



## Adhesion of RFL-treated Short-cut Aramid Fibres to Sulphur and Peroxide-cured Elastomers

10<sup>th</sup> Fall Rubber Colloquium

*Morteza Shirazi, Auke G. Talma and Jacques W. M. Noordermeer*

*University of Twente, Elastomer Technology and Engineering Department,  
7500 AE Enschede, the Netherlands  
Dutch Polymer Institute DPI, 5612 AB Eindhoven, the Netherlands*

### ABSTRACT

The performance of fibre-reinforced composites is strongly dependent on the nature and the strength of the fibre-matrix interface. Good interfacial bonding is required to ensure load transfer from matrix to reinforcing fibres. For rubber reinforced composites, Resorcinol Formaldehyde Latex (RFL) is known as a fibre surface coating which is able to provide good adhesion between rubber and fibres. But the performance of this substance in many cases can be largely affected due to exposure of the coated fibres to air and light. Moreover, most data available in literature concern sulphur-cured elastomers only.

In the present study aramid fibres are investigated. The adhesion of these fibres in compounds based on sulphur-cured NR and peroxide-cured EPDM is investigated after being coated with RFL which is the most common adhesive coating for various sort of fibres, including aramid. The effect of physical interaction between fibres and rubbers is shown to be minor, and the effect of aging of RFL on its ability to bond with rubbers using peroxide and sulphur curing systems are shown. As a result of aging, ozone is able to decrease the double bonds of the latex part of the RFL, which negatively affects the RFL-rubber adhesion in sulphur-cured systems, while it has almost no effect in peroxide-cured systems. It is also discussed that, unlike in sulphur vulcanization in which bonding happens just between the latex in the RFL and rubber, peroxide is able to generate bonds between elastomer and the resin structure of the RFL-coating.

## INTRODUCTION

Fibre-rubber composites are broadly applied. Examples of applications are car- and bicycle tyres, high-pressure hoses and conveyor belts, timing belts, V-belts and radiator hoses. By far the largest of all these areas of application are the car tyres. The application of cords in tyres is essential as the cords prevent large deformations of the rubber material when excessive forces are applied.

The properties of polymer-fibre composites are strongly dependent on the interfacial adhesion between fibre and the matrix and a stronger interfacial bond generally results in better properties. But the concept of strength of the interfacial bond is not always clear. In case of perfect adhesion, the matrix or the fibre breaks before the interfacial bond. In absence of adhesion, essentially no work is required to separate the surfaces of the matrix and fibre phases, even though the two surfaces may appear to be in contact. However, even in the case of no adhesion, work is still required to pull a fibre out of a block of the matrix because of the squeezing force exerted on the fibre as a result of mismatch in coefficient of thermal expansion and cooling down of the composite from the fabrication temperature. Between perfect adhesion and no adhesion there can be many gradations [1].

According to Allan [2], three forces need to be considered for particular problems of adhesion: Mechanical forces, Secondary (van der Waals) forces and Primary valence forces (responsible for the majority of chemical bonding). Elsewhere [3] he adds two more forces which can be important for particular applications: Electrostatic and Diffusion.

According to Gent [4]: "It has been questioned whether interfacial chemical bonds are formed at all. It has been suggested that a strong joint would be developed from dispersion forces alone and that the covalent bonding at the interface is not really necessary. It has also been suggested that a high density of interfacial bonding would be detrimental, making the joint brittle and weak. It has (now) become clear that chemical bonding at the interface is, indeed, a strengthening feature, but that it must take a particular form, using long extensible molecules at interfacial ties, to be most effective."

The most important and powerful adhesion mechanism for rubber-fibre adhesion is to form covalent bonds or chemical adhesion. A common method to increase the adhesion is by fibre surface treatment, using for example Resorcinol Formaldehyde Latex (RFL); the adhesive treatment for various types of fibres differs. Aramid fibres are normally coated with an epoxy sub-coating and an RFL-layer on the top. The latex used in many cases consists of polymerized styrene (about 15%), butadiene (about 70%) and vinyl pyridine (about 15%) monomers. The adhesive layer is applied on a cord by a so-called dipping process. Details of this process can be found elsewhere [5]. Several studies have shown that the structure of the cured RFL consists of a continuous resin phase and dispersed latex particles [6, 7].

