RECYCLING OF THERMOPLASTIC COMPOSITE LAMINATES

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UNIVERSITY OF TWENTE.

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Summary

The transportation sector, aerospace and automotive in particular, is striving to reduce vehicle weight to improve fuel economy. The high specific mechanical properties of fibre-reinforced composites make them an attractive option for reaching this goal. Among this class of materials, thermoplastic composites are becoming increasingly popular due to several benefits compared to their thermoset counterparts: superior toughness, short processing times, possibility to weld components and their easier recyclability. Recent years have shown an increase in applications and a rising demand for these thermoplastic composites. This comes with the drawback of larger volumes of industrial scrap. The combination of the high value of the scrap material and legislative incentives is pushing the industry to develop recycling solutions for this material.

This thesis proposes a new recycling route for continuous-fibre thermoplastic composites to handle the generated production scrap. It starts with the size reduction of scrap using multiple-shaft shredders to obtain flakes of centimetric size. A sieving step is then performed to recover the flakes of a desired size. The subsequent re-manufacturing process is comprised of two steps. The flakes are first fed into a low-shear mixer together with polymer granules, to melt and blend the polymer fraction with the flakes. The addition of polymer granules, virgin in this study, lowers the fibre fraction of the recyclate to enhance processability. The mixer used was selected for its ability to blend multi-layered flakes made with woven fabric to form entangled bundles, while preventing fibre breakage. The blended material is then extruded as a molten and mixed dough and is immediately transferred to a press for compression moulding. The moulding phase is carried out in an isothermal mould at a temperature lower than the polymer's melting point. As such, a dwell time of only a few minutes is enough for the part to cool down prior to being released.

The main objective is to develop the technical feasibility and economic viability of this recycling solution. This thesis focuses on the role of processing, which is evaluated by identifying and characterising the relevant material properties and their relation to the processing steps mentioned for this recycling solution.

Four aspects have been investigated: *i.* analysis of fibre length and flake size after shredding and sieving, *ii.* characterisation of the quality of mixing in doughs, *iii.* identification of the deformation mechanisms during the squeeze flow of these doughs, and *iv.* characterisation of the microstructural heterogeneities in moulded components.

The determination of the fibre length distribution is crucial as fibre length drives, among other parameters, the mechanical properties of re-manufactured components made with discontinuous-fibre composites. A novel and accurate method for characterising fibre length using pictures of shredded flakes was introduced and implemented. This method was then used to understand the

effect of flake layup, offcut size, shredding parameters and sieve sizes on the fibre length distributions. Flake layup and offcut size in particular were found to barely influence fibre length distributions.

The quality of mixing in low-shear mixed flakes was then studied. Methods were developed to characterise the quality of mixing in this material, based on image analysis of optical micrographs, using Delaunay triangulations and the scale and intensity of segregation. Said methods were then employed to improve the quality of mixing in these low-shear-mixed thermoplastic composites. Overall, both reducing the fibre length and increasing the total deformation history in the mixer were found to improve the mean quality of mixing and lower its variability.

In a further study, squeeze flow experiments were performed to identify the complex deformation mechanisms in the doughs. The activation of multiple shear planes was observed in the thickness of cylindrical disks that were squeezed in a custom-built setup. This also led to local anisotropic flow with protuberances of a few centimetres. The currently applied analytical model was not able to capture these deformations accurately. Better-mixed material should lead to more uniform deformations and give more confidence from an industrial point of view, allowing for more precise predictive modelling.

Finally, the process- and material-induced heterogeneities in moulded components were investigated and compared to other long-fibre thermoplastic (LFT) materials. The input material in this recycling route differ considerably from the pellets or chopped rovings typical for other LFTs. This study thus focused on characterising these heterogeneities for this recycling solution, and compared them to the heterogeneities in already known LFTs. Similarities were found between recycled thermoplastic composites (TPCs) and other LFTs for the studied material properties. The effect of the mixing step is particularly noticeable in the local variation of fibre fraction within moulded parts and should be improved.

Several challenges for future development of the recycling of TPCs, both technical and non-technical, are then addressed. Considering the overall results and main objective of the thesis, it was found that the mixing step is key in this recycling solution and that improvement of the quality of mixing is required.

Samenvatting

Gewichtsreductie ter bevordering van de brandstofefficiëntie is een belangrijk thema binnen de vervoerssector, in het bijzonder in de luchtvaart- en automobielin-dustrie. Vezelversterkte kunststoffen zijn een interessante optie voor dit doeleinde door de goede mechanische eigenschappen bij een laag gewicht. Binnen deze klasse materialen wordt thermoplastisch composiet een steeds aantrekkelijkere optie vanwege de voordelen ten opzichte van hun thermohardende tegenhanger, zoals een superieure taaiheid, korte procestijden, de mogelijkheid tot lassen en eenvoudigere recycling. Recentelijk is er een toename te zien in de toepassing en vraag naar dit thermoplastische materiaal. De keerzijde hiervan is de toenemende hoeveelheid industrieel afval. Door de combinatie van de hoge economische restwaarde van dit afval en wettelijke initiatieven wordt de industrie gedwongen om na te denken over de mogelijkheid tot recycling van dit materiaal.

Dit proefschrift presenteert een nieuwe recyclingroute voor de verwerking van continu-vezelversterkt thermoplastisch composiet procesafval. De hoofddoel-stelling van dit onderzoek is om de technologische en economische haalbaarheid van de beschreven recyclingroute te bestuderen. Dit proefschrift richt zich op de verwerkingsaspecten van het proces, waarbij de relaties met de relevante materiaaleigenschappen worden geïdentificeerd en gekarakteriseerd. De eerste stap in de methode is het reduceren van de afvalgrootte tot enkele centimeters, waarbij gebruikt wordt gemaakt van een meerassige versnipperaar. Middels een opvolgende zeefstap worden de snippers van de gewenste grootte herwonnen. De volgende stap bestaat uit twee delen om het materiaal te verwerken tot een product: de snippers worden eerst vermengd met ongevuld polymeergranulaat in een mixer met een lage afschuifkracht, waarin het materiaal in gesmolten toestand wordt gebracht. De toevoeging van het polymeergranulaat brengt de vezelvolumefractie omlaag wat de verwerkbaarheid ten goede komt. De geselecteerde mixer is geschikt om de meerlaagse snippers van het weefselversterkte materiaal in elkaar te vermengen terwijl het breken van vezels wordt voorkomen. In de tweede productiestap wordt het verkregen mengsel in gesmolten toestand geëxtrudeerd en direct naar de pers getransporteerd om gepersvormd te worden. Het persvormen wordt uitgevoerd in een matrijs met een temperatuur onder het smeltpunt van de polymeer. Het product blijft enkele minuten in de matrijs om af te koelen voordat het gelost wordt.

Er zijn vier aspecten onderzocht: *i.* de analyse van de vezellengte en snippergrootte na versnippering- en zeefstap, *ii.* de karakterisatie van de mengselkwaliteit, *iii.* de identificatie van de vervormingsmechanismen tijdens het persvormen van het mengsel, *iv.* de karakterisatie van heterogeniteiten in gepervormde componenten op microstructureel niveau.

De bepaling van de vezellengtedistributie is cruciaal vanwege de significante invloed op onder andere de mechanische eigenschappen van discontinu-vezel com-

posiet materiaal. Een nieuwe methode op basis van visuele analyse is gepresenteerd en geïmplementeerd voor de accurate karakterisatie van de vezellengte. Deze methode is vervolgens gebruikt om het effect van layup, de initiële grootte van het procesafval, de parameters van de versnipperaar en de zeefgrootte te bestuderen op de vezellengtedistributie. De layup en initiële grootte bleken van weinig invloed op de vezellengtedistributie.

Vervolgens is de mengkwaliteit van het proces bestudeerd. Methoden zijn ontwikkeld voor de karakterisatie en optimalisatie van de mengkwaliteit op basis van optische microscopie. De fotoanalyse maakt daarbij gebruik van Delaunay triangulatie en de segregatieschaal en -intensiteit. Het doel was het verbeteren van de mengkwaliteit en daarmee het identificeren van de onbekende mengmechanismen. Deze zijn onderzocht met een factoriale sensitiviteitsstudie met betrekking tot de menginstelling en vezellengte. Het introduceren van meer vervorming en het reduceren van de vezellengte bleken ten goede te komen aan de kwaliteit van het mengsel en deden de variatie afnemen.

In een opvolgende studie zijn squeeze flow experimenten uitgevoerd om de complexe deformatiemechanismen in het mengsel te identificeren. Met een speciaal ontwikkelde meetopstelling is de activatie van meerdere afschuifvlakken geobserveerd over de dikte van een circulair proefstuk. De aanwezigheid van meerdere afschuifvlakken leidde tot lokale anisotrope vloeit, die resulteerde in uitstulpingen van enkele centimeters langs de rand van het proefstuk. Het toegepaste analytische model was niet in staat deze deformaties nauwkeurig te beschrijven. Een hogere mengkwaliteit zal tot een meer uniforme deformatie leiden, waardoor een nauwkeurigere voorspelling mogelijk is.

Tot slot zijn de heterogeniteiten onderzocht welke tijdens het proces geïntroduceerd worden of voortkomen uit het materiaal. Het ingangsmateriaal voor deze recyclingroute zijn meerlaagse snippers die sterk verschillen van conventionele lange vezelversterkte thermoplasten, zoals gevuld granulaat of rovings. Microstructuur heterogeniteiten zoals vezeloriëntatie, percolatie, variaties in de vezelvolumefractie en het breken van vezels, verschillen mogelijk voor dit nieuwe type materiaal. De focus van deze studie is daarom gericht op het karakteriseren van de heterogeniteiten die voortkomen uit de recyclingroute, en vervolgens het vergelijken met de heterogeniteiten van conventionele lange vezelversterkte thermoplasten. Er zijn verbanden gevonden tussen de bestudeerde materiaaleigenschappen, waarbij het effect van de mengtap op de lokale variatie in vezelvolumefractie opvallend was. Deze zal daarom verbeterd moeten worden.

Een inventarisatie is gemaakt van de uitdagingen voor de toekomst van het hergebruik van thermoplastisch composiet, van technologische en niet-technologische aard. De belangrijkste resultaten beschouwend, kan worden geconcludeerd dat de mengtap een grote invloed heeft op deze recyclingroute. Tevens zijn verbeteringen nodig in de kwaliteit van het mengsel.

Résumé

Le secteur des transports, aéronautique et automobile en particulier, s'efforce à réduire la masse des véhicules afin d'améliorer la consommation de carburant desdits véhicules. Les hautes propriétés mécaniques spécifiques des composites à renforts fibreux les rendent attractifs pour atteindre cet objectif. Au sein de cette classe de matériaux, les composites thermoplastiques deviennent de plus en plus populaires grâce à de nombreux avantages comparés à leurs homologues thermodurcissables : une ténacité supérieure, des temps de fabrication réduits, la possibilité de souder des pièces ensemble et leur inhérente recyclabilité. Les dernières années ont vu une augmentation des applications et de la demande pour ces composites thermoplastiques. Cette augmentation des volumes de production arrive en parallèle d'une augmentation des déchets de production. La combinaison de la haute valeur économique de ces déchets et les incitations législatives encourage les industriels à développer des solutions de recyclage pour cette classe de matériaux.

Cette thèse propose une nouvelle solution de recyclage pour les composites thermoplastiques à fibres continues afin de traiter les déchets de production. Les travaux présentés ont été principalement menés sur des copeaux de carbone/PPS tissés et laminés. L'objectif principal de cette thèse est de développer la faisabilité technique et la viabilité économique de cette solution de recyclage. Cette thèse s'intéresse au rôle du procédé, qui est évalué par l'identification et caractérisation de propriétés matériaux et leurs relations avec les étapes de fabrication mentionnées. Une étape de tamisage est réalisée pour récupérer les copeaux de la bonne taille. La re-fabrication comporte ensuite de deux étapes. Un mixeur à faible cisaillement est alimenté d'un mélange de copeaux et de granules de polymère, puis fait fondre et mélange le polymère et les fibres. L'ajout de polymère dans ce procédé réduit le taux de fibres afin d'améliorer la processabilité. Le mixeur utilisé a été sélectionné pour sa capacité à mélanger des copeaux laminés tissés pour en faire une pâte de fibres emmêlées, tout en évitant l'attrition des fibres. La pâte de fibres emmêlées est ensuite extrudée puis est immédiatement transférée dans une presse pour être moulée par compression. La phase de moulage est réalisée dans un moule isothermique à une température inférieure à la température de fusion du polymère. Par conséquent, un délai de quelques minutes est suffisant pour que la pièce moulée refroidisse avant de l'éjecter.

Quatre aspects ont été étudiés : *i.* analyse de la longueur des fibres et de la taille des copeaux broyés et tamisés, *ii.* caractérisation de la qualité de mixage des pâtes renforcées de fibres, *iii.* identification des mécanismes de déformation apparaissant durant l'écoulement d'écrasement des pâtes, *iv.* caractérisation des hétérogénéités microstructurales de pièces moulées.

L'évaluation de la distribution des longueurs de fibres est cruciale puisque cette longueur conditionne, entre autres paramètres, les propriétés mécaniques des pièces

en composites à fibres discontinues. Une nouvelle méthode de la caractérisation de la longueur des fibres a été développée et utilise des photographies des copeaux broyés. Cette méthode a été utilisée pour comprendre l'effet de l'empilement de plis, de la taille des chutes de production, des paramètres de broyage et de tamisage sur les distributions de longueur de fibres. En particulier, l'empilement des plis et la taille des chutes affectent peu les distributions de longueur des fibres.

La qualité de mixage des pâtes mixées a été étudiée. Des méthodes ont été développées et mises en oeuvre afin de caractériser la qualité de mixage de ce matériau. Elles se basent sur l'analyse de micrographies optiques grâce à la triangulation de Delaunay, et à l'échelle et l'intensité de ségrégation. Ces méthodes ont ensuite été utilisées pour améliorer la qualité de mixage des composites thermoplastiques mixés. Une attention particulière a été portée sur la compréhension des mécanismes de mixage de ce procédé. Un plan d'expérience factoriel fractionnel a été réalisé en variant les paramètres de mixage et la longueur des fibres. Dans l'ensemble, la réduction de la longueur des fibres et l'augmentation de la déformation totale dans le mixeur permet d'améliorer la qualité de mixage moyenne et de réduire sa variabilité.

L'étude suivante s'est intéressée à des expériences d'écoulement d'écrasement afin d'identifier les mécanismes de déformation complexes dans les pâtes. Une activation de plusieurs plans de cisaillement a été observée dans l'épaisseur des échantillons cylindriques qui ont été testés. Ceci a conduit à un écoulement anisotropique avec plusieurs protubérances de quelques centimètres. La modélisation analytique utilisée n'est pas capable de capturer ces déformations de manière précise. Un matériau mieux mixé devrait conduire à des déformations plus uniformes permettant une modélisation plus précise et devrait améliorer la confiance en ce type de matériau d'un point de vue industriel.

Enfin, les hétérogénéités induites par le procédé et le matériau dans les pièces moulées ont été examinées. Le matériau initial dans cette solution de recyclage consiste en des copeaux de composites stratifiés tissés, qui sont très différents des granulés typiques des composites à fibres longues. Les hétérogénéités microstructurales telles que l'orientation des fibres, la percolation, les variations de taux de fibres ou l'attrition des fibres peuvent être différentes pour ce nouveau matériau recyclé. Cette étude s'intéresse donc à la caractérisation de ces hétérogénéités pour cette solution de recyclage, et les compare aux hétérogénéités connues dans les composites à fibres longues. Des similarités ont été trouvées entre les composites recyclés et à fibres longues pour les propriétés étudiées. L'effet de l'étape de mixage est particulièrement remarquable pour ce qui est des variations locales des taux de fibres au sein de pièces moulées.

Les résultats des chapitres précédents sont combinés et discutés dans le chapitre suivant, et mis en perspective en considérant l'objectif principal de cette thèse. Dans l'ensemble, l'étape de mixage est la clé de cette solution de recyclage

et une amélioration de la qualité de mixage est nécessaire. Plusieurs défis sont ensuite adressés pour le futur développement du recyclage des composites thermoplastiques, à la fois techniques et non-techniques.

Nomenclature

Abbreviations

5HS	5 harness satin
8-hour TWA	8-hour time weighted average
BSD	Bundle size distribution
CMT	Carbon mat thermoplastic
CM	Compression moulding
CoV	Coefficient of variation
D-LFT	Direct long fibre thermoplastic
DoE	Design of experiments
EoL	End-of-life
FLD	Fibre length distribution
FOD	Fibre orientation distribution
FVF	Fibre volume fraction
GMT	Glass mat thermoplastic
IoS	Intensity of segregation
L/D	Length over diameter
LFT	Long fibre thermoplastic
PAEK	(family of) Polyaryletherketone
PDF	Probability density function
PEEK	Polyetheretherketone
PEI	Polyetherimide
PES	Polyethersulfone
PET	Polyethylene terephthalate
PMMA	Polymethylmethacrylate
PPS	Polyphenylene sulfide
PP	Polypropylene
PSD	Particle size distribution
QoM	Quality of mixing
rpm	Rotations per minute
SoS	Scale of segregation
TPC	Thermoplastic composite
TPU	Thermoplastic polyurethane

UD	Uni-directional
UTM	Universal testing machine

Greek symbols

σ	Standard deviation of a normal distribution	
τ_{zz}	Normal stress	[MPa]
θ	Fibre orientation	[-]

Roman symbols

a	Aperture of a sieve (Chapter 2)	[m]
a and b	Major and minor axes of a fibre in the plane of observation (Chapter 3)	[m]
$\mathcal{B}_0, \mathcal{B}$	Orthogonal basis	[-]
d_0, d_f, d_c	Distances between fibre centres	[m]
$\vec{e}_1, \vec{e}_2$	Basis vector	[-]
F	External normal force	[N]
$h_0, h(t)$	Specimen heights	[mm]
$\dot{h}$	Compression speed	[mm.s ⁻¹]
k	Consistency parameter	[MPa.s ⁿ]
L	Length of a fibre in a flake	[m]
n	Power-law index	[-]
P	Centre of a fibre in the plane of observation	[-]
r, r_N	Correlation coefficients	[-]
$r_{quasi,N}, r_{cross,N}, r_{UD,N}$	Correlation coefficients	[-]
$R, r(t)$	Radii of circular specimens	[mm]
$\mathbf{T}$	Change-of-basis matrix	[-]
$\vec{u}_0$	Unit vector	[-]
$x_{N,i}$	Length fraction of the batch of flakes N for the fibre length i	[-]
$\tilde{x}_N$	Arithmetic mean of all $x_{N,i}$	[-]
$\bar{z}$	Number of fibre contacts per fibre, or coordination number	[-]

Contents

Summary	i
Samenvatting	iii
Résumé	v
Nomenclature	viii
Contents	xi
1 Introduction	1
1.1 Background and motivation	1
1.2 Recycling continuous-fibre-reinforced thermoplastics	2
1.3 Recycling TPCs by low-shear mixing	7
1.4 Objectives and scope	10
1.5 Outline	11
1.6 Acknowledgement	12
References	12
2 Shredding and sieving thermoplastic composite scrap	17
2.1 Introduction	18
2.2 Materials	21
2.3 Image processing analysis	25
2.4 Results and discussion	28
2.4.1 Reliability study	28
2.4.2 The influence of shredding settings and sieving	34
2.5 Conclusion	37
References	38
2.A Supplementary material: a predictive model for FLDs	41
3 Characterisation and improvement of the quality of mixing of doughs	47
3.1 Introduction	48
3.2 Materials	49
3.3 Low-shear mixing	51
3.4 Literature review on the experimental methods of measuring the QoM	53

3.5	Methods	57
3.5.1	Microscopy	57
3.5.2	Intensity and scale of segregation	59
3.5.3	Bundle size distribution	62
3.6	Results	64
3.6.1	Design of experiments	64
3.6.2	Reproducibility	67
3.6.3	Effect of FLDs	69
3.7	Discussion	71
3.8	Conclusion	72
	References	73
3.A	List of the QoM measurements	77
3.B	Image segmentation and correction	78
3.C	Centre-to-centre distance correction	79
3.D	Randomly-filled ellipse	82
4	Deformation mechanisms during the squeeze flow of recycled thermoplastic composites	83
4.1	Introduction	84
4.2	Materials and processes	85
4.3	Squeeze flow experiments and setup	88
4.4	Analytical modelling and validation of the experimental procedure	92
4.5	Results and discussion	94
4.5.1	Analytical modelling of the squeeze flow experiments	94
4.5.2	Deformation mechanisms	96
4.5.3	Discussion	102
4.6	Conclusion	105
	References	106
5	Process- and material-induced heterogeneities in recycled thermoplastic composites	109
5.1	Introduction	110
5.2	Materials and process	113
5.3	Measurement methods	115
5.4	Results	118
5.4.1	Visual inspection	118
5.4.2	Porosity and cracks	119
5.4.3	Variations of fibre fraction and fibre-matrix separation	120
5.4.4	Fibre attrition	123
5.4.5	Fibre orientation	125
5.5	Conclusion	127
	References	128
5.A	Details on the ribbed panel	132
6	Discussion	133
6.1	Overview of the problem	133
6.1.1	Fibre orientation	136
6.1.2	Fibre content	137
6.1.3	Fibre length	138

6.1.4	Quality of mixing	139
6.1.5	Conclusion	140
6.2	Challenges	142
6.2.1	Technical and scientific challenges	142
6.2.2	Non-technical challenges	146
6.3	Application	148
	References	150
7	Conclusions and recommendations	153
7.1	Conclusions	153
7.2	Recommendations	154
	Acknowledgments	157
	Publications	159

Chapter 1

Introduction

1.1 Background and motivation

In the transportation sector, aerospace and automotive in particular, reducing fuel consumption has become a key target because of the increase in fuel costs over the years. Two main options have been selected in these sectors, namely increasing engines' fuel efficiency and reducing vehicle weight. Regarding the latter, continuous-fibre-reinforced polymers (CFRPs), which allow for lighter products, have been increasingly used.

The aerospace industry has gradually included CFRPs to lighten aircrafts, which are now reaching 50% by weight for the recent B787 and A350 airliners [1, 2]. Most of these CFRPs consist of thermoset composites, which have been used since the 1950s. More recently, thermoplastic composites (TPCs), for which the matrix is a thermosoftening, instead of thermosetting, polymer, have entered the aerospace market. Sporadically used for non-structural parts in the 1990s initially, the market for them has increased ever since and is starting to include large structural applications [3, 4].

This increasing use is mainly due to several benefits compared to their thermoset counterparts: superior toughness, short processing times, possible automation, the option of welding components, and their easier recyclability [5]. Regarding the latter, it would probably be impossible to count the number of publications on TPCs that praised recyclability as a key benefit of TPCs over thermoset composites. Yet, recycling TPCs is still a very recent topic and is not industrialised nor standardised, to the best of the author's knowledge.

On the one hand, recycling of thermoset composites (TSCs), continuous carbon-fibre-reinforced thermosets in particular, has already been a major topic for

a few decades, with a market much larger than the one for continuous-fibre-reinforced thermoplastics. As a consequence, several sound recycling solutions have emerged and are being implemented industrially [6]. On the other hand, the recycling of TPCs is usually defined as technically easier because one of the major and most expensive steps is not required, namely reclamation of the fibres by means of thermal or chemical processes, which eliminates the matrix. Instead, the thermoplastic matrix can be melted again to form a new component. Such an approach is environmentally preferred as the thermal and chemical reclamation processes require either large amounts of energy or can produce chemical waste. The technical implementation of recycling TPCs is, however, not that straightforward since recycling TPCs is still in its infancy. Considerable developments are required to reach a level of maturity similar to that of recycling TSCs. The rise in the production of and demand for TPCs in the past few decades and their expected continuation in the coming decades is driving the development of TPC recycling. On top of that, relevant legislation, in the European Union in particular, is becoming stricter in terms of waste management, encouraging re-use and recycling instead of incineration without energy recovery or landfill [7, 8].

Currently, recycling TPCs focuses mainly on post-industrial scrap, as this constitutes the bulk of TPC waste. Most end-of-life (EoL) TPC waste has not yet reached the recycling market because most components are still in their use phase. A closer examination of post-industrial scrap revealed its diversity. Figure 1.1 shows an attempt to classify TPC scrap for the processing routes used for high-end TPCs, for instance in aerospace. The top flow chart in the figure represents a route in which unidirectional (UD) tape prepregs are placed onto a mould, and are subsequently post-consolidated and/or formed. The middle process route represents the autoclave consolidation and forming of prepregs. In the bottom flow chart, the prepregs are press-consolidated first and then formed, e.g. by stamping. The dark grey arrows represent the steps that produce scrap in these three manufacturing processes. Although many operations generate scrap, the bulk is composed of nested offcuts and trims in a consolidated form, which are thus multi-layered, potentially with various layups.

This current status of TPC scrap is a driver for the community to find solutions to recycle TPCs, considering the technical, business and societal aspects of the problem.

1.2 Recycling continuous-fibre-reinforced thermoplastics

First, a review of the work on recycling of continuous-fibre-reinforced TPC must be made. This will provide data on the recycled materials, benefits/drawbacks of the processes used, and the directions of the current research. Multiple research projects have been carried out mostly over the last decade. Table 1.1 lists an

Figure 1.1 Overview of the various main streams of production scrap during the manufacturing of TPCs. The light grey boxes represent the various processing steps, whereas the dark grey boxes highlight the operations generating scrap.

overview of recycling solutions specifically for continuous-fibre-reinforced TPCs. Although the list aims at being exhaustive, the author might have missed some solutions from screening scientific and technical literature. Some of the items in this table are projects developed internally within companies manufacturing TPCs. Such companies' recent developments are often published, if at all, in technical magazines, product pages or press releases, instead of the usual scientific communication channels. Another reason they are listed in Table 1.1 is to show the industrial interest and effort in recycling TPCs.

The table features three main aspects: the input scrap material and type, the size reduction technique and resulting fibre length distribution (FLD)/ particle size distribution (PSD) and the re-manufacturing technique with the desired final fibre volume fraction (FVF). Although all presented recycling routes differ from one another in some aspects, the materials, comminution techniques and re-manufacturing processes can be individually categorised.

Material	Scrap type	Comminution technique	FLD or PSD [mm]	Re-manufacturing technique	FVF [%]	References
G/PET	n/a	granulator	1-11	IM extrusion + CM CM	23 23 23	Chu et al. [9]
C/PEEK	n/a	hammer mill cutting mill	0.1-1 0.1-3	IM	24-43	Schinner et al. [10]
G/PP Flax/PP	production scrap	cutting mill	n/a	extrusion + CM	13-35 15-25	Schmachtenberg et al. [11]
C/PPS	weaving trims	two-shaft shredder	1-18	low shear mixing + CM	33	Janney et al. [12, 13]
G/PP	tape scrap	two-shaft shredder	38	low-shear mixing + CM	n/a	Vaidya et al. [14]
C/PEEK	component *1	electrodynamical fragmenter	1-4	CM	60*	Roux et al. [15] & Eguemann et al. [16]
G/TPU	n/a	n/a	5-25	CM	45*	Rasheed et al. [17]
C/PEEK	semi-preg scrap	chopper	5-50	†	50*	Teijin Carbon [18]
	laminated scrap	n/a †1	<10 †2	†	50*	
	laminated scrap	n/a	<3 †2	pelletising †	25	
C/PPS	laminated scrap	chopper	n/a	extrusion + CM	n/a	Premium Aerotec [19]
C/PPS	laminated scrap	+ hammer mill n/a	from <0.5 to 5-15	IM	30-50	Institut für Verbundwerkstoffe [20]
C/PPS	semi-preg scrap	chopper/guillotine	7.5-12.5	CM	50*	Rasheed [21]
G/PP	laminated scrap	chopper/guillotine	5-25	CM	47*	Moothoo et al. [22]
C/PPS	<i>laminated scrap</i>	<i>two- & four-shaft shredders</i>	<i>10-30</i>	<i>low-shear mixing + CM</i>	<i>20-35</i>	De Bruijn et al. [23, 24]
G/PP	n/a	single-shaft shredder	20-100 †2	CM	n/a*	De Bruijn et al. [25] Cetim [26]
C/PPS	laminated scrap	n/a †1	<5 †2	CM	50*	Toray Advanced Composites [27]
C/PAEK	laminated scrap	hammer mill four-shaft shredder	4.7-19 10-20	CM	n/a	Li et al. [28]
C/PEEK	laminated scrap	four-shaft shredder	5-25	CM	30-45	Vincent et al. [29]
C/PPS	semi-preg scrap	four-shaft shredder	3	dissolution + CM	25	Tapper et al. [30]
C/PP	component *1	n/a	<3	pelletising + IM	n/a	Leitat [31]
C/PPS	EoL	cryogenic grinder		pelletising + CM + thermoforming	n/a	Axval [32]

C/PEI	component *1	n/a	15-30	dissolution + solution impregnation + CM	50	Liu et al. [33]
G/PMMA	component *2	granulator	<3 ‡2	IM	13	Cousins et al. [34]
G/PP	tape scrap	chopper	<50	CM	n/a*	Van Wees [35]
C/PP						
G/PA						

*1: moulded component made from LFTs

*2: component made from continuous fibres

‡1: not described but likely a cutting mill/hammer mill based on the dimensions of the particles.

‡2: inferred from the photographs in the reference documents.

‡: provided as a semi-product

*: the re-manufacturing step was realised without lowering FVF of the initial scrap.

IM: injection moulding, CM: compression moulding

Table 1.1

List of recycling solutions for TPCs found in literature, companies’ product web-pages and press releases; ordered by date of publication. The lines in italic correspond to the recycling solution presented in this thesis. Each grey and white block represents a recycling solution studied by a single or group of research institute, company or university.

