TIME-DEPENDENT, MATRIX-DOMINATED FAILURE OF CONTINUOUS FIBER-REINFORCED THERMOPLASTIC COMPOSITES

OZAN ERARTSIN

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Summary

Composite materials have become indispensable for many engineering applications thanks to their high specific strength and tailorability of properties. Thermoplastic composites, which offer additional benefits such as recyclability and suitability for mass-manufacturing, are increasingly preferred especially in the automotive industry, which strives to decrease the weight of the electric cars for fuel-efficiency. Despite their advantages, thermoplastic composites exhibit strong time-dependent behavior in the matrix-dominated transverse and off-axis loading: strength depends on the applied strain rate and they are highly prone to creep and fatigue failure. Hence, it is of utmost importance to predict their time-dependent behavior to use them effectively in engineering applications.

Accurate prediction of the time-dependent behavior requires the identification of the failure mechanisms. Failure mechanisms under creep and fatigue loading are well known for neat thermoplastics, which play a significant role in the transverse and off-axis failure of composites. Neat thermoplastics exhibit plasticity-controlled failure at high stresses and low failure times and crack growth-controlled failure at low stresses and long times-to-failure. Although crack growth controlled nature of the failure is widely mentioned for the continuous fiber-reinforced composites, plasticity-controlled failure had not yet been identified. Hence, this thesis aims to identify the role of plasticity-controlled failure in the matrix-dominated, time-dependent failure of continuous fiber-reinforced composites, enabling accurate prediction of their time-dependent behavior.

Firstly, we aim to identify the role of plasticity-controlled failure mechanism in several unidirectional (UD) material systems loaded in the transverse direction at room temperature. Based on the experience on the neat and short fiber-reinforced thermoplastics, identification of the failure mechanisms requires the comparison of the time-to-failure under creep and fatigue loading, at the equal value of maximum stress. For plasticity-controlled failure, lifetime is longer under fatigue loading, while the opposite is valid for the crack growth-controlled failure. Besides, the identity of the failure kinetics in the tensile tests at constant-strain-rates and creep tests is an indication of the plasticity-controlled failure, which is also investigated to identify the failure mechanisms. Following these methodologies, failure mechanisms of glass/iPP, carbon/PEEK, and carbon/PEKK are identified. Plasticity is found to play a crucial role for glass/iPP, being the only mechanism observed over the whole load and timespan investigated. Unlike glass/iPP, carbon/PEEK and carbon/PEKK displayed the effects of plasticity at high stresses, while crack growth dominated the failure kinetics at low stresses.

In further studies, we aim to investigate in more detail the time-dependent behavior of the material system that shows the most evident signs of the plasticity-controlled failure, which is glass/iPP. In this aspect, the effect of elevated temperatures and off-axis angle on the time-dependent failure are investigated. Moreover, the relation between the time-dependent behavior of the neat matrix and the transversely loaded unidirectional composite is studied both experimentally and numerically with a micromechanical finite element model.

High-temperature tests are employed for transversely loaded UD glass/iPP to accelerate the failure for evaluating the failure mechanisms in long timescales and to determine the deformation processes contributing to the total time-dependent response. Similar to room temperature behavior, glass/iPP is revealed to display plasticity-controlled failure also at elevated temperatures. Moreover, similar to neat iPP, glass/iPP is shown to exhibit multi-process deformation, which is captured well by an analytical lifetime prediction method based on the Ree-Eyring approach and the concept of critical strain, in the framework of plasticity-controlled failure. Studying the relationship between the time-dependent behavior of the neat matrix and the composite, the activation energy is found to be different for the matrix and the composite. Such a trend is linked to the possible role of temperature-dependent effects such as fiber-matrix debonding and residual stresses in the time-dependent behavior of the composite.

The effect of the off-axis angle is characterized since the composite laminates used in practice have layers oriented at different angles for tailored properties. The effects of orientation and strain rate on the tensile strength are found to be factorizable, which is used for accelerated characterization of the time-dependent behavior. Employing the factorizability, the analytical lifetime prediction method is extended to take into account the effect of orientation. Moreover, an anisotropic, lamina-level constitutive model, which was developed for the short fiber-reinforced composites, is applied to predict the stress-strain response using an approach based on a single deformation process. The model successfully described the stress-strain response for a large range of off-axis angles. Further research is needed for certain angles that involve a distinct failure behavior and for taking into account the effect of multiple deformation processes on the time-dependent failure.

Lastly, the findings of the thesis are put in a broader perspective: the implication of several parameters related to loading, composite structure and the state of the matrix on the plasticity-controlled time-dependent behavior is discussed. A methodology for the prediction of the time-dependent behavior is presented.

Samenvatting

Composieten zijn tegenwoordig onlosmakelijk verbonden aan vele technische toepassingen dankzij de hoge specifieke sterkte en aanpasbaarheid van deze materiaalgroep. Thermoplastische composieten, welke ook recyclebaar en geschikt voor massa productie zijn, zijn geliefd bij de automobiel industrie door de continue ontwikkeling richting brandstofreductie. Ondanks de vele voordelen zijn thermoplastische composieten onderhevig aan sterk tijdsafhankelijk gedrag tijdens belastingen loodrecht op en afwijkend van de vezelrichting, welke gedomineerd wordt door de polymeren matrix. De sterkte van het materiaal hangt hierbij grotendeels samen met de oplegde reksnelheid, ook zijn het kruip- en vermoeiingsgedrag van hoge invloed. Om het gebruik van thermoplastische composieten efficiënter te maken is het daarom van belang om het tijdsafhankelijk gedrag van deze materialen goed te kunnen voorspellen.

Het voorspellen van het tijdsafhankelijk gedrag vereist het in kaart brengen van de verschillende actieve faalmodi. Het gedrag van pure thermoplasten onder kruip- en vermoeiingscondities is reeds bekend: plastisch gedomineerd falen treedt op bij belasting onder hoge spanningen en korte faaltijden, waar scheurgroei gedomineerd falen optreedt bij belasting onder lage spanningen en lange faaltijden. In de regel worden continu vezelversterkte materialen in verband gebracht met scheurgroei gedomineerd falen. Dit proefschrift heeft als doel de rol van het plastisch gedomineerd falen te onderzoeken voor deze materialen en onder condities welke gedomineerd worden door het tijdsafhankelijk gedrag van de matrix. Dit maakt het uiteindelijk mogelijk een goede voorspelling te maken van de levensduur.

Allereerst is het gedominateerde faalmechanisme in kaart gebracht voor diverse unidirectionele (UD) materialen. Deze werden belast in de richting loodrecht op de vezel en op kamertemperatuur. Ervaring uit de analyse van pure en kortvezel gevulde materialen is gebruikt om het faalmechanisme te herkennen, hierbij is een methode toegepast waarbij het tijdsafhankelijke faalgedrag onder kruip- en vermoeiingscondities is vergeleken, beide onder eenzelfde maximale spanning. Plastisch gedomineerd falen toont een hogere levensduur tijdens vermoeiingstesten, waar het tegenovergestelde zichtbaar is voor scheurgroei gedomineerd falen. Daarbij is ook de overlap van de kinetiek tijdens trekproeven op constante reksnelheid met kruiptesten een kenmerk van het optreden van plastisch gedomineerd falen. Met deze aanpak zijn de faalmechanismen van glas/iPP, carbon/PEEK en carbon/PEKK geïdentificeerd. Plasticiteit blijkt met name van belang voor het glas/iPP materiaal, welke te allen tijde zichtbaar was onder alle belastingscondities. Daarentegen tonen carbon/PEEK en carbon/PEKK alleen kenmerken van plasticiteit onder hoge spanningen, scheurgroei was zichtbaar onder lage spanningen.

Het onderzochte materiaal met de meeste duidelijke kenmerken van plastisch gedomineerd falen is glas/iPP, van welke de tijdsafhankelijke eigenschappen in meer detail zijn gebracht. Meegenomen in dit onderzoek zijn de invloeden van een verhoogde temperatuur en een belasting in een richting afwijkend van de vezelrichting. Het tijdsafhankelijk gedrag van de pure matrix en dat van het UD composiet is zowel experimenteel als numeriek onderzocht, dit laatste met behulp van een micromechanisch model gebaseerd op de eindige elementen theorie.

Het langetermijns faalgedrag van het UD glas/iPP materiaal is getest in de richting loodrecht op de vezel. Deze testen vonden plaats op verhoogde temperatuur om de metingen te versnellen. Ook op verhoogde temperatuur blijkt het plastische faalgedrag dominant. Belangrijk daarbij is dat het materiaal, net als puur iPP, plastisch deformeert ten gevolge van meerdere interne processen. Deze deformatieprocessen en de levensduur kunnen goed worden beschreven met een analytisch model gebaseerd op de Ree-Eyring formulering samen met het concept van een kritische spanning. Uit een vergelijk tussen het beschreven faalgedrag van een puur iPP en het gebruikte composiet volgt een verschil in activeringsenergie. Dit gedrag wordt in verband gebracht met de mogelijke rol van temperatuursafhankelijke effecten zoals de binding tussen vezel en matrix en de aanwezigheid van restspanningen in de proefstukken.

Composietlaminaten hebben in werkelijkheid meerdere lagen, elk met vezels georiënteerd in een specifieke richting. De invloed van de belastingsrichting is daarom ook in kaart gebracht. Hieruit volgt dat de invloeden van oriëntatie en reksnelheid factoriseerbaar zijn, welke gebruikt kan worden om binnen een kort tijdsbestek het tijdsafhankelijk gedrag van het materiaal te bepalen. De analytische methode welke eerder gebruikt is om levensduur te voorspellen is uitgebreid met deze factoriseerbaarheid. Daarbij is een anisotroop constitutief model, op laminaat niveau en eerder ontwikkeld voor kortvezel versterkte composieten, toegepast om het spanning-rek gedrag te beschrijven, gebruikt makend van één actief deformatie proces. Dit model is geschikt om het spanning-rek gedrag goed te beschrijven voor een groot bereik aan belastingsrichtingen. Opvolgend onderzoek is nodig naar bepaalde belastingsrichtingen welke een uniek faalgedrag vertonen, alsook om de invloed van meerdere deformatieprocessen in beschouwing te nemen.

Tot slot zijn de bevindingen in dit proefschrift in een breder perspectief geplaatst: belangrijke aspecten betreffende de opgelegde belasting, de opbouw van het composiet en de structuur van matrix zijn hierin meegenomen. Een methode is gepresenteerd welke het tijdsafhankelijke gedrag kan beschrijven.

Contents

Summary.....	i
Samenvatting.....	iii
Chapter 1: Introduction.....	1
1.1 Off-axis time-dependent failure	1
1.2 Failure mechanisms.....	3
1.3 Objective, scope, and outline.....	6
1.4 References	7
Chapter 2: Identification of plasticity-controlled creep and fatigue failure mechanisms in transversely loaded unidirectional thermoplastic composites	11
2.1 Introduction	12
2.2 Background	16
2.2.1 Plasticity-controlled failure.....	16
2.2.2 Crack-growth controlled failure	19
2.3 Experiments	21
2.3.1 Materials	21
2.3.2 Manufacturing and sample preparation	22
2.3.3 Mechanical tests	23
2.4 Results and Discussion.....	24
2.4.1 Glass/iPP.....	25
2.4.2 Carbon/PEEK.....	29
2.4.3 Carbon/PEKK.....	32
2.5 Conclusion	35
2.6 References	36
Chapter 3: Long-term failure of transversely loaded glass/iPP.....	41
3.1 Introduction	42
3.2 Experiments	45
3.2.1 Material and Sample Preparation	45
3.2.2 Crystallinity measurements	46

3.2.3	Uniaxial tensile tests.....	47
3.2.4	Microscopy	48
3.3	Results	48
3.3.1	Crystallinity	49
3.3.2	Short-term behavior.....	51
3.3.3	Long-term behavior.....	56
3.3.4	Effect of cooling rate on the short-term behavior.....	62
3.4	Conclusions.....	67
3.5	References	68
Chapter 4: Micromechanical modeling of the plasticity-controlled time-dependent failure of transversely loaded unidirectional glass/iPP		73
4.1	Introduction	74
4.2	Experiments	76
4.2.1	Processing and specimen preparation.....	76
4.2.2	The effect of cooling rate on the time-dependent behavior of iPP	78
4.3	Modeling.....	79
4.3.1	Intrinsic behavior	79
4.3.2	Constitutive model for the neat matrix	80
4.3.3	Characterization.....	82
4.3.4	Micromechanical model	86
4.4	Results	87
4.4.1	Time-dependent behavior of iPP.....	87
4.4.2	Composite simulations and composite vs. iPP comparison.....	88
4.4.3	The effect of fiber-matrix adhesion on time-dependent failure.....	91
4.5	Towards faster characterization.....	94
4.6	Conclusion.....	96
4.7	References	97
Chapter 5: Time-dependent failure of off-axis loaded glass/iPP composites		99
5.1	Introduction	100
5.2	Experimental methods and materials.....	102
5.2.1	Material and sample preparation.....	102
5.2.2	Mechanical tests	103
5.3	Experimental results.....	104
5.3.1	Constant-strain-rate tests.....	104
5.3.2	Long-term behavior and the analytical lifetime prediction method	109

5.4	Modeling of the off-axis stress-strain behavior	113
5.4.1	Anisotropic lamina constitutive model	113
5.4.2	Characterization	116
5.4.3	Finite element model	119
5.4.4	Prediction of the stress-strain response	121
5.4.5	Multi-process modeling	123
5.5	Conclusion	124
5.6	References	124
Chapter 6:	Discussion	127
6.1	The effect of several parameters on the time-dependent failure	127
6.1.1	Loading	128
6.1.2	State of the matrix	132
6.1.3	Composite structure	134
6.2	The implication of plasticity-controlled failure for Constant Life Diagrams (CLDs)	136
6.3	Towards predicting the time-dependent behavior of multidirectional laminates	137
6.3.1	Challenges and future work	139
6.4	References	140
Chapter 7:	Conclusions and recommendations	143
7.1	Conclusions	143
7.2	Recommendations	145
7.3	References	146
	Acknowledgements	147
	Publications	151

Chapter 1: Introduction

1.1 Off-axis time-dependent failure

In engineering applications, there has been an increasing demand for the use of fiber-reinforced thermoplastic composites. This demand has been driven by the need for materials suitable for mass manufacturing, recycling, and tailored properties, in addition to their high specific strength and stiffness facilitating lightweight design. With the advent of electric cars, the use of thermoplastic composites is more important than ever to decrease their weight further down and to manufacture at a high rate to keep up with the demand. Nevertheless, due to the viscoelastic nature of the thermoplastic matrix, these materials exhibit a strong time-dependence; therefore, they are highly susceptible to failure under long-term creep and fatigue loading.

The understanding and experience in the time-dependent failure of thermoplastic composites is limited. Therefore, we will illustrate the time-dependent damage of composites under long-term loading with the help of studies conducted on thermoset composites. Many studies on cross-ply and multidirectional laminates found that under creep and fatigue loading, cracking in the transverse and off-axis layers is the initial failure mechanism observed. With time under sustained load, crack density in transverse and off-axis layers increases [1–3]. An example of this is provided in Figure 1.1a, which shows the increase in the number of transverse cracks with time, observed from the edge of the sample, for a graphite/epoxy cross-ply laminate [1]. The evolution of the crack density was found to be load-dependent: although there were some exceptional cases [1], the evolution of crack density tended to accelerate with higher loads [2,3], as presented in Figure 1.1b. Having increased in number and reached the interface between the layers with different orientations, cracks in the transverse and off-axis layers may later lead to other types of damage [2–4]. This is illustrated in Figure 1.1c for cross-ply laminates, where it is shown that the delaminations start at locations where transverse cracks intersect with longitudinal layers and grow over a large area. Subsequently, ultimate failure takes place upon fiber fracture.

Although it is seen that there are different damage mechanisms interacting with each other, which govern the lifetime of multidirectional laminates, transverse cracking is usually the first damage mode to appear and it gives rise to other types of damage. One implication of this is that

delaying the cracking in transverse and off-axis layers would result in a prolonged lifetime of the whole laminate, which would be favorable for engineering applications. In addition, an understanding of the time-dependent failure of transverse and off-axis loaded layers would be fundamental to understanding the time-dependent failure of more complex, multidirectional laminates.

Figure 1.1: (a) Evolution of transverse cracks of cross-ply graphite/epoxy with time under creep load [1]. (b) Crack density vs. time at various creep loads (% of ultimate tensile strength) for cross-ply carbon/epoxy [2]. (c) Evolution of damage in cross-ply laminates based on [3,4]. Reproduced from [1,2].

Considering the general loading of a multidirectional laminate in the frame of Classical Laminate Theory (CLT), each layer experiences a combination of tensile/compressive transverse, tensile/compressive longitudinal and in-plane shear stresses in material coordinates. Ignoring the interaction between the failure modes for the time being, as in the Maximum Stress failure criterion [16], failure can be assumed to take place once any of the stresses exceed the allowable value for the corresponding stress value. Hence, studying lamina behavior with unidirectional laminates subjected to one of these loading scenarios helps one to understand also the time-dependent behavior of a multidirectional laminate. In this thesis, we will focus mostly on the matrix-dominated time-dependent failure in transverse tensile loading. Since the viscoelastic

behavior of the thermoplastic matrix plays a significant role in the transverse time-dependent behavior [5], a discussion of the long-term behavior of the neat thermoplastic matrices is crucial.

1.2 Failure mechanisms

Thermoplastic polymers exhibit three different failure mechanisms under long-term loading: plasticity-controlled failure, crack growth-controlled failure and degradation controlled failure [6–8]. These failure mechanisms have different stress dependence; hence, they are identified by different slopes in the load vs. time-to-failure curve, as shown in Figure 1.2. All mechanisms act simultaneously; however, one of them dominates the lifetime in each regime. Degradation-controlled failure, which is seen at very low stresses and long lifetimes is almost stress-independent and controlled by chemical aging and molecular degradation. Since this failure mechanism can be prevented by stabilizers, it is not considered as a limiting factor for long-term performance. Hence, degradation-controlled failure will not be considered in this thesis.

Figure 1.2: Long-term failure modes of thermoplastics.

Plasticity-controlled failure is dominant at high stresses and short lifetimes. Failure in this regime is caused by the accumulation of plastic strain. In most cases, this failure regime is characterized by an appreciable macroscopic plastic deformation for the neat thermoplastics; for instance, thermoplastic pipes display extensive bulging at high hydrostatic pressures promoting plasticity-controlled failure [8]. In the crack growth-controlled failure regime, which is seen at lower stresses and longer lifetimes, failure takes place due to a crack that is either already present or initiating at a defect or imperfection and propagating slowly until it becomes critical. This mechanism mostly leads to a brittle appearance, such as hairline cracks observed in pipes.

Since each failure regime is governed by different failure kinetics, each regime requires its own lifetime prediction method [9,10]. Hence, identification of the failure mechanisms dominant in

the load, time and temperature range of interest is of utmost importance, especially for fiber-reinforced thermoplastics, for which the macroscopical failure mode does not reveal the failure mechanism, unlike the usual trend for neat thermoplastics. For instance, short fiber-reinforced thermoplastics were observed to display the two failure mechanisms characterized by the different slopes in a load vs. lifetime plot, although they fail in a macroscopically brittle manner in both regimes [9].

For continuous fiber-reinforced composites, which also fail in a macroscopically brittle manner, the common sense is that the off-axis matrix-dominated failure is controlled by a brittle crack growth mechanism. However, as in the case of short fiber-reinforced composites [9], plasticity might play a significant role, which would require a lifetime prediction method that takes into account the kinetics of the plasticity-controlled failure. Reviews on the lifetime prediction methods for composites [11–13] show that most of the methods available do not mention the effect of failure mode. Those that mention a different failure mode at low times-to-failure and high stresses, compared to the failure mode at lower stresses and longer lifetimes, either do not deal with the matrix-dominated off-axis failure or do not consider the intrinsic failure mechanisms of the neat thermoplastics [14,15]. Hence, to propose accurate lifetime prediction methods, there is a need for the identification of the failure mechanisms associated with the long-term behavior of the neat thermoplastics in the matrix-dominated failure of thermoplastic composites.

Identifying the role of plasticity-controlled failure mechanism in the long-term behavior requires the investigation of the link between the long-term behavior characterized by creep and fatigue tests and the short term behavior characterized by constant-strain-rate tests. This is because, in the plasticity-controlled failure regime, stress dependence of the lifetime under creep loading was found to be identical to strain rate dependence of the yield stress [6,10,17]. This is illustrated for polyethylene in Figure 1.3a and Figure 1.3b, which show the dependence of the yield stress on the applied strain rate and the dependence of lifetime on creep load, respectively. Slopes of the curves in Figure 1.3a and Figure 1.3b are identical at 23°C, which implies that identical failure kinetics govern the constant-strain-rate and creep behavior.

Identical failure kinetics under short- and long-term loading is important for several reasons. Firstly, it paves the way for predicting the lifetime by making use of constant-strain-rate tests, which take short times. Secondly, it means that the factors affecting the short-term yield stress would have a major influence on the long-term behavior in the plasticity-controlled failure regime. For instance, temperature [6,17–20], processing conditions [18,20], orientation [21,22] and physical aging [23,24] all affect the short-term behavior, which correspondingly influences the long-term behavior as well. One thing this implies is that, instead of talking about long-term behavior, it is wise to mention time-dependent behavior, which inherently implies also the short-term constant-strain-rate behavior. Furthermore, identical failure kinetics also brings the

necessity to investigate the effect of the aforementioned factors on time-dependent failure. Testing at high temperatures is often preferred to accelerate the failure and assess the durability of the material for applications requiring elevated temperatures. Besides, investigating the temperature dependence of time-dependent failure is fundamental for thermoplastics since many of them exhibit thermo-rheologically-complex behavior which means that failure kinetics will be different at different temperatures [25]. iPP, which exhibits multiple deformation processes that are related to its microstructure, is an example of such materials [19,25,26]. The effect of temperature on the time-dependent behavior is also exemplified in Figure 1.3. The figure shows that a decrease in the testing temperature not only leads to lower stress levels and to an accelerated failure but the slopes of the yield stress vs. strain rate and creep stress vs. time-to-failure curves also change. Such a change in the slope implies a change also in the failure kinetics, which would need to be characterized to assess the long-term performance at long timescales or high temperatures. Another factor affecting the time-dependent behavior is the processing conditions, which do so through a change in the crystal structure and the crystallinity [18,24,27]. Figure 1.3a exemplifies this by showing that a lower cooling rate, which results in a higher crystallinity and lamellar thickness, leads to a higher rate-dependent yield stress. Correspondingly, long-term failure is also affected in a way that the failure is shifted to longer timescales, as illustrated in Figure 1.3b.

Furthermore, it is known that laminates used in engineering applications often have plies oriented at various off-axis angles. One of the reasons for this is the desire to tailor the properties along certain directions. This brings about a need for the characterization of the angle dependence of the matrix-dominated, off-axis time-dependent failure.

Figure 1.3: The effect of cooling rate during hot pressing and the testing temperature on (a) constant-strain-rate and (b) creep behavior of polyethylene. Markers represent the experimental data and lines are the fits explained in [24]. Reproduced from [24].

1.3 Objective, scope, and outline

The objective of this study is to identify the role of plasticity-controlled failure in the matrix-dominated time-dependent failure of continuous fiber-reinforced composites. The identification aims at proposing a lifetime prediction method and modeling the time-dependent behavior by taking into account the plasticity-controlled failure. To accomplish this aim, our approach will be to investigate the time-dependent failure of the transverse and off-axis loaded unidirectional (UD) composites. This is because working on UD laminates eliminates the effect of constraining layers on the time-dependent damage evolution, leading to much simpler failure kinetics, which allows one to investigate matrix-dominated failure in a more straightforward way. In addition, UD layers are the building blocks of the more complex laminates, which means that by using the finite element method or theories such as classical laminate theory, one can move from lamina to laminate level. The finite element method is especially useful for simulating the behavior of complex laminates under non-ideal loading conditions. In order to simulate the behavior of a laminate under such conditions, it is common to input the mechanical behavior of the laminae, which are the constituting blocks of the laminates, to the finite element analysis software. Hence, understanding and modeling the time-dependent behavior in the off-axis direction is fundamental and will pave the way for more realistic simulations of complex laminates used in engineering applications.

The outline of this thesis is provided in Figure 1.4. The thesis will include **four** main-body chapters. Based on the aforementioned discussion of failure mechanisms, long-term failure mechanisms will be identified first in **Chapter 2** in the transversely loaded UD laminates. This will be done on multiple material systems, namely glass/iPP, carbon/PEEK and carbon/PEKK. The rest of the thesis will focus on the time-dependent failure of the material system that shows the clearest signs of plasticity-controlled failure, which is glass/iPP. **Chapter 3** aims at the investigation of the time-dependent behavior of the transversely loaded glass/iPP at elevated temperatures and various processing conditions. A plasticity-based lifetime prediction methodology will be proposed to predict the lifetime of transversely loaded UD laminates. The time-dependent behavior of the matrix will also be characterized to investigate the link between the time-dependent failure of the neat matrix and the transversely loaded composite. **Chapter 4** aims at investigating if the differences between the time-dependent failure of neat iPP and glass/iPP experimentally observed in **Chapter 3** can be captured with a micromechanical finite element analysis. For the analysis, temperature- and time-dependent behavior of the neat matrix will be modeled using the EGP (Eindhoven Glassy Polymer) model [25,28], which was shown to work also for semicrystalline polymers [29]. **Chapter 5** will focus on unraveling the effect of orientation on the off-axis time-dependent failure. The lifetime prediction methodology presented in Chapter 2 for transverse loading at 90° will be extended to other off-axis angles. Furthermore, an anisotropic viscoelastic-viscoplastic constitutive model will be utilized to describe the time-

dependent behavior of off-axis loaded UD composites. This constitutive model will be applied to predict angle and strain-rate dependent stress-strain behavior. Having characterized the plasticity-controlled time-dependent failure in the off-axis loaded UD composite, a future application of the findings of this thesis would be to predict the time-dependent failure of complex laminate although we will not move to the laminate-level in this study.

Figure 1.4: Outline of the thesis.

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Chapter 2: Identification of plasticity-controlled creep and fatigue failure mechanisms in transversely loaded unidirectional thermoplastic composites

Abstract

In continuous fiber-reinforced thermoplastics, the macroscopic failure mode in transverse long-term failure is dominated by a brittle crack-growth mechanism. Neat thermoplastic matrices, on the other hand, generally display also a plasticity-controlled mechanism in long-term loading at elevated stress levels and/or temperature. This failure mechanism requires a different approach to lifetime prediction than crack growth, and, so far, it has not yet been observed in composites.

In this study we demonstrate the presence of the plasticity-controlled failure mechanism in long-term failure of transversely loaded unidirectional (UD) thermoplastic composites made of glass/iPP, carbon/PEEK and carbon/PEKK. The main method used is to compare the lifetime in cyclic loading to that in static loading at the same level of maximum stress, where an increase in lifetime is characteristic for plasticity controlled failure, and, vice versa, a decrease is indicative for fatigue crack growth. In addition, the applicability of a lifetime prediction method common to plasticity-controlled failure of neat thermoplastics is evaluated for the composites investigated.

The results of this study indicate that the plasticity-controlled failure was present in composites, although the extent to which the effects are present varied depending on the materials investigated. Glass/iPP showed the most explicit evidence of the plasticity-controlled failure over the entire load range experimentally covered. Its long-term failure was delayed with a decrease in the stress ratio and lifetime was predicted well using the principles of plasticity-controlled failure

2.1 Introduction

Thermoplastic composites are often used in engineering applications where they need to satisfy long lifetime requirements under creep and fatigue loading. Typical lifespans for current or potential applications might range from 15-20 years in the automotive industry to 20-25 years for aircraft and wind turbines [1,2]. Since real-time testing for such long durations is time-consuming and impractical, the need for lifetime prediction models making use of accelerated testing methodologies is vital.

For composites under off-axis creep loading, where the failure is matrix-dominated, the time-dependent failure clearly finds its origin in the time-dependent nature of the polymer matrix. Consequently, lifetime prediction methods can be used that are based on time-temperature superposition, time-stress superposition, and rate theory, where temperature and/or stress are used to accelerate the failure [3–5]. In long-term cyclic loading, the estimation of the lifetime of composite laminates is a little more challenging. Lifetime predictions are commonly based on S-N curves of UD-laminates in several loading angles, which serve as an input to predict multiaxial fatigue failure, as proposed by Hashin and Rotem [6]. In general, however, S-N curves show a strong dependence on the stress ratio R , and the performance needs to be assessed at several stress ratios. At this point, Constant Life Diagrams (CLD) serve as a practical means to predict fatigue lifetime [7–9]. Using CLDs, fatigue performance at one stress ratio can be predicted by interpolation/extrapolation of data obtained at other stress ratios. Consequently, accurate identification of the fatigue lifetime at a specific R -value will have a significant effect on lifetime prediction at other values.

One way to specify a cyclic, sinusoidal load is by using the maximum stress σ_{max} , the stress ratio R , and the applied frequency f as the main parameters. In that case, the variation of the stress ratio is commonly performed at a constant level of the maximum stress, as shown in Figure 2.1. Many studies on fiber-reinforced thermosets, performed in this way, concluded that a decrease in the stress ratio (increasing amplitude) under constant maximum stress led to a marked decrease in lifetime, indicating that failure is *accelerated*; this response will further be referred to as the “typical response”. With data obtained from the literature [10,11], Epaarachchi and Clausen [12] showed that the “typical response” was observed in longitudinal and transverse UD and quasi-isotropic woven glass/polyester laminates. Similar observations were made on epoxy-based composites with various stacking and reinforcements [7,13–18], and some thermoplastic composites [19,20]. An explanation for the observed acceleration of failure was proposed by Wevers et al. [16], who assigned the decrease in the lifetime of cross-ply carbon/epoxy composites at lower stress ratios to the damage caused by crack closure in transverse layers.

Figure 2.1: Stress vs. time for various stress ratios (R).

Remarkably, however, the “typical response” is not always observed. While some woven and transversely loaded UD epoxy composites display the typical response at temperatures far below the glass transition temperature (T_g), the trend changed at temperatures close to T_g [21,22]. This phenomenon is shown in Figure 2.2, comparing the responses in cyclic ($R=0.05$) and static loading ($R=1$) for a transversely loaded UD laminate [21]. At low temperature, lifetime clearly decreases with decreasing stress ratio, whereas at high temperature the opposite trend is observed. Such an “atypical” response was seen in carbon/PEEK composites not only around T_g [22] but also at low temperatures far below T_g [15] under transverse loading. In this study [15], cyclic loading with high R values led to longer lifetimes compared to creep loading. In all cases, the “atypical” response was assigned to a failure mechanism controlled by the mean stress [21].

Figure 2.2: Maximum stress vs. time curves for transversely loaded UD carbon/Epoxy composite below and near the glass-transition temperature. Closed and open markers represent creep and fatigue data, respectively. Lines are the least square fit to creep ($R=1$) experimental data. Reproduced from [21].

Although the observed behavior may be “atypical” for composites, it is quite common in neat thermoplastic polymers [23–25], as well as in short-fiber reinforced thermoplastic composites [24,26], synthetic fibers and ropes [27–30].

Since the time-dependent behavior of the matrix has a significant influence on that of composites, we believe that a discussion on the long-term behavior of thermoplastics will be helpful in understanding the origin of the “atypical response” observed in some composites.

The long-term behavior of thermoplastic polymers is governed by two major failure mechanisms that act simultaneously [24,31,32]: i) plasticity-controlled failure, which dominates at high stress levels, ii) slow crack growth, which manifests itself at lower stress levels. In some cases, there is also a third mechanism, degradation-controlled failure, which is typically stress-independent and controls the lifetime at extremely low stress levels [31,32]. Since we will be focusing on the stress-dependence of failure, degradation will be excluded for now.

