AROMATIC POLYAMIDE SHORT FIBRES-REINFORCED ELASTOMERS:

ADHESION MECHANISMS AND THE COMPOSITE'S PERFORMANCE PROPERTIES

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DISSERTAION

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Morteza Sadat Shirazi

born on 19th of September 1981
In Tehran, Iran

This dissertation has been approved by:

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“The eternal secrets, neither you know nor I,
And answers to the riddle neither you know nor I
Behind the veil there is much talk about us,
When the veil falls, neither you remain nor I.”

“Some are thoughtful on the way of religion
Some think that they’ve found the truth
I hear the hidden voice that may shout
O ignorants, none of you have found the right path.”

Omar Khayyam 10-11 Century

To my mother and my wife

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Introduction

Elastomers are a special class of polymeric materials. Their unique properties as high elasticity, good flexibility, high elongation at break, etc. make them suitable for different applications such as tires, hoses, conveyor belts, sealing profiles, and many others.

Despite their special morphology and structure , almost no elastomer can be used in its original form because of its low strength. Lack of crystallinity and being far above their T_g in application temperatures, makes them rather weak. This problem can be overcome by vulcanization and reinforcement. Vulcanization involves the generation of crosslinks between polymer chains usually with mono or polysulphidic bridges or with peroxides which create carbon-carbon bonds. Reinforcement is done in most cases with reinforcing fillers such as carbon black and silica. If still extra reinforcement is needed, then composites are made with different sorts of fibres. Examples of such composites are tire layers, belts and hoses.

Composites in general are well-known classes of materials and a lot of publications can be found on their different aspects. But still, though being used for a long time, the amount of literature related to composites with rubber matrices is significantly less compared to the other types of matrices, such as epoxy or polyester resins; and there are different unknown aspects in this respect. Several reasons can be mentioned to be responsible for that, for example difficulty in determining the Young's modulus of rubbers, their complicated stress-strain behaviour, co-curing between rubber and fibre-coating resulting in adhesion, etc.

Different fibres are used from a long time ago to reinforce rubber matrices. Polyester and Polyamide fibres are very well known classes of such materials. But in general the stress transfer between rubber and fibres will be poor if they are not treated to promote adhesion. Several attempts have been made to treat the fibres with different methods, among which Resorcinol Formaldehyde Latex (RFL) can be claimed to be the most successful so far and a lot of industrial examples of RFL-coated fibres can be found used to reinforce elastomers. In spite of a long tradition of using such fibres, there are still unclear points in their reinforcement mechanisms.

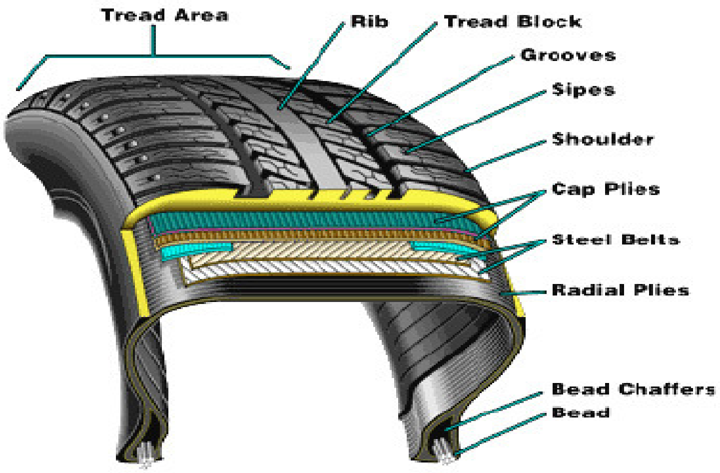

Figure 1: Construction of a tire, a well-known example of rubber composites.

Use of short fibres is rather new compared to the continuous long ones, especially for elastomer reinforcement. Though the properties of long fibre composites are generally not achievable with short fibres, the reason to replace them with short fibres is mainly to reduce the production costs, while keeping the properties acceptably high. But by making the fibres short, different questions arise. For example is it possible to use the same adhesive treatment as on the long fibres? Are the treatments as effective in reinforcement as for long fibres? Are the reinforcement mechanisms the same as for long fibres? Etc.

These and similar questions are subjects of three PhD researches funded by the Dutch Polymer Institute (DPI) which are performed in University of Twente (UT) and Leibniz Institute of Polymer Research in Dresden, Germany (IPF). The three aspects that were focused upon were:

1. The group of Elastomer Technology and Engineering at the UT: short fibre-rubber interaction,
2. IPF: the processing of short fibre reinforced composites,
3. The group of Surface Technology and Tribology at the UT: the frictional performance of short fibre reinforced rubber composites,

In the results presented here the aim was to answer questions about fibre-rubber adhesion and interaction as much as possible. After a literature review, experiments start with short fibres in the first three chapters and then two chapters deal with long fibres. The fact is that it is exactly in the same order that the research has been performed. In accordance with the title of the thesis the research was started with studying short fibre composites. Different reinforcement mechanisms and their differences with long fibres have been investigated, but as a result it was noticed that there are unknown points in the interaction between an RFL layer and elastomers regarding the effect of aging, the influence of the type of curing system, the role of polymer diffusion, etc. To investigate these aspects and to research different reinforcement mechanisms without additional effects of fibre length and dispersion, the simpler systems made with long fibres were chosen. It was tried during different chapters to explain the differences between long and short fibres as much as possible. It should also be mentioned that the set-up of the thesis is in a such way that every chapter can be read independently. Chapters 2 to 6 are papers which are either published or submitted for publication in different journals and are presented here also in the format of the separate journals, only with some adjustments.

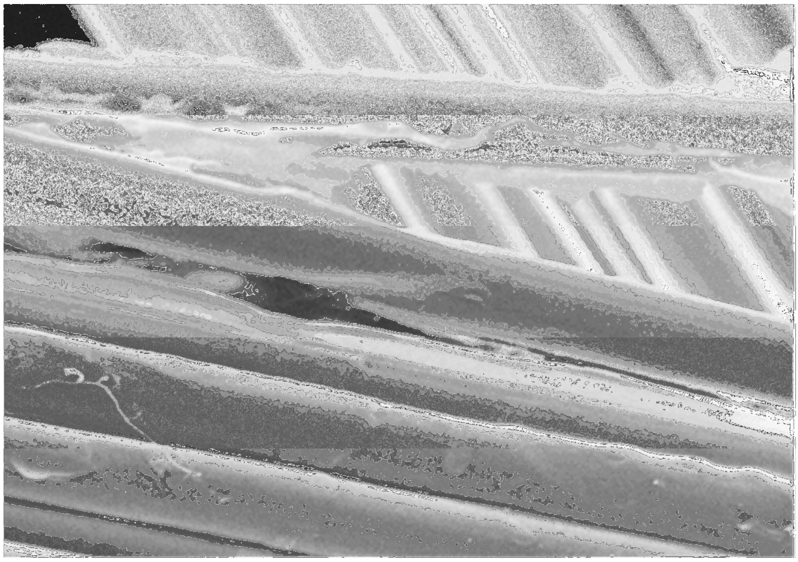

Figure 2: RFL-coated short aramid fibres.

The structure of the thesis in more details is as follows:

1. The first chapter reviews different literature sources of short-fibre reinforcement.

2. In the second chapter factors influencing reinforcement of rubbers with short aramid fibres, such as fibre surface treatments and rubber curing systems are investigated. The mechanical properties of such composites are studied and different reinforcement mechanisms are listed.

3. The third chapter deals with the differences between industrial elastomer compounds and model compounds without carbon black. Morphological studies are presented and the effects of fibre type, length, dispersion, etc. on the final properties are shown.

4. Due to the great importance of the dynamic properties of rubber parts, chapter four is dedicated to viscoelasticity of short-fibre reinforced rubbers and different factors which influence the hysteresis of such composites.

5. In the fifth chapter, the reinforcement mechanism of RFL-treated fibres is the subject of investigation. The effect of aging, and the role of chemical bonding in adhesion are the main subjects of this chapter.

6. In chapter six, due to the significant importance of adhesion of RFL-treated fibres to elastomers, the study of such fibres is continued. Here, the compatibility between elastomers and RFL and the role of polymer diffusion are paid close consideration.

7. Finally the last chapter is the overall conclusion of the thesis.

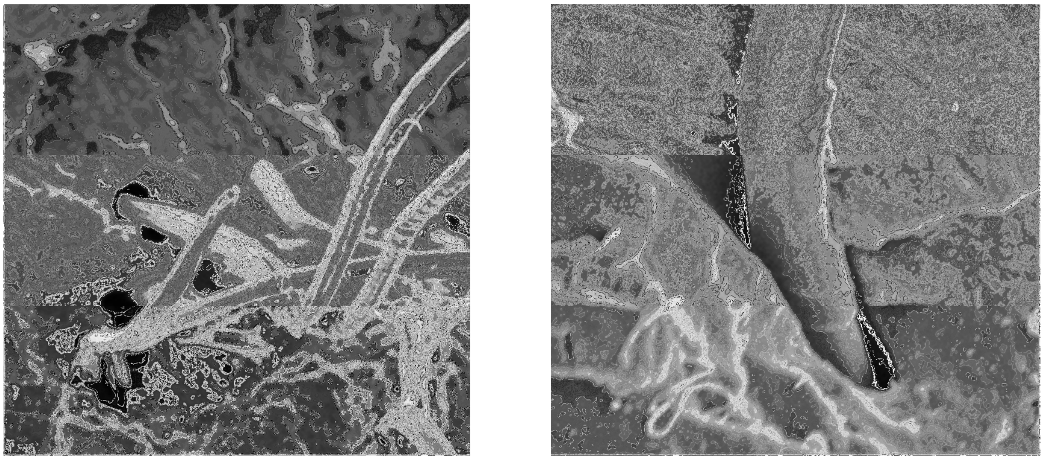

Figure 3: Short aramid fibres in tensile fracture surface of rubber composites.

Chapter 1

Review on Short Fibre-Elastomer Composites

INTRODUCTION

A composite material is defined as a macroscopic combination of two or more distinct materials having a recognizable interface or an interphase region between them. However, because composites are commonly used for their enhanced properties, the definition can be restricted to include only those materials that contain reinforcing materials. Thus, composites typically have a fibre or particle phase that is stiffer and stronger than the continuous matrix phase. In other words, a composite might be considered as a substance which consists of two or more phases acting together to produce characteristics not attainable by either constituent alone.

Fibre-reinforced rubber composites are characterized by the extremely low stiffness of the rubber matrix compared to that of the reinforcing fibres. Both continuous and short fibres are used to reinforce the rubber matrix; the most significant example for the former is the use of fibre-reinforced rubber in pneumatic tires [1]. The fibre reinforced composites with the best mechanical properties are those with continuous fibre reinforcement. Such materials cannot be adapted easily to mass production and are generally confined to products in which the property benefits outweigh the cost penalty [2].

SHORT FIBRE COMPOSITES

Short fibre reinforced composites are finding ever-increasing applications in engineering and in consumer goods. The term “short fibre” means that the fibres in the composites have a length which is neither too high to allow individual fibres to entangle with each other, nor too low for the fibres to lose their fibrous characteristics. The term “composites” as mentioned signifies that the short fibres and the rubber matrix remain recognizable in the designed material [1].

Fibre reinforcement improves the stiffness and the strength, and for many polymers it improves the toughness, though the toughness may decrease in polymers that are already tough before reinforcement. The dimensional stability is improved and, in the case of rubbery composites, better green strength is obtained. Some other benefits which can be obtained are creep resistance and better aging and weathering properties, and even improving the conductivity by adding conductive fibres for some special applications.

Generally, short fibres are used to reinforce polymers in order to improve or modify certain thermo-mechanical properties of the matrix for specific applications or to reduce the cost of the fabricated article [3]. By adding suitable fibres and by controlling factors such as the aspect ratio, the dispersion and orientation of fibres, and the fibre-matrix adhesion, significant improvements in property can be achieved with thermoplastic, thermosetting and rubbery polymers [2]. As the continuous phase of the composite, the matrix must serve not only as a protective binder, but also as the stress transfer medium between the applied forces and the short reinforcing fibres. The shear modulus of the matrix is a critical parameter in developing fibre stress, and matrix failure, usually in shear at the fibre interface, limits the reinforcing potential of the fibre [4].

Among different short fibre reinforced composites, those with rubbery matrices are obtaining an increasing importance due to the advantages they impart in processing and low cost coupled with high strength. These composites combine the elastic behaviour of rubber with strength and stiffness of fibre. Moreover, reinforcement with short fibres offers some attractive features such as design flexibility, high modulus, tear strength, etc. Short fibre reinforced rubbers are successfully used in production of V-belts, hoses, tire treads and complex-shaped mechanical goods [5, 6].

MIXING AND PROCESSING OF SHORT FIBRE COMPOSITES

Generally, Short fibre reinforced composites can be processed in a similar manner to the matrix. So, short fibres can be incorporated directly into the rubber compound along with other additives, and the resulting composites are suitable for the standard rubber processing steps such as extrusion, calendering, and the various types of moulding operations (compression, injection, and transfer) and uneconomic methods such as wrapping are not required. Economical high volume outputs are, thus, feasible. This is in contrast to the slower processes required for incorporation and placing continuous fibres [4].

On the other hand, one advantage of continuous fibre composites is the continuous nature of the reinforcement as a consequence of the highly parallel fibre orientation. In short fibre composites the fibre orientation distribution is less perfect and in many cases is random. As a result, the degree of anisotropy is generally less than in continuous fibre composites, but it is often significant and must not be overlooked by product designers [2].

Mixing- Since the dispersion process involves separation of the individual fibres from the fibre bundles, a minimum force has to be reached to overcome the aggregate entanglements. A simple theory of drag forces that describes the dispersion of carbon black into a rubber matrix also applies for fibre dispersion. The theory states that dispersion occurs only if the ratio of dispersive force to aggregative force exceeds a threshold value. Thus depending on the matrix viscosity, some minimum shear rate is required to disperse the fibres. Higher shear rates serve to improve fibre dispersion, but may be detrimental to the aspect ratio of brittle fibres. But even the slowest speeds in an internal mixer can generate sufficiently high shear rates to disperse treated cellulose fibres [4].

The dispersion of fibres in a rubber matrix can be affected by factors like mixing protocol, mixing time, and the rubber matrix viscosity. The internal mixer fill factor and mixing conditions can affect the state of fibre dispersion as well as the degree of fibre damage, which in turn alter the mechanical properties of the vulcanized composites. The mixing action is improved when the internal mixer’s chamber is less full as long as there is sufficient charge to keep pressure against the ram. Fibre dispersion is also affected by the mixing time. A longer mixing time and generation of greater energy through increasing mixing speed or the viscosity of rubber stock are favourable for improved fibre dispersion. Increasing the compound’s viscosity increases the power input, which has two beneficial effects on the mixing process: total energy input builds faster with time, and higher stresses are generated to disperse the fibres more easily from their highly concentrated initial state into the final composite [1, 7].

While mixing short fibre-rubber compounds using conventional rubber mixing equipment, it should be noted that the presence of the reinforcing fibres causes a higher rate of heat generation. To avoid scorching of the compound, it may therefore be necessary to reduce the batch size by about 10% and run the mixer at lower speed or, to use as low a volume content of short fibres as possible. A high volume content of fibres makes the compound difficult to handle in many instances; moreover, every advantage in improved properties may become obscured and expensive during processing as compared to other methods of reinforcement [1, 7].

Fibre Orientation in Processing- Fibres orient during processing and consequent fabrication, depends upon the nature of the flow, i.e. convergent, divergent, and elongational or shear. If flow is of the convergent type, the fibres align themselves in the direction of flow (parallel) and divergent flow leads to the alignment of fibres away from the direction of flow (transverse). In elongational flow, the fibre orientation takes place mainly in the direction of the applied force. In shear flow, fibre orientation can be from random to unidirectional depending on shear rate [8].

There is a linear relationship between fibre dispersion and composite tensile strength and modulus [4] and the fibre orientation also has a pronounced effect on the mode of composite fracture, thereby it influences the mechanical properties [8, 1]. Since the direction parallel to the fibre alignment shows the highest reinforcement, it is useful to control orientation to meet the anticipated loads on the fabricated part. Furthermore, the well-aligned specimen can be used to characterize the mechanical properties of the composite in a controlled and symmetric morphology. Randomized fibre patterns result only when the flow kinematics is carefully controlled to balance the orienting forces in all directions [4]. Normally the achievement of 100% orientation, in short-fibre-rubber composites is quite impractical if the standard rubber processing and fabrication techniques are used. However, depending on the fibre type and loading, and on ordinary rubber compounds, it is not difficult to orient the majority of the fibres [8, 9].

In a milling process, usually a high degree of fibre orientation can be achieved by repetitive passing through a two-roll mill. Fibre orientation depends on mill opening, number of passes, nip gap, mill roll temperature, friction ratio of the mill and mill roll speed. However, according to Goetler et al [4] mill opening is the most important factor and neither rolls speed, nor roll speed ratio have influence on fibre orientation. In extrusion the area ratio in expanding dies is the most important variable influencing fibre orientation into a circumferential direction transverse to the streamline. Other orientations are also feasible by changing the geometrical configuration of the extrusion die. In calendering, the fibre orientation occurs preferentially in the machine direction [1, 10].

Characterization of Fibre Orientation- Generally, mechanical methods like modulus measurement, ultimate tensile properties and tear strength, solvent swelling, and morphological analyses, are methods for analysing the fibre orientation [10]. Although for the composites with transparent matrix, the extent of orientation can be determined by microscopic techniques; this method is very tedious and is no more reliable than the one which infers the degree of orientation through comparison of physical property data in the direction of intended orientation (machine direction) and in a perpendicular direction [9].

The swelling method has been used by several authors [8, 11] to determine fibre orientation; this method is based on the fact that solvent swelling in a solvent is restricted by the constraining fibres. This constraint in any given direction is related to the elastic modulus in the direction. In fact, the swelling increases while increasing average fibre angle (θ) and is found to be maximum when θ becomes 90°.

Foldi [9] used a mechanical method and, from the difference in green strength in Machine Direction (MD) and Cross Machine Direction (CMD), after the milling operation, he estimated the extent of orientation as 85-95% for nylon, 75-90% for polyester, and 53-75% for glass in different Styrene Butadiene Rubber (SBR) based compounds that he tested. He also observed that there was an increasing efficiency of orientation with increasing loading for most fibres with the notable exception of the polyester, which had a tendency to ball up rather than disperse at loadings greater than 10 phr.

O’Conner [12] investigated different fibres in Natural Rubber compounds, using a microscope. He concluded that aramid and nylon tend to clump together and do not disperse easily. Ashida [10] writes that “it is difficult to mix short fibres longer than 4 mm in length in the mill and the fibres are dispersed very poorly in the composite, but short fibres of 2 mm in length are easily mixed up to 25% volume and are dispersed well in the composite”.

Fibre Breakage during Mixing and Processing- Another important factor that should be considered is that processing of short-fibre reinforced composites is always associated with certain extent of fibre breakage. Fibre length in these types of composites is critical; it should not be too long or the fibres will be entangled with each other causing problems of dispersion, on the other hand very small length of fibres does not offer sufficient stress transfer area to achieve any significant reinforcement and the fibres thus become ineffective [1]. Because of the high viscosity of rubber compounds, short fibres are buckled and broken by high shear stress during the mixing process and their fibre length distribution is different from the original length. Brittle fibres such as glass and carbon are very hard to incorporate without drastic reduction of the fibre length. They have been seen to reduce to such a low aspect ratio as to give a relatively poor performance as reinforcement for elastomers [4].

Ashida [10] mixed Chloroprene Rubber (CR) compounds with short fibres that were 6mm in length, using an internal mixer and a two-roll mill. He classified the distribution of fibre length as one of the three types depending on fibre species, as shown in figure 1. According to his results, short fibres of Poly Ethylene Terephthalate (PET) and Vinylon (trade name for a fibre, based on poly vinyl alcohol developed in Japan) retain their original length of 6 mm without breakage (breakage in negligible) (I). Nylon, aramid and rayon fibres are buckled or broken and give rise to a broad distribution in a range of shorter lengths (II). Carbon and glass fibres are broken into much smaller pieces and their lengths reduce to about 150 µm (III).

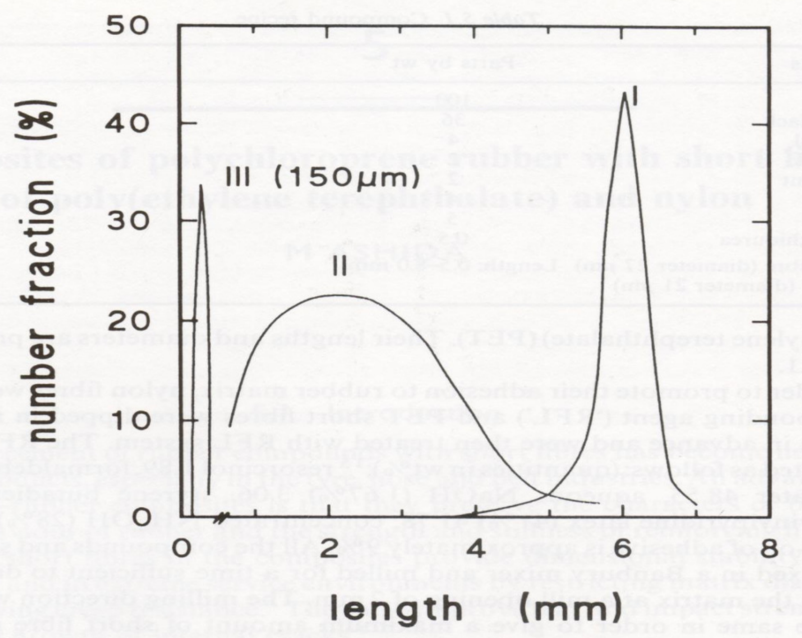

Figure 1: Length distribution of fibres after mixing [10].

MECHANICAL PROPERTIES

A major factor in the successful use of elastomers is the possibility to improve their mechanical properties by adding reinforcing ingredients such as carbon black, silica, etc. It is evident that the addition of suitable short fibres together with other fillers results in further improvement in mechanical properties. In fact, in short fibre reinforcement of rubber, the elasticity of the rubber with the strength and stiffness of the fibre are combined [3, 7]. The presence of fibres also, results in higher green strength, reduced yield point, and increased hardness. For example nylon and aramid caused 27 to 29 fold improvements in green strength over a typical control stock at only 10 phr loading [9].

Generally, the degree of reinforcement depends upon the nature of the matrix, the type of the fibre, the concentration and orientation of fibres, fibre to rubber adhesion (generation of a strong interface), fibre length and aspect ratio of the fibre [4, 5, 6].

Effect of the Nature of Matrix-The matrix material plays a major role in the composite. It serves as the stress-transfer medium between the applied forces and the discontinuous medium. The shear modulus of the matrix was shown to be critical in developing fibre stress, and generally the fibres are more effective in reinforcing higher modulus materials [13]. According to Goettler and Shen [4] short fibres are of necessity less effective in reinforcing low modulus materials than rigid ones, for the efficiency of reinforcement, that is the extent to which a discontinuous fibre can approach the performance of a continuous filament or cord, depends critically upon its modulus ratio relative to that of the matrix.

Effect of Fibre Concentration- Another factor which has great influence on the properties of composites is fibre concentration. The stress-strain curves for PET fibre-CR composites loaded with different concentrations of 2 mm fibres are shown in figure 2. The stress of the composite loaded with 5% volume fibre increases gradually as the strain is increased and, after yielding at an elongation of about 28%, a nearly constant stress is maintained similar to the behaviour of the composites containing 10% volume of fibres 1 mm long or shorter. On the other hand, for the composites loaded with fibre to over 10% volume the tensile stress increases monotonically with increasing strain until failure occurs [10].

Generally, when fibres are added to an elastomeric compound, even when the fibres are strongly bonded to the matrix, the tensile strength first drops due to a dilution effect, and then increases. In fact, when the matrix is not restrained by enough fibres, high matrix strains result at relatively low stresses. The effect is either to break or to debond the fibres before failure of the entire composite occurs. The matrix strength is diluted by the “holes” resulting from the broken or debonded fibres. Once enough fibres are used to sufficiently constrain the matrix, the addition of more fibres increases the strength of the composite even to the levels well above the strength of the matrix rubber. However this can be overdone since, as processing difficulties arise from excessive fibre loadings, imperfections occur due to extremely high viscosities, poor flow characteristics, etc [10].

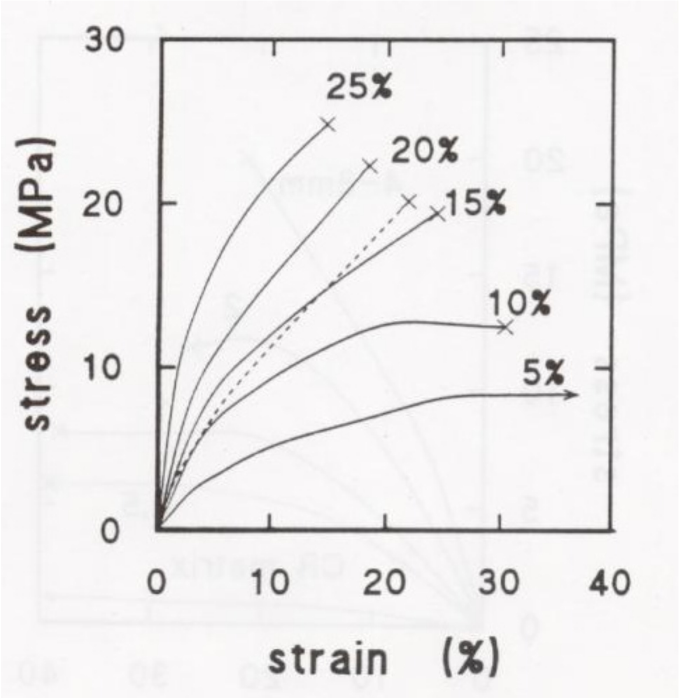

Figure 2: Effect of fibre loading on stress-strain curves of PET fibre-CR composites loaded with 2mm long fibres. Dashed line is the composite loaded with 10% volume 6mm long fibres [10].

Figure 3 gives the effect of fibre concentration in Natural Rubber (NR)/SBR-Cellulose fibre composites tested by Coran et al. [11]. This type of curve is typical of many composites. The minimum volume of fibre is known as the critical volume above which the fibre reinforces the matrix. The critical volume varies with the nature of fibre and matrix, dispersion of the fibres, fibre aspect ratio, fibre-matrix interfacial adhesion, etc. For example, the use of longer fibres can move the position of the minimum in the strength curve to lower fibre concentrations. It also can be seen that the ultimate elongation is approximately inversely proportional to fibre concentration, which could have been expected before, because the function of fibres is to restrict the composite matrix [1, 8, 11].

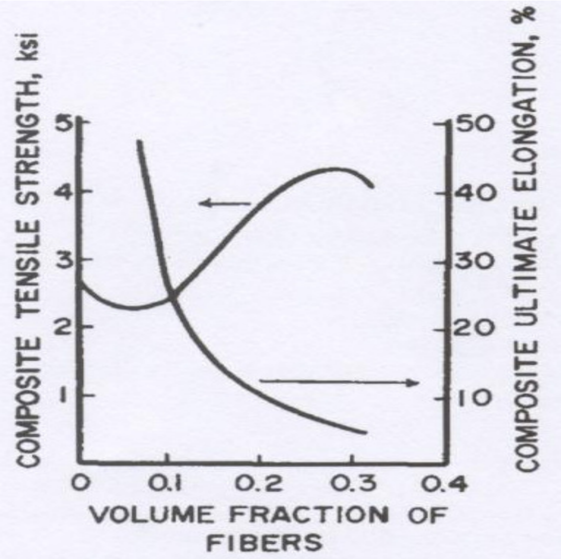

Figure 3: Effect of fibre concentration on tensile strength and ultimate elongation in NR/SBR-Cellulose fibre composites [11].

The results given by Ashida [10] show that the tensile strength of PET fibre-CR composites loaded with fibres less than 1 mm in length decreases almost linearly with increasing fibre loading, as shown in figure 4, while on loading with fibres longer than 2 mm in length the tensile strength falls steeply to the minimum value at 5% volume loading, then the plot reverses and the strength increases with further increase in fibre loading (like typical figure 3). The elongation at break of these composites falls gradually as the loading with short fibres that are 1 mm or less in length increases, which is similar to trend to the tensile strength. The elongation at break of composites loaded with fibres that are 2 mm or more in length decreases in the same way as on loading with the short fibres up to 5% volume loading, but at loadings over 5% volume it falls markedly and an inflexion point appears corresponding to a change at the minimum value of the tensile strength.