- The input material is equally distributed between C/PAEK, C/PPS, C or G/PP and other systems (with TPU, PET, PEI, PMMA matrices). The type of scrap, as described in Figure 1.1, was also found to vary. Most recycling routes considered 1. semi-preg or prepreg scrap, 2. laminated scrap, and 3. components, either EoL or manufactured for the purpose of the study. It was noticed that the collected waste in all these solutions is free from impurities, which could include glass scrims, release films or identification stickers, for instance. These are present industrially and may be difficult to separate or may reduce mechanical performance of recycled components if not separated. Not taking care of these impurities can diminish the confidence of the industry in using recycled products.
- All the recycling routes feature a size reduction step prior to re-manufacturing. The various offcuts or EoL waste come in large ranges of size, shape and thickness. This disables the direct re-use of offcuts or EoL waste to new products. Size reduction is therefore required to enable recycling solutions to obtain a homogeneous input material. In almost all cases, the size reduction step falls into one of the following two categories: 1. impact comminution (hammer mills, cutting mills, granulators, single-shaft shredders); and 2. shear/cut comminution, which can be sub-divided into two with multiple-shaft shredders and with guillotines/choppers [36]. Only the work of Roux et al. [15] stands out by using a non-mechanical size reduction technique, in the form of electrodynamic fragmentation. These various techniques result in fibre lengths or particle sizes ranging from 0.1 mm to 100 mm.
- Lastly, the re-manufacturing step in these recycling solutions tends to consist of either compression moulding, extrusion compression moulding, or injection moulding. Two exotic solutions were also applied on a few occasions. The first consists of dissolving the polymer from the composite scrap, followed by a solution impregnation step to re-impregnate fibres that are spread in a mould. The second involves thermoforming a sheet of compression moulded recycled scrap, similar to that of unreinforced polymers. The FVF in most compression moulding solutions was not lowered, e.g. by adding virgin polymer to the comminuted scrap, whereas the other re-manufacturing options require a lower FVF in order to allow the material to flow. When reduced, the FVF ranged between 13% to 50%.

Overall, most of the work presented in this table focused on implementing a recycling route, experimentally finding the right process settings, and performing various mechanical tests. The structure of the material used in all these recycling solutions is very different from standardised virgin continuous- and discontinuous-fibre composites from a processing point of view. However, extensive research on understanding how these new types of material behave during processing has been

barely done. This material-process relation is known to affect the mechanical performance of components. As such, carrying out studies on this topic would be greatly beneficial to furthering our understanding of recycling solutions and helping industrial implementation for any recycling solution reported in Table 1.1.

1.3 Recycling TPCs by low-shear mixing

Based on the preceding literature study on recycling TPCs, a recycling solution has been implemented in a research project in collaboration with the ThermoPlastic composites Research Center, the ThermoPlastic composites Application Center, GKN Fokker, Toray Advanced Composites, Cato Composite Innovations, Dutch Thermoplastic Components and Nido RecyclingTechniek. This will be the selected recycling solution for the present thesis.

The solution consists of processing steps A through E as shown in Figure 1.2, which also contains photographs of the material at every processing step. The recycling route starts with collecting post-industrial scrap at various manufacturing sites and its transport to a recycling site. Collected TPC scrap is then comminuted using multiple-shaft shredders to obtain flakes of a few centimetres in size. A sieving step is added, if necessary, to only recover flakes of the desired size. Re-manufacturing is comprised of two steps. The flakes are first fed in a low-shear mixer along with polymer granules to melt the polymer fraction and blend the flakes and the polymer. The addition of polymer granules, virgin in this study, lowers the fibre fraction of the recycle. The mixer used was selected for its ability to blend multi-layered flakes made with woven fabric into entangled bundles, while preventing fibre breakage. A molten and mixed dough is then extruded from the mixer and immediately transferred to a press for compression moulding. The moulding phase takes place in an isothermal mould at a temperature lower than the polymer's melting point. As such, a dwell time of only a few minutes is enough for the part to cool down and to be released. The lowered fibre fraction is essential to this step, in order for the dough to be able flow in the mould cavity.

The manufacturing steps in this route were selected for several reasons. Size reduction is required to homogenise the dimensions of scrap material to a size that enables processing. In the present solution, the size reduction step results in centimetric flakes in order to retain long fibres (length/diameter > 1000) and therefore good mechanical properties, strength and impact in particular [37]. Following the comminution step, the flakes may still be multi-layered. Compression moulding these thick large flakes would result in a staggered platelets system, with short failure paths resulting in low strength [17, 21, 38]. On top of that, moulding complex shapes with such systems is difficult. Direct compression moulding is thus ruled out from the possible re-manufacturing processes. Injection moulding allows for complex geometries but would drastically reduce fibre length if used.

Additionally, a pelletising step would likely be required to produce granules, since shredded flakes cannot be fed directly into an injection unit.

Overall, extrusion compression moulding is suitable for processing both prepreg and laminated TPC scrap. Shredding produces flakes with long fibres, which are barely attrited during the mixing phase. This enables the material to retain good mechanical properties. On top of that, the resulting flakes of centimetric size can be processed by the mixing device. The cycle time is also short in comparison to direct compression moulding, which is beneficial for the economic viability of this route. This recycling solution is therefore advantageous in terms of both processing and performance.

Figure 1.2 Flow chart of the low-shear mixing recycling solution.

1.4 Objectives and scope

Several areas of this recycling solution require attention. The shredding and sieving step is known to result in a distribution of flakes. These flakes are known to disentangle during the mixing phase, resulting in blended fibre bundles. The length of these bundles plays a role in the mechanical performance of moulded components. Therefore, fibre length, instead of flake size, is an important aspect to investigate. During the mixing phase, the disentanglement of flakes may vary greatly, depending on process settings for instance, resulting in variations in bundle size or their spatial distribution. These properties, fibre length and bundle size, influence the bundle aspect ratio, among other things, which is known to play a role in the dough rheology [39] and mechanical performance [40]. Properly characterising the quality of mixing is therefore crucial. In the following process step, compression moulding, the rheology of the dough determines the processibility of the material, thus determining the feasibility of filling complex geometries. Fibre length and quality of mixing are expected to affect the dough rheology, which must therefore be studied. Once moulded, the discontinuous-fibre thermoplastic retains its stochastic nature. On top of that, the flow phase in the mould cavity can also influence the material. Possible effects of the flow phase include fibre breakage due to possible high deformation rates, flow-induced orientation of the fibres, and fibre-matrix separation along the flow length or inside intricate features. Knowledge of these properties is crucial to better understand the variations in mechanical performance for instance, which are inherent to long-fibre thermoplastics (LFTs).

The overall objective is to develop the technical feasibility and economic viability of this recycling solution. This thesis focuses on the role of processing since the recycling solution presented in the previous section includes novel and poorly understood materials and processes. On the one hand, this objective will be answered by identifying and characterising the relevant material properties and their relations to the processing steps for this recycling solution. On the other hand, this thesis will determine how to improve or optimise those material properties in respect to their related processing steps.

The main material used in this study, carbon/PPS, was selected for its relevance to the aerospace industry, as it currently has the highest volume of usage among TPCs in this sector [41]. The trend in material use may shift to C/PEEK or C/PEKK in the near future when TPCs are used for large structural applications in aerospace [3]. However, this shift of material will not change the main results of this thesis because the same working principles apply for PEEK, PEKK and PPS. The collected scrap consisted of laminated carbon/PPS trims in a quasi-isotropic layup, made from Cetex® TC1100 5-harness satin. On some occasions, glass/PP and carbon/PES, in the form of LFT pellets, were also used for some of the characterisation methods or due to easier availability.

1.5 Outline

Figure 1.3 shows a schematic diagram of the thesis outline. Each chapter is reproduced from a research paper, so some details are repeated throughout the thesis. The author apologizes for any inconvenience caused by the repetition. The chapters are, however, self-contained with this format, which enables them to be read independently.

Figure 1.3 *Outline of the thesis.*

Chapter 2 investigates fibre length distributions in shredded and sieved flakes. The characterisation of fibre length distribution is crucial as fibre length drives, among other parameters, the mechanical properties of re-manufactured components made of discontinuous-fibre composites. In this chapter, a novel and accurate method to characterise fibre lengths using pictures of shredded flakes is introduced and implemented. This method was then used to understand the effect of flake layup, shredding parameters and sieve sizes on fibre length distribution.

In Chapter 3, the quality of mixing in low-shear mixed shredded flakes is studied. The first aim was to develop methods to characterise the quality of mixing in this material, based on image analysis of optical micrographs. Two methods were selected based on Delaunay triangulations, and the scale and intensity of segregation. These methods were then employed to achieve the second objective: understand how to improve the quality of mixing in these low-shear-mixed TPCs. This was investigated by performing a fractional factorial design of experiments varying several mixing settings and fibre length.

Fundamental understanding of the rheology of this new material-and-process

combination is crucial for the development of the technology. Chapter 4 considers this problem and looks at the deformation mechanisms of the recycled TPCs during the flow phase. Constant-volume squeeze flow experiments were performed under axisymmetric conditions on prepared $\varnothing 80$ mm disks of recycled carbon/PPS. The deformation mechanisms in this material, as well as their evolution during the squeezing experiment, are described thoroughly.

Chapter 5 elaborates on the process- and material-induced heterogeneities in moulded components. The input material in this recycling route consists of multi-layered woven flakes, which are very different from the pellets or chopped rovings typical for other LFTs. Microstructural heterogeneities such as fibre orientation, percolation, variation of fibre fraction, or fibre attrition may be different for this new material. This chapter thus focuses on characterising these heterogeneities for this recycling solution, and comparing them to the already known LFTs. Knowledge of these heterogeneities will provide more confidence in this material and process.

In Chapter 6, the results of the previous chapters are combined and discussed in a broader context. Finally, the main conclusions and recommendations of this thesis are presented in Chapter 7.

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Chapter 2

Shredding and sieving thermoplastic composite scrap: method development and analyses of the fibre length distributions

Abstract

Recycling of thermoplastic composites has attracted considerable attention in the recent years. Several recycling solutions include shredding scrap to centimetre-sized flakes to retain long fibres, followed by a remanufacturing step that prevents fibre breakage. Determining the exact fibre length distribution (FLD) for these routes is crucial, as it is of importance for the processability of the material as well as the mechanical performance of the recycled parts. In this chapter, novel analysis methods are introduced to calculate FLDs based on photographs of flakes. The reliability of the method and of the sampling was found to be high. The relation between flake size and FLD was studied, showing that offcut layup barely influences the FLD in comparison to flake size. The effects of shredding settings and sieving were studied, showing a strong correlation between machine parameters and FLD, whereas the offcut size was found to have no effect on FLD.

2.1 Introduction

With the demand and production of continuous fibre thermoplastic composites (TPCs) rising in the aerospace industry, the volume of production scrap has also grown and is expected to continue to grow in the future [1]. This scrap material is generated over the course several processing steps of, for instance, three of the main manufacturing routes of TPCs, as shown in Figure 2.1. There, the top flow chart represents a route where unidirectional tape prepregs, are placed into a mould, in which they are subsequently post-consolidated and/or formed. The middle process route represents autoclave consolidation and forming of prepregs. In the bottom flow chart, the prepregs are press-consolidated and then formed, e.g. by stamping. The dark-grey arrows represent the steps that produce scrap in these three manufacturing processes. Although many operations generate scrap, the bulk of the scrap is composed of nested offcuts and trims in a consolidated form, which are therefore multi-layered and may have various layups, such as in Figure 2.2a. In addition to the production scrap, end-of-life (EoL) TPC waste will later join the recyclable waste feed and become a critical issue. Recycling these streams is economically attractive because of the high value of composite waste and will probably become mandatory from an environmental perspective in the future. Several European directives have already put restrictions on disposal and require that specific waste streams be recycled [2, 3].

Several recycling solutions specific to TPCs have been implemented in recent years to convert this production scrap [4–14]. They all follow the same scheme: size reduction, sorting impurities if necessary, and manufacturing a new part. In all cases, the recycled part is manufactured with a process that resembles compression moulding of discontinuous-fibre composites. In these various approaches, the desired fibre length ranges from sub-millimetric to centimetric. Besides, some of these recycling solutions require the addition of pristine polymer to the recyclate to lower its fibre fraction [4–7], while other solutions enable processing at the input fibre fraction [6, 8–13]. Cradle-to-cradle approaches have also been proposed by some authors [9]. These recycling approaches, except the one reported by Roux et al. [9], contain a mechanical size reduction step using shredders, cutting mills or hammer mills. These types of comminution processes offer a large range of possibilities in term of output size, from powder to centimetre-sized flakes [15], depending on the requirements of the recycling route. Recently, De Bruijn [4, 5] has proposed a solution that aims to retain most of the value and mechanical performance of TPC production scrap, consisting of shredding scrap to centimetre-long flakes, melting and mixing those flakes into a dough using a low-shear mixer, and transferring the dough to a press for compression moulding. Long fibres, and therefore large flakes, are required to achieve high mechanical performance [16]. In addition, this solution is capable of processing consolidated scrap, which represents the bulk of production scrap, discarded components and EoL TPC waste.

Figure 2.1 Overview of the various main streams of production scrap during the manufacturing of TPCs. The light grey boxes represent the various processing steps, whereas the dark grey boxes highlight the operations where scrap is generated.

Figure 2.2 *Pictures of scrap material before and after shredding: (a) C/PPS offcuts prior to shredding and (b) C/PPS flakes obtained after shredding.*

In this recycling route, the micro-structure of recycled composite parts consists of entangled bundles instead of overlapping flakes such as in [8]. Both the flow behaviour of the dough during compression moulding and the mechanical properties of the recycled part will depend, among other parameters, on the fibre length distribution (FLD) [17]. As this recycling solution was developed in order to avoid breaking fibres during processing, it is important to determine the FLD of the shredded flakes rather than just the flake sizes, or particle size distribution (PSD).

Additionally, industrial applications of this recycling route may require tailored materials with specific flow behaviour or a certain part performance, in order to manufacture or certify a particular part. The production of various FLDs, with short or long fibres, with narrow or wide distributions, is an important criterion here. It is therefore essential to understand which factors influence the FLD and how to tailor these to specific requirements.

The literature already presents several methods to characterise the FLD, which can be categorised as direct and indirect. Methods are considered direct when all fibres in a sample are measured, whereas indirect methods only produce an estimated FLD. Direct measurements have been extensively used for short-fibre composites [18]. A typical example is injection moulding, where many fibre-length characterisations are carried out to determine fibre length reduction. In a significant share of these direct measurement methods, fibres are reclaimed by burning off the matrix, for instance, after which they are spread out on a piece of paper or scanner to be captured in a photograph. Image analysis is performed to determine the exact FLD [18, 19]. This methodology works well for fibres of moderate length (length/diameter (L/D) < 1000). Longer fibres may bend considerably or overlap, which makes characterisation difficult. The latter method

has been widely used for thermoset-composite recycling processes, particularly because the fibres are separated from the matrix during the process anyway [20–22]. However, many studies stopped characterising reclaimed long fibres ($L/D > 1000$) and started investigating flakes obtained from the size reduction process instead. This is primarily due to the image analysis methods used, as their technical limits are stretched at these lengths. For such long fibres, indirect measurements methods are used instead. In the case of recycling fibre-reinforced plastics, shredded scrap is sorted using sieves or air classifiers [23, 24] and the PSD is obtained based on the sorted output. The FLD is estimated indirectly by being considered equal to the PSD. This may be true [24–29] for flakes in slender cured bundles form, as particle length is equal to fibre length in this case. However, when the output flakes have an aspect ratio close to unity, such as in [5] and as shown in Figure 2.2b, the FLD can be far apart from the PSD [30]. This is mostly the case when fibre orientations differ from the principal directions of the flakes, in which case the FLD may not be approximated to the flake length. Therefore, in addition to the PSD, an alternative method is required to determine the FLD of large, possibly multi-layered, flakes. To the knowledge of the authors, this problem has, thus far, not been tackled.

The objectives of this chapter are: 1. to develop and implement a reliable method that calculates the FLD based on a batch of multi-layered flakes; 2. to understand the relations between flakes and FLD to determine whether flake shape, size and layup affect the resulting FLDs; and 3. to understand whether and how offcut size, shredding settings and sieving can influence the FLD of the resulting flakes.

The current chapter will elaborate on these three issues. Firstly, details on the materials, shredding/sieving processes, and the implemented method will be presented, followed by a results and discussion section, which will answer the objectives of this chapter.

2.2 Materials

The offcuts used in this chapter were collected at various manufacturing plants. For the purpose of this study, offcuts are defined as the remainders from the nesting or trimming stage of from prepregs or laminates (see Figure 2.1). However, the offcuts collected in this study only consist of trims from the stamp-forming stage (shown in Figure 2.2a), and trims from the press-consolidation stage (later referred as *offcut 2nd type*). Both types of offcuts consist of Toray Cetex® TC1100 carbon/PPS (C/PPS) 5-harness satin consolidated in a quasi-isotropic layup, as shown in Figure 2.2a. The trims from the stamp-forming stage were arbitrarily classified into three categories based on their offcut weight and are listed in Table 2.1. The second type of offcuts was not categorised because the offcuts in question were very similar in terms of size and is named: *C/PPS offcuts - 2nd*

type. The trims collected in this study are composed of quasi-isotropic laminates as stated above. However, this will not always be the case, as the industry can use various layups to manufacture components.

Category	Average weight [g]	Width [mm]	Length [mm]	Smallest dimension [mm]
C/PPS offcuts - small	8	60	150	20
C/PPS offcuts - medium	164	160	420	50
C/PPS offcuts - large	328	260	760	70
C/PPS offcuts - 2 nd type	n/a	50	700	80

Table 2.1 List of the offcut types used in this study. The widths and lengths are averages.

Multiple shaft shredding was the size reduction method of choice for this study for its ability to produce large and uniform flakes unlike other technologies, such as hammer mills or cutting mills [31]. Two- and four-shaft shredders manufactured by UNTHA shredding technology GmbH (hereinafter UNTHA) were used for this purpose. This type of machine was designed to shear the input material rather than impact it, as in hammer mills, which is achieved by having the shafts rotate at low speeds [31–33]. Practical experience of UNTHA and a project partner, Nido RecyclingTechniek, had shown that these machines produce a small fraction of fine particles compared to single-shaft shredders or hammer mills. Here, fine particles are defined as being five to ten times smaller than the intended main

Figure 2.3 Schematics of a shredder, top and front views in 2.3a, and inside view of a four-shaft shredder (image courtesy of Untha GmbH) in 2.3b.

output of a machine. Most flakes are therefore in the desired size range, as one can see in Figure 2.2b. The comminution mechanism of these shredders can be summarised as follows. The incoming material falls into the shredder, where teeth located on rotating blades force it to move downwards (see the blue vertically hatched areas in Figure 2.3a). The rotating blades overlap and therefore shear the material in the orange horizontally hatched area in Figure 2.3a. When a screen is placed directly beneath the blades, the flakes will either, fall through the screen, if they are small enough, or be caught by the teeth on the outer shafts, after which they are moved upwards to be shredded again. Obviously, blade width and screen size will influence the PSD. Apart from these two parameters, previous work on size reduction showed that the clearance between blades, small variations in rotational speed or sharpness of the blades/teeth have a major influence on the fracture mechanism but seem to have very little influence on the PSD [31]. Consequently, only the influence of blade width and screen size will be studied here. Various UNTHA shredders were used, depending on desired machine setting and availability, namely S20, RS30, RS40 and RS50. A summary of the shredding tests and the settings used is listed in Table 2.2. Apart from the blade width and screen size, shaft diameter, maximum torque, maximum throughput and number of shafts varied [32, 33]. The first three are known to affect the input volume and size, but not the PSD a priori. Similarly, four-shaft shredders allow the machine to be auto-cleaned, whereas the two-shaft shredder (S20) does not, but no variation in PSD is expected.

Test number	Scrap type	Blade width [mm]	Aperture of the screen [mm]	Shredder	Remarks
#1	C/PPS small	19	n/a	S20 (2-shaft)	No screen, 5 cuts
#2	C/PPS medium	19	n/a	S20 (2-shaft)	No screen, 5 cuts
#3	C/PPS large	19	n/a	S20 (2-shaft)	No screen, 5 cuts
#4	C/PPS large	29	25	RS50 (4-shaft)	1 cut
#5	C/PPS large	19	40	RS40 (4-shaft)	1 cut
#6	C/PPS large	29	40	RS50 (4-shaft)	1 cut
#7	C/PPS large	29	n/a	RS50 (4-shaft)	No screen, one cut
#8	C/PPS 2 nd type	19	40	RS30 (4-shaft)	5+2 batches
#9	C/PPS large	19	n/a	S20 (2-shaft)	No screen, 5 cuts, used for sieving

Table 2.2 *List of the various performed shredding tests. Section 2.4 will refer to the tests numbers listed here.*

Shredding experiments performed in collaboration with Nido RecyclingTechniek and UNTHA were found to produce very limited amounts of dust. The amount of dust in a workplace, especially when it comes to fibre-reinforced composites, must comply with the guidelines of the

European Scientific Committee of Occupational Exposure Limits, which recommends that workers are not exposed to more than 1 fibre/cm³ per 8-hour time-weighted average (8-hour TWA) [34]. RPS B.V. (Delft, the Netherlands), an external company certified to measure particles in workplaces, was commissioned to carry out a study on our S20 shredder to measure its small carbon fibre emissions when shredding the same C/PPS offcuts used in this study. The objective was to confirm or disprove the limited dust production with this comminution method and TPC material. Workers were given personal air sampling pumps and several stationary air pumps were installed in the lab during the measurements to record dust exposure. All fibre exposure measurements were found to be below 1% of the 8-hour TWA limit, which is a considerable safety advantage, showing the benefits of shredding thermoplastic composites. In comparison, Nido RecyclingTechniek and UNTHA had previously experienced that shredding and grinding thermoset composites produced large amounts of dust. These were personal experiences only, however, and the volume of dust generated during the thermoset composite shredding process was not measured.

After shredding, a 6 kg batch of shredded flakes was sieved using multi-stage vibrating sieves (see Figure 2.4). A set of perforated-plate sieves and woven wire sieves, specified by ASTM E323 and ASTM E11 respectively, were used with the following sizes: 2, 2.8, 4, 5.6, 8, 11.2, 16, 22.4 and 31.5 mm. The PSD of

Figure 2.4 *Photograph of the multi-stage vibrating sieves used in this study.*

sieved flakes is evidently correlated to the aperture of the sieve [23] but the exact relation is unknown, and the same goes for FLD and sieves. This study aimed to understand how sieving affects FLD, and to relate FLD to sieve size in particular.

2.3 Image processing analysis

Two alternative methods were developed to characterise the FLD of a batch of flakes. This section describes the various steps of the methods, which will later be used to characterise the FLD of shredded scrap in Section 2.4.

The steps of the two methods, named *measured-orientation method* and *assumed-orientation method*, are detailed in Table 2.3 and Figure 2.5. The differences between the two alternative methods are highlighted in Table 2.3 in italics.

Measured-orientation method:	Assumed-orientation method:
step 1: sample a batch of flakes from an initial population;	step 1: sample a batch of flakes from an initial population;
step 2a: capture photographs of the flakes — a diffuser box has been used for this purpose;	step 2: capture photographs of the flakes;
<i>step 2b: identify the fibre orientation of the top layer — this was done manually here but can be possibly performed automatically;</i>	—
step 3: convert the pictures to binary images by thresholding the flakes;	step 3: convert the pictures to binary images;
<i>step 4: generate arrays of lines oriented along the fibre direction(s) of each ply, which can be recovered from the scrap layup and the orientation of the top ply for known scrap;</i>	<i>step 4: generate arrays of lines for an arbitrary set of orientations: every 10° from 10° to 180°;</i>
step 5: intersect the binary images and their respective arrays of lines;	step 5: intersect the binary images and the arrays of lines;
step 6: compute the line length distribution of the intersected images, which is the FLD.	step 6: compute the line length distribution of the intersected images, which is the FLD.

Table 2.3 *Description of the process steps of both methods. The cells in italic highlight the differences between the measured-orientation and assumed-orientation methods.*

Specifically, the measured-orientation method requires knowledge about the offcut layup (for step 4) and the identification of the fibre orientation of the top layer (for step 2b). The identification can either be performed automatically using fibre

Measured-orientation method **Assumed-orientation method**

Figure 2.5 Sketch of the process steps for the measured-orientation (top) and assumed-orientation (bottom) analysing methods. Step numbering refers to the process description in Section 2.3.

detection tools and image analysis or manually. The purpose of this study was not to develop these fibre detection tools, which is why the fibre orientation was determined manually. Although such a measurement method indirectly estimates the FLD in each flake, it is considered to be the correct FLD by definition based on the following assumptions:

1. the flakes are flat;
2. the crimp percentage, if any, is null;
3. the edges of the flakes are sharp;
4. the fibres are not bent or sheared in the flakes.

The corrections required for these assumptions are not taken into account and may be time-consuming to implement or unknown to the user of the method. In the case of the *C/PPS offcuts - 2nd type*, assumptions 1 and 4 are valid because the offcuts originate from (flat) press-consolidated laminates. The other types of offcuts were coming from the trimming of press-formed components, which means assuming 1 and 4 is less accurate. However, visual inspection of the flakes revealed a limited number of bent flakes. Assumption 3 was found to be mostly valid for the shredded flakes in this study (see Figure 2.6). The variations induced by protruding fibres were very limited. Additionally, the crimp percentage of the 5-harness satin used in this study (see Section 2.2) is $<0.5\%$, and thus negligible [35].

Figure 2.6 Picture of some *C/PPS* flakes with a $70\text{ mm} \times 100\text{ mm}$ set square.

Contrary to the measured-orientation method, the assumed-orientation method disregards fibre orientation in the flakes by selecting an arbitrary set of fibre orientations (step 4). This way, the assumed-orientation method calculates an FLD that is independent of the actual flake layup. It does not require prior knowledge of the layup of the flakes, nor detection of the fibre orientation of the top layer. For this study, an angular increment of 10° was chosen, representing a virtually isotropic in-plane layup. The angle of 10° remained unchanged when different scrap or a different scrap layup was used. The angles are always measured in the reference orthonormal basis of the photographs (see (e_1, e_2) in Figure 2.5).

The effect of the angular increment on the resulting FLD was tested for all the following increments: 5° , 10° , 20° and 45° . Increments $< 10^\circ$ were found not to improve the accuracy of the method, and thus 10° was chosen for this study. Such a method evidently results in less accurate FLDs than when calculated with the measured-orientation method, but it can be adapted to any batch of flakes without prior knowledge about the scrap in question. Consequently, it is beneficial to determine its accuracy compared to the measured-orientation method. The first part of the following section will answer this problem.

2.4 Results and discussion

The various C/PPS offcuts were shredded and sieved, using the settings as detailed in Section 2.2: blade width, screen size and offcut size. Overall, most flakes had a shape resembling a parallelogram or a trapezoid as shown in Figure 2.6, while the average flake size was found to vary with shredding settings.

The first subsection will address the reliability of the methods defined in Section 2.3, particularly the reliability of the assumed-orientation method in respect to its manual counterpart. Additionally, possible reasons that explain the discrepancy and similarity between these two methods will be discussed. Consecutively, the assumed-orientation method will be used to characterise FLDs in order to clarify which parameters affect FLDs and to which extent.

2.4.1 Reliability study

Batches were sampled randomly for the two implemented methods. Since this may induce statistical variability, a reproducibility and repeatability study was performed first, using the measured-orientation method. Six kilograms of flakes were obtained from shredding *C/PPS 2nd type* using an RS30 with a 19 mm blade width and a 40 mm screen size. These were then kept stationary after shredding to prevent the finer particles from sinking to the bottom of the container. Seven batches were sampled without replacement, i.e. flakes were drawn once and not returned to the population, from the top of the container. The first five batches were sampled by the first operator and the last two by another operator on a different day.

Measured-orientation method

The FLDs of the seven batches were calculated using the measured-orientation method. Examples of such FLDs are shown in Figure 2.7a, which can be characterised as a uni-modal distribution peaking at around 20 mm, which is

Figure 2.7 Comparison of FLDs of batches calculated using the measured-orientation method or assumed-orientation method to show the correlations between batches and between methods.

close to the blade width of 19 mm. This apparent correlation will be discussed in further paragraphs. These distributions were found not to fit with regular probability density functions that might characterise FLDs, such as log-normal [17] or Weibull [36, 37]. This is mostly due to the characteristic long tail and high peak of the presented FLDs. All seven batches resulted in FLDs similar to Figure 2.7a. A correlation coefficient, r_N , based on the Pearson correlation coefficient, can be calculated to quantify this similarity [38]. Ideally, r_N would be the correlation coefficient between the FLD of batch number N and the FLD of the parent population. However, due to the difficulty of calculating the FLD of the entire population, the weighted average of the seven batches is considered to be the best approximation. Thus, r_N compares the FLD of each batch to this average:

$$r_N = \frac{\sum_{i=1}^n (x_{N,i} - \tilde{x}_N)(X_i - \tilde{X})}{\sqrt{\sum_{i=1}^n (x_{N,i} - \tilde{x}_N)^2 \sum_{i=1}^n (X_i - \tilde{X})^2}} \quad (2.1)$$

where N refers to batch number N (from 1 to 7), $x_{N,i}$ is the length fraction (or volume in this case) of batch N for the fibre length i , $\tilde{x}_N$ refers to the arithmetic mean of all $x_{N,i}$ and X refers to the weighted average of the seven batches. Table 2.4 lists the r_N for the seven batches, which are all larger than 0.978. Even though these numbers are close to 1, it is difficult to objectively conclude whether they are large enough. As an example, Figure 2.7a displays two FLDs that each have an r_N of 0.985, showing what level of variability is expected

for such an r_N . To sum up, it can be concluded that the sampling method induces a low statistical variability from the r_N coefficients in Table 2.4 as well as from the FLDs displayed in Figure 2.7a. It is also important to note that these levels of correlation can be achieved for small batches (Table 2.4), featuring between 59 and 93 flakes per batch. This improves the robustness of industrial recycling solutions. Batch-process routes, such as in [4, 5, 10], result in virtually identical FLDs from one batch to another.