Since both failure mechanisms, plasticity and crack growth, typically possess quite different kinetics, the transition between the two is generally visible as a change in the slope of the stress-dependence of the lifetime, as shown in Figure 2.3b. But that is not the only distinction between the two; there is also a marked difference in their response upon a variation in the stress ratio at a constant value of the maximum stress. In the crack-growth-controlled regime, the lifetime is dominated by the steady growth of the cracks that initiate at imperfections in the material. Failure takes place when the crack reaches a critical length, dictated either by geometry (e.g. wall thickness) or the critical stress intensity factor, and becomes unstable. In this regime, cyclic loading induces an accelerated crack propagation rate, resulting in a marked decrease of the lifetime compared to creep loading; the “typical response” as observed in composites. The accelerated growth in cyclic loading can be explained by damage accumulation in the fibrils of the craze at the crack-tip, as a result of bending or even crushing of fibrils, formed in the craze at the crack-tip, during the unloading phase of a cycle (crack closure) [33].

Figure 2.3: Schematic illustration of (a) static and cyclic load vs. time and (b) plasticity- and crack growth-controlled regimes under these loads typical for neat and short fiber-reinforced thermoplastics. Figures are drawn based on the findings in [24].

In plasticity-controlled failure, applied stress causes plastic flow that leads to a gradual accumulation of plastic strain. When the level of accumulated plastic strain exceeds a critical level, strain localization is triggered and failure occurs. In cyclic loading, at the same maximum stress, the average stress level is lower than in creep loading, resulting in a slower accumulation of plastic strain, and, hence, an increase in lifetime [24]; the “atypical response”. Consequently, the response in the plasticity-controlled regime is opposite to that observed in the crack-growth regime. This is illustrated in Figure 2.3, where the stress dependence of the lifetime is presented for two load cases: static and cyclic loading. In both cases, we observe both failure mechanisms; the transition between them visible by the change in slope over the two regimes. Upon cyclic loading, at the same maximum stress, the lifetime is observed to increase in the plasticity controlled regime, and decrease in the crack growth regime [26]. This marked difference in the response of both failure mechanisms makes the comparison of lifetime in static and in cyclic loading, at the same level of the maximum stress, an effective method to identify the underlying failure mechanism. Identification of the failure mechanisms is important since lifetime prediction methods are based on different principles for each failure mechanism [23,24,26,34–36]. Proper identification also aids in proposing the right steps to improve the lifetime of the material, since a method that improves performance in one failure regime, may be detrimental for the other regime [23,37]. Well-known examples are the effect of annealing, which improves the performance in the plasticity-controlled regime, but is ineffective/detrimental for crack growth [23,37–39]; and the effect of an increase in molecular weight, which strongly favors crack growth [40,41], but is ineffective in the plasticity regime.

Although the aforementioned plasticity-controlled failure mechanism was revealed to be present in the long-term behavior of short fiber-reinforced composites [24,26], its role in that of continuous fiber-reinforced composites has not yet been studied. Hence, the aim of this study is to investigate if the plasticity-controlled failure mechanism, which we think might be linked to the aforementioned “atypical response”, plays a role also in the long-term behavior of thermoplastic composites. Since this matrix-related phenomenon is expected to be critical especially in the transverse direction, transversely loaded UD laminates will be used for the investigation.

One might argue that transversely loaded UD laminates are not used in practice and their failure mechanisms are different than those observed in multidirectional laminates. This is correct; however, it is very straightforward to study matrix-dominated failure kinetics in UD laminates since failure takes place by the evolution of a single crack spanning the cross-section. In cross-ply laminates, multiple cracks initiate in the transverse layers, which grow, increase in number and eventually initiate other types of damage such as delamination, leading to ultimate failure [42–44]. This makes it more complex to observe matrix-dominated failure kinetics by studying cross-ply laminates. Besides, since the time-dependent failure of transverse layers affects the

lifetime of the whole laminate [42–44], studying the failure kinetics of the transversely loaded UD laminates gives a valuable insight into the long-term behavior of multidirectional laminates.

In the scope of this research, the creep responses of various transversely loaded UD composites, glass/iPP, carbon/PEEK and carbon/PEKK, are determined at room temperature. Cyclic loading, which has different effects on the lifetime in the plasticity- and crack-growth-controlled failure regimes, is applied to identify the dominant failure mechanism. To investigate the extent to which the principles of plasticity-controlled failure apply, a lifetime prediction method based on the plasticity-controlled failure of thermoplastics is employed [24,34].

In the remaining part of this paper, Section 2.2 elaborates on the plasticity- and crack-growth-controlled long-term failure mechanisms of thermoplastic polymers and their lifetime prediction methods. Furthermore, the effect of stress ratio and frequency on the lifetime in each failure mechanism will be discussed here, which will help to identify the dominant failure mechanism. In Section 2.3, the experimental methodology will be introduced. Section 2.4 includes both the results and a discussion of how plasticity-controlled failure manifests itself in the materials studied. Finally, Section 2.5 concludes the study.

2.2 Background

2.2.1 Plasticity-controlled failure

Plastic deformation in polymers is related to stress-induced chain mobility; the application of stress induces an enhanced state of main-chain segmental mobility, which induces a continuous and dynamic change of chain conformation, resulting in plastic flow [45].

In a creep test under constant load, three stages of deformation are present, which are named as the primary, secondary, and tertiary creep. Primary creep is the viscoelastic region where strain rate decreases with time and strain. During secondary creep, the strain rate reaches a constant steady rate of plastic flow, which subsequently gradually accelerates (tertiary creep), eventually leading to strain localization and failure.

In the secondary creep stage, the polymer behaves as a fluid; it deforms at a constant (plastic) flow rate under a constant stress. Another situation where such a steady flow is observed is at the yield point in a tensile test, where there is a small region where stress is constant under a constant rate of strain. Bauwens-Crowet et al. [46] were the first to demonstrate that the state of deformation in both conditions is equivalent. Their results are summarized in Figure 2.4, which shows that the stress-dependence of the flow rate during secondary creep follows the same

trend as the strain rate dependence of the yield stress observed in tensile tests. It is clear that the flow kinetics are equivalent for both load cases. This equivalency implies that the stress-dependence of the flow rate during secondary creep can be estimated from tensile tests at different strain rates.

Figure 2.4: Ratio of the engineering yield stress to temperature vs logarithm of the strain-rate at yield in creep and constant-strain-rate tests. Reproduced from Bauwens-Crowet et al. (1974) [46].

The flow or deformation kinetics of polymers can be described by Eyring's activated flow theory [47] where the relationship between the plastic flow rate $\dot{\epsilon}_{pl}$ and the applied stress σ is described as:

$$\dot{\epsilon}_{pl}(\sigma, T) = \dot{\epsilon}_0 \exp\left(-\frac{\Delta U}{RT}\right) \sinh\left(\frac{\sigma v^*}{kT}\right), \quad (2.1)$$

where $\dot{\epsilon}_0$ is a rate factor, ΔU is the activation energy of the molecular relaxation mechanism, v^* is the activation volume, T is the absolute temperature, k is the Boltzmann's constant and R is the universal gas constant.

Equation (2.1) accounts for multiple factors that affect the development of the plastic flow rate. The rate factor $\dot{\epsilon}_0$ is related to molecular mobility and; therefore, the only parameter influenced by the thermodynamic state. The Arrhenius term and the sine hyperbolic part cover the temperature and stress dependence of the plastic flow rate, respectively.

Under isothermal conditions, the terms $\dot{\epsilon}_0 \exp\left(-\frac{\Delta U}{RT}\right)$ and $\frac{kT}{v^*}$ will be constants, which can be denoted as $\dot{\epsilon}_{0,T}$ and σ_0 , respectively. Then, Equation (2.1) can be rearranged to obtain the stress σ at yield in a constant-strain-rate test in terms of the applied strain rate $\dot{\epsilon}$:

$$\sigma = \sigma_0 \sinh^{-1} \left(\frac{\dot{\epsilon}}{\dot{\epsilon}_{0,T}} \right). \quad (2.2)$$

For $\sigma \gg \sigma_0$, Equation (2.2) reduces to Equation (2.3), which clearly shows the well-known linear relationship between the yield stress of polymers and the logarithm of the applied strain rate:

$$\sigma = \sigma_0 \ln(\dot{\epsilon}) - \sigma_0 \ln \left(\frac{1}{2} \dot{\epsilon}_{0,T} \right). \quad (2.3)$$

In some cases, the polymer's yield response contains contributions of two processes [48–50], and the yield stress can be described by:

$$\sigma = \sum_{i=I,II} \sigma_{0,i} \sinh^{-1} \left(\frac{\dot{\epsilon}}{\dot{\epsilon}_{0,T,i}} \right), \quad (2.4)$$

which is based on the generalized expression for viscosity proposed by Ree and Eyring [51]. Here, the stresses due to primary and secondary transitions, named as process *I* and *II*, respectively, are assumed to be additive and act in parallel.

The rate expression mentioned above can be used effectively to estimate the resulting plastic flow rate for arbitrary values of the applied stress and temperature. To extend this to an effective lifetime prediction, we make use of an experimental observation. For many neat and short fiber-reinforced thermoplastics it was demonstrated that the product of the plastic flow rate ($\dot{\epsilon}_{pl}(\sigma)$) in a creep test with the corresponding time-to-failure (t_f) is constant [23,26,34,35,52–54]. The constant can be seen as a critical level of accumulated plastic strain ϵ_{cr} , required for the initiation of strain localization and failure. This leads to:

$$\dot{\epsilon}_{pl}(\sigma) \cdot t_f = \epsilon_{cr}, \quad (2.5)$$

which implies that a double logarithmic plot of the flow rate during secondary creep versus the corresponding time to failure will yield a line with a slope of -1 [55]. In isothermal creep, the resulting lifetime can be estimated using:

$$t_f = \frac{\epsilon_{cr}}{\dot{\epsilon}_{pl}(\sigma)}, \quad (2.6)$$

where $\dot{\varepsilon}_{pl}(\sigma, T)$ was already described by Equation (2.1) and can be obtained using the short-term constant strain-rate tests. In polymers, an increase in stress or temperature will lead to an increase in the molecular mobility and thus cause a higher rate of plastic flow leading to accelerated failure.

For situations where the stress varies in time, Equation (2.6) is no longer applicable and the accumulation of plastic strain has to be monitored over time. In the case of cyclic loading, the plastic strain accumulated in a single cycle is:

$$\varepsilon_{pl,acc,cycle} = \int_0^{t_{cycle}} \dot{\varepsilon}_{pl}(\sigma(t')) dt'. \quad (2.7)$$

Lifetime under cyclic loading is calculated from the number of cycles required to attain the critical strain:

$$t_f = \frac{\varepsilon_{cr}}{\varepsilon_{pl,acc,cycle}} \cdot t_{cycle} = \frac{\varepsilon_{cr}}{\varepsilon_{pl,acc,cycle}} \cdot \frac{1}{f}, \quad (2.8)$$

where f is the frequency of the cyclic loading, t_{cycle} is the cycle time, and $\varepsilon_{pl,acc,cycle}$ is the plastic strain accumulated in a single cycle (Equation (2.7)). In general, the amount of accumulated plastic strain during a certain period in cyclic loading will be lower than that accumulated at the same maximum stress in static loading. Consequently, the lifetime under cyclic loading will be longer. Furthermore, a change in frequency does not result in a shift in the cyclic lifetime [23,24,35].

2.2.2 Crack-growth controlled failure

This failure mechanism takes place at relatively lower loads compared to the plasticity-controlled failure and is dominated by the slow growth of individual cracks. Cracks may either form during service due to loads at locations of stress concentration such as internal defects [56,57] or pre-exist due to processing and/or handling of the product. Especially for fiber-filled systems, cracks can be assumed to already exist in the material. After the crack has formed, it will grow slowly and steadily until it reaches a critical length, dictated either by geometry or the critical stress intensity factor, leading to unstable growth and, eventually, to final fracture. The gradual growth of the crack can be estimated using Paris' Law [58] which relates the crack propagation rate $\frac{da}{dt}$ to the stress intensity factor K_I at the crack tip by Equation (2.9):

$$\frac{da}{dt} = A \cdot K_I^m, \quad (2.9)$$

where A and m are the experimentally determined constants. Equation (2.9) describes a linear relationship between the logarithm of the crack growth rate and the logarithm of the stress intensity factor, which depends on the applied stress, initial crack size, and the geometry of the specimen. Equation (2.9) can be integrated from the time the crack is assumed to initiate until failure to get the lifetime. The integration and some subsequent simplifications consequently lead to Equation (2.10), which describes a linear relationship between the applied stress and time-to-failure in double logarithmic scale [26,59]. This is in contrast to what is observed in the plasticity-controlled failure, where the relationship is linear in a semi-logarithmic plot. t_f in Equation (2.10) is the time-to-failure, m is the aforementioned experimentally determined constant from the crack propagation experiments, and c_f is a factor which is a function of A , m , and both the initial and final crack length.

$$t_f = \left(\frac{\sigma}{c_f}\right)^{-m}. \quad (2.10)$$

It should be noted that even though the total lifetime is dominated by crack growth, both plasticity- and crack growth-controlled failure mechanisms may take place during service until the failure. After all, the formation of crazes that lead to cracks is a plasticity-controlled phenomenon [60]. However, since the lifetime is dominated by crack growth, the time for a crack to grow critical has to be substantially longer than the time to initiate a crack [60].

In the case of cyclic loading, the crack propagation rate at a specific stress intensity factor increases with the stress ratio, which *decreases* the lifetime (acceleration of failure) [23,24,39,61]. An illustrative example of this response is shown in Figure 2.5 where the crack propagation kinetics of a polyethylene pipe grade is presented for various values of the stress ratio R [61]. This “typical response” is opposite to that observed in plasticity controlled failure, and this characteristic can be used to identify the underlying failure mechanism. The accelerated crack propagation rate with decreasing stress ratio R may be explained by bending- or crushing-induced damage to the fibrils of the craze in the crack tip during the unloading phase [33].

Figure 2.5: Crack propagation rate of PE versus the maximum stress intensity factor for various stress ratios R . Markers represent experimental measurements and the lines are guides-to-the-eye. Reproduced from [61].

To predict lifetime under cyclic loading, the crack propagation rate in Equation (2.9) can be expressed in terms of the maximum-stress-intensity-factor K_{max} in a load cycle. Since it has been shown that the Paris' Law exponent m is approximately the same for both cyclic as static loading conditions, the parameter c_f is the only parameter that is subject to change [24,26]. Thus, to predict the creep lifetime by using cyclic tests, c_f of the creep loading can be obtained by extrapolating the c_f values obtained from cyclic tests at various stress ratios to $R=1$. Here it should be noted that, although the lifetime in cyclic loading is typically strongly frequency-dependent, the extrapolation procedure will always yield the same c_f value for $R=1$; irrespective of the frequency used [26].

In addition to the stress ratio, the frequency can also be varied in cyclic loading. At a fixed stress ratio, an increase in the frequency was observed to result in lower c_f values [26,62]. According to Equation (2.10), this implies a shorter lifetime when the frequency is increased. Such an effect of frequency on lifetime was observed also in [23]. This trend is different from the effect of frequency in the plasticity-controlled failure regime; hence, the effect of frequency can also be used for the identification of failure mechanisms.

2.3 Experiments

2.3.1 Materials

Three different materials were utilized in this study. Glass reinforced UD tape with a polypropylene matrix with a weight averaged molecular weight of $M_w = 150$ kg/mol and a

polydispersity index (M_w/M_n) of 5.2 was kindly provided by SABIC FRT. Cetex® TC1200 carbon/PEEK tape was purchased from TenCate and carbon/PEKK laminates made of Solvay's APC™ tapes were kindly provided by Fokker Aerostructures. Note that only carbon/PEKK was provided as a laminate, while the other materials were received as tapes. Fiber volume fractions (v_f) and the thicknesses of the tapes, stacking sequence of the corresponding laminates are shown in Table 2.1.

Table 2.1: Material data according to the supplier and datasheets [63,64] and laminate stacking.

Material	v_f [%]	Tape Thickness [mm]	Laminate Stacking
glass/iPP	45	0.25	[90] ₈
carbon/PEEK	59	0.15	[90] ₁₂
carbon/PEKK	58	0.14	[90] ₁₄

2.3.2 Manufacturing and sample preparation

Glass/iPP and carbon/PEEK laminates were manufactured using compression molding, while Carbon/PEKK laminates were manufactured at Fokker Aerostructures by vacuum bagging in an autoclave. The reader is referred to the datasheet of the tape [64] for the processing parameters of carbon/PEKK. The following discussion about the manufacturing of the laminates will concern only glass/iPP and carbon/PEEK laminates.

Table 2.2: Processing parameters of the laminates. Values for carbon/PEKK are taken from [64].

Material	Consolidation temperature [°C]	Consolidation pressure [bars]	Dwell time [min]	Cooling rate [°C/min]
glass/iPP	220	2	10	4.4
carbon/PEEK	385	20	20	5
carbon/PEKK	371	7	20	Max 20

Initially, tapes are cut in required dimensions according to the size of the picture frame mold utilized. The picture frame was placed in a press and heated up to the consolidation pressure. In the meantime, a small pressure of about 1 bar was applied to ensure the contact and heat transfer between the plates of the press and the mold. Once the consolidation temperature was reached, the pressure was increased to the consolidation pressure and kept at that level until the end of the pressing cycle. Cooling started after a dwell at the consolidation pressure and temperature. Approximate cooling rates applied, which are dictated by water cooling, consolidation temperatures and pressures, and dwell times for each material are listed in Table 2.2.

The specimens were cut from the laminates by using a diamond saw with the help of cutting water to prevent over-heating. While glass/iPP was tested in uniaxial tension, carbon/PEEK and

carbon/PEKK were tested under 3-point bending due to a large number of specimens failing at or close to clamps in uniaxial testing of these material systems. For both uniaxial and 3-point bending testing. Dimensions of specimens are listed in Table 2.3, and Figure 2.6 shows the schematic drawing of the specimens.

Table 2.3: Specimen dimensions.

Uniaxial tests				
Material	Width [mm]	Grip length [mm]	Grip-to-grip sep. [mm]	Thickness [mm]
glass/iPP	20	20	80	2
3-point bending tests [61]				
Material	Width [mm]	Span length [mm]	Specimen Length [mm]	Thickness [mm]
carbon/PEEK	15	35	52.5	1.75
carbon/PEKK	15	40	60	2

Figure 2.6: Schematic drawing of (a) 3-point bending and (b) uniaxial test specimens. The drawings at the top and bottom part of the figure correspond to the front and top views, respectively.

2.3.3 Mechanical tests

In this study, three types of mechanical tests are conducted, which are constant-strain-rate, creep and fatigue tests. As mentioned before, glass/iPP was tested in uniaxial tension, while

carbon/PEEK and carbon/PEKK were tested under 3-point bending to avoid failure at the clamps. All the tests except some of the constant-strain-rate tests of carbon/PEKK were carried out at room temperature. Constant-strain-rate, creep and fatigue tests (with a frequency (f) of 0.06 Hz) were conducted using Zwick/Roell Z005 and Z5.0 universal tensile testers equipped with load cells with capacities of 2.5 kN and 5 kN. For uniaxial fatigue tests of glass/iPP, a servo-hydraulic MTS testing system equipped with a 2.5 kN load cell was used. For flexural fatigue tests with a frequency of 1 Hz and 10 Hz, an Instron ElectroPuls E1000 with a 1 kN-capacity load cell was utilized.

Constant-strain-rate tests were conducted at constant crosshead speeds that correspond to strain rates from 10^{-7} s^{-1} to 10^{-1} s^{-1} . Strains measured from crosshead displacements are utilized to plot strength vs. applied strain rate curves and Sherby-Dorn plots. A clip-on extensometer was utilized to plot stress vs strain curves in uniaxial tests as in Figure 2.7. For 3-point bending tests, the maximum tensile stress and strain rate occurring at the outer surface and mid-length of the specimens were considered and calculated according to [65]. In constant-strain-rate tests, at least 3 specimens were tested per strain rate. In creep and fatigue tests, the maximum stress was applied in less than 10 s. Frequencies and stress ratios utilized in fatigue loading for each material are summarized in Table 2.4. All the fatigue tests were done with a sinusoidal stress waveform except the one with $f=0.06 \text{ Hz}$, which was done with a sawtooth waveform.

Table 2.4: Frequencies and stress ratios utilized in the fatigue tests performed. “(s)” denotes the sawtooth waveform.

glass/iPP	carbon/PEEK	carbon/PEKK
$f = 1 \text{ Hz}, R = 0.1$	$f = 0.06 \text{ Hz}, R = 0.1 \text{ (s)}$	$f = 1 \text{ Hz}, R = 0.1$
$f = 10 \text{ Hz}, R = 0.1$	$f = 1 \text{ Hz}, R = 0.1$	$f = 10 \text{ Hz}, R = 0.1$
	$f = 10 \text{ Hz}, R = 0.1$	

2.4 Results and Discussion

In this section, first, the applicability of the lifetime prediction method for the plasticity-controlled failure to the composites will be discussed. This will require a comparison of the short- and long-term behavior. Subsequently, the effect of stress ratio and frequency on the lifetime will be investigated to identify the failure mechanisms. Results of glass/iPP will be reported first, which will be followed by carbon/PEEK and carbon/PEKK.

2.4.1 Glass/iPP

In the “Background” section, we introduced a lifetime prediction methodology for plasticity-controlled failure which was based on identical yield conditions in constant-strain-rate and creep tests. In this method, the yield was taken as the moment when stress attains a maximum constant value in a constant-strain-rate test and the strain rate reaches a minimum constant value in a creep test. To investigate whether these conditions hold also for composites, we will discuss constant-strain rate and creep behavior in more detail.

Figure 2.7: Stress-strain behavior of glass/iPP measured by constant-strain-rate tests.

Figure 2.7 presents the stress-strain curves obtained from constant-strain-rate tests at various strain rates. It demonstrates that while glass/iPP tends to display macroscopic yielding at low strain rates, it shows pre-yield failure at higher strain rates. Strength increases considerably with strain rate, while the opposite is valid for strain-to-failure. In the linear, low-stress range it can be observed that the modulus also increases considerably with strain rate. Figure 2.8a shows the evolution of strain with time during creep (note that the creep load is applied in the first 10 seconds, which is subtracted from the time-to-failure). Upon an increase in the creep stress, initial strain levels and creep rates increase and time-to-failure decreases. The data in Figure 2.8a can be used to plot the evolution of the creep rate as a function of strain, a so-called Sherby-Dorn plot [55], which is given in Figure 2.8b. It is seen in the Sherby-Dorn plot that the strain rate decreases continuously in the primary creep regime. At high loads, failure tends to take place before the secondary creep regime is reached. At lower loads, secondary creep, and therefore macroscopic plastic flow, is observed.

Figure 2.8: (a) Strain vs. time and (b) Sherby-Dorn plots from creep tests of glass/iPP.

Since macroscopic yield is not reached at every test, the maximum stress attained, which is the “tensile strength”, will be considered when we discuss the strain-rate dependence of the short-term strength. Likewise, regardless of the presence of macroscopic yield in creep, which is termed also as “plastic flow”, the minimum creep rate is taken into account to analyze its dependence on creep stress. In Figure 2.9a, the strain-rate dependence of the tensile strength is presented at various strain rates, indicated by circular markers. It can be recognized that the transverse strength of glass/iPP has a linear relationship with the logarithm of the applied strain rate, similar to that observed in neat polymers. The full line in Figure 2.9a is a line of best fit with Equation (2.3), resulting in the parameters provided in Table 2.5.

To analyze the equivalence between the failure observed in constant-strain-rate and creep tests, the minimum creep rates obtained from Figure 2.8b are also plotted in Figure 2.9a (diamond markers), showing excellent agreement. Despite the fact that pre-yield failure was observed in some tensile and creep tests, the stress-dependence of the minimum creep rate is, similar to the case of plastic flow kinetics (Figure 2.4), equivalent to that observed in constant-strain-rate experiments. The long-term performance, measured in static (creep) as well as in cyclic loading, is presented in Figure 2.9b, which shows maximum applied stress versus the time-to-failure for glass/iPP under creep and fatigue loading.

Figure 2.9: (a) Creep stress dependence of the minimum creep rate superimposed on the plot of the strain rate dependence of the tensile strength. (b) Creep and fatigue ($R=0.1$) behavior of glass/iPP. Line in (a) is described by Equation (2.3). Lines in (b) are the lifetime predictions according to Equations (2.6) and (2.8). Error bars represent a confidence interval of 95%.

Figure 2.10: Minimum creep rate versus time-to-failure for glass/iPP. Markers represent experimental data and the line represents the fit with Equation (2.5).

The lifetimes measured in creep are plotted versus the corresponding minimum creep rate in Figure 2.10, in a double logarithmic presentation. The data shows a trend that corresponds well with the slope of -1 that is expected for plasticity controlled failure [66], and the drawn line is a fit with Equation (2.5), yielding the critical strain, ϵ_{cr} , listed in Table 2.5. The full line in Figure 2.9b represents the lifetime in static loading represented by Equation (2.6), using the parameters listed in Table 2.5. Hence, the slope of this line is identical to that of the strain rate dependence of the tensile strength, but opposite in sign; it is clear that the data is well represented by this description. This is not surprising, given the equivalence in the deformation kinetics of both loading histories, demonstrated in Figure 2.9a.

Table 2.5: Fit parameters for glass/iPP.

σ_0 [MPa]	$\dot{\epsilon}_{0,T}$ [s^{-1}]	ϵ_{cr}
0.82	$1.03 \cdot 10^{-14}$	$1.2 \cdot 10^{-3}$

A strong confirmation of the role of plasticity is found in the response of long-term cyclic loading. Figure 2.9b also presents the lifetime measured in cyclic loading at frequencies of 1 and 10 Hz, which show a marked *increase* of lifetime compared to that in static loading. Additionally, it is observed that the stress-dependence of the lifetime is very comparable for both frequencies experimentally covered. Both observations give evidence that failure in this regime is plasticity-controlled [23,24,35]. Further support is found in applying the framework for the prediction of plasticity-controlled failure (represented by Equations (2.7) and (2.8)) to *predict* the lifetime in cyclic loading using the parameters listed in Table 2.5, which are determined from the strain rate dependence of the tensile strength (parameters σ_0 and $\dot{\epsilon}_{0,T}$), and the stress-dependence of the lifetime in static loading (ϵ_{cr}).

The resulting *prediction* of the lifetime in cyclic loading, represented by the dashed line in Figure 2.9b, agrees excellently with the data experimentally obtained. The method yields the same predictions for $f=1$ Hz and $f=10$ Hz, which is clarified in Figure 2.11 where the accumulation of plastic strain is presented as a function of time. In static loading, the accumulation of plastic strain evolves at a constant, high rate, evidenced by the steep slope of the line. In cyclic loading, such a high rate is observed only at the high stress levels of the load cycles, followed by an almost inactive region in the low-stress region. As a result, the average rate is far lower compared to that of static loading, leading to longer failure times. The shift in the lifetime resulting from the delayed accumulation of plastic strain is almost 1 decade, which is significant.

All these observations give evidence that the long-term behavior of glass/iPP is plasticity-controlled over the entire load range experimentally covered although the deformation was significantly localized due to the fiber reinforcement.

Figure 2.11: Accumulation of plastic strain as a function of time for glass/iPP under static and cyclic loading at the same value of the maximum stress. A representative stress profile for static and cyclic loading is given in Figure 2.3.

2.4.2 Carbon/PEEK

Figure 2.12: (a) Transverse stress-strain response of carbon/PEEK at various strain rates and (b) Sherby-Dorn plots of carbon/PEEK from creep tests at various stress levels.

Figure 2.12a shows the stress-strain curves for carbon/PEEK laminates loaded transversely at different strain rates. In contrast to the stress-strain response of glass/iPP, macroscopic yield is never observed and the modulus is almost insensitive to the applied strain rate. Sherby-Dorn plots for various creep loads, presented in Figure 2.12b, only show signs of macroscopic plastic flow at some tests. A thing to note is the large amount of scatter in the data; in Figure 2.12b different creep stresses result in flow rates that are close to each other. In addition to the scatter in creep, the material also exhibits considerable scatter in its transverse strength measured under constant-strain-rate, presented in Figure 2.13a, where the dependence of minimum creep rate on the creep stress is also presented. The average standard deviation in the strength of

carbon/PEEK is 11.4% of its mean strength at 10^{-4} s^{-1} (with a confidence interval of 95%), which is almost twice the value for glass/iPP, which is 6.1%.

Despite the large scatter, the minimum creep rate data in Figure 2.13a, represented by the diamond markers, follow the general trend and are well within the error band. The full line in Figure 2.13a is a fit with Equation (2.3), using the parameters provided in Table 2.6. The long-term performance of carbon/PEEK is presented in Figure 2.13b, where the maximum applied stress is plotted versus the time-to-failure for both static (creep) as well as and cyclic (fatigue) loading. Similar to the procedure for glass/iPP, a double logarithmic plot of the minimum creep rate versus the corresponding time-to-failure is constructed; represented in Figure 2.14. The data shows a clear trend with a slope of -1 and is well described by Equation (2.5), yielding the value of the critical strain ε_{cr} listed in Table 2.6. Using the ε_{cr} , in combination with the kinetic parameters σ_0 and $\dot{\varepsilon}_{0,T}$ also shown in Table 2.6, Equation (2.6) leads to a creep lifetime prediction in Figure 2.13b shown by the full line and the error band: the creep data in Figure 2.13b follow a low slope which is comparable to the slope of the line in Figure 2.13a. This correspondence between short- and long-term behavior agrees with the principles of the plasticity-controlled failure.

Figure 2.13: (a) Creep stress dependence of the minimum creep rate superimposed on the plot of the strain rate dependence of the tensile strength. (b) Creep and fatigue ($R=0.1$) behavior of carbon/PEEK. The line in (a) is described by Equation (2.3) and the gray error band indicates the average scatter in the rate-dependent strength with a confidence interval of 95%. In (b), the full line and the error band are the predictions for creep according to Equation (2.6) and the dashed line is the prediction for $f=0.06\text{ Hz}$ (Equation (2.8)), while the other lines are guides-to-the-eye. Fit parameters for the full lines are given in Table 2.6.

Figure 2.14: Minimum creep rate versus time-to-failure for carbon/PEEK. Markers represent experimental data and the line represents the fit with Equation (2.5).

Table 2.6: Fit parameters for carbon/PEEK.

σ_0 [MPa]	$\dot{\epsilon}_{0,T}$ [s^{-1}]	ϵ_{cr}
1.34	$3.24 \cdot 10^{-39}$	$2.5 \cdot 10^{-4}$

Figure 2.15: Influence of frequency on the cycles-to-failure for carbon/PEEK. Lines are guides-to-the-eye.

Next, the fatigue behavior of carbon/PEEK will be discussed. Cyclic testing of this material is carried out at frequencies of 0.06 Hz, 1 Hz, and 10 Hz. It can be seen in Figure 2.13b that cyclic loading with a frequency of 0.06 Hz and a stress ratio of 0.1, represented by the black square markers, follow a trend that is similar to the creep data. This would be expected in the case of plasticity-controlled failure, shown by the cyclic lifetime prediction according to Equation (2.8), using the parameters from Table 2.6, represented by the dashed line in Figure 2.13b. However, the increase in lifetime is not very clearly observed in the experimental data. This is thought to

be related to the scatter in the time-dependent strength. Upon an increase in frequency to 1 Hz, the failure kinetics change, indicated by a strong change in slope that is characteristic for the onset of crack-growth controlled failure. This is confirmed by the experimental results at 10 Hz, represented by the green triangular markers, where the time-to-failure is clearly reduced compared to the 1 Hz data, whereas the kinetics of both (slope) compare well. Our observations concerning the change in failure kinetics from creep to fatigue ($f=1, 10$ Hz) agree well with the findings of Nakada et al. [15] on the long-term behavior of transversely loaded carbon/PEEK, where cyclic data with $f=2$ Hz and $R=0.05$ and creep data have a pronounced difference in the slopes of stress vs time-to-failure curves. Moreover, when we plot the fatigue data versus cycles-to-failure, see Figure 2.15, the 1 Hz and 10 Hz data collapse, indicating that the lifetime for these frequencies is controlled by the number of cycles-to-failure. However, this is not the case for the high-stress region where the $f=0.06$ Hz data is located. At high stresses, we enter the plasticity-dominated region and the slope of the data becomes lower. Lin et al. [67] reported a similar trend for the cyclic behavior of an angle-ply carbon/PEEK laminate, whose behavior is also matrix dominated. Overall, these results suggest that failure mechanisms of carbon/PEEK under cyclic loading depends on the load level: while at higher loads the contribution of plasticity is recognizable, at lower loads crack-growth-controlled failure dominates.