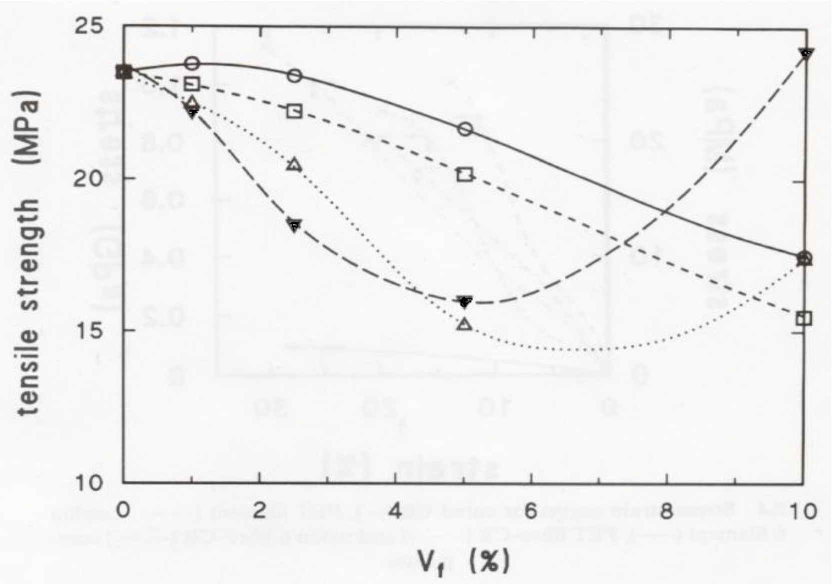

Figure 4: Effect of fibre loading (V_f) on tensile strength of PET fibre-CR composites loaded with fibres of (○): 0.5mm, (□): 1mm, (Δ): 2mm, and (▼): 4mm in length [10].

O'Connor [12] investigated the effect of fibre content on tensile strength and Young's modulus for different fibres- NR with a hexamethylenetetramine, resorcinol (HR) bonding system; tensile strength in longitudinal direction and Young's modulus in transverse direction can be seen in figures 5 and 6. Tensile strength in the transverse direction also was measured which showed a complete independence of fibre content and type. In this case, the strength depends on the elastomer matrix, which is weakened by the presence of transversely aligned fibres.

Effect of Fibre Length-As pointed out above, fibre length has a great importance in reinforcement. It is because of two main reasons [14]:

1- The fibre length controls how effective the fibre is in carrying load,
2- The number of fibre ends affects the fibre/fibre interaction, and the average strain enhancement the fibres will experience, as a consequence of the strain concentration from fibre ends.

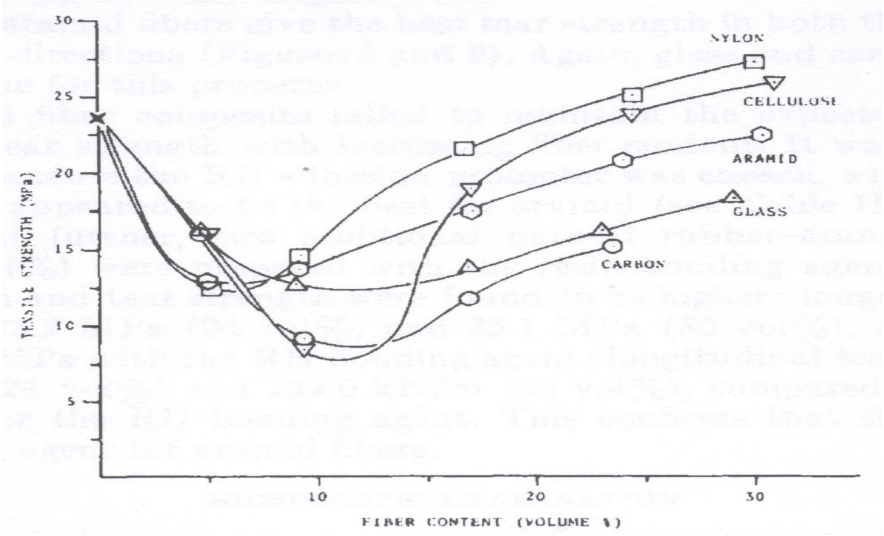

Figure 5: Effect of fibre content on tensile strength of various short fibres reinforced natural rubber ; HR bonding system; longitudinal fibre direction [12].

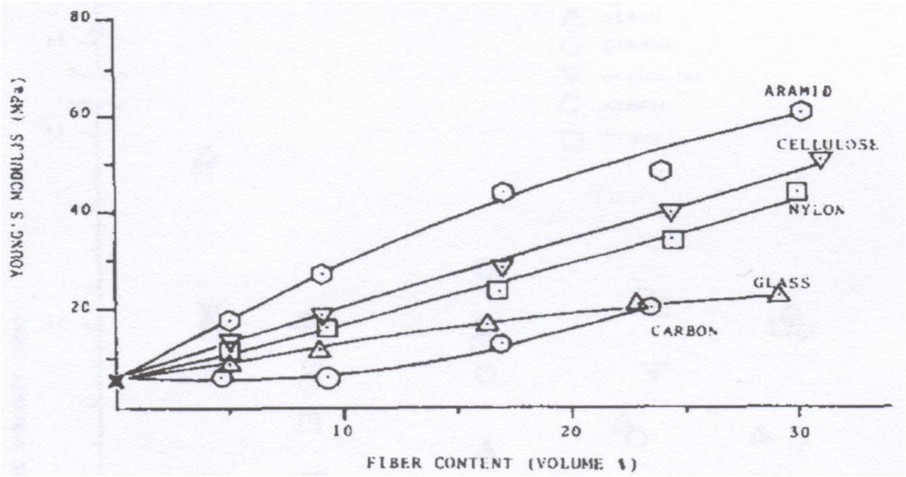

Figure 6: Effect of fibre content on Young's modulus of various short fibres reinforced natural rubber; HR bonding system; Transverse fibre direction [12].

The distance along the fibre to go from zero loads to the applied load (or some percentage of the applied load) is called the stress transfer length. For fibres with higher aspect ratios, there will be a long, uniformly stressed region in the middle of the fibre. In a long fibre composite (LFC) the majority of the fibre will see this uniformly strained region because of the long-fibre length. In a short fibre composite (SFC) only a small section will see the uniformly strained region. Therefore, the inability of a SFC to reinforce as well as a LFC lies in the smaller length of the constant load region in the middle of the fibres and more regions of load transfer near the fibre ends [14].

It is clear from above definition that there is a minimum length of fibres, which is needed for effective stress transfer. This length is called the critical fibre length and it is twice the stress transfer length; below which the fibres cannot be loaded to reach the applied composite strain, or loaded high enough to cause failure. Fibre slip occurs when the fibre length is less than the critical fibre length; because no effective stress transfer is possible in this condition [1, 14]. The critical fibre length (l_c) for fibres with uniform radius can be calculated with [1]:

$$(l_c/l) = (\sigma_{fu}/2\tau_y) \qquad (1)$$

Where l is the fibre length, σ_{fu} is the ultimate fibre strength and τ_y is the matrix yield stress in shear.

The effect of fibre length on the stress-strain curves for PET fibres-CR composites loaded with 10% volume fibre is shown in figure 7. It can be seen that for composites loaded with PET fibres from 4 to 8 mm in length, the tensile stress increases monotonically with strain until on elongation under 20% at about 20 MPa stress. For composites loaded with PET fibres that are 1 mm or less in length, the tensile stress increases gradually with increasing strain until the yield point at an elongation of about 20%, and then it approaches a plateau. In contrast, the composite loaded with 2 mm PET fibres breaks soon after the yield point. Therefore, it seems that 2 mm is the critical fibre length to reinforce this class of composites [10].

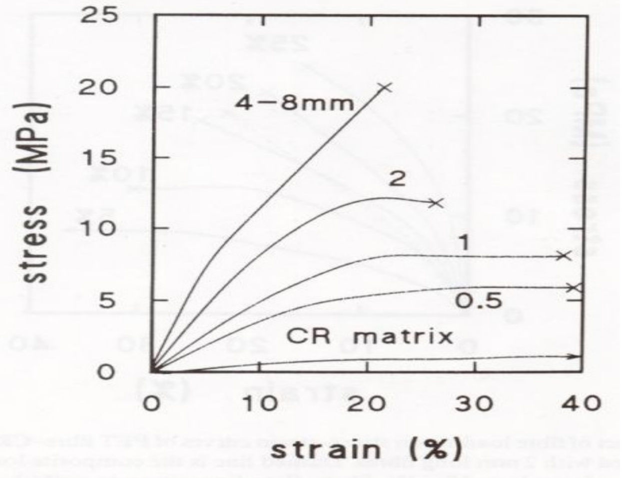

Figure 7: Stress-strain curves for PET fibres-CR composites loaded with 10 volume % fibres, different fibre lengths [10].

The effect of fibre length on the tensile stress required to produce a given extension is shown in figure 8 for composites loaded with 10% volume PET fibre. The tensile stress of composites in the direction perpendicular to the fibre direction at an elongation of 100%, increases considerably as the fibre length is increased up to 2 mm, after which it remains nearly constant as the fibre length is increased from 2 to 8 mm. The tensile stress of composites in the direction of fibre orientation at an elongation of 10% increases rapidly and almost linearly as the fibre length is increased up to 2 mm, but with fibres of 2 mm or more in length the tensile stress increases much more slowly with fibre length. In the direction perpendicular to the fibre direction, short fibres in the composites act in a manner similar to that of fillers such as calcium carbonate or clay; that is, the fibres have a reinforcing effect on the matrix rubber by acting as massive crosslinks. It is noted that the mechanical properties of PET fibre-CR composites change non-linearly at a fibre length of about 2 mm. Consequently, the CR composites reinforced with short fibres give rubber-like or fibre-like behaviour, depending on the fibre loading and the fibre length and orientation [10].

Interfacial Effects-As pointed out before, the mechanical properties also depend strongly on fibre-rubber interaction which itself depends on the interface or the interfacial region (interphase). In different sources it can be seen that the researchers mixed these two concepts up [8, 14]. The interphase is a region at least several molecular layers thick whose properties are intermediate between those of the fibre and matrix phase while a sharp interface does not refer to any intermediate layer.

Matrix molecules may be anchored to the fibre surface by chemical reaction or absorption, which determine the extent of adhesion. The adhesion can also be promoted by an additional constituent added to the composite as a bonding agent or as an interlayer between the two components of the composite [8].

According to Mehan and Schadler [14] the strength of the interface/ interphase will determine the stress-transfer length. Stronger, tougher interfaces will lead to higher interfacial shear strength and shorter stress transfer length. Thus more of the fibre will carry the applied load. A weaker or more brittle interface/interphase will have a longer stress transfer length, and relatively less of the fibre will carry the applied load.

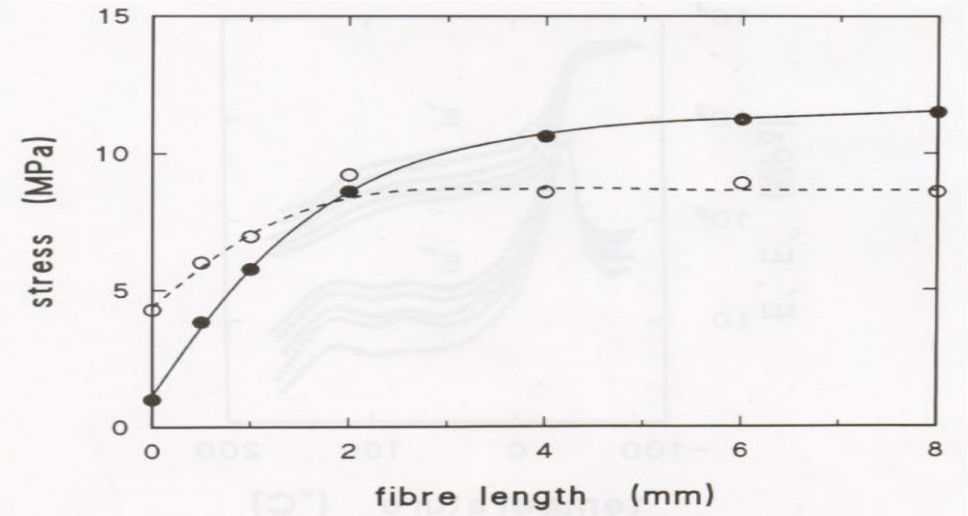

Figure 8: The effect of fibre length on the tensile stress required to produce a given extension for PET fibre-CR composites loaded with 10% volume fibres; (●): parallel to fibre direction at 10% extension; (○): normal to fibre direction at 100% extension [10].

A weak interface/interphase drastically reduces the longitudinal and transverse strength, the flexural strength and the compression strength. On the other hand, an increase in the interfacial strength leads to a substantial increase in the tensile strength and modulus of a short fibre composite [15, 16]. Poor adhesion increases the critical fibre length since mechanical friction at the interface must take the place of adhesion. Good adhesion can nearly double the tensile strength and elongation to break compared to a composite in which the adhesion is poor [15].

The nature of the interface/interphase has a large influence on the mode of failure and the toughness of the composite, too. A strong interface would promote crack propagation across the fibres, whilst a weak interface/interphase would promote failure by fibre debonding and pull-out [17].

There are two general methods to increase the adhesion between fibre and rubber matrix [4, 18]:

1. by the use of the hexamethylenetetramine, resorcinol, and a high-surface-area hydrated silica (HRH) system which is incorporated in the rubber mix.
2. by fibre surface treatments using for example Resorcinol Formaldehyde Latex (RFL).

Adhesive treatments for various types of fibres are different. The adhesive layer is applied on a cord by a so-called dipping process. Schematic view of this process can be seen in figure 9. After applying the adhesive layer on the fibre it can be cut into short fibres.

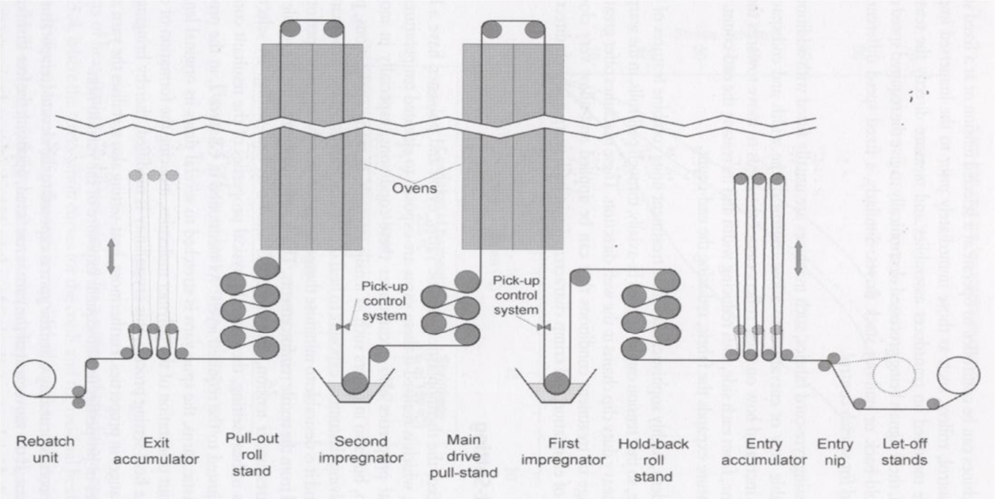

Figure 9: Schematic view of dipping process [19].

There are many important parameters in the dipping process which have great influence on the final adhesive properties, some of these parameters are: resin to latex ratio, type of rubber latex, dip pick-up which is amount of adhesive layer on fibre, heat treatment of fibres and pH of the dip. A review on these parameters has been done by Wennekes [20]. Each of these variables and even type of adhesive coating can be different for each fibre, according to its nature. Moreover, more inert fibres like Aramid, needs two stage dipping, first applying a pre-dip and then applying RFL; but for other kind of fibres like Nylon one stage dipping is enough and RFL can be applied directly on fibre surface. More information about dipping process can be found in [19].

While applying tensile force, if the fibres are not bonded, a pull-out will result without breakage of the fibres. Thus the strength or load-bearing property of the fibres is not fully used [11].When there is no bonding between the fibre and the matrix, the fibre can slip past from the matrix under tension, but when there is bonding between the fibre and the matrix, there will be shear at the interface between the matrix and the fibre, which leads to increase mechanical loss [3].

The quantitative determination of adhesion is not possible in the case of short-fibre reinforcement of rubber. However, it can qualitatively be assessed either by stress-strain curves or by SEM analysis of the fracture surfaces, and also by the swelling method [21, 22].

Typical stress-strain curves for different fibres- nitrile rubber with no bonding agent and with HRH bonding agent can be seen in figures 10 and 11 [12]. It can be seen in these figures that, for samples tested in the longitudinal direction, the addition of the bonding agent significantly improves the strength at yield for each type of composite. However, in these cases, the strength at break is not improved, except for the nylon fibre composite. Young's modulus is improved considerably for the glass, carbon, cellulose, and aramid fibres containing composites.

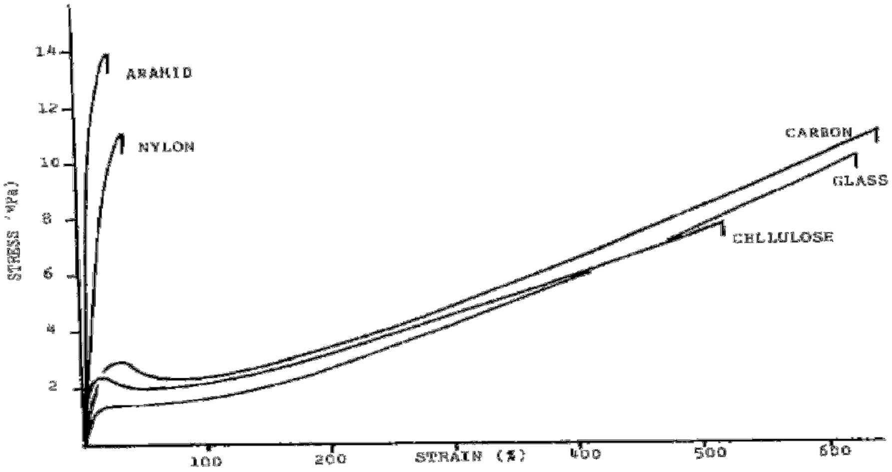

Figure 10: Typical stress-strain curves for different fibres- nitrile rubber with no bonding agent. 9% volume fibres; tested in longitudinal fibre direction [12].

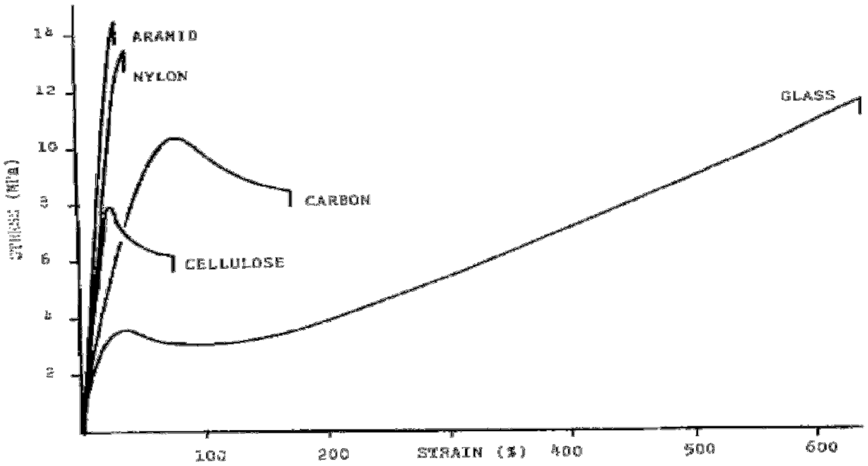

Figure 11: Typical stress-strain curves for different fibres- nitrile rubber with an HRH bonding agent. 9% volume fibres; tested in longitudinal fibre direction [12].

Samples tested in the transverse fibre direction show some improvement in mechanical properties, but not nearly the magnitude of increase observed for the longitudinal direction. In this case, the composite properties depend primarily on the properties of the rubber matrix, and increased fibre-matrix adhesion does not play an important role [12].

In another research [3] authors have concluded that addition of both treated (acetylated) and untreated fibres (short sisal) increases the modulus in a natural rubber based compound. The effect was more pronounced in the case of the treated fibre than in the case of the untreated fibre, at the same loading. In the case of untreated fibre up to 17.5% volume loading, the tensile strength in the longitudinal direction decreased and thereafter the strength increased. For acetylated fibres up to 12% volume loading, the tensile strength in the longitudinal direction decreased and thereafter increased. For transversely oriented fibre, the composite tensile strength decreased continuously for both acetylated and untreated samples [3]. Geethmma et al. [8] also pointed to results that show that sodium hydroxide treatment of coir fibre will enhance the bonding of coir fibre with NR matrix.

According to Nielsen and Landel [15] the strength of the interfacial bond between the two phases is an important factor in determining the transverse strength of a composite too. They write that the longitudinal tensile strength is affected by the strength of the interfacial bond only in the case of relatively short fibres. The transverse strength is generally less than the strength of the matrix. However, in some kinds of composites, good adhesive bonding gives a somewhat higher transverse tensile strength than does poor bonding. In other cases of good adhesion, the fibres restrain the matrix, giving rise to biaxial stresses and reduced elongations to break; under these conditions, the composite with poor adhesion may have the higher transverse strength.

In fact the concept of strength of the interfacial bond is not always clear. If there is perfect adhesion, the matrix or the fibre breaks before the interfacial bond. If there is no 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 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 the mismatch in coefficient of the thermal expansion and cooling down of the composite from the fabrication temperature.

Between perfect adhesion and no adhesion there can, of course, be many gradations of practical adhesion [15].

Other Topics in Mechanical Properties- The tear test also can be viewed as a means for estimating the ultimate properties of rubber. Some authors even believe that it describes the behaviour of the material at the failure zone better than a simple tension test. Generally, adding short fibres will improve tear strength by blunting or diverting growing crack tips [4, 5].

O’Connor [12] compared the results of the tear test for different short fibre natural rubber systems, with a HRH bonding system and observed that in different examined systems, nylon and aramid fibres give the best tear strength in both the longitudinal and transverse direction.

According to Abrate [13] low fibre loadings can elevate the tear strength of the composite above that of the matrix. For higher concentrations, strain concentration between closely packed fibres promotes tearing parallel to the fibre direction, reducing tear strength. Imperfect or random fibre alignment can also increase tear strength.

Kumar et al. [22] did experiments on SBR-short sisal fibre systems and concluded that increasing the fibre content increases the tear strength in longitudinal direction more than in the transverse direction; and the maximum tear strength is in mixtures containing bonding agent.

Among different investigations, only Cataldo [23] observed a drawback in tear test by the addition of short fibres. He writes that the presence of milled carbon fibres leads to a reduction of tear strength of at least 20%.

Adding short fibres to elastomers also affects on their fatigue life. Fatigue damage generally is associated with the generation of cracks in the matrix, or with dewetting and destruction of the polymer-fibre bonding, or by combination of the two effects [13, 15]. Heat build-up can be another major factor in decreasing fatigue life at high frequencies. The mechanical damping of a composite, especially near the interface and fibre ends, generates heat that cannot be dissipated easily at high frequencies and high loads. As the temperature rises, the damping increases more, and the polymer strength and stiffness decrease; catastrophic failure can follow quickly [15].

Rajeev [1] writes that “short fibre reinforcement generally has a negative effect on flex fatigue, particularly at high fibre loading and high strain. According to him heat build-up of these composites is also higher. The mechanical loss near the fibre-matrix interface accounts for the higher heat build-up. His investigations showed that increase in fibre loading increases the heat build-up.

According to Foldi [9], considerable heat build-up results above 10 phr loading with good reinforcers which can restrict the utility of a fibre-reinforced elastomers perpendicular to the stroke. He says that fibre length has no significant effect on heat build-up. On the other hand, Cataldo [23] investigated short milled carbon fibres-elastomer composites. He tested the samples in a Goodrich flexometer where the specimens were tested in compression under a standard load and stressed at 35 Hz, and a decrease in heat build-up was observed. He believes that significant increase in hardness because of adding these short fibres causes this reduction.

Nielson and Landel [15] mention that fatigue life greatly decreases as the applied stress is increased. They write that up to aspect ratio of about 200, fatigue life increases with the length of the fibres. Another investigation [10] has been done on the specimens of PET short fibre-CR composites, loaded with 10 volume % of 6 mm fibres, which were extended parallel to the fibre orientation under repeated constant displacement to 5% of static strain and ±2.5% of sinusoidal repeated strain. Figure 12 shows the stress and the surface temperature of the composites during the tests at 5 and 25 Hz frequency. At the frequency of 25 Hz, the stress decreases rapidly from 100 cycles to 5000 cycles and after that the composites registers a constant stress until 10000 cycles. The surface temperature of the composite rises steeply from 250 cycles to 5000 cycles and reaches the highest value at 7500 cycles; then the temperature falls slowly until 10000 cycles, which corresponds to the stress decay of the composite under fatigue. At a frequency of 5 Hz, the stress decreases gradually and the surface temperature raises only a little.

In the case of the cured CR compound, the surface temperature rises slightly after 1500 cycles. Because the rubber matrix can be regarded as a macroscopically homogeneous material which generates little heat under fatigue, the rising temperature of the composite is caused by differential displacements among the three components of fibre, interfacial region and rubber matrix. Under the higher frequency, the interfacial region between the fibres and the rubber matrix is destroyed in 5000 cycles and much heat is generated in the composite due to rapid displacement. The stress decay from 100 cycles to 5000 cycles becomes steeper, with increasing fibre loading for PET fibre-CR composites.

The PET fibre-CR composites loaded with 6 mm long 10 volume % have been extended in various directions from parallel to perpendicular to the fibre direction. Figure 13 shows that the rise in temperature becomes lower with increasing angle to the fibre direction. The symmetry axis of the temperature distribution makes higher inclination to the extensional direction as the extension angle increases. At the angle of 90°C, the temperature distribution in the composite is fairly similar to that in the cured CR compound. The stress and the surface temperature of the composite gradually approach those of the cured CR compound as the angle to the fibre direction increases. These results again suggest that the stress decay and the rising temperature are caused by shear deformation of the interfacial region along the fibre direction.

Uchiyama et al. [24] investigated the frictional behaviour of short fibre reinforced rubbers; they found that the friction coefficients for the short fibre reinforced rubbers are lower than those for the matrix rubber. Even on wet surfaces the friction coefficient of the short fibre reinforced rubbers is lower than that of unfilled rubber at low sliding speeds. They found minimum wear rates when the short fibre orients normal to the mating surface.

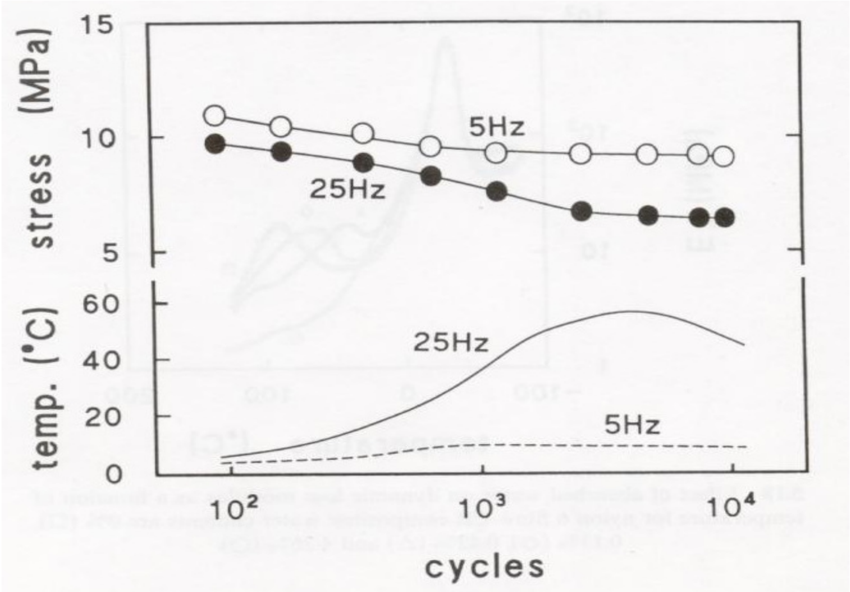

Figure 12: Stress decay and the surface temperature of PET-CR composites under repeated strain [10].

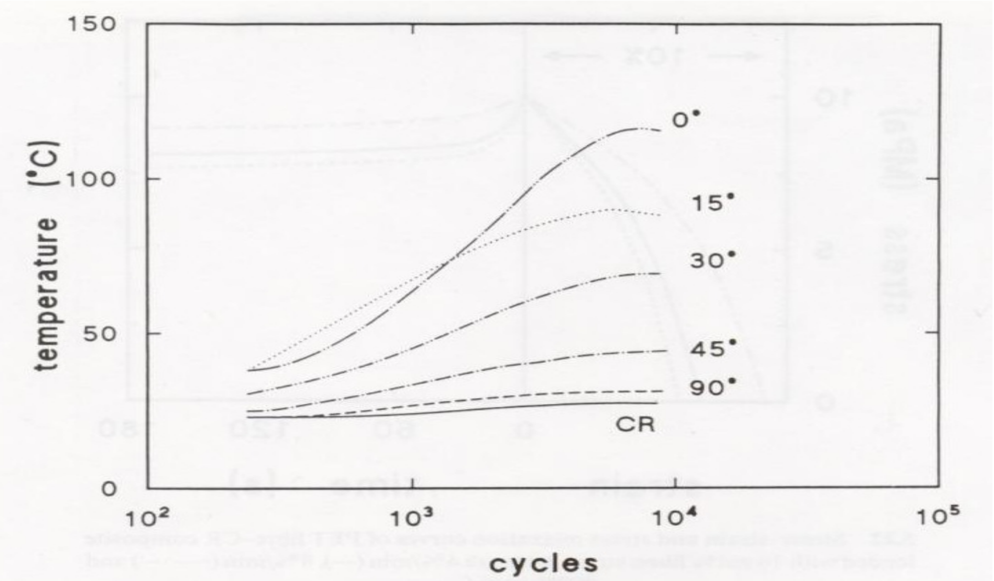

Figure 13: The temperature increase of PET-CR composites, at different fibre angles, under repeated strain [10].