Batch	#1	#2	#3	#4	#5	#6	#7
r_N	0.985	0.990	0.985	0.980	0.991	0.978	0.986
Flakes per batch	63	63	64	61	93	59	60
$r_{\text{quasi},N}$	0.986	0.990	0.975	0.989	0.961	0.973	0.982
$r_{\text{cross},N}$	0.950	0.960	0.885	0.882	0.923	0.925	0.970
$r_{\text{UD},N}$	0.854	0.907	0.696	0.811	0.853	0.904	0.896

Table 2.4 Correlation coefficients of the batches used for the reliability study as defined in Equations (2.1) and (2.2).

Assumed-orientation method

Next, the assumed-orientation method was employed to calculate FLDs, which were compared to those computed with the measured-orientation method. As a reminder, the assumed-orientation method disregards the actual flake layout when computing FLDs. All the flakes in the current study are shredded quasi-isotropic offcuts. However, the industry uses or will use various layouts to manufacture TPC components. Therefore, the accuracy of the assumed-orientation method must be tested against various flake layouts. For that purpose, the actual layout of the seven batches of flakes was considered when analysing the flakes (the case presented in the previous paragraphs), or they were considered to have a virtual layout (cross-ply and unidirectional (UD)). The resulting FLDs for each layout configuration were then compared to the results of the assumed-orientation method. Correlation coefficients were calculated between the FLDs computed using the assumed-orientation method and the FLDs calculated with the measured-orientation method for each layout situation and for all seven batches. An expression of such a coefficient is defined as:

$$r = \frac{\sum_{i=1}^n (x_i - \tilde{x})(y_i - \tilde{y})}{\sqrt{\sum_{i=1}^n (x_i - \tilde{x})^2 \sum_{i=1}^n (y_i - \tilde{y})^2}} \quad (2.2)$$

where x and y refer to the two FLDs to be compared. Similarly to Equation (2.1), x_i corresponds to the volume fraction for the fibre length i of the FLD represented by x , and $\tilde{x}$ is the arithmetic mean of all x_i . The various layouts are denoted by

$r_{quasi,N}$, $r_{cross,N}$ and $r_{UD,N}$. The names *quasi*, *cross* and *UD* refer to the layup (true or virtual) of the flakes when running the measured-orientation method. As before, N corresponds to the batch number, ranging from 1 to 7. Table 2.4 lists the results for these three coefficients for all batches and Figure 2.7b shows a few typical FLDs to help visualise the correlation levels between the assumed-orientation method and the measured-orientation method for different layups.

Table 2.4 highlights that all $r_{quasi,N}$ and $r_{cross,N}$ coefficients are very high. The $r_{UD,N}$ coefficients, on the contrary, show some deviations, as they range from 0.70 to 0.91. The FLDs in Figure 2.7b illustrate an example for batch 1, computed with a virtual UD layup on the one hand and with the assumed-orientation method on the other. This results in a mediocre correlation between the two FLDs, validated by $r_{UD,1} = 0.854$. Although the two FLDs look different, the major characteristics are well captured: a high peak at 20 mm, a very good correlation for fibres smaller than 20 mm and a long tail for long fibres.

Two main results can be derived from this study of the assumed-orientation method. Firstly, the assumed-orientation method can be used instead of the measured-orientation method, as it characterises FLDs well when flakes have a quasi-isotropic layup, which is the case in this study (see Section 2.2). Secondly, the results on $r_{quasi,N}$, $r_{cross,N}$ and $r_{UD,N}$ seem to show that flake layup hardly influences the FLD in most cases, as opposed to flake shape.

Discussion

The possible origins of the influence of flake layup and shape on the FLD are discussed here. First, flakes obtained from multiple-shaft shredders mainly look like parallelograms, or possibly quadrilaterals, as shown in Figures 2.2b and 2.6. As offcuts might be shredded from any orientation, fibres might also have any orientation, irrespective of flake layup, indicated as θ in the referential of the flake (see Figure 2.8). However, there are two phenomena limiting the influence of θ on FLD. To make matters simpler, consider a single rectangular flake. Figure 2.8a illustrates that variations in fibre length ($\Delta L(\theta)$) are small when θ is small, whereas variations in $L(\theta)$ are large for large angles, in which θ is defined with respect to either of the principal directions of a parallelogram flake (e_1 and e_2 in Figure 2.8). When the fibres are randomly oriented in the flakes, there will be many more fibres with a length close to the flake width and flake height. Consequently, the offcut layup has less influence on the FLD than the flake shape and size. Figures 2.8b and 2.8c highlight the areas of constant fibre length in grey. It is clear from these figures that there are more fibres of length $L(\theta)$ for a small angle θ than for a large angle. This, again, indicates that there are more fibres with a length close to the flake width and flake height when the fibres are randomly oriented in flakes.

These phenomena demonstrate that FLDs are dependent on flake size and shape as well as on the orientation in which the offcuts were shredded. However, the

offcut layout has no influence when the orientation of the offcuts in the shredders is completely random. The shredding experiments performed in this study showed that this orientation seemed random if the hopper is large enough to be fed by offcuts in every orientation. Measurements were made for a batch of flakes that closely matches these conditions: *C/PPS offcuts - large* shredded with an RS40 shredder (test #5 in Table 2.2). The fibre orientation of the top layer was measured from pictures of the flakes. The orientation of flakes on the pictures was also set to be the 0° reference. A histogram plot of the results is shown in Figure 2.9. The number of fibres is relatively low around 20° – 25° and 60° – 65° , while relatively high numbers of fibres are found at 0° , 45° and 90° . However, these peaks are fairly flat and most angles are well distributed. The offcuts used in this section, *C/PPS 2nd type*, have a much larger aspect ratio and were fed into the shredder less randomly. As a consequence, the orientation distribution of the top layer is more centred at 0° and 90° . Because of this, one would expect variations between the FLDs computed with the measured-orientation method for various flake layouts. These differences are visible for the UD case (see Table 2.4). The $r_{UD,N}$ coefficients vary, indeed showing correlations that range between marginal and good. Still, the $r_{quasi,N}$ and $r_{cross,N}$ coefficients are high confirming that offcut layout has far less influence on FLD than flake size.

Additionally, the argument for a single rectangular flake can be extended to explain the shape of the FLDs. As there are more fibres with a length close to the flake width and flake height, it is expected that the FLD can be obtained from the

Figure 2.8 Sub-figures 2.8a, 2.8b and 2.8c show two reasons that explain the non-dependence of layout in FLDs and the presence of peaks in the FLDs (Figure 2.7a): there are more fibres for small angles and the fibre length distribution is scattered when θ increases.

distribution of flake width and height. This statement becomes more accurate for flakes with a high aspect ratio as it strengthens the two phenomena. It also remains true for variations in flake size, as there are independent of flake size. However, changes in flake shape can diminish the effects. This should be studied case by case and probably depends on flake convexity and the number of edges of the flake in question. One of the possible representations is to use maximum and minimum Feret diameters, which correspond to the maximum and minimum lengths of a random shape that can be measured with a calliper [39]. Figure 2.10 shows the distribution of these minimum and maximum Feret diameters of flakes obtained from the image processing analysis. The distribution of the minimum Feret diameters is narrow, peaking at 22 mm, while the maximum Feret diameter ranges from 20 mm to 100 mm. This explains the peak at 20-22 mm in Figure 2.7, obtained with a 19 mm blade width, as well as the long tail next to this peak. The discrepancy between blade width and the minimum Feret diameter can be explained by various factors. On one hand, blade clearance and wear of the shredder may lead to slightly larger cuts than the expected 19 mm. On the other hand, the observed flakes have small protruding fibres or broken particles next to the flakes, which artificially increase the Feret diameters.

Nevertheless, the assumed-orientation method was shown to reliably capture FLDs of quasi-isotropic flakes.

Figure 2.9 Measured distribution of the fibre orientation of the top layer for the flakes of the batch number #5.

Figure 2.10 Length distributions of the minimum and maximum Feret diameters for a batch of flakes, showing a narrow peak for the minimum diameter and a wide distribution for the maximum diameter.

2.4.2 The influence of shredding settings and sieving

The results of the previous section explained the development and reliability of the methods, especially the assumed-orientation method, which will be used for the rest of the study. These results enable us to proceed to the last aim of the chapter: to understand whether and how, offcut size, shredding settings and sieving influence the FLD of the resulting flakes. Three cases are tested in this section.

- The first considers offcuts of different sizes shredded with the same parameters, to determine whether offcut size influences the FLD of the shredded flakes. Three offcut sizes were used for this purpose.
- The second case tests the influence of varying shredding parameters, namely blade width and screen size, on the FLD. Shredding experiments with four combinations of blade width and screen size were performed.
- The third case involves the sieving of shredded flakes, to determine the relation between sieve size and FLD. A set of different sieves was used to sieve one batch of flakes.

First, offcuts of the various sizes listed in Table 2.1 were shredded using an S20, a two-shaft shredder without a screen. The shredded output was fed through the shredder four times to create multiple cuts and to simulate the effect of a screen. A visual inspection revealed that slightly more fine particles were produced than with the four-shaft plus screen system. A single batch was sampled and analysed for each of the three offcut sizes. The corresponding FLDs are displayed in a boxplot in Figure 2.11 (top three rows). The peak location is also indicated and is situated at 20 mm for all three cases, which was expected as the blade width is 19 mm (one of the dashed lines in Figure 2.11). Besides, the scatter of the FLD, regardless of whether interquartile range or 90 % spread is considered, is nearly constant. For comparison purposes, a correlation coefficient was calculated between the FLDs resulting from tests #1 & #3, and #2 & #3, following Equation (2.2). This resulted in $r_{\#1,\#3} = 0.910$ and $r_{\#2,\#3} = 0.990$ respectively, which confirms their apparent correlation. Although FLDs shift slightly towards longer fibres when offcut weight increases, this effect is very limited compared to the differences between the average offcut weight and size (see Table 2.1).

Secondly, the shredding parameters of four-shaft shredders were varied while processing the same type of offcuts. The following combination of blade width [mm] and screen size [mm] were used: (29 - 25), (19 - 40), (29 - 40) and (29 - no screen). The bottom four rows in Figure 2.11 summarise the resulting FLDs, and one batch was sampled and analysed for each combination of settings. Similarly to the previous case, the peak value is equal to blade width when screen size,

- material category
(blade width [mm] -
screen size [mm])

Figure 2.11 *FLDs (left) and PSDs (right) of various flakes in a boxplot form. The first three rows illustrate variations of FLD when the offcuts vary in size, whereas the last four rows correspond to flakes shredded with various settings. The dashed lines at 19 mm and 29 mm highlight the blade width of the shredders used in this study.*

if applicable, is larger than the blade width (tests #5, #6 and #7). Otherwise, when the screen is smaller than the blade width, the shredded flakes had much smaller fibre lengths (tests # 4 and #6). This is a direct consequence of flakes being cut multiple times in the shredder before they pass through the screen. For those tests, flake area was also measured by means of image analysis, confirming the results. The average flake area for test #4 was 379 mm², while #5 and #6 resulted in 603 mm² and 950 mm² respectively. In addition, larger blade widths result in larger flakes and shift the bulk of FLDs to longer fibres (tests #5 and #6), as a result of increased flake size.

Overall, the seven FLDs in Figure 2.11 show that the bulk of fibre lengths is narrowly distributed at the peak, in addition to having long tails on the right-

hand side. This is in accordance with the findings of the previous section.

Thirdly, flakes shredded from C/PPS large offcuts (19 mm blade - no screen - 5 cuts) were sieved using a multi-stage vibrating sieve, as described in Section 2.2. One batch of flakes was sampled from the material resting on each sieve. The FLDs were calculated and are shown in Figure 2.12 in a boxplot form. The aperture of the sieves from between which the flakes were retrieved, is overlaid on the FLDs. As expected, based on the results of the previous section, the FLDs are directly correlated to their related sieves. Flake size is linked to the sieve aperture, and so is the FLD. A small percentage of flakes did not pass through the 22.4 mm sieve. This may be due to the S20 shredding machine, to which no screen could be attached, which might produce these large flakes. The fraction of flakes retrieved from the 11.2 mm and 22.4 mm sieves represents 70%, which is in agreement with the expectations and previous results: most of the flakes have a size close to the blade width. The flakes resting on sieves of aperture 8 mm and lower start to delaminate when using this shredding system and these blade/screen parameters. Importantly, different comminution techniques may induce delamination of flakes at different flake sizes from what it observed here. This primarily depends on the

Figure 2.12 *Boxplots of the FLDs of sieved flakes. Each row corresponds to flakes resting on each sieve of the multi-stage sieve. The apertures of the corresponding sieves, which are written on the left-hand side, are indicated with round symbols over the boxplots.*

dominant comminution mechanism, impact or shearing [15].

2.5 Conclusion

The objective of this chapter was to develop and implement a new method that calculates FLD from a batch of multi-layered flakes. Recycling routes, such as those presented in [5] can benefit greatly from knowing the fibre lengths in the recyclate. The next step was to use this newly implemented image processing method to understand whether and how shredding parameters can influence FLD, as well as seeing how FLD could be adjusted by means of sieving.

In this study, an image processing method that disregards the actual flake layup was successfully implemented and used to calculate FLDs from pictures of flakes. It was found that FLD is closely related to flake size and is barely affected by offcut layup, if the offcuts are fed into the shredder at random orientations. This characteristic extends the validity of the method to shredded composites when there is no prior knowledge of the layup. However, the methods and the results remain valid only if flakes do not delaminate during the shredding process.

Additionally, the researchers noticed that production scrap can vary in size. However, this was shown to have no influence on FLD/PSD, which is a significant result when setting up a pilot plant or production line to recycle collected scrap. Along the same lines, it was demonstrated that sampling batches from a population of shredded flakes is reproducible even when batches are as small as 60 flakes. Such a stable FLD/PSD, from batch to batch or in a continuous process, will be a minimum prerequisite for any application requiring reproducible part performance.

Finally, it was shown that changing the blade width and screen shifted FLD location and peak, as well as modifying the overall scatter of FLDs. Sieving provides a simple way to separate fine and coarse particles. It was also found that the aperture size of the sieves is closely correlated to the FLD of flakes resting on each sieve. These results were obtained with flakes shredded from quasi-isotropic offcuts but the authors believe that similar results can be expected if the scrap layup varies.

This study focused on TPCs, but the results presented here, as well as the assumed-orientation method, can be easily used for the recycling of thermoset composites. Although recycling solutions for thermoset composites are different from those for TPCs, the comminution step can be similar, which results in similar needs to characterise FLDs.

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2.A Supplementary material: a predictive model for FLDs

The results from the main body of the chapter showed that the FLDs are directly related to the flake size (Section 2.4.1), and that the shredding settings and sieving largely influence the FLDs. At the current state, there is no explicit formulation between the machine settings, the flake sizes and the FLDs. The objective of the supplementary section is to determine a fast and reliable method of predicting the FLDs of flakes based on limited parameters, such as shredding and sieving settings. This would help to predict the output of shredding and sieving systems not used for this study for instance.

It was noticed in Section 2.4 that the probability density functions (PDFs) that commonly fit FLDs for short and long fibre composites [17, 36, 37] failed to properly fit the FLDs in this chapter. In particular, the Weibull and log-normal PDFs fail to capture both the long tail and the high peak simultaneously. Two *a priori* options exist to fit FLDs. Firstly, a PDF can be formulated from scratch to make it fit the FLDs of this chapter, but this lacks physical understanding. Additionally, the eventual large number of fitting parameters and its possible lack of re-usability makes this method inadequate. Secondly, a bimodal PDF with identical modes, i.e. peak locations, can be used to characterise the tall peak on one hand and the long tail on the other hand. However, this method is not an elegant way of representing uni-modal probability distribution.

A third simpler approach was developed and implemented to generate FLDs from limited inputs. The main steps of this new method are illustrated in Figure 2.A. 1. It starts by generating three lists of N numbers following any given PDF. N rectangular flakes are then generated characterised by their widths, lengths and fibre orientations corresponding to the three lists of generated numbers. Each

Figure 2.A. 1 Schematic description of the method that generates a set of rectangular flakes and computes their FLD.

rectangular flake is then ‘filled’ with lines, which are representing fibres. The FLD of each flake is calculated from the line length distribution. The FLD is then computed by summing the FLD of each flake.

The method was used to simulate FLDs of the batches presented in Section 2.4.1, i.e. *C/PPS offcuts - 2nd type* shredded with a 19 mm blade and 40 mm screen. As a first guess, a Dirac delta distribution peaking at 19 mm (noted D(19)) was chosen for the flake widths because it represents the blade width accurately. A uniform distribution between 0 mm and 80 mm (noted U(0,80)) was arbitrarily chosen for the flake lengths from the observations of the maximum Feret diameters (Figure 2.10). The orientation distribution of the fibres in the flakes was chosen to be uniform. A total of 1000 flakes are generated for each computation. The resulting FLD was compared to the FLD of the weighted average of the seven batches from Section 2.4.1, using the Pearson correlation coefficient described in Equation (2.2) (page 30), resulting in $r = 0.63$. Observations of the FLD revealed a peak too narrow compared to the FLDs calculated from image processing, which may be due to the Dirac delta function. Thus D(19) was replaced by a normal distribution, with a mean at 19 and a varying standard deviation (1, 3, 5 or 7) (noted N(19,5²) for instance when $\sigma = 5$). Distributions were chosen instead of a single Dirac peak to better simulate the effects of offcuts being shredded, as the histogram of the minimum Feret diameters in Figure 2.10 shows a distribution. Two reasons can explain this deviation from the expected Dirac peak. On one hand flakes may be cut multiple times resulting in widths smaller than the blade width. On the other hand, large flakes might be created as by-products and can fall through the shredder and screen. The resulting correlation coefficients are listed in Table 2.A.1 on the left for these four cases, showing a much higher correlation when the distribution of the flake width is wide.

Flake widths	Flake lengths	r	Flake widths	Flake lengths	r
D(19)	U(0,80)	0.63	N(19,3 ²)	N(38,6 ²)	0.92
N(19,1 ²)	U(0,80)	0.76	N(19,5 ²)	N(38,10 ²)	0.95
N(19,3 ²)	U(0,80)	0.90	N(19,7 ²)	N(38,14 ²)	0.95
N(19,5 ²)	U(0,80)	0.94	N(29,3 ²)	N(58,6 ²)	0.86
N(19,7 ²)	U(0,80)	0.94	N(29,5 ²)	N(29,10 ²)	0.89
			N(29,7 ²)	N(29,14 ²)	0.88

Table 2.A.1 *Correlation coefficients calculated from Equation (2.2) (page 30) between FLDs calculated using the method presented in this section for various input distributions, and FLDs obtained from the image processing analysis.*

Regarding the length of the flakes, a first estimation of the effect of the apertures of the screen on the flake size would be to limit flakes larger than the aperture diameter to fall through the screen. However, the aperture diameter is 40 mm in this case, which is evidently smaller than most maximum Feret diameters (Figure 2.10, page 33). A closer look at the Feret diameters of the flakes seem to highlight that the maximum Feret diameters are twice longer than the minimum diameters. This suggests that flakes have on average an aspect ratio of two. Therefore, the distribution of the flake lengths was set to be twice the distribution of the flake widths, as an educated input for the method implemented in this section. The distribution of widths and lengths was set as $N(19, \sigma^2) \times N(38, (2\sigma)^2)$, where σ can range from three to seven without much effect. The correlation coefficients for three cases are listed in Table 2.A.1 showing good agreement between the modelled FLDs and the FLDs computed from the assumed-orientation method. Figure 2.A. 2a shows the comparison between the two FLDs for $\sigma = 5$, and helps to visualise the correlation achievable with a single machine input, the blade width.

Figure 2.A. 2 FLDs calculated with two methods for two situations, offcuts shredded with a 19 mm blade in 2.A. 2a and a 29 mm blade in 2.A. 2b. The solid lines correspond to FLDs generated using the method presented in this section with an educated input for the distribution of flake widths and lengths. The dotted lines show the FLDs computed from the image processing analysis for batches of the two situations.

Eventually, another situation was tested to validate the results. The offcuts were those shredded with a 29 mm blade and a 40 mm screen, which correspond to the test #6 in Table 2.2 (page 23). The FLD of the output flakes was computed using the assumed-orientation method, and is shown in Figure 2.11 (page 35). Similarly to the previous paragraph, an educated input based on the blade width was used,

i.e. $N(29, \sigma^2) \times N(58, (2\sigma)^2)$ for the flake widths and lengths respectively, with σ ranging from three to seven. The correlation coefficients between the FLDs computed from the image processing method and from the generated rectangles are listed in Table 2.A.1 and show good agreements. Figure 2.A. 2b shows the FLDs calculated with both methods, for $\sigma = 5$, to illustrate the achievable level of correlation.

By extending this work, predictions of FLDs with a relatively high confidence can be achieved for various shredders configurations with only one physical parameter, the blade width. Several assumptions are however necessary: the screen size is larger than the blade width, the offcuts to be shredded are initially larger than the expected flake size, the cutting mechanism of the shredders is similar to the shearing in multi-shaft shredders, the orientation of the offcuts during shredding is close to random.

Following these results, the next step is to focus on the FLDs of sieved flakes. The boxplots in Figure 2.12 (page 36) seem to correlate well to the aperture of their respective sieves. Hence, the objective is to determine whether the FLD can be directly calculated from the sieve aperture.

The sieves used for this study were perforated plates with square openings as defined in ASTM E11. The sieves were stacked in a way that the aperture area of each sieve is the exact double of the sieve below. Therefore the apertures in any given sieve are squares of length a and diagonal $a\sqrt{2}$, and the apertures of the sieve above have a length $a\sqrt{2}$. A priori, $a\sqrt{2}$ seem to be a good factor to scale each batch of sieved flakes. Thus the FLD of the flakes resting on each sieve in Figure 2.12 was divided by the diagonal of its respective aperture $a\sqrt{2}$, to form normalised FLDs. Figure 2.A. 3 displays those normalised FLDs for most sieved flakes. The flakes resting on the 2 mm and 2.8 mm sieves are not included because they are too fine for such an analysis. In addition, the FLD of the flakes before sieving, which correspond to the shredding test #3 in Figure 2.11, was normalised by dividing the fibre lengths by the shredder's blade width. A correlation coefficient was calculated between each normalised sieved FLD and the normalised non-sieved FLD, following Equation (2.2). The coefficients are displayed in Figure 2.A. 3 and show very good correlation. Therefore, a simple equation can be formulated to express the FLD of sieved flakes as a function of the FLD of non-sieved flakes:

$$\text{FLD}_{\text{sieve length}=a} = \frac{a\sqrt{2}}{\text{blade width}} \text{FLD}_{\text{non-sieved}} \quad (2.3)$$

Additionally, the FLDs of sieved flakes are highly correlated to the sieves where flakes are resting on. As explained in Section 2.4.1, FLDs are well related to the shape of their respective flakes. It was found that the aspect ratio of these flakes is similar in all sieved batches, which can explain the high correlation coefficients. More than 90% of flakes in all batches have an aspect ratio between 1 and 4. In

Figure 2.A. 3 *FLDs of sieved flakes after being normalised. On the top row, the FLD of the non-sieved flakes is normalised with the blade width and used as a reference to calculate correlation coefficient with all other FLDs of sieved flakes.*

comparison, 90% of the flakes of the reference batch have an aspect ratio between 1.1 and 3.6.

The first part of the appendix concluded on the prediction of FLDs for shredding systems. The newly implemented method confirmed its ability to predict the FLDs for various systems with a high correlation, and from a single physical parameter. This second part showed to be able to determine the FLDs of flakes after sieving, only by knowing the sieve sizes and the FLD before sieving. This later FLD can be calculated from the image processing of pictures of flakes, or from the method introduced in this section.

Chapter 3

Characterisation and improvement of the quality of mixing of doughs from recycled thermoplastic composites

Abstract

A low-shear mixer was used to blend large thermoplastic composite flakes into a molten mixed dough, which was then compression moulded. This process is a key step in a novel recycling solution for thermoplastic composites. This study used shredded C/PPS flakes, originating from consolidated laminate scrap. These flakes are about 20 mm in size, and contain woven fabric reinforcement, making them far different from regular pellets, and therefore more difficult to mix. A study was carried out to characterise the quality of mixing (QoM) of the blended doughs, and, as a main objective, to understand how to improve the QoM of mixed doughs. In order to achieve this, the effect of mixing settings and fibre length on the QoM were studied. The QoM was characterised by means of image analysis of a large set of cross-sectional microscopy images, based on which the scale and intensity of segregation of the fibre clusters were evaluated. Bundle size distribution was determined by applying Delaunay triangulations to cluster the fibre centres. These methods were found to be suitable for characterising the QoM of such doughs. Increasing the mixing time and mixing speed were identified as key ways to improve the mixing process. With the current mixing machine, it is also suggested not to use fibres longer than 15 mm on average in order to limit intra-dough variability. For doughs made of fibres longer than 15 mm, improvements on the mixing device could sufficiently increase the QoM.

3.1 Introduction

The application of long fibre thermoplastics (LFTs) attracted considerable interest in the past decades [1, 2]. On one hand, they offer and allow for an increased geometrical complexity, from a design point of view, compared to continuous fibre composites. On the other hand, they exhibit mechanical properties intermediate to short and continuous fibre composites. Several categories of LFTs have been brought to market including thermoplastic bulk moulding compounds [3, 4], glass mat thermoplastics and LFT pellets [2, 5, 6]. During the same period, the production and demand of continuous fibre thermoplastic composites (TPCs) has increased considerably, leading to a rise in TPC production scrap. The economic benefits of recycling this scrap, in conjunction with environmental and legislative incentives, have encouraged the development of recycling solutions for TPCs. Recently, both De Bruijn et al. [7, 8] and Janney et al. [9] separately developed a recycling route for TPC scrap inspired by the processing of LFT pellets. A schematic view of the recycling solution implemented by De Bruijn is shown in Figure 3.1. Production offcuts, such as trims and nesting scrap, are first collected and shredded into flakes. Most often, these flakes are multi-layered material and may consist of woven fabric, similar to those in De Bruijn et al. [8] and in Chapter 2. and as shown in Figure 3.1. Flakes are then processed in a blender to form a molten mixed dough that is transferred directly to a press for compression moulding. The mixing phase used in this study is similar to the mixing of LFT pellets. The pellets or flakes are processed in a device that melts the polymer and disperses the fibres. However, mixing of flakes described here can be substantially more difficult than mixing LFT pellets that have been designed to disperse easily [5].

Figure 3.1 *Schematic flow chart of the chosen recycling solution. The top row illustrates the various processing steps while the bottom row shows the material state between each step.*

The subsequent processing step, after mixing, involves squeezing the mixed dough into a mould. Its flow behaviour depends on the amount of fibres, fibre length, the interaction of fibre bundles in the dough, and thus the dispersion of bundles. Once a component has been moulded, its mechanical properties are also linked to fibre length and the dispersion of fibre bundles. A previous study by De Bruijn [7] showed that mixing the multi-layered TPC flakes significantly improves the mechanical properties of the moulded panels, compared to compression moulding of non-mixed flakes. This improvement is mainly driven by the micro-structural change: from stacked, thick flakes to homogeneously entangled fibre bundles. Additionally, the recycling solution presented here prevents fibre attrition during mixing by using a low-shear mixer, in order to limit the reduction in mechanical properties, which depend on the fibre length. The mixing of flakes, and the resulting micro-structure, is therefore crucial for the recycling process. Consequently, a proper understanding of the mixing step is required, as well as a good definition of the quality of mixing (QoM) of mixed flakes. A suitable characterisation method for QoM must be developed and implemented.

The previous studies have sought to tackle the problem of characterising the QoM of fibre reinforced plastics with various methods [10–24], mainly based on image analysis of microscopy images. Most of these methods were inspired by a large corpus on spatial statistics [25–29], but the methods implemented for fibre composites often lack the mathematical rigour of the latter.

The present chapter will deal with the mixing step in the recycling solution developed by De Bruijn et al. and characterise the QoM of the mixed material, with the objective of understanding how to improve the QoM of mixed doughs. In order to achieve this, several aspects of the QoM that can be applied to fibre reinforced composites will be selected from literature and implemented. Finally, the effects of mixing settings and fibre length on QoM will be studied.

The first two sections will detail the material and mixing technology used in this study. The details of the experimental study are introduced in Section 3.3. Next, Section 3.4 will discuss the proposed definitions to characterise the QoM, as well as listing current methods used for fibre composites. The selection and implementation of the methods is then detailed in Section 3.5. The methods are applied to characterise the effect of mixing settings and fibre length on QoM, which are presented in Section 3.6.