For RFL-coated cords in matrices with sulphur-curing systems, it is suggested that diffusion of sulphur takes place from the rubber compound into the RFL dip film. Sulphur can interact with the latex portion of the RFL and rubber matrix and can form a sulphur cross-link [8]. The migration of sulphur, Zinc and accelerators into the RFL dip has been proved with EDX measurements [9-11].

A drop of adhesion measured after RFL aging for sulphur-cured systems is reported by other researchers [12-13]. The highest concentration of curatives is in the interface of RFL-

Latex [9-10] and it is known that the capacity of sulphur as a crosslinking agent requires allylic protons that are provided by unsaturation (double carbon-carbon bonds) in the elastomer chains [14]. If the saturation of double bonds as the result of ozone attack decreases in the outer layers, the possibility of interfacial bonding between latex and rubber decreases. Atmospheric ozone reacts readily with C=C double bonds, leading to the breakage of molecules on the surface. As a result, small, deep fissures (i.e. ozone cracks) are formed if the rubbers are exposed to ozone and stretched by more than about 10%. Cracks 1 mm long appear in unprotected rubber after a few weeks of exposure to typical outdoor ozone (typically ca. 5 parts per 100 million)[15].

Wenghoffer [13] showed that the decrease in adhesion level of RFL-coated cords in an aging process becomes faster when the concentration of ozone increases. Hartz and Adams [16] also reported that the adhesion drop of RFL-coated cords in rubbers is much faster when they are exposed to ozone, and ozone-UV systems compared to several other environments. It is explained that the adhesion loss due to aging is the result of addition reactions to the olefinic double bonds to reduce unsaturation sites for cure.

In a previous study [17] mechanical properties of two different rubbers, Natural rubber (NR) and Ethylene Propylene Diene rubber (EPDM) reinforced with short aramid fibres, coated with Standard treatment (St) and RFL-coated (applied on an epoxy pre-coating) have been investigated. The standard treatment is an oily substance applied on the fibre surface to facilitate the processing of the fibres and does not have a negative effect on adhesion [18]. The results showed that in all cases, peroxide-curing systems lead to a better degree of reinforcement than sulphur-curing. In the present study, doing different tests on long fibre composites, the chemical bonding as the strongest type of interaction between RFL and these rubbers, and the effect of curing systems are further investigated in order to shed more light on the main mechanisms involved in creating a strong, durable bond.

## EXPERIMENTAL

Materials: two types of elastomers were used: Natural Rubber (NR): SMR CV60 and Ethylene Propylene Diene Rubber (EPDM): Keltan<sup>®</sup> 8340A with 5.5 weight percent Ethylidene Norbornene (ENB) content, and 55 and 39.5 weight percents of Ethylene and Propylene respectively. The fibres were aramid type: poly(para-phenylene terephthalamide) or PPTA, Twaron<sup>®</sup> type 1000, 1680 dtex produced by Teijin Aramid B.V.; The RF and RFL-coatings preceded by an epoxy pre-coating took place on a Litzler single end Computreater.

Two masterbatches were made in a 150 liter industrial internal mixer. The compositions of the two compounds which can be considered as a typical truck tire tread and a radiator hose compound are presented in Table I. The curatives were added on a laboratory two roll mill. Fibres with three different kinds of surface treatments have been used. The treatments were Standard Finish, RF (without Latex) and RFL-coating.

The cure characteristics of the compounds were measured with a Rubber Process Analyzer (RPA) of Alpha Technologies, and according to the results the compounds were cured at 140°C for NR and 170°C for EPDM for their  $t_{90} +6$  minutes.

The surface tension of fibres and rubbers has been determined by measuring the contact angle of the liquids with known surface tensions, namely water and CH<sub>2</sub>I<sub>2</sub>. For rubbers, to avoid the effect of surface oxidation, the measurements have been done on fresh surfaces made by cutting, creating a cross section of the materials.

For aging, RFL-coated fibres were exposed to atmospheric conditions at room temperature for 1 week. Some of the fibres were kept away from light, which are referred in the text as aged in darkness.