VISCOELASTIC PROPERTIES OF SHORT FIBRE REINFORCED COMPOSITES

The constraint of the rubber matrix due to the presence of the fibres is apparent in creep and stress relaxation, just as it is in the instantaneous mechanical properties. Time dependent deformations occurs in the composites, but they are more related to the matrix than to the fibres [11].

Figure 14 compares longitudinal tensile stress relaxation data for a typical NR-cellulose fibre composite and for the unconstrained matrix rubber. The resistance to relaxation conferred by the fibres is apparent.

After 30 minutes the force was removed, and after 30 minutes tension set was measured. A tension set of 4% was found for the matrix rubber, but it was less than 0.5% for the composite. From this one would expect excellent creep behaviour in the cellulose-rubber composites, as is indeed the case. General reduction of creep by adding short fibres is also mentioned by other authors [1].

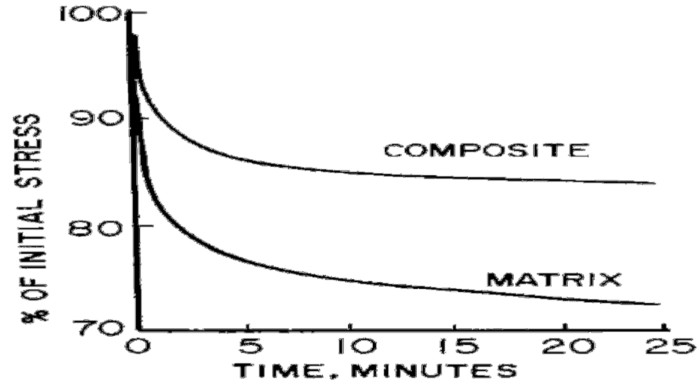

Figure 14: Typical stress relaxation curve for rubber matrix and short fibre composite [11].

Figure 15 gives the creep curve for NR-SBR composites which were reinforced by cellulose fibres to give a longitudinal Young's modulus of about 480 MPa. Resistance to creep is best provided by wood-cellulose fibres since they are less extensible than either nylon or polyester.

The effect of the fibres on composite creep behaviour is not unlike the effect on ultimate elongation or the inverse of the effect on Young's modulus. This is indicated by figure 16 which is the relationship between creep and Young's modulus.

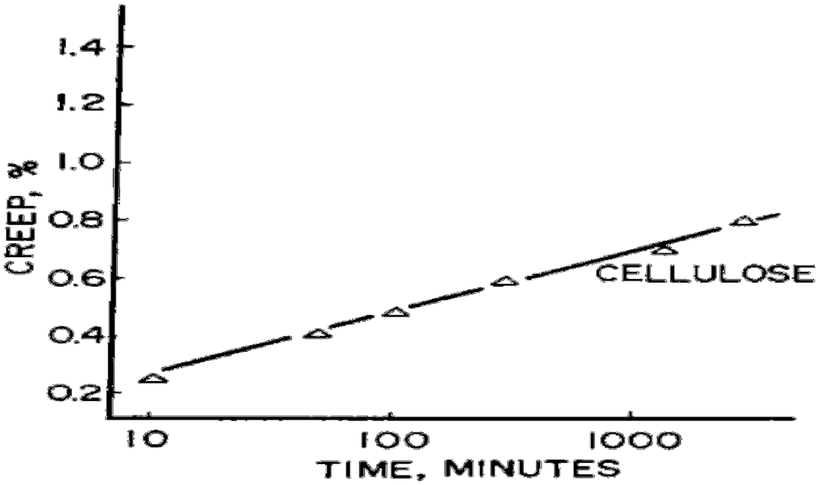

Figure 15: Tensile creep in NR-SBR-cellulose fibre composites at 70°C under 6.89 MPa load **[11].**

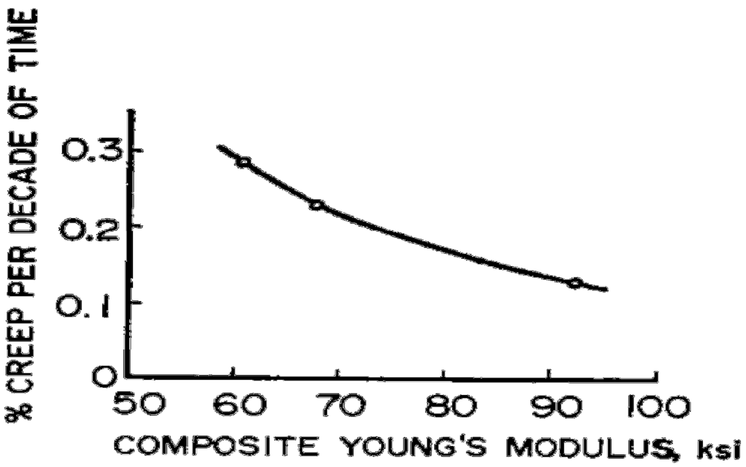

Figure 16: Creep as a function of composite modulus at 70°C under 6.89 MPa load **[**11**].**

The effect of the volume fraction of fibres on the tensile storage modulus E' and loss modulus E" in the fibre direction for PET and Nylon 6 fibres-CR composites loaded with fibres of 6 mm in length was investigated by Ashida [10]. The storage modulus of PET and nylon 6 fibre samples, were higher than that of cured CR compound by a factor of more than 100 over the whole temperature range above 0°C. The rubbery state of cured CR compound is in the range 0-160°C, in which the storage modulus of the composites decreases linearly with rising temperature. The storage modulus of the nylon 6 fibre-CR composites displayed similar behavior, but the modulus of the composite loaded with 15 volume% fibre had the same value as the composite with 12.5% fibre, because nylon 6 fibres tend to buckle during mixing and so a uniform dispersion of the fibres is not obtained in the matrix. Therefore the effect of increasing fibre loading for nylon 6 fibre-CR composites does not appear when the loading is over 12.5 volume%.

It was obvious that both E' and E" increase to higher values with increasing fibre loading. In addition, the storage modulus of PET fibre-CR composites given in figure 17 as a function of temperature for different fibre lengths shows that in the rubbery region the storage modulus of composites loaded with fibres shorter than 1 mm in length has a similar concave curve to the CR compound, and the storage modulus of composites loaded with fibres longer than 2 mm in length gives straight lines. For the composites loaded with fibres that are 2 mm or less in length, the elastic modulus increases linearly as the fibre loading is increased, as shown in figure 17, and the slope increases with the fibre length up to 2 mm and is constant over the range of fibre length from 4 to 8 mm.

Varghese et al. [3] investigated NR-sisal fibre systems. They concluded that with an increase of the temperature, the storage modulus of both treated (acetylated) and untreated composites decrease. The decrease is due to the deterioration of the fibre-matrix adhesion at higher temperatures. Tan δ values increase with increased fibre loadings. They also found that the high interfacial bonding of treated fibres with the rubber matrix is evident from the higher tan δ values for untreated fibres. When there is bonding between the fibre and the matrix, there will be shear at the interface between the matrix and the fibre, which leads to increased mechanical loss. The high storage modulus of the well-bonded composite supports the fact that the load transfer between the fibre and the matrix occurred through the strong fibre-rubber interface.

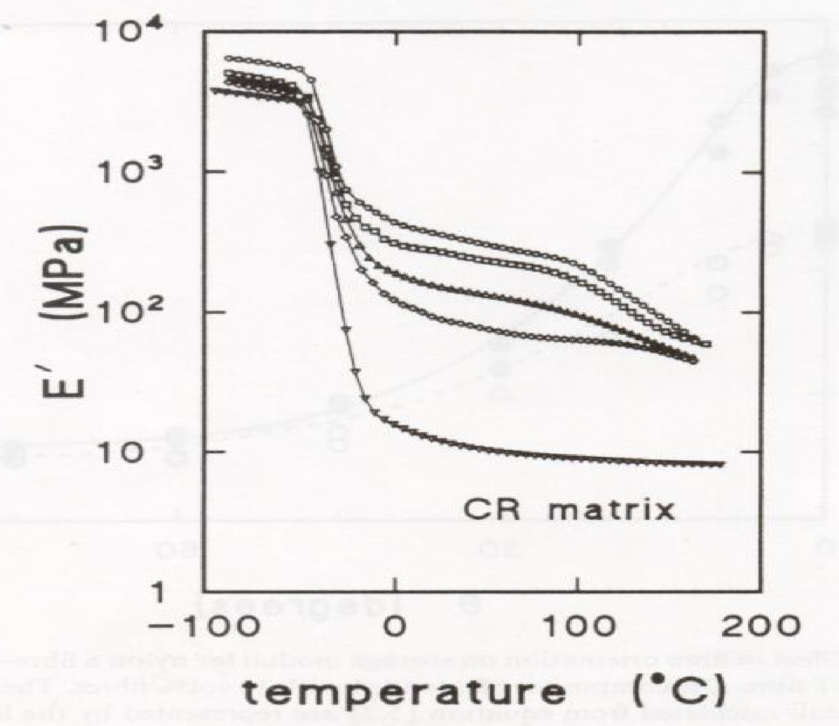

Figure 17: Effect of fibre length on storage modulus for PET fibre-CR composites loaded with 10 volume % fibres; fibre lengths are (◊): 0.5 mm, (Δ): 1 mm, (□): 2 mm, and (○): 4-8 mm [10].

Results by other authors [21] also support this fact that the increase in adhesion increases the storage modulus and mechanical loss per cycle in dynamic conditions. Their experiments also showed that the tan δ values decrease with increasing temperature, and the decrease is sharper at a higher loading (> 10 phr) of treated fibres. Generally, these drops in the mechanical loss and modulus with the increase in temperature indicate a possible deterioration of the adhesion at higher temperatures [21].

According to above discussion, the quality of the adhesion in composites can be evaluated by measuring that part of energy dissipation contributed by the interfaces/interphases; the interface/interphase part can be obtained by separating the fibre and matrix from the total composites [16]:

$$\tan \delta_{in} = \tan \delta_{comp} - \tan \delta_s \qquad (16)$$

$$\tan \delta_s = (\tan \delta_f \, . \, E_f V_f + \tan \delta_m \, . \, E_m V_m) \, / \, (E_f V_f + E_m V_m) \qquad (17)$$

where m and f represent matrix and fibre respectively; tan δ_{in} is the internal energy dissipation due to poor adhesion from the interface, which can be used for evaluating the interfacial adhesion; tan δ_s is the effective loss tangent for a composite with perfect interfacial adhesion, tan δ_{comp} is the measured internal energy dissipation of the composite system. So, by measuring the total system energy dissipation in terms of tan δ, and knowing tan δ and the dynamic modulus of the components, as well as the volume fraction of fibres, the dissipation due to the poor interfacial adhesion can be determined.

REINFORCEMENT THEORIES

Based on a simple blend rule, the storage modulus of long fibre composites for longitudinal direction can be given by the parallel model as follows [10]:

$$E_{c,L} = E_f V_f + E_m V_m = (E_f - E_m) V_f + E_m \qquad (2)$$

where E_c, E_f and E_m are the storage modulus values for the composite, fibre and matrix and V_f and V_m are the volume fractions of fibre and matrix, respectively. This parallel model is based on the assumption that matrix and fibres are strained to the same extent. The findings suggest that the fibres are bonded strongly to the matrix so that the fibre strain equals the matrix strain in the range of the tensile deformation which is applied to the composite. Consequently, if equation (2) is modified as follows [10]:

$$E_{c,L} = \alpha(E_f - E_m)V_f + E_m \qquad (3)$$

where α is a coefficient depending on fibre length, the resulting equation can be applied to short fibre composites.

Based on equation (3) Ashida [10] obtained equation (4) for short PET fibres-CR composites for fibre lengths longer than 3 mm (l is the fibres length):

$$E_c = 0.34l\,(E_f - E_m)V_f + E_m \qquad (4)$$

So, the storage modulus of a short fibre-CR composite can be obtained from the storage modulus of the component materials, the fibre length and fibre loading by using equation (3).However, the tensile stress differs according to the diameter of the fibres and it suggests that the coefficient α depends on the elastic modulus and the diameter of the short fibres used.

The logarithmic law of mixing is a well-known way to calculate the transverse modulus of many composites composed of two phases as shown below [10]:

$$\log E_{c,T} = V_m \log E_m + V_f \log E_m = \log E_m + V_f \log (E_f / E_m) \qquad (5)$$

Ashida [10] found that for RFL treated short cut PET fibres-CR matrixes, this equation should be modified as below:

$$\log E_{c,T} = \log E_m + \gamma V_f \log (E_f / E_m) \qquad (6)$$

where γ is a factor depending on the character of the interphase between fibres and matrix, that is the degree of bonding force. If the fibre is not treated with RFL solution, the γ value is unity because no interphase is formed between fibres and rubber matrix, and log $E_{c,T}$ increases with increasing fibre loading according to the volume effect. When the fibre is treated with RFL solution, the apparent volume fraction of fibre becomes larger than the true volume fraction of fibre with increasing adhesion, that is, γV_f is larger than V_f and γ is larger than unity.

The modulus of the composites can also be theoretically calculated using the well-known Halpin-Tsai equation given by:

$$E_{c,L} = E_m \{[1+ 2 (l / d) \eta_L V_f] / [1- \eta_L V_f]\} \qquad (7)$$

$$E_{c,T} = E_m [(1+ 2 \eta_T V_f) / (1+ 2 \eta_T V_f)] \qquad (8)$$

$$\eta_L = [(E_f / E_m)-1] / [(E_f / E_m) +2(l/d)] \qquad (9)$$

$$\eta_T = [(E_f / E_m)-1] / [(E_f / E_m) +2] \qquad (10)$$

where $E_{c,L}$ and $E_{c,T}$ are Young's modulus of the composite in the longitudinal and transverse direction respectively, and d is diameter of the fibre [1].

These equations reveal that in order to utilize the potential of the fibre for reinforcement and approach the limit $E_f V_f$, the fibre aspect ratio should be larger with higher E_f / E_m ratios. Reinforcement by short fibres is more efficient for relatively small E_f / E_m ratios. In fact, within the range of fibre aspect ratios achievable in practice, the composite modulus reaches a asymptotic value, and then large increases in fibre modulus bring only minor changes in the modulus of the composite [13].

Another equation for Young's modulus of the short fibre composites is proposed by Derringer, which is an empirical equation; a and b are constants [20]:

$$E = E_m - 1 + \exp (a V_f^b) \qquad (11)$$

In addition to the mentioned equations, there are another theories and equations proposed by different authors to calculate the modulus of short fibre composite. A review on these models has been done by Abrate [13].

Generally, the analysis of mechanics of short fibre-rubber composites is more difficult than that for continuous fibre-rubber composites. This is because of the fact that fibre end effects are important in short fibre reinforcement which are absent in the case of continuous fibre reinforcement.

In short fibre reinforced composites there is non-uniformity in the stress transfer between the fibre and the matrix. A perfect fibre orientation is not possible with short fibre reinforcement unlike in the case of continuous fibre reinforcement. In short fibre composites, the efficiency of fibre reinforcement depends on the maximum tensile stress that can be transferred to the fibre by the shearing mechanism between the fibres and the matrix. Since the matrix has a lower modulus, the longitudinal strain in the matrix is higher than that in adjacent fibres. Assuming a perfect bond between the fibre and the matrix, the difference in longitudinal strain creates a shear stress distribution across the fibre-matrix interface. In this condition, maximum reinforcement would be achieved when the fibres are long enough so that maximum stress transfer occurs.

Equation (12), proposed by Rosen, calculates the minimum fibre length, needed for complete stress transfer (l). Several assumptions were made: the effect of adjacent fibres on the stress distribution is ignored and so is the effect of fibre-end geometry; the fibre stress is zero at the end and increases gradually as load is transferred from the matrix to the fibre, and both fibres and matrix behave elastically [1, 13]:

$$l/d = \{0.5\ (E_f / E_m) / [(1\text{-}V_f^{0.5}) / V_f^{0.5})]\}^{0.5} \qquad (12)$$

where d is fibre diameter. The minimum fibre aspect ratio required to obtain complete stress transfer is called the effective aspect ratio, which can be derived from equation (12). This parameter decreases slightly with increasing fibre loading and is affected in a major way by the fibre-to-matrix modulus ratio.

Analysis of the stress distribution in an idealized composite showed that discontinuous fibres can contribute a maximum of only 6/7 of their strength to the strength of the composite. This ratio decreases to 1/2 for many cases. Such simplified analysis indicates that the full strength potential of the fibres cannot be used in discontinuous form [13].

The theoretical strength of a short fibre reinforced composite is given by [17]:

$$\sigma_{cu} = C\ \{\Sigma\ [(\tau_i l_i V_i) / (2r)] + \Sigma\ \sigma_{fu} V_j [1\text{-}\ (l_c / (2l_j))]\} + \sigma_m\ (1\text{-}V_f) \qquad (13)$$

where σ_{cu} is the ultimate strength of the composite, σ_{fu} is the ultimate strength of the fibre, σ_m is the matrix strength at failure, τ_i is the interfacial shear strength, C is the orientation efficiency, l_c is the critical fibre length, l_i and l_j are sub-critical and super-critical fibre lengths, respectively, V_i and V_j are the fibre volume fractions of the sub-critical and super-critical fibre lengths, respectively, V_f is the overall fibre volume fraction, and r is the fibre radius.

It can be seen from above equation that the strength is affected by many parameters. The first two terms on the right of the above equation account for the varying short transfer lengths in short fibre systems. In continuous fibre systems, the equation reduces to the simpler rule of mixtures relationship.

The strength of the composite has been observed to increase linearly with fibre volume fraction V_f as predicted by equation (13). Systems with too high or too low V_f may deviate from this linear relationship due to fibre embrittlement of the matrix and fibre interaction, respectively. This phenomenon is more pronounced in a system with short fibre lengths and a weak fibre-matrix interface.

It has been shown [25] for short –fibre systems that the reinforcement efficiency (η) of aligned short fibres increases with fibre length l. when $l/l_c > 10$, η approaches 95% of that of aligned continuous fibres.

However, in practice, initiation of matrix failure at the fibre ends due to stress concentration severely reduces the stress of the composites.

There are also simpler models that are modified forms of rule of the mixture like equations (3) and equations (14) and (15) [14]:

$$E_c = \chi_1\chi_2 E_f V_f + E_m V_m \qquad (14)$$

$$\sigma_{cu} = \chi_3\chi_4 V_f \sigma_{fu} + V_m \sigma_{mu} \qquad (15)$$

The factors that represent the effect of fibre orientation are χ_1 and χ_3. The factors that express the fibre length effect or the effective length of the fibre carrying load are χ_2 and χ_4. For fibres that are randomly directed in a plane χ_1 and χ_3 are usually taken to be 3/8, and for the three dimensionally random cases the value would be 1/5. More details about these χ factors can be found in the paper of Fu and Lauke [26].

SUMMARY AND CONCLUDING REMARKS

Rubber fibre composites are an important class of engineering materials due to combining unique rubber properties with strength of fibres. Among these sorts of composites, those with short fibres have gained a special attention because in short fibre containing composites a good balance between improvement in mechanical properties and production costs is achievable. The research in this field was started more than 40 years ago and till recent years, still different researches covering a wide range of materials, processing, final properties of such materials, etc. are published as papers or filed as patents [27-30]. In this literature survey the aim was to cover the most notable publications in this respect.

Generally, adding short fibres will increase green strength, tensile strength, elastic modulus, hardness and tear strength of a rubber compound; but they may have a negative effect on heat build-up, flex fatigue and elongation at break. There are many parameters affecting the final properties of short fibre rubber composites, among them nature of fibre and matrix, fibre concentration, fibre orientation and dispersion and fibre-rubber interaction have great importance.

In fact, the reinforcing effect of fibres arises from stress transfer from rubber medium to them. Owing to several researches which have been done in that field, many things are clear now; a stronger and tougher interface/interphase would result in better stress transfer and better final properties and weak and brittle interface/interphase leads to poor properties. But, still the concept of interface/interphase and its effect on final properties is not that clear. One reason for that is that there is no direct method to measure the adhesion in short fibre reinforced composites and indirect methods are also more qualitative rather than quantitative. So it is rather difficult to determine the degree of adhesion and to use the factor relating to that to develop a reinforcing theory for these composites or even to modify existing theories.

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Chapter 2

Factors Influencing Reinforcement of NR and EPDM Rubbers with Short Aramid Fibres

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ABSTRACT

Among short fibre reinforced composites, those with rubbery matrices have gained great importance due to the advantages they have in processing and low cost, coupled with high strength. These composites combine the elastic behaviour of rubbers with strength and stiffness of fibres.

In this research aramid fibres have been chosen because of their significantly higher modulus and strength, compared to other commercial fibres. Compounds based on NR and EPDM are prepared. Short aramid fibres with different kinds of surface treatments, standard finish and RFL-coating result in different rubber-fibre interfaces. The reinforcing effect of these short aramid fibres is characterized by mechanical and viscoelastic experiments, and by studying the fracture surfaces with electron microscopy techniques. Related to the fibre coating and rubber curing system, sulphur- or peroxide-based, different reinforcement mechanisms are observed, where the combination of peroxide-cured EPDM with RFL-treated fibres is the only case showing clear signs of chemical adhesion. In all other combinations there are only indications of mechanical interactions of the fibres with the rubber matrices, due to bending/buckling of fibres, dog-bone shaped fibre ends and surface roughness due to the RFL-coating.

INTRODUCTION

Fibre reinforced composites with the best mechanical properties are those with continuous fibre reinforcement. Such materials cannot be adapted easily to mass production and are generally limited to products in which the property benefits outweigh the cost penalty. [1] Alternatively, short fibres are used to reinforce polymers in order to improve or modify the thermo-mechanical properties of the matrix for specific applications or to reduce the cost of the fabricated article.[2] By adding suitable fibres and by controlling factors such as the aspect ratio, the dispersion and orientation of the fibres, and the fibre-matrix adhesion, significant improvements in properties can be achieved with thermoplastic, thermosetting and rubber polymers.[1]

Among different short fibre reinforced composites, those with rubber matrices are gaining increasing importance due to the advantages they impart in processing and low cost coupled with high strength. These composites combine the elastic behaviour of rubber with strength and stiffness of the fibres. Moreover, reinforcement with short fibres offers some attractive features such as design flexibility, high modulus, tear strength, etc. Short fibre reinforced rubbers have been successfully used in production of V-belts, hoses, tire treads and complex-shaped mechanical goods.[3, 4]

Generally, the degree of reinforcement depends upon the nature of the matrix, the type of fibres, the concentration and orientation of the fibres, fibre to rubber adhesion (generation of a strong interface), fibre length and aspect ratio of the fibres.[3, 4, 5] Poor adhesion increases the critical fibre length, which is the minimum length of fibres needed for effective stress transfer, since mechanical friction at the interface must take the role of adhesion. Good adhesion can nearly double the tensile strength and elongation at break compared to a composite in which the adhesion is poor.[6]

A common method to increase the adhesion is by fibre surface treatment using for example isocyanate or Resorcinol Formaldehyde Latex (RFL); the adhesive treatment for various types of fibres differs. The adhesive layer is applied on a cord by a so-called dipping process. Details of this process can be found elsewhere.[7]

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 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.[6] There exist several earlier studies concerning rubber reinforcement with short fibres. Mainly glass fibres and different types of natural fibres such as Jute fibres were investigated.[8-11] Some attempts also have been made in the past [12] to try different ingredients as adhesion promoters between fibres and rubber, but RFL treatment of the fibres has been recognized to be the most effective to enhance the adhesion.

In the present work, the reinforcement of two types of widely used rubbers, Ethylene Propylene Diene Rubber (EPDM) and Natural Rubber (NR) is investigated in the form of typical radiator hose and truck tire tread compounds, with short aramid fibres.

EXPERIMENTAL

Materials: Twaron® aramid short fibres were supplied by Teijin Aramid B.V., the Netherlands, with initial length of 3 mm and fibre diameter of 10-12 microns. These fibres were chosen because of their significantly higher modulus and strength compared to other commercial fibres. Two types of elastomers have been chosen: Natural Rubber (NR): SMR CV60; and Ethylene Propylene Diene Rubber (EPDM): Keltan® 8340A with 5.5 weight percent ENB content and respectively 55 and 39.5 weight percents of Ethylene and Propylene contents, from DSM Elastomers, the Netherlands. The compositions of the compounds are presented in Table I. Carbon blacks N220 and N550 were obtained from Evonik GmbH (formerly Degussa), Germany. The oil type added to EPDM compounds was Sunpar® 2280 paraffinic oil and to NR was naphthenic oil. ZnO was Red Seal quality of Union Minière, Belgium, and stearic acid was a technical quality grade. PolyEthyleneGlycol (PEG2000) was obtained from Merck, Darmstadt, Germany. Sulphur and Tertiary-Butyl-BenzothiazolSulfenamide (TBBS) were provided by Rhein Chemie, Germany. Trimethylolpropane-trimethacrylate (TRIM) and Perkadox 14/40 peroxide were obtained from AkzoNobel, Deventer, the Netherlands. Polymerized 1,2-dihydro-2,2,4-trimethylquinoline (TMQ) came from Flexsys, Belgium.

Table I: Compound Recipes.

Component	**A**	**B**	**C**	**D**
NR	100	-	100	-
EPDM Keltan 8340A	-	100	-	100
Carbon black N-22O	55	-	55	-
Carbon black N-550	-	105	-	105
Oil	8	60	8	60
Stearic acid	2	1	2	2
ZnO	5	-	5	5
6PPD	2	-	2	-
TMQ	1.5	-	1.5	-
Wax	2	-	2	-
PEG2000	-	2.5	-	2.5
TBBS	1.5	-	-	2
Sulphur	1.5	-	-	2
Perkadox 14/40	-	7.5	7.5	-
TRIM	-	4	4	-

Two masterbatches were made in a 150 litre industrial internal mixer. The curatives and short fibres in various loadings were added on a laboratory two roll mill. The mill was warmed to 40°C and the nip was set to 1.5mm and fibres were mixed for 6-7min. Compounds with short aramid fibres, with two different kinds of surface treatment, added to the masterbatches, were prepared. Although the fibres with the two different coatings showed different tendencies for dispersion on the two roll mill, the mixing conditions were were kept the same for all cases. The different treatments of the fibres were standard finish (StF) which is an oily substance added on the fibre surface to facilitate processing, and Resorcinol Formaldehyde Latex (RFL) coating. It has been shown elsewhere that the standard finish has no negative influence on the adhesion of cords to rubbers.[13]

The goal of this research was to investigate the effect of adding small amounts of fibres to two commercial compounds on dynamic and mechanical properties. Although adding short fibres could give the possibility to reduce the amount of filler in the compound as an alternative reinforcing material, in the present study, the amount of carbon black was kept the same as for the compound without fibres.

Methods: The cure characteristics of the compounds were measured with a Rubber Process Analyser (RPA) of Alpha Technologies, and according to the results the compounds were cured for their t_{90} +2 minutes in a Wickert hot press WLP1600, at 100 Bar pressure. In order to obtain the preferred orientation of the fibres, before putting into the mould, 20gr of each compound which was the amount needed to fill the mould, was passed several times through a two roll mill, to make a sheet which could fill the mould. The milling direction was considered as longitudinal direction of fibre orientation.

Tensile tests were done, using a Zwick Z1.0/TH1S tensile tester, speed 200 mm/min, in the longitudinal direction of fibre orientation on the samples containing each kind of treated fibres, and the fractured surfaces of tensile bars were studied with electron microscopy using a bench-top NeoScope JCM-500 device, after coating the samples with a very thin layer of platinum. Dynamic Mechanical Analysis was done on samples using a Metravib Viscoanalyser DMA+150, in strain sweep mode, at the frequency of 10Hz and ambient temperature.

RESULTS

Fibre length and dispersion: Results obtained from studying fibre length and fibre dispersion in model gum stocks, the same compounds but without carbon black and oil, showed that fibre length decreased during mixing. It was observed however, that by keeping the same nip distance of the two roll mill, after short mixing, the change in fibre length with time was relatively little. The weight average length obtained for fibres with different treatments in NR and EPDM was approximately between 2.3 to 2.7 mm. RFL-treated fibres ended up with higher length in both NR and EPDM after mixing compared to StF-coated fibres.

A dispersion study of the model gum stocks showed that fibres with StF-treatment don't disperse well in NR, tending to form agglomerates of fibres, while they disperse fairly well in EPDM: Figure 1. RFL-treated fibres tend to form smaller agglomerates in both NR and EPDM matrices.

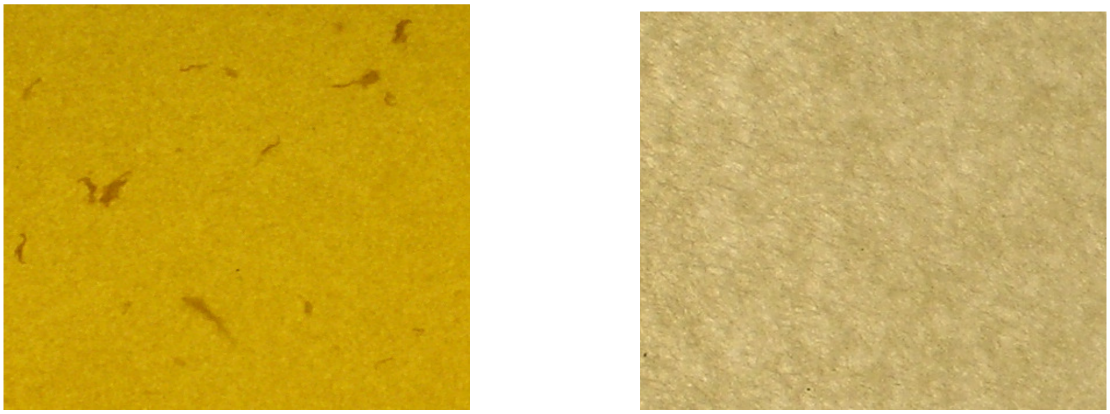


Figure 1: Dispersion of StF-fibres in gum stocks of NR: left; and of EPDM: right.