3.2 Materials

The scrap material used for this study was collected at the forming stage of various manufacturing sites. It consists of laminated TPC offcuts, made of Toray Cetex® TC1100 5HS carbon/PPS (C/PPS) at 50% fibre volume fraction (FVF), as shown in Figure 3.1 (1. trims). The carbon fabric is woven with tows that

Figure 3.2 *Inside view of a four-shaft shredder (image courtesy of UNTHA GmbH).*

contain 3,000 fibres each. The offcuts were shredded in-house using a two-shaft shredder made by UNTHA shredding technology GmbH, Austria (see Figure 3.2). The output flakes can be seen in Figure 3.1 (2. shredded flakes). Some batches of shredded flakes were sieved with a multi-stage vibrating sieve. The fibre length distribution (FLD) of the output flakes, as well as the shredding and sieving process, were previously characterised in Chapter 2. The FLDs of the categories of flakes used in this study are shown in Figure 3.3. *C/PPS L* and *C/PPS M* correspond to the flakes that first passed through the sieves with an aperture of 22.4 mm and 11.2 mm, respectively, before failing to pass through the sieves with an aperture of 16 mm and 8 mm, respectively. In addition *C/PPS S* consists of a blend of the flakes that failed to pass through the sieves with an aperture of 2.8 mm and 4 mm. *C/PPS LFT* pellets with 3 mm fibres were used to compare the QoM of the recycled material with commercially available pellets. These pellets are known as Luvocom®1301/XCF/30 and are produced at 30% fibre weight fraction,

Figure 3.3 *FLDs of the various types of flakes used in this chapter.*

or approximately 24% FVF. This study also used polymer granulates to dilute the flakes or pellets during the mixing stage, namely Fortron® 0214 PPS granulates by Celanese. Two other materials were used for comparison purposes:

- short fibre pellets that were injection moulded at 40% fibre weight fraction (or around 32% FVF) with fibres of 200 μm in length;
- single-layer woven fabric prepregs measuring $10 \times 10 \text{ mm}^2$, which were compression moulded at 50% FVF. Note that this material is not mixed in any way. More information on the material and processes can be found in [30].

3.3 Low-shear mixing

After the offcuts had been shredded, the resulting flakes or pellets were fed into a low-shear mixer together with PPS granulates to dilute the fibre suspension to 20% FVF. The device was developed and manufactured at the Centre of Lightweight Structures in the Netherlands in 1998 [31]. Contrary to typical screw extruders, the low-shear mixer consists of a heated hollow cylinder with a 70 mm diameter, and features three eccentrically-located heated rods rotating inside. An illustration of this device is shown in Figure 3.4. The three rods are placed at different distances from the axial centre of the cylinder (Figure 3.4 on the right). The mixer is fed by means of a hopper located on the cylinder. After feeding, a piston pushes the

Figure 3.4 A schematic of the low-shear mixing device is shown on the left. It highlights several key elements that are explained in Section 3.3. The cross-section A-A is drawn on the right-hand side of the figure.

material inside the cylindrical cavity, which closes the feed opening. The heated rods then start to rotate around the axial centre at a speed varying from 5 rotations per minute (rpm) to 15 rpm, for 5 to 20 minutes. During this phase, the polymer starts to melt, causing the flakes to delaminate, the woven structure of the plies to loosen, and eventually the bundles to spread into clusters of various sizes. At the end of the mixing phase, the piston pushes the material out of the mixer, which is now a molten, mixed dough. During the entire mixing process, the material is not compressed and consequently only fills part of the cavity, ranging from 20% to 50%. The rest is filled with air and, possibly, volatile by-products. As a result, the extruded dough is very porous, and even swells a small amount when pushed out, reaching a final diameter of 100 mm after ejection from the cylinder and gate, which both have a diameter of 70 mm.

In this mixing device, the rotation speeds of the low-shear mixer are typically 10 rpm and the distance between the rotating rods and the cylindrical cavity is about 10 mm. This results in very low shear rates compared to those found in typical screw extruders. As a consequence, fibres are less prone to breaking during the mixing phase. Besides, the low-shear mixer allows for a batch-type process rather than the continuous process typical for screw extruders, as a result of which

Test number	Material	Mixing time [min]		Mixing speed [rpm]		Filling fraction [%]	Temperature [°C]	Remarks
#1	non-sieved	10	5	21	320			run of the DoE
#2		20	5	50				
#3		10	15	50				
#4		20	15	21	320			
#5		10	5	50	360			
#6		20	5	21				
#7		10	15	21				
#8		20	15	50	360			
#9	non-sieved	15	10	35	340			run of the DoE
#10	LFT pellets	20	10	21	340			3 mm long fibres
#11	C/PPS L							sieved flakes
#12	C/PPS M							
#13	C/PPS S	20	10	21	340			sieved flakes
#14	non-sieved	20	15	50	320			repetition of #8
#15		10	5	21	320			repetition of #1
#16	non-sieved	20	5	21	360			repetition of #6

Table 3.1 List of the various doughs manufactured and tested.

the residence time of the material is equal for all particles. The low-shear device is still in its prototype phase and has not been studied extensively. Therefore the mechanisms of mixing in such a device are still poorly known.

A fractional factorial design of experiments (DoE) of resolution IV was performed by varying the mixing speed, mixing time, cavity filling ratio and mixing temperature. Two levels were chosen for these four factors in addition to a central point. The doughs and their mixing settings are listed in Table 3.1. The resolution (IV) of the DoE makes it possible to identify the significance and strength of the main factors. However, the two-factor interactions for such a resolution are confounded with other two-factor interactions so they will not be analysed in order to prevent interpretation errors. The reproducibility of the mixing process was investigated by producing an extra dough for three of the DoE settings (see tests #14, #15, #16 in Table 3.1). Some doughs were also produced with various FLDs – rows #10 to #13 in Table 3.1.

3.4 Literature review on the experimental methods of measuring the QoM

The study of mixing and segregation is a field of spatial statistics that, over the past decades, has been widely applied to various fields of science, ranging from ecology to the material blending [14, 27, 32]. A first comprehensive definition of QoM was proposed by Danckwerts in 1952 [25] by introducing two aspects: the intensity of segregation (IoS) and the scale of segregation (SoS). The IoS corresponds to the coefficient of variation (CoV) of the concentration of species in the system, also known as evenness [28]. With regard to blending fibre composites, it refers to the CoV of the local fibre fraction. The SoS represents a characteristic length of segregation, or clustering, in the system. SoS represents, for instance the maximum striation thickness for mixed fluids, or the size of fibre clusters for fibre composites. Figure 3.5 shows a visual representation of good and poor IoS and SoS, with each sub-figure representing a cross-sectional micrograph of fibre composites. The studies that followed Danckwerts extended his initial work and defined other aspects of segregation [28]. *Exposure* corresponds to the rate of change in segregation, which has some importance along the length of screw extruders, for instance. *Density* is a measure of the mass or volume of one of the constituents per unit volume or area. Lastly, *centralisation* corresponds to the aggregation of a constituent away from its centre.

The first two aspects of segregation were continuously measured in various fields related to spatial statistics [14, 27, 32] by adapting the measurement methods for IoS and SoS to specific situations. IoS and SoS are particularly well-suited for the mixing of discontinuous-fibre composites and have been studied by various

Figure 3.5 *Schematic cross-sections of fibre reinforced composites with various degrees of evenness (IoS) and clustering (SoS). Figures 3.5a to 3.5d show cross-sections overlaid with square quadrats that are subdivided into 4×4 cells. Figures 3.5e to 3.5h show the same cross-sections and their Voronoi diagrams, generated from the centre of the fibres. The dual graph of the Voronoi diagram, the Delaunay tessellation, is only shown in Figure 3.5e for clarity.*

authors [10–24]. The latter three aspects of segregation – namely exposure, density and centralisation – have been scarcely used for fibre composites and polymer blends.

The problem presented in this chapter is similar, in a way, to other mixing problems for discontinuous-fibre composites or polymer blends, and can be summarised as follows. Two immiscible species, fibres and polymer, are initially highly segregated in the form of large clusters of flakes (large multi-layered flakes) and polymer granulates. During mixing, the flake structure delaminates and disentangles into loose bundles, eventually leading to a more even distribution of fibres in the dough. Measuring IoS and SoS only requires a snapshot of the final state of the dough to be measured, while the exposure can be difficult to determine for mixed discontinuous-fibre composites because it is usually only possible to capture the final state. Regarding the centralisation, Kukukova et al. [28] state

that ‘it does not add information about the mixing problem beyond the scale and intensity of segregation’. However, poor mixing of fibre bundles can lead to a situation in which they are locally well dispersed (good IoS and SoS), but accumulate in some areas.

The characterisation of the QoM of fibre-reinforced plastics is diverse. Most research is based on image analysis of cross-sectional microscopy. Several methods have been implemented and can be categorised as follows.

Methods based on quadrats

Several authors worked with cross-sectional microscopy of fibre composites divided into square grids of various sizes. The fibre fraction or the presence of fibre in each cell is measured and recorded. Figures 3.5a to 3.5d represent quadrats filled with fibres at various degrees of evenness and clustering. Inoue et al. [10] and Spowart et al. [11] measured QoM by determining a *box-counting dimension* of the presence of fibres in the cells. This is indirectly related to the SoS of the fibre clusters. Li et al. [12] also worked on cross-sectional micrographs of fibre-reinforced concrete and measured the CoV of the local fibre fraction in the cells. Using the CoV of local fibre fraction is found to lead to the closest estimation of the IoS for such a system, sufficiently characterising the dispersion of fibres in the system. Normalising it to the CoV of the non-mixed material allows for the measurement of the improvement of evenness due to mixing. This is a better measure than just the CoV for comparing mixers or for identifying how various materials behave in a mixer. Besides, the variation in CoV per cell size has scarcely been studied, and may lead to novel results.

Methods based on microstructural features

Le Baillif et al. [13] compounded cellulose fibre reinforced polypropylene using a twin screw extruder and characterised the dispersion of fibres using cross-sectional microscopy. They measured the distribution of the size of the fibre clusters, which is an estimation of the SoS. Yazdanbakhsh et al. [14] formulated a new definition of particle dispersion, *dispersive work*, as the minimum amount of work per domain to move all particles to a uniform state of equally distant particles. It is therefore based on the distribution of the particle locations in the domain. Wang et al. [15] mixed carbon fibre reinforced cement and measured the dispersion of fibres with the aid of 3D tomographic images. A dispersion coefficient was defined as the CoV of the size of fibre clusters.

Various researchers determined fibre dispersion by either considering the size of agglomerates or their CoV. The former seems to be a good measure of the SoS, whereas the latter characterises the poly-dispersity of fibre clusters in a blend but hardly indicates the SoS, or any aspect of QoM defined in [28]. *Dispersive work*, as defined by Yazdanbakhsh et al., may be a good measure of either

clustering, evenness or centralisation in some situations. Nonetheless, it is not capable of distinguishing systems made up of large clusters from those with poor centralisation.

Methods based on Delaunay triangulation

Several researchers characterised the QoM of discontinuous-fibre composites based on photographs (made by optical or electron microscopes) using the Delaunay triangulation or its dual graph, the Voronoi diagram [16–21]. Voronoi diagrams are constructed on the centroids of the particles, from which several statistical quantities are measured. Figures 3.5e to 3.5h show the Voronoi diagrams of four schematic cross-sections of fibre composites, with various levels of IoS and SoS. The figures highlight the differences in Voronoi cell sizes and cell distributions for these four situations. In most cases, the distribution of the areas of the Voronoi cells was used. Additionally, the distribution of the mean near-neighbour distance, which can be output from the Delaunay triangulation (see Figure 3.5e), was computed. It was found that the CoV of the mean near-neighbour distance or the CoV of the Voronoi cell sizes are a powerful tool to characterise the homogeneity of the samples. However, such a measure hardly differentiates between the evenness of particle dispersion (IoS) and their clustering (SoS). Considering two systems, one with poor evenness and a second highly clustered, one can find many fibres with both close and distant neighbours, leading to a similar measure (see Figures 3.5g and 3.5f). Additionally, in all aforementioned studies the mean near-neighbour distance was measured as the Euclidean distance between fibre centroids in 2D microscopic images. Discontinuous cylindrical fibres can orient themselves in any direction in a composite specimen, which means that a cross-sectional micrograph of such a specimen shows fibres as ellipses of various eccentricities and orientations. The actual distance between fibres, however, is the distance between their centrelines, which depends on the ellipse parameters when cut in a 2D plane. Therefore, the Euclidean distance between fibre centroids leads to interpretation errors if the ellipses' eccentricities and orientations are not taken into account.

Methods based on physical measurements

Several studies on discontinuous-fibre reinforced composites characterised QoM by performing global physical measurements. Yang et al. [22] and Ozyurt et al. [23] worked with carbon-fibre-reinforced cement and measured the electrical resistance of their specimens to determine fibre dispersion. Similarly, Yenjaichon et al. [24] used electrical resistance tomography to determine the QoM of kraft pulp suspensions. Although these measurement methods can be non-destructive, they struggle to distinguish the various aspects of segregation, in particular IoS and SoS.

Conclusion

Cross-sectional microscopy appears to be a relevant method of characterising the QoM of discontinuous fibre composites. The stochastic nature of these materials requires a considerable number of microscopic photographs to provide statistically satisfactory results. The CoV of the local fibre fraction is found to be a pertinent measure of IoS, which represents the evenness of a sample. However, the CoV characterises the material, not the mixing technology, which is why it should be normalised to the CoV of the local FVFs in the initially non-mixed material to measure the improvement in evenness thanks to the mixing step. This measurement method was introduced by Danckwerts [25] and later used for various mixing problems [28]. The normalised CoV appears to be a better measure to compare different materials after mixing, or different mixing systems, and it will therefore be examined in this study. Close attention will also be paid to the effect of cell size on IoS, since, to the knowledge of the authors, it has not been reported in relevant literature. No previously investigated measure of SoS seemed adequate for fibre-reinforced composites, which is why one close to the general definition mentioned in Kukukova et al. [28] will be implemented.

The measurement of fibre clustering using Delaunay triangulation appears to be valuable for discontinuous-fibre composites. The exact determination of the fibre clusters might not be the prime objective when characterising QoM, but this does drive the mechanical and rheological properties of the LFTs. As of yet, little attention has been paid to correcting the distances and areas with the ellipses' orientation and eccentricity. This correction is implemented in this chapter to help measure the size of fibre clusters in a more precise way.

A detailed description of the methods is outlined in the following section.

3.5 Methods

3.5.1 Microscopy

In the recycling process developed by De Bruijn et al. [7], the dough is directly transferred from the mixer to a press for compression moulding in a matter of seconds. For this study, the state of the material right after mixing was studied using cross-sectional microscopy. However, directly after mixing, the doughs are too porous to be prepared for microscopy. Therefore, the doughs were half-pressed to a thickness varying between 15 mm and 20 mm. It was found that the compression of these doughs occurs in two stages. In the initial pressing stage, most void pockets close, while the dough does not flow outwards. During the second stage, the dough starts to flow and the remaining void pockets close. A dough thickness of about 15-20 mm was found to be the end of the first pressing stage. It is assumed that the structure and arrangement of the fibres are identical

in the extruded doughs and the half-pressed doughs, except for the out-of-plane orientation of fibres. Especially, it is assumed here that the local relative variations in fibre volume fraction and the clusters of fibres remain the same as in the non-pressed doughs.

The stochastic nature of the dough makes quantitative analyses of its microstructure by micrography difficult. However, an extensive microscopy study can provide sufficient data to obtain reliable statistical measurements. In the present study, the following procedure was adopted to gather data for measurements of the QoM. First, each half-pressed dough was cut to produce sections of roughly 10 mm width (see Figure 3.6). Six sections were cut per dough – two from the front, the middle and the rear areas – and were then embedded and polished. Two large cross-sectional micrographs were taken for each section at a $\times 700$ magnification and were automatically stitched to $20,000 \times 20,000$ pixels each, representing an area of $6 \text{ mm} \times 6 \text{ mm}$. Hence, twelve large microscopic images were obtained per dough, representing an analysed area of roughly 430 mm^2 . Parts of such micrographs are shown in Figures 3.7a and 3.7e. Microscopic images of the non-mixed material, i.e. the flakes and LFT pellets, were also captured for the calculation of the IoS (see following section). Microscopic photographs of the other two materials, the injection moulded short fibre composites and the compression moulded flakes (see Section 3.2), were also made to compare their QoM to those of the doughs.

Figure 3.6 Photographs of a dough after mixing and after being half-pressed. The locations of the microscopy specimens in the dough are highlighted in white on the half-pressed dough.

Image segmentation was executed automatically on each picture, using the peak locations of each image histogram to determine the fibre, matrix and porosity fraction. Details on this operation can be found in Appendix 3.B.

At first, a large-scale measurement of the evenness of the doughs was determined. For each dough, the FVFs of the twelve microscopic images were first calculated and then grouped by their location in the dough: front, middle or rear (see

Figure 3.6). This resulted in an estimate of the global variations in FVF, which will be analysed in Section 3.6.

Figure 3.7 Visualisation of the image processing analysis that computes the local FVFs. The example is limited to two sections of $2.4 \text{ mm} \times 2.4 \text{ mm}$ taken from the large micrograph in 3.7a, i.e. they represent the distribution of FVFs, for three different cell sizes, where each cell displays its local FVF in grey. The grayscale represents the fibre volume fraction, ranging from 0% in white to 100% in black. Similarly, Figures 3.7f to 3.7h represent the FVF in the micrograph in 3.7e for various cell sizes.

3.5.2 Intensity and scale of segregation

The segmented cross-sectional micrographs are divided into a grid of various cell sizes (from $18.75 \mu\text{m}$ to $600 \mu\text{m}$). The FVF of each cell is computed, excluding the fraction of porosity, i.e. $FVF = \text{Area}_{\text{fibres}} / (\text{Area}_{\text{totalcell}} - \text{Area}_{\text{porosity}})$. Note that if the porosity fraction in any cell is larger than 30%, this cell is discarded from the analysis. The CoV of the local FVFs is recorded per image for each grid size. The same calculation was performed for the initially non-mixed materials,

i.e. blends of flakes and polymer or pellets and polymer. The IoS is defined as the ratio of the CoV between two microscopic pictures: the half-pressed doughs over the initially non-mixed flakes - polymer combination (see Figure 3.8 for an illustration of the method). Figures 3.7a and 3.7e display two micrographs with a clear difference in QoM. The top picture presents large clusters of fibres with moderate evenness. The bottom picture shows the opposite: small clusters and considerable evenness. Figures 3.7b to 3.7d and 3.7f to 3.7h show the grids of FVFs for various cell sizes ($75 \mu m$, $150 \mu m$ and $300 \mu m$) where the greyscale represents the FVF, ranging from 0% in white to 100% in black. It is clear from the grids that the CoV of the local FVFs will give different results for both micrographs, thus resulting in different degrees of IoS.

The calculation of SoS starts with the grid of local fibre fraction with cells of $18.75 \mu m$, computed from the microscopy images. Image segmentation is performed on the grid into two phases with the FVF respectively below and above the median

Figure 3.8 Representation of the calculation of the IoS of mixed doughs. In the cross-sectional micrographs, the fibres are in white, the polymer in grey and porosities are in black. The same procedure is applied for the dough made of LFT pellets, for which the CoV before mixing is calculated from microscopic images of the initial LFT pellets.

FVF (see Figure 3.9). Considering the newly segmented image as a matrix, the maximum striation thickness of the high FVF clusters, i.e. the maximum height of the white regions in Figure 3.9e, is measured for each column. The average of the maximum striation thicknesses of all columns is calculated, which gives the measure of the SoS. Figure 3.9 shows the grid of FVFs from the two micrographs in Figures 3.7a and 3.7e, as well as the segmentation by FVF. Figure 3.9b has much larger clusters than Figure 3.9d, which are detected by the measure of the SoS, $400\text{ }\mu\text{m}$ and $175\text{ }\mu\text{m}$ respectively. This method is sensitive to the orientation of the micrographs in the cross-sectional specimen. However, all micrographs were taken with the same orientation to prevent this issue.

In addition, an artificial random distribution of fibres was created to represent the

Figure 3.9 Figures 3.9a and 3.9c show the local FVFs of the microscopic images of Figure 3.7. Figures 3.9b and 3.9d are the segmented images of 3.9a and 3.9c respectively, where the areas of higher fibre fraction are shown in white. The SoS is the average of the striation thicknesses of the white regions. The bottom figure, (e), illustrates the calculation of SoS from the segmented images.

QoM of an almost perfectly even dough. For that, a 2D space was randomly filled with non-overlapping ellipses at 20% coverage (see Appendix 3.D), from which the IoS and SoS were measured. This random fill represents a mixing situation that is difficult to achieve in reality, but it is still far more segregated than a perfectly uniform distribution of fibres. This artificial random distribution helps to visualise the theoretical limit of evenness and clustering achievable for mixed C/PPS dough.

3.5.3 Bundle size distribution

An additional method was implemented to determine the size of the fibre clusters in each image, which can range from a single loose fibre to 3,000 clustered fibres.

Images of the segmented fibres were used for this purpose. In the segmented micrographs presented here, adjacent fibres may appear to be joint because of the segmentation step. However, an accurate description of the clusters of fibres requires fully disjoint fibres. A watershed algorithm was applied to the segmented images to overcome this issue. Figure 3.10b shows the segmented image after applying a watershed analysis. Most fibres are disjointed from one another. However, flat ellipses, which correspond to fibres parallel to the microscopic plane, may be cut by the watershed algorithm, thereby outputting multiple domains of a single fibre. These numerical artefacts seemed limited compared to the benefits of applying a watershed algorithm.

A Delaunay triangulation was then performed on all fibre centres on each image (Figure 3.10c). A refinement technique was needed to cluster the fibres that are close to each other. Figure 3.10d illustrates the result of the refinement technique. The clusters of fibres are clearly disjointed from one another, although some fibres are wrongly attributed to another cluster. This issue artificially increases or reduces the number of fibres per cluster, but the overall effect was found to be limited. The number of fibres per cluster is calculated from the list of connected components in the refined Delaunay graph, which is then converted to the bundle size distribution (BSD).

In the aforementioned refinement technique, all segments longer than three fibre diameters, corresponding to a regular hexagonal configuration at 10% FVF, are discarded. A corrected fibre-to-fibre distance was calculated to take into account ellipse eccentricities and orientations. A detailed description of the calculations can be found in Appendix 3.C.

Exceptionally, some flakes did not blend properly in the mixer, which meant that layers of packed fibres remained. This refinement technique is not able to cluster the various tows. It results in a cluster of several tens of thousands of fibres, which clearly does not correspond to the actual cluster sizes as the maximum number of fibres per tow is 3,000 (the initial tow size). Instead, these large clusters

are counted as n clusters of 3,000 fibres, with n the largest integer satisfying $n \leq \frac{\text{number of fibres}}{3000}$, i.e. the quotient of the division.

Figure 3.10 *Visualisation of the intermediate steps of the algorithm implemented to determine the BSD of cross-sectional micrographs. Figures 3.10a shows the input cross-sectional micrograph while 3.10b displays the segmented fibres after the fibres were disjointed using a watershed. Figures 3.10c and 3.10d show the Delaunay triangulation before and after the refinement technique (Section 3.5.3). The refined triangulation was used to compute the BSD in each micrograph.*

3.6 Results

The half-pressed doughs listed in Table 3.1 were prepared for microscopy and analysed according to the methods presented in Section 3.5. Initially, the DoE was analysed to determine the effect of mixing settings on QoM. The results of the reproducibility study are presented next. Then, the effects of the various FLDs on QoM are analysed and discussed.

3.6.1 Design of experiments

Figure 3.11a shows the IoS for all cell sizes, of the distinct twelve micrographs made from dough #5. The IoS is always smaller than one, which indicates a mixed state that is, as expected, less segregated than the initial non-mixed material. Besides, the IoS of the randomly filled 2D space is plotted under *random fill* with a dotted line (Figure 3.11). It is most probable that the IoS of all doughs are bounded by one and the IoS of *random fill*. A hatched region was therefore added to the figure to represent a domain of the IoS that cannot be reached for the doughs in this study. One may note the large scatter between these twelve lines, which is why a grey bounding region depicting the maximum and minimum values of the IoS are shown around the mean values plotted with a line as shown in Figure 3.11b. This graph illustrates that three measures are important:

- the mean IoS: it represents the evenness of the local FVF, as defined in Section 3.5.2. In order to make the analysis simpler, only the IoS for a cell size of $150\ \mu\text{m}$ is considered in detail for the DoE. This value was chosen due to its similarity to the initial bundle size, approximately $150\ \mu\text{m}$ in thickness at normal FVF. This size is assumed to be a relevant scale to determine the evenness of this material. Lower IoS values equal a better evenness of the fibres in the sample.
- The bandwidth of the IoS (height of the grey band), which corresponds to the intra-sample variability of evenness. The analysis of the DoE was performed only for the bandwidth at $150\ \mu\text{m}$, similarly to the mean of IoS. A small bandwidth indicates limited variability of evenness between the twelve micrographs.
- The effect of cell size on the IoS is described by the slope of the IoS as a function of cell size. It expresses the rate of change of evenness within the studied scale range. Steep slopes indicate that fibre bundles become evenly spaced at a large scale. Gradual slopes show that the local variations in FVF hardly decrease when increasing the scale.

Figure 3.11 *The IoS of various doughs analysed for the DoE. Figures 3.11a and 3.11b show the IoS of dough #5. In 3.11a, the twelve solid lines are the IoS of all micrographs for this dough, while in 3.11b they are represented as a mean value and a grey band bounding the extrema. Figure 3.11c highlights the mean IoS of several doughs processed with various mixing settings. Figure 3.11d shows the IoS of another dough with its mean value and extrema highlighting the variations of IoS in a dough.*

An analysis of variance of the three measures of the DoE was performed. For all cases, a level of significance of 0.05 was selected, as it is common practice, to distinguish the effects that significantly influence the measures of the QoM. A first consideration showed that increasing the mixing speed decreased the bandwidth. Both the mixing speed and mixing time were found to decrease the mean IoS. The mixing speed, mixing temperature and mixing time were all found to decrease the slope of the mean IoS.

The effects of the mixing settings on the mean IoS, the bandwidth and the slope are illustrated in Figure 3.11. The mean IoS of several doughs is displayed in

Figure 3.11c where doughs #1 and #5 were processed at a low mixing speed and for a short amount of time, whereas doughs #8 and #7 were processed at a high mixing speed and for varying amounts of time.

Further, Figure 3.11a shows the intra-sample variability, which can be of a similar magnitude as the variations between the IoS of doughs made with various settings (Figure 3.11c). This urged us to reconsider the reliability of considering the mean IoS and bandwidth separately. Therefore, the analysis of the DoE was carried out for six repetitions, corresponding to the six sections in each dough. The results show again that mixing speed and mixing time influence the IoS; with a more significant effect (p-value 5 to 10 times lower) as compared to the analysis of the mean IoS. The strength of the significant factors is similar for both studies, with mixing speed having stronger influence than mixing time. As a conclusion, although intra-sample variability is high, the mixing speed and mixing time have a strong and significant effect on the IoS.

Next, the SoSs of the doughs were analysed. The average SoS of the nine doughs was found to vary between $260\ \mu\text{m}$ and $420\ \mu\text{m}$ (see Table 3.A.1 in the Appendix), which is a small range, when compared to the SoS of the *random fill* ($101\ \mu\text{m}$) and indicates that fibre-dense regions are of comparable size. However, the intra-sample variation of SoS varies considerably, from $150\ \mu\text{m}$ to $430\ \mu\text{m}$. Again, mixing time and mixing speed were found to reduce the SoS.

The study of the effect of the mixing settings on the IoS and SoS showed that both the total amount of shear (mixing time and mixing speed) and the shear rate (mixing speed) significantly improve QoM on multiple levels: they reduce the IoS, SoS and the intra-sample variability. However, the low-shear mixer does have some limitations. A comparison of the IoS and SoS obtained for the best mixed doughs with those of the *random fill* confirms that the evenness and clustering of the doughs can still be improved, at least from a theoretical point of view.

Studying the microscopic images also revealed that fibres are far from evenly distributed or aggregated in small clusters, even after long mixing times and high mixing speeds, although it is also clear that longer mixing time and higher speed improve evenness and clustering. This phenomenon is highlighted in Figure 3.12 which also shows the variations of FVF at a large scale, where the FVF of each micrograph is calculated and grouped according to its dough and its location in this dough. The solid line and the grey band represent the mean and extrema of the FVFs for each location respectively. The doughs processed at 5 rpm for 10 min and 20 min – #1 & #5, and #2 & #6 respectively – all show very large variations in FVF, whereas FVF variations are much lower for the doughs processed at 15 rpm (#3, #4, #7 and #8). This seems to indicate that mixing speed has a more pronounced effect than mixing time. The results of the analysis of variance also confirmed this for the IoS and the SoS. Additionally, the micrographs show that a combination of large and small fibre clusters are found in doughs mixed at

5 rpm. Fewer large clusters are found in dough processed at 15 rpm. This result is visualised in Figures 3.13b, which plots the BSD of several doughs. This figure is the output of the refined Delaunay triangulation and shows the volume fraction of bundles of every given size. The fractions of large bundles ($\geq 1,000$ fibres) and small bundles (≤ 100 fibres) indicate whether the initial tows of 3,000 fibres were well dispersed. The figure shows that doughs #1 and #6 (5 rpm) had very similar BSDs with more than 30% of their volume consisting of large bundles, while the BSD of #8 (20 min, 15 rpm) results in a much lower fraction of large bundles.

In conclusion, the analysis of variance shows that mixing time and speed improve all measures of QoM, with mixing speed having a stronger effect than mixing time. This observation was confirmed by analysing the BSD, the large-scale variations of FVF and the micrographs of doughs.

Figure 3.12 Large scale variations of the FVF for the nine doughs analysed in the DoE (left block, ordered according to the DoE in Table 3.1), and the three repetitions (right block) for the reproducibility study. The black lines and the grey bands show the mean and the extrema respectively.