2.4.3 Carbon/PEKK

Figure 2.16: (a) Transverse stress-strain response of carbon/PEKK at various strain rates, and (b) Sherby-Dorn plots of carbon/PEEK from creep tests at various stress levels.

Figure 2.16a shows the stress-strain curves for carbon/PEKK laminates loaded transversely at different strain rates. Similar to carbon/PEEK, there is no sign of macroscopic yield, the modulus is also insensitive to the applied strain rate. Sherby-Dorn plots for various creep loads, presented in Figure 2.16b, show the predominance of pre-yield failure. Similar to Carbon/PEEK, there is also

substantial scatter in the performance. This is clearly observed in Figure 2.17a, where the transverse strength measured under constant-strain-rate is presented including the minimum creep rate data. The average standard deviation in the strength of carbon/PEKK is 13.6% of its mean strength at 10^{-4} s^{-1} (considering strain rates from 10^{-6} s^{-1} to 10^{-3} s^{-1} and a confidence interval of 95%).

The minimum creep rate data suggests a change in slope with decreasing strain rate. Such behavior is quite common in unfilled thermoplastics and may be related to:

i) *Multiple deformation processes contributing to the stress*

The stress contributions of two individual deformation processes with different deformation kinetics [48–52,66,68]; these stress contributions act additively (Equation (2.4)), and the change of slope is related to the onset of the stress contribution of the second process.

ii) *Physical aging*

The amorphous phase of PEKK is in the glassy state and subject to physical aging. The result is an increase in the yield stress in time. This process is accelerated by stress, which may lead to a selective increase of the yield stress at low strain rates where the material is under stress for longer periods of time [23,62,69–71].

Figure 2.17: (a) Creep stress dependence of the minimum creep rate superimposed on the plot of the strain rate dependence of the tensile strength and (b) creep behavior of carbon/PEKK. Note that the minimum creep rates plotted are all from completed creep tests, i.e., they do not belong to run-out tests. The lines in (a) and (b) are described by Equations (2.4) and (2.6), respectively. Error bands indicate the average scatter in the rate-dependent strength with a confidence interval of 95%.

In both cases, the strain rate at which the transition is observed should increase with an increase in the testing temperature. The transverse strength data of carbon/PEKK measured at a temperature of 70 °C, presented in Figure 2.17a with the black circular markers, clearly gives

evidence of such a shift. This indicates that additional kinetics is involved, which can be related to a second deformation process or physical aging, but the reason for the slope change cannot be identified uniquely. The standard approach for the identification would be to perform creep tests and monitor the increase of the (yield) strength in time [62,69–71]. For this, multiple samples would need to be tested at the same creep load for different loading times, and subsequently subjected to a constant-strain-rate experiment to determine the strength. Given the large amount of scatter in the carbon/PEKK laminates, such a study is not conducted.

Although the exact reason for the deviation cannot be determined, it is clear from Figure 2.17b, where the maximum applied stress is plotted versus the time-to-failure in static loading, that the long-term response has kinetics that compares well to that at low strain rates in Figure 2.17a. To directly compare the strain rate dependence of the strength to the long-term data, the data in Figure 2.17a was fitted using the Ree-Eyring expression given in Equation (2.4); the fit should be regarded as a guide-to-the-eye. However, the obtained expression could, in combination with a critical strain ε_{cr} , be used to predict the lifetime in static loading, represented by the full line and error band in Figure 2.17b. The critical strain is determined from a double logarithmic plot of the minimum creep rate data versus the corresponding time-to-failure, represented in Figure 2.18, from a fit of the data with Equation (2.5). The data again shows a clear trend with a slope of -1, and is well described by Equation (2.5), yielding a value for the critical strain ε_{cr} of 10^{-4} .

From Figure 2.17b, it is clear that the creep lifetime data also displays a lot of scatter. Within experimental error, however, it appears to agree with the estimates following from the plasticity-controlled failure kinetics. Yet, due to the severe scatter, it is hard to give a definitive assignment of the failure mechanism. At this point, it is helpful to discuss the effect of cyclic loading on long-term failure kinetics.

Figure 2.18: Minimum creep rate versus time-to-failure for carbon/PEKK. Markers represent experimental data and the line represents the fit with Equation (2.5).

Figure 2.19a presents the stress dependence of the lifetime of carbon/PEKK in cyclic loading at frequencies of 1 Hz and 10 Hz and a stress ratio $R=0.1$. Figure 2.19a shows that under cyclic loading at 1 Hz, the stress dependence of time-to-failure shows a steeper slope compared to creep loading, indicating a change in the failure kinetics. Moreover, the scatter seems to be reduced, which might also suggest a different failure mechanism than in creep loading. Figure 2.19a also demonstrates that failure is accelerated by an increase in frequency, which agrees with crack growth-controlled failure. In order to investigate this further, the maximum applied stress is plotted against the number of cycles-to-failure in Figure 2.19b. Similar to the observation in Figure 2.15 for carbon/PEEK, failure appears to be controlled by the number of cycles, rather than by time; a response that is typical for crack-growth controlled failure.

Figure 2.19: The effect of frequency on (a) time-to-failure and (b) cycles-to-failure for carbon/PEKK. The lines are guides-to-the-eye.

2.5 Conclusion

In the present work, we investigated whether the “plasticity controlled” failure mechanism, which had previously been identified for neat thermoplastics, also plays a role in the long-term behavior of transversely loaded UD composites.

The plasticity-controlled failure mechanism dominated both creep and fatigue behavior of glass/iPP over the entire load range covered. Application of creep and cyclic loading (investigating the effect of stress ratios of 1 and 0.1) and comparing the lifetime at the same maximum stress was used as a method for the identification of failure mechanisms. A decrease in the stress ratio led to an increase in the lifetime. Time-to-failure was independent of the frequency of the cyclic loading. An excellent relationship was observed between short-term

constant-strain-rate tests and long-term creep and fatigue tests. This served as a method to predict the lifetime under long-term loading using short-term tests.

Nevertheless, the dominant failure mechanism was observed to be dependent on the load type and level for carbon/PEKK and carbon/PEEK. Creep failure of both materials showed indications of plasticity-controlled failure through the relationship between creep and the constant-strain-rate tests and different failure kinetics (such as the slope of stress vs time-to-failure graph) compared to fatigue behavior at lower loads. At low loads, an increase in the frequency accelerates the cyclic failure and cycles-to-failure is independent of the frequency. Thus, cyclic failure of carbon/PEEK and carbon/PEKK can be classified as crack-growth-controlled for a large load range. However, fatigue behavior at higher loads showed a clear contribution of plasticity indicated by a change in the slope of the stress vs time-to-failure graph.

Regardless of the dominant failure mechanism, the deformation was highly localized for all materials, which led to a brittle macroscopic appearance of the fracture surface.

Creep tests of all materials showed that a “critical strain”, which is independent of the magnitude of long-term loading, exists, similar to the behavior of neat thermoplastics in the plasticity-controlled regime. This is also an indication of the plasticity-dominated creep behavior of all materials we investigated. This critical strain was helpful for the prediction of the lifetime under plasticity-controlled failure conditions.

All in all, the identification of the failure mechanisms was concluded to be essential for the composites studied. Since plasticity-controlled failure is heavily influenced by parameters such as processing conditions, testing temperature, and physical aging; its identification is expected to have a high impact to account for the effect of these parameters on the characterization of long-term performance of thermoplastic composites in future studies.

2.6 References

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Chapter 3: Long-term failure of transversely loaded glass/iPP

Abstract

Thermoplastic composites are prone to creep and fatigue failure under transverse loading, where the behavior is matrix-dominated. Hence, lifetime prediction methods are necessary for their use in engineering applications; and proposing the right lifetime prediction methodology requires long-term failure mechanisms to be identified. In Chapter 2, at room temperature, glass/iPP was shown to exhibit plasticity-controlled failure, which is a long-term failure mechanism intrinsic to the high-stress response of neat thermoplastics.

In this study, the aim is to identify the failure mechanisms at high temperatures, which accelerates the failure and helps to reach time scales longer than those studied at room temperature, and, based on the mechanisms, propose a lifetime prediction methodology. Furthermore, it is also aimed to address the effect of cooling rate on time-dependent behavior. As a methodology, we study the time-dependent behavior of the neat matrix as well to reveal the link between the behavior of the composite and the neat matrix.

Testing at elevated temperatures revealed that similar to neat iPP, glass/iPP also showed multi-process (plasticity-controlled) deformation kinetics. Ree-Eyring approach [1] was used to model the multi-process failure. Similar to the observations at room temperature in Chapter 2, failure kinetics under constant-strain-rate and creep tests were found to be identical, which allowed us to use a creep lifetime prediction methodology based on short-term tests. Application of cyclic loading decelerated the failure, which pointed out that the lifetime was controlled by plasticity also at higher temperatures: a switch to crack-growth-controlled failure was not detected. The cooling rate was found to have a profound influence on the time-dependent failure: a decrease in the cooling rate led to considerable embrittlement, which altered the failure kinetics such as the rate dependence.

3.1 Introduction

Thermoplastic composites have recently drawn increasing attention thanks to their advantages such as light-weight, high specific strength, recyclability and suitability for mass-manufacturing. Their use is expected to increase even more with the growing interest in electric cars following the new governmental policies in an attempt to reduce CO₂ emissions. Glass fiber reinforced iPP, which combines the strength of glass fibers and cost-effectiveness of iPP, stands as a strong candidate for the aforementioned engineering application. Nevertheless, these materials are prone to long-term (creep and fatigue) failure due to the time-dependent behavior of the matrix [2–5]. Understanding the long-term behavior of thermoplastic composites is essential for lifetime predictions, which is required for safe and reliable application of load-bearing composite products.

Long-term failure is crucial especially in the transverse direction, where the matrix dominates the overall response. In multidirectional laminates under long-term loading, multiple cracks are formed in the transverse layers [6–8]. These cracks may later cause other types of damage such as the delamination and lead to ultimate failure. Hence, matrix-dominated time-dependent damage plays a critical role in the long-term behavior of thermoplastic composites. A feasible and straightforward approach to studying matrix-dominated long-term behavior is to study the long-term behavior of UD (unidirectional) laminates, which eliminates the effects of the neighboring plies on the damage development in the transverse layers. In contrast to the damage evolution in multidirectional laminates, the evolution of a single crack governs the lifetime of transversely loaded UD laminates.

Since the transverse behavior of the composites is matrix-dominated, a discussion of the intrinsic long-term behavior of thermoplastics is useful. Short fiber-reinforced [9] and neat thermoplastics [10–12] show two main stress-dependent long-term failure mechanisms: plasticity-controlled failure and slow crack growth. These mechanisms are illustrated in Figure 3.1 for polyethylene, which is a commonly studied material for pressurized pipe applications [10]. Plasticity-controlled failure is seen at high stress levels and short failure times. In this regime, applied stress leads to plastic flow, which causes failure once a critical level of accumulated plastic strain is exceeded. Slow crack growth is observed at lower stresses and longer timescales and displays a steeper slope in the stress vs. time-to-failure curve. In this regime, lifetime is dominated by the steady growth of cracks that form from precursors or that are already present, until they reach a critical length and become unstable. Since the two mechanisms possess different kinetics, the change from plasticity to crack growth is accompanied by a change in slope, as shown in Figure 3.1.

Figure 3.1: Hoop stress vs. lifetime data showing plasticity (hollow markers) and crack growth-controlled (full markers) failure regimes for a high-density polyethylene pipe subjected to pressure. Markers with an arrow indicate run-out tests. Reproduced from [10].

Identification of the failure mechanisms mentioned is important for matrix-dominated long-term behavior since each failure mechanism requires a different method for lifetime prediction and improvement. For this reason, in Chapter 2, we identified the failure mechanisms in transversely loaded thermoplastic composites tested at room temperature, where glass/iPP was one of the materials studied. In that study, the stress range experimentally covered led to failure mostly in a day, and only a single slope was observed in the long-term stress vs. lifetime plot, which did not signal a change in the failure mechanism. Based on a methodology for identifying the failure mechanisms, we revealed that plasticity was the dominant mechanism in the experimental range covered, in contrast to the common understanding in composites that their long-term failure is controlled by a brittle crack growth mechanism. Extension of this study to longer time scales, which would be encountered in the practical applications, is necessary, whereas conducting long tests is experimentally demanding and not practical. Therefore, there is a need for accelerating the long-term failure, which can be achieved via testing at elevated temperatures. High-temperature testing helps to accelerate the failure especially in the plasticity-controlled regime, which was the failure mechanism observed for glass/iPP in Chapter 2. An example of this can be found in the work of Lang et al. [10], where increasing the temperature of a medium-density polyethylene by 10°C accelerates the failure in the plasticity-controlled regime by about 3 decades, in contrast to only half a decade for the crack-growth-controlled regime.

Another benefit of long-term testing at elevated temperatures is that it can help to identify the different deformation processes in the plasticity-controlled failure of thermo-rheologically complex materials [13]. iPP is known to be one of such materials exhibiting multiple deformation processes that contribute to the time-dependent strength [14–16]. Each process has different

kinetics, which results in a change in the slope of the creep stress vs. time-to-failure curve in the plasticity-controlled regime when the time scale of a long-term test at a certain temperature is enough for one of the processes to relax [16,17]. Thus, understanding and determining the temperature and stress dependence of each process helps to develop accurate methods to predict long-term failure and interpret the changes in the trends seen over the experimental time scale.

Last but not least, real engineering applications often require the investigation of the time-dependent behavior at elevated temperatures. For example, in the automotive industry, low weight requirements lead to smaller volumes, resulting in hotter engine compartments. Besides, there is a growing interest in the automotive industry to produce car cross beams and leaf springs made of thermoplastic composites, for which design temperatures up to 65°C and 80°C, respectively, may be needed [18–21].

In addition to temperature, processing history is also known to have a profound effect on short- and long-term behavior of thermoplastics and their composites. The cooling rate has been observed to influence crystallinity [17,22–29] and crystalline microstructure [22,23,29–32] of both fiber-reinforced and neat iPP. In addition, fiber-matrix adhesion is also known to be influenced by the cooling rate [23,24,27,29,33]. Changes in the above-mentioned aspects combined will strongly affect the stress-strain response, long-term and impact behavior of the thermoplastic-based materials. If we focus on the effect of cooling rate on matrix-dominated properties of PP composites, many studies found that the interlaminar fracture toughness decreases with a decrease in cooling rate [22,23,27–29,32]. This was attributed mostly to interspherulitic failure which is a result of weak bonding between the spherulites. On the other hand, it is common in the studies on neat semi-crystalline polymers to attribute the embrittlement at low cooling rates to a low density of tie chains connecting the lamellae [34–36]. Embrittlement was observed also in the tensile strength: Wafai et al. [37] observed that low cooling rates result in embrittlement in the tensile behavior of the neat impact polypropylene, which leads to low in-plane shear strengths for its glass-reinforced composite. An opposite trend was observed by Kabbani and El Kadi [38]; however, no explanation was provided for the trend observed. None of the latter two studies on the transverse tensile strength mentions the effect of cooling rate on the time-dependent behavior; hence, there is a lack of research about the effect of cooling rate on time-dependent behavior of transversely loaded UD laminates. Furthermore, given the complexities and many parameters involved in the effect of cooling rate on transverse time-dependent behavior, we believe that it is essential to investigate its effect on our specific material of interest.

The aim of this study is to investigate and predict the temperature-dependent long-term behavior of transversely loaded UD glass/iPP under static and cyclic fatigue loading and to identify the effect of cooling rate (using three different cooling rates). Long-term tests will be

conducted at several temperatures ranging from room temperature up to 110°C. Strain rate- and temperature-dependent short-term behavior will be characterized to be used for the lifetime prediction based on the plasticity-controlled failure of neat polymers [9,12]. Time-dependent behavior of the neat matrix will also be studied to investigate the link between the behavior of the neat matrix and the composite.

3.2 Experiments

3.2.1 Material and Sample Preparation

Glass-reinforced UD tape with a polypropylene matrix with a weight averaged molecular weight of $M_w = 150$ kg/mol and a polydispersity index (M_w/M_n) of 5.2 was kindly provided by SABIC FRT. The volume and weight fraction of the fibers in the prepreg is 45% and 70%, respectively. Each prepreg had a width of 110 mm and a nominal thickness of 0.25 mm. The neat matrix used was of the same grade as the matrix of the prepreg.

A stack with $[90]_8$ lay-up was prepared in a picture frame mold of 390 mm by 390 mm to be pressed in a Fontijne hot press at the Composite Production Laboratory of the University of Twente. The stack was heated to 220°C, kept at that temperature for consolidation for 10 minutes and then cooled to room temperature. A consolidation pressure of 2 bars was applied. Three different cooling rates, named as slow, medium and fast, were utilized. To obtain the slow cooling rate, the press was shut off and the laminates were cooled by free convection while keeping the pressure on. The medium cooling rate was achieved by activating the water cooling system of the press at its full capacity. For fast cooling, initially, a laminate was pre-consolidated with the medium cooling rate. Later, the laminate was re-heated to 220°C in the mold in an oven to erase the previous manufacturing history and rapidly transferred to the press with cold plates to apply pressure and cool down. The cooling rate was measured by a thermocouple placed at the mid-thickness of the laminate for all cases. The approximate cooling rates that were achieved in the temperature range of crystallization (based on differential scanning calory experiments) are shown in Table 3.1. After making the laminates, composite specimens were cut using a diamond saw. Water was used while sawing to prevent over-heating. Rectangular specimens had a thickness of 2 mm, grip-to-grip separation of 100 mm, width of 20 mm and a grip length of 20 mm.

Table 3.1: Cooling rates applied in for the composite laminates and neat iPP.

Material	Naming	Cooling rate [°C/min]
glass/iPP	Slow	0.7
	Medium	5
	Fast	30
iPP	Slow	< 1
	Controlled cooling	10
	Quenching	1800

Neat iPP was both manufactured and mechanically tested at the Polymer Technology Laboratory of the Eindhoven University of Technology. A Fontijne dual hot press was used. Three different cooling rates were applied: slow cooling, controlled cooling and quenching, which are shown in Table 3.1. A consolidation temperature of 220°C was used for all cases. For slow and controlled cooling, a consolidation pressure of 37.5 bars and a dwell time of 5 minutes were applied. Slow cooling was obtained by shutting the press off and letting the plates cool by free convection, and controlled cooling was achieved by cooling the plates of the press by water at a programmed cooling rate of 10°C/min. For quenching, a consolidation pressure of 25 bars and a dwell time of 3 minutes were used. After the consolidation, the plate was transferred to the cold pair of press plates, which were at 17°C. Since iPP plates were manufactured using different equipment in a different laboratory, the cooling rates obtained were not exactly the same as those of composite plates. For this reason, the cooling rates of neat iPP plates are named as controlled cooling and quenching to differentiate them from the cooling rates used for the composites as shown in Table 3.1. Tensile specimens of the neat matrix material are dumbbell-shaped tensile bars dimensioned according to ISO 527-2-1BA and ISO 527-2-5B for the “quenching” and “controlled-cooling” conditions, respectively.

3.2.2 Crystallinity measurements

Crystallinity was measured by utilizing a Mettler Toledo Differential Scanning Calorimeter (DSC). Composite samples were cut by using a diamond saw from the plates. Since there might be a gradient of cooling rate through the thickness of the laminate, each sample was cut to include all layers of the laminate in order not to have a biased measurement that is representative of only certain layers. For the tests of neat iPP, granules were used and the cooling rate was imposed by the DSC. Composite and neat iPP samples weighed around 12 mg and 7 mg, respectively. At least 3 samples were tested per cooling rate.

DSC tests were performed in two different ways. In the first case, a single scan was carried out using as-manufactured samples. Samples were heated above the melting temperature at a rate of 10°C/min and the heat of melting was determined to calculate the crystallinity. Only the composite samples were tested in this manner. Silicone oil of around 3 mg was used at every run

to enhance the thermal contact between the pan and the sample. Silicone oil was scanned in DSC without a composite sample to determine its heat capacity, which was later used to compensate for the heat transfer to the oil during DSC scans of the composite samples. In the second approach, two consecutive DSC scans are employed. In the first scan, samples were melted and subsequently cooled at constant rates of 0.7, 5, and 20°C/min imposed by the DSC. In the next scan, samples were re-heated at 10°C/min to determine the heat of melting. The second approach was employed to have comparable cooling rates for composites and neat iPP since they were not manufactured with the same cooling rates. Both neat iPP and the composite were tested in this manner. Note that the highest cooling rate imposed by DSC, 20°C/min, was lower than the fast cooling rate of the as-manufactured composite (30°C/min) due to the operation limits of the DSC. The samples were first heated at a heating rate of 10°C/min to 220°C/min to erase the previous manufacturing history, held at that temperature for 5 minutes and afterwards cooled at the cooling rate required. In the second run, the samples were heated to 220°C again to obtain the melting peak that is required for the crystallinity calculation. The silicon oil was not used for the samples for which the cooling rate was imposed by the DSC since after the first melting run the bottom surface of the sample is assumed to have good contact with the pan.

Eventually, the crystallinity is calculated using the formula:

$$X = \frac{\Delta H_m}{\Delta H_f(1 - w_f)} \cdot 100, \quad (3.1)$$

where X is the percent crystallinity, ΔH_m is the heat of fusion (endothermic) determined from the DSC tests, ΔH_f is the heat of fusion (endothermic) of a 100% crystalline material, and w_f is the weight fraction of fibers [39]. w_f was taken as 70% for composites based on the data provided by the tape manufacturer and 0 for the neat iPP. ΔH_f was taken as 207 J/g according to [40].

In addition to the DSC tests, wide-angle x-ray diffraction (WAXD) of the as-manufactured composite plates were also carried out for morphological analysis. A copper anode was used; X-ray wavelength was 1.54 Å. WAXD patterns were recorded with an Eiger 2R 500K detector with a pixel size of 72 x 72 μm^2 located at a distance of 38 mm. For all measurements, the scattering intensity from the background was subtracted from the total intensity.

3.2.3 Uniaxial tensile tests

For composites, creep tests and constant-strain-rate tests up to strain rates of 10^{-2} s^{-1} were conducted using Zwick/Roell universal tensile testers equipped with load cells with capacities of 2.5 kN and 5 kN. Constant-strain-rate test at a strain rate of 10^{-1} s^{-1} at room temperature was

conducted using an Instron 8516 servo-hydraulic testing system thanks to its ability to perform tests at high rates. For the fatigue tests of glass/iPP, a servo-hydraulic MTS testing system equipped with a 2.5 kN load cell was used. For iPP, constant-strain-rate and creep tests are performed on a Z010 Zwick Material Testing Machine equipped with a 1 kN load-cell and fatigue experiments are performed on a servo-hydraulic MTS testing system with a 2.5 kN load-cell. For constant-strain-rate experiments, constant crosshead speeds corresponding to strain rates ranging from 10^{-7} s^{-1} to 10^{-1} s^{-1} are used. In creep and fatigue tests, the maximum stress was applied in 10 s. Fatigue load was introduced in a sinusoidal wave, with a stress ratio of 0.1 and using frequencies (f) of 1 and 10 Hz. The machines were equipped with a temperature chamber for high-temperature testing. The testing temperature ranged from room temperature up to 110°C . The samples were kept in the hot chamber for 10 minutes before performing the high-temperature tests.

3.2.4 Microscopy

Optical microscopy and scanning electron microscopy (SEM) were carried out to investigate the effect of cooling rate on the fracture behavior of glass/iPP constant-strain-rate specimens tested at a strain rate of 10^{-4} s^{-1} . For optical microscopy, a Keyence digital microscope was used. Samples were embedded in epoxy such that the side surface of the fractured specimen can be observed. The samples were later polished using several grades of sandpaper (600, 1200, 2000 and 4000 grits) and a colloidal silica suspension. For the SEM analysis, a Jeol SEM JSM-7200F device was used. Prior to microscopy, the samples were dried for a day at 80°C in a vacuum oven to prevent degassing during SEM observation. Afterwards, they were gold-sputtered with Jeol Auto Fine Coater to form a conductive layer that prevents the charging of the specimen. The fracture surfaces of the specimens were positioned perpendicular to the incident electron beam.

3.3 Results

In this section, crystallinity results will be presented first. Subsequently, temperature and strain-rate-dependent short-term behavior will be discussed, followed by the long-term behavior, where the findings on short-term behavior will be used for the lifetime prediction methodology. The last part of the results section deals with the effect of cooling rate on the time-dependent behavior. In every sub-section, the behavior of the composite will be compared to that of the neat matrix. Note that the constant-strain-rate, creep, and fatigue data of the composite cooled with the medium cooling rate and tested at room temperature is obtained from Chapter 2.

3.3.1 Crystallinity

Figure 3.2a and Figure 3.2b show examples of melting curves of the composite and neat iPP, respectively. The figures show that there are variations in the melting temperatures: as the cooling rate is increased, the shape of the melting peak moves towards lower temperatures, and, in the case of the neat iPP cooled at 20°C/min, double melting peaks are observed. Possible reasons for double melting peaks are the formation of different crystal phases and structures, variations in the crystal sizes and recrystallization [41–44]. Although α -phase is the most common crystal structure formed under moderate conditions [45], a less-ordered form of α -phase may also form under high cooling rates [41,42]. Moreover, the addition of nucleating agents may result in the formation of β -phase, which has a lower melting temperature than the α -phase [45,46]. Since each phase leads to a different scatter pattern, XRD analysis will help understand whether the double melting peak and lower melting temperature observed in some cases are due to different crystal phases. Hence, WAXD profiles of the composite samples cooled with different rates are provided in Figure 3.3a. Figure 3.3a shows that the samples cooled with different cooling rates all display peaks at $2\theta = 9.5^\circ, 11.3^\circ, 12.5^\circ, 14.2^\circ$, and 14.7° , which are common for the α -phase. However, the sample cooled with 30°C/min exhibits an additional peak located around $2\theta = 10.7^\circ$, which is typical for the β -phase [13]. This might explain why multiple peaks and variations in the peak melting temperatures are observed. Another support for the formation of β -phase can be found in Figure 3.3b, which presents cooling curves and peak crystallization temperatures (T_c). Figure 3.3b shows that for cases where either one melting peak at a lower temperature or double melting peaks are observed (glass/iPP 20°C/min, iPP 20°C/min and 5°C/min), T_c lies in the range of 100°C–120°C. In this temperature range, growth rate of β -phase is higher than that of α -phase, which would favor the formation of β -phase [45].

Figure 3.3b also shows that, as expected, the higher the cooling rate, the lower is the crystallization temperature. Furthermore, comparing the T_c of the composite and the neat iPP at the same cooling rate, it is seen that fibers contribute to shifting the T_c to higher temperatures, possibly acting as nucleating agents.

Figure 3.2: DSC melting curves of (a) composites and (b) neat iPP processed with different cooling rates indicated on the curves. (Heating rate: 10°C/min).

Figure 3.3: (a) WAXD profiles of composite samples manufactured with different cooling rates. Gray dashed line indicates the amorphous halo, and the scatter angle is scaled for a wavelength of 1.04 Å. The peaks belong to α -phase unless otherwise indicated. (b) Effect of fiber reinforcement and cooling rate on the crystallization temperature.

Based on the DSC curves, crystallinity is calculated as explained in Section 3.2.2, and the values are shown in Table 3.2 and Table 3.3. Crystallinity is observed to decrease with an increase in the cooling rate both for neat iPP and composite. Furthermore, the level of crystallinity of glass/iPP is higher compared to that of neat iPP, which again shows that fibers are likely to act as nucleation agents. Also note that, at the same cooling rates, regardless of the way cooling rate is imposed, the crystallinity and also the scatter values are similar for the composites; see Table 3.2 and Table 3.3.

Table 3.2: Crystallinity of as-manufactured glass/iPP composites based on first heating in DSC measurements.

Cooling rate	Slow (0.7°C/min)	Medium (5°C/min)	Fast (30°C/min)
Degree of crystallinity (%)	54.8±2.4	52.1±3.6	48.6.0±3.1

Table 3.3: Crystallinity of neat iPP and the composite (G/iPP) based on second heating in DSC measurements (cooling rates are imposed by the DSC in the first scan).

Cooling rate	Slow (0.7°C/min)	Medium (5°C/min)	20°C/min
Degree of crystallinity (%) iPP	51.2±1.0	47.8±0.9	46.2±1.3
Degree of crystallinity (%) G/iPP	55.0±3.9	52.0±3.8	50.1±2.4

3.3.2 Short-term behavior

In this sub-section, the temperature and strain-rate dependence of the tensile strength of the composite will be discussed and compared with the neat iPP. Since quenched iPP was tested at more temperatures than the iPP manufactured with the controlled cooling rate, mainly quenched conditions will be considered for iPP. For composites, experimental evidence on the medium cooling rate will be discussed for the same reason.

Figure 3.4a shows the stress-strain curves of iPP at various temperatures and strain rates. Yield stress, which is the stress at the maximum in the stress-strain curve, shows a substantial dependence on both the temperature and strain rate. An increase in temperature leads to a decrease in the yield stress, whereas an increase in the strain rate leads to a higher yield stress. Similarly, as shown in Figure 3.4b and Figure 3.4c, composites also exhibit a high strain-rate and temperature dependence. Nevertheless, comparing Figure 3.4a to Figure 3.4b and Figure 3.4c, it can be noticed that unlike iPP, the composite displays macroscopic yield only at high temperatures and low strain rates.

The temperature and strain rate dependence of the (yield) strength is presented in Figure 3.5a for the neat iPP, and Figure 3.5b for the composite. In Figure 3.5a, two different regions can be observed with respect to the strain rate dependence: a region at high temperatures and/or low strain rates, where the slope is low, and a region at lower temperatures and/or higher strain rates where the slope is much steeper. This phenomenon is well-known and related to the fact that two separate molecular deformation processes are contributing to the stress [16,17].

Figure 3.4: (a) Stress-strain graphs of iPP-Q (quenched) and (b,c) glass/iPP-med (medium cooling rate) at various temperatures and strain rates.

Figure 3.5: (a) Strain rate and temperature dependence of yield stress of iPP-Quenched and (b) tensile strength of glass/iPP-medium. Markers are experimental data and lines are descriptions according to

Equation (3.3) using the parameters in Table 3.4.

In the case of neat iPP, which is a semicrystalline polymer, these processes are related to the microstructure consisting of crystalline lamellae and amorphous regions. One of the processes is related to the intralamellar deformation caused by crystallographic slip processes [47]. This process is thought to contribute to the total stress at all temperatures and strain rates investigated. At high temperatures and low strain rates, where the slope is low, this process is the only one contributing to the stress. At lower temperatures and higher strain rates, the interlamellar process also starts to contribute to the stress. This process is the well-known α -relaxation, which is also observed in Dynamic Mechanical Thermal Analysis as a transition around 80°C [48]. Although the deformation finds its origin in the interlamellar amorphous regions, the rate-determining step is chain diffusion throughout the crystalline stem [48]. This relaxes tie chains, allowing the interlamellar region to be sheared [49].

Since the mechanical response of the composites is matrix-dominated in the transverse direction, it is not surprising that similar changes in slope are also observed in Figure 3.5b. Comparing Figure 3.5a and Figure 3.5b, it can be recognized that, at the same temperature, the change in the slope takes place at lower strain rates for the composite than for the neat iPP. This is likely to be related to strain localization in the composite, where the applied strain rates are locally amplified due to the heterogeneous microstructure. Another thing to note is the change in the slope of the data points in Figure 3.5b at room temperatures and at strain rates greater than 10^{-3} s^{-1} , which is likely to stem from the contribution of a third process. Such an additional process was revealed also by Caelers et al. [16] for neat iPP and it was linked to the glass transition of the bulk amorphous phase [16,49].