Reinforcement mechanisms and mechanical properties: Figure 2 shows the tensile test results of the compounds without fibres (WF) and of those containing 5phr short fibres in longitudinal direction of fibre orientation. It should be noted that the orientation of the fibres is much more complicated compared to for example glass fibres, because they remain curved and wavy in the compounds. So the compounds are also fortified considerably in direction transverse to the main fibre orientation. To obtain an indication about the degree of orientation, tensile tests for NR (A) and EPDM (B) containing 5phr standard-finish treated fibre have been done also in transverse direction. As an indication, the tensile stress in longitudinal direction vs. the values in transverse direction at 10% elongation, was 1.12 for NR and 1.3 for EPDM.

Another thing which should be noted is that adding higher volume contents of fibres makes the compounds difficult to process. Therefore it has been recommended by others, to use as low a volume content of short fibres as possible. [14, 15] In the present study adding only 5 phr fibres did not result in noticeable changes in the processing behaviour. The Mooney viscosities did not show a considerable increase either; for instance the increase in Mooney (1+4) at 120° C in the EPDM compound by adding 5phr standard finish-treated fibres was only 1 Mooney unit.

Adding fibres causes a drop in elongation at break and tensile strength, as expected [16], but also results in higher stresses in both low and high strain regimes. Particularly eye-catching is that the reinforcement in sulphur-cured NR (A), especially with RFL-treated fibres is far less than in peroxide-cured EPDM (B). This is highlighted in Figure 3, where the reinforcement factors: the ratio of the stress of a reinforced composite at a certain elongation to the stress of the corresponding compound without fibre at the same elongation, are compared. In the case of NR (A) no large effect of RFL fibre treatment is observed, while for EPDM (B) the effect of the RFL-coating is relatively high, particularly in the range of low elongations till even more than 100% strain. The tensile stress of peroxide-cured EPDM (B) containing RFL-treated fibres increases fast in the beginning, reaching a shoulder, then decreases slightly and later on increases again. This indicates that at the beginning of the tensile test, at low strains, the applied load is mainly transferred to the fibres because of good interaction between peroxide-cured EPDM and the RFL-treated fibres. Apparently, this is not the case for NR. Additional proof for the adhesion of RFL-treated fibres to EPDM (B) compound is that only in that case, SEM pictures of the tensile fracture surface show rubber sticking to the fibre surfaces while in other samples no sign of fibre-rubber adhesion was observed: Figure 4.

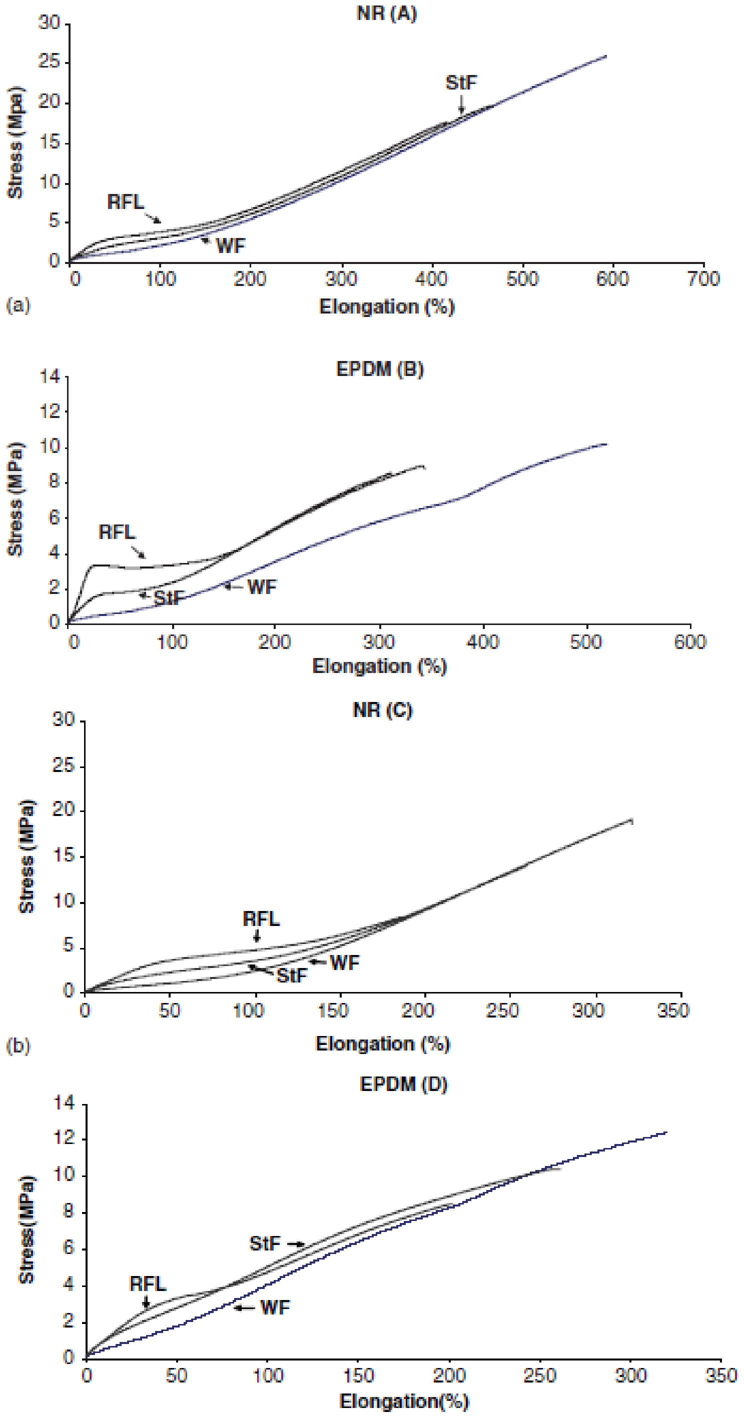


Figure 2: Tensile properties of 5 phr fibre-loaded sulphur-cured NR (A), peroxide-cured EPDM (B), peroxide-cured NR (C), and sulphur-cured EPDM (D) compounds, in longitudinal direction of fibre orientation. WF: Without Fibre; StF: Standard Finish; RFL: Resorcinol Formaldehyde Latex.

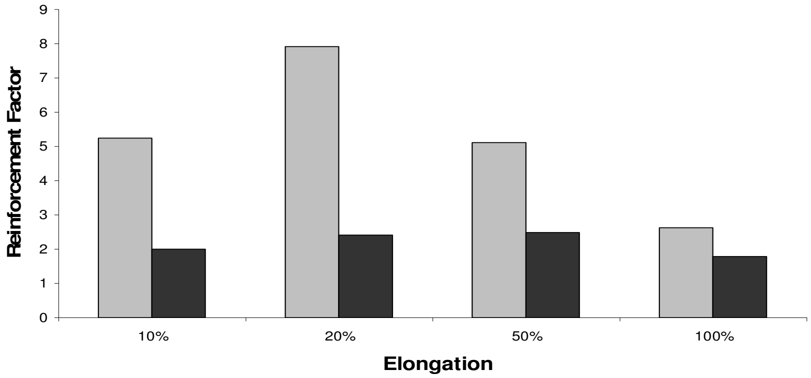
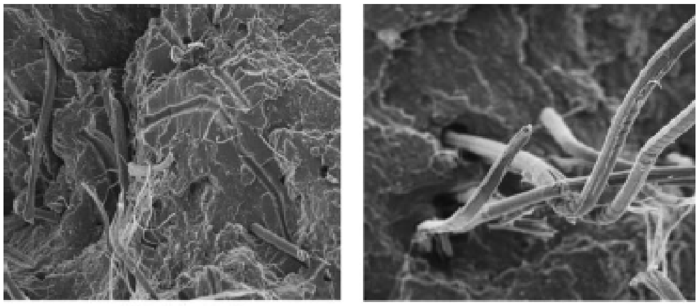
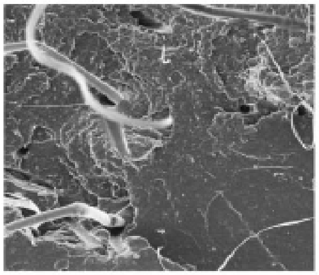


Figure 3: Reinforcement Factor; Black: NR (A); Gray: EPDM (B).

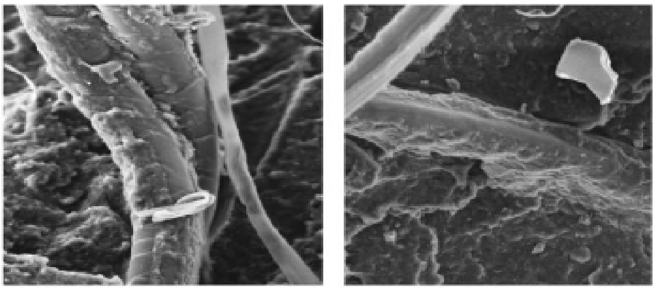


NR (A) – StF

NR (A) – RFL



EPDM (B) – STF



EPDM (B) – RFL

Figure 4: SEM pictures of fibres in tensile fractured surfaces.

Considering the improvement in tensile properties of the composites containing fibres treated with standard finish, the increase in stress at both low and high elongations for all composites (A)-(D), Figure 2, and the lack of chemical adhesion between fibres and rubbers in most cases, it is clear that mechanical interaction is of main importance in this fibre reinforcement. The main origins of mechanical interaction have been identified in this study. The first one is roughness of the fibre surface because of fibre bending. Figure 5 shows two pictures of the surface of free standing aramid fibres, in the right picture the fibre is bended/ buckled, and Figure 6 shows a fibre in a tensile fracture surface. The surface becomes rough in bending due to the highly crystalline layer structure of these fibres. Bending/buckling happens a lot of times during mixing, causing this roughness to occur along the contour of the fibres.

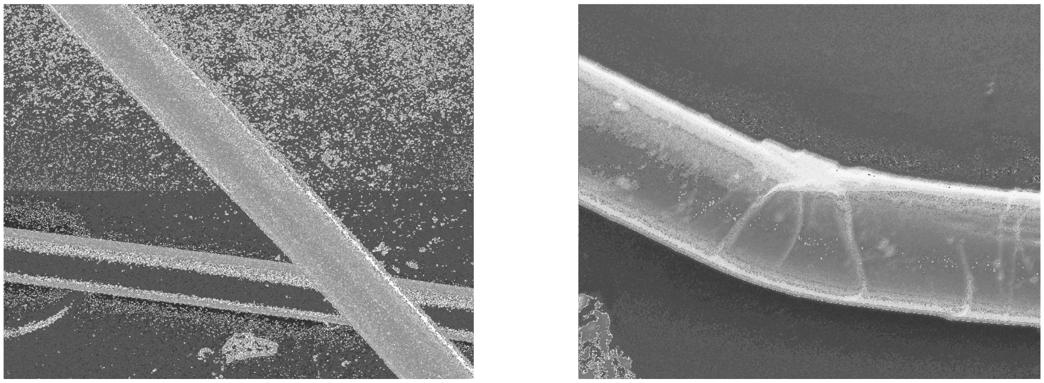


Figure 5: Free standing and buckled short aramid fibres (StF).

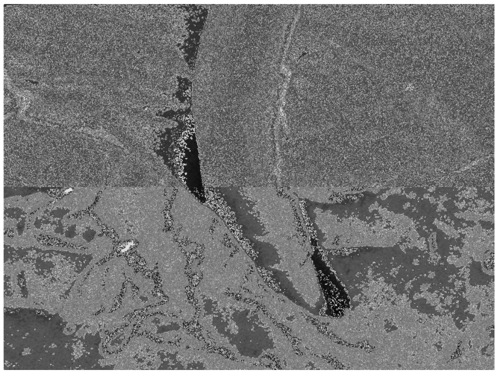


Figure 6: Short aramid fibre (StF) in tensile fracture surface.

The second origin of mechanical interaction is fibre ends which have been deformed in the cutting process. Figure 7 shows the end of a bundle of dog-bone shaped short fibres. The diameter of the individual fibres is considerably larger at the ends, caused by the cutting. These end parts can resist pulling out of the rubber matrix by acting as anchors. The third origin of mechanical reinforcement is roughness of the fibre surface due to its coating, important in the case of RFL-treated fibres: Figure 8. This is also a reason that, although no sign of chemical adhesion was observed in sulphur-cured NR (A) compounds, still the compound containing RFL-treated fibres shows slightly better tensile properties compared to the same compound containing standard finish treated fibres.

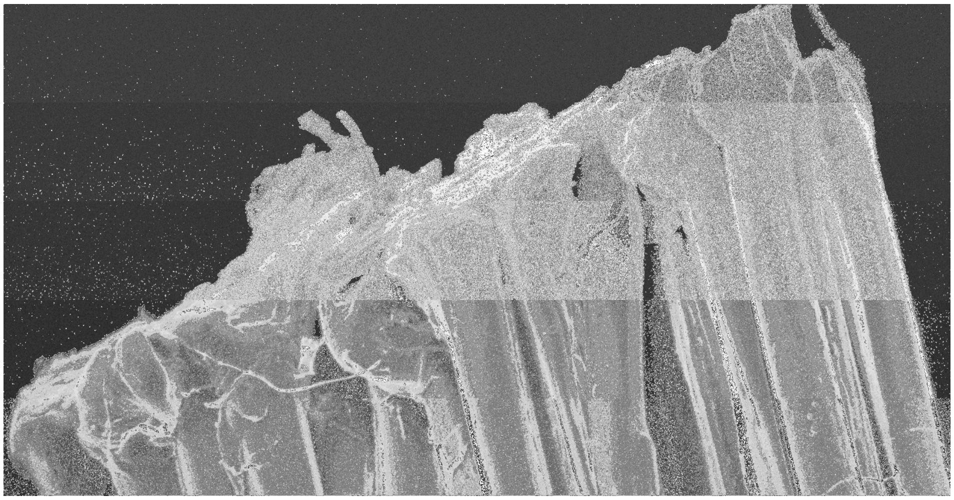


Figure 7: Dog-bone shape fibre ends.

Figure 8: Roughness of RFL-coated short fibres.

The effect of curing system: Two other compounds have also been made: peroxide-cured NR (C) and sulphur-cured EPDM (D), to investigate the effect of curing system on adhesion: Table I. The tensile curves and the reinforcement factors are also presented in Figures 2, 9 and 10. It appears that with the peroxide curing system for NR (C), RFL-treated fibres show improved tensile properties over sulphur cured NR (A). But particularly eye-catching is the reinforcement achieved with RFL-treated fibres in peroxide-cured EPDM (B) over sulphur-cured (D), where for the latter no sign of chemical adhesion to RFL-treated fibres can be seen in the tensile curve; also the reinforcement factors are very low compared to peroxide-cured EPDM. In the SEM pictures of tensile fractured surfaces of the two compounds NR (C) and EPDM (D) containing StF- as well as RFL-coated fibres, no sign of chemical adhesion was observed either. By comparing Figures 9 and 10 it can be seen that changing curing system, has considerably improved the reinforcing factor in all cases, even for the StF-coated fibres when there is no RFL-coating present.

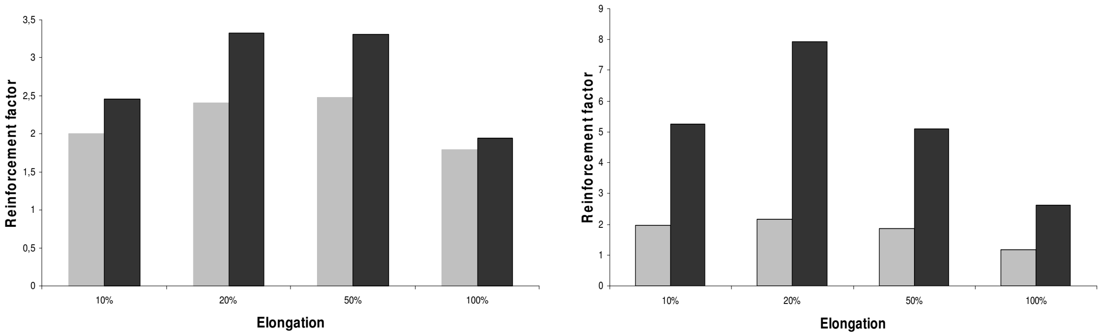


Figure 9: Reinforcement Factors; Left: NR, Right: EPDM, containing 5phr RFL-coated fibres, measured in longitudinal direction; Grey: Sulphur-cured, Black: Peroxide-cured.

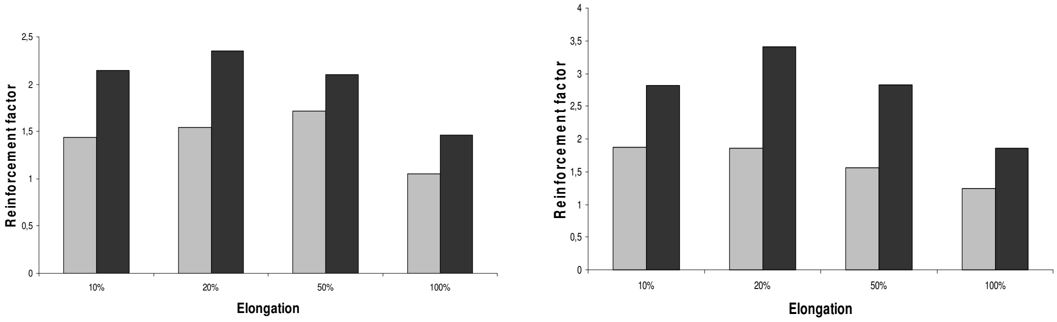


Figure 10: Reinforcement Factors; Left: NR, Right: EPDM, containing 5phr StF-treated fibres in longitudinal direction; Grey: Sulphur-cured, Black: Peroxide-cured.

Dynamic Mechanical Properties: Figures 11 and 12 show the results of storage modulus and tanδ, with δ the loss angle, measured with DMA in strain sweep tests. The compounds were loaded with 3 phr fibres instead of 5 phr, in order to reduce possible interactions between the short fibres, which might result in a contribution to the measured viscoelastic properties, especially in tanδ. The measurements were done in tension mode, in longitudinal direction of fibre orientation at ambient temperature. It can be seen from figure 11 that in both cases, NR and EPDM, RFL shows the highest storage modulus, although this difference is not always very significant because of the small amount of fibres added. In the sulphur-cured NR, StF fibres perform better than WF for strains till 3%, while this range is wider till 6 % for EPDM. In all cases, increase in the strain results in less difference between the fibre-filled compounds and the compound without fibres; and also between compounds containing the StF and RFL fibres. Another important output of a dynamic test is the loss angle or tanδ. The rubber-fibre interface can have its own contribution to the loss angle, and the quality of the interfacial adhesion in composites can be evaluated by measuring that part of energy dissipation. [10]

The results of tanδ, are presented in Figure 12. The compounds containing RFL-treated fibres show lower tanδ compared to the compounds containing StF-coated fibres. These results are in accordance with the tensile data and show the advantage of RFL-treated fibres, even in the case of no chemical adhesion, over StF-treated fibres in two very common applications: sulphur-cured NR and peroxide-cured EPDM compounds. In the case of peroxide-cured EPDM (B), it can be seen that adding StF-coated fibres results in an increase in tanδ, because of additional loss mechanisms due to slippage on the interface of fibre-rubber. Adding RFL-treated fibres reduces tan delta to almost the same level as for the compound without fibres, because of the chemical bond between fibre and rubber.

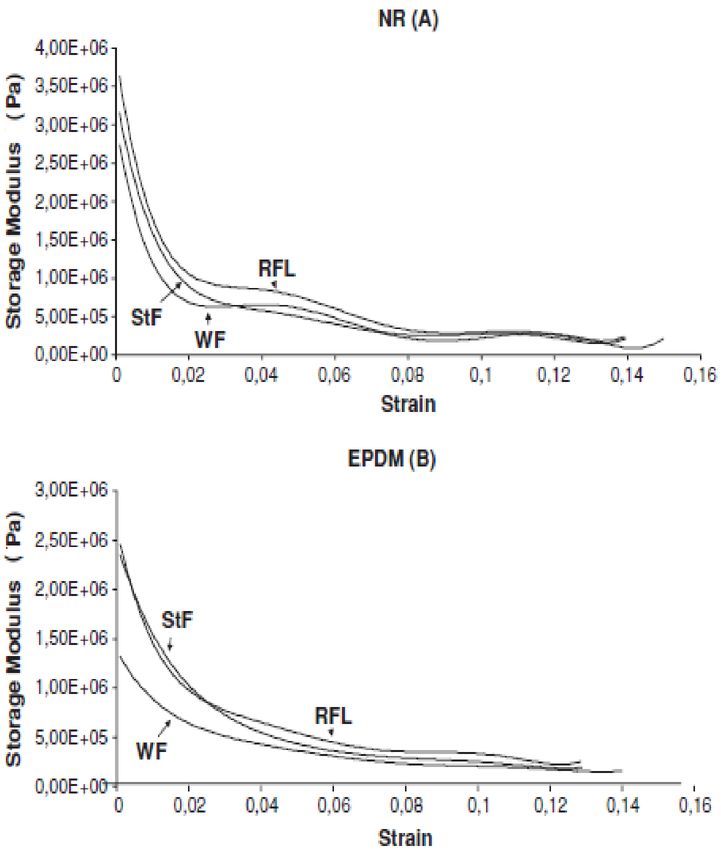
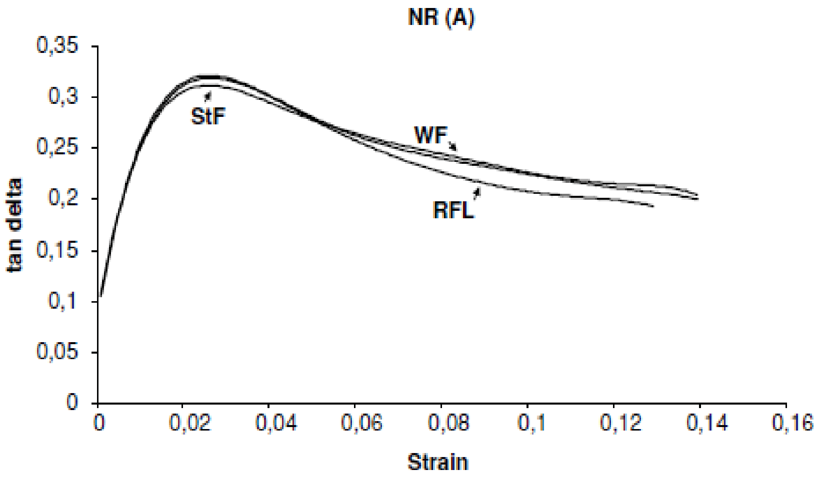


Figure 11: Storage modulus derived from strain sweep DMA measurements on 3 phr fibre loaded sulphur-cured NR and peroxide-cured EPDM compounds at ambient temperature for various fibre treatments.

It may be expected that, when RFL-treated fibres are added to peroxide-cured EPDM (B), because of the chemical bond between RFL and the bulk rubber matrix and the consequent increase in elastic modulus as a result of reinforcement, the tanδ could even be lower than for the compound without fibres. The reason that this doesn't happen is that in the production of the short fibres, RFL is applied on cords which consist of bundles of fibres, with the cord being cut later-on to make the short fibres. There is always a considerable fraction of fibres which were in the middle of the bundles that remain uncoated: Figure 13. Considering also the low concentration of fibres, this can be a reason that there is almost no difference between storage modulus of StF and RFL-treated fibres loaded EPDM at strains below 3%.



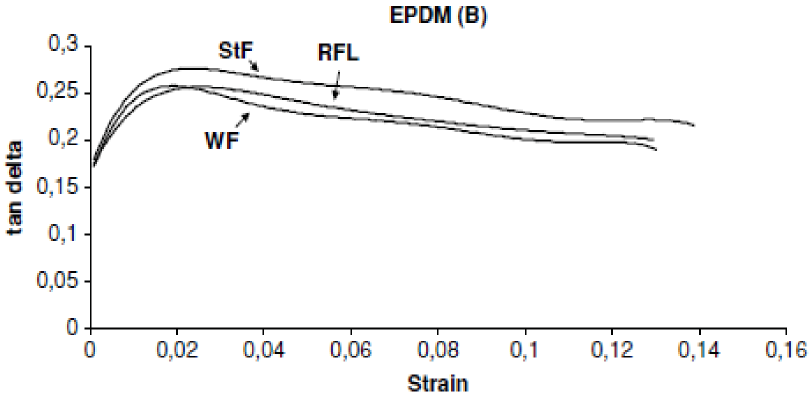


Figure 12: Loss factor tan δ derived from strain sweep DMA measurements on 3 phr fibre loaded sulphur-cured NR and peroxide-cured EPDM compounds at ambient temperature for various fibre treatments.

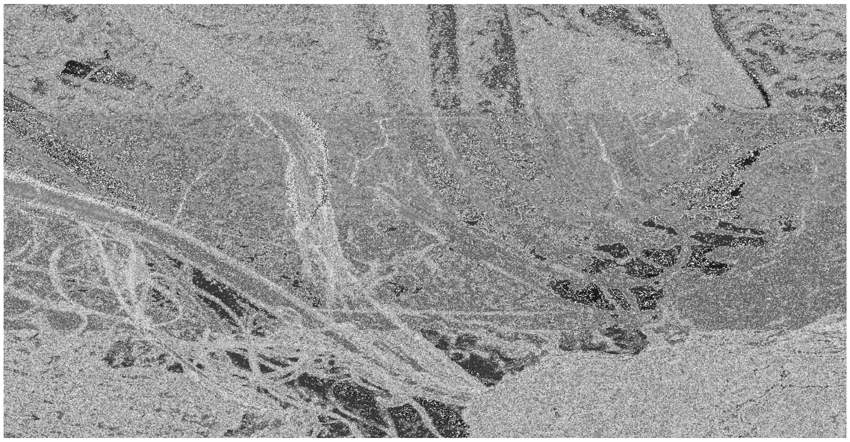


Figure 13: Peroxide-cured EPDM (B) with RFL-treated fibres, partially uncoated.

In the case of sulphur-cured NR (A) there is no considerable change in tanδ with adding StF-treated fibres. One possible reason can be that because of the much higher modulus of the NR compound compared to EPDM, the contribution of the loss mechanisms at the interface of only 3 phr fibres to tanδ of the composite is not significant.

DISCUSSION

It has become clear that compared to the very common use of RFL-treated textile cords in sulphur cured NR compounds, there are other mechanisms involved in the case of short RFL-treated fibre reinforcement. For RFL-treated cords previous research has shown that in sulphur-cured NR, sulphur and accelerators migrate through the RFL-rubber interface and create bonds across the phase-boundery.[18,19] The mechanism proposed was that sulphur forms bonds between the vinyl-pyridine latex in the RFL and the bulk rubber. From this perspective it was quite unexpected that the present results indicate a rather poor adhesion between RFL-treated short aramid-fibres and all sulphur-cured rubbers, whether NR or EPDM. This may be due to uneven RFL-coating on the various fibres, as cut out of RFL-treated multi-fibre cords. Even more surprising is that peroxide-curing gives better adhesion than sulphur-curing for all combinations, with RFL- fibres. Most conspicuous is the very good adhesion achieved between RFL-treated fibres and peroxide-cured EPDM. EPDM can well be vulcanized with peroxides and apparently the radicals generated during that process also manage to react with the RFL-layer around the others. Whether the latex-particles play here the main role or the resorcinol-formaldehyde matrix is at this point not clear and needs further study.

It has been mentioned[20, 21] that RFL loses its adhesion properties with sulphur-cured rubber rather fast when exposed to air, which can be due to oxidation of the latex-moiety in the coating. This oxidation is quoted to be rather fast and happens only within a few days. It could therefore well be conceived that oxidation of the RFL-treated fibres is responsible for the phenomena observed. In our research, no clear sign of chemical bonding between RFL-treated short fibres and sulphur-cured NR was found. The effect of oxidation has also been investigated by using some RFL-coated short fibres which were provided well packed and sealed to prevent oxidation. Using those fibres in NR-compound (A), no difference in tensile properties were found, compared to the same compound with the same amount of RFL treated fibres, stored for quite a long time without particular precautions. Additional proof of no effect of oxidation can be found in the practice in industry: from the moment that RFL-treated cords are purchased from a fibre producing company, till the time that they are used in actual compounds, shipping and storage may take several weeks, while the rolls of these cords are not sealed in such a way that no oxygen can reach the cords. Commonly no differences in practical performance are seen in all cases.

CONCLUSIONS

In the different short fibre / rubber systems examined, clear chemical adhesion only happened in the case of peroxide-cured EPDM with RFL-treated fibres. This phenomenon was most clearly reflected in the tensile curve of this system, showing a large reinforcement factor particularly at tensile elongations of <100%. But the reinforcement stays in place over the whole range of accessible elongations till break. In addition, curing system has been shown to be a determining factor in Fibre-rubber interaction. Particularly an improved interaction between EPDM rubber and short aramid fibres, with RFL-treatment has been observed by using Peroxide curing system due to formation of chemical interaction between fibres and the rubber.