3.6.2 Reproducibility

The previous results showed that intra-sample variability is of great importance, and the same might apply to inter-sample variability. Three doughs made with various mixing settings (#1, #6 and #8) were replicated (#15, #16 and #14,

respectively) to investigate the reproducibility of the mixing process. The mean IoS of the six doughs is plotted in Figure 3.13a. Their large-scale variations in FVF are displayed in Figure 3.12. The findings from the previous section indicate that dough #1 has a moderate QoM for all measures. Dough #6 showed some improvement due to a longer mixing time. Dough #8 demonstrates that it is among the doughs with the highest QoM in the study due to a long mixing time and a high mixing speed.

Limited inter-sample variability would lead to a clear grouping of IoS by mixing settings: #1 & #15, #6 & #16, and #8 & #14. However, the measurements in Figure 3.13a show non-groupable lines for all doughs. The situation is different, however, when looking at the large-scale variation of FVF (Figure 3.12). Clearly, doughs #1 and #15 have very high variations of FVF. Doughs #6 & #16 show reduced variability, whereas #8 & #14 exhibit very limited variations of FVF. Additionally, the BSD was also analysed for these six doughs (Figure 3.13b). Two separate groups can easily be identified. The BSDs of doughs #8 & #14 are clearly distinct from the other four: they have a higher fraction of small bundles (smaller than sixteen fibres) and a small fraction of large bundles (larger than 1000 fibres). The other four doughs cannot, however, be grouped by mixing settings, as was the case for the mean IoS. The fraction of large bundles in these doughs is nonetheless considerable, ranging from 20% to 40%. Dough #16 is particularly striking, as it has the second worst IoS and the largest fraction of large bundles, but a small

Figure 3.13 The IoS and the BSD of the doughs analysed for the reproducibility study.

large-scale variation of FVF (Figure 3.12). Nevertheless, its SoS and the slope of the mean IoS are average (see Table 3.A.1 in the Appendix section).

3.6.3 Effect of FLDs

The last set of experiments concerns the effect of the FLD on the QoM. Sieved flakes and LFT pellets were used as described in Section 3.2. Figure 3.14 aggregates the IoS, the BSD and the variations of FVF for the four doughs #10, #11, #12 and #13. Table 3.2 summarises the measures of the QoM for the four doughs. It also shows the standard deviation of the local FVF for the two comparison materials and the randomly filled 2D space. As a reminder, the IoS is defined as the improvement in evenness of the local FVF due to mixing. The results show that the evenness of LFT pellets improves less than for the other three doughs. However, its standard deviation of FVF is lower than for the doughs, showing a more even distribution of fibres. The standard deviations in Table 3.2 also highlights the differences between the compression moulded flakes (non-mixed), the moulded LFT and short fibre pellets, and the doughs made from sieved flakes: the evenness of the smallest flakes is almost as good as the moulded short and long fibre composites.

Dough	Material	Mean SoS at 18.75 μm [μm]	Mean IoS at 150 μm [$\times 10^{-1}$]	Bandwidth at 150 μm [$\times 10^{-1}$]	Slope of the IoS [-]	Standard deviation of the FVFs at 150 μm [$\times 10^{-1}$]
#10	LFT pellets	177	2.0	0.64	-0.67	0.30
#11	C/PPS L	310	1.6	0.54	-0.53	0.79
#12	C/PPS M	224	0.94	0.35	-0.72	0.52
#13	C/PPS S	207	0.67	0.13	-0.80	0.42
compression-moulded non-mixed flakes						1.49
injection-moulded SFT pellets						0.35
artificial random fill						0.17

Table 3.2 Summary of the measures of the QoM for the doughs processed with various FLDs. The standard deviations of local FVF are also listed for two comparison materials and the randomly filled space.

Figure 3.14 (a) The IoS, (b) the BSD and (c) the large scale variations of FVF of the doughs processed with various FLDs.

The effect of flake size and FLD on QoM is evident for all measurements. Shorter fibres reduce IoS and SoS, and lead to a steeper slope of the IoS. The intra-sample variations for IoS and SoS steadily decrease with the reduction in FLD (see Table 3.2). Additionally, in the dough processed with the smallest flakes, only 2% of bundles were larger than 1,000 fibres, which is far lower than the 20% - 40% range obtained for large flakes (Figures 3.14b and 3.13b). However, there is still a large difference between the BSDs of the dough made from LFT pellets and from the smallest flakes, but this was expected due to the completely different nature of the input material. In addition, the large-scale variations of FVF mainly reduce from large to medium-size flakes. The doughs #10, #12 and #13 all show similar large-scale variations of FVF, for which no improvement is noticeable with a reduction in fibre length. This may be a limit for the prototype mixer used in this study (Figure 3.14c).

3.7 Discussion

When considering the whole recycling route studied in this chapter, the QoM obtained during the mixing phase affects the flow behaviour of the material in the mould and its mechanical properties afterwards. The industrial application of this recycling technology requires that moulded components have consistent mechanical properties, and hence low intra-part variability and good reproducibility. Additionally, the flow behaviour of the dough is partially determined by the number of bundle-bundle interactions, which translates to the bundle aspect ratio among others [33, 34]. The homogeneity and reproducibility of the flow behaviour of the doughs are also important factors, which can be improved by reducing intra- and inter-sample scatter. The conditions necessary to address these issues can be derived from different aspects of the QoM. This leads to several measures of QoM that are to be either minimised or be optimised.

- Limited large scale variations of FVF are required. Figures 3.12 and 3.14c demonstrate that variations of just a few percent can be achieved.
- The IoS and the intra-sample variability of IoS are other properties to be minimised. A locally even distribution of FVF helps reduce variability both in terms of rheology and part performance.
- A high reproducibility of QoM, all aspects combined, is also a key to the successful application of such a technology.
- BSD has a major effect on both flow behaviour and mechanical performance. On one hand, a considerable fraction of small bundles drastically increases the number of fibre-fibre interactions, which increases the apparent viscosity [33], where the upper limit is set by the flow distance in the mould and the size of the intricate features to fill. On the other hand, a substantial fraction of large bundles reduces the average bundle aspect ratio, which tends to limit the theoretical mechanical properties of the moulded component [35]. Nonetheless, it is rather difficult to draw a conclusion on the optimum BSD without a proper study of its effect on the flow behaviour of doughs as well as on the mechanical properties of moulded parts.

Regarding the list of criteria above, well mixed doughs (long mixing time, high mixing speed) do show improvement of IoS, intra-sample variability of IoS, and large-scale variations of FVF. It was, however, found that the reproducibility of doughs is moderate for all measured aspects of QoM, although only two doughs were analysed per setting. This lack of reproducibility can also be caused by the limitations in sample size: twelve microscopic images of $6 \times 6 \text{ mm}^2$ per dough. In terms of the process window, the oxidation of the polymer is more severe for long

mixing times in the presence of oxygen, which should be prevented in order to limit the degradation of the polymer. The results also pointed out that increasing the mixing speed is a more effective way to improve QoM than increasing mixing time. Thus, the authors recommend increasing the mixing speed to limit polymer degradation, although high shear rates may break fibres during mixing. This has not been a problem yet with the current mixing prototype, which has technical limitations that prevent its use at higher rpm. In addition, it was found that the SoS of all the doughs were close, and of the same order of magnitude; in comparison to other finely-clustered materials, i.e. the injection-moulded short-fibre composites and the artificial random distribution of fibres. On the contrary, the BSD varied drastically with respect to mixing settings and FLDs. Hence, it is supposed that BSD and SoS do not exactly characterise the same aspects of QoM, or do not characterise them with the same strength. BSD is an important material property, as explained in the previous bullet list. This may indicate that the method chosen to measure SoS is not the most suitable for this type of material or mixing technology.

Concerning the effect of FLD on the QoM of doughs, large improvements are noticed between doughs #11/C/PPS L and #12/C/PPS M for all measures of QoM. These improvements seem to saturate between #12/C/PPS M and #13/C/PPS S; and the large-scale variations of FVF, in particular, are comparable (Figure 3.14c). Therefore, the authors recommend using small flakes in this process, especially with a mean fibre length smaller than 15 mm.

3.8 Conclusion

An experimental study was carried out to understand how to improve the QoM of mixed doughs, made of long-fibre-reinforced polymers. Contrary to other LFT processes and materials, the flake material and the mixer used in this study are unconventional. The material consisted of multi-layered, woven-fibre reinforced composites plus polymer granulates. The mixer had a very low rotation speed to prevent fibre breakage, thereby limiting blending efficiency. Several aspects of QoM were selected from literature, namely evenness and clustering, and implemented for this study. The experimental methods involved image analysis of a large set of cross-sectional micrographs. The analysis was based on quadrats to measure IoS and SoS, and on refined Delaunay triangulation to measure BSD. Choices were made to measure the following aspects from the extensive set of cross-sectional micrographs:

- IoS, or evenness of the local FVFs;
- SoS, representing a measure of the clustering of fibres;

- intra-sample variations of IoS, SoS and FVFs;
- BSD, describing the size distribution of fibre clusters.

The methods developed and implemented in this chapter were found adequate for the material in this chapter, as well as to characterise the QoM of other LFTs. The refinement technique performed on the Delaunay triangulation is definitely beneficial, as it quantifies a material property of LFTs: bundle sizes. This property can also be used for the micro-mechanical modelling of LFTs. The IoS is a good measure to compare other mixing devices to the one used in this study, or to compare the doughs with other materials. Further developments of this recycling technology or of LFT material should consider the measurement of the IoS as a benchmark, similar to the current practice for polymer blends [36]. Finally, it is not sure whether the current implementation of SoS measurement provides information beyond the IoS and BSD.

The effects of mixing time, mixing speed, temperature and filling ratio on QoM were analysed by performing a fractional factorial DoE. It was found that the mixing time and mixing speed are the main drivers to improve QoM for all measures. The reproducibility of the QoM in doughs was inspected and was found to be marginal. On the other hand, the effect of the FLDs on QoM was clear for all measures: smaller flakes significantly improve the QoM. The recommendations for better mixing for this particular mixing setup are first to shred scrap to a smaller size, yielding a mean fibre length under 15 mm. In addition, further improvements can be made to the mixing machine by blending at higher shear rates. This can be achieved by modifying the mixer design, but special care should be taken to minimise fibre breakage. It is still unclear whether the best QoM obtained in this study is sufficient. Further work is required to understand the effect of QoM on the flow behaviour of doughs and, subsequently, on mechanical properties of moulded parts.

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3.A List of the QoM measurements

Test number	Material	Mixing time [min]		Mixing speed [rpm]		Filling fraction [%]	Temperature [°C]	Mean SoS at 18.75 μm [μm]	Bandwidth of the SoS at 18.75 μm [μm]	Mean IoS at 150 μm [×10 ⁻¹]	Bandwidth of the IoS at 150 μm [×10 ⁻¹]	Slope of the mean IoS
#1	non-sieved	10	5	21	320		416	288	3.6	1.6	-0.33	
#2		20	5	50			390	427	3.1	1.6	-0.36	
#3		10	15	50			318	156	2.6	1.4	-0.47	
#4		20	15	21	320		318	373	2.5	1.0	-0.51	
#5		10	5	50	360		419	238	3.1	1.5	-0.36	
#6		20	5	21			339	233	3.4	1.8	-0.47	
#7		10	15	21			308	252	2.9	0.88	-0.51	
#8		20	15	50	360		262	171	1.9	0.73	-0.58	
#9	non-sieved	15	10	35	340		320	205	2.7	0.74	-0.49	
#10	LFT pellets	20	10	21	340		177	36	2.0	0.64	-0.67	
#11	C/PPS L						310	229	1.6	0.54	-0.53	
#12	C/PPS M						224	106	0.94	0.35	-0.72	
#13	C/PPS S	20	10	21	340		207	66	0.67	0.13	-0.80	
#14	non-sieved	20	15	50	320		219	110	0.96	0.58	-0.69	
#15		10	5	21	320		309	210	3.2	2.5	-0.50	
#16	non-sieved	20	5	21	360		324	90	3.0	0.92	-0.46	
	compression-moulded flakes†						325	134	n/a	n/a	n/a	
	injection-moulded SFT pellets†						149	1	n/a	n/a	n/a	
	artificial random fill						101	n/a	0.038	n/a	-1.60	

†: For these two materials, four large microscopic images were taken and analysed, instead of the twelve micrographs for the half-pressed doughs.

Table 3.A.1 Summary of the measurement results of the QoM for the samples studied in this chapter.

3.B Image segmentation and correction

The image segmentation of all cross-sectional micrographs was automatically performed by the peak locations of the image histogram. A section of a micrograph is shown in Figure 3.B.1a; its histogram is shown in Figure 3.B.1b. The histogram contains a grey level peak for the epoxy (mounting resin for polishing), the PPS matrix and the fibres. The average grey level between epoxy & matrix, and between matrix & fibres is chosen to segment the images in the three phases (see the image segmentation axis in Figure 3.B.1a).

The magnified fibre at the bottom-left corner of Figure 3.B.1a emphasizes a black contour around the fibre, being an optical artefact captured by the microscope. Such a defect systematically lowers the measured FVF of the image. Therefore, a global correction was performed for the FVF of each image. It was assumed that a large number of micrographs was enough to represent the correct FVF of the samples, 20% on average. The global average FVF of the sixteen doughs $\times$ twelve micrographs was set to 20%. The results of this correction are shown in Figures 3.12 and 3.14c.

0.596 0.404

Figure 3.B.1 Section of a cross-sectional micrograph on the left, showing that fibres, matrix and filled porosities have a different grey level. A close-up of a fibre shows its spurious black envelope. The three grey levels are highlighted in the histogram of the image on the right. Automatic segmentation is performed based on the peak locations of the histogram.

3.C Centre-to-centre distance correction

The micrographs studied in this chapter are cross-sections of discontinuous fibre composites. The cross-sections of cylindrical fibres with the micrography plane are ellipses with various eccentricities and orientations. In Section 3.5.3, the Delaunay triangulation of the ellipse centres is refined by discarding centre-to-centre segments longer than a threshold distance. This refinement technique is required to cluster the various fibre bundles. However, the Euclidean centre-to-centre distance in the plane of observation does not rigorously measure the distance between the fibres.

Consider the following situation; two ellipses in contact along their major axes in the microscopy plane have a longer Euclidean centre-to-centre distance than two touching fibres whose cross-sections are circles (see Figure 3.C.2 (a)). Yet, the true distance between the centres is one fibre diameter in both cases. The relation with the observed distance depends on the orientations and eccentricities of the two ellipses. Thus, a corrected centre-to-centre distance is required to accurately distinguish the various clusters. The objective of this section is to define such a corrected distance.

The strategy implemented here is to consider a sleeve of polymer growing radially around two fibres until the sleeves touch. When the fibres are cut in the micrography plane, the cross-sections of the sleeves are also elliptical with the

Figure 3.C.2 Schematics of cross-sections of cylindrical fibres in a micrography plane. The few drawn cases highlight the differences between the Euclidean centre-to-centre distance d_0 and the true distance between the fibres d_c in comparison to the fibre diameter d_f .

same orientation and eccentricity as their parent fibre (see Figure 3.C.2 (b) to (d)). In the micrography plane, a non-normal orthogonal basis can be associated with each fibre and its sleeve (see Figure 3.C.3). The elliptical sleeves grow radially and isotropically in their respective bases.

At the junction point of the two sleeves (Figure 3.C.2 (b) to (d)), the sleeves have grown by the same amount in their respective bases. The corrected centre-to-centre distance, noted d_c , corresponds to the size of these sleeves of polymer and is in all cases $\leq d_0$. This distance is related to the change-of-basis matrices of each ellipse's basis and the direction of $\overrightarrow{PP'}$, as elaborated mathematically in the following paragraphs.

Figure 3.C.3 illustrates the cross-section of two fibres F_P and $F_{P'}$, in the plane of observation. The fibres are oriented differently from each other, leading to different ellipse orientations and eccentricities in the cross-sectional plane, whose centres are noted P and P' . Each ellipse is determined by its major axis, minor axis and orientation in the reference orthonormal basis of the cross-sectional plane, $\mathcal{B}_0$: (a, b, θ) and (a', b', θ') respectively for F_P and $F_{P'}$. For all fibres analysed in this chapter, $b' = b = \text{fibre diameter}$. Let $\overrightarrow{u_0}$ be the unit vector in $\mathcal{B}_0$ collinear to $\overrightarrow{PP'}$.

Figure 3.C.3 Illustration of two fibres of different orientations and eccentricities. Their centre points are P and P' , and their related fibre parameters are used for the calculation of the corrected centre-to-centre distance. Note that $\mathcal{B}$ and $\mathcal{B}'$ are orthogonal non-normal bases, because their unit vectors correspond to the length of the ellipse axes.

Additionally, consider an orthogonal basis for each ellipse, $\mathcal{B}$ and $\mathcal{B}'$, whose unit vectors correspond to the axes of the ellipses. The change-of-basis matrix from $\mathcal{B}$ to $\mathcal{B}_0$ is:

$$\mathbf{T} = \begin{pmatrix} \frac{a}{b} \cos(\theta) & \frac{a}{b} \sin(\theta) \\ -\sin(\theta) & \cos(\theta) \end{pmatrix} \quad (3.1)$$

Therefore, $\mathbf{T}^{-1}\vec{u}_0$ is the unit vector $\vec{u}_0$ expressed in $\mathcal{B}$, and $|\vec{PP'}| \times \|\mathbf{T}^{-1}\vec{u}_0\|$ represents the length $|\vec{PP'}|$ expressed in basis $\mathcal{B}$. Similarly, $|\vec{PP'}| \times \|\mathbf{T}'^{-1}\vec{u}_0\|$ is computed for the basis $\mathcal{B}'$.

As stated above, the elliptical sleeves grow radially and isotropically in their respective bases. If one of the ellipses were a circle, the sleeve would grow proportionally to $|\vec{u}_0|$ (with $|\vec{u}_0| = 1$). However, for the ellipse centred in P , the radius along $\vec{u}_0$ grows $\|\mathbf{T}^{-1}\vec{u}_0\|^{-1}$ faster (this expression is ≥ 1). Thus the average growth factors of the two sleeves' radii are proportional to:

$$r = \frac{\|\mathbf{T}^{-1}\vec{u}_0\|^{-1} + \|\mathbf{T}'^{-1}\vec{u}_0\|^{-1}}{2} \quad (3.2)$$

with $r \geq 1$. From this, it is straightforward that the ratio d_0/d_c is the ratio of r over $|\vec{u}_0|$. Here $d_0 = |\vec{PP'}|$, i.e. the measured distance between P and P' in the orthonormal basis $\mathcal{B}_0$ of the micrography plane. d_c is the corrected centre-to-centre distance mentioned earlier. Hence this ratio is:

$$\frac{d_0}{d_c} = \frac{\|\mathbf{T}^{-1}\vec{u}_0\|^{-1} + \|\mathbf{T}'^{-1}\vec{u}_0\|^{-1}}{2} \quad (3.3)$$

and the expression of d_c is:

$$d_c = \frac{2|\vec{PP'}|}{\|\mathbf{T}^{-1}\vec{u}_0\|^{-1} + \|\mathbf{T}'^{-1}\vec{u}_0\|^{-1}} \quad (3.4)$$

Note that this expression of d_c is also the harmonic mean of $|\vec{PP'}| \times \|\mathbf{T}^{-1}\vec{u}_0\|$ and $|\vec{PP'}| \times \|\mathbf{T}'^{-1}\vec{u}_0\|$. This corrected centre-to-centre distance was calculated for all segments of the Delaunay triangulation and used for the refinement.

3.D Randomly-filled ellipse

Figure 3.D.4 *Comparison of the fibre distribution obtained from the randomly filled 2D space (a) and from a cross-sectional micrograph of a dough (b).*

Chapter 4

Deformation mechanisms during the squeeze flow of recycled thermoplastic composites

Abstract

A novel recycling route for thermoplastic composites (TPCs) has been implemented recently, which comprises the following steps: shredding of TPC offcuts to flakes of a few centimetres, melting and blending of the flakes in a low-shear mixer, extrusion of a molten mixed dough and its transfer to a press for compression moulding. Fundamental understanding of the rheology of this recycled material is crucial for applying the technology. The present chapter will focus on the deformation mechanisms of the recycled thermoplastic composites during squeeze flow. Constant-volume experiments were performed under axisymmetric conditions on prepared $\varnothing 80$ mm disks of recycled carbon/PPS. Experiments were executed at different closing rates, and with specimens of various fibre fraction and fibre length to study their influence on the rheology of the disks. As a first approximation, the material response was modelled assuming a power-law constitutive equation, leading to poor results. A detailed study of the present deformation mechanisms revealed complex macroscopic behaviour during the squeezing experiment, mainly due to the activation of multiple shear planes. These complex mechanisms were found to largely deviate from most assumptions required for simple analytical modelling. It is hypothesized that better-mixed material will lead to more uniform deformations. This would also decrease the local anisotropy of the material, making it easier to model.

4.1 Introduction

The past decade has seen the introduction of several recycling solutions for thermoplastic composites (TPCs), either by research institutes, universities or companies [1–9]. The impetus for these recent developments has a couple of reasons. First, TPC demand and production has increased drastically since their first applications [10, 11], leading to large amounts of production scrap with considerable economic value. Secondly, legislative incentives are encouraging re-use or recycling in all industrial sectors [12].

These new recycling solutions all feature discontinuous-fibre composites and are very diverse in terms of the type of scrap, size reduction and re-manufacturing method. The used scrap can vary from prepreg materials to laminates, with unidirectional or woven reinforcements. A size reduction technique is selected to obtain particles ranging from 0.1 mm to 100 mm. A manufacturing step then converts the TPC particles to a new semi- or end-product, often by means of compression moulding [2, 4], injection moulding [6] or extrusion-compression moulding [1, 3].

For these manufacturing techniques, the feasibility of obtaining the desired end-product is driven by the rheology of the recycled compound, similar to the case of long fibre thermoplastics (LFTs). Therefore, understanding and characterising the flow behaviour of such recycled materials is a major topic. Extensive characterisation and modelling work has been carried out using squeeze flow experiments on glass mat thermoplastics (GMTs) [13–17], on randomly-oriented strands [18, 19], and on recycled chopped prepregs [2]. Although squeeze flows are transient and inhomogeneous, compared to the flow in shear rheometers for instance, they are appreciated for their similarity to industrial compression moulding. In such previous studies, the material behaviour during squeeze flows was found to vary drastically based on the structure of the fibre networks tested. In the previous example, GMTs are stacked sheets of entangled bundles usually longer than 25 mm, while the randomly-oriented strands and the recycled chopped prepregs are systems of staggered platelets of one to two centimetres.

The structure of the fibre network in recycled components is likely different for the various recycling solutions, because of the diversity of scrap, size reduction and re-manufacturing technique. This would lead to different flow behaviours and deformation mechanisms during the compression moulding phase. However, the industrial implementation of such recycling solutions requires processing guidelines regarding the flow phase. Rheological characterisation is therefore a crucial step. This chapter aims to characterise the deformation mechanisms during the squeeze flow of TPCs recycled with the solution introduced by De Bruijn et al. [1]. In this work, the re-manufacturing steps consist of melting and blending flakes and polymer granulates in a low-shear mixer, followed by compression moulding of the mixed compound in an isothermal mould. The mixing step is known to result in

local variations of the quality of mixing (QoM) of the mixed compound (Chapter 3). This leads to differences in bundle sizes and spatial distribution of the bundles, which could result in local variations of the dough rheology.

Constant-volume squeeze flow experiments were carried out first on a relevant control material to validate the experimental procedure, in regard to the setup and materials tested at the ThermoPlastic composites Research Center. Experiments under similar conditions were then performed on recycled C/PPS. Experimental results will be analysed using a closed-form model for power-law fluids. The chapter follows with detailed descriptions of the deformation mechanisms based on video observations of squeezed specimens.

4.2 Materials and processes

Two materials were used in this study: recycled carbon/polyphenylenesulfide (C/PPS) and virgin carbon/polyethersulfone (C/PES). The latter material was used for experimental validation purposes only.

The C/PPS was collected at various manufacturing sites and consisted of offcuts trimmed after stamp-forming. The trims were made of laminated 5HS, with tows of 3,000 fibres each, Cetex® TC1100 in a quasi-isotropic layup. Next, the scrap was shredded in-house using a two-shaft shredder from UNTHA GmbH, and sieved with a multi-stage vibrating sieve (Chapter 2). The flakes resting on several sieves were recovered for the present chapter and their fibre length distributions (FLDs), which were analysed previously, are shown in Figure 4.1. Three batches were collected: 1. the flakes that failed to pass through apertures of 16 mm, later referred as *C/PPS L*; 2. the flakes that failed to pass through the 8 mm sieve, called *C/PPS M*; and 3. *C/PPS S*, a blend of the flakes that failed to pass through the sieves with apertures of 2.8 mm and 4 mm. Here, subscripts *L*, *M* and *S* indicate long, medium and short respectively. A photograph of shredded flakes, similar to *C/PPS L* is shown in Figure 4.2.

Boxplots of the FLDs studied in chapter

Figure 4.1 FLD of the shredded flakes used in this chapter, analysed in Chapter 2.

Figure 4.2 Photograph of the flakes *C/PPS L*.

The flakes were then processed in a low-shear mixing device to produce molten and mixed doughs. Additional PPS granules (Fortron® 0214) were added in with the flakes in the mixing device to lower the fibre volume fraction (FVF) from an initial 50% to 26% or 20%. The chosen mixing device was selected to prevent fibre attrition by mixing at low shear rates, but may lead to a limited QoM, i.e. the evenness and clustering of fibres, as shown in Chapter 3.

The device consists of a heated hollow cylinder of 70 mm in diameter, with three eccentrically-located heated rods rotating inside. In the present study, all doughs were processed at 330°C for 20 min and at 10 rotations per minute. The filling ratio of the cavity with flakes and granules was 50%, the rest being filled with air. After being pushed out, the dimensions of the molten mixed doughs were about $\varnothing 100 \text{ mm} \times 300 \text{ mm}$. They were then directly transferred to a press to be semi-pressed to a height of 15 mm. The pressing of doughs takes place in two stages, as reported in Chapter 3. In the first compression stage, the void pockets present in the dough are closed while the dough barely flows outwards. The material starts to flow and the last void pockets close only in the second phase. The height of 15 mm was found to be at the transition between the two stages and therefore best suited for the production of specimens for squeeze flow experiments.

Five or six disks of $\varnothing 80 \text{ mm} \times 15 \text{ mm}$ were then cut from each semi-pressed dough. A region of 2 cm in width along the perimeter of the doughs was trimmed before cutting the disks to prevent edge effects. Photographs of each step are shown in Figure 4.3.

Figure 4.3 Photographs of the manufacturing of squeeze flow specimens at various stages.

During the mixing step, the flakes first delaminate, the woven structure loosens, and the bundles spread into smaller fibre-clusters. When combined with the FLD, the bundle size distribution (BSD) is a good indication for the number of bundle-bundle interactions per unit volume [20, 21]. Chapter 3 demonstrated that the BSD varies with FLD, as shown in Figure 4.4, which shows the BSD for the three selected flake sizes. It reveals that mixing short-fibre flakes leads to smaller clusters

of fibres. The various fibre lengths, bundle sizes and their respective entanglement are expected to lead to inhomogeneous flow behaviour. Therefore, the rheological behaviour of the three types of doughs, *C/PPS L*, *M* and *S*, will be studied.

Figure 4.4 Bundle size distribution (BSD) measured in the mixed doughs in Chapter 3 for the three sizes of flakes studied in this chapter.

Prior to the characterisation of this material, our approach, consisting of the squeeze flow experiments, the model and the setup, was validated. A more uniform, yet similar, material was used for this purpose: C/PES chopped unidirectional flakes at 25% FVF. The material consists of fibre bundles of a constant 11 mm in length embedded in PES. Disks of 80 mm in diameter and 10 mm in height were consolidated in a cylindrical mould. Figure 4.5 shows photographs of the flakes and consolidated disks. In comparison, the C/PPS and C/PES disks have

Figure 4.5 Photographs of C/PES flakes of 11 mm (a) and the manufactured specimen for squeeze flow measuring ø80 mm × 10 mm (b).

similar dimensions, FVF and FLDs. They also have a random, mostly in-plane, fibre orientation distribution (FOD). The C/PES disks are expected to behave similarly to previously studied LFTs such as GMT or randomly oriented strands, and therefore have a behaviour that can be accurately modelled analytically as shown in [15, 22]. The edges of the C/PPS and C/PES disks are different. The C/PPS disks have bundles cut off on their edges, but the FOD is unaffected. Manufacturing of C/PES disks using a circular picture frame allows for uncut fibres but influences the FOD along the edges.

4.3 Squeeze flow experiments and setup

The experimental study in this chapter consists of constant-volume squeeze flow experiments performed with a setup developed in-house. The setup was designed to fit universal testing machines (UTMs), in this case an Instron 5982. It is based on a standard die set of $246 \times 246 \text{ mm}^2$, and therefore features a large working surface, enabling the squeezing of large specimens. Figures 4.6 and 4.7 show a photograph of the setup and a drawing to illustrate the main components.

The setup is heated using heat cartridges inserted in each half-mould and controlled with incorporated thermocouples (see Figure 4.7 and ⑦ in Figure 4.6). Three guiding rods and bushings are installed to enforce the parallelism between the two half-moulds, as well as preventing relative planar movement. A spherical and planar joint, in the form of a spherical seat and a compression platen, respectively, link the setup to the UTM. These two joints are locked prior to testing, with the squeeze flow setup installed, under a compressive load of 3 kN, in order to compensate for any misalignment of the upper and lower Instron rods and to prevent large bending moments in the load cell. This over-constrained mechanism leads to friction between the guiding rods and bushings, but it was found limited to a few hundred newtons, which is not significant for the tested materials, both at room and processing temperature.

After cutting the disks, annotations were marked on the top and bottom surfaces to determine the initial stick or slip conditions. In particular, the circumference of the top and bottom surfaces was painted. Prior to testing, the mould surfaces were coated with a release agent, Marbocote 227 CE, to ease de-moulding of the squeezed specimens. Once the disks were prepared and the setup was installed, the experimental procedure for both C/PPS and C/PES disks was as follows.