Strap Peel Adhesion Force (SPAF) tests were done on long fibre composites in accordance with ASTM D 4393. Composites were made with cord and rubber layers with the test specimen dimensions of length: 110±5 mm and width: 20 mm. The build-up of layers was: rubber (2mm) - cord - rubber (1mm) - cord - rubber (2mm). The samples were cured in a hot press at 140°C (NR) and 170°C (EPDM) for their t<sub>90</sub> + 6 min. The peel tests were performed at a rate of 100 mm/min. To do the adhesion tests also in the shear mode (Lap Shear), the same type of SPAF samples were used, but cut differently and the force was applied to them in such a way that the interface was exposed to shear, see figure 2.

## RESULTS AND DISCUSSION

Figure 3 and 4a show the result of SPAF tests for NR and EPDM compounds containing St and RFL coated fibres. As was expected no chemical bond happens between St fibres and either EPDM or NR, resulting in significantly lower peeling force and no rubber coverage remaining on the fibres, which shows that failure happens in the adhesive mode exactly on the interface.

The effect of secondary (Van der Waals) forces is reflected in the thermodynamic work of adhesion which can be calculated by Dupré equation:

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12} \quad (1)$$

i.e. the thermodynamic work of adhesion, W<sub>a</sub>, is equal to the sum of the surface free energies of the two substances less the interfacial free energy. The surface tension values and the interfacial tensions can be determined based on the contact angle measurements of the liquids with known surface tensions with equations below: [19]

$$(1 - \cos\theta_1) \gamma_1 = 4\{(\gamma_1^p \gamma_s^p / \gamma_1^p + \gamma_s^p) + (\gamma_1^d \gamma_s^d / \gamma_1^d + \gamma_s^d)\} \quad (2)$$

$$(1 - \cos\theta_2) \gamma_2 = 4\{(\gamma_2^p \gamma_s^p / \gamma_2^p + \gamma_s^p) + (\gamma_2^d \gamma_s^d / \gamma_2^d + \gamma_s^d)\} \quad (3)$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - [4 \gamma_1^d \gamma_2^d / (\gamma_1^d + \gamma_2^d)] - [4 \gamma_1^p \gamma_2^p / (\gamma_1^p + \gamma_2^p)] \quad (4)$$

θ<sub>1</sub> and θ<sub>2</sub> are contact angles of liquid 1 and 2, γ<sup>p</sup> is the polar and γ<sup>d</sup> is the dispersive surface tension values for each solvent and the solid surface (polymer). The total surface tension of the solvent (1) would be (γ<sub>1</sub><sup>p</sup> + γ<sub>1</sub><sup>d</sup>) and for the solvent (2), (γ<sub>2</sub><sup>p</sup> + γ<sub>2</sub><sup>d</sup>). The results of contact angle measurements, the calculated surface tension γ for the rubbers, the interfacial tension between rubbers and fibres and the work of adhesion are presented in Tables 2-3. Here, water and CH<sub>2</sub>I<sub>2</sub> were used with surface tension values of:

Water (72,8): dispersive = 21,8 and polar = 51,0

Diiodomethane (50,8): dispersive = 50,8 and polar = 0,0

As can be seen both rubbers have higher work of adhesion with St-fibres which is not in accordance with the SPAF results, figure 3, which indicates that RFL-coated fibres have much better adhesion to both EPDM and NR. This is an indication that secondary Van der Waals forces are not the main source of adhesion in these chosen systems. As a consequence, regarding the mode of the application of the force, the strong interaction for RFL-coated fibres must then be due to chemical interaction.

Figure 5 and 4b present the SPAF results after aging for the RFL-coated fibres in both matrices. The sulphur-cured NR loses adhesion strength very fast by aging. This is even more dramatic when the fibres are not kept in darkness. Please note that the rate and extend of the decrease of adhesion depend also on the actual rubber formulation.

The peel strength of the peroxide-cured EPDM sample however remains unchanged. The aged RFL fibres showed total rubber coverage after the tests for EPDM and no coverage for NR, indicating that strong bonds form between aged-RFL and EPDM resulting in failure in the bulk of rubber: cohesive failure. There is no strong interaction between aged-RFL and NR and failure happens on the interface.

The shear tests show also the same trend, though the drop in properties after aging for NR is not as dramatic as for the SPAF test: figure 6. This can be attributed to the additional effect of the other reinforcement mechanism: mechanical interlocking between the fibres roughened as the result of application of the RFL layer, and the surrounding matrix, which is an important parameter when a shear force is applied on the surface of fibres.