The two-process yield response observed in Figure 3.5a and Figure 3.5b is commonly modeled using the so-called modified Eyring approach [50,51]. In this approach [1], the kinetics of each process is described using Eyring's activated flow theory [52], where each process has its own parameters such as the activation energy and volume. For each process, the theory describes the plastic flow rate under an applied stress σ at a specific temperature as follows:

$$\dot{\epsilon}_{pl}(\sigma, T) = \dot{\epsilon}_0 \exp\left(-\frac{\Delta U}{RT}\right) \sinh\left(\frac{\sigma v^*}{kT}\right), \quad (3.2)$$

where $\dot{\epsilon}_0$ is a rate factor, ΔU is the activation energy, v^* is the activation volume, T is the absolute temperature, k is the Boltzmann's constant and R is the universal gas constant. Rearranging Equation (3.2) and summing the stress contribution from both processes, strain rate ($\dot{\epsilon}$) and temperature dependent total stress is obtained by:

$$\sigma = \sum_{i=I,II} \frac{kT}{v_i^*} \sinh^{-1} \left(\frac{\dot{\epsilon}}{\dot{\epsilon}_{0,i}} \exp \left(\frac{\Delta U_i}{RT} \right) \right), \quad (3.3)$$

where the subscript i indicates the processes I and II . For $\sigma \gg kT/v^*$, Equation (3.3) can be simplified into:

$$\sigma = \sum_{i=I,II} \left(\frac{kT}{v_i^*} \ln \left(\frac{2\dot{\epsilon}}{\dot{\epsilon}_{0,i}} \right) + \frac{\Delta U_i}{v_i^*} \cdot \frac{k}{R} \right). \quad (3.4)$$

In order to fit Equation (3.4) to the data shown in Figure 3.5, a fitting procedure similar to the one described in [53] is used. Activation volume and energy of each process are assumed to be constant [15–17]. The resulting fit parameters are presented in Table 3.4. It is observed in Figure 3.5 that the Eyring approach describes the failure kinetics well, where the lines are described by Equation (3.3) using the parameters presented in Table 3.4. Activation energies and volumes of iPP shown in Table 3.4 are comparable with the values found by van Erp et al. [17]. A comparison of the rate constants is avoided since they depend highly on the state of the material such as the physical age of amorphous domains [13], which is sensitive to processing and service conditions. When we compare the parameters of glass/iPP with those of iPP, we see that activation energies tend to be less for composites, especially for the process I, as shown in Table 3.4. This observation is surprising since the activation energy takes the temperature dependence of deformation into account, which is expected to be identical for the composite and the neat matrix as the matrix, which is the same in both cases, is the deforming constituent. We aim to elaborate on the possible reasons for this observation in Chapter 4 with the help of micromechanical analysis.

Table 3.4: Eyring parameters for iPP-Quenched and glass/iPP-medium.

Material	v_I^* [nm ³]	v_{II}^* [nm ³]	ΔU_I [kJ/mol]	ΔU_{II} [kJ/mol]	$\dot{\epsilon}_{0,I}$ [s ⁻¹]	$\dot{\epsilon}_{0,II}$ [s ⁻¹]
iPP	15.9	2.9	465	166	$5.9 \cdot 10^{51}$	$3.0 \cdot 10^{23}$
glass/iPP	11.5	7.9	254	157	$3.2 \cdot 10^{25}$	$1.7 \cdot 10^{18}$

Figure 3.6: Comparison of (a) stress-strain curves and (b) temperature and rate dependence of the yield stress of neat iPP processes by quenching and controlled cooling. Markers in (b) are experimental data and lines are descriptions according to Equation (3.3) using the activation volumes and energies in Table 3.4 and rate constants in Table 3.5.

So far, we have compared the behavior of quenched neat iPP to the composite which was cooled at a far slower rate due to the availability of more iPP data at the quenched cooling rate. We do not expect a problem in doing so since it was previously shown that the activation energy and volume are not affected by the cooling rate [17]. The only parameter that was shown to change with cooling rate is the rate constant [17], which results in a shift of the fit in the x-axis, thus affecting the comparison of the strain rate at shift from single-process to two-process response. Hence, to check if the yield kinetics of iPP processed with controlled cooling rate can be described by changing the rate constant and its strain rate at shift from single-process to two-process response is still higher compared to the composite, we compare the yield kinetics of iPP processed by quenching and controlled cooling at two temperatures in Figure 3.6. It is seen in the figure that controlled cooling condition results in an improved tensile strength compared to quenching. This is in line with the common trend in thermoplastics: lower cooling rates induce a higher crystallinity and lamellar thickness leading to a higher yield stress [54,55]. As shown by van Erp et al. [17] and confirmed in Figure 3.6b, yield kinetics can be predicted well by using the same activation energies and volumes, but different rate constants (provided in Table 3.5). Comparing Figure 3.5b and Figure 3.6b, it is confirmed that the transition from single-process to two-process response still occurs at a lower strain rate in the composites compared to iPP cooled with the controlled cooling rate, which we previously linked to strain localization.

Table 3.5: Comparison of rate constants for quenched and controlled-cooled iPP.

Material	$\dot{\epsilon}_{0,I} [s^{-1}]$	$\dot{\epsilon}_{0,II} [s^{-1}]$
iPP quenched	$5.9 \cdot 10^{52}$	$3.0 \cdot 10^{23}$
iPP controlled cooling	$2.0 \cdot 10^{48}$	$2.5 \cdot 10^{22}$

3.3.3 Long-term behavior

Creep behavior

Figure 3.7: (a) Creep strain vs time and (b) creep strain rate vs strain for the composite tested at 90°C and 23°C under different creep stress levels. Gray arrows indicate an increase in creep stress.

Creep behavior of the composite is presented in Figure 3.7a, which shows the evolution of creep strain with time at 90°C, and also 23°C, for comparison. As expected, a decrease in the creep stress leads to an increase in the time-to-failure. The data shown in Figure 3.7a can be used to plot the evolution of the creep strain rate with creep strain, a so-called Sherby-Dorn plot [56], as in Figure 3.7b. Sherby-Dorn plots of specimens tested at 90°C reveal three different regions: the

primary creep region where the creep strain decreases, the secondary creep region where the plastic flow rate is constant, and the tertiary creep (at some stress levels) where the strain rate increases until the material eventually fails. It can be argued that the existence of the secondary creep regime, also referred to as “macroscopic flow”, is promoted by an increase in the testing temperature, given that glass/iPP tested at room temperature did not exhibit macroscopic flow at all stress levels as shown in Figure 3.7a. The magnitude of the plastic flow rate depends on the applied stress: as the creep stress is lowered, a lower plastic flow rate is observed.

Lifetime Prediction

It was shown in previous works that the lifetime of the neat iPP can be successfully predicted in the framework of the plasticity-controlled failure [16,17]. In Chapter 2, we demonstrated that the plasticity was the dominant failure mechanism in the long-term behavior of glass/iPP tested at room temperature. Thus, in this section, we are going to use the lifetime prediction methodology for the plasticity-controlled failure which was discussed in detail in Chapter 2 and also in [9,12].

Figure 3.8a and Figure 3.8b show plastic flow rates from Sherby-Dorn plots plotted against applied creep stress and the strain rate dependence of the (yield) strength for the neat iPP and the composite, respectively. Both figures show that an excellent agreement can be observed between the constant-strain-rate and creep tests. Similar to the constant-strain-rate data, an increase in the testing temperature leads to a change in the dependence of the plastic flow rate on the creep stress, which is indicated by a change in the slope of the creep data. The correspondence between the constant-strain-rate and creep data means that stress and temperature-dependent plastic flow rate ($\dot{\epsilon}_{pl}(\sigma, T)$) under a long-term load can be calculated once the constant-strain-rate failure kinetics is characterized by Equation (3.3).

Plotting the plastic flow rates versus time-to-failure in a double logarithmic plot as shown in Figure 3.9a reveals that most of the data lie on a line with a slope of -1. This indicates that the product of plastic flow rate and time-to-failure is a constant, named as the critical strain (ϵ_{cr}), which is calculated to be 0.066. This observation is used to define a failure criterion: in the framework of the plasticity-controlled failure, failure takes place when the accumulated plastic strain $\epsilon_{pl,acc}$ exceeds the critical strain, which can be summarized by the following expression:

$$\epsilon_{pl,acc} = \int_0^t \dot{\epsilon}_{pl}(\sigma, T, t') dt' \quad \text{failure when} \quad \epsilon_{pl,acc} = \epsilon_{cr}, \quad (3.5)$$

where the plastic flow rate is expressed as a function of the time (t') to take into account the change in plastic flow rate during cyclic loading. This allows one to apply Equation (3.5) not only to creep but also to cyclic (fatigue) loading.

It should be noted that at higher temperatures and lower plastic flow rates, the data in Figure 3.9a tends to deviate from the line. The specimens that deviate from the line also had a macroscopically brittle failure, while the others failed in a ductile manner. Hence, the deviation might indicate a change in the failure kinetics, which will be investigated further when creep lifetime predictions are presented.

Figure 3.8: (a) Rate- and temperature-dependent tensile strength together with creep stress dependence of the plastic flow rate for (a) iPP and (b) glass/iPP. Full and open markers represent the constant-strain-rate and creep data, respectively. Gray markers in (a) represent the creep samples that exhibited macroscopically brittle failure. Lines are descriptions according to Equation (3.3) using the parameters in Table 3.4.

Figure 3.9: Plastic flow rate vs time-to-failure at various creep stress levels for (a) iPP-Quenched and (b) glass/iPP-medium. In (a), gray markers represent the samples that failed macroscopically brittle, while the others represent macroscopically ductile failure. Lines are traces of constant critical strain values indicated on figures.

Figure 3.10: Temperature-dependent creep behavior of (a) iPP and (b) glass/iPP. In (a), gray markers represent the samples that failed macroscopically brittle, while the others represent macroscopically ductile failure. Lines except gray-colored ones are lifetime predictions according to Equation (3.5), whereas the gray lines are guides-to-the eye.

Let us now turn our attention to Figure 3.9b, which illustrates the concept of critical strain for the composite. Some high-temperature data with long failure times are not plotted due to the aging effects during testing. Firstly, the data at 23°C and 50°C clearly indicate that the concept of critical strain holds for the composite at these temperatures. Nevertheless, the observation is less clear for higher temperatures. For 90°C and 110°C, creep datapoints with longer time-to-failure tend to follow a slope steeper than “-1”. Similar to iPP, this might be due to embrittlement; however, since the macroscopic failure mode is brittle for composites regardless of the temperature and load level, a strong statement cannot be made at this point. Another observation that can be made in Figure 3.9b is that the critical strain depends on the testing temperature, in contrast to what was seen for the iPP. The critical strain increases from 0.0012 at room temperature to 0.0036 at 50°C, which might indicate that the material’s ability to experience plastic deformation increases with temperature. Note also that the critical strains calculated for the composite are significantly lower than that of iPP due to the localized deformation in the composite resulting from the fiber reinforcement. This is not surprising considering also the lower creep strain levels observed for the composite, as shown in Figure 3.7. For the lifetime prediction, critical strains of 0.0012 and 0.0036 are used for the room temperature and other temperatures, respectively.

Figure 3.10a presents the effect of temperature on the creep behavior of iPP and the lifetime predictions. Creep strength shows a considerable dependence on the temperature. Moreover, the slope of the creep data indicating the stress dependence of the time-to-failure shows a change at high temperatures and/or low strain rates. This is a sign that failure kinetics of the

short-term behavior, which show multiple slopes due to multiple failure processes, have implications on the creep behavior. Lifetime prediction indicated by the lines describes most of the data well; however, the creep data at high temperatures and low stresses deviate from the prediction indicating a change in the failure kinetics and mode: also shown by the macroscopic failure mode, failure becomes brittle. These data points are exactly the ones that deviate also from the line describing a constant critical strain in Figure 3.9a.

Next, with Figure 3.10b, stress and temperature-dependent creep behavior of the composite and its prediction is discussed. It can be seen in Figure 3.10b that high temperatures lead to a remarkable decrease in the creep strength also for the composite: for instance, when the temperature is raised from room temperature to 90°C, the creep strength decreases by half. Similar to neat iPP, two different slopes are observed, which indicate two different failure processes. This is a remarkable sign that the creep behavior of the neat matrix plays a significant role on the creep behavior of the transversely loaded composite. At high temperatures, there is not a significant change in the trend of the data with decreasing creep stress; thus, a transition from plasticity- to crack growth-controlled failure cannot be detected. Eventually, the lifetime prediction shown by the lines captures the two-process failure kinetics and describes most of the creep data reasonably well. This shows that the lifetime prediction method based on the plasticity-controlled failure of neat thermoplastics can be successfully applied to transversely loaded glass/iPP as well.

Cyclic behavior: identification of failure mechanisms

Since the crack growth-controlled failure mechanism is active at lower stresses compared to plasticity-controlled failure and it leads to a steeper slope compared to the plasticity-controlled failure, a switch to the crack growth controlled failure might be the underlying reason for the deviation of iPP creep data points from the lifetime prediction at high temperatures and/or long time scales (Figure 3.10a). Previous research has shown that the application of cyclic loading and comparing the lifetime at the same maximum stress helps to identify the underlying long-term failure mechanism [2,9,57]. In the plasticity-controlled regime, cyclic loading leads to a longer lifetime compared to creep loading, while in the crack growth controlled regime the trend is opposite, as illustrated in Figure 3.11. Moreover, while the time-to-failure is frequency independent in the plasticity-controlled regime, it is highly frequency dependent in the crack growth-controlled regime where the higher the frequency, the lower is the time-to-failure. Given these observations, to investigate the underlying failure mechanisms further, static (creep) and cyclic (fatigue) behavior of the composite and the neat iPP will be compared. Furthermore, the lifetime prediction method that was previously introduced will be applied to cyclic long-term loading.

Figure 3.11: (a) Static and cyclic (same stress ratio, two different frequencies) load vs. time and (b) plasticity- and crack growth-controlled regimes under these loads.

Figure 3.12: Creep and cyclic behavior of (a) iPP and (b) glass/iPP at room temperature and a high temperature. In (a), gray markers represent the samples that failed macroscopically brittle, while other markers represent macroscopically ductile failure. Lines except gray-colored ones are lifetime predictions according to Equation (3.5), whereas the gray lines are guides-to-the eye.

Figure 3.12 presents the creep and fatigue ($R = 0.1$, $f = 1$ and 10 Hz) data of the composite and the neat iPP at 23°C and elevated temperature. Firstly focusing on iPP, it is seen in Figure 3.12a that at 23°C cyclic loading with $f = 10$ Hz results in longer failure times compared to creep, which indicates the dominance of plasticity. Similarly, at 80°C , failure shifts to longer timescales with the application of cyclic loading with $f = 10$ Hz. Therefore, comparison of creep and fatigue data ($f = 10$ Hz) indicates that the failure is plasticity-controlled. However, similar to creep data, at lower stress levels slope of the fatigue data changes and the macroscopic failure becomes brittle. To have a better understanding of the underlying failure mechanisms, the effect of frequency is

also investigated at 80°C by applying cyclic loading with $f = 1$ Hz. It can be seen that at high loads the lifetime is independent of the frequency, which indicates the dominance of the plasticity-controlled failure. However, in the low-stress regime, 10 Hz leads to shorter lifetimes compared to 1 Hz, which is typical for the crack growth-controlled failure. Thus, an intermediate type of failure is believed to be present at low creep stresses at 80°C: while the stress ratio dependence suggests plasticity-controlled failure, the frequency dependence indicates crack growth-controlled failure. Cyclic lifetime prediction indicated by the dashed lines mostly underpredicts the lifetime experimentally observed, which is more evident at 80°C. This might stem from the stress and temperature-induced aging, which is known to affect the failure kinetics of semicrystalline polymers [2,58,59]. As demonstrated in [2] for PEEK, cyclic loading might lead to a stronger stress-induced physical aging compared to static loading, which might explain why the cyclic lifetime of iPP is underpredicted given that the aging effects are not taken into account in the lifetime prediction method implemented in this study. To check if aging plays a role, one would need to conduct creep experiments with thermo-mechanical pre-treatments to investigate their effect on long-term behavior.

Figure 3.12b presents the effect of cyclic loading on the long-term behavior of the composite. As also shown previously in Chapter 2, the failure is plasticity-dominated at room temperature, which is indicated by longer time-to-failure under cyclic loading and the frequency independence of the lifetime. It can be seen in the figure that, for the same reasons, plasticity-controlled failure is dominant also at 90°C. Therefore, a switch to crack growth-controlled failure cannot be detected in the composite at elevated temperatures. This shows that an intermediate failure mechanism as discussed for neat iPP is not observed for the composite. Also different from iPP is that the lifetime prediction for cyclic loading indicated by the dashed lines fits the data reasonably well and the shift in lifetime to longer timescales is less. Fiber-matrix debonding and defects, which also contribute to the transverse failure of composites, might counteract to the effects of the possible aging in the matrix phase, leading to a smaller shift of lifetime compared to the neat iPP.

3.3.4 Effect of cooling rate on the short-term behavior

In this section, the effect of the cooling rate on the strain-rate-dependent short-term behavior will be studied. The influence of the cooling rate on the short-term behavior of the neat iPP was already shown in Figure 3.6. In the figure, it was shown that the controlled cooling rate (10°C/min) results in an improvement in the tensile strength compared to quenching. This trend is in line with the increasing crystallinity of the pure iPP with a decrease in the cooling rate as shown in Table 3.3 if we assume, in a straightforward manner, that the higher crystallinity should lead to a higher yield stress. In addition, higher yield stress for the controlled cooling rate can be explained also by an increase in the lamellar thickness, indicated by a lower rate constant in Table 3.5 [17,54,55]. The increase in strength is accompanied by a reduction of the strain-to-

failure, as can be seen in Figure 3.6 at room temperature, although the macroscopic yield is still observable. On the other hand, the slowest cooling rate, which was obtained by shutting the press off, resulted in a high level of embrittlement. The as-manufactured plate was full of voids and cracks, which did not allow us to cut samples. Thus, no tension tests were conducted for this case.

A different trend is observed in the effect of cooling rate on transversely loaded fiber-reinforced iPP. Firstly, the slowly cooled laminate was intact, which made it possible to test it. However, as can be seen in Figure 3.13, slow cooling resulted in the lowest strength and strain-to-failure. Although the crystallinity was seen to increase when the cooling rate was lowered as shown in Table 3.2, the transverse tensile strength decreased considerably. This observation implies that the crystallinity itself is not governing the transverse strength of the composite. Moreover, as shown in Figure 3.13b, the strain-rate-dependence of the tensile strength is characterized by different slopes for different cooling rates: strain rate sensitivity becomes lower as the cooling rate is lowered. This can be an indication that different failure mechanisms are present as a result of different cooling rates.

Comparing the effect of the cooling rate on the short-term behavior of the neat matrix and the composite, we see that the slowest cooling rate leads to embrittlement for both materials. Nevertheless, the effect of the moderate (controlled cooling and medium) and fast (quenching and fast) cooling rates are different for the two materials, as observed in Figure 3.6 and Figure 3.13. For neat iPP, quenching (300°C/min) leads to a lower strength compared to controlled cooling (10°C/min), while for the composite fast cooling (30°C/min) results in a higher strength compared to medium cooling rate (5°C/min). One thing to note is that the cooling rates applied for the composite were lower, which are more likely to lead to embrittlement. Moreover, even when the same cooling rates are considered for both materials to measure the cooling rate-dependent crystallinities as in Table 3.3, the levels of crystallinity in the composite was observed to be higher. Hence, an enhanced crystallization might also play a role in the stronger effects of embrittlement observed for the composite.

Figure 3.13: (a) Representative stress-strain curves and (b) the dependence of the tensile strength on the strain rate for the transversely loaded glass/iPP composites tested at 23°C. Markers in (b) represent the experimental data. Lines for slow and fast cooling are guides-to-the-eye, while the line for medium cooling rate is the description according to Equation (3.3) using the parameters in Table 3.4.

To investigate the reason for the cooling rate dependent embrittlement of the composite, SEM and optical microscopy of the fractured samples are carried out, which were tested at a constant strain rate of 10^{-4} s^{-1} . SEM images made perpendicular to the fracture surface, and optical micrographs made perpendicular to the side face of the samples along the fracture surface, are provided in Figure 3.14. First, investigating the SEM images shown in the left column, we see that the images of the fracture surface agree with the level of embrittlement observed in Figure 3.14. Slow cooling case results in highly brittle failure where blocks of the matrix material dominate the fracture surface. The fibers are mostly covered with the blocks of matrix. On the other hand, as the cooling rate is increased, the extent of plastic deformation increases, which is indicated by some changes in the microstructure such as the highly deformed matrix material seen in the SEM image of the fast cooling.

Analyzing the optical micrographs shown in the right column in Figure 3.14, it is seen that the fibers are usually surrounded by the matrix in slow cooling, which agrees with the SEM image that shows blocks of matrix on the fibers. In contrast, the tendency for fiber-matrix debonding increases at higher cooling rates. Such a difference might be a result of the strength of brittle failure under the slow cooling rate being closer to or lower than the fiber-matrix interface strength. Besides, voids are present along the fracture path of the slowly cooled laminate, unlike for the other cooling rates. Since crystallization from the melt results in an increase in the density as the spherulites are formed, the region between the spherulites may experience shrinkage, leading to voids [60,61]. Hence, slow cooling, which leads to a higher level of crystallinity and larger spherulite size, may favor the formation of more voids as in [62].

Figure 3.14: (left) SEM images of fracture surfaces (right) optical microscopy images of the edges of the fractured glass/iPP processed with slow, medium and fast cooling rates. SEM images are made perpendicular to the fracture surface and optical microscopy images are made perpendicular to the side surface of the specimen, along the fracture surface.

As mentioned previously in the introduction, semi-crystalline polymers are already known to be prone to embrittlement at extremely slow cooling rates [34–36], which can be explained by

several reasons. Firstly, slow cooling is known to promote the reeling-in of tie chains connecting the lamellae, which decreases the tie chain density. Tie chains, which act as load transducers between the lamellae, are responsible for the interlamellar deformation process for iPP (also named as the α relaxation) [49]; hence, a lower tie chain density would mean that the contribution of this deformation process to total stress would be reduced. Molecular weight also plays a significant role in the embrittlement by controlling the amount of tie chains: a lower molecular weight leads to a decrease in the number of tie chains, promoting the embrittlement [30,35,36,63]. The iPP grade used in this study has a relatively low molecular weight ($M_w = 150$ kg/mol), which might contribute to the embrittlement. Moreover, a decrease in the tie chain density leads to a decrease in the resistance to cavitation, also promoting the embrittlement [63]. This can be especially critical for the transverse loading of composites, where high hydrostatic stresses are present.

Besides, the embrittlement in semi-crystalline polymers may also be linked to the inter-spherulitic failure [30,31]. Promoted by slow cooling, the inter-spherulitic failure results from a weak bonding between the spherulites due to impurities, voids and elastic discontinuity at spherulite boundaries [30]. Many studies on composites attributed the embrittlement observed at slow cooling rates to this phenomenon [22,23,29,32]. Inter-spherulitic failure might have contributed to the embrittlement observed for the material used in this study as well; in fact, the “reeling in” phenomenon might have led to a weak bond between the spherulites, similar to its effect in the interlamellar region.

Since the temperature dependence of the strain-rate-dependent strength gives an idea about the different failure processes contributing to the tensile strength, the high-temperature behavior of the composite cooled with medium and slow rate is compared in Figure 3.15 to investigate further the underlying failure mechanisms. For the medium cooling case, different slopes at room temperature and 110°C indicate that both the intralamellar and interlamellar processes are active at the room temperature, while at 110°C and low strain rates only the intralamellar process exists. Towards the higher strain rates at 110°C, an increase in the slope can be detected, which is thought to be due to the contribution of the interlamellar failure process. Turning our attention to the slow cooling case, we see that the slopes at both testing temperatures are comparable and a change in the slope is not observed, which may indicate that deformation processes are the same in the temperature and strain rate range studied. In the light of this observation, it is thought that the interlamellar failure, which is seen at low temperatures and/or high strain-rates, might have been suppressed due to the reeling-in of tie chains connecting the lamellae.

Figure 3.15: Strain rate and temperature dependence of tensile strength for glass/iPP processed with slow and medium cooling rates. Markers represent the experimental data. Lines for slow cooling are guides-to-the-eye, while those for medium cooling rate are descriptions according to Equation (3.3) using the parameters in Table 3.4.

3.4 Conclusions

In this study, we have investigated the temperature-dependent long-term behavior of transversely loaded glass/iPP. Besides, the effect of cooling rate on the strain rate-dependent short-term strength was studied.

Elevated temperatures were observed to decrease the long-term strength significantly. Furthermore, a change in the failure kinetics, in other words, stress-dependence of the time-to-failure, was observed at high temperatures. This was related to the plasticity-controlled, multi-process deformation (interlamellar and intralamellar failure) of neat iPP which also shows such a change in the failure kinetics. Hence, it can be said that plasticity-controlled, time-dependent failure of the neat matrix has a substantial influence on that of the composite. Multi-process deformation kinetics was successfully captured by the Ree-Eyring equation [1].

Comparison of the lifetime at the same maximum stress at elevated temperatures revealed that cyclic loading leads to longer times-to-failure compared to creep loading for glass/iPP. Furthermore, the time-to-failure was independent of the frequency of the cyclic loading. Hence, plasticity was concluded to control the long-term behavior also at high temperatures, in addition to room temperature. Eventually, a switch to crack growth-controlled failure could not be detected for the composites, although the neat iPP showed the characteristics of both the plasticity- and crack growth-controlled failure at high temperatures.

A lifetime prediction method based on the plasticity-controlled failure of neat polymers, which makes use of the identity of the short- and long-term failure kinetics and the concept of critical strain, was employed for composites. The method led to reasonable lifetime predictions. The critical strain was observed to be temperature-dependent, unlike for the neat iPP.

An increase in the cooling rate led to a decrease in the degree of crystallinity for both neat and reinforced iPP. The degree of crystallinity was higher in the composite at the same cooling rates. This was thought to be due to fiber reinforcement acting as a nucleating agent. The effect of reinforcement can also be seen in the higher crystallization temperatures for the composites compared to the neat iPP.

For the composite, an increasing level of crystallinity did not correspond to a higher strength. Instead, the strength, ductility, and strain-rate dependence decreased significantly at low cooling rates. The embrittlement was thought to be linked to interlamellar and/or inter-spherulitic failure, which may be both promoted by a decrease in the tie chain density under slow cooling rates.

This study has shown that matrix-dominated time-dependent failure of glass/iPP is plasticity-controlled and extensively affected by the temperature, processing conditions, and the time-dependent behavior of the neat matrix. Hence, the effects of the aforementioned factors should be taken into account while designing glass/iPP products for long-term creep and fatigue as well as strain-rate dependent short-term loading.

3.5 References

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Chapter 4: Micromechanical modeling of the plasticity-controlled time-dependent failure of transversely loaded unidirectional glass/iPP

Abstract

Transversely loaded thermoplastic composites display pronounced time-dependent behavior which originates mostly from the time-dependence of the thermoplastic matrix. In this study, we investigate the relation between the time (rate) and temperature-dependent behavior of the neat and transversely loaded unidirectional continuous glass fiber reinforced polypropylene. Plasticity-controlled time-dependent stress-strain response of the neat iPP is modeled using the Eindhoven Glassy Polymer (EGP) model, which is subsequently employed in a micromechanical finite element model with a representative volume element comprising hexagonally packed fibers. The time-dependent behavior is characterized using Eyring's activated flow theory and Eyring parameters (activation volume and energy) are compared to investigate the link between the time-dependent behavior of the neat iPP and the composite. Simulations showed that the activation energies of the two materials were similar, unlike the experimental observation where composite had significantly lower activation energy. Moreover, stress levels of the composite were higher than that of the matrix, which also contradicted the experimental observations, suggesting the presence of failure at the fiber-matrix interface. Incorporating the effect of non-adhering fibers in the RVE, stress levels and the strain rate sensitivity (slope of yield stress vs. strain rate curve) of the composite dropped below those of the neat iPP, similar to experimental observations. The presence of non-adhering fibers did not affect the activation energies.

4.1 Introduction

Transverse failure of the continuous fiber-reinforced thermoplastic composites displays a pronounced dependence on the applied strain rate. This response originates mostly from the intrinsic time-dependent behavior of the neat matrix, which dominates the overall behavior of the composites when they are loaded in the transverse direction. Hence, it is of importance to investigate the link between the time-dependent behavior of the composite and the neat matrix.

In Chapter 3, we investigated the time-dependent behavior of the transversely loaded glass/iPP and its relation to that of the neat iPP. It was revealed that similar to the neat iPP, plasticity-controlled failure governed the time-dependent behavior of the composite. This was evidenced by the identical kinetics of the strain rate dependence of the tensile strength and the stress dependence of the time-to-failure under creep and fatigue loading, which allowed us to predict the lifetime based on the characterization of the temperature and strain rate dependence of the tensile strength and the concept of critical strain. Strain rate and temperature dependence of the (yield) strength was modeled using Eyring's activated flow theory [1,2] and Eyring parameters were compared to investigate the link between the time-dependent behavior of the two material systems.

Figure 4.1: (a) Strain rate and temperature dependence of yield stress of iPP-Quenched and (b) tensile strength of glass/iPP-medium. Markers represent the experimental data and lines are described by Equation (4.1) using the parameters shown in Table 4.1. Figures are reproduced from Chapter 3.

According to Eyring's activated flow theory, rate- and temperature-dependent (yield) strength of the two materials shown in Figure 4.1 was modeled by:

$$\sigma = \sum_{i=1,II} \frac{kT}{v_i^*} \sinh^{-1} \left(\frac{\dot{\epsilon}}{\dot{\epsilon}_{0,i}} \exp \left(\frac{\Delta U_i}{RT} \right) \right), \quad (4.1)$$

where k is the Boltzmann's constant, T is the temperature, v_i^* is the activation volume, $\dot{\epsilon}$ is the applied strain rate, $\dot{\epsilon}_{0,i}$ is the rate constant, ΔU_i is the activation energy and R is the gas constant. Note that the subscript i stands for the processes I and II , whose stress contributions act additively. These processes are related to the deformation mechanisms in the micro-scale: for iPP, processes I and II symbolize the intralamellar and interlamellar deformation, respectively [3]. At low strain rates and/or high temperatures, where the slope is low, the stress response is only due to the stress contribution of the process I . At high strain rates and/or low temperatures, process II also contributes to the total stress, leading to a stronger strain rate dependence of the yield stress. Eventually, via a fit procedure on the experimental data shown in Figure 4.1, Eyring parameters, presented in Table 4.1, were determined.

Table 4.1: Eyring parameters for Equation (4.1) to describe the lines in Figure 4.1.

Material	v_I^* [nm ³]	v_{II}^* [nm ³]	v_{I+II}^* [nm ³]	ΔU_I [kJ/mol]	ΔU_{II} [kJ/mol]
iPP	15.9	2.9	2.5	465.3	166.0
glass/iPP	11.5	7.9	4.7	254.1	157.4

Comparing the time- and temperature-dependent behavior of the composite and the neat iPP based on the Eyring parameters shown in Table 4.1 and the rate- and temperature-dependence of the (yield) strength shown in Figure 4.1, the following differences are noted:

- The activation energy of the process I of the composite is significantly lower, almost half of that of the neat iPP.
- Stress levels and the slope of the yield stress vs. $\log(\text{strain rate})$ plot in the region where both processes are active are lower for the composite (note that the slope is inversely proportional to the activation volumes shown in Table 4.1).
- At a specific temperature, the strain rate at which the stress response shows a change in the rate dependence, which signals a shift from the one-process to two-process response, is lower for the composite. In other words, the application of a lower strain rate is sufficient for the process II to contribute to the total stress of the composite, which we attributed to the possible strain localization in composites in Chapter 3.