A specimen is placed in the centre of the setup at a low temperature ($< 80^\circ\text{C}$). The two half-moulds are then heated-up to 320°C (360°C for the C/PES disks). Once a stabilised temperature is reached within the half-moulds, the friction between the rods and bushings is measured by moving the upper mould up and down a couple of times without the specimen. The *friction force*, defined as the maximum absolute load during this step, is recorded. The top half-mould is lowered until

Figure 4.6 Photograph of the squeeze flow setup, with the following highlighted elements: ① Instron spherical seating, ② thermal insulation, ③ guidance pin, ④ guidance bushing, ⑤ mould surface platen, ⑥ LVDT, and ⑦ thermocouples and heat cartridges.

Figure 4.7 Drawing of the squeeze flow setup illustrating the location of the various elements.

contact with the specimen is made. The contact force is here arbitrarily defined as *friction force* + 150 N. The value of 150 N was found to assure contact between the specimen and the mould surfaces, but not enough to start squeezing the material. The initial specimen height, h_0 , was measured from linear variable differential transformers (LVDTs). The specimen heats up to the processing temperature, while holding the cross-head position. For a few specimens, the temperature at the centre of the specimen was measured. A waiting time of 15 min was found to be sufficient for the materials studied here. The specimen is then compressed at a constant speed until it reaches 25% of its initial height h_0 . The compression speed $\dot{h}(t)$ is controlled from the LVDTs. The height $h(t)$ and normal force are recorded from the LVDTs and load cell. Finally, the specimen and setup are cooled while holding a constant load of 1 kN.

Two LVDTs were used to record the specimen height, in the front and back of the setup, to measure possible lack of parallelism in the y-direction (see Figure 4.7 for the axis system), which was found to be $< 0.025^\circ$. The other two sides of the setup support the power and temperature units, which disable parallelism measurements in the x-direction. Videos of the experiments were also recorded from the front (see Figure 4.7) to analyse the deformations of the specimens.

For each material and for each FVF and FLD combination that was tested, experiments were performed at various closing speeds, ranging from $10^{-1.5}$ mm/s to 10^0 mm/s, and repeated two to four times (see Table 4.1). Because of the limits of our UTM, the range of closing speeds in this study is different from the typical moulding speeds used in industrial presses for such materials, which usually range from 10^1 mm/s to 10^2 mm/s [23]. The heating method is also different in these experiments as specimens are heated through conduction via the hot mould, while the recycling solution features an already molten dough that is transferred into a cold mould. Here, cold is defined as below the polymer's melting temperature. This also means that the squeeze flow experiments are performed in isothermal conditions, whereas in the recycling solutions, the doughs cool down while they are compression-moulded.

Material	Fibre length [mm]		Fibre volume fraction [%]	Closing speed [mm/s]	Number of repetitions
C/PES	15 mm	25	$10^{-1.5}$	3	
			10^{-1}	3	
			$10^{-0.5}$	3	
			10^0	3	
C/PPS	S	20	10^{-1}	3	
			$10^{-0.5}$	3	
			10^0	3	
		26	10^{-1}	2	
			$10^{-0.5}$	2	
			10^0	2	
	M	20	$10^{-1.5}$	3	
			10^{-1}	4	
			$10^{-0.5}$	4	
			$10^{-0.25}$	3	
			10^0	4	
		26	10^{-1}	2	
			$10^{-0.5}$	2	
			10^0	2	
		L	10^{-1}	2	
			$10^{-0.5}$	2	
			10^0	2	
		26	10^{-1}	2	
			$10^{-0.5}$	1	
			10^0	2	

Table 4.1 List of the performed squeeze flow experiments.

4.4 Analytical modelling and validation of the experimental procedure

Analytical modelling

The rheology of long fibre suspensions during squeeze flow is a well-studied topic. Most classes of LFTs that are processed by compression moulding were examined in such a way. It is a transient experiment with complex deformations, but is very close to the compression moulding that is used in industrial processes in practice.

A general first approach to the modelling of the squeeze flow of LFTs is to consider the fluid compound as a single-phase power-law fluid, with a scalar viscosity. An analytical solution to this problem exists for the following assumptions:

- the experiments are isothermal, with the polymer fully molten;
- the material is assumed to be single-phased;
- the material is assumed to be incompressible;
- the inertia term is neglected;
- the specimens are sticking to the wall boundaries;
- the lubrication assumption is considered valid;
- the material flow is axisymmetric.

It was observed that the semi-pressed doughs contain a void fraction of >10% that likely decreases during the squeezing. Besides, the fibre bed in both C/PPS and C/PES disks initially decompacts when heated to the processing temperature. This conflicts with the incompressibility assumption, which can be valid for the fibres and matrix taken alone for the studied conditions. The derivations of the equations of motion and volume flow rate are not detailed in this chapter but can be found, for instance, in Bird et al. [24]. It leads to the following equation, usually referred as the *Scott equation* [24]:

$$F(t) = \frac{(-\dot{h})^n}{h^{2n+1}} \left(\frac{2n+1}{n} \right)^n \frac{2\pi k}{n+3} R^{n+3} \quad (4.1)$$

where $F(t)$ is the normal force [N], $-\dot{h}$ and h are the compression speed [mm/s] and specimen height [mm] respectively, n and k are the power-law index [-] and consistency parameter [MPa.sⁿ], and R is the initial specimen radius [mm].

During the squeeze flow experiments, performed at fixed $\dot{h}$, several mechanisms can affect the apparent viscosity of the suspension. Instantaneous coefficients, n and

k , should be determined for fixed h/h_0 instead of a fixed $\dot{h}$ to include the evolving fibrous network, where h_0 is the initial specimen height [mm]. Equation 4.1 should be rewritten to a more functional form to take this into account. It requires the introduction of the compressive strain rate $\dot{\epsilon} = \dot{h}/h$ [s^{-1}], which is the derivative of the Hencky strain $\epsilon = \ln(h/h_0)$. Rewriting Equation 4.1 leads to

$$\tau_{zz} \left(\frac{\dot{h}}{h}, \frac{h}{h_0} \right) = \frac{F(t)}{\pi r^2} = \left(\frac{-\dot{h}}{h} \right)^n \left(\frac{h_0}{h} \right)^n \left(\frac{2n+1}{n} \right)^n \frac{2k}{n+3} \left(\frac{R}{h_0} \right)^{n+1} \quad (4.2)$$

where τ_{zz} is the normal stress [MPa]. This equation is used to fit experimental data for fixed h/h_0 , which requires experiments performed at multiple compression speeds $\dot{h}$.

Validation of the experimental procedure

The squeeze flow experiments performed with the C/PES disks, a relevant control material, are analysed first to validate the experimental procedure. Figure 4.8a shows the evolution of the normal stress as a function of the compression ratio h/h_0 , for all tested speeds. Each plot corresponds to the mean value of three repetitions. For $h/h_0 > 0.5$, the plots show start-up effects in combination with the friction of the setup and non-fully developed flows that makes analysis inappropriate. This study thus only focuses on $h/h_0 < 0.5$. Figure 4.8b displays the same normal stress as a function of the strain rate $\dot{h}/h$ instead, from which

Figure 4.8 Results of the experiments performed with C/PES disks. The symbols and error bars represent the average and extrema of normal stresses respectively. The coloured lines on the right show the power-law fit for Equation 4.2 for various values of h/h_0 .

Equation 4.2 was fitted for constant h/h_0 . Some power law fittings are highlighted with solid lines in Figure 4.8b. The extrema of the normal stress are displayed as error bars around the symbols. This limited discrepancy in the squeeze flow results and the good power-law fit show the reliability and accuracy of the experimental procedure for the currently used well-defined material.

The power-law index and consistency parameter can be calculated using the slope of the fitted equation and its intercept respectively. This becomes clear when taking the logarithm of Equation 4.2:

$$\ln \tau_{zz} = n \ln \left(\frac{-\dot{h}}{h} \right) + \ln \left[\left(\frac{h_0}{h} \right)^n \left(\frac{2n+1}{n} \right)^n \frac{2k}{n+3} \left(\frac{R}{h_0} \right)^{n+1} \right] \quad (4.3)$$

Further study on this material could analyse the obtained power-law index and consistency parameter, but this is not the aim of this chapter.

4.5 Results and discussion

4.5.1 Analytical modelling of the squeeze flow experiments

Regarding the experiments with the C/PPS material, two cases are analysed in detail in this section: *C/PPS L* at 20% FVF (Figure 4.9) and *C/PPS M* at 20% FVF (Figure 4.10). These samples highlight the typical material response obtained

Figure 4.9 Results of the experiments performed with C/PPS L disks at 20% FVF. The symbols and error bars represent the average and extrema of normal stresses respectively. The coloured lines on the right show the power-law fit for Equation 4.2 for various values of h/h_0 .

for all sets of experiments with the C/PPS disks (see Table 4.1), which is why the other sets are not detailed here.

For the first case with C/PPS *L* at 20% FVF, squeeze flow experiments were performed at 10^{-1} mm/s, $10^{-0.5}$ mm/s and 10^0 mm/s with two repetitions each. The dotted lines in Figures 4.9a and 4.9b are the average normal stress, while the extrema are displayed with error bars. Only the case of $h/h_0 < 0.5$ is studied for the same reasons as for the C/PES disks. Similar to Figure 4.8, the power-law fit matches the average normal stress well. However, the extent of the scatter makes the fit unreliable. The non-linearity of τ_{zz} in Figure 4.9a for $h/h_0 < 0.5$ is translated into increasing slopes of the fitted Equation 4.2 in Figure 4.9b. This results in an increasing fitted power-law index n with the reduction of h/h_0 .

The second case, with C/PPS *M* disks at 20% FVF as shown in Figure 4.10, highlights a different situation. Squeeze flow experiments were again performed at multiple compression rates ranging from $10^{-1.5}$ mm/s to 10^0 mm/s (see Table 4.1). The first observation is that the normal stresses vs. compression rate (Figure 4.10a) are barely ordered with the closing rates, contrary to the previous case (Figure 4.9a).

Figure 4.10 Results of the experiments performed with C/PPS *M* disks at 20% FVF. The symbols and error bars represent the average and extrema of normal stresses respectively. The coloured lines on the right show the power-law fit for Equation 4.2 for various values of h/h_0 .

Regarding the analytical modelling, it is clear from Figure 4.10b that a reliable fit is not possible and that the scatter is rather large. The analyses of the other sets of experiments, i.e. C/PPS *L*, *M* and *S* at 26% FVF and C/PPS *S* 20% materials, revealed similar behaviour to the last two sets of experimental data included in this section, and therefore are not described in detail. Although C/PPS *L* 26% and C/PPS *S* 20% were expected to behave differently, this was not observed.

Overall, the results of the squeeze flow experiments with C/PPS suggest that one or several of the modelling assumptions are not valid. The observations of the material being squeezed showed that both the single-phase flow assumption and the assumption of axisymmetric behaviour appear to be invalid. The following section will assess these concerns.

4.5.2 Deformation mechanisms

The following paragraphs will examine the deformation mechanisms during the squeezing of C/PPS disks based on several aspects: 1. the fully squeezed disks from the experiments described in the previous section, 2. a disk squeezed partially to identify the initial mechanisms, and 3. video recordings made during the squeeze flow experiments.

Fully squeezed disks

First of all, the visual inspection of the squeezed specimens reveals a flow front with various degrees of anisotropy. Scans of the squeezed specimens were realised using a flat-bed scanner to measure this anisotropy. Ellipses were fitted to the scanned specimens for that purpose. The ellipses' aspect ratios, i.e. major-axis-length over minor-axis-length, were calculated for all scanned specimens and ranged from 1.02 to 1.34. Figure 4.11 shows a few squeezed specimens with different eccentricities in order to illustrate this subject. As stated in Section 4.2, several disks were cut from each semi-pressed dough. Due to the stochastic nature of the material and the various FLD and FVF involved, the various doughs may have different structures leading to different aspect ratios of the squeezed disks. Similarly, the compression speed can influence the aspect ratios. These concerns were studied first by grouping the aspect ratios of the squeezed disks in respect to the dough from which they originate. No clear influence of the doughs on the aspect ratios of the squeezed disks was noticed (Figure 4.12a). In a similar fashion, the influence of the compression speed and FVF on the aspect ratio of the squeezed specimen was also studied, resulting in no visible correlation (Figure 4.12b). Additionally, it was found that the centre of the fitted ellipses does not always match the centre of the squeezed specimens, although the distance between the two centres is rather small (< 5 mm). This preferential flow direction could be caused by a lack of parallelism between the press plates, but this was measured and found to be very limited.

(a) C/PPS S - 26%

(b) C/PPS M - 20%

(c) C/PPS M - 20%

Figure 4.11 Scans of a few representative squeezed specimens. (a) and (c) are exceptionally round and elliptic respectively. (b) shows severe protuberances and depressions around the circumference. (c) and (d) correspond to protuberances flowing next to each other and protuberances shearing away from each other respectively.

Figure 4.12 *Measurements of the specimens' aspect ratios after squeezing. Each symbol is the aspect ratio of one specimen. The aspect ratios were grouped based on their affiliation to a type of dough (a) or to a combination of compression speed and FVF (b). The connected symbols in (a) belong to one dough, while those in (b) belong to one combination of compression speed and FVF. The connected symbols are alternating between grey and black to make the distinction between them visible.*

The radial flow distance of a few specimens was also measured and is shown in Figure 4.13 for the two squeezed specimens in Figures 4.11b and 4.11c. The black solid lines represent the closest fitted ellipses to the specimen contours, ellipses which are also superimposed to the specimens in Figure 4.11. Local variations in flow distance are possible with such a material, which can be seen as the specimen contours do not perfectly match the ellipses. It is reasonable to assume that variations in flow radii up to one fibre length are inherent to this material. These boundaries were added to Figure 4.13 using dashed lines. The actual specimen contours are outside these boundaries on numerous occasions, revealing variations larger than one fibre length. In many places, these variations are either due to circular protuberances of a few centimetres flowing further outwards, or due to lumps of materials stuck together that could not flow further. The protuberances were also found to flow next to each other, as in the area (c) in Figure 4.11b). In some occasions, the protuberances also shear away from each other when flowing outward ((d) in Figure 4.11c).

(a) Specimen in Figure 4.11b

(b) Specimen in Figure 4.11c

Figure 4.13 Visualisation of the radial flow distance of squeezed disks. The solid black lines represent the closest ellipse fitted to the specimen contour. The dashed lines are upper and lower margins with an offset of ± 5 mm corresponding to half the average fibre length.

Partially squeezed disk

A partially squeezed specimen was produced in order to obtain more insight into how the observed deformation mechanisms start. A disk of 40 mm in diameter and 15 mm in height was squeezed until $h/h_0 = 0.7$ and cooled down. Prior to squeezing, photographs were taken of the side surface and then stitched together (Figure 4.14 - top). A photograph of the specimen after partial squeezing is shown in Figure 4.15, which highlights the large-scale, lobed-like deformations occurring in this specimen. The relative orientation and deformation of the partially squeezed specimen is superimposed to the original figure in Figure 4.14 to

Figure 4.14 *Stitched photographs of the circumference of a $\varnothing 40$ mm disk before squeezing (top). The bottom figure shows the same photograph superimposed with the identified flow regions: skin layers in (1), flowing core layer in (2), and shear planes in (3).*

identify the different surface structures in the non-squeezed and partially squeezed specimen. On the one hand, the top and bottom surfaces stuck to the mould walls (region (1)). On the other hand, the core region flowed outward (region (2)). During squeezing, the transition between the two regions, skin and core, seems to be a plane of nearly in-plane shear. It was observed that the top and bottom skins are more mixed than the core region. This can be seen in Figure 4.14 - top from the change of colour intensity. These differences mostly originate in the mixing step.

Figure 4.15 *Front view of the semi-squeezed specimen presented in Figure 4.14. The numbered regions also correspond to those in this figure. The dashed lines are the identified shear planes.*

The molten flakes and polymer granules are sheared by the heated rods during the mixing stage. Figure 4.16 aids understanding of the mixing mechanisms by showing cross-sectional sketches of the material before mixing (a), during mixing (b) and after being pressed (c). The mixer features three eccentrically-located heated rods rotating inside a hollow cylindrical cavity. The rods are placed at different distances from the axial centre of the cylinder and placed closer to the edges than to the centre. It can lead to an improved QoM on the circumference of the extruded dough. When semi-pressed, the well-mixed phase end up on the top and bottom, becoming the two well-mixed skin layers. This results in the skin and core regions identified in Figures 4.14 and 4.15.

Figure 4.16 *Schematics of cross-sectional views of the mixer processing flakes and polymer. The centre is hardly mixed because of the rod locations.*

Video recordings

Lastly, the video recordings of the squeeze flow experiments were analysed to understand the evolution of the flow. The deformation mechanisms in all these recordings were found to be similar to those described for the semi-squeezed disk.

Figure 4.17 shows one disk being squeezed at various instants, which has been selected for its visual clarity. The dashed lines represent the shear planes identified. For the specimen shown, the skin-core distinction was less visible, and the material seems less layered compared to the one in Figure 4.15. During the initial pressing stages, the specimen had a barrel shape that is typical for uniaxial compression with non-slip boundary conditions at the walls. Then, a few shear planes became active, possibly very close to the mould walls, and lobed-like structures (hereinafter named daughter plates) flowed outward. From the examination of the squeezed specimens, it was found that only a few did not stick to the walls, as demonstrated by the fact that their initial marker annotations flowed. In comparison, most specimens still showed circular painted marks at the centre after squeezing as in Figure 4.11.

Figure 4.17 *Front view photographs of a specimen being squeezed at various instants showing the development of the flow front.*

4.5.3 Discussion

Side and top views

The flow behaviour of the disks can be divided into two categories based on the previous observations, illustrated in Figure 4.18. These two categories seem to mainly depend on the disks' QoM. In Figure 4.18, the t_1 , t_2 and t_3 are used to define characteristic moments of the flow for both cases. The mechanisms at t_1 appeared early, at $h/h_0 \simeq 0.7$, while t_3 is characteristic for the last flow phase for $h/h_0 < 0.3$ and t_2 is intermediate to the two. The lobes of material flowing outward, as observed previously, are called daughter plates. More specifically, daughter-1 and daughter-2 plates flowed out of the cylindrical specimen and daughter-1 plates respectively (see Figure 4.18).

The left side presents the deformations observed in the semi-squeezed disk (Figure 4.15), where a clear skin-core distinction was observed. The further squeezing of such specimen leads to a daughter-2 plate shearing out from the daughter-1 plate. This multi-stage squeezing mechanism was also observed in the video recordings. The radial flow of the daughter plates is illustrated from a top view in Figure 4.19 as hatched regions. Figure 4.11b highlights these daughter plates as © in a scanned specimen. As the daughter plates flow away from each other, extensional flow occurs at the interphase between them and may lead to a

drastic separation, as in (d) - Figure 4.11c.

The right side of Figure 4.18 illustrates the situation of a more homogeneous disk being squeezed. This is possibly a consequence of an improved QoM of the parent dough. Instabilities probably already exist within the disk at t_1 which leads to the activation of shear planes, which can be seen at t_2 . The material then flows independently between the shear planes and/or the wall boundaries with a combination of shear and plug flow. At t_3 , the various daughter plates partially merge.

For most disks after testing, a demarcation line (between the parent and daughter plates) shown as (a) in Figure 4.18 is still visible in the squeezed specimens. It translates into the initial full-stick boundary conditions of the disks. Partial slip boundary conditions were observed in some cases, which could originate from better coating of the release agent on the mould surfaces. The coating wears off

Figure 4.18 Drawing the observed deformation mechanisms during the squeezing of recycled C/PPS disks. The two cases illustrate two slightly different mechanisms. (a): demarcation line between the parent and daughter plates.

Figure 4.19 *Drawing of deformations mechanisms from a top view. The dotted circle represents the initial un-squeezed disk. The hatched regions on the right are daughter plates flowing radially.*

over the course the multiple uses, leading to a different release efficiency before and after re-applying it.

Specimens with short fibres were found to be better mixed than those with long fibres, as reported in Chapter 3. It was expected that short-fibre specimens would behave more according to case 2, while long-fibre specimens would behave more like case 1. However, both short- and long-fibre specimens were found to have a combination of the two types of deformations described above. No correlation between the type of doughs and the deformations mechanisms was found upon visual inspection of all specimens. A similar lack of correlation can be observed between specimens with high and low FVF.

Possible causes

The mechanisms detailed above are hypothesized to originate from the mixing stage. During mixing, the flakes and granules are blended by rotating rods inside the cavity as seen in Figure 4.16. The locations of these heated rods prevent proper mixing in the centre of the mixer's cavity. Then, when the dough is pushed out and pressed subsequently, the well-mixed outer layer becomes the top and bottom skins, as sketched in Figure 4.16 (b) and (c). The interface between the well-mixed skin layers and the region of poor mixing is likely an instability that leads to a shear plane when squeezed.

These observations seem to also support the existence of instabilities even when the whole dough is well-mixed. Overall, such deformation mechanisms during the squeeze flow of long-fibre composites were not previously observed, nor described, to the knowledge of the authors.

Challenges

The development of these mechanisms during squeeze flow makes modelling more challenging. The local anisotropy of the flow and the growth of daughter plates make the calculation of the average normal stress nearly impossible, either from video recording or volume conservation. The material is also not homogeneous across its thickness. Even when considering local single-phase flows, the various skin/core regions have different boundary conditions that evolve during the experiment. Modelling this behaviour may require a different approach, for instance one similar to Kuhn [25] or Hayashi [26, 27]. Both approaches consider a mechanistic model that simulates the fibres or bundles as beam elements coupled with the polymer melt (as solid elements). This modelling strategy is able to capture the local anisotropy of the fibre reinforced fluid during moulding. However, fibre-fibre interactions are not taken into account, which may be crucial to capture the shear planes observed in this chapter.

Besides, the disks were cut from semi-pressed doughs (see Figure 4.16), de facto removing their edges (the well-mixed layer) and their influence on the flow behaviour. A possible solution would be to perform experiments with circular semi-pressed doughs, i.e. avoiding the need for the additional cutting step to create squeeze flow samples. However, the manufacturing of small circular doughs seems difficult. Semi-pressing doughs in a circular picture frame could work. This would also constrain the dough to be a disk with sharp corners, altering its shape from an unconstrained flow (see the edges of the semi-pressed dough in Figure 4.3).

Even so, the difficulty to model this material's flow behaviour does not hinder its application. Recent progress by the authors [28, 29] towards applications was mostly realised empirically. Work on deformation mechanisms and flow behaviour of this material is still needed to stimulate industrial parties' confidence in it, and thus stimulate its use.

4.6 Conclusion

This chapter is aimed at understanding the flow behaviour of C/PPS recycled by low-shear mixing. Axisymmetrical squeeze flow experiments with recycled C/PPS disks were performed in a setup developed in-house. C/PPS disks were prepared for various FLDs and FVFs to test and model the flow behaviour.

The experimental procedure and setup are suitable to characterise large LFT specimens, especially regarding the high temperature and the relatively large range of compression speeds. A drawback was identified concerning the manufacturing of specimens. Cutting disks from a dough removes the well-mixed edges and their effect on the rheology. In an industrial setting, the doughs are transferred to a press for compression moulding. The identification of the effects of the dough

edges on its rheology is thus important. Further research on this topic should consider manufacturing circular doughs to prevent removing this edge effect.

It was found that simplistic modelling approaches cannot accurately capture the flow behaviour of the specimens. The main reason for this is the complex deformation mechanisms taking place during the flow of the specimens. The main mechanism is related to the activation of shear planes across the thickness of the specimens that leads to daughter plates flowing radially from the parent plate. Some variations were found between the specimens but could not be related to FLD or FVF. It is hypothesised that the variations in deformation mechanisms are related to the local QoM, i.e. varying from well-mixed bundles to barely-mixed flakes. No correlation was found between the different deformation mechanisms and the various types of dough. Doughs that are mixed better than those tested in this study are imperative in order to have more homogeneous materials, that are in turn expected to have more uniform deformation mechanisms. Even so, the identification of these complex mechanisms and the difficulty of modelling them are not detrimental to the application of this technology, as progress is also made in this direction [29].

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Chapter 5

Process- and material-induced heterogeneities in recycled thermoplastic composites

Abstract

A novel recycling solution for thermoplastic composites (TPCs) was recently implemented. The processing steps comprise shredding of TPC offcuts to flakes of a few centimetres, melting and blending of the flakes in a low-shear mixer, extrusion of a molten mixed dough and subsequent compression moulding in a press. This material and process are similar to the compression moulding of long fibre thermoplastics (LFTs) that have been in the market for decades, such as glass mat thermoplastics (GMT) or direct-LFT. However, the input material in this recycling route consists of multi-layered woven flakes, which is very different from the pellets or chopped rovings of other LFTs. Process- and material-induced heterogeneities such as fibre orientation, percolation, variation of fibre fraction, or fibre attrition may be different for this new material. The development of this recycling technology and future industrial applications require more confidence in the material and process. The objective of this study is to characterise these heterogeneities for this recycling solution, and compare them to those generated in regular LFTs. It was found that the process- and material-induced heterogeneities of the recycled TPCs are similar to other LFTs, for the aspects listed here: fibre orientation, percolation, variation of fibre fraction and fibre attrition. In comparison to GMT, the effect of the mixing step is particularly noticeable on the local variation of fibre fraction within the panels. Industrial applications of this recycling route will benefit from this similarity, as it improves the confidence in the material and process combination.

5.1 Introduction

The use of continuous-fibre-reinforced thermoplastic composites (TPCs) has increased in the past decades in various industrial sectors, with a large focus in aerospace [1]. The ever-increasing TPC applications also leads to increasing amounts of production scrap, generated during various manufacturing steps. The combination of economic value of the TPC scrap and legislative incentives is pushing the industry to reuse or recycle this material more and more [2, 3]. As a consequence, several companies and research institutes involved in TPCs have developed recycling solutions specific to TPCs in recent years [4–12]. In all of the implemented recycling routes, scrap material is first sorted and comminuted to the desired size, ranging from particles of a few millimetres to a few centimetres. The recycling solutions then proceed with a remanufacturing step that turns the composite particles into an end- or semi-product.

De Bruijn et al. [4] recently introduced a novel recycling solution involving shredding of scrap to produce flakes of a few centimetres, melting and blending of the flakes in a low-shear mixer, and extrusion of a dough that is directly transferred to a press for compression moulding (Figure 5.1). The low-shear mixing step was chosen for its ability to retain long fibres during mixing, while disentangling the flake structure. Additional polymer granules are added to the flakes in the mixing phase to lower the fibre fraction. Details on the mixing process used in this study are available in Chapter 3 of this thesis. The mixing process provides the opportunity to process long fibres, known to exhibit high stiffness, strength and impact properties [13]. After the extrusion, the molten dough is a concentrated suspension of poly-dispersed bundles, with a distribution of fibre lengths. The pressing phase is carried out in an isothermal mould, at a temperature lower than

Figure 5.1 *Schematic flow chart of the chosen recycling solution. The top row illustrates the various processing steps while the bottom row shows the material state between each step.*

the polymer's melting point, enabling fast pressing and a de-moulding step that only takes minutes [14].

The process and materials used by De Bruijn et al. are similar to the compression moulding of glass mat thermoplastics (GMT), carbon mat thermoplastics (CMT) or direct-long fibre thermoplastics (D-LFT), which have been developed over the past decades [15–18]. In those processes, a molten material, which can be a dough or a stack of sheets, is placed in a mould with partial coverage, and subsequently pressed to flow the material into all of the intricate features of the cavity. The molten material described here is a highly concentrated suspension of fibres in a thermoplastic matrix at the moment of pressing, with the fibre length ranging from 3 mm to 100 mm. The fibres may be bundled together into clusters of various sizes. These highly concentrated fibre suspensions of long fibres (henceforth, long fibres are defined as those longer than 10 mm) feature some microstructural heterogeneities, which are inherent to this type of material and their evolution is often flow-induced [19].

From literature on LFT, several microstructural properties are known to be affected by the process, in turn affecting mechanical properties, and leading to heterogeneities in LFTs:

- Porosity and cracks: the compression moulding of LFTs may not eliminate all void pockets. These were mostly found in regions with limited consolidation pressure. On the one hand, this can occur on the edges of panels. On the other hand, jammed regions can lead to resin rich regions that also lack pressure [20]. The location, percentage and type of porosity can affect the part performance. Cracks can occur during the cooling phase of the moulded part, due to the stress induced by the fibre bed and polymer shrinkage on the polymer.
- Fibre-matrix segregation and variations of fibre volume fraction (FVF): the flow of polymer and fibres of a concentrated suspension can lead to restriction of fibre movement, fibre bridging or jamming [18, 21, 22]. This can contribute to a decrease in fibre fraction along the flow or in some intricate features such as ribs [18]. Besides, the material itself may have local variations of fibre fraction that do not average out during the flow phase [17]. Moreover, the mixing step studied in this chapter was found to result in uneven distribution of the fibres (Chapter 3). The pressing of these doughs may lead to variations in fibre fraction in the moulded component. Overall, the FVF is a major parameter influencing material properties. Its variation within a part does affect mechanical performance.
- Fibre length reduction, or attrition: several studies on LFTs confirmed that the compression moulding step can result in fibre damage and breakage [17, 18, 23]. Although the mixing step in the recycling solution of De Bruijn et al.

was chosen for its ability to limit fibre breakage, the forces in the moulding step may induce fibre damage that leads to fibre attrition. A decrease in fibre length is known to affect the mechanical properties [13].