Next to potential chemical bonding, mechanical interaction between fibres and rubber matrix plays an important role. The fibres are long enough to be embedded in a curled manner in the rubber matrix. This impedes pulling out of the rubber matrix, next to surface phenomena on the fibres, as bending/buckling, dog-bone shaped fibre ends and surface roughness due to the RFL-coating. So, even in absence of chemical adhesion, adding short aramid fibres improves the mechanical properties of rubber compounds because of mechanical interaction.

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Chapter 3

Influence of Fibre Type and Dip-Coating on the Composite Properties of EPDM Compounds Reinforced with Short Aramid Fibres

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ABSTRACT

There is a renewed interest in the application of short aramid fibres in elastomers due to the considerable improvement in mechanical and dynamic properties of the corresponding rubber composites. Possible applications of short aramid fibre reinforced elastomers are tires, dynamically loaded rubber seals, diaphragms, engine mounts, transmission belts, conveyer belts and hoses.

Our studies are related to the investigation of dispersion, length distribution and fibre-matrix interaction of two types of short aramid fibres, uncoated and Resorcinol Formaldehyde Latex (RFL)-coated, in ethylene-propylene-diene rubber (EPDM). Since the detection of the polymer fibre morphology in rubber compounds is hampered in the presence of carbon black, which is typically used in industrial elastomer compounds, fibre length, fibre length distribution and dispersion are investigated in corresponding carbon black-free model compounds. Optical methods, scanning electron microscopy, and tensile testing are employed to explore the short aramid fibre reinforced elastomer composites. The effects of morphology and fibre-matrix interaction on the mechanical properties of composites are discussed.

Regarding fibre type, it is shown co-poly-(paraphenylene/3,4'-oxydiphenylene terephthalamide): PP/ODPTA fibres end up with higher final length than poly(para-phenylene terephtalamide):PPTA which results in considerably higher mechanical properties of corresponding rubber compounds. For each fibre type, higher final length as a result of RFL-coating, and the interaction to rubber matrix are the key factors which overcome even the negative effect of poorer dispersion of RFL-coated fibres. The differences between the adhesion of short aramid fibres and aramid cords are also discussed.

INTRODUCTION

In the past a wide variety of short fibres has been studied to reinforce elastomers. Natural fibres, mainly cellulose[1-3], sisal[4-5], jute[6-7], silk[8], coir[9], bamboo and oil palm, have the advantage that they are made from renewable resources and sometimes show a rather good bonding to rubber due to better mechanical interlocking compared to synthetic fibres. Their complicated fabrication and lower reinforcement factors are disadvantages.

Compared to natural, synthetic fibres like nylon[10], polyester[11], glass[3], melamine[12], carbon[13] and aramid [3,10] have better tolerances in shape and uniformity because they are produced in a continuous manner. Nevertheless, brittle fibres based on carbon and glass are not commonly used for reinforcement of elastomers, since they undergo dramatic breakage during processing. Due to the lower breakage and the considerable improvement of tribological properties of the resulting rubber composites[14-15] there is an increasing interest in the application of short aramid fibres in elastomers.

To obtain optimal performance of such short fibres in elastomers, the following factors are critical: i) dispersion of bundles to filament level, ii) keeping a high aspect ratio during compounding and processing, iii) controlled orientation in the desired direction for application and iv) strong interaction to the matrix elastomer to transfer the load from matrix to fibres via shearing forces exerted on the interface.

One of the important features which should be considered in application of short aramid fibre-rubber composites is the chemical inertness of the aramid surface. Absence of proper coating, leads to lack of chemical interaction between fibre and elastomer resulting in reduced interaction.[16] Application of sizing on the fibre surface can also result in dispersion problems.[17] It has been shown elsewhere that elastomer short aramid fibres containing composites even in absence of chemical adhesion, still gain a considerable degree of reinforcement due to mechanical interactions as result of roughened fibre surface due to bending, dog-bone shape fibre ends and the roughness of the coating itself.[18]

Several attempts have been carried out by different researchers to develop surface modified aramid fibres to improve the interaction with the surrounding polymer matrix[19-21]. An already well known method is the application of a Resorcinol Formaldehyde Latex (RFL) dip to improve the adhesion of long fibres to elastomer matrices. The adhesive layer is applied on a cord by a so-called dipping process. Details of this process can be found elsewhere.[22] The adhesion mechanisms of RFL-treated cords with sulphur-curing elastomers have been comprehensively studied.[23] For EPDM with a peroxide- curing system reinforced with short RFL-coated aramid fibres, it was also shown that chemical bonds are created across the interface, which lead to a significant reinforcement.[18]

In the present study, using two different types of short para-aramid fibres: poly(para-phenylene terephtalamide) (PPTA), and co-poly-(paraphenylene/3,4'-oxydiphenylene terephthalamide) (PP/ODPTA), the influence of RFL-treatment on the resulting morphology and macroscopic properties is investigated in two EPDM compounds: a typical radiator hose compound and the corresponding model compound based on only elastomer, fibres and curatives.

EXPERIMENTAL

Materials: PPTA (Twaron®) and PP/ODPTA (Technora®) short aramid fibres were supplied by Teijin Aramid B.V., Arnhem, the Netherlands, with an initial length of about 3 mm and a filament diameter of 10-12 microns. Both fibre types were coated with two different surface coatings, referred to as standard finish (Stan) and Resorcinol Formaldehyde Latex (RFL). The standard finish 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[21], and RFL as mentioned is commonly used in cord-reinforced elastomer composites to improve adhesion.

EPDM Keltan® 8340A with 5.5 wt.% Ethylidene Norbornene (ENB) and respectively 55 and 39.5 wt.% of Ethylene and Propylene contents, from DSM Elastomers B.V., the Netherlands was used as matrix. It was cured by a peroxide system. Table I shows the different components used in phr. Trimethylolpropane-trimethacrylate (TRIM) and Perkadox® 14/40 peroxide were obtained from AkzoNobel, Deventer, the Netherlands. Carbon black N550 was obtained from Evonik GmbH (formerly Degussa), Germany. The oil type was Sunpar® 2280 paraffinic oil from Sun Oil Company. Stearic acid was a technical quality grade and Poly-Ethylene-Glycol (PEG2000) was obtained from Merck, Darmstadt, Germany.

Table I: Compound Recipes.

Components	EPDM Model	EPDM Model +PPTA	EPDM Model +PP/ODPTA	EPDM Hose	EPDM Hose +PPTA	EPDM Hose +PP/ODPTA
EPDM Keltan 8340A	100	100	100	100	100	100
Carbon black N-550	-	-	-	105	105	105
Oil	-	-	-	60	60	60
Stearic acid	-	-	-	1	1	1
PEG2000	-	-	-	2.5	2.5	2.5
Perkadox 14/40	1.5	1.5	1.5	7.5	7.5	7.5
TRIM	0.6	0.6	0.6	4	4	4
PPTA with Stan/RFL	-	1	-	-	5	-
PP/ODPTA with Stan/RFL	-	-	1	-	-	5

Due to the different components the volume percentage of the fibres differed for constant parts per hundred rubber in the hose compound and the corresponding model compound. It is 0.6 Vol.% for the model compound and 1.4 Vol.% for the hose compound.

Methods: In the first processing step of the model compound half of the matrix was kneaded for 2 min in a laboratory internal mixer (Haake Rheomix 610p, Thermo Fisher Scientific, Karlsruhe, Germany). After that the short aramid fibres were added together with the other half of the rubber. The standard mixing parameters were set as follows: degree of fill of 70%, initial chamber wall temperature of 90°C and rotor speed of 40 rpm. After incorporation of the fibres for specific fibre mixing time t_{mix} the material was passed once through a laboratory two roll mill (Polymix 110L, Servitec Maschinenservice GmbH, Wustermark, Germany) to make sheets with a thickness of about 0.5 mm. These sheets were inspected visually to quantify the macroscopic dispersion. Afterwards the incorporation of curatives as well as orientation of fibres was carried out on a two roll mill in a second processing step. The general orientation of the fibres was considered to be the milling direction.

The curing behavior was determined by means of a rubber process analyzer Scarabaeus SIS V50 (Scarabaeus Mess- und Produktionstechnik GmbH, Langgons, Germany) at 170°C with an amplitude and frequency of 0.2 degrees and 0.83 Hz, respectively. Oriented rubber sheets and samples were then piled into the compression mold by preserving the fibre orientation and cured at 170°C for t_{90} + 2 min under pressure of 10 MPa in a hot press (Fortijne Grotnes BV, Vlaardingen, the Netherlands).

While for study purposes, the model compound was mixed in several steps; the masterbatch of the hose compound was made in a 150 lit industrial internal mixer and later on, curatives and fibres were simply added on a laboratory two roll mill. The curing characteristics were determined and the samples were cured in a similar way as the model compound. To determine the mechanical properties, five S2 type tensile bars were punched out in fibre direction and tests were performed according to ISO 527 with cross-head speed of 200 mm/min using a 1 kN load cell installed in a tensile testing machine from Zwick GmbH, Ulm, Germany. Tests were executed in longitudinal direction of fibre orientation, corresponding to the milling direction.

The initial fibre length distribution (FLD) before mixing was determined by measuring 100 random bundles with a digital caliper. To characterize the FLD after incorporation of the fibres into the model compounds, films with a thickness of 15 microns were compression molded from the unvulcanized material by the hot press. In the next step fluorescence microscopy was executed. A microscope in reflection mode (Axio Imager A1m von Carl Zeiss Jena GmbH, Germany) was used to record images of these films with a magnification of 5x, which were later compiled with software (MethaMorph SPOT Insight) to images with an area of about 250 mm^2. FLD was then determined by counting the length of about 200 fibres. Fibres touching the edge and those with diameter below the normal thickness were left out. Automated detection of length with software as it is standard for glass fibres[24] failed due to curvature and junction points of the aramid fibres. From the obtained fibre length distribution the weighted average of length l_w was calculated as:

$$l_w = \frac{\sum N_i \cdot l_i^2}{\sum N_i \cdot l_i} \qquad (1)$$

where N_i is the number of fibres with a length l_i. The ratio of weighted fibre length before mixing, $l_{w\ \text{initial}}$, and after mixing, $l_{w\ \text{mix}}$, was termed r_w and calculated in percent according to:

$$r_w = \frac{l_{w\ \text{mix}}}{l_{w\ \text{initial}}} \cdot 100 \quad (\%) \qquad (2)$$

Confocal laser scanning microscopy (CLSM) is a well-established technique to visualize the 3D-morphology of short fibre composites, as is commonly used for glass fibre reinforced thermoplastics[25]. To determine the orientation of the model compounds, 2 mm thick S2 tensile bars were punched out of a vulcanized sheet. The parallel part in the middle section (3.15 x 6.3 mm^2) of these tensile bars was then scanned with CLSM (TCS SP5, Leica Microsystems, Wetzlar, Germany) before testing it in a tensile testing machine. The penetration depth of the laser was limited to ~400 microns. Scanning electron microscopy (SEM) was also used to study the fractured tensile test bars made of short fibre composites. SEM was executed with the help of a bench-top NeoScope JCM-500 device, after coating the samples with a very thin layer of platinum.

As there is no direct way to measure adhesion of short fibres to polymer matrices, Strap Peel Adhesion Force (SPAF) tests were done on a long fibre (cords) reinforced hose compound 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 (2 mm) - cord - rubber (1 mm) - cord - rubber (2 mm). The samples were cured in the hot press at 170°C for t_{90} + 2 min. The peel tests were performed at a rate of 100 mm/min.

RESULTS AND DISCUSSION

Dispersion: Dispersion is an important criterion to evaluate the compound quality since agglomerates (clusters of several filaments) may act as crack initiators under load. Figure 1 shows the results of the dispersion studies for the differently treated short fibres in the EPDM model compound prepared in the internal mixer. The PPTA fibres with RFL-coating showed incomplete dispersion in the form of agglomerates containing several filaments (see Figure 1b). The applied shear forces during mixing were too low in this case to overcome the cohesive strength of the dip, which made the filaments stick together. For PP/ODPTA fibres this behaviour was not observed. In this case the RFL-dipped fibres dispersed even better than those with standard dip.

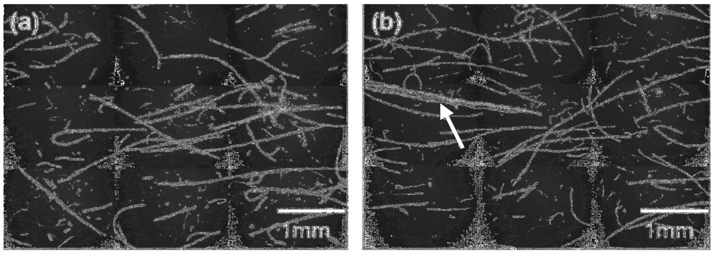


Figure1: Typical images for dispersion: EPDM model compound with a): PPTA Stan and b): RFL finish; arrow shows a PPTA RFL agglomerate.

Fibre length: Due to the fact that aramid fibres contain several levels of superimposed microscopic and macroscopic structures e. g. crystalline structures, pleat structures, fibrillar structures and skin-core structures,[26] they fibrillate and shorten as a result of their unique morphology. This property becomes critical when we consider the high shear and the buckling forces occurring during mixing into elastomers.

To compare the states before and after mixing into the EPDM model compound, the weighted average of fibre length l_w and the ratio of weighted fibre length before and after, r_w were calculated: and are displayed in figure 2. The two fibre types reached different r_w values after mixing. While PP/ODPTA could maintain values above 86%, those for PPTA decreased to a significant extent. This is caused by the different chemical structure as mentioned in the materials section. Fibres dipped with RFL mainly kept higher lengths after mixing compared to those with standard finish. This can be explained by a protective effect of the RFL-dip, which diminishes fibrillation and shortening of the fibres. For PPTA the agglomerates as seen in figure 1b play hereby an important role, since they can withstand buckling during mixing better and therefore prevent fibre breakage. However, after the second processing step of incorporating the curatives on the mill, the PPTA fibres decreased again in length down to values of 1 mm for standard finish and 1.8 mm for the RFL-dip. PP/ODPTA fibres keep a high residual l_w value above 2.6 mm irrespective of the dip.

Morphology: CLSM images taken from tensile test bars show the different morphologies found for the two fibre types and dips in the tensile bars: figure 3. Generally all fibre types either with Stan or RFL dip are oriented in the direction of tension of the corresponding tensile bars. However the fibres are not straight anymore like initially. Due to intensive buckling during the mixing process, kinking points are observable.

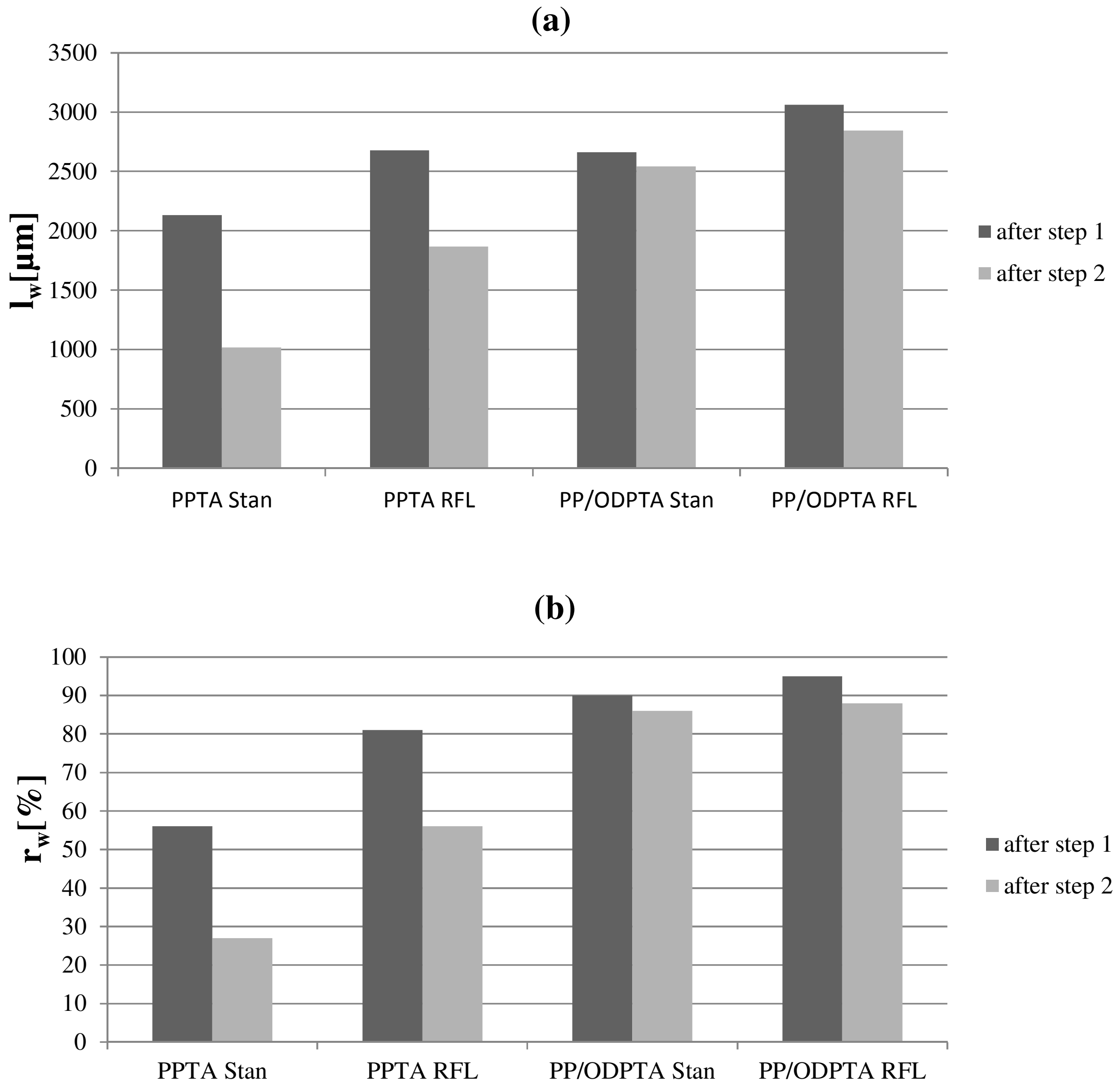


Figure 2: a): Weighted fibre length l_w, and b):fibre breakage ratio r_w after processing step 1 and 2 in EPDM model-compound for PPTA and PP/ODPTA with Stan and RFL dip.

Comparing PPTA with (a) Stan or (b) RFL-dip it is clear that the fibre length in the case of RFL is higher. For PPTA with standard finish a significantly higher degree of fibrillation and shortening of the fibres is observed. Also the agglomerates containing several filaments shown in figure 1b can be seen in case of the RFL- dip. When comparing the two coatings for PP/ODPTA a higher length in case of (d) RFL-dip can be seen. Also the higher remaining length for PP/ODPTA compared to PPTA with standard dip is confirmed.

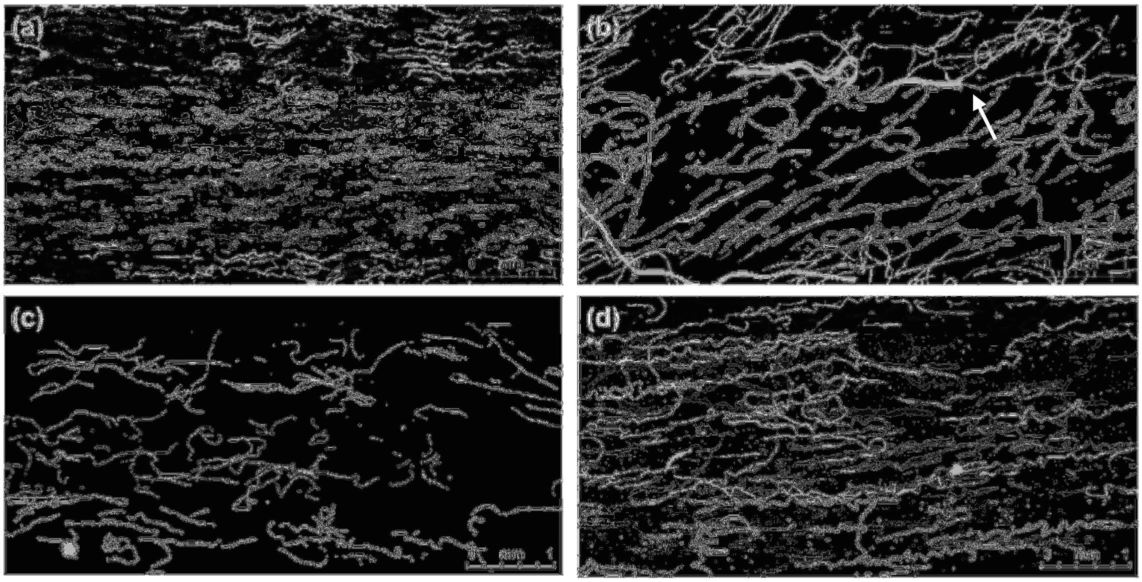


Figure 3: CLSM Images for best orientation for 1 phr fibres in EPDM; PPTA with a): Stan, and b): RFL; and PP/ODPTA with c): Stan, and d): RFL. Arrow shows a PPTA RFL agglomerate.

Fibre-matrix interaction: The results of SPAF tests on the composites made of the hose compound with long PPTA-cords are presented in figure 4. As it can be seen, the RFL-treated cords show much higher interaction to the rubber compound compared to the standard dip cords.

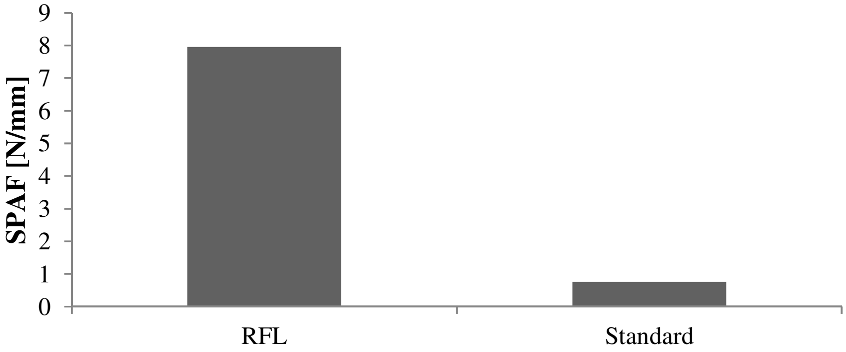


Figure 4: Results of SPAF tests for long fibre elastomer-adhesion.

Figure 5 shows the samples after the SPAF test. The RFL-treated cords were still fully covered with rubber, while the standard cords had no coverage after the test. This is an indication of good adhesion for RFL-coated and poor adhesion for the Stan fibres.

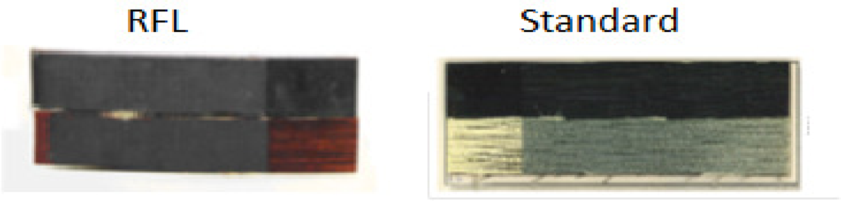


Figure 5: The peeled samples after performance of SPAF test.

This observation may not be applied to short fibres without reserve. Short fibres are produced by cutting full cords after treatment and as mentioned, they gain roughness during the mixing process and this increases the interaction with the surrounding rubber matrix. Second, the RFL-layer on cords is thicker, compared to the short fibres. This is caused by the processing of such fibres. Figure 6 shows part of the cross-section of an RFL-coated aramid cord. The cord consists of a bundle of filaments and as can be seen the coating is mainly on the outer side. This explains the found agglomerates for PPTA with RFL dip in figure 1b. They consisted of two to four filaments and were glued together by the dip while the applied shear forces during mixing were too low to separate them.

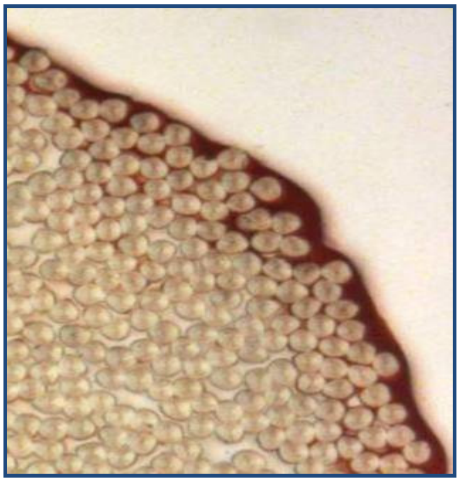
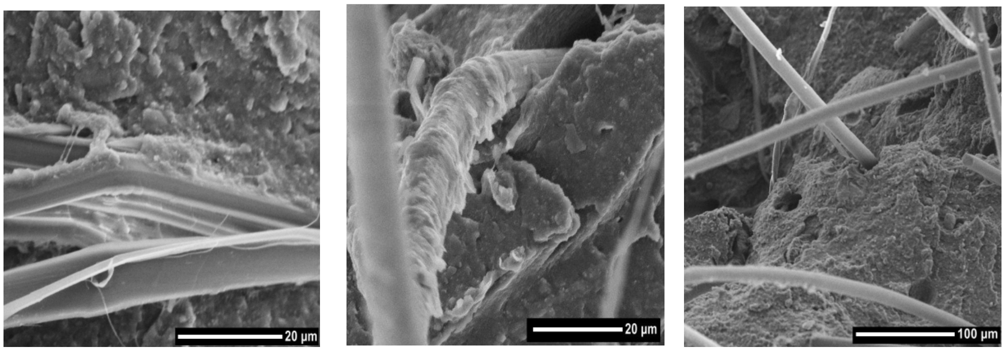


Figure 6: Part of cross-section of an RFL-coated aramid cord.

The amount of the RFL-dip on the cord after the dipping process, called dip pickup may differ. Various researchers have reported that the adhesion increases as a function of dip pickup and reaches a saturation point.[27-28] To produce short fibres, the coating is usually performed in such a way that the dip diffuses more into the cord, so that the inner filaments also become coated . However, always some filaments will still remain uncoated. And the thickness of RFL-coating on the individual filaments is not comparable with the coating on a full cord. This results in a part of the filaments which generate good bonding to the surrounding matrix; and a part which do not, because they are either uncoated or not sufficiently coated. This effect is displayed in figure 7. In the left picture, a sufficiently coated filament remains bound to the rubber matrix; in the middle picture, the dip pick up was not enough to generate good bonding, and in the right picture filaments are uncoated.



(a) (b) (c)

Figure 7: SEM pictures of fracture surface of the hose compound reinforced with 5 phr short RFL-coated aramid fibres. a): sufficiently coated filament; b): insufficiently coated filament and c): uncoated filaments.

Despite the fact that the adhesion of RFL-treated short aramid fibres could not reach the level of the adhesion of a cord; as can be seen in figures 8 and 9, still the reinforcement in the EPDM compounds with RFL-treated fibres is much higher than for the same compound with standard dipped fibres.

Mechanical properties: The mean average stress-strain curves in fibre direction are displayed as engineering stress versus strain in figures 8 and 9 for the EPDM model compounds and hose compounds, respectively. Generally, as already mentioned PP/ODPTA fibres show less breakage, and as a result of that the reinforcement effect is higher compared to PPTA. This results in a steeper initial slope of the stress-strain curve and for the model compound, also significantly reduced elongation at break. For the two investigated fibre treatments the RFL-dip shows improved reinforcement compared to standard finish in the model as well as in the hose compounds. In case of the combination of PPTA with RFL, despite the formation of agglomerates of fibres in the matrix, the higher final length and the better interaction of RFL-dip with the rubber matrix compared to Stan, result in higher initial slope and higher stress in a considerable strain range. The stress values for the hose compounds exhibit a characteristic yield point till where the fibre-rubber interface is still is contributing to the stress values. For higher strains the load is only carried by the rubber matrix itself. A similar behavior was found by Naskar and Shibulal[29] for short PP/ODPTA fibres in an ethylene- octene copolymer.

Although the fibre volume contents and recipes were different, the trends for the reinforcement of the used fibre treatments and –types in terms of initial slope are similar for EPDM hose and model compounds.

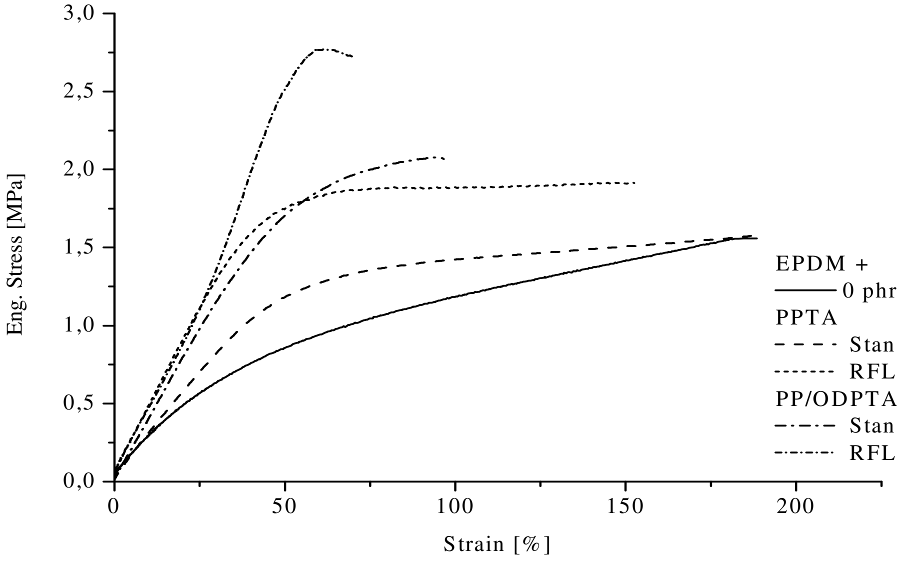


Figure 8: Stress strain curves for EPDM model systems in fibre direction with 1 phr of different fibre types and coatings. 0 phr indicates the reference sample without fibres.