Given the aforementioned differences in the Eyring parameters for neat and reinforced iPP, it is crucial to understand why such differences would be observed. Especially, the change in the activation energy is striking: activation energy takes the temperature dependence of deformation into account, which is expected to be identical for the composite and the neat matrix since the matrix, which is the same in both cases, is the deforming constituent.

An efficient tool in this aspect is the micromechanical finite element analysis, which offers extensive possibilities in investigating the effect of various parameters such as residual stresses as a result of processing, poor fiber-matrix adhesion, etc. on the homogenized composite

response by isolating the effect of the parameter of interest. In literature, there are numerous studies on the micromechanical finite element analysis of the transversely loaded composites. Although it is not the point of this study to review them here in detail, one can realize that most of the studies are based on thermoset-matrix composites. A review of some of these studies can be found in [4]. Few studies are available about the micromechanical modeling of fiber-reinforced thermoplastic composites [5,6]. Given that the stress-strain response of iPP exhibits extensive dependence on strain rate, temperature, and hydrostatic pressure [7], and, in addition, it displays multi-process behavior as seen in Figure 4.1, a matrix constitutive model that is capable of accounting for these effects is required. A sophisticated model that can be used for this purpose is the Eindhoven Glassy Polymer (EGP) model [8–10]. Although this model was originally developed for glassy polymers, it was successfully applied to semicrystalline polymers such as iPP [11]. Moreover, it was successfully employed in the micromechanical modeling of the filled fiber reinforced polymers [12,13]. Thus, EGP will be used to describe the time-dependent behavior of the neat iPP.

The purpose of this study is to investigate the relationship between the time-dependent behavior of the neat and glass-reinforced iPP with the help of micromechanical analysis and to understand the reason for the aforementioned changes in the Eyring parameters experimentally observed. Time- and temperature-dependent stress-strain response of the neat iPP will be modeled using the EGP model, and subsequently implemented in a micromechanical model of the transversely loaded composite with a representative volume element consisting of hexagonally packed fibers. Simulations will be carried out at various strain rates and temperatures, based on which Eyring parameters will be determined and compared to the experimental observations.

Note that an RVE with hexagonally packed, uniformly distributed fibers definitely does not represent the real microstructure of the composite, which would lead to quantitative errors in properties such as tensile strength, modulus of elasticity, and strain; however, we are after a more qualitative description rather than a quantitative description. That is to say, we do not aim to predict the stress-strain response of the composite experimentally observed, but rather we aim to observe the trends in the change of Eyring parameters such as activation volume and energy, for which the uniform fiber distribution will suffice.

4.2 Experiments

4.2.1 Processing and specimen preparation

The experimental data shown in this chapter is taken from Chapter 3. Below, the materials,

manufacturing, sample preparation, and mechanical testing will be summarized.

Glass-reinforced UD tape with a polypropylene matrix with a weight averaged molecular weight of $M_w = 150$ kg/mol and a polydispersity index (M_w/M_n) of 5.2 was kindly provided by Sabic. Volume and weight fraction of the fibers in the prepreg is 45% and 70%, respectively. Each prepreg had a width of 110 mm and a nominal thickness of 0.25 mm. The neat matrix used is of the same grade as the matrix of the tape.

A stack with $[90]_8$ lay-up was prepared in a picture frame mold of 390 mm by 390 mm to be pressed in a Fontijne hot press. The stack was heated to 220°C, allowed to consolidate at that temperature for 10 minutes at a pressure of 2 bars, and then cooled to room temperature with the pressure on. Cooling was achieved by activating the water cooling system of the press at its full capacity, which led to a cooling rate of around 5°C/min (medium cooling rate in Chapter 3). After making the laminates, composite specimens were cut using a diamond saw. Water was used while sawing to prevent over-heating. Rectangular specimens had a thickness of 2 mm, grip-to-grip separation of 100 mm, a width of 20 mm and a grip length of 20 mm.

Neat iPP was manufactured using a Fontijne dual hot press with 2 different cooling rates, which are named as quenching (1800°C/min) and controlled cooling (10°C/min). This press consists of two plates that are used to heat the mold and two cold plates kept at 17°C that are used to quench the mold. For the quenched cooling, after the mold was kept at the consolidation temperature of 220°C and pressure of 25 bars for a dwell time of 3 minutes, it was transferred to the cold plates for cooling which resulted in a cooling rate of around 1800°C/min. For controlled cooling, after the consolidation took place at a temperature of 220°C and a pressure of 37.5 bars for 5 minutes, the plates of the press were cooled at the programmed cooling rate of 10°C/min. Tensile specimens of the neat matrix material are dumbbell-shaped tensile bars dimensioned according to ISO 527-2-1BA and ISO 527-2-5B for quenched and controlled cooling, respectively.

Mechanical tests considered in this study are mostly the constant-strain-rate tensile tests that are conducted to determine the strain rate dependence of the (yield) strength. Some creep test results on the stress dependence of the plastic flow rate are also provided to complement the former data. For composites, the tests were conducted using Zwick/Roell 2005 and Z5.0 equipped with load cells with capacities of 2.5 kN and 5 kN. For iPP, tests were performed on a Z010 Zwick Material Testing Machine equipped with a 1 kN load-cell. The machines were equipped with a temperature chamber for high-temperature testing. For constant-strain-rates, constant crosshead speeds corresponding to strain rates ranging from 10^{-7} s⁻¹ to 10^{-1} s⁻¹ were used. The testing temperature ranged from room temperature (23°C) up to 110°C. The samples were kept in a hot chamber for 10 minutes before performing the high-temperature tests.

4.2.2 The effect of cooling rate on the time-dependent behavior of iPP

Before moving on to the modeling and comparison of the experimental behavior and the simulations, since the neat iPP was manufactured employing two different cooling rates, their effect on the time-dependent behavior will be summarized, as previously done in Chapter 3. The cooling rates employed for the manufacturing of iPP are 10°C/min (controlled cooling) and 1800°C/min (quenching). Although the controlled cooling rate of the neat iPP is more comparable to the cooling rate applied for the composite (5°C/min), quenched iPP was tested in a wider range of temperatures, from which the Eyring parameters were determined. Hence, the modeling, which will be carried out in the next section, will be based on the experimental data of the quenched iPP, which is shown in Figure 4.1a. Since the activation volumes and energies are, to a good approximation, constant for different processing conditions based on the observation van Erp [14] made, using the data of the quenched iPP will not pose a problem for the comparison of activation volume and energy between the neat iPP and the composite. However, since the processing conditions affect the rate constants $\dot{\epsilon}_{0,i}$ in Equation (4.1) and, thus, the stress levels considerably, the data of iPP with controlled cooling will be utilized to compare the stress levels of the simulations and experimental observations. To verify the observation of van Erp [14], the rate-dependent yield stress of the iPP with different cooling rates is plotted in Figure 4.2, where the lines are Eyring fits according to Equation (4.1) using the Eyring parameters presented in Table 4.2. It can be seen that the use of the same activation volumes and energies and different rate constants yields a reasonable description of the time-dependent behavior of the iPP manufactured with different cooling rates, verifying the observation of van Erp [14].

Since the rate constants depend highly on the processing conditions, in the introduction section, their comparison for the composite and the neat iPP (quenched), which were processed with different cooling rates, was not mentioned.

Table 4.2: Comparison of Eyring parameters for quenched and controlled-cooled iPP and the composite.

Material	v_I^* [nm ³]	v_{II}^* [nm ³]	ΔU_I [kJ/mol]	ΔU_{II} [kJ/mol]	$\dot{\epsilon}_{0,I}$ [s ⁻¹]	$\dot{\epsilon}_{0,II}$ [s ⁻¹]
iPP (quenching)	15.9	2.9	465.3	166.0	$5.9 \cdot 10^{51}$	$3.0 \cdot 10^{23}$
iPP (controlled cooling)	15.9	2.9	465.3	166.0	$2.0 \cdot 10^{48}$	$2.5 \cdot 10^{22}$
glass/iPP	11.5	7.9	254.1	157.4	$3.2 \cdot 10^{25}$	$1.7 \cdot 10^{18}$

Figure 4.2: Dependence of the yield stress on the applied strain rate for iPP processed with different cooling rates. Markers represent the experimental data and lines are described by Equation (4.1) using the parameters shown in Table 4.2. The figure is reproduced from Chapter 3.

4.3 Modeling

4.3.1 Intrinsic behavior

Figure 4.3: Intrinsic stress-strain response of a polymer measured in a uniaxial compression test. The image is reproduced from [15].

The intrinsic stress-strain response of a material refers to its true stress-strain behavior during homogeneous deformation [15]. As most polymers display strain localization in extension, intrinsic behavior should be measured by using another method that ensures homogeneous deformation. A common method to obtain homogeneous deformation is uniaxial compression testing. Figure 4.3 shows a typical true stress vs. true strain graph of a glassy polymer measured in a uniaxial compression test. At low loads, the behavior is linear viscoelastic. As the stress

increases, we encounter the nonlinear viscoelastic region, where, along with the linear viscoelastic region, the deformation is fully reversible upon the removal of the stress. As the stress increases further, stress-induced plastic flow leads to an irreversible deformation at the yield point. Yield is followed by strain softening which takes place due to material's reduced resistance to plastic flow. After strain softening, orientation of the polymer molecules leads to strain hardening [16], which can be seen as an increase in the stress at high strains. The constitutive model (EGP) that will be presented in the next section is capable of modeling the aforementioned intrinsic behavior. The effect of multiple deformation processes, applied strain rate and temperature are captured well by the model.

4.3.2 Constitutive model for the neat matrix

Figure 4.4: Mechanical analog of the model, based on [10].

According to the EGP model [8–10], total stress is composed of driving and hardening stresses, whose responses are additive as follows:

$$\sigma = \sigma_s + \sigma_r, \quad (4.2)$$

where σ_s represents the driving stress, which takes intermolecular interactions into account,

and σ_r represents the hardening stress which accounts for the contribution of the oriented network of molecules to the total stress with a neo-Hookean relation where the hardening stiffness is represented by G_r . The driving stress is decomposed into its hydrostatic and deviatoric components represented by σ_s^h and σ_s^d , respectively, as follows:

$$\sigma_s = \sigma_s^h + \sigma_s^d. \quad (4.3)$$

The hydrostatic stress is related to the volume change and defined as:

$$\sigma_s^h = K(J - 1)\mathbf{I}, \quad (4.4)$$

where K is the bulk modulus and J is the volume change ratio. The deviatoric stress is further additively decomposed into stress contributions of the processes I and II , which are represented by $\sigma_{s,I}^d$ and $\sigma_{s,II}^d$, respectively, in Equation (4.5):

$$\sigma_s^d = \sigma_{s,I}^d + \sigma_{s,II}^d. \quad (4.5)$$

The total deviatoric stress of each process is modeled by multiple nonlinear Maxwell elements with stress-dependent viscosities (and hence stress-dependent relaxation times) that are connected in parallel, as shown in Figure 4.4. Total deviatoric driving stress is given by:

$$\sigma_s^d = \sigma_{s,I}^d + \sigma_{s,II}^d = \sum_{i=1}^n G_{I,i} \tilde{\mathbf{B}}_{e,I,i}^d + \sum_{j=1}^m G_{II,j} \tilde{\mathbf{B}}_{e,II,j}^d, \quad (4.6)$$

where n stands for the number of modes for process I , m represents the number of modes for process II , $G_{x,k}$ and $\tilde{\mathbf{B}}_{e,x,k}^d$ represent the shear modulus and the deviatoric part of the isochoric left Cauchy Green strain tensor for process x and mode k (where $x = I, II$ and $k = i, j$), respectively. It was shown in the previous studies [8,10,17] that the incorporation of multiple Maxwell elements is essential to capture the nonlinearity in the pre-yield regime.

The plastic deformation rate tensor $\mathbf{D}_{p,x,k}$ of process x and mode k is given by:

$$\mathbf{D}_{p,x,k} = \frac{\sigma_{s,x,k}^d}{2\eta_{x,k}(T, \bar{\tau}_x, p, S_{a,x}, R_x)}, \quad (4.7)$$

where $\eta_{x,k}$ is the modified Eyring viscosity that takes into account the influence of temperature (T), equivalent stress of the process x ($\bar{\tau}_x$), hydrostatic pressure (p), thermodynamic state ($S_{a,x}$) and softening (R_x). Strain softening depends on the equivalent plastic strain $\bar{\gamma}_p$ and can be described with a special function whose details can be found in [9]. Evolution of the equivalent

plastic strain is controlled by the equivalent plastic strain rate, which is taken as equal to the plastic strain rate of the mode with the highest relaxation time in the process I , as described in [11]. For convenience, the terms $S_{a,x}$ and R_x are combined into a single term $S_{A,x} = S_{a,x} \cdot R_x(\bar{\gamma}_p)$. The modified Eyring viscosity $\eta_{x,k}$ is expressed as:

$$\eta_{x,k} = \eta_{0,x,k,ref}(T) \frac{\bar{\tau}_x/\tau_{0,x}}{\sinh(\bar{\tau}_x/\tau_{0,x})} \exp\left(\frac{\mu_x p}{\tau_{0,x}}\right) \exp(S_{A,x}), \quad (4.8)$$

where $\eta_{0,x,k,ref}$ is the temperature-dependent reference viscosity, $\tau_{0,x}$ is the characteristic stress, and μ_x is the pressure dependence factor. $\eta_{0,x,k,ref}$ is defined as:

$$\eta_{0,x,k,ref}(T) = A_{0,x,k} \tau_0 \exp\left(\frac{\Delta U_x}{RT}\right), \quad (4.9)$$

where $A_{0,x,k}$ is a temperature-independent constant (with a unit of time), R is the gas constant, and ΔU_x is the activation energy [15]. The characteristic stress is related to shear activation volume $v_{s,x}^*$ through the relation:

$$\tau_{0,x} = k_B T / v_{s,x}^*, \quad (4.10)$$

where k_B is the Boltzmann's constant.

4.3.3 Characterization

This section explains how the parameters required for the constitutive model are determined. The bulk modulus K is taken as $1.66 \cdot 10^3$ MPa from [11]. One of the parameters required is the pressure dependence factor μ , which is especially important for the modeling of composites due to the triaxial stress state that evolves when composites are loaded in the transverse direction. Based on the work of Klompen et al. [9], assuming a model with a single process and mode, the yield stress under 1-D tensile loading in the presence of a superimposed hydrostatic pressure p_0 is expressed as:

$$\sigma_y = \frac{3\tau_0}{\sqrt{3}+\mu} \left[\ln\left(2\sqrt{3} \frac{\eta_{0,ref}(T)}{\tau_0} \dot{\epsilon}\right) + \frac{\mu p_0}{\tau_0} + S_A \right] + \frac{\sqrt{3}}{\sqrt{3}+\mu} \sigma_r(\lambda_y), \quad (4.11)$$

where $\sigma_r(\lambda_y)$ is the hardening stress at yield (at the draw ratio of λ_y) and its explicit expression is:

$$\sigma_r(\lambda_y) = G_r(\lambda_y^2 - \lambda_y^{-1}), \quad (4.12)$$

where G_r is the strain hardening modulus. From Equation (4.11) it can be seen that, at a fixed strain rate, the slope of σ_y vs p_0 line will be $\frac{3\mu}{\sqrt{3}+\mu}$. Since we have not conducted tests at different hydrostatic pressures to determine the pressure dependence factor, this slope is taken from [7], which results in $\mu = 0.13$. The slope of the line that characterizes the dependence of the yield stress on the applied strain rate $\dot{\epsilon}$ is $\frac{3\tau_0}{\sqrt{3}+\mu}$. This slope is also equal to the characteristic stress $\sigma_0 = \frac{k_B T}{v^*}$, where v^* is the uniaxial tensile activation volume given in Table 4.1. This leads to $\tau_{0,\alpha} = 0.16$ MPa and $\tau_{0,\beta} = 0.87$ MPa at $T = 23^\circ\text{C}$.

It was shown in the previous studies [11,18] that, especially at high temperatures, iPP does not exhibit pronounced strain softening and strain hardening. Based on this observation and on the fact that the tensile tests conducted in this study lead to localized deformation; hence they cannot describe the post-yield behavior, we neglect the effect of softening and hardening and assume a perfectly plastic behavior. This implies that strain hardening modulus and the state parameters are set to zero: $G_r = 0$ and $S_{A,\alpha} = S_{A,\beta} = 0$. Since the strain hardening is neglected, the total stress will be equal to the driving stress, from which the other parameters will be extracted.

The main parameters that are required by the model are reference shear viscosities and shear moduli of the Maxwell elements, which define the time-dependent behavior of the individual modes. In order to extract these constants, a method based on time-stress superposition is used. Developed by van Breemen et al. [10], this method requires only a single stress-strain curve obtained at a certain constant-strain-rate. Upon choosing a discrete spectrum of relaxation times, the driving stress vs. strain curve is fitted with Boltzmann's superposition integral incorporated with a stress-reduced-time to determine the moduli and viscosity of each mode.

To determine the constants of the process I , temperature of 80°C and strain rate of 10^{-4} s^{-1} are chosen since, under these conditions, only process I contributes to the total stress, as seen in Figure 4.1. Choosing about 1 mode per decade based on the recommendation in [10], the fit obtained is shown in Figure 4.5a. Total relaxation modulus vs. time and the relaxation moduli of the individual modes vs time are illustrated in Figure 4.5b. Relaxation times of the individual modes are shown with circular markers in the figure. It can be observed that while every single mode has an almost constant modulus before the relaxation time is reached, the total response which is obtained by the summation of the relaxation moduli of the modes shows a relaxation modulus gradually decreasing with time. This captures the nonlinear stress-strain behavior experimentally observed. Finally, the spectrum of moduli of elasticity and viscosities in the loading direction are converted to shear viscosities and moduli according to [8].

The spectrum determined is transferred to other temperatures by using the ratio of reference viscosities at different temperatures. Following Equation (4.9), the ratio of the reference

viscosity at temperature T to the reference viscosity at a reference temperature is:

$$\frac{\eta_{0,x,k,ref}(T)}{\eta_{0,x,k,ref}(T_{ref})} = a_{I,T}(T) = \frac{T}{T_{ref}} \exp\left(\frac{\Delta U}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right). \quad (4.13)$$

By using Equation (4.13) with $T_{ref} = 80^\circ\text{C}$, $T = 23^\circ\text{C}$ and the activation energy of the process I shown in Table 4.1, the spectrum of reference viscosities of the process I is shifted to $T = 23^\circ\text{C}$, which is illustrated in Figure 4.6a with the curves of the relaxation modulus vs. time at 80°C and 23°C . Stress-strain response of the process I is predicted with the spectrum obtained, which is displayed in Figure 4.6b. Note that the stress-strain response is linear at low strains with a steep transition to non-linearity as the strain increases. Such linear behavior at low strains is due to the unavailability of modes at short relaxation times, which results from shifting the spectrum. Unavailability of modes at short timescales means that very little relaxation takes place, leading to an almost constant relaxation modulus, as shown in Figure 4.6a, and, thus, to a linear stress-strain relationship. Table 4.3, which presents the relaxation times of the modes of the process I for both 23°C and 80°C , also illustrates this phenomenon: even the lowest relaxation time at 23°C is greater than the highest relaxation time at 80°C .

Figure 4.5: (a) Experimental stress-strain curve and the fit obtained using the model with parameters for the process I shown in Table 4.3. (b) Relaxation modulus (extensional) vs time curve of the process I , based on (a). In (b), solid lines indicate the individual modes and the dashed line represents the total response. Circular markers indicate the relaxation times.

Unlike process I , process II cannot be identified independently since there is no experimental condition where only the process II contributes to the total stress. Hence, we use a fictive spectrum for the process II , which, at $T = 23^\circ\text{C}$ and strain rate of 10^{-3} s^{-1} , where both processes are observed, yields at the stress that is determined by subtracting the yield stress of the process I from the experimentally observed total stress; and has the same strain-at-yield as the process I . Although the spectrum of the process II captures the temperature and rate dependence of

the yield stress, the loading path, i.e. modulus vs. time, predicted by the simulations will be different from the behavior experimentally observed for the neat iPP for cases involving the contribution of the process II. Since we are concerned with the yield conditions, this approach will be sufficient for the present study. Relaxation modulus vs. time curve of the process II is shown in Figure 4.7 and the spectra of the reference zero shear viscosities $\eta_{0,i,ref}$, shear moduli G_i and the relaxation times λ_i of both processes are tabulated in Table 4.3 and Table 4.4, respectively (note that $\eta_{0,i,ref} = G_i \cdot \lambda_i$).

Figure 4.6: (a) Total relaxation modulus (extensional) vs. time curve of the process I at $T=80^\circ\text{C}$ and $T=23^\circ\text{C}$. (b) Contribution of the process I to the total stress at $T = 23^\circ\text{C}$ and strain rate of 10^{-3} s^{-1} .

Figure 4.7: Relaxation modulus (extensional) vs. time curve of the process II at $T = 23^\circ\text{C}$, where solid lines indicate the individual modes and the dashed line represents the total response. Circular markers indicate the relaxation times.

Table 4.3: Spectrum for the process I at $T=23^{\circ}\text{C}$ and 80°C .

Mode	G_i [MPa]	$\eta_{0,i,ref}$ [MPa·s] $T=23^{\circ}\text{C}$	λ_i [s] $T=23^{\circ}\text{C}$	λ_i [s] $T=80^{\circ}\text{C}$
1	7.70e+00	1.11e+29	1.44e+28	9.73e+14
2	2.63e+01	1.37e+29	5.19e+27	3.50e+14
3	2.22e+00	7.72e+26	3.48e+26	2.35e+13
4	4.80e+00	6.89e+26	1.44e+26	9.70e+12
5	7.31e+00	1.72e+26	2.35e+25	1.59e+12
6	1.88e+00	1.76e+25	9.39e+24	6.34e+11
7	2.04e+00	3.22e+24	1.58e+24	1.07e+11
8	4.37e+00	2.78e+24	6.36e+23	4.30e+10
9	5.42e+00	3.45e+23	6.37e+22	4.30e+09
10	5.07e+00	3.23e+22	6.36e+21	4.30e+08
11	6.07e+00	3.86e+21	6.36e+20	4.30e+07
12	6.59e+00	4.18e+20	6.35e+19	4.29e+06
13	7.44e+00	4.71e+19	6.34e+18	4.28e+05
14	7.96e+00	5.02e+18	6.31e+17	4.26e+04
15	8.32e+00	5.25e+17	6.30e+16	4.26e+03

Table 4.4: Spectrum for the process II at $T = 23^{\circ}\text{C}$.

Mode	G_i [MPa]	$\eta_{0,i,ref}$ [MPa·s]	λ_i [s]
1	1.19e+01	1.31e+06	1.10e+05
2	6.87e+00	3.12e+05	4.54e+04
3	1.09e+01	5.71e+04	5.23e+03
4	1.02e+01	1.00e+04	9.78e+02

4.3.4 Micromechanical model

The finite element model for the composite is developed in ABAQUS® assuming plane strain conditions. Mesh is dominantly formed by 4-node bilinear plane strain quadrilateral CPE4 elements, while few elements are 3-node linear plane strain triangular CPE3 elements. The RVE has a uniform, hexagonal fiber stacking. The dimensions of the RVE are arranged such that the fiber volume fraction is equal to the nominal fiber volume fraction given in the material datasheet, which is 45%. To reduce the computation time, a quarter of the RVE is modeled, as shown in Figure 4.8. Symmetric boundary conditions are applied: the nodes on the line OA are fixed in the y -direction and the nodes on the line OC are fixed in the x -direction. Furthermore, the x -displacement of the nodes on the line AB is constrained to be equal to x -displacement of the node at point B. Likewise, y -displacement of the nodes on the line BC is set to be the same as that of the node at point B. The loading is applied as a time-dependent displacement, which depends on the engineering strain rate desired, at node B towards the $+x$ -direction. Homogenized RVE stress is determined by dividing the reaction force in the x -direction at the

load node (node B) by the cross-sectional area of the surface perpendicular to which it is applied to. The homogenized engineering strain is determined by dividing the x -displacement of the node B by the initial length of the line OA. The material model is input as a UMAT subroutine, which is run with the implicit solver. For the neat iPP, a solid model with a single 8-node linear brick C3D8 element is utilized to simulate the rate and temperature-dependent stress-strain response.

Figure 4.8: RVE of the composite where dark and light colors indicate the glass fibers and iPP, respectively.

4.4 Results

4.4.1 Time-dependent behavior of iPP

In this section, stress-strain behavior of the neat iPP at various strain rates and temperatures will be explained. To begin with, stress-strain graphs of the neat iPP at $T = 50^\circ\text{C}$ and $T = 110^\circ\text{C}$ are provided in Figure 4.9a. In the figure, it can be seen that compared to 110°C , rate dependence of the yield stress at 50°C at higher strain rates is greater since the process *II* starts to contribute to the total stress in addition to the process *I*. Note that the predictions at $T = 50^\circ\text{C}$, shown in Figure 4.9a, display a linear stress-strain behavior at low strains, similar to Figure 4.6b, due to the unavailability of modes at short relaxation times.

Extending the study to a larger range of strain rates and temperatures, picking the yield stresses and superimposing them on the experimental data as shown in Figure 4.9b, we see that the EGP

model captures the temperature dependence of the yield stress of the neat iPP quite well.

Figure 4.9: (a) Stress-strain curves of iPP from simulations for $T = 50^\circ\text{C}$, 110°C and $\dot{\epsilon} = 10^{-5}$, 10^{-4} , 10^{-3} , 10^{-2} s^{-1} . (b) Dependence of yield stress on the strain rate and temperature predicted by the model (simulations) and its comparison to experimental data (markers) and its Eyring fit (lines according to Equation (4.1) using the parameters shown in Table 4.1).

4.4.2 Composite simulations and composite vs. iPP comparison

The homogenized stress-strain curves of the composite obtained from the simulations are provided in Figure 4.10a. Similar to the neat iPP, the rate dependency at high rates at 50°C is greater than the rate dependence at 80°C and 110°C . This demonstrates that the two-process failure behavior of the transversely loaded glass/iPP composite can be captured with the model utilized. All curves exhibit yield, evidenced by the maximum, constant stress in the stress-strain curves. For the characterization of the time-dependent behavior via Eyring fit, the maximum stress is taken as the (yield) strength. This approach is in line with the experimental behavior at high temperatures and/or low strain rates, where yield is observed as shown in Figure 4.11. Same criterion is applied also for the simulations at low temperatures and/or high strain rates although experimentally pre-yield failure is observed under these conditions.

The two-process yield behavior of the composite is illustrated in Figure 4.10b for a large range of temperatures and strain rates and it is compared to the neat iPP. Firstly, it is seen that, similar to experimental observations, the strain rate at the shift to two process-region is lower for the composite. The shift can be explained by the magnified strains in the composite microstructure, as illustrated in Figure 4.12. In Figure 4.12, while the strain rate applied is 10^{-3} s^{-1} , the local strains reach 10^{-2} s^{-1} , which is 10 times the applied strain rate.

Figure 4.10: (a) Stress-strain curves of the composite obtained by simulations for $T = 50^\circ\text{C}$, 80°C , 110°C and $\dot{\epsilon} = 10^{-6}$, 10^{-5} , $10^{-4} s^{-1}$. (b) Dependence of yield stress on the strain rate and temperature according to the simulations of the composite and the neat iPP. Markers in (b) represent simulation results and lines are Eyring fits (Equation (4.1)) using the parameters shown in Table 4.5.

Figure 4.11: (a) Stress-strain curves of the composite obtained by experiments (a) at $T = 23^\circ\text{C}$ and 90°C at various strain rates ($1.3 \cdot 10^{-7}$ - $1.3 \cdot 10^{-4} s^{-1}$ for 23°C and 10^{-6} - $10^{-3} s^{-1}$ for 90°C), (b) at a strain rate of $10^{-4} s^{-1}$ at various temperatures.

Figure 4.12: Distribution of the strain rate in x -direction in the RVE for $T = 80^\circ\text{C}$ and $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$ at an instant close to yield.

Table 4.5 Eyring parameters of the neat iPP and the composite from simulations and experiments.

Material	v_I^* [nm ³]	v_{II}^* [nm ³]	v_{I+II}^* [nm ³]	ΔU_I [kJ/mol]	ΔU_{II} [kJ/mol]
iPP (exp.)	15.9	2.9	2.5	465.3	166.0
glass/iPP (exp.)	11.5	7.9	4.7	254.1	157.4
glass/iPP (sim.)	13.5	3.3	2.7	464.8	160.3

The yield stresses shown in Figure 4.10b are used to determine the Eyring parameters of the RVE simulations and these parameters are shown in Table 4.5. It is remarkable that the activation energies of the processes I and II from the composite simulations are almost the same as those of the neat iPP, which contradicts with the experimental observations. Moreover, as illustrated in Figure 4.13a, composite simulations lead to higher stress levels compared to the neat iPP, which also contradicts the experimental observations shown in Figure 4.13b. Note that the simulations in Figure 4.13a are based on the data of the quenched iPP since quenched iPP was tested at a large range of temperatures, which enabled us to determine the Eyring parameters. However, the comparison of the experimental behavior in Figure 4.13b is made with the iPP with controlled cooling since its cooling rate is closer to that of the composite.

An important reason for the aforementioned discrepancy in the stress levels is thought to be because the fiber-matrix interface failure, which plays a significant role in the transverse behavior of the composites, is not taken into account in the RVE used for this study. To investigate the effect of the fiber-matrix interface failure on the time-dependent failure of the composite, we study an extreme case: in the next section, the effect of *no adhesion* between the fiber and matrix on the time-dependent behavior will be presented.

Figure 4.13: (a) Comparison of the rate dependent strength for the neat iPP (quenched) and the composite at $T = 23^\circ\text{C}$, where the data indicated by markers are taken from the simulations. Lines are Eyring fits (Equation (4.1)) with parameters from Table 4.5 and Table 4.6. (b) Comparison of the rate-dependence of the (yield) strength for the neat iPP (controlled cooling) and the composite, where the data is from the experiments. In (b), in addition to the constant-strain-rate data, creep stress vs. plastic flow rate data are also provided. The line for the composite is the Eyring fit with parameters from Table 4.1 while the line for the neat iPP is a guide-to-the-eye.

4.4.3 The effect of fiber-matrix adhesion on time-dependent failure

To check the effect of the fiber-matrix adhesion on the time-dependent behavior, certain regions in the fiber-matrix interface in the RVE are modeled with no adhesion between the two constituents. Two RVEs are developed: one with only a single non-adhering fiber, and the other one with two non-adhering fibers. The RVEs with non-adhering fibers are illustrated in Figure 4.14, where a small displacement is applied to the RVEs to show the debonded regions clearly. For the RVE with one non-adhering fiber, the arc DF on the surface of both the matrix and fiber is divided into two arcs DE and DF where the length of the arc DE is chosen to be 5% of the length of arc DF. Subsequently, the arcs are seeded and meshed such that the node E separates the connected and debonded region. The nodes on the arc DE that are on the fiber are tied to those on the matrix by tie constraints. For the nodes on the arc EF both on the fiber and matrix, a normal surface-to-surface contact is defined. Contact property is chosen as hard contact, which does not allow the transfer of tensile stress across the interface. The contact is enforced using a standard penalty stiffness. Tangential contact is assumed to be frictionless. A similar procedure is followed in order to develop the RVE with two non-adhering fibers. Note that the boundary conditions on the edges of the RVE are the same as those applied for the RVE without debonding.

Figure 4.14: RVEs with (a) one and (b) two non-adhering fiber(s). A small displacement is applied to the RVEs to show the debonded regions clearly.

Figure 4.15: Stress-strain graphs of the simulations of the neat iPP and composite with different RVEs at $T = 80^\circ\text{C}$ and $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$.