This lap shear test can also be representative for the tensile properties of the rubber reinforced with short fibres, tested in longitudinal direction of fibre orientation [17]. For such samples it has been observed that:

1. Using already aged RFL-coated short fibres, still a considerable degree of reinforcement was obtained, and
2. Peroxide curing system resulted in higher degree of reinforcement both for EPDM and NR.

For NR with the sulphur curing system it can be argued that aging might result in the removal of carbon-carbon unsaturation in the latex part of the RFL on the surface due to the exposure to ozone, which restricts its ability to take part in the co-vulcanization process with the rubber phase. On the other hand, for peroxide curing systems the existence of the double bonds is not necessary, as it is known<sup>20</sup> that peroxides are able to react equally well with saturated polymer chains.

But a question still remains. Does peroxide like sulphur generate bonds just between rubber and latex or is it able to react with the resin part of RFL as well? To investigate that, some fibres were coated with just RF (without Latex). The SPAF and Lap Shear results are presented in figures 7, 8, 4c and 4d. In both SPAF and Lap shear results, NR shows no indication of adhesion to RF-coated fibres. The adhesion drops till close to the St-coated fibres and no sign of rubber coverage could be detected on the fibres after the test. But for peroxide cured EPDM the situation is rather different. The drop in adhesion by replacing RFL-coating with RF is not as much as for the sulphur-cured NR and some degree of rubber

coverage is observable on the fibres after the tests. This indicates that peroxide indeed has the ability to react with both the resin structure and the latex.

## **CONCLUSIONS**

The adhesion of RFL-coated fibres to two different industrial rubber compounds with peroxide and sulphur curing systems have been investigated with SPAF and lap shear tests. The results showed that un-aged RFL is able to generate good adhesion to both rubbers. The calculation of physical forces proved that these cannot be responsible for the strong interaction between RFL-coated fibres and elastomers. It was shown that mechanical interlocking increases the total interaction between (roughened) fibres and rubbers when the tests are done in the shear mode.

Tests with RF-coated fibres and aged RFL-coated fibres, showed that in sulphur-cured NR, chemical bonds are generated with the latex particles in the RFL structure, so that rubber and latex co-vulcanize. Aging results in saturation of the outer surface of the latex which in addition contains the highest concentration of curatives. As a result the adhesion forces decrease significantly. For peroxide-cured EPDM, chemical bonds are also generated between latex and rubber, but peroxide is able to connect the rubber to the resin as well to some extent. Considering this and also the fact that peroxide is able to generate cross-linking even in polymers with saturated chains, the adhesion between such systems and rubbers should not be affected by aging. This latter has been proved by the adhesion experiments.

## **ACKNOWLEDGEMENT**

This study is part of the research program of the Dutch Polymer Institute (DPI), under project # 664. The authors gratefully acknowledge Teijin Aramid B.V. for their supports and Dr. M. de Rooij from the department of surface and tribology, University of Twente for his comments.