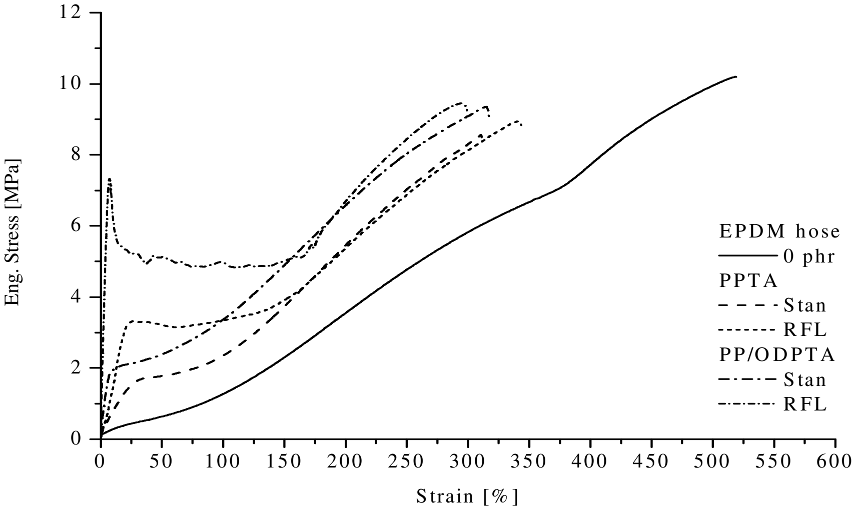


Figure 9: Stress strain curves for EPDM hose compound in fibre direction with 5 phr different fibre types and coatings. 0 phr indicates the reference sample without fibres.

CONCLUSIONS

This work is related to the investigation of composite morphology and interaction of short aramid fibres in an EPDM radiator hose compound and its corresponding model system. Optical and electron microscopy techniques were used to correlate the composite morphology to the mechanical properties obtained from tensile testing. PPTA fibres with RFL-dip could not be dispersed completely to filament level due to the glueing effect of the dip. Irrespective of the mixing time, PP/ODPTA fibres could better withstand the applied shear stresses during mixing and maintain a high level of fibre length, which resulted in better mechanical properties in composites reinforced with these fibres compared to those reinforced with PPTA fibres. On the other side, the RFL-dip acted as protective layer and prevented the fibres from excessive breaking, which was especially the case for PPTA.

With short fibres, reinforcement worked as the result of a combination of chemical and mechanical interactions, and RFL in particular was able to generate chemical bonds to EPDM matrix. Despite chemical bonding only happened between a part of RFL-treated filaments and EPDM rubber, still composites containing these fibres showed better mechanical properties compared to those reinforced with standard finish. The reason for this superiority is not only the partial chemical bonds. There are two more factors which should be considered: better mechanical interlocking of the RFL-treated fibres and the surrounding matrix (due to the roughness of the coating), and the higher final length of these fibres after mixing.

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Chapter 4

Viscoelastic Properties of Short Aramid Fibres Reinforced Rubbers

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ABSTRACT

Among short fibre reinforced composites, those with rubber matrices have gained great importance due to the advantages they have in processing and low cost, coupled with high strength. These composites combine the elastic behaviour of rubbers with strength and stiffness of fibres. Reinforcement with short fibres offers attractive features such as design flexibility, high modulus, tear strength, etc. The degree of reinforcement depends upon many factors such as: the nature of the rubber matrix, the type of fibre, the concentration and orientation of the fibres, the fibre to rubber adhesion and fibre length.

One of the main features related to this class of composites is their hysteretic properties which are of great importance especially in dynamic applications such as tire treads. In this research, short aramid fibres with different kinds of surface treatments: Standard Finish and Resorcinol Formaldehyde Latex (RFL)-coating, have been applied in two different carbon black filled rubber compounds based on Natural Rubber (NR) and Ethylene Propylene Diene Rubber (EPDM). The dynamic properties of the compounds have been measured as influenced by the different kinds of fibre treatments on rubber-fibre interaction. Finally, the contribution of the interfaces and/or interphase layers to the loss properties are characterized.

INTRODUCTION

Fibre reinforced composites with the best mechanical properties are those with continuous fibre reinforcement. Such materials cannot be adapted easily to mass production and are generally limited to products in which the property benefits outweigh the cost penalty. [1] Alternatively, short fibres are used to reinforce polymers in order to improve or modify the thermo-mechanical properties of the matrix for specific applications or to reduce the cost of the fabricated article. [2] By adding suitable fibres and by controlling factors such as the aspect ratio, the dispersion and orientation of the fibres, and the fibre-matrix adhesion, significant improvements in properties can be achieved with thermoplastic, thermosetting and rubber polymers. [1]

Among different short fibre reinforced composites, those with rubber matrices are gaining increasing importance, due to the advantages they impart in processing and low cost coupled with high strength. These composites combine the elastic behaviour of rubber with strength and stiffness of the fibres. Short fibre reinforced rubbers have been successfully used in production of V-belts, hoses, tire treads and complex-shaped mechanical goods. [3, 4]

Generally, the degree of reinforcement depends on the nature of the matrix, the type of fibres, the concentration and orientation of the fibres, fibre to matrix adhesion (generation of a strong interface) and aspect ratio of the fibres. [3, 4, 5] Poor adhesion increases the critical fibre length, which is the minimum length of fibres needed for effective stress transfer, since mechanical friction at the interface must take the role of adhesion. Good adhesion can nearly double the tensile strength and elongation at break compared to a composite in which the adhesion is poor. [6]

A common method to increase the adhesion is by fibre surface treatment, using for example isocyanate or Resorcinol Formaldehyde Latex (RFL); the adhesive treatment for various types of fibres differs. The adhesive layer is applied on a cord by a so-called dipping process. Details of this process can be found elsewhere. [7]

The concept of strength of the interfacial bond is not always clear. In case of perfect adhesion the applied stress can be properly transferred from matrix to the fibres and failure mode will not be phase separation: the matrix or the fibres break 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 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. [6]

Besides the increased strength of the short fibre composites, their viscoelastic properties are also of great importance, especially in dynamic applications. Friction forces of tires are related to the value of the loss angle [8], and the relation between rolling resistance and wet grip of tires to the hysteretic properties is also well-known. Hess and Klamp [9] referred to the work done by Khromov and co-workers [10], who examined a blend of Styrene Butadiene rubber/Butadiene rubber and concluded that a drop of only 0.022 in tan δ results in 5% reduction in tire rolling resistance.

There are studies [2, 11, 12] which show that adding short fibres generally results in an increase in storage modulus of rubbers in a considerable range of fibre loadings and temperatures. It has been also observed that increase in adhesion increases the storage modulus and mechanical loss per cycle under dynamic conditions. [13]

Furthermore the interface and interfacial bonding affects the loss properties of composites. [2, 13] It has been suggested that the quality of the interfacial adhesion in the composites can be evaluated by measuring that part of energy dissipation which is contributed by the interfaces, which can be obtained by subtracting the loss of fibre and matrix from the total loss of the composites. [14] Gibson [15] found higher damping of aramid fibres than glass fibres in an epoxy resin. Nielson and Landel [6] observing higher damping of the aramid fibres compared to the glass fibres in an epoxy resin, concluded that this may be due to poor adhesion of aramid fibres, but at least some of the damping is due to the high damping of the aramid fibre itself compared to the negligible damping of a glass fibre.

Tensile test results and a study on fracture mechanics of Natural Rubber (NR) and Ethylene Propylene Diene Rubber (EPDM) compounds reinforced with short aramid fibres, treated with Standard Finish (St), an oily substance used to facilitate spinning, and RFL were presented elsewhere. [16] It was shown that adding fibres to the compounds causes a drop in ultimate tensile strength and elongation at break, but also results in higher stresses in both low and high strain regimes. Although in all cases RFL-treated fibres showed to lead to the best mechanical properties, reinforcement in sulphur-cured NR especially with RFL-treated fibres was significantly less than in peroxide-cured EPDM. It was argued that clear chemical adhesion only happened in the case of peroxide-cured EPDM reinforced with RFL-treated fibres, and that in the other cases reinforcement was due to mechanical interaction. The results of fibre length studies [17] in EPDM and NR compounds, without carbon black, showed that in both matrices RFL-treated fibres ended up in slightly higher fibre length after mixing. A Scanning Electron Microscopy (SEM) study on the fracture surfaces of the carbon black filled rubbers showed that the fibres treated either with St or RFL coating did not break as the result of applied tensile force, which shows that they were still above their critical length.[16] So, fibre breakage was not a critical factor in determining the final properties of the composites.

In the present work, in relation to the previous research, the viscoelastic properties of these two types of widely used rubbers, Ethylene Propylene Diene Rubber (EPDM) and Natural Rubber (NR) are investigated in the form of typical radiator hose and truck tire tread compounds, reinforced with short aramid fibres. The aim was to study how the viscoelastic properties of these rubbers are affected by adding short aramid fibres and how the two types of reinforcement, chemical and mechanical, work out in these viscoelastic properties.

EXPERIMENTAL

Materials: Twaron® aramid short fibres were supplied by Teijin Aramid B.V., the Netherlands, with average initial length of 3 mm and fibre diameter of 10-12 microns. Two types of elastomers were used: NR: SMR CV60; and EPDM: Keltan® 8340A with 5.5 weight percent Ethylidene Norbornene (ENB) content, and 55 and 39.5 weight percents of Ethylene and Propylene respectively, from DSM Elastomers B.V., the Netherlands. Carbon blacks N220 and N550 were obtained from Evonik GmbH (formerly Degussa), Germany. The oil types added to the EPDM and NR compounds were Sunpar® 2280 paraffinic oil from Sun Oil Company and Nytex 840 naphthenic oil from Nynas, respectively. ZnO was Red Seal quality from Union Minière, Belgium, and stearic acid was a technical quality grade. PolyEthyleneGlycol (PEG2000) was obtained from Merck, Darmstadt, Germany. Sulfur and t-Butyl-Benzothiazol-Sulfenamide (TBBS) were provided by Rhein Chemie, Germany.

Trimethylolpropane-trimethacrylate (TRIM) and Perkadox 14/40 peroxide were obtained from AkzoNobel, Deventer, the Netherlands. Polymerized 1,2-dihydro-2,2,4-trimethylquinoline (TMQ) came from Flexsys, Belgium.

Methods: Two masterbatches were made in a 150 liter industrial internal mixer. The compositions of the two compounds are presented in Table I. The curatives and short fibres were added on a laboratory two roll mill. Two different kinds of surface treatments have been used for the aramid fibres. The treatments were St and RFL coating. It was shown elsewhere that the standard finish has no negative influence on the adhesion of cords to rubbers. [18]

Table I: Compound Recipes (phr).

Component	NR	EPDM
NR	100	-
EPDM	-	100
Carbon black N-220	55	-
Carbon black N-550	-	105
Oil	8	60
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

The cure characteristics of the compounds were measured with a Rubber Process Analyser (RPA) of Alpha Technologies, and according to the results the compounds were cured for their t_{90} +2 minutes in a Wickert hot press WLP1600, at 100 bar pressure in sheets of 1.9mm thickness. In order to obtain a preferred orientation of the fibres, 20 gr of each compound - the amount needed to fill the mould - was passed several times through a two roll mill. The milling direction was considered as longitudinal direction of fibre orientation.

Dynamic Mechanical Analysis were done using a Metravib Viscoanalyser DMA+150, in tension mode; storage moduli and loss angles of the samples were measured in temperature sweep, strain sweep, and frequency sweep tests. To reach minimum error, the tests were performed at least on 3 samples of every compound. For NR compounds the standard deviation was usually low; for example in temperature sweep tests above the glass transition temperature range, it was below 1%, and in strain sweep tests, below 3%. For EPDM in some cases, to reach a minimum level of error up to 6-7 samples of the same compound had to be tested until at least 3-4 similar curves close to each other with a standard deviation less than 3%, were obtained. The first tests were done without the application of a pre-strain which is closest to practical use of most rubber goods in dynamic applications. A second set of tests were done with application of a static elongation, pre-strain, larger than the applied dynamic strain values, to remain in the elongation regime. In any case, only the data with an acceptable standard deviation are reported.

Elongation set tests have been done on 3 samples of each compound containing 5 phr fibres. Stripes with a length of 82 ± 1 mm and width of 10 mm were cut out of the cured sheets with thickness of 1.9 mm in parallel direction of fibre orientation. The samples were stretched for 30 ± 1.5% of their initial length. After 24 hours at room temperature the samples were released and after 30 minutes their lengths were measured. The elongation set is reported as the permanent increase in length in percent divided by the applied elongation.

RESULTS

The carbon black filled compounds were loaded with 3 phr fibres, in order to avoid possible interactions between the short fibres, which happens at higher concentrations resulting in a significant contribution to the measured viscoelastic properties. In fact, previous results on model systems (without carbon black) showed that this does not happen till 5 phr loading. [17] The viscoelastic properties of the samples have been evaluated by tests in temperature, strain, and frequency sweep modes, to give a rather complete picture of the viscoelasticity of the composites under different practical conditions.

Temperature sweep measurements: The storage moduli of NR and EPDM compounds in temperature sweep tests, without pre-strain are shown in figure 1 . It can be seen that the addition of fibres generally results in an increase in storage modulus, especially in the temperature range above T_g. For NR this is even more clear in the temperature range above 0°C than at lower temperatures. It also can be seen that RFL- treatment leads to more reinforcement compared to St-fibres. The storage moduli of the EPDM compounds also increase considerably with inclusion of RFL-treated fibres.

The tan δ results for the temperature sweep tests, without pre-strain, figure 2, show that for NR the compound with RFL-treated fibres generally has the lowest tan δ throughout the whole temperature range, even lower than for the compound without fibres. It can also be seen that in both NR and EPDM compounds in the range above room temperature St-fibres generally result in the highest loss angle. An interesting point here is the difference between the loss angle curves of the compounds at the tan δ peak or glass transition temperature, where RFL shows the lowest tanδ peak and the compound without fibres (WF) the highest for both polymers. Having a closer look at figure 1, it turns out that with passing the glass transition temperature the drop in storage modulus of fibre-filled composites is less compared to the WF-compounds. This trend is similar to the results of tensile tests: at elongations up to 100%, RFL-treaded fibres lead to the highest stresses, and St-treated fibres still result in higher stress compared to WF-compounds. [16]

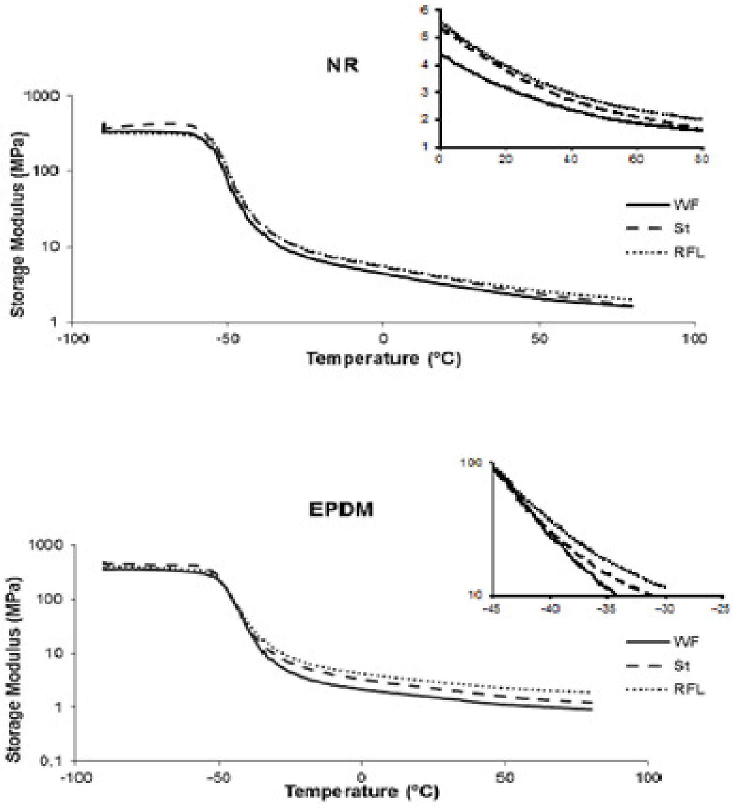

Figure 1: Storage moduli from temperature sweep DMA measurements at 0.1% strain, without pre-strain, frequency of 10 Hz for various fibre treatments. WF: Without Fibre; St: Standard Finish treated; RFL: RFL-treated.

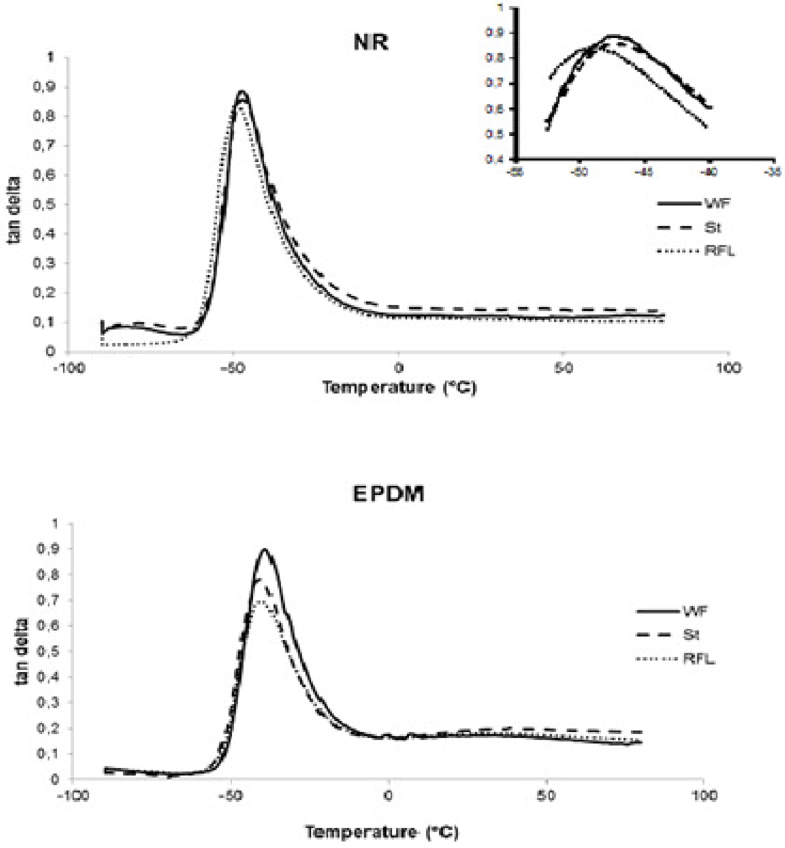

Figure2: Loss factor tanδ derived from temperature sweep DMA measurements at 0.1% strain, without pre-strain, frequency of 10 Hz for various fibre treatments. WF: Without Fibre; St: Standard Finish treated; RFL: RFL-treated.

Figure 3 shows that for NR compounds, without pre-strain, at a higher dynamic strain of 5%, the difference between the various tan δ curves is more pronounced in the range above room temperature. This test was done on the NR compounds mainly to represent rolling resistance as an important tire property in a more severe conditions of higher strain. The rolling resistance of a tire is represented by the loss angle of the compound in the range between 30°C and 70°C which is the running temperature range of tires.[19] It can be seen that the NR-compound containing RFL treated fibres has a considerably lower loss angle, despite the fact that the reinforcement mechanisms involved in this case are mainly mechanical of nature [16] and, unlike for RFL-treated cords, no chemical bonds occur between rubber and the coating on the fibres. It can also be seen that at 5% of strain, St-treated fibres do not negatively affect rolling resistance relative to the compound without fibres. An attempt was also made to perform a temperature sweep test on EPDM compounds at 5% of strain, but the scatter in the data was too high to be presented here.

The same temperature sweep tests in low strains have been done on the samples with application of 0.2% of static pre-strain and the results of storage modulus and tan δ were comparable with the results of the same test without pre-strain, which are not presented to avoid unnecessary additional pictures.

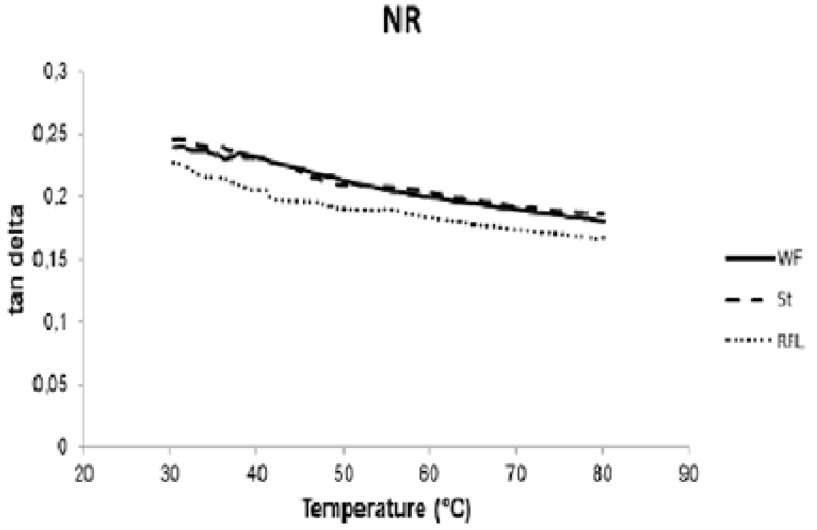

Figure 3: Loss factor tan δ derived from temperature sweep DMA measurements at 5% strain, without pre-strain, frequency of 10 Hz for various fibre treatments.

Strain sweep measurements: Figure 4 shows storage moduli measured in strain sweep tests, without pre-strain at ambient temperature of 20°C. It can be seen that again in both cases, NR and EPDM, over a wide strain range RFL-treatment of the fibres results in the highest storage modulus, although this difference is not always very significant because of the small amount of fibres added. In the NR compound, St-fibres perform better than WF for strains till 5%, while this range is wider for EPDM. In all cases, increase in strain results in less difference between the fibre-filled compounds and the compound without fibres. The loss angles obtained from the strain sweep tests, without pre-strain at ambient temperature, figure 5, show that in a considerable range of strains, the NR compound reinforced with RFL-treated fibres has the lowest tan δ, while there is almost no change in loss angle of the NR compound as a result of adding St-treated fibres in comparison with WF.

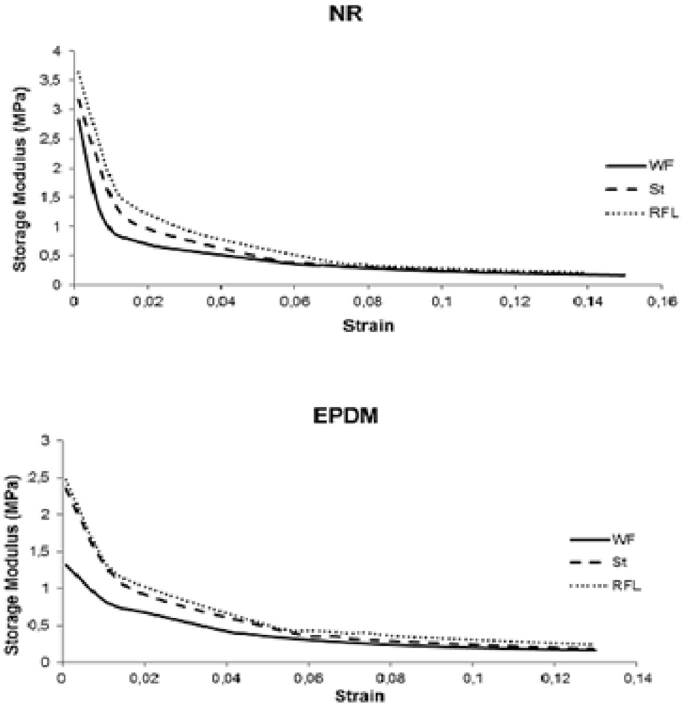

Figure 4: Storage moduli from strain sweep DMA measurements on 3 phr fibre loaded NR and EPDM compounds at ambient temperature, without pre-strain, frequency of 10 Hz, for various fibre treatments.

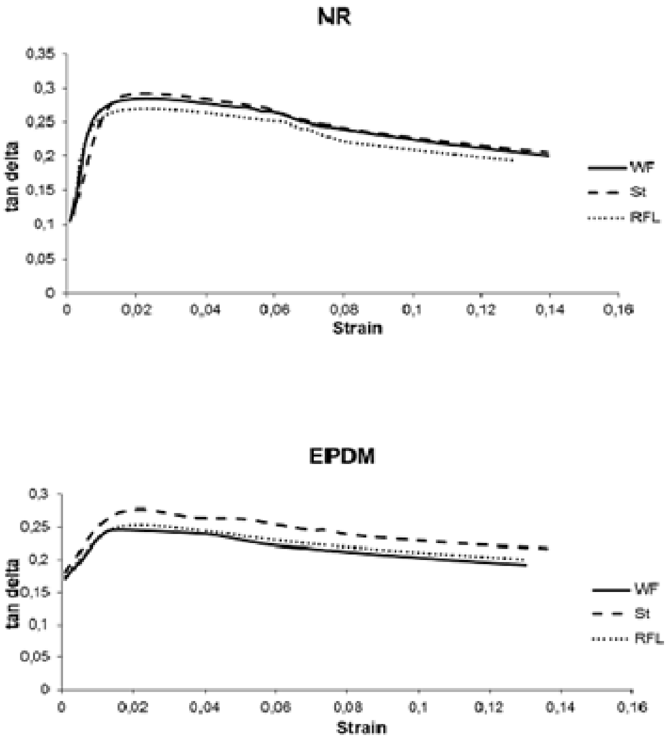

Figure 5: Loss factor tan δ derived from strain sweep DMA measurements at ambient temperature, without pre-strain, frequency of 10 Hz, for various fibre treatments.

In the tan δ graphs for EPDM, figure 5, without pre-strain and at very low dynamic strains, adding fibres results in almost no change in tan δ. This is in accordance with the results presented in figure 2 in the temperature range between 0 and 20°C. At slightly higher strain of about 1%, the interface effect is pronounced and St-fibres show higher loss compared to the compound without fibres, while RFL-coated fibres give a lower tan δ than St-fibres. This can be due to the absence of chemical bonding for the St- fibres. Where a high tan δ can be an indication of mechanical loss/hysteretic effects due to mutual friction between rubber and the fibres on the interface, the lower level of tan δ for the RFL-coated fibres suggests that there is less mechanical loss than with St-coating.

Strain sweep tests after applying a pre-strain of 10%, larger than the dynamic strain values of up to 9%; have also been performed on the samples: figures 6-7. The main difference between the storage modulus results here is seen for NR, while the storage modulus of EPDM shows the same trends as the tests without pre-strain. For NR the application of a pre-strain, reduces the benefits of RFL-treated fibres. While for NR the interaction with all fibres is mainly mechanical and not chemical of nature, it is clear that this kind of interaction mainly acts at low elongations.

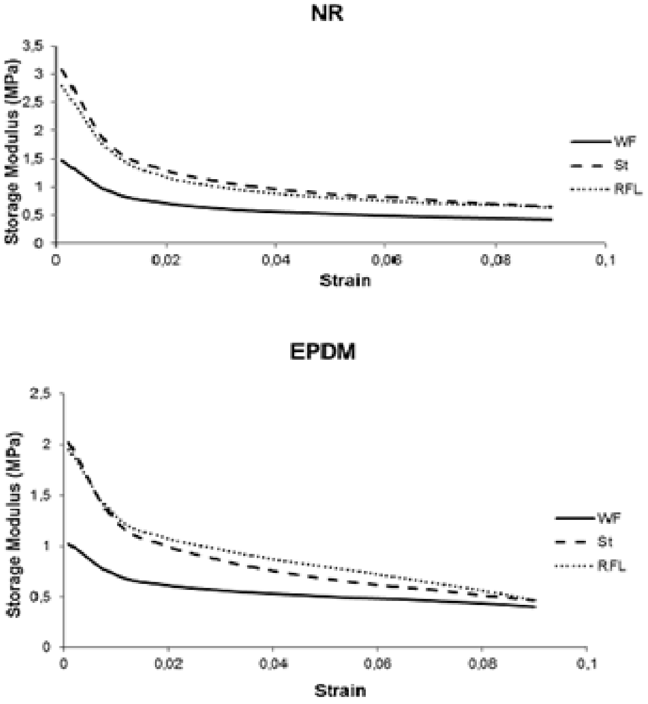

Figure 6: Storage moduli from strain sweep DMA measurements, with application of 0.1 (=10%) pre-strain, on 3 phr fibre loaded NR and EPDM compounds at ambient temperature, frequency of 10 Hz, for various fibre treatments.