The stress-strain response obtained from the simulations with non-adhering fibers is provided in Figure 4.15 at a strain rate of 10^{-4} s^{-1} . It can be recognized in the figure that the RVEs with non-adhering fibers lead to lower stresses compared to the RVE with perfect adhesion. As the size of the region in the RVE with no adhesion gets larger, stress levels drop further. Furthermore, both RVEs with non-adhering fibers lead to lower stresses compared to the neat iPP, which agrees with the experimental observations, as presented in Figure 4.13b at $T = 23^\circ\text{C}$. To obtain the Eyring parameters for the RVEs with non-adhering fibers and to compare them with those from the RVE with perfect adhesion, the simulations are carried out at various temperatures and strain rates. Picking the yield stresses from these simulations, the dependence of the yield stress on the strain rate and temperature for the two cases with debonding are plotted in Figure 4.16 and compared with the neat iPP. The Eyring parameters determined are presented in Table 4.6.

Figure 4.16: Yield stresses (markers) and Eyring fits (lines) for the simulations of iPP and RVE with (a) one non-adhering fiber (b) two non-adhering fibers. Open markers represent the simulations of the neat iPP, and the closed markers represent the simulations of the composite. Lines are Eyring fits (Equation (4.1)) using the parameters in Table 4.6.

Table 4.6: Eyring parameters for the RVEs with non-adhering fibers and iPP. “sim.” indicates “simulation”.

Material	ν_I^* [nm ³]	ν_{II}^* [nm ³]	ν_{I+II}^* [nm ³]	ΔU_I [kJ/mol]	ΔU_{II} [kJ/mol]
iPP (sim.)	15.9	3.3	2.7	465.0	163.7
glass/iPP (sim., 1 non-adhering fiber)	39.4	11.2	8.7	478.9	160.3
glass/iPP (sim., 2 non-adhering fibers)	49.4	13.3	10.5	480.5	162.5

Comparing the Eyring parameters of the composite with non-adhering fibers with those of the neat iPP based on Table 4.6, it is seen that, similar to the trend experimentally observed as shown in Figure 4.13b, the rate sensitivity (slope of the yield stress vs. $\log(\text{strain rate})$ curve) obtained by composite simulations is lower than that of the neat iPP, revealed by higher activation volume of the composite for the region where both deformation processes contribute to the total stress. Moreover, the larger the size of the fiber-matrix interface with no adhesion, the lower the slope of the yield stress vs. $\log(\text{strain rate})$ curve (strain rate sensitivity).

When the activation energies obtained by composite simulations are compared, it can be concluded that the simulations with non-adhering fibers do not lead to lower activation energies compared to the neat iPP, contrary to the experimentally observed trend presented in Table 4.1. Rather, the activation energies remain almost constant regardless of the geometry employed in the simulations.

It should be noted that, in our model, fiber-matrix-debonding was not modeled as a

temperature-activated failure mechanism, which means that the only temperature-dependent deformation mechanism is that of the neat matrix. As the temperature dependence of the neat matrix is the same for neat iPP in the RVEs with and without debonding, the activation energies, which are related to the temperature dependence of the failure, are identical for all cases. Based on this, we can hypothesize that the introduction of effects into the RVE, which leads to temperature-dependent failure, would result in a change in the activation energy compared to the neat iPP. An example of such effects is the residual stress since the residual stress is expected to be different at different testing temperatures due to a change in the temperature difference between the stress-free temperature and the testing temperature [19].

Alternatively, the presence of another failure mechanism in the composite with an activation energy lower than that of the neat matrix would also result in a lower activation energy for the composite compared to the neat matrix. Fiber-matrix debonding, which is highly dependent on the sizing, could be an example of such a failure mechanism [20]. Nevertheless, in this study, we are not going to investigate the effect of these factors.

4.5 Towards faster characterization

Plotting the rate-dependent strength of the neat iPP and composite with different RVEs in the double logarithmic scale as in Figure 4.17, it can be seen that although the strain rate sensitivity is different for the different cases in the semilogarithmic scale, the differences disappear to a large extent in the double logarithmic scale. Considering the simulations with debonding, which result in yield stresses lower than those of the neat matrix (similar to the experimentally observed trend) it can be claimed that debonding leads to a decrease in the stress levels while the slope in the double logarithmic scale remains almost the same. The parallelity in the double logarithmic scale implies that the rate-dependent strength of the composite can be obtained by applying a shift factor to the rate-dependent strength of the neat matrix as follows:

$$\sigma_{composite}(\dot{\epsilon}, T) = \sigma_{iPP}(\dot{\epsilon}, T) \cdot S_{composite}, \quad (4.14)$$

where $S_{composite}$ is the shift factor of composite associated with a certain type of RVE. The amount of debonding determines the location of the curve characterizing the rate dependence of the strength in the y-axis. Hence, $S_{composite}$ changes with the extent of debonding.

Investigating if such parallelity is also observed experimentally, at 23°C we plot the data of iPP (controlled-cooling) along with the composite in Figure 4.18. In Figure 4.18a, the full line is the Eyring fit for the experimental data of the composite. The dashed line is constructed by shifting the full line (Eyring fit for the composite data) with a shift factor according to Equation (4.14)

and it describes the iPP data reasonably well. Hence, we can claim that for 23°C assumption of parallelity in the double logarithmic scale gives a reasonable approximation to rate-dependent strength of the composite.

Parallelity in the double logarithmic scale we observed in the micromechanical analyses and to some extent in the experimental data was experimentally observed also for the short fiber-reinforced iPP by Pastukhov [21]. This observation implies that the characterization of the time-dependent behavior of the composite can be done in a faster way: given the time-dependent behavior of the neat matrix, by conducting constant-strain-rate tests of the composite at a single strain rate, the shift factor can be determined. Subsequently, assuming parallelity in the double logarithmic scale, yield stress at other rates can be predicted. This significantly reduces the time required to characterize the time-dependent failure of the composite, which is often cumbersome due to the amount of material needed and experiments that need to be carried out. Especially for engineering applications that require a quick but an educated guess for the time-dependent mechanical behavior of composite materials based on the time-dependent behavior of the neat matrix, using the approach of shift factor can be seen as an alternative approach with reasonable accuracy.

Figure 4.17: Rate-dependent yield stress for iPP and composite with different levels of fiber-matrix adhesion, determined by simulations at 23°C, plotted in the semi-logarithmic (a) and double logarithmic (b) scales. Markers represent the simulations. Lines are Eyring fits according to Equation (4.1) using the parameters in Table 4.6.

Figure 4.18 Experimental data for the composite and the neat iPP (controlled cooling) at 23°C (a) and 80°C (b) where open and full markers represent the data from the creep and constant-strain-rate tests, respectively. Solid line is the Eyring fit for the composite data according to Equation (4.1) using the parameters in Table 4.1. Dashed line is obtained by shifting the full line with a shift factor, according to Equation (4.14).

4.6 Conclusion

In this study, a micromechanical finite element analysis was conducted to investigate the relationship between the time-dependent behavior of the neat iPP and its transversely loaded UD composite, and to seek explanations for the experimentally observed differences between them. Stress-strain response of the neat iPP was modeled with the EGP model and it was implemented in a micromechanical finite element model of the composite with an RVE containing hexagonally stacked fibers. Simulating the stress-strain behavior at various strain rates and temperatures, Eyring parameters of the composite are determined. Later, Eyring parameters and the time-dependent behavior of the composite obtained by simulations are compared with the experimental observations.

Two-process time- and temperature-dependent yield behavior of the neat matrix was captured also in the micromechanical simulations of the transversely loaded composite. The experimental observations on the lower strain rates for composite at which the response changes from 1-process to 2-processes are supported also by the micromechanical simulations. Simulations showed that the localization of the strain in the RVE is responsible for the trend observed.

Composite simulations resulted in activation energies and strain rate sensitivity (slope of the yield stress vs. $\log(\text{strain rate})$ curve, related to activation volume) similar to those of the neat matrix, contradicting the experimental observations which showed lower activation energies and strain rate sensitivity for the composite. Besides, stress levels of the composite were higher

than that of the neat matrix, unlike the experimental observations. Upon this observation, it was decided to include the effect of non-adhering fibers in the RVE, which, in reality also plays a role in the transverse failure of composites, to investigate its influence on the time-dependent failure.

The introduction of deadhesion between the fiber and matrix resulted in lower stress levels for the composite compared to the neat iPP. Furthermore, the strain rate sensitivity of the composite was also lower than that of the neat iPP, similar to the experimental observations. The size of the fiber-matrix interface with no adhesion affected the strain rate sensitivity: the larger the debonded region, the lower the strain-rate sensitivity. However, the activation energy was not sensitive to the adhesion: neat iPP and composite simulations with different levels of adhesion all resulted in close activation energies.

The simulations show that the strain rate sensitivity (and thus, activation volume) is sensitive to the temperature-independent effects such as the deadhesion between the fiber and matrix, while the activation energy is not. Lower activation energy experimentally observed for the composite may be originating from the presence of another thermally-activated failure mechanism such as time- and temperature-dependent interface failure [22,23] with an activation energy lower than that of the neat matrix.

4.7 References

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Chapter 5: Time-dependent failure of off-axis loaded glass/iPP composites

Abstract

In Chapters 2 and 3, it was demonstrated that the time-dependent failure of transversely loaded UD glass/iPP was fully plasticity-controlled and an analytical lifetime prediction method was used to describe the relation between the applied stress and time-to-failure without describing the stress-strain behavior. In the present work, the aim is to extend our previous study to other off-axis angles by investigating the effect of the off-axis angle on the time-dependent failure of UD glass/iPP, and to predict the time-dependent, anisotropic stress-strain response.

Glass/iPP specimens with different off-axis angles are tested at various strain rates, creep and fatigue loads to characterize the anisotropic and time-dependent mechanical response. It is demonstrated that the angle- and strain-rate dependence of the tensile strength is decoupled, which makes it possible to characterize the angle dependence at a single strain rate and the strain rate dependence at a single angle. Moreover, similar to transverse loading, off-axis failure was also observed to be plasticity-controlled. Based on these observations, the aforementioned analytical lifetime prediction method is adapted for the off-axis loading, which eventually leads to a good agreement with the experimental long-term data. In the second part of the study, an anisotropic, viscoelastic-viscoplastic macro-scale (lamina level) constitutive model [1] is applied to UD glass/iPP. Angle and rate dependence of the strength were captured by Hill equivalent stress and Eyring flow rule, respectively. The decoupling of the effects of angle and strain rate on the off-axis strength simplified the characterization of the angle and time-dependent behavior for modeling. A method for extracting the model parameters is presented. The model describes the angle- and rate-dependent nonlinear stress-strain behavior of UD composites reasonably well.

5.1 Introduction

Thermoplastic composites find ever-increasing use in engineering applications. Being relatively new and still less common than their thermoset counterparts, their use brings new challenges in understanding and predicting their mechanical behavior. These materials exhibit significant time-dependence in off-axis loading: they are highly prone to creep and fatigue failure [2–6], and their stress-strain response depends significantly on the applied strain rate [7–11]. Hence, one of the main challenges is the development of predictive models capturing their time-dependent behavior, which is crucial to exploiting the full potential of these materials. Since the time-dependent behavior of the neat matrix plays a significant role in the off-axis failure, as shown in Chapters 2, 3, and 4 for the transverse loading, a discussion of the time-dependent failure of the neat thermoplastics is important to understand the behavior of the composites.

Under long-term creep loading, neat thermoplastics may exhibit plasticity, crack-growth, and degradation-controlled failure mechanisms [12–14], which is schematically illustrated in Figure 5.1. Among these, plasticity- and crack growth-controlled mechanisms depend highly on the applied stress. Plasticity-controlled failure results from the accumulation of plastic strain and it is dominant at high stresses and relatively short time scales. Crack growth controlled failure occurs due to cracks, which are either already present in the material or have formed due to the loading, reaching a critical length after they have slowly propagated. This mechanism is present at low stresses and long time scales and results in a less pronounced stress dependence of the time-to-failure, as schematically shown in Figure 5.1. Due to the change in failure kinetics, lifetime prediction methods for each regime are also different; hence, identification of the failure mechanisms is of high importance. Motivated by the fact that plasticity-controlled failure had not been identified for the continuous fiber-reinforced composites, in Chapters 2 and 3 we discovered that the time-dependent failure of glass/iPP was extensively dominated by the plasticity. This was shown by the delayed failure under cyclic loading, identical failure kinetics in the constant-strain-rate and long-term tests, and a critical strain-governed lifetime, which are all typical characteristics for material systems displaying plasticity-controlled failure [13, 15–18]. Nevertheless, these studies were limited to transverse loading (loading angle of 90°). Since multidirectional laminates practically used in engineering applications have off-axis layers oriented in various directions, it is essential to investigate the time-dependent failure in other off-axis loading angles as well.

Figure 5.1: Long-term failure mechanisms of thermoplastics.

Most studies on creep and fatigue of the off-axis loaded composites make use of a linear relationship between the applied stress and lifetime in a semi- or double-logarithmic plot, based on empirical, phenomenological or damage mechanics based approaches [3, 19–24]. Such a relationship in the material directions is later plugged in a macroscopic strength criterion such as Tsai-Hill [25] or Hashin-Rotem [26] to describe the off-axis angle dependence of the creep and fatigue behavior [2, 21]. Although these studies came up with a relation that described the lifetime under off-axis loading, most of them focus on epoxy and PEEK composites and a lifetime prediction method based on the plasticity-controlled failure of the thermoplastic composites is missing. Hence, their use may lead to an erroneous description of the failure kinetics for glass/iPP, which displays pronounced plasticity-controlled failure.

Besides predicting time-to-failure, modeling the orientation- and time-dependent stress-strain response of the off-axis loaded thermoplastic composites is also of high interest. This has potential uses in the prediction of the time-dependent response of multidirectional laminates since the off-axis loaded laminae can be considered as the building blocks of multidirectional laminates. A sophisticated model available for this purpose is the anisotropic, viscoelastic-viscoplastic macro-scale constitutive model developed by Amiri-Rad et al. [1], which was successfully used to predict the anisotropic time-dependent behavior of short fiber-reinforced composites. The model of Amiri-Rad et al. [1] incorporates the viscoelastic nature of the neat thermoplastics well in the constitutive model of the composite. This helps to accurately model the effects of parameters such as temperature, strain-rate and thermo-rheologically complex behavior [27], which play a remarkable role in the matrix-dominated failure of composites. Thus, this model will be applied to off-axis loaded UD glass/iPP in the present study.

The anisotropic viscoelastic-viscoplastic constitutive model [1] that will be applied in this work was developed based on extensive research on the time-dependent failure of short fiber-reinforced and oriented thermoplastics. A study by van Erp et al. [28] on the influence of molecular orientation on the anisotropic response of drawn iPP demonstrated that the strain

rate dependence of the yield stress in various loading directions were observed to be parallel in a double logarithmic plot. This finding implied that the influences of strain rate and loading angle were multiplicatively separable; also referred to as *factorizable*. The factorizability facilitated the modeling of the effect of orientation and strain rate. Besides, constant-strain-rate and creep behavior exhibited identical failure kinetics, which was along with plasticity-controlled failure kinetics [13,17]. The time-dependent anisotropic yield was modeled using an associated flow rule with anisotropic Hill effective stress [29] and Eyring's flow theory [30]. This model was confined to predicting yield conditions and time-to-failure under constant-strain-rate and creep loading, respectively. Amiri-Rad et al. [1] improved van Erp et al.'s model by adding anisotropic, rate-dependent viscoelasticity and, as a result, they successfully simulated the anisotropic viscoelastic-viscoplastic stress-strain response of short-fiber-reinforced polycarbonate. This versatile model offered the advantage of simulating not only the constant-strain-rate response but also creep and fatigue response in the plasticity-controlled regime by using the same constitutive model.

This study aims to investigate the effect of off-axis loading angle on the time-dependent failure of glass/iPP and to predict the time-dependent behavior. The initial part of the study will serve as an extension of Chapters 2 and 3, which identified the plasticity-controlled failure mechanism in the transversely loaded glass/iPP, to other off-axis angles. Time-dependent failure will be characterized by conducting constant-strain-rate, creep and fatigue tests at room temperature. An analytical lifetime prediction method, which is an extension of the method presented in Chapters 2 and 3 from transverse loading to other off-axis angles, will be introduced. In the second part of the study, the above-mentioned macroscopic, anisotropic, lamina-level constitutive model [1] will be applied to predict the off-axis, angle and strain rate dependent stress-strain response.

5.2 Experimental methods and materials

5.2.1 Material and sample preparation

Glass-reinforced UD tape with a polypropylene matrix with a weight averaged molecular weight of $M_w = 150$ kg/mol and a polydispersity index (M_w/M_n) of 5.2 was kindly provided by SABIC FRT. The tape has a fiber volume and weight fraction of 45% and 70%, respectively. The dimensions of the tape are 110 mm (width) x 0.25 mm (nominal thickness). The tape was cut in 390 mm-long strips to be laid in a picture-frame mold with dimensions of 390 mm x 390 mm. The stack had eight layers, which can be shown with the laminate designation $[90]_8$, and was pressed using a Fontijne press. A low pressure was applied to ensure contact and facilitate heat transfer between the plates of the press and the mold while heating the mold to the consolidation temperature of

220°C. When the consolidation temperature was reached, the pressure was increased to the consolidation pressure of 2 bars and kept constant until the end of the press cycle. After a dwell time of 10 minutes at the consolidation temperature and pressure, the plates were first cooled by air down to 200°C, and then by water down to room temperature. The cooling rate obtained was measured to be 5°C/min.

Samples were cut from the unidirectional laminates with a diamond saw using the water as a coolant. Rectangular specimens with rectangular sandpaper tabs are utilized. Dimensions of the specimen are presented in Figure 5.2. As shown in the figure, the angle between the fiber orientation and the loading direction is named as the off-axis angle ϕ .

Figure 5.2: Schematic drawing of the specimen.

5.2.2 Mechanical tests

For constant-strain-rate and creep tests, a Zwick Roell testing machine with a 50 kN load cell was used. For fatigue tests, a hydraulic Instron 8516 with a load cell of 100 kN was utilized. Constant-strain-rate tests of the off-axis UD specimens were conducted at constant crosshead speeds, which correspond to strain rates in the range of 10^{-6} - 10^{-3} s^{-1} . A clip-on extensometer with a gauge length of 25 mm was used while testing some specimens to record stress-strain data to be used for characterization and validation of the viscoelastic-viscoplastic model. Creep and maximum fatigue loads were applied in 10 seconds. Fatigue tests were conducted with a stress ratio of 0.1 and a sinusoidal waveform. Constant-strain-rate and creep tests were conducted in various off-axis angles, while fatigue tests were conducted only at 45°. For comparison, constant-strain-rate, creep and fatigue data of the transverse angle 90° are frequently referenced from Chapter 2.

In addition to the off-axis specimens, longitudinally loaded UD specimens were also tested to determine the modulus of elasticity in the fiber direction, longitudinal tensile strength, and the Poisson's ratio. Tests were carried out only at a strain rate of 10^{-4} s^{-1} . To determine the Poisson's ratio, 2-D Digital Image Correlation (DIC) was conducted using Aramis software. A speckle pattern was formed by applying black-colored spray paint directly on the specimens' surface. This was sufficient to get enough contrast between the specimen surface and the speckle pattern since the specimens had a white color.

5.3 Experimental results

5.3.1 Constant-strain-rate tests

Figure 5.3: (a) Specimens after failure, where the failure path is indicated by a red, dashed line for the sample with $\phi = 45^\circ$. (b) Engineering stress vs. engineering strain curves of UD specimens with various fiber orientations at $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$ (for $\phi = 90^\circ$, $\dot{\epsilon} = 1.3 \cdot 10^{-4} \text{ s}^{-1}$).

Figure 5.3a shows the specimens with different off-axis angles after failure. As can be seen in the figure, failure takes place along the fiber direction. This means that fiber failure does not contribute to the failure of the off-axis loaded specimens. On the other hand, longitudinal failure (0°) is fully fiber-dominated. Figure 5.3b displays the stress-strain graphs of UD specimens with various orientations at a strain rate of 10^{-4} s^{-1} . The tensile strength increases as the angle gets smaller. Modulus is almost constant in the range of $\phi = 90^\circ$ – 45° , while it increases with decreasing angles in the range of $\phi = 45^\circ$ – 0° . A considerable nonlinearity in the stress-strain response is observed for all off-axis angles. Moreover, strain-to-failure at other off-axis angles is remarkably higher than that for $\phi = 90^\circ$. This could be caused by the contribution of shear deformation induced by extension-shear coupling, which does not play a role at 90° . In the longitudinal loading, the stress-strain curve is mostly linear up to failure; hence, the deformation is predominantly elastic.

To investigate the strain rate dependence of the strength, constant-strain-rate tests are conducted also at 10^{-6} , 10^{-5} , and 10^{-3} s^{-1} . Figure 5.4a, which is plotted on a semi-logarithmic scale, shows that off-axis loading leads to a linear relationship between the tensile strength and the logarithm of the strain rate, similar to the observations for $\phi = 90^\circ$ in Chapters 2 and 3. In addition, the slope of the tensile strength vs. applied strain rate curve increases as the off-axis angle gets smaller, which means that the sensitivity of the tensile strength to a change in the applied strain rate increases. When the figure is plotted on a double-logarithmic scale as in Figure

5.4c, it is striking to observe that the data at different angles are parallel to each other. This implies that the strain rate and angle dependence of the tensile strength can be multiplicatively decomposed, i.e., they are factorizable, similar to previous observations on the oriented PP [27] and various short and long fiber reinforced thermoplastics [6]. In other words, strain-rate dependent strength at an arbitrary off-axis angle can be obtained by the multiplication of rate-dependent strength at a reference angle with a shift factor, which can be summarized as:

$$\sigma_{\phi}(\dot{\epsilon}, \phi) = \sigma_{ref}(\dot{\epsilon}) \cdot g(\phi), \quad (5.1)$$

where σ_{ϕ} is the rate and off-axis angle-dependent tensile strength at the off-axis angle ϕ , $\sigma_{ref}(\dot{\epsilon})$ is the rate-dependent strength at the reference off-axis angle of choice and $g(\phi)$ is the angle-dependent shift factor. The factorizability implies that the rate-dependent tensile strength can be characterized at a single angle (reference angle) and the orientation (off-axis angle) dependence of the tensile strength can be characterized at a single strain rate, which significantly simplifies the characterization procedure. This observation will be used both for the analytical lifetime prediction method and the anisotropic lamina-level constitutive model.

Initially, strain rate dependence of the tensile strength will be characterized based on Eyring's activated flow theory [30]. Although glass/iPP is known to possess multiple deformation processes, which was shown in Chapter 3, at room temperature the rate-dependent strength can be captured with a combined, single process for a certain range of strain rates where the slope of tensile strength vs. logarithm of strain rate curve is constant. Examining Figure 5.4a, a change in slope is not observed; hence, single-process modeling will be carried out. In this case, based on Eyring's activated flow theory [30], the rate-dependent strength in the reference direction is expressed as in Equation (5.2), where $\dot{\epsilon}_{0,T}$ stands for the rate factor and σ_0 represents the characteristic stress at room temperature:

$$\sigma_{ref}(\dot{\epsilon}) = \sigma_0 \ln(\dot{\epsilon}) - \sigma_0 \ln\left(\frac{1}{2} \dot{\epsilon}_{0,T}\right). \quad (5.2)$$

Equation (5.2) is fitted with the experimental data in the reference angle of 90° , which results in the Eyring constants given in Table 5.1.

Next, orientation dependence of the tensile strength will be described at a single strain rate, which is chosen as 10^{-4} s^{-1} . A common approach for describing the orientation dependence of the tensile strength is using Hill's anisotropic failure criterion [29]. According to this criterion, regardless of the orientation, failure takes place at the same Hill equivalent stress $\bar{\sigma}_H$ given by:

$$\bar{\sigma}_H^2 = F(\sigma_{22} - \sigma_{33})^2 + G(\sigma_{33} - \sigma_{11})^2 + H(\sigma_{11} - \sigma_{22})^2 + 2L\sigma_{23}^2 + 2M\sigma_{13}^2 + 2N\sigma_{12}^2, \quad (5.3)$$

where

$$\begin{aligned} F &= \frac{1}{2} \left(\frac{1}{R_{22}^2} + \frac{1}{R_{33}^2} - \frac{1}{R_{11}^2} \right), & L &= \frac{3}{2R_{23}^2}, \\ G &= \frac{1}{2} \left(\frac{1}{R_{11}^2} + \frac{1}{R_{33}^2} - \frac{1}{R_{22}^2} \right), & M &= \frac{3}{2R_{13}^2}, \\ H &= \frac{1}{2} \left(\frac{1}{R_{11}^2} + \frac{1}{R_{22}^2} - \frac{1}{R_{33}^2} \right), & N &= \frac{3}{2R_{12}^2}. \end{aligned} \quad (5.4)$$

σ_{ij} in Equation (5.3) represents the stress components in the material directions and the indices 1, 2, and 3 represent the fiber direction, in-plane transverse direction, and the out-of-plane transverse direction, respectively. The constants R_{ij} in Equation (5.4) define the material anisotropy where R_{11} , R_{22} , and R_{33} are the ratios of tensile strengths in the material coordinates to the reference tensile strength σ_{ref} . Likewise, R_{12} , R_{13} , and R_{23} are defined as the ratios of shear strength in the material directions to the reference shear strength $\tau_{ref} = \frac{\sigma_{ref}}{\sqrt{3}}$. Choosing $\phi = 90^\circ$ as the reference angle and assuming transverse isotropy, $R_{22} = R_{33} = 1$. Assuming plane stress, stress components in the 3-direction are zero; hence, determining only R_{11} and R_{12} is sufficient. R_{11} can be determined from the coupon tests as the ratio of tensile strength in the longitudinal direction to the tensile strength in the reference (transverse) direction. Eventually, the only parameter that needs to be determined is R_{12} .

Expressing the stress components in Equation (5.3) as functions of the stress in the loading direction and the off-axis angle, orientation-dependent tensile strength can be described as follows:

$$\begin{aligned} \sigma_\phi &= \bar{\sigma}_H \cdot g(\phi), \\ g(\phi) &= [F \sin^4 \phi + G \cos^4 \phi + H(\cos^2 \phi - \sin^2 \phi)^2 + 2N \sin^2 \phi \cos^2 \phi]^{-\frac{1}{2}}. \end{aligned} \quad (5.5)$$

After setting $\bar{\sigma}_H = \sigma_{ref}(\dot{\epsilon})$ at $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$, R_{12} is determined by fitting Equation (5.5) with the experimental data at 10^{-4} s^{-1} . The resulting Hill parameters are shown in Table 5.1. In Figure 5.4b, the Hill fit using these parameters and the corresponding $g(\phi)$ are shown with a line and the experimental data at 10^{-4} s^{-1} are shown with markers. It can be seen that Hill fit describes the data well, except at $\phi = 10^\circ$.

Using the $g(\phi)$ determined, the predictions for the orientation and strain rate dependent

tensile strength using Equation (5.2) are shown with solid lines in Figure 5.4a and Figure 5.4c. It can be seen that although the rate dependence was characterized at a single strain rate and the orientation dependence was characterized at a single strain rate, the predictions describe the data quite well, except at $\phi = 10^\circ$ where the strength is underpredicted. This is caused by the fact that $g(\phi)$ determined by Hill fit cannot describe the data at $\phi = 10^\circ$ well. To show the capabilities of the model also for $\phi = 10^\circ$, the shift factor for this angle is artificially increased to 8.2 to have a good fit with the data, which is shown with dashed-dotted lines in Figure 5.4a and Figure 5.4c. The dashed-dotted lines show that if the dependence of the angle is described well for $\phi = 10^\circ$ as well, the behavior at this angle can also be predicted well.

Figure 5.4: Orientation and strain rate dependent tensile strength in (a) semi-logarithmic and (c) double-logarithmic plot of the tensile strength vs. applied strain rate. Markers are experimental data, lines are descriptions by Equation (5.1). (b) Off-axis tensile strength at various off-axis angles at a strain rate of 10⁻⁴ s⁻¹ with Hill fit and $g(\phi)$. (d) Rate-dependent tensile strength at various angles shifted vertically to 90°.

Next, using the shift factors, rate-dependent tensile strength at different angles will be shifted to the reference off-axis angle, $\phi = 90^\circ$. While doing this, the shift factor for $\phi = 10^\circ$ is again taken as 8.2, which is the value used for the fits with dashed-dotted lines in Figure 5.4a and Figure 5.4c, while for the other angles shift factors described by $g(\phi)$ are used. To differentiate the shift factors used for plotting Figure 5.4d from the ones obtained by $g(\phi)$, the notation $g^*(\phi)$ is used in Figure 5.4d. Eventually, shifting the data vertically using the shift factors, the data at different off-axis angles are shown to collapse and form a master curve, supporting the observation that rate- and strain-rate-dependence are factorizable. This observation shows that despite pre-yield failure is observed for $\phi = 90^\circ$, unlike for the other off-axis angles, failure kinetics are still related, shown by the same rate dependence in the double logarithmic scale.

Table 5.1: Parameters for the analytical lifetime prediction method.

Eyring parameters		Hill parameters		
σ_0 [MPa]	$\dot{\epsilon}_{0,T}$ [s ⁻¹]	R_{11}	R_{12}	R_{22}
0.82	$1.03 \cdot 10^{-14}$	40	2.05	1

An important observation is made when we compare the data shown in Figure 5.4c with the data of the neat matrix from Chapter 3 and the data of long fiber-reinforced iPP with two different orientations from the work of Pastukhov [6], as presented in Figure 5.5. It is seen that the data of the neat matrix and long fiber-reinforced iPP are also parallel to the data of the composite at different angles in a double logarithmic plot. This observation suggests that the failure kinetics of the neat matrix governs the time-dependent behavior of the fiber-reinforced matrices. Hence, the time-dependent behavior of the reinforced material systems with various fiber orientations can be obtained from the time-dependent behavior of the neat matrix by introducing a shift factor that accounts for the effect of fiber reinforcement on tensile strength. The shift factor shifts the reference tensile strength vs. strain rate curve of the neat matrix, which determines the rate dependence, in the vertical direction in a double logarithmic plot. This paves the way for fast and easy characterization of the time-dependent behavior of reinforced thermoplastics. Note that the stress levels at the UD transverse loading ($\phi=90^\circ$) are lower compared to the neat matrix, which was attributed in Chapter 4 to the presence of fiber-matrix interface failure.

Figure 5.5: Orientation and rate-dependent tensile strength. UD: unidirectional continuous fiber-reinforced composite, LFC: long fiber-reinforced composite.

5.3.2 Long-term behavior and the analytical lifetime prediction method

In this section, the experimental data on the loading angle dependence of the creep and fatigue behavior will be shown and an analytical lifetime prediction method based on the plasticity-controlled failure will be presented.

Creep tests are conducted at various off-axis angles and load levels to record the evolution of creep strain over time. This data can be used to construct Sherby-Dorn plots [31], which show the evolution of the strain rate as a function of strain. Sherby-Dorn plots are provided in Figure 5.6 for $\phi = 10^\circ$ and 30° at various creep stress levels. As seen in the plots, the creep strain rate decreases gradually and approaches a constant minimum value, which is termed as the macroscopic plastic flow. The plastic flow rate decreases as the creep stress is lowered.

For material systems exhibiting plasticity-controlled failure, multiplication of the plastic flow rate with time-to-failure is a constant, which is termed as the “critical strain”. In Chapter 2, we showed that the concept of critical strain holds for glass/iPP loaded at $\phi = 90^\circ$. Plotting plastic flow rate (minimum creep rate) versus time-to-failure as in Figure 5.7a, we observe that the concept of critical strain holds also for the other off-axis angles, which is implied by the data collapsing on lines with slopes of -1. Furthermore, the critical strain is observed to increase with a decrease in ϕ . This trend is plotted in Figure 5.7b, which shows that the dependence of the critical strain on the off-axis angle can be described by a linear relationship. Hence, for the lifetime prediction, the fit shown by the line in Figure 5.7b will be used to describe the relation between the critical strain and the off-axis angle.

Figure 5.6: (a) Sherby-Dorn plots from the creep tests at (a) $\phi = 10^\circ$ and (b) $\phi = 30^\circ$.