## REFERENCES

1. L. E. Nielson and R. F. Landel, *Mechanical Properties of Polymers and Composites*. Ch. 8, 2nd ed., Marcel Dekker, New York (1994).
2. K. W. Allen, *Journal de Physique* **3**, 1511 (1993).
3. K. W. Allen, *Int. J. of Adh. & Adhesives* **23**, 87 (2003).
4. N. Gent, *Int. J. Adh. & Adhesives* **1**, 175 (1981).
5. D. B. Wooton, *The Application of Textiles in Rubber*. Ch. 5, Rapra Publishing, Exeter, UK (2001).
6. G. Gillberg and L.C. Sawyer, *J. Appl. Polym. Sci.* **28**, 3723 (1983).
7. D.B. Rahrig, *J. Adhes.* **16**, 179 (1984).
8. R. Durairaj, *Resorcinol: Chemistry Technology and Applications*. Ch. 6, Springer Pub., Germany (2005).
9. B. Wennekes, *Adhesion of RFL-treated Cords to Rubber*. Ph.D. Thesis, University of Twente, the Netherlands, Enschede (2008).
10. W.B. Wennekes, R.N. Datta and J.W.M. Noordermeer, *Rubber Chem. Technol.* **81**, 523 (2008).
11. B.C. Begnoche and R.L. Keefe, *Rubber Chem. Technol.* **60**, 689 (1987).
12. E. K. Bradley, *Humidity and atmosphere affect dipped cord adhesion properties, Rubber and Plastic News*, p 46–48, May (1984).
13. H. M. Wenghoefer, *Rubber Chem. Technol.* **47**, 1066 (1974).
14. C. P. Rader, *Basic Elastomer Technology*. Ch.7.A, K. C. Barnawal and H. L. Stephens (Eds.), American Chemical Society, Rubber Division, USA (2001).
15. A. Y. Coran, *J. Appl. Polym. Sci.* **87**, 24 (2003).
16. R. E. Hartz and H. T. Adams, *J. Appl. Poly. Sci.* **21**, 525 (1977).
17. M. Shirazi and J. W. M. Noordermeer, *Rubber Chem. Technol.* **84**, 187 (2011).
19. P. J. de Lange, P. G. Akker, S. Willemsen, and R. N. Datta. *J. Adh. Sci. Technol.* **23**,139 (2009).
19. S. Wu, *Polymer interface and adhesion*. Ch. 3 and 5, Marcell Dekker pub., USA (1982).
20. J. B. Class and P.R. Dluzneski, *Basic Elastomer Technology*, Ch. 7.B, K. C. Barnawal and H. L. Stephens (Eds.), American Chemical Society, Rubber Division, USA (2001).

**Table 1: Composition of compounds.**

<i>Component</i>	<i>NR</i>	<i>EPDM</i>
NR (SMR CV60)	100	-
EPDM (Keltan <sup>®</sup> 8340A)	-	100
Carbon Black (N220)	55	-
Carbon Black (N550)	-	105
Oil	8 (Nytex 840)	60 (Sunpar <sup>®</sup> 2280)
Stearic acid	2	1
ZnO	5	-
6PPD	2	-
TMQ	1.5	-
Wax	2	-
PEG2000	-	2.5
TBBS	1.5	-
Sulphur	1.5	-
Perkadox 14/40	-	7.5
TRIM	-	4

**Table 2: Contact angles and surface tension of fibres and rubbers.**

<i>Material</i>	<i>Angle (deg.)</i>		<i>Surface tension (mJ/m<sup>2</sup>)</i>		
	<i>H<sub>2</sub>O</i>	<i>CH<sub>2</sub>l<sub>2</sub></i>	<i>Total</i>	<i>Disperse</i>	<i>Polar</i>
Standard Fibres (St)	32,7	26,7	75	45	30
RFL dipped fibre	112,3	55,4	32	32	0
EPDM	102.9	57	33.2	32	1.2
NR	106.7	56.6	32.2	32.2	0

**Table 3: Interfacial tension and work of adhesion (mJ/m<sup>2</sup>).**

	<i>St</i>		<i>RFL</i>	
	Interfacial Tension	Work of Adhesion	Interfacial Tension	Work of Adhesion
<i>EPDM</i>	32.2	76	24.2	40
<i>NR</i>	32.1	73.8	0	63.9

Figure 1: Proposed RFL morphology.

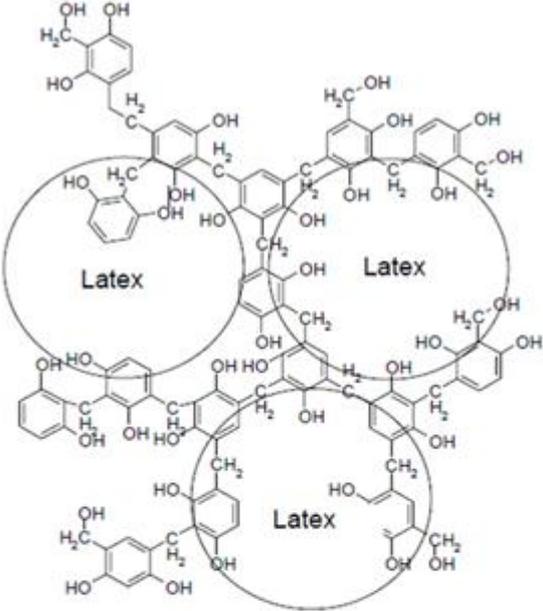


Figure 2: Sample preparation for shear test (Lap Shear).