- Fibre orientation distribution (FOD): during compression moulding of doughs, the flow of polymer and fibres is coupled. The fibres orient themselves due to interactions with the flow field and contact amongst themselves. In the case of highly concentrated suspensions with long fibres, the interactions between the fibres are accentuated. This is known to result in an FOD with systematic deviations compared to results of suspensions assumed to behave as single-phase flow, largely used for commercial numerical simulations [18, 19]. Fibre orientation has a major effect on the mechanical properties of fibre reinforced composites. As such, its characterisation is crucial.
- Sink marks: the polymer crystallisation and cooling down during the compression moulding phase leads to shrinkage. This may eventually create sink marks at thick regions or local thickness variations. This is known to occur in LFTs when large resin-rich regions exist [5].

Contrary to GMT, CMT or D-LFT, the input material in the recycling solution of De Bruijn et al. consists of multi-layered woven flakes that disentangle in the mixing process. This may lead to differences in the type of heterogeneities as well as differences in their relation to the process conditions. Nonetheless, the development of industrial applications for this recycling solution is in progress [14], and revealed a scatter in the mechanical properties [4]. The further development and use of this recycling solution requires improved confidence in the material-process combination, and therefore a better understanding of these microstructural heterogeneities. Hence, the objective of this chapter is to characterise the material heterogeneity and its link to the process, as well as to benchmark it to similar LFT processes and materials. This chapter focuses on the aspects listed above.

The experimental characterisation of these properties will be studied using various methods: cross-sectional microscopy, C-scanning and X-ray radiography, density measurements, fibre attrition and orientation measurements. First a description of the materials is presented in Section 5.2, and then the methods used in this study are described in Section 5.3. A subsequent section will present the results before concluding the chapter.

5.2 Materials and process

Two materials were used for this study, carbon/PPS (C/PPS) and glass/PP (G/PP). C/PPS scrap material has been collected at various manufacturing sites and consists of the trimming edges of stamp-formed components. It was made of laminated Cetex® TC1100 5HS C/PPS at 50% FVF. The trims were shredded in-house using a two-shaft shredder, an S20 from Untha GmbH. The fibre length distribution (FLD) of the resulting shredded flakes was previously characterised (Chapter 2) and is shown in Figure 5.2. It is characterised by a peak at 20 mm and a long tail for longer fibres. The C/PPS flakes (see Figure 5.3a) were then processed in a low-shear mixer with PPS granules added in to lower the FVF from the initial 50% to 19%, 26% or 35%. The material was mixed for 20 min at 10 rotations per minute (rpm) and moulded at 200 bar and 20 mm/s with a mould at 180°C, if not stated otherwise.

Figure 5.2 *FLD of the shredded flakes used in this chapter, analysed in Chapter 2.*

Figure 5.3 *(a) shredded C/PPS flakes, (b) square C/PPS flake of 20 mm × 20 mm, (c) G/PP pellets of 15 mm.*

Figure 5.4 Photograph of a C/PPS ribbed panel. The two close-ups on the right show details on ribs and rib crossings.

Two types of panels were manufactured in this study: a flat panel and a ribbed panel both measuring $305 \times 305 \text{ mm}^2$. The ribbed panel was designed to test the manufacturability of several geometrical features, following the guidelines in use for GMT [16]. The panel is shown in Figure 5.4 with a few highlights, and includes the following features (see also drawing in Appendix 5.A):

- An increase in thickness along the edges, to simulate component landing [14]. Such an increase is usually required for the assembly of LFT components using rivets.
- Ribs with various height-to-width ratios, from 2:1 to 4.5:1. Two quarters of the panel include various types of ribs to test the effect of the rib type at different flow distances on the filling behaviour.
- Various types of rib crossings: normal intersection, knockout at and coring at intersection.

The FLD measured on the flakes was assumed to remain the same during mixing, but fibre attrition was expected in the moulding phase. From a statistical point of view, it is difficult to reliably measure the FLD after attrition when the input FLD is spread. Therefore, characterisation of the fibre attrition was performed with different flakes. Cross-ply 5HS C/PPS laminates were consolidated and then cut into squares of $20 \times 20 \text{ mm}^2$ (see Figure 5.3b). This way, the square flakes

resemble the shredded flakes in terms of their laminated and woven structure, but the constant fibre length of the square flakes makes the measurement of fibre attrition statistically more reliable. These flakes were diluted to 20% FVF in the mixing step and then processed with the default settings.

Next to the C/PPS, several panels were moulded with readily-available virgin LFT glass/PP (G/PP) pellets, with fibres of 15 mm, as shown in Figure 5.3c. The pellets were added at 40% fibre weight fraction, or approximately 19% FVF. The G/PP panels were mixed for 15 min at 5 rpm, and moulded at 45 bar and 200 bar for the flat and ribbed panels respectively. The moulds were pre-heated to 80°C and were closed at 20 mm/s.

5.3 Measurement methods

Visual inspection and cross-sectional microscopy

Visual inspection was first carried out on all panels to scrutinise the part quality. Surface defects such as improper filling or insufficiently mixed regions were searched for. Cross-sectional microscopy was extensively used on C/PPS flat and ribbed panels. Cross-sections were cut at various locations, embedded, polished and inspected with an optical microscope.

Fibre orientation distribution and fibre attrition

The measurements of fibre attrition and FOD were performed on burnt-off specimens.

The FOD was characterised on one quarter panel of G/PP, as shown in Figure 5.5, which also highlights the location of the dough prior to pressing. The quarter panel was cut into nine pieces of approximately $50 \times 50 \text{ mm}^2$. Each piece was placed in an oven at 550°C in an air environment for three hours in order to have complete matrix burn-off. The resulting fibrous structure was then placed under a camera mounted vertically. The fibre bundles were picked up with tweezers continuously while the camera took photographs of the fibre bed every 10 seconds. A square caul sheet was placed under the fibre bed and served as a reference to correct for geometrical distortion. A schematic of the set-up is visualised in Figure 5.6. The map of the fibre bundle locations and orientations was obtained from manual identification of each unique fibre bundle in the images recorded by the camera. The calculation of the local orientation tensors results in the FOD on the quarter panel. Approximately 2,000 bundles were picked up and identified in the process. It is possible to estimate the FOD in the panels with this method. Yet, the scatter in the dispersion of the fibre bundles during the mixing and moulding phase makes the identification of bundles complex and therefore makes very accurate measurements difficult.

Figure 5.5 Photograph of a G/PP flat panel, highlighting the locations of the dough prior to the moulding phase, and of the quarter panel analysed for the FOD measurements.

Figure 5.6 Schematic of the method used to record the locations of the bundles to measure the FOD. The left picture is an example of the pictures recorded by the camera during the continuous pick-up. It shows a stack of fibre bundles that are framed by a caul sheet.

The fibre attrition was measured for both a G/PP and a C/PPS panel. A flat panel was moulded for each of the two cases, from which a square specimen of four times the input fibre length in width was cut off (see Figure 5.7 on the left). The glass fibres all measured 15 mm in the input pellet, while the carbon fibres were all 20 mm long before mixing. As in the previous analysis, the square specimens were placed in an oven at 550°C until complete matrix burn-off. As shown in the left diagram of Figure 5.7, the fibres located on the edges of the cut specimens may be cut, and must be removed from the analysis. Therefore, all fibres located in a border of one fibre length in width around the specimen were removed after

Figure 5.7 *Schematic of the selection of fibres for the fibre attrition method. A square of four times the fibre length is cut from a panel. The matrix of this specimen is burnt-off in an oven. Fibres located in a perimeter of one fibre length in width may be cut, thus must be removed from the analysis. Therefore, only the central square of two fibre length is kept for the fibre length analysis.*

matrix burn-off. The reclaimed fibres, in the centre square (Figure 5.7 - right), were spread on a flat surface and photographed. The FLD of the reclaimed fibres was determined by manual identification of the fibres in the pictures.

Density measurements

The local variations in FVF of several C/PPS panels were determined via density measurements. For the ribbed panels, each rib and flat section of several quarter panels was analysed (see Figure 5.8). The individual specimens weighed between 0.5 g and 1 g for the ribs, and around 1.5-2 g for the flat sections. Regarding the analysis of the FVFs for the flat panels, 32 pieces were cut from each half-panel, with each piece weighting between 4 g and 6 g. Each cut specimen was weighed while immersed in air and in ethanol at a measured temperature. The density and FVF of each specimen was then calculated according Archimedes' principle based on the two measurements and following the operating guidelines of Mettler Toledo, assuming no porosity.

C-scan inspection and X-ray photography

A few non-destructive inspection techniques were also investigated to determine whether they would be applicable for such a material. Several C/PPS panels, flat and ribbed, were C-scanned by GKN Fokker. Additionally, several G/PP and

Figure 5.8 Photograph of a C/PPS ribbed panel, highlighting the locations of the quarter panels analysed for the density and FVF measurements.

C/PPS panels, both flat and ribbed, were analysed via X-ray radiography by X-RIS (Liège, Belgium). The X-ray generator was set to a voltage ranging between 80 kV and 140 kV, and an amperage between 100 μA and 300 μA .

5.4 Results

5.4.1 Visual inspection

The C/PPS and G/PP ribbed panels were visually inspected to detect filling defects, resin rich regions, regions of poorly mixed fibres and weld lines. The panels were visually homogeneous when looking at the patterns on the surface for both C/PPS and G/PP panels. However, some regions in a few C/PPS panels were whiter, presumably because of lower fibre content locally. These resin-rich regions form up to one cluster per panel and do not seem flow-dependent. On the contrary, they likely originate in the mixed doughs: a layer of molten polymer was sometimes detected on the piston during the extrusion of the doughs, which was then partially transferred to the rear of the doughs.

Complete filling of the ribbed panels was found to be successful for an FVF below 26% for C/PPS and up to 35% for G/PP. Similarly, the C/PPS doughs at 35% could not fill flat panels completely. The cooling of the polymer during moulding increases the macroscopic viscosity, i.e. that of the dough, until the viscosity is too high to flow further with the available 200 bar pressure and 20 mm/s. The flow problems at high FVF are attributed to the increased number of fibre-fibre interactions in the high FVF doughs. Moulding G/PP was easier due to reduced fibre interactions compared to C/PPS, i.e. the average bundle aspect ratio is

different. The C/PPS panels that were fully filled included some filling defects smaller than 1 mm^3 in a few ribs, most likely resulting from the solidification and related shrinkage of the matrix during moulding. Weld lines were sometimes detected near a panel edge, for all types of panels: flat or ribbed, G/PP or C/PPS.

5.4.2 Porosity and cracks

The presence of porosity was further inspected via cross-sectional microscopy images. The micrographs revealed nearly void-free sections in most locations of the examined C/PPS panels (see Figure 5.9). Clusters of void pockets were only observed at steep thickness increases and on the edges of the panels, as in Figure 5.9-*right*. Figure 5.10 shows a cross-sectional microscopy highlighting the typical clusters of void pockets found in these locations. The size of these pockets ranges from $50 \mu\text{m}$ to $150 \mu\text{m}$ and their morphology is irregular [24]. The presence of void pockets in these regions may be the result of a pressure drop during cooling down, which is expected for these regions. Similar results were also found by Wakeman et al. [25] during the moulding of GMT.

Figure 5.9 *Cross-sectional micrograph of a thickness increase, taken on one of the C/PPS panel's edge.*

The presence of porosity was also investigated via C-scanning and X-ray radiography on C/PPS panels. The examination of the C-scans of C/PPS panels was found to corroborate the limited fraction of porosity observed from cross-sectional micrographs. Conversely, X-ray radiography by absorption seems to hardly distinguish regions with porosity from regions with local variations of the material structure. Yet, high magnification X-ray photographs were able to spot cracks at weld lines, which can be seen in Figure 5.11, for instance, where a crack was observed due to the thermal shrinkage of the two sides of the line. Aside from the crack on the weld line, no other cracks, possibly originating from matrix shrinkage, were observed by microscopy, contrary to some findings of Rasheed [5] on the non-mixed compression moulding of C/PPS flakes at high FVF.

Figure 5.10 Cross-sectional micrograph highlighting a region with the typical void pockets found around the edges and at thickness increases.

Figure 5.11 Close-up of an X-ray photograph (positive mode) on a weld line. A small crack is visible at this weld line in white (top-right corner).

This very limited porosity fraction, while difficult to measure accurately, confirms the assumption of 0% porosity used for the density measurements, detailed in Section 5.3.

5.4.3 Variations of fibre fraction and fibre-matrix separation

Density measurements were performed on four flat C/PPS panels at various quality of mixing. The local variations of FVF were obtained from the density measurements, assuming no porosity. The variations of FVF were also measured in the doughs manufactured with the same mixing settings and input flakes in Chapter 3. Table 5.1 summarises the results and qualitatively classifies the mixing quality of the panels and doughs as poor or good, based on the findings of Chapter 3. The results reveal a correlation between the standard deviations of the doughs and panels: improving the quality of mixing of the doughs increases the homogeneity of the panels. The difference between the standard deviations of doughs and panels may be due to the different measurement methods and sample sizes.

For all four panels, the variations in FVF were found to be grouped in large clusters, with a few clusters of higher and lower FVF per panel. However, no reduction in FVF was observed along the flow length, indicating an absence of flow-induced percolation for this material. As a consequence, it is suggested that the variations of FVF in the flat panels are only a result of the mixing technology, or the random distribution of fibres as in GMT and CMT [17]. The low-shear mixing technology was chosen for its ability to not break fibres, with the drawback of a limited shear rate and mixing efficiency in comparison to screw

Mixing quality	dough temp.	Mixing settings			Standard deviation of FVF in:	
		mixing speed	mixing time	fill ratio*	the flat panels (32 measur. per panel)	the doughs † (12 measur. per dough)
poor {	320 °C	5 rpm	10 min	21%	2.5%	6.1%
	360 °C	5 rpm	10 min	50%	2.2%	5.7%
good {	320 °C	15 rpm	20 min	21%	1.4%	2.9%
	360 °C	15 rpm	20 min	50%	1.6%	2.6%

*: during the mixing process, the material is not compressed and only fills part of the cavity, ranging from 20% to 50%.

†: results from Chapter 3

Table 5.1 Summary of measurements of the variations of FVF for C/PPS flat panels and doughs.

extruders. Improvements in the quality of mixing were found feasible with such technology (Chapter 3), likely leading to improvements in the variations of FVF in the moulded panels.

Density measurements were also performed on C/PPS ribbed panels at nominal FVFs of 26%. The local FVF was determined for all flat and all rib sections in the selected panels based on the Archimedes principle. Figure 5.12 shows the results for quarter panels, where all coloured cells represent a measurement of FVF, for either a rib or a flat section, and where the dough flowed from the centre of the

Figure 5.12 Measurements of the FVFs in all ribbed and flat sections for three quarter panels. The quarter panels (b) and (c) belong to the same ribbed panel (bottom-right and bottom-left quarters from Figure 5.8 respectively), while (a) is from a different panel. The selected panels are not especially well-mixed, in order to study the limits of the material and process, but were both processed with the same settings.

		Figure 5.12a	Figure 5.12b	Figure 5.12c
Flat sections	[min. - max.]	[21% - 34%]	[26% - 31%]	[23% - 29%]
	standard deviation	4.4%	1.3%	1.6%
Rib sections	[min. - max.]	[16% - 33%]	[22% - 32%]	[10% - 29%]
	standard deviation	3.9%	2.5%	3.8%
Average difference: rib sections – flat sections		-2.5%	-2.5%	-4.3%

Table 5.2 Several statistics calculated from the distribution of FVFs of the quarter panels in Figure 5.12.

panels towards the edges (Figure 5.12a). Errors in weight measurements in air and ethanol were found to account for variations up to 1% of FVF. Table 5.2 summarises some statistics for these three quarter panels. It was found that the variations of FVF are grouped in clusters and not affected by the flow, similar to the results of the flat panels. For instance, Figures 5.12a and 5.12c show regions with high and low FVF respectively in two corners instead of a decrease from the centre to the edges. Most notably, the region of low FVF in Figure 5.12c is located exactly on the region with a resin layer on the surface, mentioned earlier. This confirms that whiter regions, i.e. with higher resin content on the surface, have a low through-thickness FVF on average. The ribs were found to have a

Figure 5.13 (a) cross-sectional micrograph in a C/PPS rib, focusing on two bundles being locked, and (b) location of the locked bundles in the rib. The circle and the curve in (a) respectively highlight a bundle perpendicular to the cut plane, and the in-plane bundle locked around the former.

reduction of FVF of 2% – 4% on average compared to their surrounding flat sections, independently from the rib height-to-width ratio. Still, a few ribs were found to have an FVF higher than the flat sections around them. Fibre-matrix separation was not found to be more severe for tall or thin ribs. Similarly, no difference was found between ribs parallel and perpendicular to the flow direction. The reduction in FVF in ribs has been studied in details for GMT [18, 21, 22], both experimentally and numerically and this reduction was also found to occur in multiple situations: ribs parallel or perpendicular to the flow direction, and ribs located close or far from the initial position of the dough. Kuhn et al. [18] analysed the causes for the fibre-matrix segregation phenomenon in the ribs. They observed bundle locking at multiple locations in the ribs via X-ray tomography. However, it is unclear whether Kuhn used stitched or non-stitched GMT, which can alter the interpretation of the results. Similar bundle locking was observed by Wakeman et al. [25] in flat regions along the flow length. Such phenomena were also observed in the ribbed panels made from C/PPS and G/PP in this study. Figure 5.13 presents a cross-sectional micrograph highlighting this locking in a C/PPS rib. The bundle that is circled in Figure 5.13 is perpendicular to the cut plane, while the bundle following the curve is mostly in plane. Figure 5.14 shows an X-ray photograph of a G/PP ribbed panel where several locked bundles were observed close to the edges of the panel.

Figure 5.14 *Top view X-ray photograph of a G/PP ribbed panel highlighting bundle locking (white arrows).*

5.4.4 Fibre attrition

Carbon and glass fibre bundles were assumed to not break during the mixing phase, which was selected for its low shear forces. The moulding phase, on the contrary, can result in fibre attrition, as observed in a previous study [26]. Fibre attrition of G/PP and C/PPS was measured following the method described in Section 5.3.

The glass fibres after burn-off were found not to be reduced in length. On the other hand, the length of the carbon fibres was reduced as shown in Figure 5.15. About 50% of the fibre bundles remained at 20 mm, their original length, while the rest were reduced to lengths varying from 2 mm to 20 mm. The difference in fibre attrition between G/PP and C/PPS can be attributed to multiple factors: the different matrix viscosity under the processing conditions, and the bundle aspect ratios. Contrary to the findings of Caba et al. [26] with C/PP mat, the percentage of short fibres, i.e. smaller than 1 mm, is very limited. It is yet unclear why such a discrepancy exists between the results of G/PP and C/PPS on the one hand, and C/PP on the other hand, considering that the moulding conditions in all cases are very similar.

Figure 5.15 FLD after moulding of a C/PPS dough, highlighting the fibre attrition happening during the moulding of a C/PPS dough. All fibres measured 20 mm before the mixing and moulding phases.

Figure 5.16 Estimate of the fibre length reduction in the moulding phase for an input FLD measured in shredded C/PPS flakes. The fibre length reduction factor in Figure 5.15 is used for the calculation.

The findings on fibre attrition in the moulding phase are substantial for micro-modelling of the mechanical properties of the panels [4]. For the current purposes, however, the experimental measurements were performed using flakes of a constant fibre length of 20 mm. In order to extend these results to the case of shredded flakes, experimental measurements could be performed for these flakes. However, the FLD of these flakes is broad, ranging from 2 mm to 80 mm, and subject to variation. Accurate measurement of the fibre length reduction is hardly possible in this case, because a large number of experiments would be required to obtain a statistically reliable measure of the attrited FLD. Instead, an estimated fibre

length reduction in the case of shredded flakes was calculated. The FLD prior to processing was measured from the flakes (Chapter 2) and is shown in Figure 5.16 as a solid line. Based on that, each fibre length was assumed to be attrited similarly to the measured 20 mm long fibres (Figure 5.15). I.e. each fibre length experiences the same ‘length reduction factor’, shown in the second X-axis of Figure 5.15. The estimated reduced FLDs were calculated for all fibre lengths of the solid line distribution (Figure 5.16), and then combined to form the dashed FLD in the same figure. There is a visible, but small, reduction of the fibre lengths, which could result in a very limited impact on the overall mechanical performance of the material. This estimation may be conservative, as longer fibres tend to break more, and fibres shorter than 10 mm tend to break less, leading to a narrower distribution. The effect on mechanical performance is expected to be limited as bundles with fibres longer than the average of about 20 mm, which are more prone to break, exceed the critical bundle length.

5.4.5 Fibre orientation

The fibre orientation of moulded panels was characterised in-plane for a quarter G/PP flat panel using the method described in Section 5.3. The out-of-plane component of the fibre bundles was inspected via cross-sectional microscopy for the C/PPS ribbed panels. It is clear that the G/PP pellets and C/PPS flakes have different mesostructures, which leads to differences in fibre-fibre interactions and FODs in the doughs. Even so, the C/PPS flake structure loosens well in the mixing process, leading to entangled bundles similar to the microstructure in G/PP doughs. The characterisation of the in-plane FOD for the case of G/PP provides indications regarding the FOD of panels moulded with this recycling solution, which is expected to be similar to the FOD of moulded C/PPS.

Figure 5.17 shows the results of the G/PP quarter panel after burn-off. The identified fibre bundles from image analysis are displayed on the left side. The dough was placed in the centre of the panel, which is shown in the upper right corner of the images, and then flowed toward the edges. Figure 5.5 in the previous section illustrates the location of the analysed quarter panel. The right side shows a representation of the FOD using the local second-order orientation tensors that were computed from the distribution of bundle orientations and locations. The ellipses’ axes and orientations translate into the diagonal terms of the diagonalised second-order orientation tensors and the direction of its eigenvectors respectively [18, 27].

The ellipse’s orientations and eccentricities show that most fibres are oriented perpendicular to the flow direction. This result was expected from previous work on the rheology of SFT and LFT [18, 19], from Jeffery’s equation [28, 29], and considering the moulding conditions in this study: a no-slip condition on the (cold) walls of the mould is assumed and the material exhibits fountain-flow

Figure 5.17 Location and orientation of the identified bundles from a quarter G/PP panel (on the left) and its the local FOD represented by orientation tensors (on the right).

Orientation tensors
from experimental
measurements

Orientation tensors
from MoldFlow

Figure 5.18 Fibre orientation tensors exported from MoldFlow for a simulation of compression moulding of a G/PP dough.

behaviour. Notably, the ellipses in Figure 5.17 present large local variations of fibre orientation. These originate from the bundle interactions, and when bundles orient themselves in the flow, this creates local jamming, which is highly dependent on the initial conditions.

Most modelling approaches to compute fibre orientation treat the fibre suspensions as a single-phase fluid, with the fibre orientation taken into account with models derived from the Folgar-Tucker equation [19, 29]. The flow of highly concentrated long-fibre suspensions was proven to deviate from these single-phase flows [19], which was also found in GMT [18, 19].

A comparison between the FOD calculated with these single-phase models and the FOD measured experimentally was made, to determine the extent of the deviation. Regarding the single-phase flow, a numerical simulation of the compression moulding of a molten LFT dough was performed using MoldFlow using material properties very similar to the experimentally used G/PP LFT pellets. The calculation of the fibre orientation in MoldFlow is based on developments of the Folgar-Tucker equation [29, 30], which includes a diffusion coefficient that takes into account the interactions between fibres during the flow to a varying level of accuracy. The material for this simulation was G/PP LFT pellets with a set length of 10 mm, and an initial in-plane 2D random FOD. The orientation tensors of the bottom-left quarter panel at the last time step were exported and are shown in Figure 5.18. Similar to the experimental measurements, the fibres orient themselves mainly perpendicular to the flow direction in the MoldFlow simulation. As expected, the single-phase flow results in a homogeneous FOD,

which does not present any local variation. Simulations of LFTs using single-phase flow, especially for the present recycling solution, can still provide an estimate of the FOD of moulded components. In turn, they can help predicting mechanical performance or warpage in the moulded panels.

Apart from the in-plane FOD of moulded panels, fibre orientations may have an out-of-plane component. A strong out-of-plane component definitely leads to variations in mechanical performance compared to a solely in-plane FOD. Therefore, the out-of-plane component of the moulded flat and ribbed panels was investigated, from cross-sectional micrographs. It was found that all flat regions have primarily in-plane fibre orientation as long as the thickness does not exceed 3.5 mm. Otherwise, the FOD contains a large out-of-plane component in the core regions, as in Figure 5.9. This phenomenon also appears for thick ribs, compared to thin ribs, with their core regions containing bundles that are not parallel to the mould walls. The orientation of the ribs, perpendicular or parallel to the flow direction, was found to barely influence this phenomenon.

5.5 Conclusion

A novel recycling solution for TPCs, recently introduced by De Bruijn et al. [4] consists of the following steps: shredding, low-shear mixing and compression moulding. This recycling solution shares similarities with the compression moulding of GMT, CMT or D-LFT, both in terms of processing and material properties. However, several features make this material-and-process combination specific for this approach, with the input material, consisting of multi-layered woven flakes of a few centimetres combined with the low-shear mixing step, minimising fibre fracture but having possible limited mixing efficiency (Chapter 3).

Such highly concentrated LFT suspensions have inherent heterogeneities induced by the process or by their stochastic structure, which are known to affect the mechanical properties of moulded components. These heterogeneities include, not exhaustively, fibre orientation, fibre attrition, fibre-matrix separation, variations of fibre fraction, and fibre microstructure.

Previous research work has characterised such heterogeneities for GMT, CMT and D-LFT. The objective of the current study was to determine whether the new recycling solution and TPC scrap have such heterogeneities for C/PPS and G/PP, and if so, to compare them to the already existing LFTs described above.

The results showed that the heterogeneities in the recycled TPCs are similar to those in other LFTs:

- Little to no porosity was observed in compression-moulded C/PPS and G/PP

panels from quality inspection. Cracks may exist at weld lines, but should be prevented, as detailed in GMT guidelines.

- Some variations of FVF within the moulded flat and ribbed panels seem to originate from the input mixed doughs. Large improvements of the quality of mixing are known to be possible and are expected to lead to reduced variations of FVF (Chapter 3).
- Flow-induced fibre-matrix separation was limited and only observed in intricate features such as ribs, but not along the flow length, which is in accordance with results on GMT [18].
- Fibre attrition during the moulding phase only occurred for C/PPS, at a limited extent compared to former findings on CMT [26].
- The fibre orientation was found to deviate from the FOD results of single-phase flow simulations, as expected from such a material. Yet, the fibres mostly orient perpendicularly to the flow direction. These results are completely in agreement with general findings on the FOD in highly concentrated suspensions of long fibres [19]. The out-of-plane component of the fibre orientations was also investigated and found to be limited for sections thinner than 3.5 mm.

The similarity between the recycled TPCs and GMT or CMT is positive with respect to the understanding of this material. It improves confidence in this novel recycling solution and helps the further development of industrial applications.

Regarding the studied non-destructive inspection, several conclusion can be drawn. C-scans of C/PPS panels were successful in detecting material homogeneity in terms of porosity, yet limited conclusions can be made with this technique when it comes to small cracks, fibre orientation, fibre fraction or weld lines. X-ray radiography was better capable of detecting fibre orientation (for G/PP) and weld lines (for C/PPS). The measurement of fibre orientations from the radiographs seems challenging, and proper crack detection requires multiple, possibly laborious, radiographs. Moreover, porosities are much harder or even impossible to detect with X-ray. Other potential inspection techniques could be thermography or CT-scanning, but these have not yet been investigated in this project.

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5.A Details on the ribbed panel

Figure 5.A.1 Top view drawing of the ribbed panel highlighting the various ribs.

Rib	height [mm]	width [mm]
A	6	3
B	9	2
C	7.5	2.5
D	9	4.5
E	9	3

Table 5.A.1 Details of the ribs highlighted in Figure 5.A.1.

Chapter 6

Discussion

The previous chapters looked at a novel recycling solution, studying material properties and their relation to the processing steps. The first section within this chapter combines the previous results and puts them into perspective, while considering the main objective of the thesis. Several challenges identified for the development of recycling thermoplastic composites will then be addressed and detailed in a subsequent section. Finally, the last section will present a demonstrator that was developed to validate the technical feasibility and economic viability of the presently proposed recycling solution.

6.1 Overview of the problem

The work presented in this thesis concerns the recycling of thermoplastic composites (TPCs) by means of shredding, sieving, low-shear mixing and compression moulding. This solution was demonstrated to be able to process laminated scrap and to largely retain long fibres during processing. Hence, high-value TPC scrap such as C/PPS trims can be recycled while maintaining a high value. However, recycled materials can only be used for high-end applications if the relations between materials, processing and performance are well understood. The combination of the processes and the structure of the material presented is new in comparison to already known and standardised long-fibre composites. As a consequence, it is not yet well understood and effort needs to be put to fill this knowledge gap.

The technical feasibility and economic viability of this recycling solution is based on a couple of different objectives: performance should be maximum, consistent and predictable, while the process cycle time should be minimum or remain below a

threshold value. Considering the stochastic nature of the material being processed, these performance and processing objectives relate to specific material properties evolving during processing, as well as their relation to the process.

The results from the previous chapters helped identify some of the various interrelations between the material properties and are illustrated in Figure 6.1. The chapter numbers refer to the location where each subject is studied in more detail in this thesis. This scheme, however, follows a chronological order, from collection to re-manufacturing, and does not provide any detail on the actual relations.

The following subsections will address each of the identified important material properties separately. Their importance is discussed and put into relation to the objectives of performance and processing.