Figure 5.7: (a) Minimum creep rate vs. time-to-failure for various off-axis angles. (b) Dependence of critical strain on the off-axis angle.

The concept of the critical strain is used for lifetime predictions in the plasticity-controlled failure regime if the stress-dependence of the plastic flow rates in creep tests is identical to the rate dependence of the tensile strength in constant-strain-rate tests [17]. Such a relation paves the way for predicting the long-term creep lifetime using constant-strain-rate tests that take short times. Hence, it is of interest to investigate the relationship between short-term constant-strain-rate tests and long-term creep tests. Observing that creep stress dependence of the plastic flow rate and strain-rate-dependence of the tensile strength were identical, Bauwens-Crowet [32] postulated that the steady-state reached in creep tests of glassy polymers during plastic flow is identical to the steady-state at yield in constant-strain-rate tests. We showed in Chapters 2 and 3 that the same condition holds also for glass/iPP loaded at $\phi = 90^\circ$. To investigate if constant-strain-rate and creep tests are related also at the other off-axis angles, stress-dependent plastic flow rates obtained from the Sherby-Dorn plots for $\phi = 10^\circ$, 30° , and 45° are superimposed on

the plot of the tensile strength vs. logarithm of the applied strain rate, as presented in Figure 5.8a. In addition to $\phi = 90^\circ$, an excellent relationship is observed between the constant-strain-rate and creep tests at the other off-axis angles. Being a sign of plasticity-controlled failure [13, 17], this relation allows the utilization of the plasticity-controlled lifetime prediction methodology which expresses the time-to-failure as:

$$t_f = \frac{\varepsilon_{cr}}{\dot{\varepsilon}_{pl}(\sigma)} \quad (5.6)$$

for an arbitrary orientation where ε_{cr} is the critical strain and $\dot{\varepsilon}_{pl}$ is the stress-dependent plastic flow rate which is calculated from the Eyring equation [30]. We showed in Figure 5.7 that the critical strain depends on the off-axis angle. In addition, we showed in Figure 5.4 that the stress at an arbitrary off-axis angle can be reduced to the reference angle with the shift factor $g(\phi)$. Hence, Equation (5.6) is modified as:

$$t = \frac{\varepsilon_{cr}(\phi)}{\dot{\varepsilon}_{pl}(\sigma_\phi)}, \quad (5.7)$$

$$\dot{\varepsilon}_{pl}(\sigma_\phi) = \dot{\varepsilon}_{0,T} \sinh\left(\frac{\sigma_\phi / g(\phi)}{\sigma_0}\right), \quad (5.8)$$

where $\varepsilon_{cr}(\phi)$ is the off-axis angle-dependent critical strain, $\dot{\varepsilon}_{pl}(\sigma_\phi)$ is the plastic flow rate at the angle ϕ , $\dot{\varepsilon}_{0,T}$ and σ_0 are provided in Table 5.1.

Based on Chapter 2, in the case of cyclic loading with a constant-amplitude loading, accumulated plastic strain per cycle needs to be calculated for the lifetime prediction as follows:

$$t_f = \frac{\varepsilon_{cr}(\phi)}{\varepsilon_{pl,acc,cycle}} \cdot t_{cycle} = \frac{\varepsilon_{cr}(\phi)}{\varepsilon_{pl,acc,cycle}} \cdot \frac{1}{f} \quad (5.9)$$

$$\varepsilon_{pl,acc,cycle} = \int_0^{t_{cycle}} \dot{\varepsilon}_{pl}(\sigma_\phi(t')) dt', \quad (5.10)$$

where t_{cycle} is the cycle time and f is the frequency of the cyclic loading.

Figure 5.8: (a) Stress dependence of the minimum creep rate superimposed on the graph showing the strain-rate-dependence of the tensile strength at various off-axis angles. (b) Creep and fatigue behavior ($R = 0.1$, $f = 1$ Hz) at various off-axis angles. Open markers in (a) and (b) represent the creep data. Closed markers in (a) and (b) stand for constant-strain-rate tests and fatigue tests, respectively. Lines in (a) are described by Equation (5.1). Solid and dashed-dotted lines in (b) are described by Equation (5.7) and the dashed lines are described by Equation (5.9). For $\phi = 10^\circ$, shift factor is taken as 8.2 instead of the value determined by $g(\theta)$.

The analytical lifetime prediction method is used to predict the long-term creep and fatigue ($R = 0.1$ and $f = 1$ Hz) data presented in Figure 5.8b, where the prediction is shown with the lines (dashed line: fatigue, solid and dashed-dotted line: creep) and the experimental data is shown by the markers. Overall, the prediction provides an excellent description of both creep and fatigue data. Slight overprediction of lifetime at $\phi = 45^\circ$ is linked to the fact that creep data for this angle shown in Figure 5.8a lie below the line that characterizes the failure kinetics. Similar to the data at $\phi = 90^\circ$, the application of cyclic loading at $\phi = 45^\circ$ also results in a longer lifetime at the same maximum stress compared to creep loading. A longer lifetime under fatigue loading was associated with the plasticity-controlled failure following the previous research of Kanters et al. [13] on short fiber-reinforced composites and our work on transversely loaded UD continuous fiber-reinforced composites presented in Chapters 2 and 3. Hence, this observation shows that plasticity-controlled failure dominates the failure of off-axis loaded glass/iPP over a large time range, in addition to the previous observations on the identical failure kinetics in constant-strain-rate and creep tests and the applicability of the concept of critical strain. Another sign for the plasticity-controlled failure is that the creep and fatigue stress vs. time-to-failure curves for different angles are parallel to each other in a double logarithmic plot, similar to the parallelism of the short-term data shown in Figure 5.8a. It was revealed by Pastukhov [6] that such parallelism can be observed only in the plasticity-controlled regime, while in the crack growth-controlled regime slope changes with angle. Hence, to conclude, the aforementioned signs of plasticity-controlled failure explain the excellent agreement between the experimental data and lifetime predictions using the principles of plasticity-controlled failure.

5.4 Modeling of the off-axis stress-strain behavior

5.4.1 Anisotropic lamina constitutive model

In this section, the constitutive model to describe the macroscopic anisotropic response of the laminae (UD off-axis laminates) will be introduced. The modeling will be based on a single-process approach, since, as mentioned previously, the curves of tensile strength vs. $\log(\text{strain rate})$ of glass/iPP shown in Figure 5.4a display a constant slope at room temperature in the range of strain rates experimentally covered. This allows modeling of the total stress response, which is the summation of the stress response of multiple processes, with an imaginary, combined process, simplifying the characterization and modeling procedure remarkably.

The model, developed by Amiri-Rad et al. [1], considers two contributions to stress that act in parallel. One of them is the driving stress, which represents the contribution of intermolecular secondary interactions between the chains that control the viscoelastic deformation in the pre-yield regime and the plastic flow at yield. The other contribution is the hardening stress which accounts for the elastic deformation of the entangled polymer network. Although the model is capable of modeling the hardening behavior, in our analysis the contribution of strain hardening will not be taken into account since the stress-strain graphs of the off-axis loaded composites shown in Figure 5.3b do not display a strain-hardening regime. Based on the findings in [33,34], multiple Maxwell elements with different relaxation times are used to describe the viscoelastic deformation in the nonlinear pre-yield regime. A mechanical analog of the model is presented in Figure 5.9, where the number of branches represents the number of modes used to capture the nonlinearity. Note that, in contrast to the modeling of neat polymers by the Eindhoven Glassy Polymer (EGP) model, both the spring and the dashpot in Figure 5.9 are anisotropic. Since the Maxwell elements are connected in parallel, the total Cauchy stress σ is expressed as the summation of the stresses in all branches as in:

$$\sigma = \sum_{i=1}^n \sigma_{s,i}, \quad (5.11)$$

where $\sigma_{s,i}$ represents the driving stress of mode i and n is the total number of modes. To capture the rate-dependence as observed in the experiments, which is described by a linear relationship between the yield stress and the logarithm of the strain rate, an Eyring type viscosity is used. Hence, the viscosity of each Maxwell element, $\eta_i(\bar{\epsilon})$, decreases exponentially with the applied stress [34]. In a constant-strain-rate test, as the strain, and thus stress, increases, different Maxwell elements relax at their respective relaxation times. When the mode with the highest relaxation time relaxes, a steady state is reached: at constant stress, the material flows

at the applied strain rate, which is taken as the yield point.

Figure 5.9: Mechanical analog of the model.

Total deformation gradient $\mathbf{F}$ is decomposed into its elastic ($\mathbf{F}_{e,i}$) and plastic ($\mathbf{F}_{p,i}$) parts as follows:

$$\mathbf{F} = \mathbf{F}_{e,i} \cdot \mathbf{F}_{p,i}, \quad (5.12)$$

where $\mathbf{F}_{p,i}$ transforms the reference configuration to a stress-free intermediate configuration and $\mathbf{F}_{e,i}$ brings the material to the current state. To calculate the stress in each branch using the linear anisotropic law, the second Piola-Kirchhoff stress $\hat{\mathbf{S}}_{s,i}$ is used, which is related to the Cauchy stress $\boldsymbol{\sigma}_{s,i}$ as follows:

$$\hat{\mathbf{S}}_{s,i} = J \mathbf{F}_{e,i}^{-1} \cdot \boldsymbol{\sigma}_{s,i} \cdot \mathbf{F}_{e,i}^{-T}, \quad (5.13)$$

where J is the volume ratio and $\mathbf{F}_{e,i}$ is the elastic part of the deformation gradient tensor for mode i and the hat symbol ($\hat{}$) represents the intermediate state [1].

Elastic Green-Lagrange strain and the rate of plastic deformation tensors are based on the elastic and plastic deformation gradient tensors, respectively, as shown in Equations (5.14) and (5.15), where sym stands for the symmetric part of the tensor:

$$\hat{\mathbf{E}}_{e,i} = \frac{1}{2} (\mathbf{F}_{e,i}^T \cdot \mathbf{F}_{e,i} - \mathbf{I}) \quad (5.14)$$

$$\hat{\mathbf{D}}_{p,i} = \text{sym}(\dot{\mathbf{F}}_{p,i} \cdot \mathbf{F}_{p,i}^{-1}). \quad (5.15)$$

The elastic Green-Lagrange strain is used to calculate the stress $\hat{\mathbf{S}}_{s,i}$ according to the linear

orthotropic law as follows:

$$\hat{\mathbf{S}}_{s,i} = {}^4\hat{\mathbf{C}}_i : \hat{\mathbf{E}}_{e,i}, \quad (5.16)$$

where ${}^4\hat{\mathbf{C}}_i$ is the 4th order orthotropic stiffness tensor. In the material coordinates, the stiffness matrix for the mode i is expressed as [1, 34]:

$$\underline{\mathbf{C}}_i = \begin{bmatrix} \frac{1 - \nu_{23}\nu_{32}}{E_{22,i}E_{33,i}\Delta_i} & \frac{\nu_{21} + \nu_{31}\nu_{23}}{E_{22,i}E_{33,i}\Delta_i} & \frac{\nu_{31} + \nu_{21}\nu_{32}}{E_{22,i}E_{33,i}\Delta_i} & 0 & 0 & 0 \\ \frac{\nu_{12} + \nu_{32}\nu_{13}}{E_{11,i}E_{33,i}\Delta_i} & \frac{1 - \nu_{13}\nu_{31}}{E_{11,i}E_{33,i}\Delta_i} & \frac{\nu_{32} + \nu_{12}\nu_{31}}{E_{11,i}E_{33,i}\Delta_i} & 0 & 0 & 0 \\ \frac{\nu_{13} + \nu_{12}\nu_{23}}{E_{11,i}E_{22,i}\Delta_i} & \frac{\nu_{23} + \nu_{21}\nu_{13}}{E_{11,i}E_{22,i}\Delta_i} & \frac{1 - \nu_{12}\nu_{21}}{E_{11,i}E_{22,i}\Delta_i} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{12,i} & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{23,i} & 0 \\ 0 & 0 & 0 & 0 & 0 & G_{13,i} \end{bmatrix}, \quad (5.17)$$

where

$$\Delta_i = \frac{1 - \nu_{12}\nu_{21} - \nu_{23}\nu_{32} - \nu_{31}\nu_{13} - 2\nu_{21}\nu_{32}\nu_{13}}{E_{11,i}E_{22,i}E_{33,i}}. \quad (5.18)$$

Having obtained the stress at each branch, the equivalent stress needs to be determined, as it will be needed later to determine the anisotropic plastic flow. The equivalent shear stress $\bar{\tau}_i$ for each branch is found from:

$$\bar{\tau}_i = \frac{\bar{\sigma}_i}{\sqrt{3}}, \quad (5.19)$$

where $\bar{\sigma}_i$ is the Hill effective stress [1]. After the stress is transformed to material coordinates represented by indices 1, 2 and 3, Hill effective stress is obtained using the components of the stress tensor as follows [1,29]:

$$\begin{aligned} \bar{\sigma}_i^2 = & F(\underline{S}_{s,i,22} - \underline{S}_{s,i,33})^2 + G(\underline{S}_{s,i,33} - \underline{S}_{s,i,11})^2 + H(\underline{S}_{s,i,11} - \underline{S}_{s,i,22})^2 \\ & + 2L\underline{S}_{s,i,23}^2 + 2M\underline{S}_{s,i,13}^2 + 2N\underline{S}_{s,i,12}^2, \end{aligned} \quad (5.20)$$

where the constants F , G , H , L , M , and N define the anisotropy of the material and they were already introduced in Equation (5.4).

The equivalent stress at each Maxwell branch results in an equivalent plastic flow rate $\dot{\bar{\gamma}}_{p,i}$ which depends on the viscosity as follows [1,36]:

$$\dot{\bar{\gamma}}_{p,i} = \bar{\tau}_i / \eta_i(\bar{\tau}). \quad (5.21)$$

As mentioned before, the viscosity of each branch decreases with the total equivalent stress $\bar{\tau}$ according to Eyring rule [30]:

$$\eta_i(\bar{\tau}) = \eta_{0,i} a_\tau(\bar{\tau}), \quad (5.22)$$

where a_τ is the stress shift function defined as:

$$a_\tau(\bar{\tau}) = \frac{\frac{\bar{\tau}}{\tau_0}}{\sinh\left(\frac{\bar{\tau}}{\tau_0}\right)}. \quad (5.23)$$

In Equation (5.22) and (5.23), $\eta_{0,i}$ represents the zero shear viscosity of each mode and τ_0 is the characteristic shear stress defined as $\tau_0 = \sigma_0 / \sqrt{3}$ [33]. Based on the anisotropic viscoplasticity model proposed by van Erp et al. [28], the rate of plastic deformation tensor is related to the equivalent plastic flow rate by the following relation:

$$\hat{\mathbf{D}}_{p,i} = \dot{\bar{\gamma}}_{p,i} \hat{\mathbf{N}}_i. \quad (5.24)$$

In Equation (5.24), $\hat{\mathbf{N}}_i$ determines the direction of the plastic flow according to [1,28]:

$$\hat{\mathbf{N}}_i = \frac{\partial \bar{\tau}_i}{\partial \mathbf{S}_{s,i}}. \quad (5.25)$$

5.4.2 Characterization

In this section, we are going to introduce how the parameters of the anisotropic lamina constitutive model are determined. These include Eyring and Hill parameters, elastic anisotropy parameters and the spectrum of viscosities and moduli.

As mentioned before, although glass/iPP is known to possess multiple deformation processes, the response can be captured with a combined, single process at room temperature for a certain

range of strain rates. Initially, the characteristic shear stress is determined from the strain rate dependence of the tensile strength at the reference angle, which is chosen as $\phi = 90^\circ$. Equivalent shear stress is related to σ_0 provided in Table 5.1 through the relation $\tau_0 = \frac{\sigma_0}{\sqrt{3}}$ and is shown in Table 5.2.

Since the strain-rate and off-axis angle dependence of the tensile strength is factorizable, the characteristic stress is determined only at the reference off-axis angle. Likewise, Hill parameters which characterize the anisotropy in the tensile strength are determined only at a single strain rate, which is 10^{-4} s^{-1} . Although the Hill parameters were already determined in Section 5.3.1 for the analytical lifetime prediction method, they needed to be fine-tuned for the constitutive model since they led to higher stress levels compared to the experimental response. Hence, R_{12} was decreased to 1.7 for the constitutive model. Eventually, the new set of Hill parameters for the constitutive model is provided in Table 5.2.

The next step is to characterize the elastic anisotropy. Modulus of elasticity in the longitudinal and transverse directions (E_{11} and E_{22}) and the Poisson's ratio (ν_{12}) are determined by coupon tests conducted at a strain rate of 10^{-4} s^{-1} . In addition to these, the linear orthotropic elasticity requires the in-plane shear modulus G_{12} also to be determined to fully characterize the elasticity parameters. Nevertheless, unlike E_{11} , E_{22} and ν_{12} , G_{12} is not measured directly but instead determined by a trial and error approach to have a good prediction of the stress-strain response at different angles. The moduli determined, shown in Table 5.2, are used to form the stiffness tensor in the material coordinates shown in Equation (5.17). Although the stiffness tensor has 9 independent elasticity constants, transverse isotropy in continuous fiber-reinforced composites reduces this number to 5, where independent constants are E_{11} , $E_{22} = E_{33}$, $G_{12} = G_{13}$, $\nu_{12} = \nu_{13}$ and $G_{23} = \frac{E_{22}}{2(1+\nu_{23})}$.

Table 5.2: Parameters for the constitutive model.

Eyring parameter	Hill parameters			Orthotropic elasticity constants			
τ_0 [MPa]	R_{11}	R_{12}	R_{22}	E_{11} [GPa]	E_{22} [GPa]	ν_{12}	G_{12} [GPa]
0.47	40	1.7	1	36.30	8.47	0.26	1.72

Spectrum determination

The spectrum of moduli and relaxation times can effectively be determined using a single stress-strain curve with the procedure proposed by van Breemen et al. [33]. This procedure requires the choice of a discrete number of (extensional) relaxation times λ_i^e at which subsequently the moduli E_i of each mode is determined by fitting the experimental data to the stress expression that follows from time-stress superposition and the Boltzmann's integral. Following this procedure, which was also applied in [1], the moduli are obtained at an off-axis angle ϕ_{spect} by

using the characteristic stress at that angle.

Based on [1], it is assumed that the moduli in the material coordinates (E_{11} , E_{22} , G_{12}) are distributed in the same way among different modes as the moduli at ϕ_{spect} . For instance, the longitudinal modulus E_{11} can be written as a sum of the moduli of different modes $E_{11,i}$ as follows:

$$E_{11} = \sum_{i=1}^n E_{11,i} = \sum_{i=1}^n m_i E_{11} \quad (5.26)$$

$$\sum_{i=1}^n m_i = 1,$$

where $E_{11,i}$ is the modulus of each mode in the longitudinal direction and m_i is a weight factor that accounts for the contribution of each mode to the total moduli. This assumption eventually leads to:

$${}^4\mathbf{C}_i = m_i {}^4\mathbf{C}, \quad (5.27)$$

where ${}^4\mathbf{C}_i$ is the elastic stiffness tensor of each mode, ${}^4\mathbf{C}$ is the total elastic stiffness tensor.

Figure 5.10: (a) Stress-strain curve of the tensile test at $\phi = 30^\circ$ and $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$. (b) Total relaxation modulus vs. time obtained from (a).

To determine the spectrum, the stress-strain curve at $\phi_{spect} = 30^\circ$ and $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$ is utilized, which is presented in Figure 5.10a. Our experience has shown that the off-axis angles such as ϕ

$= 20^\circ$ or 45° can also be used to extract the spectrum. However, the transverse angle (90°) should not be used to extract the spectrum since at $\phi = 90^\circ$ failure takes place at low strains; thus, a reliable spectrum cannot be obtained to describe the high-strain behavior observed at the other angles. Another reason is that the model proposed leads to macroscopic yield at the tensile strength, which holds for all the off-axis angles except 90° , as seen in Figure 5.3b. Eventually, the total relaxation modulus vs. time for $\phi = 30^\circ$ is shown in Figure 5.10b. The total relaxation modulus $E(t)$ shown in Figure 5.10b is the sum of the contribution of all the modes according to:

$$E(t) = \sum_{i=1}^n E_i \exp\left(-\frac{t}{\lambda_i^e}\right), \quad (5.28)$$

where λ_i^e is the elongational relaxation time of each mode.

Subsequently, using the procedure mentioned, the moduli in the reference angle $\phi = 90^\circ$ are determined, which are provided in Table 5.3 along with the zero shear viscosities and elongational relaxation times.

Table 5.3: Spectrum at $\phi = 90^\circ$ according to the single-process approach ($\eta_{0,i} = \eta_{0,i,e}/3, \eta_{0,i,e} = E_i \lambda_i^e$).

Mode	$\eta_{0,i}$ [MPa·s]	E_i [MPa]	λ_i^e [s]
1	1.37e+13	1.29e+03	3.19e+10
2	1.93e+12	3.80e+02	1.52e+10
3	3.32e+10	5.95e+02	1.67e+08
4	4.08e+10	1.53e+02	8.00e+08
5	2.92e+10	2.28e+02	3.84e+08
6	2.58e+10	4.21e+02	1.84e+08
7	8.25e+09	5.87e+02	4.21e+07
8	1.46e+09	6.71e+02	6.51e+06
9	2.01e+08	6.00e+02	1.01e+06
10	3.34e+07	6.44e+02	1.56e+05
11	5.46e+06	6.81e+02	2.40e+04
12	8.98e+05	7.26e+02	3.71e+03
13	1.36e+05	7.09e+02	5.74e+02

5.4.3 Finite element model

Amiri-Rad et al. [1] implemented the constitutive model presented in a UMAT subroutine (implicit analysis) to be used in ABAQUS. In the current work, this subroutine is used to run simulations. The details about the numerical implementation, hence, can be found in their study

[1].

A finite element model of the specimen with its actual dimensions mentioned in Section 5.2.1 is constructed with 60 linear 3-D solid C3D8 elements, as shown in Figure 5.11. The strain-rate-dependent displacement $u(t)$ is applied on two reference points indicated by yellow dots in Figure 5.11, which are kinematically coupled in the loading direction (x) to the nodes on the surface they are placed.

Figure 5.11 Mesh used in the finite element model.

Mesh dependence

The effect of mesh refinement is checked for $\phi = 15^\circ$ and $\phi = 30^\circ$. Although Hill parameters used for the mesh refinement study ($R_{11} = 20$, $R_{12} = 1.7$, $R_{22} = 1$) are different than those shown in Table 5.2 which are used for obtaining the results presented in the next section, this will not affect the conclusion about the effect of mesh refinement. For the mesh refinement study, in addition to the mesh used in this study, simulations are run also with a finer mesh consisting of 240 elements (1 x 6 x 40 elements along thickness x width x length). As illustrated in Figure 5.12, the results are mesh-dependent for small angles such as $\phi = 15^\circ$ in the viscoplastic region at high strains, while at $\phi = 30^\circ$ there is no mesh dependence. Although the results are seen to be mesh dependent, further mesh refinement is avoided and the simulations in this work are run with the coarse mesh due to extremely long simulation times (more than 2 days for the 240-element model). Hence, the use of coarse mesh enabled us to perform more analyses in a limited timeframe and to investigate more conveniently the effect of parameters used in the model on the prediction, helping to fine-tune them.

Figure 5.12: Mesh dependence of the stress-strain behavior for $\phi = 15^\circ$ and $\phi = 30^\circ$ with $R_{11} = 20$, $R_{12} = 1.8$, $R_{22} = 1$.

5.4.4 Prediction of the stress-strain response

In this section, stress-strain curves experimentally obtained and those predicted by the simulations will be compared. To obtain the engineering stress from the simulations, the reaction force in the reference points is divided by the nominal cross-sectional area, which is 40 mm². Engineering strain is obtained based on the displacement of two nodes in the middle portion of the specimen which are 24 mm away from each other in the loading direction, shown by the red dots in Figure 5.11. This distance is very close to the gage length of the extensometer, which is 25 mm. Note that black-colored nodes in Figure 5.11 can also be used to determine the strain, which gives the same result as the red-colored nodes.

Initially, stress-strain curves for the off-axis angles $\phi = 10^\circ$ - 45° will be considered. Figure 5.13a shows the stress-strain curves at these angles at a strain rate of 10^{-4} s^{-1} , where solid lines are predictions according to the model, and markers represent the experimental data. It can be recognized that the predictions according to the viscoelastic-viscoplastic lamina model describe the experimentally observed angle-dependent nonlinear stress-strain curves quite well for the angles in the range of $\phi = 15^\circ$ - 45° . The success of the predictions can be attributed to the good description of the angle-dependent yield stress with Hill criterion, the initial moduli at different angles, and the spectrum of modes relaxation of which at their respective relaxation times determines the nonlinear path between the initial moduli and yield stresses. On the other hand, the prediction at $\phi = 10^\circ$ deviates from the experimental curve. A reason for that could be the deviations from the intended angle in specimen preparation or testing (specimen placement in clamps). To illustrate this effect, stress-strain curves taking into account a deviation of $\pm 1^\circ$ in the angle are shown with dashed lines. It is seen that the predictions are highly influenced by slight deviations in the angle for $\phi = 10^\circ$ and the experimentally obtained stress-strain curve is described well by the simulation at $\phi = 9^\circ$.

Figure 5.13b shows the predictions and experimental stress-strain curves at different strain rates at $\phi = 30^\circ$. As shown in the figure, the stress-strain behavior at different rates is predicted to a good extent. Although the rate dependence of the yield stress is captured well, compared to the experimental data, the predictions are less sensitive to the strain rate at low strains. A way to tackle this problem is to fine-tune the spectrum at low relaxation times. Moreover, two-process modeling may also improve the rate dependence of the predictions since the time-dependence of each process is different and the overall rate dependence at a specific strain depends on the relative stress contribution of each process at that strain.

Figure 5.13: Experimental stress-strain curves (markers) and predictions (lines) (a) at a strain rate of 10^{-4} s^{-1} for various angles and (b) at $\phi = 30^\circ$ for various strain rates. Dashed lines in (a) represent simulations at $\phi = 9^\circ$ and $\phi = 11^\circ$.

Figure 5.14: Experimental stress-strain curves (markers) and predictions with $R_{22} = 1$ (solid lines) and $R_{22} = 1.2$ (dashed lines) for (a) $\phi = 90^\circ$ at $\dot{\epsilon} = 1.3 \cdot 10^{-4} \text{ s}^{-1}$ and (b) $\phi = 20^\circ$ and $\phi = 45^\circ$ at $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$.

Next, the prediction will be compared with the experimental behavior for $\phi = 90^\circ$. Figure 5.14a

shows that the experiments lead to premature failure; in other words, the stress-strain curve does not exhibit a yield point, unlike the observation for the other off-axis angles. On the contrary, the prediction represented by the full line displays a yield point. This is not surprising since the model is built in such a way that it will predict yield conditions at the tensile strength, where the dependence of the tensile strength on the off-axis angle is controlled by the Hill parameters. Moreover, it can be seen that the prediction represented by the full line deviates from the experimentally-determined stress-strain curve at high strains. This can be explained by the differences in failure behavior between the angle at which the spectrum is obtained ($\phi = 30^\circ$) and the angle at which the prediction is made ($\phi = 90^\circ$). Experimentally, at $\phi = 30^\circ$, the strains are much larger compared to $\phi = 90^\circ$, which may be linked to the presence of shear deformation at $\phi = 30^\circ$. Hence, the spectrum obtained at $\phi = 30^\circ$ will lead to high strains when it is shifted to 90° . To predict the stress-strain response at $\phi = 90^\circ$, it can be assumed that the $\phi = 90^\circ$ specimen would have yielded at a stress value higher than the tensile strength experimentally observed if premature failure did not take place. Implementing this effect by increasing R_{22} from 1 to 1.2, the prediction obtained with $R_{22} = 1.2$ for $\phi = 90^\circ$ is shown with the dashed line in Figure 5.14a. It can be seen that the new prediction describes the experimental data well in the strain range experimentally covered. It should be born in mind that when R_{22} is artificially increased, a stress-based failure criterion is needed. In Figure 5.14a, the stress level set as the failure criterion is indicated by the gray-colored horizontal dotted line. Using $R_{22} = 1.2$, the stress-strain behavior at other off-axis angles can also be predicted. The effect of increasing R_{22} on the stress-strain behavior is illustrated in Figure 5.14b for $\phi = 20^\circ$ and $\phi = 45^\circ$. It can be seen that for a small off-axis angle such as $\phi = 20^\circ$, R_{22} does not have a significant effect. The effect is more apparent for $\phi = 45^\circ$, where $R_{22} = 1.2$ leads to higher stress levels. However, since the prediction with $R_{22} = 1$ showed slightly lower stresses compared to experimental behavior at $\phi = 45^\circ$, increasing R_{22} improves the prediction.

5.4.5 Multi-process modeling

In this work, we introduced and applied the constitutive model assuming that a single process governs the failure kinetics. Modeling with a single process was sufficient for the range of strain rates covered at room temperature. On the other hand, in reality, glass/iPP exhibits two processes (process *I* and *II*) that contribute to the total stress at room temperature for the range of strain rates we considered, which was shown in Chapter 3. Hence, it can be stated that two-process modeling is more physically-sound and represents the failure kinetics better. For instance, as mentioned previously, the strain-rate-dependence of the pre-yield regime may be improved with the two-process modeling. Moreover, two-process modeling would be needed if the stress-strain behavior needs to be described for various temperatures and/or a larger range of strain rates. This is because unlike the room temperature and the strain rates we studied, at elevated temperatures and/or low strain rates, only process *I* contributes to the total stress-

strain response, which implies a change in the deformation kinetics that cannot be taken into account with a single-process approach. Hence, multi-process modeling requires time-dependent off-axis behavior to be characterized at elevated temperatures as well, which is a subject of future research.

5.5 Conclusion

In this study, we investigated the time-dependent failure of the off-axis loaded unidirectional glass/iPP composites. Tensile strength vs. applied strain rate curves for different off-axis angles were parallel in a double logarithmic plot. This observation meant that the effects of the off-axis angle and strain rate on the tensile strength are decoupled: it was possible to characterize the angle dependence at a single strain rate and the rate dependence at a single off-axis angle, which facilitated the characterization of the anisotropic time-dependent behavior. Identical failure kinetics were observed in constant-strain-rate and creep tests. As the constant-strain-rate and creep behavior were related, applied creep/fatigue stress vs. time-to-failure plots at different off-axis angles were also parallel in a double-logarithmic plot. Based on these observations, the analytical lifetime prediction method presented in Chapters 2 and 3 for transverse loading is extended to other off-axis angles, which led to an excellent agreement with the creep and fatigue data. Plasticity-controlled failure, which was previously identified for transversely loaded glass/iPP, was seen to dominate the time-dependent failure at other off-axis angles as well.

This study also included the modeling of the time-dependent off-axis stress-strain response of glass/iPP using an anisotropic viscoelastic-viscoplastic lamina constitutive model [1] which was previously developed for short fiber-reinforced composites. The applied model, which makes use of the aforementioned decoupling, successfully predicted the off-axis angle and strain-rate dependent stress-strain response of glass/iPP by using a single-process approach which reduced the characterization and modeling efforts significantly. Successful description of the UD off-axis (or lamina) behavior using this model paves the way for modeling the time-dependent behavior of multidirectional laminates, which is important for a wide range of engineering applications. The lamina constitutive model applied in this study can be used, in essence, to simulate creep and fatigue response as well by employing a failure criterion as in [1], which is a subject of further research.

5.6 References

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Chapter 6: Discussion

In the main chapters of this thesis, the role of plasticity-controlled failure is identified in the matrix-dominated time-dependent behavior of thermoplastic composites. The identification aimed at proposing a lifetime prediction methodology based on the plasticity-controlled failure mechanism. The role of plasticity-controlled failure is identified under various conditions such as different temperatures, loading angles, and processing conditions. In this chapter, initially, the effect of these parameters on the time-dependent behavior will be discussed. Additionally, other parameters affecting the time-dependent behavior, which are not studied in this thesis, will also be discussed. Subsequently, the findings of this thesis will be put in a broader perspective: they will be used to ponder upon the implications of the plasticity-controlled failure on a common lifetime prediction method used in practice, the Constant Life Diagram (CLD). In the last part of the discussion, the attention will be directed towards multidirectional laminates: based on the outline provided in the introduction, a procedure to predict the time-dependent, plasticity-controlled failure of multidirectional laminates will be introduced and challenges pertaining to it will be explained.