This was also confirmed by the results of tensile tests, as presented in our previous work.[16] It was shown there that in a static tensile test the reinforcement factor, defined as the stress of the composite at a certain elongation divided by the stress of the corresponding WF compound at the same elongation, is higher for low elongations. That is because in processing of the composites, the rubber can form itself around the roughness of the fibre before being cured. So, after curing, it is difficult to pull the fibre out of the first position. At higher strains, after changing the mutual position of the fibre-surrounding matrix, the reinforcement may still take place due to frictional forces between fibres and rubber, but to a relatively lesser extent. Another important factor is that: the RFL-coated fibres used in this research had a dip pick up of 12-15 weight percent, so that using the same weight, the number of RFL-treated fibres is 12-15% less than St-fibres. So, it is readily understood that by lack of chemical adhesion, and by removing the most effective part of mechanical interaction as a result of applying a large enough pre-strain, St-fibres can even lead to a slightly higher storage modulus than RFL-treated fibres. Loss angle results show again no advantage of RFL-treated compared to St-fibres fibres in NR, in spite of a general decrease in tan δ for both fibre-filled compounds compared to the compound without fibres.

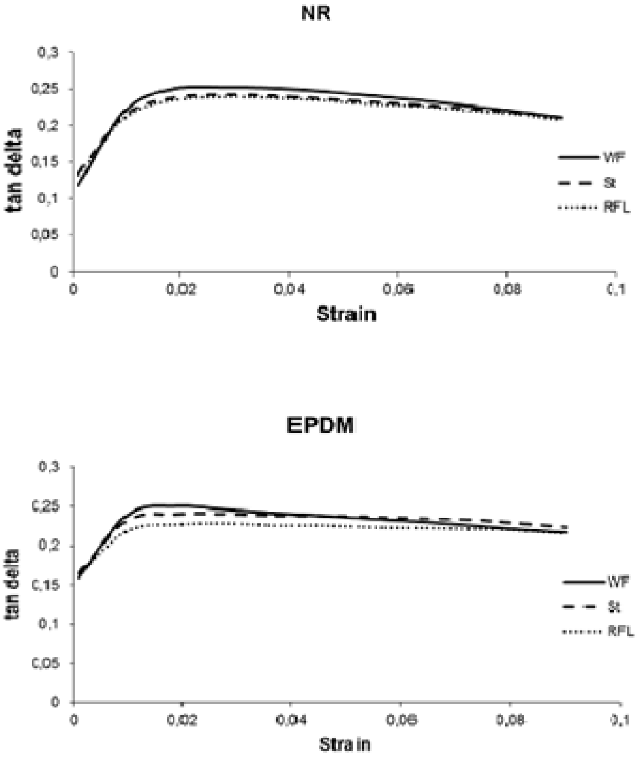

Figure 7: Loss factor tanδ derived from strain sweep DMA measurements at ambient temperature, frequency of 10 Hz, Pre-strain of 0.1 (=10%), on 3 phr fibre loaded NR and EPDM compounds for various fibre treatments.

For EPDM, the chemical adhesion still gives an advantage to RFL-treated fibres, even with this amount of pre-strain. It can also be seen that with increasing strain, the RFL-curve approaches the St-curve as the result of breakage of the chemical bonds at higher strains.

Frequency sweep measurements: Frequency sweep tests have been performed on both NR and EPDM samples at 0.5% strain without pre-strain and the results are presented in figure 8. It has been tried to do the tests also with pre-strain, but the data scattering was outside an acceptable range, so the results are not presented.

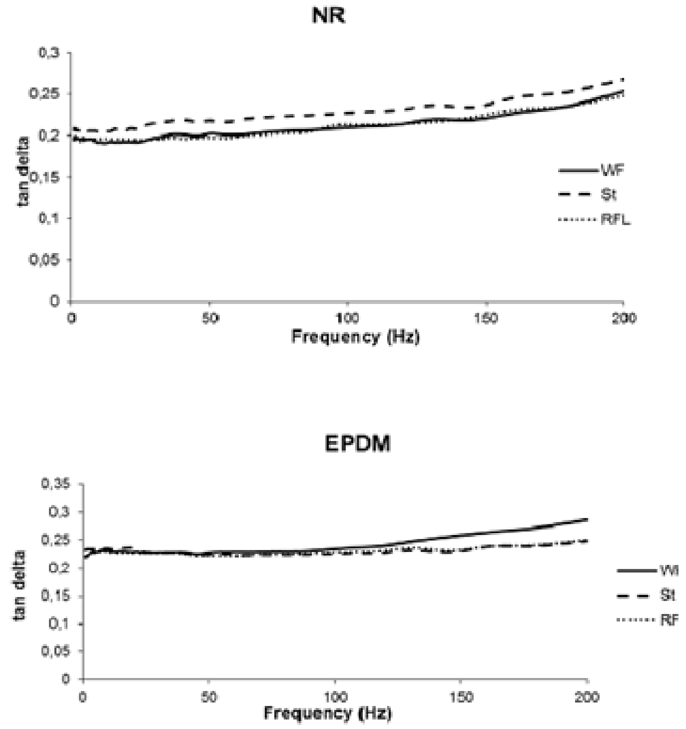

Figure 8: Loss factor tanδ derived from frequency sweep DMA measurements at ambient temperature, without pre-strain, strain of 0.5%, on 3 phr fibre loaded NR and EPDM compounds for various fibre treatments.

For EPDM at increased frequencies, the mechanical interaction between fibres and rubber prevents or limits mutual sliding with the corresponding energy dissipation and becomes the dominant effect: tan δ values of these fibre-filled compounds are lower than for the compound without fibres. For NR, there is not much difference between the compound without fibres and the compound containing RFL-treated fibres, but in this low strain regime of 0.5% RFL leads to lower loss angles in the whole frequency range compared to St-fibres. Comparing this with the strain sweep test results it can be seen that in the stiffer matrix of NR, the degree of reinforcement is more sensitive to strain rather than to frequency.

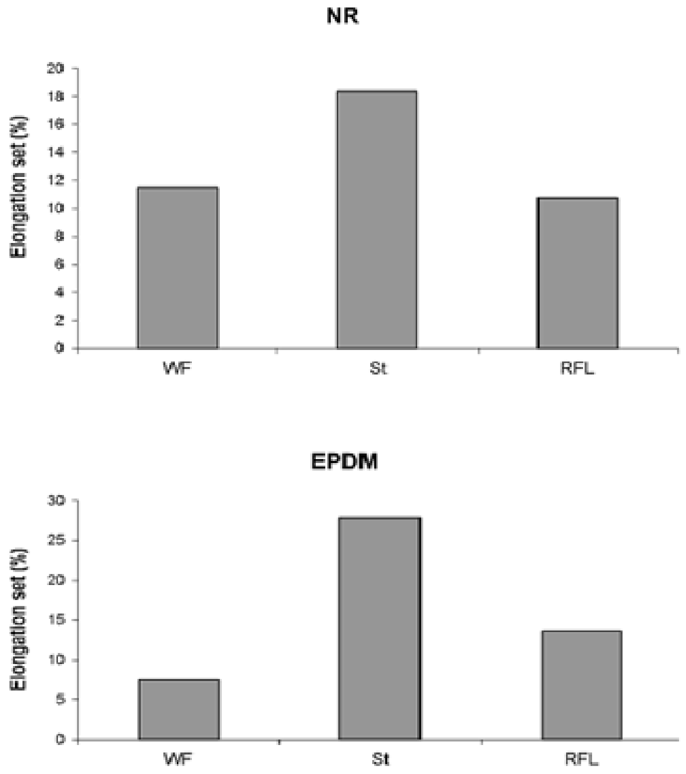

Figure 9: Elongation sets, 24 hours, ambient temperature, NR and EPDM compounds with 5phr fibre loading.

Elongation set: To investigate the rubber-fibre interaction and sliding of rubber along the fibre surface by a different method, elongation set tests have been performed on the samples. As this is a rather primitive mechanical test with lower sensitivity compared to DMA, the fibre contents had been increased slightly, to 5phr. The results are presented in figure 9. For both NR and EPDM, adding St-treated fibres results in a considerable increase in the set. This is more pronounced for EPDM compared to NR. The interesting point is that replacing the St-treated fibres with RFL-treated, the set decreases to a large extent. St-fibres are not able to form chemical bonds, resulting in weaker interfaces. So the rubber can more readily slide along the fibre surface, which in the static test of elongation set is reflected in a higher value, and in dynamic tests in a lower storage modulus and higher loss angle compared to RFL-treated fibres.

DISCUSSION

Adding fibres in fact means generating interfaces (and in some cases interphases) into a material. If the rubber would be perfectly and ideally bonded to the fibres' surface, the storage modulus would increase and the contribution of the interface to the loss modulus would not be significant. But in practice there is no perfect and totally uniform bonding taking place and reinforcement happens by combined effects of several mechanisms. It the present study, for St-fibres there is no chemical bond, but for RFL-fibres part of the fibres which are properly coated, depending on the curing system, are able to generate chemical bonds to the rubber matrix [16]. Rubber which is not chemically attached to the fibres can partially slide along the fibre surface and so create friction. This results in increasing elongation set or additional losses in dynamic loading. Despite that, in a considerable range of strains, temperatures and frequencies, reinforcement still has a possible effect in the sense that it keeps the loss values at the same level as for the compound without fibres or even lowers these to some extent. It is also possible to decrease the set properties by improving fibre-rubber interaction.

An example of using St-fibres to increase the storage modulus of rubbers without negative effects on loss properties, is NR with pre-strain. If in actual practice a NR compound is under permanent load and subjected to a dynamic stress, 3 phr of fibres without treatment can enhance the dynamic properties. For RFL treated fibres with higher degree of reinforcement the situation is even better. Generally, adding RFL-treated fibres to a compound results in increasing storage modulus, with almost no negative effects or even a decrease in tan δ. This can be attributed their higher interaction with the rubber matrix, chemical as well as mechanical.

CONCLUSIONS

The viscoelastic properties which are of great importance in dynamic applications, especially in tires, have been investigated in different modes. It was shown that mechanical and chemical interactions between short fibres and a rubber matrix, which are the reasons for an increase in storage modulus, can affect loss properties in different ways, depending on the type of matrix, temperature, dynamic strain and the possible application of a static pre-strain.

There are two main influencing factors which should be considered: 1/ Reinforcement as a result of interaction between fibres and rubber which results in an increase in storage modulus of the composite; 2/ If there is no perfect interphase and fibres and rubbers are not fully bonded, sliding of the rubber matrix along the fibre surface causes additional losses due to friction.

In general it will not be possible to obtain similar reinforcement with short fibres compared to long ones; considering the advantage of the lower processing costs of short fibre-reinforced composites, there is still room for improvement in the their applications. It has been shown that chemical interaction is not the only mechanism for reinforcement of rubbers with short fibres, but that mechanical interactions are also of great importance.

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Chapter 5

Adhesion of RFL-coated Aramid Fibres to Sulphur and Peroxide Cured Elastomers

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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, because of their significantly higher modulus and strength compared to other commercial fibres. 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 only 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 tires 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].

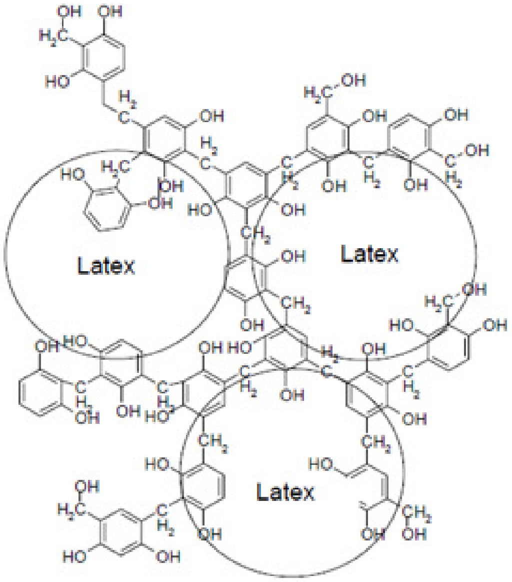

Figure 1: Proposed RFL morphology.

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® 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 terephtalamide) or PPTA, Twaron ® type 1000, 1680 dtex produced by Teijin Aramid B.V.; The RF and RFL-coatings 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.

Table I: The composition of compounds.

Component	NR	EPDM
NR (SMR CV60)	100	-
EPDM (Keltan® 8340A)	-	100
Carbon Black (N220)	55	-
Carbon Black (N550)	-	105
Oil	8 (Nytex 840)	60 (Sunpar® 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

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_2I_2. 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_{90} + 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.

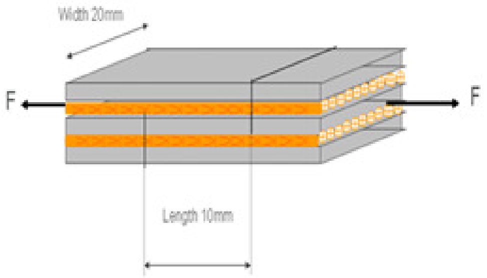

Figure 2: Sample preparation for shear test (Lap Shear).

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.

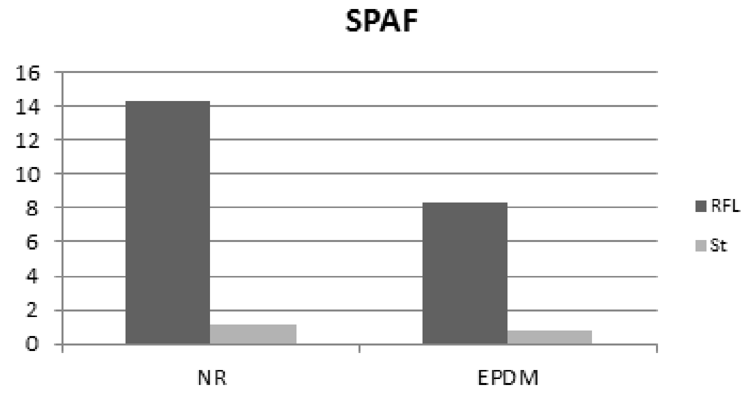

Figure 3: SPAF results (N/mm).

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

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

i.e. the thermodynamic work of adhesion, W_a, 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]:

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

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

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

θ_1 and θ_2 are contact angles of liquid 1 and 2, γ^p is the polar and γ^d is the dispersive surface tension values for each solvent and the solid surface(polymer). The total surface tension of the solvent (1) would be ($\gamma_1^p + \gamma_1^d$) and for the solvent (2), ($\gamma_2^p + \gamma_2^d$) .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.

Table II: Contact angles and surface tension of fibres and rubbers.

Material	**Angle (deg.)**		**Surface tension (mJ/m^2)**		
	H_2O	CH_2I_2	Total	Disperse	Polar
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 III: Interfacial tension and work of adhesion (mJ/m^2).

	St		**RFL**	
	Interfacial Tension	Work of Adhesion	Interfacial Tension	Work of Adhesion
EPDM	32.2	76	24.2	40
NR	32.1	73.8	0	63.9

Here, water and CH2I2 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.

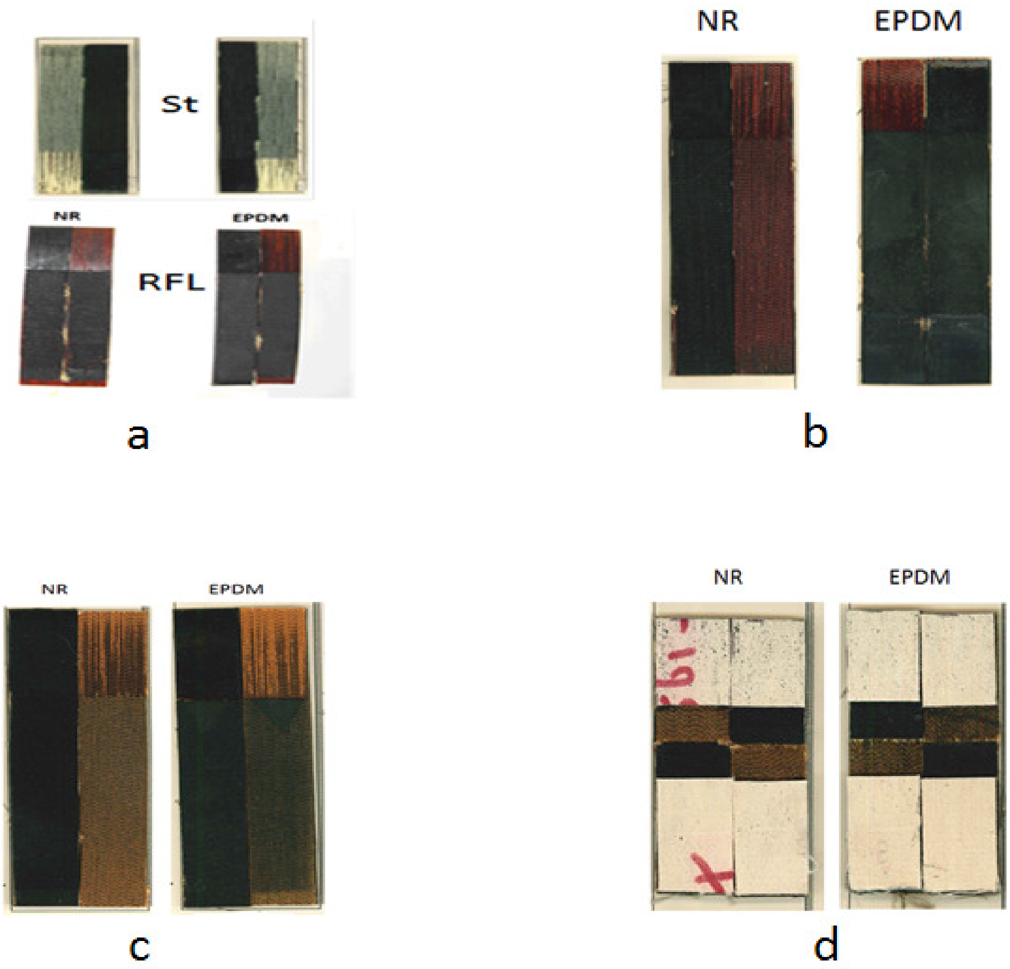

Figure 4: Samples after SPAF/ Lap shear tests.

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.

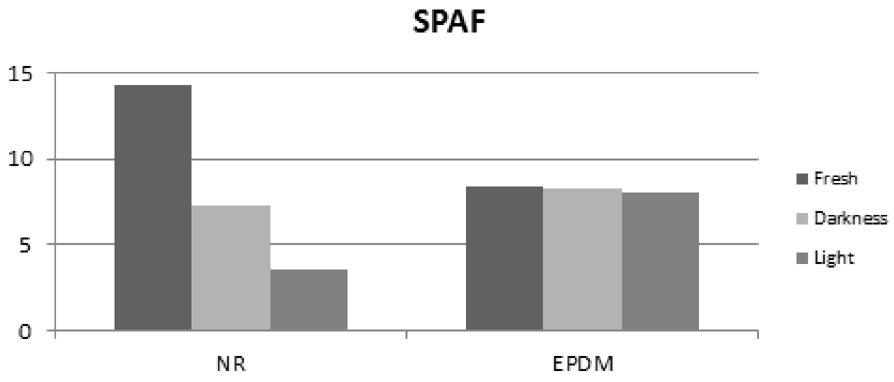

Figure 5: SPAF results(N/mm) for RFL-coated fibres fresh and after 1 week aging.

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.

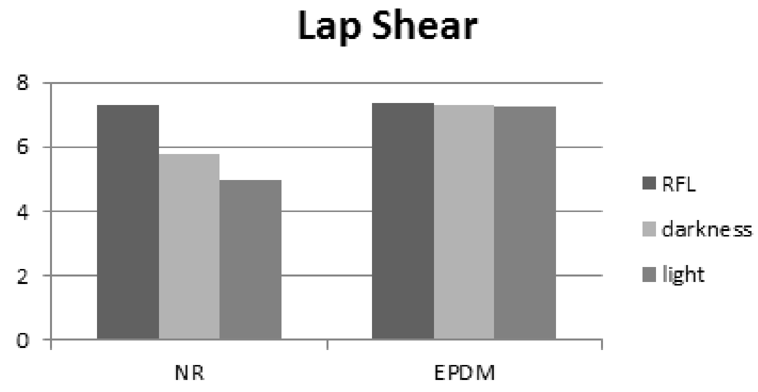

Figure 6: Lap shear (MPa) results for RFL-coated fibres fresh and after 1 week aging.

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[20] that peroxides are able to react equally well with saturated polymer chains.

But a question still remains. Does peroxide like sulphur generate bonds only 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 only RF (without Latex). The SPAF and Lap Shear results are presented in figures 7, 8, 4c and 4d.

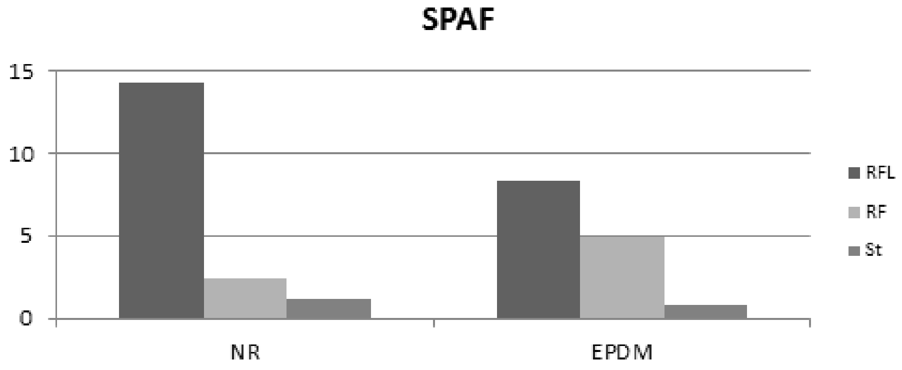

Figure 7: SPAF results (N/mm) for RFL, RF and St-treated fibres.

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.

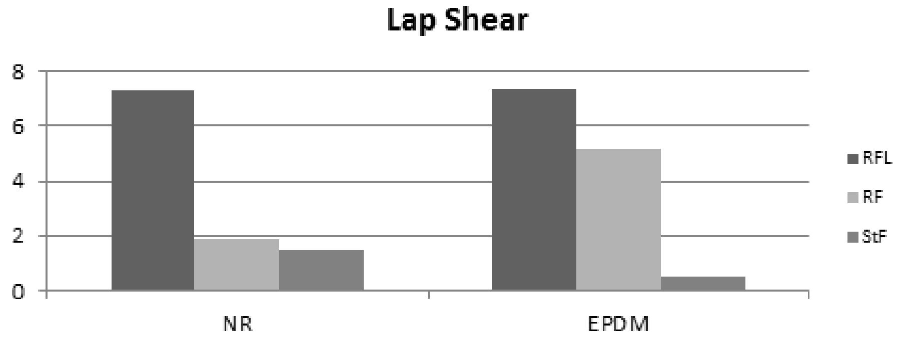

Figure 8: Lap shear (MPa) results for RFL, RF and St-treated fibres.

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.

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Chapter 6

Adhesion of RFL-coated Aramid Fibres to Elastomers: the Role of Elastomer-Latex Compatibility

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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.

In the present study aramid fibres are investigated, because of their significantly higher modulus and strength, compared to other commercial fibres. Their adhesion after being coated with RFL, in compounds based on Natural Rubber (NR) and in NR blended with a small amount of Styrene Butadiene Rubber (SBR) is investigated. It is shown that though having very similar tensile properties, the latter compound has much better adhesion to RFL which is also less sensitive to RFL aging, compared to the pure NR compound. It is argued that an interphase region is formed between RFL and the elastomer, which is stronger for the compound containing SBR due to its enhanced compatibility with the latex part of the RFL.

INTRODUCTION

Reinforced composites with the best mechanical properties are those with continuous fibre reinforcement. Alternatively, short fibres are also used to reinforce polymers in order to improve or modify the thermo-mechanical properties of the matrix for specific applications or to reduce the cost of the fabricated article [1].

Generally, the degree of reinforcement depends on the nature of the matrix, the type of fibres, the concentration and orientation of the fibres, fibre to rubber adhesion by generation of a strong interface, and the aspect ratio of the fibres [2,3,4]. Poor adhesion increases the critical fibre length, an important factor in the case of short fibres, which is the minimum length of fibres needed for effective stress transfer. 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 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 [5].

It is widely believed that adhesion is not a simple phenomenon to be described by only one source of interaction. Allan [6] writes: “Since 1922, there have been a number of attempts to develop a single explanation or theory which would account for all the varied aspects of adhesion. However, it is now clear to account for various areas of the whole range of phenomena which may be described as adhesion.”

In literature several forces have been mentioned which need to be considered for particular problems of adhesion, of which the most important are [6, 7]: Mechanical forces, Secondary (van der Waals) forces and Primary valence forces, mainly responsible for chemical bonding, and Diffusion.

For fibre reinforcement of elastomers 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 in particular are normally coated with an epoxy sub-coating and an RFL-layer on top. The latex used in an RFL formulation 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[8]. Several studies have shown that the structure of the cured RFL consists of a continuous resin phase and dispersed latex particles [9,10]: figure 1.

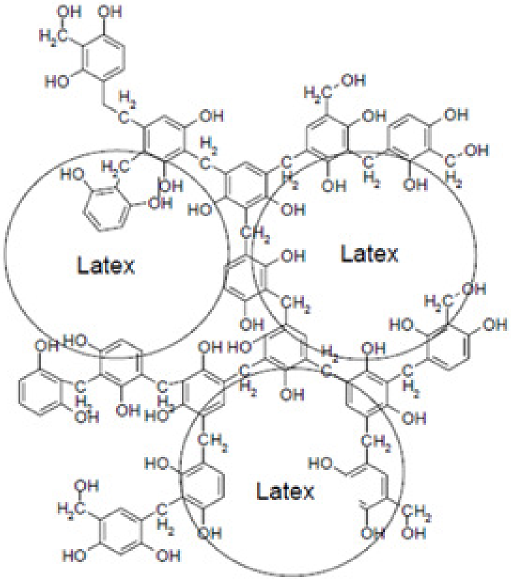

Figure 1: Proposed RFL morphology.

For RFL-coated fibres in elastomer matrices with sulphur-curing systems, it has been suggested that diffusion of sulphur from the rubber compound into the RFL dip film happens. Because of this the sulphur can interact with the latex portion of the RFL and the rubber matrix and form a sulphur cross-link [11]. In our previous research [12] it was shown that for peroxide cured systems bonding happens between rubber and both the latex and resin part of the RFL. It has also been discussed that secondary van der Waals forces are not considerably contributing to adhesion between RFL-coated fibres and elastomers either, and can easily be neglected. On the other hand chemical bonds were shown to be responsible for good adhesion between RFL-coated fibres and both sulphur and peroxide cured elastomers. The role of mechanical interlocking which is of particular importance in short fibres, has also been discussed [13].

The migration of sulphur, zinc and accelerators into the RFL dip has been demonstrated with EDX measurements [14-16]. But, despite the emphasis on curative migration from the elastomer into the RFL-layer, the role of polymer chain diffusion in these particular cases is mostly neglected.

In general if two polymers are in sufficiently close contact, parts of the long chain molecules can diffuse across the interface. This might result in interpenetration and eventually disappearance of the interface [17]. Wake [18] states that the interdiffusion of polymers across an interface is possible when the polymers are at temperatures above, preferably greatly above, their glass transition temperatures (T_g). Another fundamental feature of diffusion is that thermodynamic compatibility must exist between the materials. This pre-requisite can be easily satisfied for two non-polar elastomers with similar chain back-bones. According to Allan [7] for bonding of two elastomers above their T_gs, the concept of the interdiffusion of polymer chain segments had been developed convincingly. Wool [19] believes that even in the case of macroscopic thermodynamic incompatibility; an atomically sharp interface between two incompatible polymers will not be stable. Although there is an enthalpy debt to be paid if a chain of polymer A starts to diffuse into polymer B, there is still a small entropy gain. In another paper [20], he classified five different time regions for polymer diffusion: (1) Short-range Fickian diffusion of individual chain segments, (2) Rouse relaxation between chain entanglements, (3) Rouse relaxation of the whole chain, (4) Reptation (snake-like movement) diffusion and (5) Fickian long-range diffusion. The fastest relaxation (1) takes place on the order of a single statistical segment, so lateral displacements are quite small. Time scale (5) occurs at long times when the chain loses all memory of its initial conformation. To give some feeling for the time scales he gives data for polystyrene of molecular weight of 245000 (g/mole), at the 118°C welding point: the Rouse relaxation time between chain entanglements with average diffusion distance of 30 Å, is 10s and the Rouse relaxation time of the whole chain with average diffusion distance of 60 Å, is 21 mins., while for reputation with average distance of 110 Å a long time of 1860 mins. is needed.

Crocker [21] has written a review paper on elastomers and their adhesion in 1969. He quotedthe substantial works of Vasenin [22, 23] on polymer diffusion theory and its application to adhesion. He examined the concentration dependence of diffusion rate in polymers, and the effect of double bonds and cross-sectional area of the diffusing molecule.

He pointed out that for inter-diffusion to happen, it must be possible both thermodynamically and kinetically. He stated that for interpenetration depths of less than 200-600 monomer units, debounding would be by chain slippage, while for greater penetration, chain breakage needs to occur.

For rubber systems crosslinks should also be considered. For such cases Voyutskii [24] explained that co-vulcanisation phenomena, similar to adhesion of polymers, include diffusion displacement of macromolecules or their segments, especially intensive at the initial vulcanisation period when the formation of crosslinks has not yet begun. The only difference is that the process of mutual penetration of molecular chains is sooner or later interrupted by the superimposed vulcanisation process, anchoring the diffused macromolecules or their segments by strong chemical bonds.