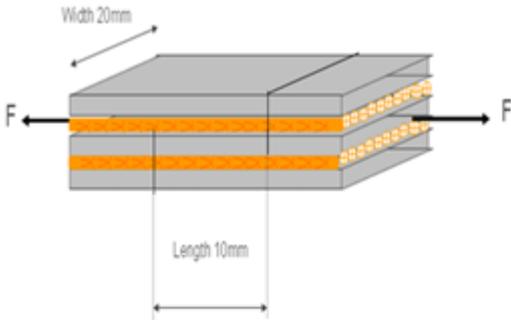


Figure 3: SPAF results (N/mm).

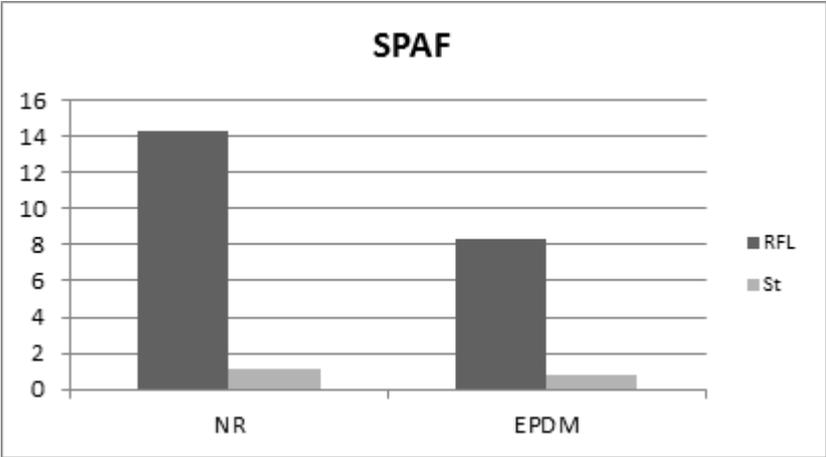


Figure 4: Samples after SPAF/ Lap shear tests.

- a. SPAF samples NR and EPDM with St and RFL-coated fibres.
- b. SPAF samples NR and EPDM containing RFL- coated fibres 1 week aged in light.
- c. SPAF samples NR and EPDM with St and RF-coated fibres.
- d. Lap shear samples NR and EPDM with St and RF-coated fibres.

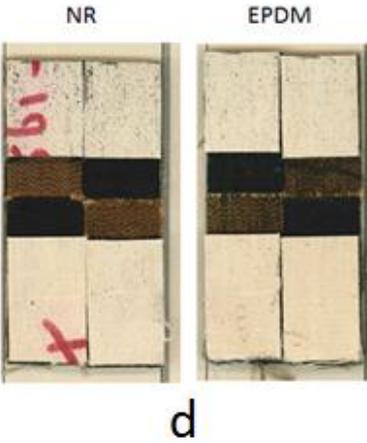
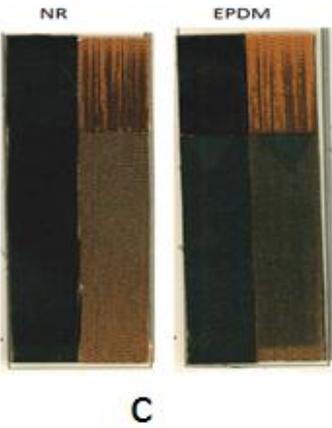
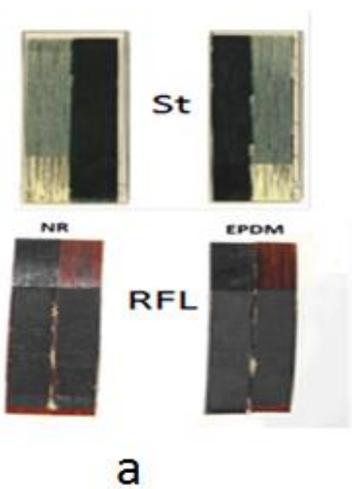


Figure 5: SPAF results(N/mm) for RFL-coated fibres fresh and after 1 week aging.