6.1.1 Fibre orientation

In the recycling route studied in this thesis, fibre orientation is never homogeneous, whether this could mean uniformly random or uniformly oriented, for instance. Instead, fibre orientation is a distribution that varies with location. In particular, Chapter 5 showed that the fibre orientation distribution (FOD) is affected by the flow field and the fibre-fibre interactions. It was found to range from nearly uni-directional (UD) to in-plane isotropic, which drastically affects local mechanical performance of moulded components. The flow-induced aspect of the FOD is strongly influenced by the part design, thus mould cavity, and the initial position of the dough. The material in this recycling solution is similar in that regard to glass mat thermoplastics (GMTs) or sheet moulding compounds (SMCs).

Local non-homogeneities of the FOD were observed due to the fibre-fibre interactions during the flow phase, which are inherent to highly concentrated long-fibre suspensions. These fibrous systems can be characterised by the number of contacts per fibre-bundle, also known as the mean coordination number $\bar{z}$, which for these materials is always above 2 [4]. The material used in this study, with bundles of about 20 mm in length and with a fibre volume fraction (FVF) >20% result in $\bar{z}$ well above 10. This evidently increases the effect of fibre interaction during flow and creates opportunities for local variations. In comparison, dilute or semi-dilute fibre suspensions have $\bar{z} < 1$, which show limited fibre interactions and their effect on FOD. The reproducibility of these non-homogeneities was not investigated per se, but the causes of variations observed within compression-moulded plates could also lead to part-to-part variations. Due to the stochastic nature of the material, bundle sizes, lengths, locations and orientations vary from dough to dough, leading to different fibre-fibre interactions. The FOD can vary locally from part to part, similarly to its local variations within a part. Besides, it is also suggested that well-mixed doughs reduce the inter-part variability, as well as a consistent and possibly automated material transfer from the mixer to the press. Good quality of mixing (QoM) also reduces the average bundle size, therefore increasing both the bundle aspect ratio and $\bar{z}$. Short fibres and low FVF would also improve reproducibility due to easier mixing and reduced number of fibre-fibre interactions. This can improve predictability and consistency of the performance, but negatively affect the maximum achievable performance. An equilibrium in terms of fibre length must be found but is currently unknown.

Regarding the predictability of the FOD, similarities were found with standard FOD simulations for short fibre composites (Chapter 5). These FOD simulations could be used for first approximations of the FOD when the engineer requires predictions of mechanical performance [4, 5]. Local non-homogeneities of FOD are however not taken into account and there is currently no accepted theory to accurately predict the FOD of highly concentrated long-fibre suspensions.

Finally, the local FOD can lead to variations in fibre compaction. Intuitively,

aligned fibres are easier to pack than fibres that are oriented isotropically in-plane. These variations are part of a larger category of flow-induced fibre-matrix segregation, which itself is influenced by the part design and is discussed in the following section.

6.1.2 Fibre content

The maximum reachable FVF of any discontinuous-fibre composite is lower than for continuous-fibre composites, mostly because of the entanglement of discontinuous fibres and bundles. In the recycling route presented in this thesis, the FVF was tested experimentally between 20% and 50%. On the one hand, a low FVF is preferable as it allows for easier moulding and filling of complex features. This is caused by the expected reduced number of bundle-bundle contacts. In that regard, anything above 35% FVF is deemed impossible especially for thin parts (<4 mm) with large areas ($>300 \times 300 \text{ mm}^2$) based on experiments, due to the long flow length and the short time at melt in the presented recycling route (Chapter 5). On the other hand, higher FVF increases stiffness, but an upper limit is usually found for strength. Such a limit was found between 35% and 50% for C/PPS recycled with the presented solution [2]. Apart from the effect of fibre content on processibility and mechanical performance, FVF can also influence QoM. During the mixing step, the two phases, matrix and flakes, must be blended evenly. It is currently unknown whether low or high FVF facilitates mixing. An optimum may exist depending on the type of mixer and the mixing mechanism selected. However, this may be an irrelevant problem since the FVF is mostly selected based on processibility and performance constraints. Overall, a sweet spot was found experimentally between 20% and 30% to balance processibility (Chapter 5) and mechanical properties [2, 3].

This range is in accordance with the FVF used in GMTs, which are typically processed with an FVF varying from 15% to 30%. Such a fibre fraction is usually a balance between reaching the maximum packing fraction of random long-fibre composites and the process constraints. Calculating the maximum packing fraction for this type of fibre network is challenging because of the fibres being flexible, bundled and oriented randomly. Closed-form solutions for *unforced packing* of rigid rods exist [6], but they do not provide information when compressed flexible fibres are used. In that regard, analytical relations between the normal stress and FVF were developed with good agreement to experiments. They cannot, however, set an upper limit to the maximum FVF due to the possible network rearrangements, either reversible or irreversible, and fibre breakage, both occurring experimentally. The optimum FVF also depends on the process route, its constraints, and the type of discontinuous reinforcement. For thin parts with a large area, an FVF of 50-60% is known to be possible for thin UD or woven flakes that are compression moulded with a dwell time of 10-20 minutes at melt [7], while 35% is currently the limit for

the proposed recycling solution.

Variations of FVF within and between components were also observed, which can increase the probability of failure upon loading, therefore increasing the variance of the mechanical property tested. This leads to lower allowable mechanical properties which is detrimental to the industrial applications of such a material. These variations are related to the dual-phase flow behaviour and to the quality of the input material. In literature, the former is usually referred to as fibre-matrix segregation [8, 9] and was found to be limited to the filling of intricate features such as ribs (reduction of FVF of 2-4%), and not present along the flow length. The latter, and most crucial in this recycling solution, concerns the variations already present in the mixed doughs. With the current mixer, it was possible to achieve standard deviations of FVF of 1.5%. Improvements of QoM, thus variations of FVF in the doughs, are known to be technically possible compared to what has already been tested. In comparison, consolidated flat panels of C/PP and C/PET mat thermoplastics (CMTs) were found to account for a standard deviation of FVF below 0.5% [10]. It would be beneficial to the presented recycling solution to reach levels similar to these CMTs to largely improve the consistency of mechanical performance.

6.1.3 Fibre length

The fibre length distribution (FLD) was determined accurately in shredded flakes. Guidelines to tailor it to requirements were found, mostly revolving around the shredder's blade width and sieve apertures. Both offcut size and layup were found to barely affect the FLD of shredded flakes. Therefore, the collection of any continuous-fibre TPC scrap of sufficient size would result in substantially the same FLD, discarding possible variability at this stage. Besides, batches of shredded flakes as small as 50 flakes, taken from the same initial population, also result in the same FLD. As a consequence, the number of flakes required to manufacture one component (50-100 flakes) is already enough to average out the differences between flakes. Chapter 2 showed that in the phase prior to mixing, the FLD is accurately known and is extremely consistent.

Fibre breakage was then found to occur in the subsequent processing steps for C/PPS, which can negatively affect mechanical performance. With the current setup and process parameters, the attrition was limited and the bulk of fibres remained in the 10-30 mm range, assumedly having a limited effect on mechanical properties. This fibre length reduction was assumed to take place mainly during the moulding step because the current mixing step works at low shear rates and speeds. Different types of mixer or different moulding conditions can lead to more fibre breakage, therefore to much shorter fibres compared to the FLD in flakes. Severe attrition is common in screw extruders for instance, with reductions up to an order of magnitude. This can lead to a detrimental reduction in mechanical

properties compared to what could be achieved with the input FLD if no attrition occurs.

After mixing and moulding, the fibre lengths might not be evenly distributed in a component, or even from component to component. In this regard, constant fibre length is probably a better choice than the distribution output by the selected shredding technology to improve part uniformity. An example of constant fibre length can be found in the thesis of Rasheed [11], in which square flakes of constant length are processed without fibre attrition. On top of that, the current definition of QoM cannot capture the evenness of the distribution of fibre length. The characterisation of QoM only considers two phases at the moment, matrix and fibres, to define their evenness or clustering. Instead, the evenness and clustering could be defined in a system of $N+1$ phases ($N \geq 1$), for the N various fibre length classes present in the system and the matrix.

6.1.4 Quality of mixing

The quality of mixing is a multi-scale aspect that ranges from the size of a cluster of a few tens of fibres to the size of a dough. It is crucial to obtain a homogeneous QoM, both intra- and inter-sample in order to obtain consistent performance. The study of mixing in Chapter 3 showed that the mean and variation of QoM improve in parallel for the two considered aspects of mixing, intensity and scale of segregation, and at all scales (from microscopic to macroscopic).

The results of Chapter 3 also detail possible ways to improve QoM. First, small flakes (size of 5-10 mm in this thesis) are easier to mix, possibly due to the reduced bundle entanglement per flake in comparison to flakes of 20 mm and above. Yet, small flakes, and therefore short fibres, negatively affect the mean mechanical performance. As QoM improves with small flakes, the variations in mechanical performance also decrease. The optimum flake size to balance the mean performance and consistency is currently unknown. Second, an improved QoM can be achieved with a longer mixing time or a high mixing speed. The former leads to more thermal degradation of the polymer during the mixing phase and increases the total cycle time, which can negatively affect the economic viability of the processing route. The latter increases the shear rates during the mixing phase and consequently increases the probability of fibre attrition.

Additionally, the effect of the FVF on QoM is currently unknown for the present low-shear mixer and for any mixer processing a combination of multi-layered woven flakes and polymer granules. Diluting flakes at 50% FVF to a dough of 20% or 30% was possible. It is however unknown whether either of the two diluted FVFs gives a better QoM.

Improved QoM was found to lead to smaller bundles, which increase the number of bundle-bundle contacts leading to a higher macroscopic viscosity. The work of

Chapter 4 focused on the rheological behaviour of doughs during squeeze flow. Their behaviour was found to be heterogeneous, due to a layered structure. Improved QoM resulted in a more homogeneous dough structure and more uniform flow behaviour at the cost of an increased macroscopic viscosity. The improvement of the homogeneity of the dough structure, resulting in more uniform flow behaviour, outweighs the drawbacks of the accompanied increase of the macroscopic viscosity.

6.1.5 Conclusion

Several material properties of the mixture of flakes and resin and their local variations are evolving during processing. The results documented in the chapters of this thesis, together with the discussion in the previous sections revealed complex relations between various material properties, the processing steps and part performance. Table 6.1 presents an overview of these relations. It shows how a factor (processing step, property) in the row x influences or imposes constraints on other factors (in y). The strength of the relations was qualitatively assessed and is displayed using varying grey levels: for strong relations; for medium-strength relations and for low-strength relations. Blank cells correspond to no known relation or not appropriate.

	Shredding	Sieving	Mixing settings	Moulding settings	Part design	Macroscopic viscosity	Performance	Mean FVF	Var. FVF	FLD	FLD attrition	FOD	FOD consistency	Mean QoM	Var. QoM	Degradation
Shredding																
Sieving																
Mixing settings																
Moulding settings																
Part design																
Macroscopic viscosity																
Performance																
Mean FVF																
Var. FVF																
FLD																
FLD attrition																
FOD																
FOD consistency																
Mean QoM																
Var. QoM																
Degradation																

Table 6.1 *Assessment of the relations between material properties, processing and performance for the current approach. The grey level of each cell shows the strength of the relation: ■ strong; ■ medium-strength; ■ low-strength. This table shows how a factor (processing step, property) in the row x influences or imposes constraints on other factors (in y).*

6.2 Challenges

The recycling solution presented in this thesis was shown to be feasible. Thorough understanding of the relations between processing and material properties was gained. The results of this thesis provide a clear future research focus. The following sections will discuss the challenges identified, classifying them in either technical or non-technical. The former concerns challenges that require engineering or scientific research, while the latter deals with the business side required to industrially implement such a recycling solution.

6.2.1 Technical and scientific challenges

Improving the mixing phase

The study in Chapter 3 aided understanding the possible improvements in QoM with measurements of evenness and clustering of the mixed system. Figure 6.2 shows the coefficient of variation of mixed systems, with data taken from Chapter 3, with the round symbols corresponding to mixed doughs made from shredded flakes, and the diamond symbols signifying low-shear mixed long-fibre thermoplastics (LFTs) and injection-moulded short-fibre thermoplastics (SFTs). Likewise, Figure 6.3 shows the bundle size distribution for those mixed systems. Figure 6.2 highlights the drastic improvement of evenness of injection-moulded SFTs over the low-shear mixed shredded flakes. The coefficient of variation of injection-moulded SFTs almost reaches the practical limit hypothesized in Chapter 3 with a random filling of non-overlapping ellipses (*random fill*).

Figure 6.2 Coefficients of variation of FVF for multiple discontinuous-fibre composites, with data collected in Chapter 3.

Figure 6.3 Bundle size distribution of multiple discontinuous-fibre composites.

It is clear that improving evenness is possible for discontinuous-fibre composites and Chapter 3 indicated that this takes place simultaneously with the reduction of the average bundle size (Figure 6.3). However, two factors might hinder reaching this optimum point with the current low-shear mixing of large multi-layered flakes.

- In practice, the prototype low-shear mixer cannot reach this optimum point. It is limited by its maximum mixing speed and the expected pure stretching mechanism. On top of that, the mixing time is limited by the thermal stability of the polymer at high temperature. In order to drastically improve QoM while limiting the processing time, it is advised to look for chaotic mixers, which improve QoM quadratically with mixing time or speed [12]. Examples include helical static mixers (main mixing mechanism: *stretch, cut and stake*) or double-screw extruders (main mixing mechanism: *stretch and fold*) [12], with the latter already used for LFTs.
- Secondly, fibre breakage might occur during mixing, especially if shear rates are excessively high. High mixing speed or harsh stretch-and-fold mixers can cause similar problems and should therefore be avoided, if retaining long fibres is the objective. Common double-screw extruders usually attrite fibres to a large extent, yet special screw designs can lead to limited fibre attrition.

The optimum reachable QoM for multi-layered woven flakes without altering the FLD is unknown, but looking into this topic is a major research direction to consider for the technical development of this recycling solution.

Unidirectional tape material

The work presented in this thesis focused on multi-layered woven material. This type of material was selected for its relevance in the current production of high-end TPCs. Future trends show a shift towards UD tape material that allows for automated processing of large parts [13]. The recycling of this type of material is similar from a processing point of view. However, mixing UD material is different. There is no weave structure to be loosened before obtaining fibre-bundles. Therefore, mixing UD tape material should be easier than mixing woven material. As a side note, the UD tapes are commonly used at a higher FVF in high-end applications, typically around 60%, which requires further dilution during mixing.

Overall, studying of mixing for UD tape material should definitely be considered, in order to achieve similar or better QoM than the one already found in the present thesis. For UD tapes as well as for woven material, high reproducibility is crucial to the performance of recycled components.

Finally, if the QoM for these two types of material is similar, they are expected to behave similarly in the processing steps following mixing.

Polymer degradation and crystallinity

The thermal history of the polymer phase and its exposition to oxygen at high temperature change its chemistry and crystallinity, in turn influencing the mechanical properties of the parent TPC and the performance of components [14]. The recycling of TPCs with the solution presented in this thesis evidently affects the polymer as the material is heated up in the mixer for a long time.

With the current low-shear mixer, the material is mixed in presence of air. This may degrade the polymer and negatively affect its crystallinity [15]. The presence of air is a known drawback of the current mixing prototype, which should be fixed before assessing the degree of crystallinity in this processing route. Additionally, thermal degradation also leads to cross-linking, which increases the polymer viscosity and thus the macroscopic viscosity of the dough [16]. Following mixing, the fast cooling step during compression moulding is similar to what TPCs experience during stamp-forming for instance, possibly leading to similar degree of crystallinity, at least for non-degraded polymers. Additionally, TPC scrap material already has a former thermal history from the manufacturing of virgin components, which can be different within a batch of scrap and can be possibly unknown.

The degradation and crystallinity of the polymer were not characterised in this thesis, even though these are crucial, because of the known drawback of the mixer employed here that does not offer an accurate representation of the conditions of an industrial setting. The extent of polymer degradation in recycled components

and its effect on the degree of crystallinity is unknown and should therefore be addressed in future research.

Pollution in TPC scrap

Most of the TPC scrap used in this study was free from impurities. The main material consisted of a single type of post-industrial waste (trims from press-forming), single material type and grade (Cetex® TC1100 5-harness satin) laminated in a quasi-isotropic layup, originating from a single manufacturing site. This is not a realistic representation of the generated post-industrial scrap in general. Discussions with fellow engineers in the field and visits to shop floors of TPC manufacturing sites provided considerable knowledge on the impurity level of TPC scrap. Figure 6.4 shows some examples of pollution that can be found in this post-industrial TPC scrap. Additionally, end-of-life waste, which can be highly polluted, will also require recycling. Most research work currently focuses on clean production scrap (Chapter 1) in order to develop the technical feasibility of any recycling solution. However, the recycling of most or all TPC waste will require solutions to handle polluted waste, either by sorting it or by down-cycling.

Figure 6.4 *Examples of polluted TPC waste, not limited to C/PPS: (1) release films, (2) oxidised matrix, (3a) sandwich structures, (4) inserts, (5) overmoulded polymer on TPC, (3b) glass scrim.*

Non-destructive inspection

Quality inspection for long-fibre composites is an important aspect that is required for industrial applications, similarly to the current status of inspection with continuous-fibre composites. Further study is required to better understand how to assess component quality for recycled materials.

Non-destructive inspection was investigated to some extent by means of C-scanning and X-ray radiography. Several material-property features were observed for either G/PP or C/PPS. Yet, no solid conclusion could be drawn from these preliminary results.

Prior to continuing research on this topic, it is also crucial to define the aspects that should be characterised. A non-exhaustive list of the observed defects or material properties (Chapter 5) includes local void fraction, FOD, local FVF or the presence of bundle locking due to flow. Besides, the understanding of the effects of these defects and properties on mechanical performance is still limited for this recycling solution [1–3].

6.2.2 Non-technical challenges

The recycling of continuous-fibre-reinforced TPCs has not yet entered its industrial phase to the knowledge of the author. Although considerable technical developments have been tackled regarding the recycling of TPCs over the past decade, multiple questions should be answered before large scale industrial applications emerge. Previous work of fellow researchers and engineers on the recycling of thermoset composites (TSCs) is a good example to understand what is to be expected for TPCs. In 2011, Pimenta and Pinho [17] pointed out several key challenges regarding recycling TSCs, most of which are currently relevant for TPCs:

- From a business perspective, “market identification and product pricing” have to be determined along with life cycle analyses.
- A global strategy bringing together collectors, recyclers and users in a network must be developed. Similar approaches already exist for the recycling of polymers with the Plastic Recyclers Europe and the Association of Plastic Recyclers (North America).
- Network members must cooperate to develop a functional supply chain.
- A market for recycled products, which matches the market demand for recycled components and the supply of waste, should be established.

In addition, personal discussions with TPC experts enabled the author to identify several other challenges before industrial applications of recycled TPCs are fully implemented.

- Traceability of waste along the recycling route must be maintained and the recycled products should be certifiable especially if aerospace TPC waste is recycled to aerospace products.
- Legislative incentives should be stronger to discourage or ban landfill. The cost of landfill in the European Union is currently up to 100€/ton [18], which is negligible compared to the price of aerospace TPCs in use. This does not encourage the aerospace sector to become more active regarding recycling.
- Engineers should be trained to develop recycling in their companies, to be able to design recycled products and understand the economic value in scrap material.

In the past decade, the recycling of continuous-carbon-fibre TSCs has grown considerably and the industry has seen the establishment of several recyclers such as ELG Carbon Fibre Ltd (United Kingdom) or carboNXT GmbH (Germany). The current main logistic status for recycling TSCs involves the collection of waste at various manufacturing sites and their transport to recycling companies. The sorting, comminution and fibre reclamation steps are performed at the recyclers, which then sell recycled fibres as a semi-product. Material also needs to be re-certified if required. Different grades of carbon fibres may be blended together making recycled carbon fibres a blend product. Recyclers are to set a competitive price for recycled carbon fibres in order to establish a market.

Regarding continuous-fibre TPCs, the recycling market is evidently not mature enough to answer all the issues listed above and implement industrial solutions similar to that of TSCs. Additionally, the volume of high-end TPC waste is small compared to continuous-carbon-fibre TSC waste, which makes the out-sourcing recycling approach of TSC not economically viable for TPCs. Yet, small steps in the direction of industrial recycling can help the researchers and engineers move forward. The first industrial stepping-stone for the recycling of TPCs could take a different path than for TSCs, which solves some of these issues.

In-source recycling approach

The following approach was mainly developed considering the high-end TPC market, which makes recycling more economically viable due to the high value of the material. The approach consists of fully in-sourcing recycling at the manufacturing sites. Scrap material is collected and sorted within a site, then shredded and re-manufactured in-house. The recycled components become part of the product portfolio of the company.

The application of this recycling approach to the aerospace market allows for recycling post-industrial scrap from an aerospace program into components for the same program. First of all, this approach simplifies the material traceability significantly since materials of the same batch can end up both in the virgin and recycled components for the same assembly. The virgin material being already certified, its recycling to aerospace applications is further eased. The logistics behind this approach are evidently easier than having to form a network of scrap producers, collectors and recyclers. Yet it requires the manufacturing site to produce enough scrap for recycling to be economically viable and requires the company to have engineers trained to design recycled parts. The supply-demand paradigm can be solved, at least partially, when such an approach is implemented for multiple aerospace programs for multiple components. This way, most of the recyclable scrap produced at a manufacturing site can be recycled into parts to be assembled to the virgin structures.

This approach is possible for TPCs because manufacturing processes required for recycling are either inexpensive (shredding), already known or in use (extrusion compression moulding). This opportunity is not present when recycling TSCs due to the thermal or chemical fibre reclamation processes. Applications of such recycling route should be assessed considering the possible net-shape components, complex geometries and fast processing time. These can lead to both weight and cost reductions for well-chosen stiffness-dominated designs in comparison to their legacy counterparts that are either metallic or continuous-fibre reinforced plastics. Nevertheless, this approach might not be the selected global solution when looking 30 years from now when TPCs are employed at a larger scale, but has the advantage to be viable for small volumes of high-value scrap which is the current situation for TPCs.

6.3 Application

The technical feasibility and economic viability of the recycling solution presented in this thesis is illustrated with an access panel demonstrator developed in collaboration with GKN Fokker (the Netherlands) and the ThermoPlastic composites Application Center (the Netherlands). This panel sought to demonstrate the possibility of using the in-source recycling approach detailed earlier to recycle high-end TPCs into aerospace applications.

The strategy relied on recycling post-industrial scrap from the manufacturing of TPC ruddervators for the Bell V-280 Valor into access panels for the same aircraft's V-tail [3, 19]. TPC scrap is collected at GKN Fokker and recycled using the solution presented in this thesis.

The technical development of the access panel followed the traditional 'Building Block Approach' [3], the knowledge gathered in this thesis and in the work of De

Bruijn et al. [1, 2]. Coupons were first tested to determine allowable mechanical properties. Manufacturing guidelines and process parameters were identified from the work in this thesis, especially from Chapters 3 and 5, in order to select possible design features for this panel. Upon iterating the access panel design, the most critical design detail was tested for validation. The finalised design was put to production and is shown in Figure 6.5. Prior to the delivery of access panels to the client, the panels were tested on component level under real case loading conditions. Further details on the technical development of this demonstrator is available in [3].

Figure 6.5 *Aerospace demonstrator developed with GKN Fokker and TPAC [3]. The edges are coated with a primer paint, which is why they appear light blue.*

This demonstrator also showed that weight reductions are possible using this recycling solution over traditional continuous-fibre composites, especially for these non-structural stiffness-dominated designs [3]. Significant cost reductions were found possible due to the short cycle time of such a recycling solution and the inexpensive input material, consisting on mostly in-house scrap. Regarding the present access panel, a flight test demonstration with both the virgin TPC structure and recycled TPCs components installed on the aircraft is scheduled for 2019.

Overall, this collaborative work demonstrated the feasibility and viability of designing an aerospace TPC structure using virgin material alongside with recycling the former TPC structure's scrap into non-critical components for the same assembly. Most engineers are currently not trained to design recycled TPC components, possibly because the primary objective is performance, among others criteria, over material efficiency. If more emphasis were put to material efficiency, the further developments and applications of recycling would lead to the possibility to deliver near-zero-waste TPC shipsets in aerospace.

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Chapter 7

Conclusions and recommendations

7.1 Conclusions

The recycling of thermoplastic composites by means of shredding, low-shear mixing and compression moulding was investigated in this thesis. The main objective was to develop the technical feasibility and economic viability of this recycling solution, with a focus on identifying and characterising the relevant material properties and their relation to the processing steps for the present recycling solution. This section summarises the main conclusions from the obtained results.

- Multiple-shaft shredders are suitable to comminute consolidated thermoplastic composites (TPCs) into flakes of centimetric size. This technique barely produces dust and fine particles thanks to the size reduction mechanism that shears the incoming material instead of impacting it. Analysis tools were developed and implemented to measure the fibre length distribution (FLD) of flakes, which can be performed automatically with high accuracy. Such methods could be implemented in inline scanning devices to measure the FLD right after shredding for instance. These methods helped to understand how to tailor FLD to specific requirements, making use of blade width and sieving. Shredding TPC scrap was also found to show very little variability for two reasons. Firstly, the scrap size and layup barely affect the FLD of shredded flakes. Secondly, the FLD of single flakes is different for each flake, but the number of flakes used to manufacture a part similar to the flat and ribbed panels in this thesis (50-100 flakes) is already enough to average out the differences between the flakes. This results in extremely reproducible FLDs in series production of recycled components.

- During the mixing phase, the multi-layered and woven structure of flakes are disentangled to bundles of varying size, with limited attrition, if any. Low-shear mixing is also capable of lowering the fibre fraction of flakes evenly by the addition of virgin polymer granules. A study on the quality of mixing was performed, using image analysis of cross-sectional micrographs. Improving the quality of mixing for all measured aspects was found possible by using flakes with shorter fibres or by increasing the total deformation, which can be performed by increasing the mixing time or mixing speed.
- The stochastic nature of recycled TPCs is similar to that of long-fibre composites such as glass mat thermoplastic (GMT), sheet moulding compound or bulk moulding compound. The fibrous network has inherent heterogeneities originating from the mixing process and material itself. In the present recycling solution, the quality of mixing was found to be a major cause of some of those heterogeneities. Improving the quality of mixing can result in more reproducible components.
- The squeeze flow of this material revealed complex macroscopic behaviours, with the activation of multiple shear planes in the thickness of the material, which makes modelling challenging. These likely originate from the poor mixing phase. Additionally, no clear distinction of behaviour was found when changing the fibre content or the FLD of doughs, although this was expected. The improvement of the quality of mixing due to the shorter fibres or the low fibre content is probably not enough to change the flow behaviour of doughs.
- In terms of design and processing guidelines, complex geometrical features are possible, which in turn are beneficial to part performance. It was found that following the usual guidelines for GMT to design and process parts give satisfactory results.

7.2 Recommendations

The work in this thesis constituted a first step towards understanding the material and process interactions in the presented recycling solution. This section proposes some recommendations for future work on the recycling of TPCs based on the results and conclusions of this thesis.

- The degree of crystallinity of the matrix, if semi-crystalline, is an important parameter that drives its mechanical properties. In turn, it influences the mechanical properties of the parent TPC, and thus the performance of components under load conditions. It was not studied in this thesis

but deserves attention for future research. The degree of crystallinity is strongly affected by the TPC's thermal history, which includes the mixing and compression moulding phase for the present recycling solution.

- The quality of mixing of the doughs with the current mixer could be improved upon. Although the results showed ways to improve the quality of mixing, the present mixer had some technical limitations. If an upgraded version of the low-shear mixer were considered, it would be advisable to look at chaotic mixing mechanisms, instead of the current linear and pure stretching mechanism.
- Impurities in scrap were observed. Their separation from the TPC waste has not been studied in detail but deserves attention. If they are not separated from the TPC waste, they can negatively affect mechanical properties, although this effect is currently poorly quantified.
- Non-destructive inspection was investigated by means of X-ray radiography and C-scanning, yet the study was not extensive enough to lead to solid conclusions. Further study is required to assess the possibility of quality inspection for recycled TPCs made of long fibres, because non-destructive inspection of recycled components will likely become required when recycling is implemented industrially.
- This thesis focused on the recycling of multi-layered and woven TPCs as a main material. In the TPC sector, woven fabrics are currently more often used than UD tapes. This trend may however shift in the future because UD tapes can help reaching higher production rates thanks to possible automated placement and make the manufacturing of large structures possible. In order to anticipate for this possible shift, future work should consider the recycling of UD TPC tapes, both in a prepreg and consolidated form. In particular, it would be advisable to study the mixing of UD material in order to achieve similar quality of mixing (intensity and scale of segregation) for both woven and UD material. In turn, this would lead to similar behaviour in the subsequent processing steps for both types of material.

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Guillaume Vincent

Publications

Journal articles

1. G.A. Vincent, T.A. de Bruijn, S. Wijskamp, M.I. Abdul Rasheed, M. van Drongelen, R. Akkerman. Shredding and sieving thermoplastic composite scrap: Method development and analyses of the fibre length distributions. Published in: *Composites Part B: Engineering*, 176, **2019** (Chapter 2 of this thesis).
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9. I. ten Bruggencate, T.A. de Bruijn, G.A. Vincent, F.W.J. van Hattum. Design, manufacturing and testing of a safety shoe nose cap from recycled glass fibre polypropylene. *SAMPE Europe Conference 2019 Proceedings*, **2019**, Nantes, France.

Awards

1. CAMX 2019 'Unsurpassed Innovation Award' finalist. A rotorcraft access panel from recycled carbon PPS. Anaheim, CA, USA. September 2019.
This submission is a collaboration between TPAC, TPRC, GKN Fokker and the other TPC-Cycle consortium partners. Details on the demonstrator can be found in Section 6.3 of this thesis.