6.1 The effect of several parameters on the time-dependent failure

The parameters affecting the time-dependent failure of the composites are categorized as:

- state of the matrix
- composite structure
- loading.

These parameters are schematically shown in Figure 6.1. The parameters (partly) studied are placed on the left and the parameters that were not studied are located on the right-hand side of the schema. Considering a straight-forward Classical Laminate Theory (CLT) approach, under time-dependent global loading, each lamina of a multidirectional laminate experiences a combination of transverse tension/compression, longitudinal tension/compression and in-plane shear loads. Matrix phase of the laminae experiences local stress states that are affected by the structure of the composite (lamina) which includes the effects such as fiber volume fraction, residual stresses, processing parameters, adhesion between fiber and matrix, etc. These stresses

later result in matrix-dominated time-dependent failure, which depends on the intrinsic time-dependent failure of the matrix (plasticity or crack growth controlled failure mechanism) affected by the state of the matrix (temperature, crystallinity imposed by cooling rate, etc.).

Figure 6.1: Parameters affecting the matrix-dominated time-dependent behavior of composites. Chapters in which the parameters are studied are indicated in parentheses.

6.1.1 Loading

Frequency, stress ratio, and constant-strain-rate behavior

The main method used for the identification of the failure mechanism was to investigate the influence of stress ratio and frequency on the lifetime, which have different effects on time-to-failure in plasticity and crack growth controlled failure regimes. These effects are summarized with a schematic drawing for an idealized case in Figure 6.2 for both plasticity- and crack growth-controlled failure. In addition to this, the relation between constant-strain-rate and creep behavior was also investigated to identify plasticity-controlled failure.

Figure 6.2: The influence of (a) stress ratio (R) and (b) frequency (f) on time-to-failure in plasticity and crack growth controlled failure regimes.

Based on the identification methods used, it was shown in Chapter 2 that glass/iPP, which is tested at room temperature, displayed the clearest signs of plasticity-controlled behavior. Plasticity was the dominant failure mode over the experimentally covered load range. Its creep and constant-strain rate behavior were related: the stress dependence of the minimum creep rate and strain rate dependence of the tensile strength were identical. Moreover, at the same maximum stress, cycling loading led to an increase in time-to-failure compared to static creep loading and the time-to-failure under cyclic loading was found to be frequency-independent. On the other hand, the extent of plasticity-related failure depended on factors such as frequency, load level and stress ratio for carbon/PEEK and carbon/PEKK. While they showed a relation between their short- and long-term behavior to some extent, the plasticity effects were evident mostly at high creep and fatigue loads and high stress ratios. At lower loads, time-to-failure decreased with a decrease in stress ratio and increase in frequency; and cycles-to-failure was independent of the frequency, which is typical for the crack growth-controlled failure.

The influence of the off-axis angle

In Chapter 5, the off-axis tensile tests revealed that the strain-to-failure is considerably higher for all off-axis angles tested (10° - 45°) compared to the transverse loading. In addition, the stress-strain curves under off-axis loading tended to display macroscopic yield, which is also different from the behavior under transverse loading.

Despite such differences, similar to transverse loading, the failure kinetics for constant-strain-rate and creep tests were identical and cyclic loading led to longer lifetimes compared to creep. Hence, plasticity-controlled failure was concluded to control the time-dependent failure of off-axis loaded UD laminates as well. Another remarkable observation was that yield stress vs. strain

rate curves at different angles are parallel to each other in the log-log scale, which also means that the failure kinetics at different angles are similar despite the aforementioned differences in the macroscopic deformation. The parallelity implies that the constant-strain-rate behavior at an arbitrary angle can be predicted by using the time-dependent failure at a reference angle and applying an angle-dependent shift factor. This makes it possible to “decouple” the effects of strain rate and angle on the tensile strength: rate dependence can be characterized at a single angle and angle dependence can be characterized at a single strain rate for accelerated characterization of the angle- and rate-dependent strength. Since short- and long-term tests are related, using the right critical strain for the corresponding angle, the characterization is extended to long-term loading. It should be borne in mind that the accelerated characterization scheme explained is associated with the plasticity-controlled failure, while the crack growth dominated failure would necessitate other approaches for characterization. To illustrate, Pastukhov’s [1] observations on short-fiber reinforced polycarbonate revealed that in the plasticity-controlled regime, time-dependent behavior exhibited parallelity in log-log scale similar to our observation; however, at lower loads and longer timescales where crack growth-controlled failure was dominant, a decrease in the off-axis angle led the slope of stress vs. time-to-failure to increase, as illustrated in Figure 6.3. Hence, it is of high importance to identify the governing failure mechanisms also for the off-axis loading.

Figure 6.3: Schematic illustration of the effect of off-axis angle θ on the failure kinetics in plasticity and crack growth controlled failure. The image is reproduced from [1].

In addition, plasticity-controlled deformation and failure of the glass/iPP paved the way for modeling the angle and time-dependent stress-strain behavior of UD laminates using the anisotropic constitutive model presented in [2], which was previously developed for short fiber-reinforced composites, where modeling made use of the above-mentioned path for accelerated characterization. Ability to model off-axis UD constitutive behavior has a pivotal role in modeling the plasticity-controlled time-dependent behavior of the multidirectional laminates since off-axis loaded laminae are building blocks of a multidirectional laminate. At the end of this chapter,

a roadmap will be introduced for predicting the time-dependent behavior of multidirectional laminates.

Before moving on to the next section, it should also be mentioned that the constitutive model of the lamina was used to simulate only the constant-strain-rate behavior in this thesis due to time limitations. In essence, the constitutive model is able to describe the creep response as well. Note that in constant-strain-rate tests a failure criterion was not necessary since simulations exhibit constant stress at yield, which was taken as the end of the simulation for all angles except 0° and 90° . However, a failure criterion should be defined for creep tests, similar to the procedure followed in [2] for short fiber-reinforced composites.

Other loading configurations

As previously mentioned, based on a straight-forward CLT approach, a lamina may experience various loading scenarios. In this thesis, we studied the matrix-dominated failure with transverse and off-axis loaded UD laminates subjected to tensile loads. Since off-axis loading leads to both transverse and in-plane shear stresses, the effect of in-plane shear loading is studied in a non-direct way. The role of plasticity under other loading scenarios are briefly discussed below.

Under compression transverse to the fibers, failure usually takes place at an inclined plane parallel to fibers [3,4], in contrast to transverse tensile failure where the failure tends to take place at a plane perpendicular to the loading direction. Failure is dominated by the shear stresses on the plane of fracture, which is highly matrix-dominated [3,4]. Although fiber-matrix debonding also plays a role here [5,6], its effect was found to be less compared to transverse tensile loading [7]. For these reasons, it can be expected that a high level of plasticity-related phenomena would be observed if the matrix-dominated time-dependent failure was studied under transverse compression.

In longitudinal tensile loading, failure is dominated mostly by fibers. However, depending on the relative stiffnesses of the fiber and matrix, plasticity of the matrix might play a role in the time-dependent failure [8]. In longitudinal compression, depending on the fiber-matrix adhesion [9], micro-buckling of fibers plays a significant role [4,9–12], which requires the matrix to be sheared; hence, the plasticity of the matrix would be expected to play an important role there.

As a next step, cross-ply and/or multidirectional laminates can be studied experimentally to investigate the role of plasticity-controlled failure in the time-dependent failure of more complex laminates. In this case, multiple transverse cracks would develop in the transverse and off-axis layers [13–15]. Whether plasticity would dominate or not can be checked by recording the transverse crack density over time and comparing the crack densities under static and cyclic loading at discrete times. For plasticity-controlled damage, at the same maximum stress, a lower transverse crack density would be expected in cyclic loading compared to static loading.

6.1.2 State of the matrix

Temperature

Chapters 2 and 3 showed that for transversely loaded UD glass/iPP failure was dominated by plasticity not only at room temperature, but also at high temperatures up to 110°C: lifetime under cyclic loading was higher compared to creep, time-to-failure was frequency-independent, and, furthermore, failure kinetics in constant-strain-rate and long-term tests were identical. The temperature was shown to have a profound influence on the time-dependent failure of glass/iPP: short and long-term strength decreased considerably with temperature. Moreover, elevated temperatures helped to identify the different plasticity-controlled deformation processes contributing to the time-dependent failure, similar to the neat iPP. Identification of the multiple deformation processes was found to be important for accurate lifetime predictions (Chapter 3) and constitutive modeling of the stress-strain-behavior (Chapter 4). However, it was shown that for a short range of strain rates and time-to-failure at a constant temperature, lifetime predictions (Chapter 2) and constitutive modeling (Chapter 5) can be made using a single deformation process to simplify the characterization of the time-dependent behavior.

Testing temperature with respect to the T_g

It was shown in Chapter 2 that plasticity effects were far more evident for glass/iPP, compared to carbon/PEEK and carbon/PEKK. Hence, why glass/iPP and other material systems would show such a difference in their long-term behavior should be questioned. A primary difference between the different material systems is that the testing temperature (room temperature) is above the T_g of iPP, while it is way below the T_g of both PEEK and PEKK, where testing above T_g is known to promote plasticity due to an enhancement in the segmental chain mobility in the matrix phase. Even for transversely loaded epoxy-matrix composites, increasing the testing temperature above T_g led to a change in the failure mode from crack growth to plasticity-dominated failure [16].

The influence of an increase in the temperature on the time-to-failure can be visualized in Figure 6.4. In the figure, the slope of the line indicating the plasticity-controlled region at low temperature is based on the creep data of carbon/PEEK at 23°C. The slope of the line indicating the crack growth-controlled region is based on the fatigue data of carbon/PEEK at 1 Hz and 23°C since creep data for the crack growth-controlled region is not available and the horizontal location of the line is not relevant for the current discussion. Rather, the plasticity- to crack growth-controlled-transition points, which are marked in the figure with circles, are of interest. Vertical location of the line showing plasticity-controlled region at high temperature is based on our own experimental data on carbon/PEEK at 120°C, which is around (just below) T_g . Assuming that an increase in the temperature from room temperature to a high temperature around T_g

leads to a larger shift in the plasticity-controlled region than in the crack growth-controlled region as in the figure, we see that the transition point shifts to longer lifetimes. This implies that at high temperature, load and time range at which plasticity-controlled failure is dominant will be larger. Hence, if crack growth is not accelerated considerably by temperature, an increase in the temperature might lead to plasticity-dominated failure over a large load range. The validity of this claim should be verified for PEEK by studying its crack growth controlled failure kinetics at high temperatures.

Figure 6.4: The effect of temperature on long-term behavior. The circles indicate the transition from plasticity to crack growth controlled failure.

Cooling rate

For glass/iPP, based on the findings in Chapter 3, a decrease in the cooling rate resulted in lower stress levels and strains-to-failure leading to extensive embrittlement at the slowest cooling rate (0.7°C/min), which was supported by microscopy images of the fracture location. In addition, strain rate sensitivity also decreased with the cooling rate, which showed that changing the cooling rate altered the failure mechanism. Due to the change in the failure mechanism, the change in the time-dependent behavior caused by the cooling rate could not be modeled directly by changing the rate factor in the Eyring Equation and keeping the other parameters (activation energies and volumes) as constant, unlike what is proposed in [17].

It can be stated that to benefit from higher strengths and levels of plasticity, higher cooling rates should be opted for. Considering our experimental work, most of our data, however, was not based on the highest cooling rate we studied (30°C/min). This is because our press was not able to cool at such high rates and the method we used to manufacture the fast-cooled laminate was not reproducible, which is also the reason for the non-availability of specimens for the long-term tests at this cooling rate.

Time-dependent behavior of the neat matrix

In Chapter 3, multi-process, thermo-rheologically complex behavior that is exhibited by neat iPP was also observed for glass/iPP, which was a clear sign that time-dependent behavior of the neat matrix and the composite was linked. Nevertheless, activation volumes and energies needed to model the time-dependent behavior of these materials were not identical: both the rate sensitivity (in the region where both deformation processes act) and activation energy of the composite was lower than those of the neat iPP. An explanation for such a difference was searched for in the scope of Chapter 4 with a micromechanical study. The time-dependent behavior of the iPP was modeled by the EGP model and subsequently input to the micromechanical finite element model of the transversely loaded composite. Simulations using an RVE assuming perfect bonding between the fiber and matrix led to Eyring parameters that are similar to those of neat iPP, which contradicted with the experimental observations.

Comparing the strain-rate dependence of the tensile strength of the composite and the neat iPP, the curves of yield (strength) vs. strain rate were parallel in a double logarithmic plot. This helps to predict the time-dependent behavior of the composite using a shift factor that accounts for the change in the stress levels once the time-dependent behavior of the neat matrix is known. Such an observation was made also by Pastukhov [1] for short fiber-reinforced composites.

6.1.3 Composite structure

Fiber-matrix adhesion

Fiber-matrix debonding is known to be crucial in transverse tensile loading. Motivated by this and the observation that the micromechanical RVE simulations with perfect fiber-matrix adhesion led to higher stress levels for the composite compared to the neat iPP, contradicting the experimental observations, the effect of fiber-matrix adhesion was studied in Chapter 4 to investigate its effect on the time-dependent behavior of the composite.

Incorporation of regions with no adhesion between the fiber and matrix in the RVE led to lower stress levels and strain rate sensitivity (slope of the yield stress vs. $\log(\text{strain rate})$ curve) for composites compared to the neat iPP, in agreement with the experiments. Hence, it can be stated that the fiber-matrix adhesion affects the strain rate sensitivity of the composite, in addition to the stress levels. Nevertheless, unlike the experimental observations, the activation energies calculated for the RVEs with non-adhering fibers were the same as that of the neat matrix. Hence, a complete link between Eyring parameters of iPP and glass/iPP could not be established. For more accurate simulations, process-induced residual stresses and time- and temperature-dependence of the fiber-matrix adhesion should also be studied, which would have an influence on the time-dependent failure of the composite affecting the Eyring parameters.

Fiber volume fraction

The effect of fiber volume fraction (v_f) was not studied in this thesis explicitly; however, it was significantly different for the materials studied: v_f was 45% for glass/iPP, while it was around 60% for carbon/PEEK and carbon/PEKK, for which the extent of plasticity-controlled failure was found to be lower. At this point, let us investigate the SEM images of the fracture surface of carbon/PEEK specimens tested under creep ($\sigma = 104$ MPa) and fatigue ($f = 10$ Hz, $\sigma = 75$ MPa) with the help of Figure 6.5a and Figure 6.5b, respectively. The specimens belong to different failure regimes; however, they both exhibit fiber-matrix debonding as a prominent failure mechanism regardless of the loading type and stress level. Hence, a higher fiber volume fraction compared to glass/iPP would lead to a higher possibility of having fiber-matrix debonding, which may explain the dominance of crack growth-dominated failure over a large load range for carbon/PEEK and carbon/PEKK. This hypothesis should be verified experimentally in further research with carbon/PEEK and carbon/PEKK tapes with lower v_f 's. Nevertheless, there is no supporting evidence for the proposed claim in the literature: one of the few studies about the effect of fiber volume fraction on the fatigue strength of transversely loaded UD composites was on carbon/epoxy laminates and claims that increasing the fiber content from 30% to 55% leads to an improvement in the fatigue strength [18].

(a)

(b)

Figure 6.5: SEM image of the fracture surface of carbon/PEEK specimens (a) tested under creep at 104 MPa (b) tested under fatigue at $\sigma_{max} = 75$ MPa with $R = 0.1$ and $f = 10$ Hz.

6.2 The implication of plasticity-controlled failure for Constant Life Diagrams (CLDs)

In this section, we aim to discuss what would be the implications of plasticity-controlled failure for CLDs, which is one of the common lifetime characterization methods for composites [19,20].

CLDs show combinations of stress amplitude (σ_a) and mean stress (σ_m) corresponding to certain levels of lifetime at specific stress ratios. Typically, using simple approaches such as S-N curves, lifetime is characterized at several stress ratios, with which the lifetime at other stress ratios can be predicted by interpolation. Several methods are available which propose a different number of stress ratios for characterization and also different ways of interpolation between those [19]. One important issue with CLDs is about how to treat the strength at zero stress amplitude. Most of the models utilize ultimate tensile and compressive strengths determined at a constant-strain-rate for this case, which was shown to result in a high discrepancy between the experimental data and predictions at high stress ratios [21]. To avoid this, and since static strength of our material is highly time-dependent, we will use creep strengths for the case $\sigma_a = 0$ as in [22].

To illustrate the effect of plasticity-controlled failure on the CLD, room temperature long-term data of glass/iPP from Chapter 2 is used, for which plasticity was observed to be the dominant failure mechanism throughout the experimental load range covered. Experimental data is available only at stress ratios of 0.1 and 1; however, using the lifetime prediction method introduced in Chapter 2, lifetime at other stress ratios of 0.3, 0.5, 0.7, and 0.9 are also calculated and depicted in Figure 6.6a. Based on this figure, a CLD is constructed, which is shown in Figure 6.6b where constant lifetime is indicated by full lines. The first thing to note is, as stated before, the pronounced time-dependence for $R = 1$ where $\sigma_a = 0$. Hence, typical CLD approaches that interpolate the lifetime between an R value and the static constant strength (UTS) would result in high errors especially for high R values. Next, change in lifetime under constant maximum stress will be discussed, which we used as a method to identify the failure mechanisms. For this purpose, we introduce a dashed line with a slope of -1 along which the maximum stress is constant. When we move from $R = 1$ towards $R = 0.1$ along the line, we traverse constant-life-lines with increasing lifetimes. This is because the slopes of constant-life-lines are steeper than that of the dashed line. If the failure was crack growth controlled, the slopes of the constant-life-lines would have been lower compared to the dashed line, as illustrated in Figure 6.7. Based on this figure, it can be stated that one should be careful if the governing failure mechanism changes with stress ratio as observed in [23]. Such a change would alter the trend of CLD, which would require a special way to construct the lines of constant lifetime; in other words, the method of interpolation would change.

Figure 6.6: (a) Maximum applied stress vs. time-to-failure for long-term loading of glass/iPP with $R = 0.1, 0.3, 0.5, 0.7, 0.9, 1$ according to Equation 2.8. (b) CLD based on (a) where lifetimes of $10^1, 10^2, 10^3, 10^4, 10^5$ s are indicated by full lines. The dashed line is a locus for constant maximum stress.

Figure 6.7: Schematic representation of the effect of failure mechanisms on the trend of CLDs. Full lines indicate the path for the constant life for plasticity and crack growth controlled failure mechanisms. Dotted lines represent different R values. The dashed line is a locus for constant maximum stress.

6.3 Towards predicting the time-dependent behavior of multidirectional laminates

In this section, a roadmap for the prediction of the time-dependent behavior of multidirectional laminates will be introduced. The constitutive model presented in Chapter 5 describes the angle and time-dependent behavior of a lamina. To simulate the time-dependent behavior of the laminate, the constitutive model can be used as an input for each lamina in the finite element

model of a multidirectional laminate.

Although two deformation processes govern the time-dependent behavior of glass/iPP (Chapter 3), for a certain range of strain rates where both processes contribute to the stress, the time-dependent behavior of off-axis loaded glass/iPP can be described with an imaginary, combined, single process. Hence, to simplify the characterization process, the use of the combined, single-process approach is recommended if the transversely/off-axis loaded material does not display a change from two-process to one-process behavior in the strain rate range of interest. This is usually the case for glass/iPP at room temperature if strain rates that are not too low or high are not of interest, see Chapter 3.

Since the angle and rate dependence of the time-dependent off-axis strength is decoupled, characterizing the rate dependence at a single off-axis angle is sufficient, which can be chosen as 90° for simplicity. In this thesis, this was carried out in Chapters 2 and 3, which can be seen in the outline presented in Figure 6.8. Also thanks to the decoupling, angle dependence is characterized at a single strain rate. The elastic anisotropy should be determined based on the dependence of the modulus of elasticity in the loading direction on the off-axis angle. In the spectrum of loading angles from the longitudinal loading at 0° to transverse loading at 90° , moduli should be determined at least at three angles to characterize the elastic anisotropy. This can be done at 90° and 0° , in addition to the angle at which spectrum is obtained, which is chosen in Chapter 5 as 30° . Based on the strength determined at these 3 loading angles, Hill parameters can also be determined to describe the orientation-dependent yield stress. Since the modeling approach for transverse loading requires a failure criterion to be defined, the strengths determined at the transverse angle 90° can be used as a failure criterion at that angle. To determine the spectrum of viscosities and moduli, stress-strain curve for the off-axis angle of 30° at a single strain rate is used. Overall, these are the set of tests that should be conducted to determine the anisotropic time-dependent failure of a lamina with the least amount of experimental work. In future studies, the implementation of the anisotropic lamina constitutive model in finite element analyses of multidirectional laminates is of high interest to predict their time-dependent behavior.

This thesis showed that the factors related to the state of the matrix have implications on the plasticity-controlled failure, which was discussed in the first section of this chapter. Hence, it is relevant to discuss briefly how the aforementioned factors can be taken into account in the prediction of time-dependent behavior.

Temperature dependence of the time-dependent behavior: To take the temperature dependence into account, different processes contributing to the total stress should be identified and their failure kinetics (characteristic stress, activation energy) should be determined, which requires the characterization of the time-dependent behavior in a wide range

of temperatures and strain rates as shown in Chapter 3. Temperature dependence should be characterized not only for transverse loading as in Chapter 3, but also for other off-axis angles.

Cooling rate (and aging): van Erp [17] showed that the failure kinetics of iPP with various cooling histories can be described with the same activation volume and energies and the effect of cooling rate on the failure kinetics can be captured by changing the rate constant in the Eyring equation. However, our observations in Chapter 3 showed that strain rate sensitivity, hence activation volumes, were significantly different for different cooling rates, which implied a change in the failure mechanism. Therefore, to account for the effect of cooling rate for glass/iPP, time and rate dependence should be fully characterized for the cooling rate of interest. However, for a material system that does not show such a change in the failure mechanism, the effect of the cooling rate can be captured by introducing a state parameter that shifts the viscosity of the Maxwell elements, an example of which can be found in [24]. The introduction of a state parameter would also be useful for capturing the effect of physical aging in the time-dependent behavior of materials [25,26], which was discussed for carbon/PEEK and carbon/PEKK in Chapter 2.

Time-dependent behavior of the neat matrix: The parallelity of the curves of (yield) strength vs. strain rate in a log-log plot for the neat iPP and composite loaded in the off-axis direction, as discussed in Chapter 5, can accelerate the characterization of the angle and time-dependent lamina behavior if the time-dependent behavior of the matrix is known a priori. However, for simulations at multiple temperatures and/or a large range of strain rates, care should be taken for the activation energies, which are found to be different for the neat matrix and the composite.

6.3.1 Challenges and future work

Prediction of the time-dependent deformation of multidirectional laminates involves several other challenges. One of the challenges is the introduction of failure (damage initiation) and damage evolution criteria. The current model results in yield (maximum, constant stress in the stress-strain curve) for the constant strain-rate simulations of the off-axis loaded UD laminates, which can be taken as the end of the simulation. However, in the simulations of complex parts with a multidirectional layup, some layers in certain locations of the part may reach yield far earlier than the rest of the part; hence, the load-bearing capacity of such regions should be decreased. This requires setting a damage initiation criterion followed by a damage evolution pattern. A failure criterion is needed also for the creep simulations since the strain keeps increasing under constant creep load. An example can be found in the work of Amiri-Rad et al. [2], where a strain-based failure criterion is employed for creep simulations of the short fiber-reinforced composites using the anisotropic, time-dependent constitutive model applied in Chapter 5 of this thesis. Another challenge for the simulations is accounting for the differences in the in-situ strength of a lamina in a multidirectional laminate and the UD strength determined

by coupon tests during characterization, known as “the in-situ effect”. This requires the identification of the effect of the constraining layers on the in-situ strength [27]. Kawai and Honda [28] found that neglecting the in-situ effect causes very conservative predictions for the fatigue lifetime of the off-axis fatigue loaded cross-ply carbon/epoxy laminates. Finally, for simulations of the multidirectional laminates, the capability of predicting the delamination is crucial since delamination plays a significant role in the progressive failure of the multidirectional laminates [29,30]. These are subjects of future research.

Figure 6.8: Outline of the thesis. Reproduced from Chapter 1.

6.4 References

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Chapter 7: Conclusions and recommendations

7.1 Conclusions

This thesis focused on the identification of the role of plasticity-controlled failure mechanism in the time-dependent, matrix-dominated failure of thermoplastic composites. The identification is aimed at predicting the time-dependent failure of thermoplastic composites by taking plasticity-controlled failure into account. Time-dependent behavior was studied on transversely (glass/iPP, carbon/PEEK, carbon/PEKK) and off-axis (glass/iPP) loaded laminates. Carbon/PEEK and carbon/PEKK were tested mainly at room temperature, while the time-dependent behavior of glass/iPP was evaluated also at elevated temperatures. Main conclusions of this thesis are listed below:

- Plasticity-controlled failure, an intrinsic failure mechanism of neat thermoplastics, plays a role also in the time-dependent behavior of UD composites although the deformation is highly localized and in some cases, a high scatter is observed, unlike neat thermoplastics. The extent of the role of the plasticity depends on the material system.
- Investigating the effect of frequency and stress ratio on time-to-failure, glass/iPP is shown to display plasticity-controlled failure over the whole experimental range covered: at the same maximum stress, time-to-failure increases with a decrease in the stress ratio of the fatigue loading. Moreover, time-to-failure is independent of the frequency.
- Glass/iPP displays identical failure kinetics in constant-strain-rate and creep tests: strain rate dependence of the tensile strength and creep stress dependence of the minimum creep rate are found to be identical, which is typical for plasticity-controlled failure. This helps in formulating an analytical lifetime prediction methodology based on the failure kinetics observed in the constant-strain-rate tests that take short times. The identity holds regardless of the presence of macroscopic yield.
- For transversely loaded carbon/PEEK and carbon/PEKK, the role of plasticity depends on the load levels. At high creep and fatigue loads, stress dependence of time-to-failure is low, comparable to the low strain rate dependence of the tensile strength, although the data in both tests have high scatter. The comparable failure kinetics is attributed to the effect of plasticity. At low stresses, stress dependence of time-to-failure is controlled by a far steeper slope, implying a change in the failure kinetics. A decrease

in stress ratio and an increase in frequency leads to shorter lifetimes. These, along with the frequency independence of cycles-to-failure, are signs of the crack growth controlled failure at low stresses.

- The product of the minimum creep rate and time-to-failure is, to a good approximation, constant for different material systems. This phenomenon is typical for the plasticity-controlled failure and the constant is termed as “the critical strain”. Once the failure kinetics are described based on constant-strain-rate tests, the critical strain is used to predict the time-to-failure. Critical strain is observed to depend on temperature and off-axis angle for glass/iPP.
- A switch to crack growth controlled failure is not detected for transversely loaded glass/iPP at high temperatures. Rather, testing glass/iPP at high temperatures, different plasticity-controlled deformation processes that contribute to its time-dependent behavior is identified, similar to neat iPP. Multi-process deformation kinetics was captured by Ree-Eyring equation. Compared to iPP, activation energy and strain rate sensitivity (slope of (yield) strength vs. $\log(\text{strain rate})$ plot) were found to be lower for the composite.
- Micromechanics simulations show that lower strain rate sensitivity of glass/iPP can be caused by (temperature-independent) fiber-matrix debonding. The lower activation energy for the composite is attributed to the presence of an additional temperature-dependent mechanism such as temperature-dependent fiber-matrix debonding.
- The cooling rate has a significant effect on the time-dependent behavior of glass/iPP. As the cooling rate is lowered, both strength and strain rate sensitivity decrease. This signals a change in the failure mechanism, which is confirmed by the microscopy images of the fracture surface showing an increasing level of embrittlement as the cooling rate is lowered.
- Under off-axis loading, angle and strain rate dependence of the tensile strength of glass/iPP is factorizable. This means that angle and rate dependent strength at an arbitrary off-axis angle can be determined by multiplying the rate dependent strength at a reference angle with an angle-dependent shift factor. Given that constant-strain-rate and creep tests exhibit identical failure kinetics, this significantly reduces the effort in the characterization of the time-dependent behavior.
- The anisotropic viscoelastic-viscoplastic lamina constitutive model (Chapter 5) developed for short fiber-reinforced composites [1], which makes use of the aforementioned factorizability, describes the strain rate and angle dependent stress-strain response of off-axis laminates well. This model can be used in future studies to describe the lamina behavior in finite element simulations of the time-dependent

behavior of multidirectional laminates.

7.2 Recommendations

- Physical aging is mentioned as a possible source for the trends observed in several instances throughout the thesis, such as the change in the stress dependence of the minimum creep rate for carbon/PEKK in Chapter 2. For a better understanding of the role of plasticity-controlled failure in time-dependent failure, the physical aging should also be studied as in [2,3].
- Only glass/iPP is tested extensively at elevated temperatures. The role of plasticity should be identified for a larger range of temperatures for other material systems as well. As mentioned in the Discussion chapter, elevated temperatures might favor plasticity-controlled failure.
- While glass/iPP does not exhibit a high scatter, carbon/PEEK and carbon/PEKK do. Studying these materials systems more elaborately as we did for glass/iPP would require a statistical approach more detailed than the one applied in Chapter 2.
- Since the neat iPP and glass/iPP are manufactured in different laboratories using different equipment, the cooling rates applied are not the same for the two materials. Although this should not be a problem for the comparison of activation energies based on the previous observations [4], stress levels are affected by the cooling rate. Hence, for accurate quantitative comparisons between the neat matrix and its composite, using the same processing conditions is recommended. This would also be helpful in setting a failure criterion in the micromechanical simulations of the composite, based on the comparable experimental data of the neat matrix and the composite.
- For the micromechanical modeling, the time-dependent behavior of the neat iPP was characterized using the data from tensile tests. In tensile tests, due to localization of the deformation, only the pre-yield region can be taken as the intrinsic stress-strain response of the material. Hence, characterization of the time-dependent behavior by conducting uniaxial compression tests would be recommended to model also the post-yield response of the polymer.
- In Chapter 5, while strain rate dependence is characterized in the transverse and off-axis loading, it is not characterized in longitudinal loading. Modeling the time-dependent behavior of multidirectional laminates would require the characterization of time-dependent behavior in the longitudinal direction as well. Moreover, the capability of the model in predicting the strain rate dependence should be validated at more angles (currently, the validation is done only at the off-axis angle of 30° due to

the unavailability of stress-strain data obtained with an extensometer at various strain rates at the other off-axis angles).

- In Chapter 5, while the spectrum obtained at $\phi=30^\circ$ describes the stress-strain response at the off-axis angles well, this was not the case for the transverse loading ($\phi=90^\circ$) where a macroscopic yield is not observed, unlike other angles. A simple approach to tackle this issue is presented, which proposed artificially increasing the Hill stress at $\phi=90^\circ$ to push the yield region of the prediction curve to higher stress values so that a stress-based failure criterion can be used at the transverse tensile strength experimentally observed. Although simple, by proposing using a spectrum of moduli and viscosities obtained at $\phi=30^\circ$ to determine the stress-strain response of transverse loading, this approach ignores the fact that transverse loading and off-axis loading have significantly different stress-strain curves: strain levels for the transverse loading are far smaller. Hence, the approach for the prediction of the transverse stress-strain behavior should be improved.
- To be able to use the lamina constitutive model presented in Chapter 5 for a larger range of loading conditions (strain rate and temperatures), a thorough high-temperature off-axis characterization is recommended.
- The experimental work in this thesis was concerned only with unidirectional laminates loaded in tension. It is recommended to study other UD loading configurations and multidirectional laminates to enhance the understanding of the role of plasticity-controlled failure in more general loading scenarios.

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