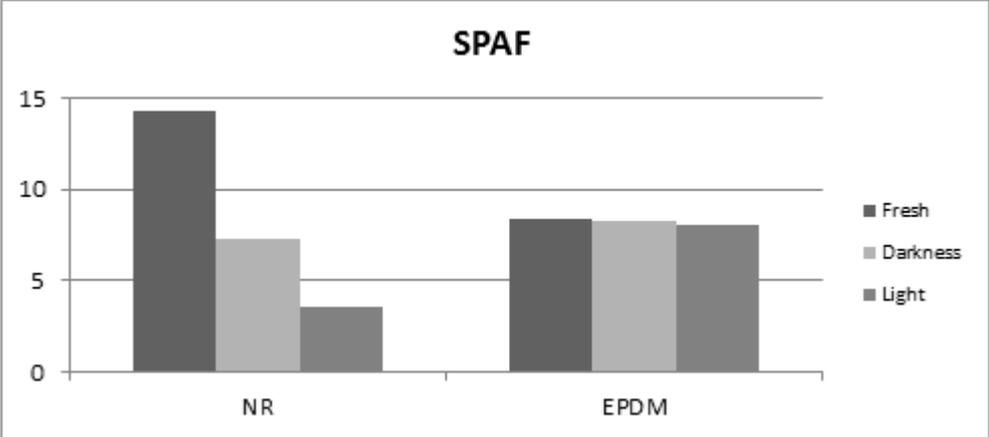


Figure 6: Lap shear (MPa) results for RFL-coated fibres fresh and after 1 week aging.

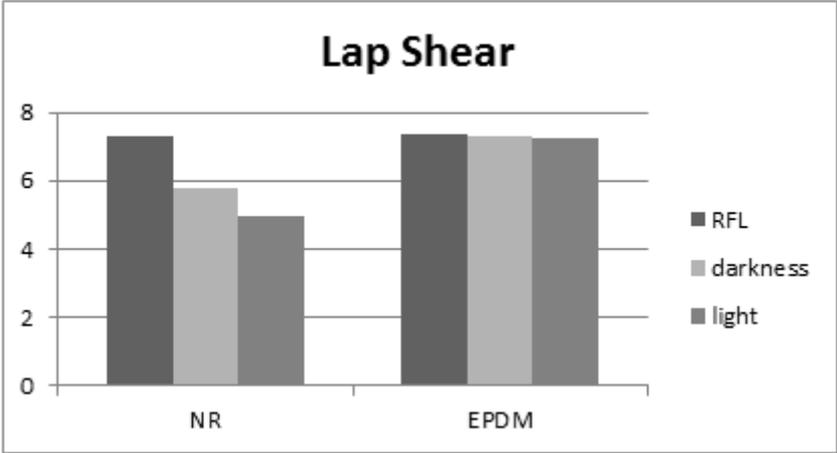


Figure 7: SPAF results (N/mm) for RFL, RF and St-treated fibres.

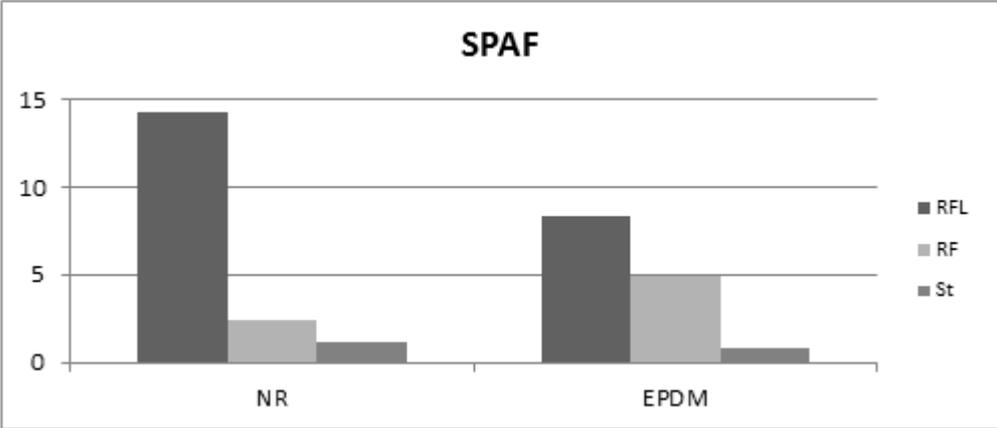


Figure 8: Lap shear (MPa) results for RFL, RF and St-treated fibres.