The present study was performed to give more insight into the adhesion phenomena between RFL-coated aramid cords and rubbers, especially the importance of compatibility and inter-diffusion of the polymers used for the rubber matrices and for the latex part of the RFL. Two types of matrices were chosen, based on Natural Rubber (NR) and NR blended with a small amount of Styrene Butadiene Rubber (SBR). The two compounds are quite similar, where in the latter only 5 phr of the NR is replaced with SBR which has a closer structural similarity to the latex part of RFL.

EXPERIMENTAL

Two compounds were prepared based on NR and a NR/SBR blend. The compositions are given in Table I. Mixing of the compounds were done in industrial scale internal mixers at Trelleborg, Kampen, the Netherlands. The mixings were done in two stages: first the masterbatches were prepared without curatives; the rotor speed was 30 rpm, fill factor 74% and discharge temperature 140°C; then after 24 hour leaving the compounds to rest, in a second step the curatives N-Cyclohexyl-2-benzothiazyl sulphenamide (CBS) and Sulphur, were added to the mixtures with rotor speed of 18 rpm and discharge temperature of 110 °C. The total mass of the compounds was 210 Kg.

Table I: The composition of compounds.

Component	NR	NR/SBR
NR (SMR-10)	100	95
SBR 1502	----	5
Carbon Black (N660)	50	50
Perkasil (KS 408)	10	10
Oil (Nytex 840)	10	10
Zinc oxide	5	5
Stearic acid	1	1
6PPD	1	1
TMQ	1	1
Tackifier (SP 1068)	1	1
CBS	0,9	0,9
Sulphur	4	4

The continuous fibres (cords) were poly(para-phenylene terephtalamide) (PPTA), Twaron ® type 1000, 1680 dtex produced by Teijin Aramid B.V.; the RFL-coatings preceded by an epoxy pre-coating were applied on a Litzler single end Computreater.

The cure characteristics of the compounds were measured with a Rubber Process Analyzer (RPA2000) of Alpha Technologies, and according to the results the compounds were cured in a hot press for their t_{90} +6 mins. at 150°C.

To prepare the compounds with short-fibres, 5 phr of such fibres with the initial length of 3mm were added on a laboratory two roll mill. The milling direction was considered as longitudinal direction of fibre orientation. These compounds were cured for the same t_{90}+6 mins. at 150°C. Tensile tests were performed using a Zwick Z1.0/TH1S tensile tester, speed 200 mm/min.

Strap Peel Adhesion Force (SPAF) tests were done on continuous fibre composites in accordance with ASTM D4393. 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 150°C for their t_{90} + 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 in such a way that the interface was exposed to shear: figure 2.

The adhesion tests were performed also with aged RFL. As light has a synergistic effect with ozone in aging processes, to provide better control of the process of aging, they were done under atmospheric conditions in darkness.

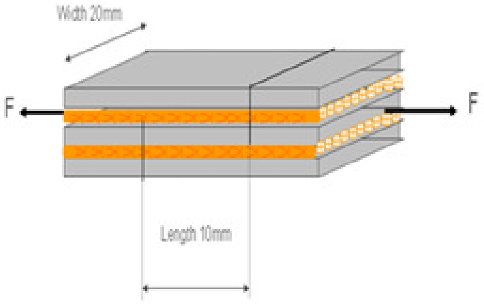

Figure 2: Lap Shear test samples,

The migration of sulphur and zinc from the elastomer phase into the RFL-layer has been investigated with Energy Dispersive X-ray spectrometry (EDX). For ease of measurement the RFL was prepared on an aluminium foil and subsequently co-vulcanised to the rubber compounds using a compression set mould. The samples were pressed at a temperature of 150°C for their t_{90}+6 mins. This procedure is schematically shown in figure 3. After cooling the samples with liquid nitrogen, sections were perpendicularly cut, to prepare surfaces for EDX tests. The SEM-EDX equipment used was a LEO 1550 FEG/Thermo Noran instrument, model Vantage. The accelerating voltage was 15 kV and the samples were coated with carbon for better electrical conductivity.

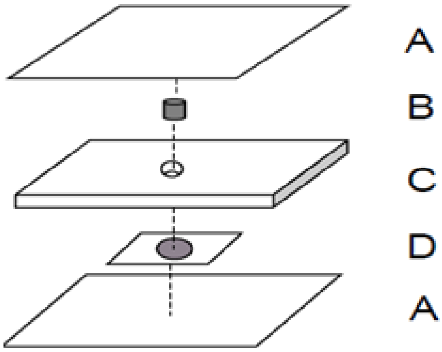

Figure 3: A: press plates, B: rubber compound, C: compression set mould, D: cured RFL-layer on aluminium foil.

RESULTS AND DISCUSSION

The tensile test results for the two compounds are presented in figure 4. The two samples are practically identical in tensile properties and replacing only a small amount of NR with SBR does not cause a noticeable change in the tensile values.

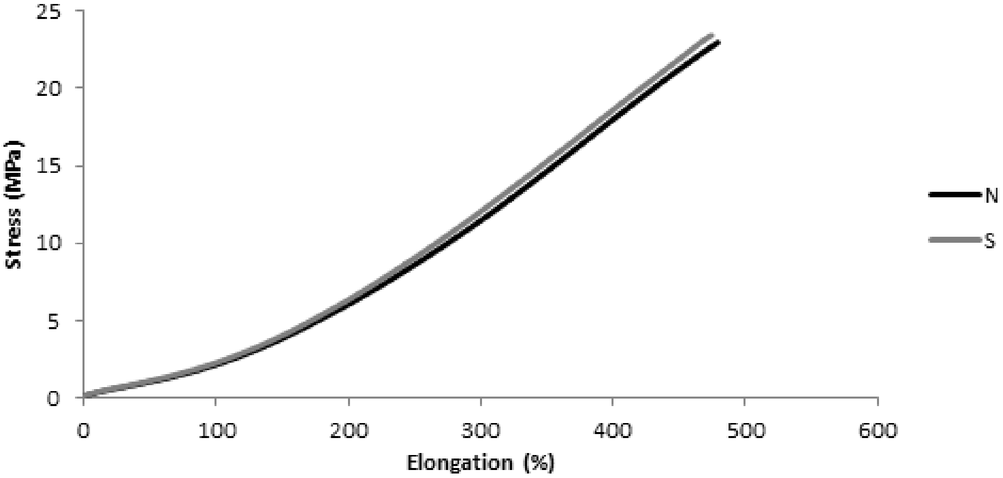

Figure 4: Tensile results for NR(N) and NR/SBR(S) compounds without fibres.

Table II: SPAF and Lap Shear results for RFL-coated continuous fibres in NR and NR/SBR compounds.

	SPAF (N/mm)	Lap Shear (MPa)
NR (N)	13.5	6.6
NR/SBR (S)	16.5	7.5

Interesting is that there is a difference in adhesion of RFL-coated continuous fibres to the two compounds, measured either in the SPAF or Lap Shear tests: Table 2. Even after aging of the RFL-coated fibres for 4 weeks, still the compounds containing 5 phr SBR, showed higher adhesion compared to the pure NR compound, measured either in SPAF or Lap Shear tests: figure 5.

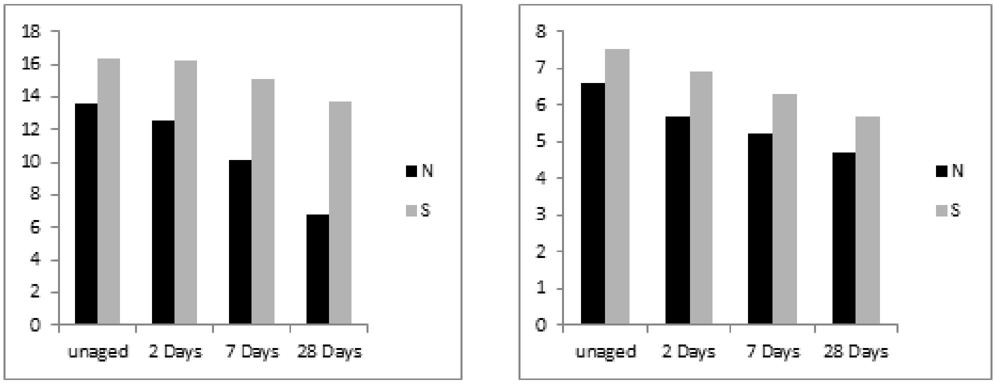

Figure 5: Adhesion results of RFL-coated continuous fibres in NR (N) and NR/SBR (S) against aging; Left: SPAF(N/mm), Right: Lap Shear (MPa).

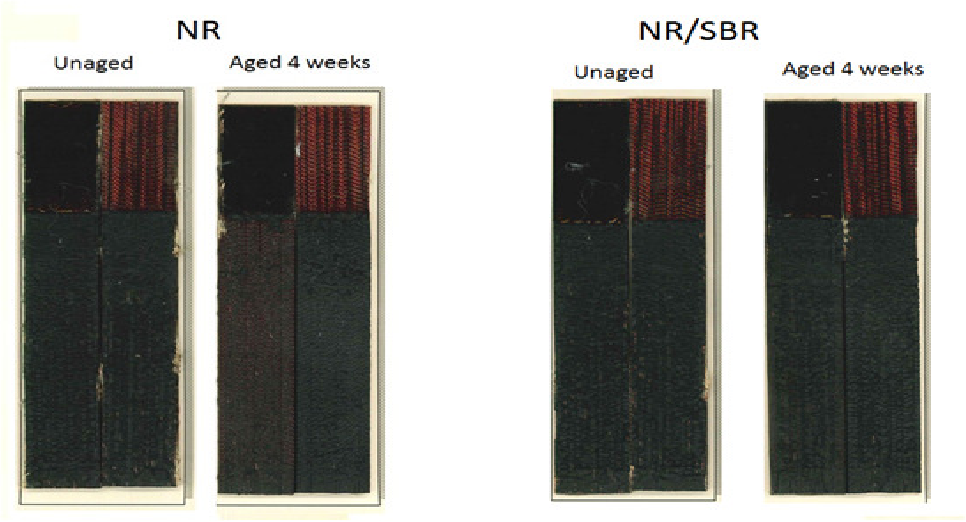

Figure 6: SPAF samples of NR and NR/SBR with unaged and 4 weeks aged RFL-coated continuous fibres.

Having a closer look at the failure mode shows that both the NR and NR/SBR compounds with unaged RFL-coated continuous fibres fail in the bulk of the elastomer: cohesive failure with full rubber coverage on the fibres after the tests. As the aging process proceeds, the failure becomes partly adhesive (fibre dip-rubber failure) resulting in some fibres without rubber coverage; the proportion of such fibres is higher for the NR compound than for NR/SBR, figure 6, to demonstrate that the adhesion of NR with unaged and aged RFL improves when a small amount is replaced by SBR.

Comparable results were observed in short fibre reinforcement. The used short RFL-coated fibres had already been stored in a dark place for a long period; still it was observed that after adding 5 phr of such fibres, the reinforcement effect was higher for the NR/SBR compound than for the pure NR compound: figures 7 and 8.

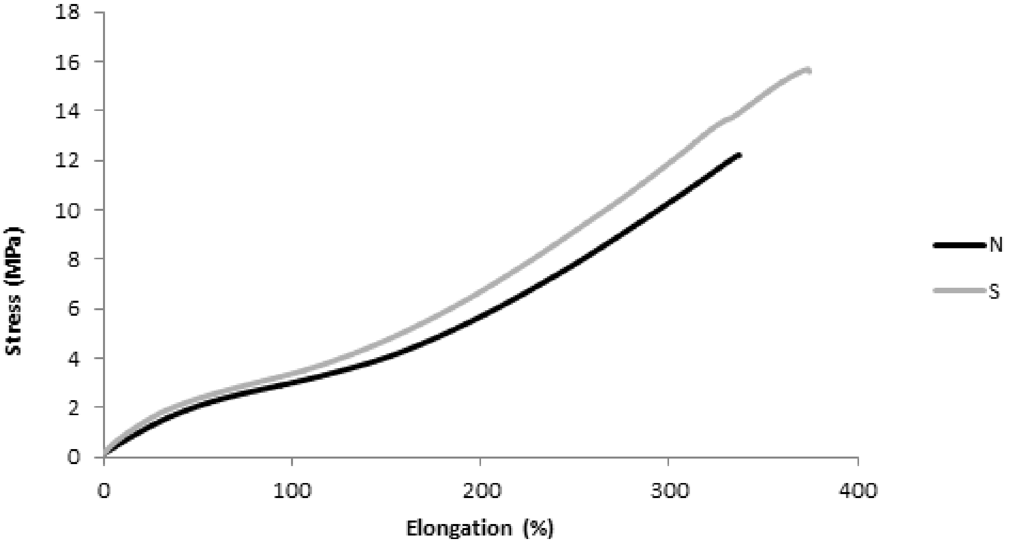

Figure 7: Tensile curves of NR (N) and NR/SBR (S) compounds containing 5phr RFL-coated short fibres, in longitudinal direction of fibre orientation.

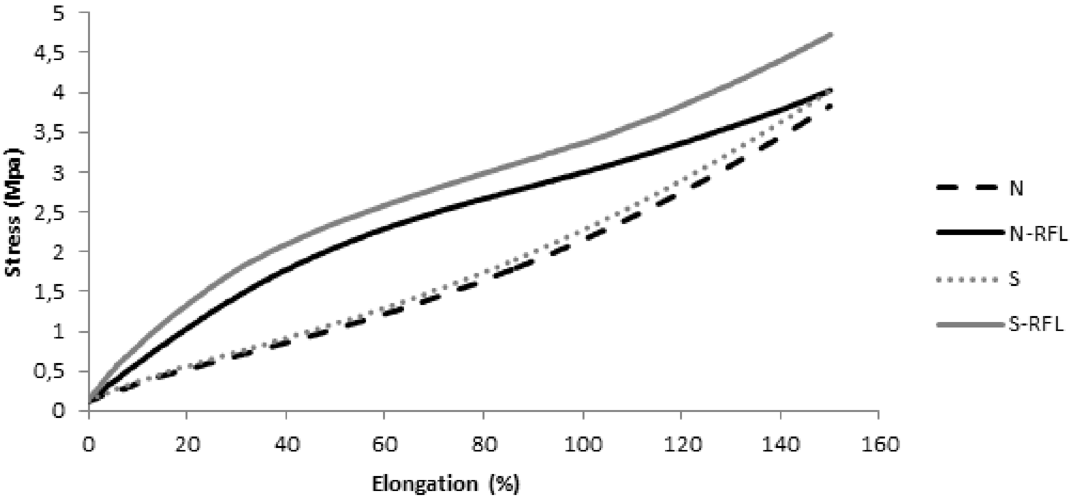

Figure 8: Tensile curves of NR (N) and NR/SBR (S) compounds without fibres and containing 5phr RFL-coated short fibres, in longitudinal direction of fibre orientation at lower elongations of 0 to 150%.

Evaluating these phenomena, two possibilities can be considered:

1. There is a difference in migration of curatives from the two compounds into the RFL layer. A high density of interfacial bonding makes a joint brittle and weak [25]. A higher concentration of sulphur in the contact region of RFL and elastomer, might cause over-curing and form a brittle layer which affects adhesion negatively.
2. The adhesion of elastomers to RFL-coated fibres is influenced by polymer diffusion: the mutual diffusion of elastomer and the latex part of the RFL. The degree that chains inter-diffuse, resulting in forming an interphase layer is important in adhesion properties.

Curatives migration: Figure 9 shows a SEM picture of the samples and EDX scan line. The scan results show no major difference in sulphur counts for unaged-RFL co-cured with the NR or NR/SBR compounds: figure 10. Also the line scans for 1 week aged-RFL co-cured with the two compounds, figure 11, does not show an increase in the sulphur amount at a sharp interface or a broad interphase region which might result in brittleness or any other change which can affect the adhesion negatively or account for the better adhesion of the NR/SBR blend compared to the pure NR compound. The results for zinc were also quite similar and no clear difference was observed in all cases.

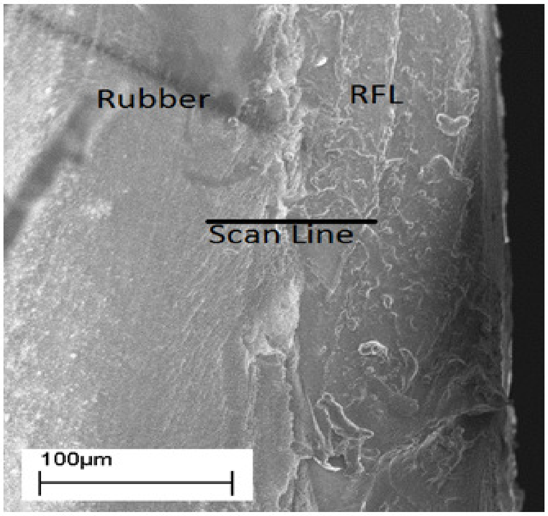

Figure 9: EDX scan line from the bulk of rubber to the bulk of RFL across the interface.

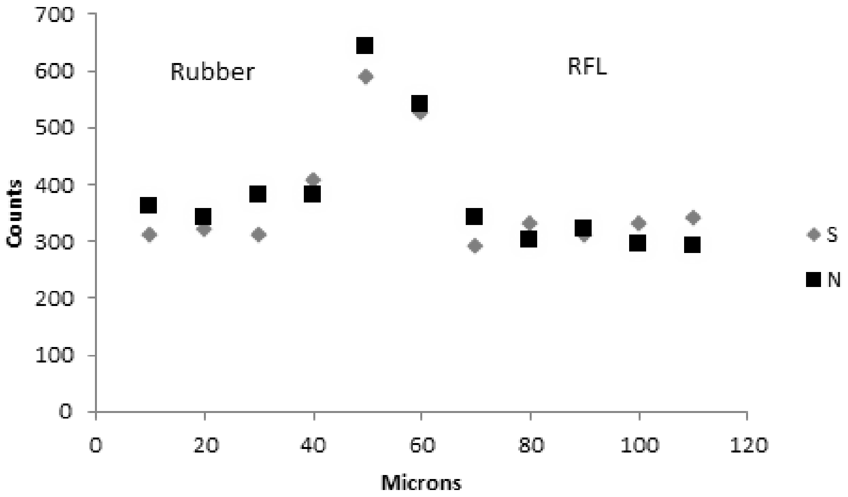

Figure 10: Sulphur counts in line scan for unaged RFL layer, co-cured with NR (N) and NR/SBR (S). Left: Rubber, Right: RFL, the area around 50 microns corresponds to the contact region.

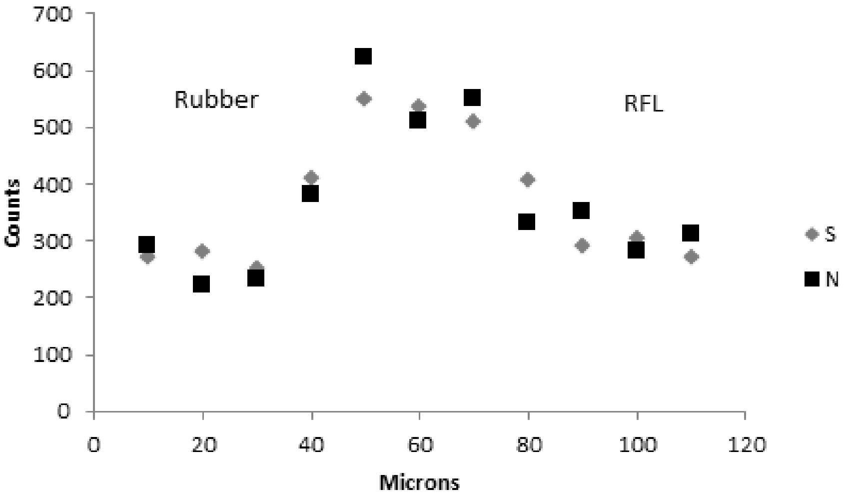

Figure 11: Sulphur counts in line scan in 1 week aged RFL layer, co-cured with NR (N) and NR/SBR (S). Left: Rubber, Right: RFL, the area around 50 microns corresponds to the contact region.

From these SEM-EDX results it can be concluded that the decrease in adhesion properties as a result of aging is not due to a change in curatives migration; the peaks at the interfacial region are not higher than those for unaged RFL and are not sharper after aging, but even broader. This means that the chance of forming over-cured areas which can act as stress concentration points in smaller after aging. It can also be seen that the difference in adhesion properties of the pure NR and the NR/SBR compounds cannot be related to different curatives migration patterns.

Polymer diffusion: The main pre-requisite for polymer diffusion is thermodynamic compatibility between two phases. Though in different literatures [26-29] different numbers are reported for the solubility parameters of NR and Poly Butadiene which forms almost 70% of the latex in RFL, it can be expected from their molecular structures that their respective values are fairly close. So, one may reasonably expect that NR has a good thermodynamic compatibility with the latex. But, the chemical structure of the SBR which contains 22-25% styrene and 75-78% butadiene is even closer to that of a latex part of the RFL. So, one can also expect more thermodynamic compatibility between the latex and SBR, compared to NR.

In rubber reinforcement with RFL-coated fibres, the high temperature used for curing facilitates chain movements by diffusion. It was also shown by Green and Kramer [30] that the lower the molecular weight of a polymer, the faster the diffusion. In this sense also the low molecular weight of the latex in RFL can also be considered a factor favouring diffusion.

On the other hand, if there were no diffusion, a sharp interface would have been formed and the chemical bonds would only form on this interface which would result in a weak and brittle joint. So, with reference to the explanation of Voyutskii [24] for the co-vulcanisation in the introduction part, it would be more logical to consider that we have a combination of the chain diffusion and crosslinking which results in the formation of an interphase layer rather than a sharp and distinct interface. A closer look at the cross-section of the RFL-rubber samples shows that at higher magnifications the two phases are mingled to some extent in their contact area: figure 12. It is then expected that increasing the compatibility between the phases results in a stronger interphase which in turn makes the adhesion stronger. Adding SBR to a NR compound has such an effect, which results in better compatibility with the latex part of RFL and a stronger (and maybe thicker) interphase, reflecting in better adhesion properties.

The aging results also can be argued to favour the discussion above. It is well-known that ozone has affinity with the double bonds in elastomers and those with unsaturated chains must be protected by adding antiozonants. In rubber articles which consist of elastomers with unsaturated chain backbones, such as tires, ozone attack causes small cracks on the surface and degrades it gradually. It should be noticed that like other gases ozone can also diffuse into the rubber. After a sufficient time of penetration and reaction with elastomer chains, ozone leaves a degraded layer on the surface [31]. RFL is practically a several microns thick film, not protected from ozone with any sort of antiozonant. Aging time results in increasing the thickness of the degraded layer of the RFL-coating. The rubber with more diffusion affinity would have the chance to be cross-linked with the double bonds in the RFL latex phase which are still intact, resulting in a better adhesion.

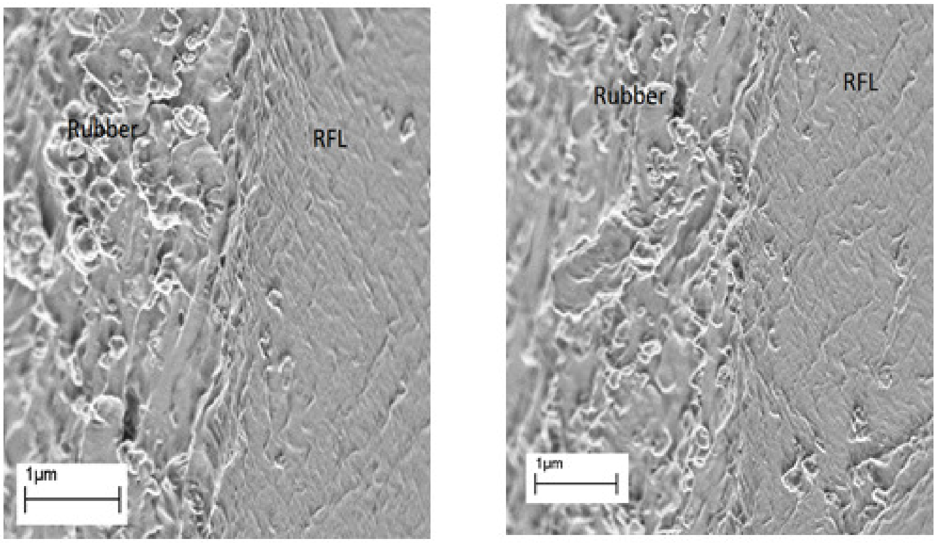

Figure 12: Cross section of RFL-layer co-cured with rubber, Left S-RFL, Right: N-RFL.

Looking at industrial applications one can find more proofs for that. Tire factories commonly do not have a dipping unit and buy RFL-coated fibres. These fibres are kept away from light and not from air. Considering the whole shipping and storage time, there is a considerable time span between applying the coating on the fibres and processing of the tire layers by making fibre-rubber composites. According to the shown SPAF results for the NR compound, the RFL-coated fibres must have lost a considerable amount of their capability to generate chemical bonds, but still show a practically acceptable adhesion to rubbers. There are two points which should be considered here:

1. The adhesion of fibres to rubbers in the tire industry is frequently tested by performing a H-adhesion test which essentially is a shear test, closer to practical tire applications compared to the SPAF test, as the fibre surface is sheared. While performing the test in shear mode, mechanical interlocking between fibres and rubbers becomes also important and should be added to the total adhesion value as the result of chemical and physical forces. Applying RFL on the surface of the fibres increases their roughness [12, 13] which enhances the frictional forces between RFL-treated fibres and the surrounding matrix. Figure 5 also shows that the adhesion of the NR compound to RFL-coated fibres which is less sensitive to RFL aging, decreasing with a slower rate when the test is done in shear mode (Lap shear) than the peeling mode of the SPAF test.
2. Pure NR is not common in tire layers and usually blends with SBR are used which has been shown to give better adhesion performance even after aging of the RFL layer because of the better compatibility and ability to form a stronger interphase.

CONCLUSIONS

The adhision of the RFL-coated fibres (especially continuous fibres) to elastomers, strongly depends on the chemical bonding. But it should be noticed that a good adhesion is not obtained by bonding between the RFL and elastomer across a sharp interface. However, forming a strong layer of interphase is of great importance. Increasing the compatibility between NR and the latex of RFL by adding only a small amount of SBR in the compound results in a stronger interphase which results in turn in better adhesion properties to RFL-coated fibres. Even if the fibres are aged and the number of carbon-carbon double bonds is reduced due to ozone reaction, better compatibility causes better mutual diffusion of latex of the RFL and the elastomer chains which increases the chance of co-vulcanization between rubber and intact latex chains in greater depth from the initial contact zone. This can partly compensate the negative effect of RFL aging.

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Summary and Conclusions

in English and Dutch

The current thesis consists of a chapter as literature review in which different scientific sources and the results of investigation of various researchers are reviewed, followed by 5 chapters (2 to 6) and an appendix covering the results of the experimental work performed. The results can be divided in 3 main sections:

Section 1: Short-fibre rubber composites.

In the first section rubber composites reinforced with short aramid fibres are focused upon; the reinforcement mechanisms and the mechanical and viscoelastic properties of the composites are explored.

- In the second chapter, short fibre reinforced NR and EPDM rubbers are the subjects of investigation. In the different short fibre-rubber systems examined, clear chemical adhesion only happened in the case of peroxide-cured EPDM with RFL-treated fibres. This phenomenon was most clearly reflected in the tensile curves for this system, showing a large reinforcement factor particularly at tensile elongations below 100%. Next to potential chemical bonding, mechanical interaction between fibres and rubber matrix plays an important role. Surface phenomena on the fibres, as bending/buckling, dog-bone shaped fibre ends and surface roughness due to the RFL-coating cause mechanical interlocking. So, even in the absence of chemical adhesion, adding short aramid fibres improves the mechanical properties of rubber compounds because of the mechanical interaction.
- Chapter three describes the results of the investigation of the composite morphology and interaction of two different types of short aramid fibres in an EPDM radiator hose compound and its corresponding model system. PPTA fibres with RFL-dip could not be dispersed completely to filament level due to the gluing effect of the dip. Irrespective of the mixing time, PP/ODPTA fibres could better withstand the applied shear stresses during mixing and maintain a high level of fibre length, which resulted in better mechanical properties in composites reinforced with these fibres compared to those reinforced with PPTA fibres. On the other side, the RFL-dip acted as protective layer and prevented the fibres from excessive breaking, which was especially the case for PPTA. It was shown that for RFL-coated fibres, chemical bonding only happens between a part of RFL-treated filaments and EPDM rubber.

Still the composites containing these fibres showed better mechanical properties compared to those reinforced with standard finish. The reason for this superiority is not only the partial chemical bonds, but two more factors are involved: better mechanical interlocking of the RFL-treated fibres and the surrounding matrix (due to the roughness of the coating), and the higher final length of these fibres after mixing.

- Due to the importance of viscoelastic properties in performance of a lot of rubber parts, especially tires, the dynamic properties of the short fibre-reinforced compounds are the subject of the fourth chapter. It was shown that mechanical and chemical interactions between short fibres and a rubber matrix, which are the reasons for an increase in storage modulus, can affect loss properties in different ways, depending on the type of matrix, temperature, dynamic strain and the possible application of a static pre-strain. In this respect two main influencing factors needed to be considered: 1) Reinforcement as a result of interaction between fibres and rubber which results in an increase in storage modulus of the composite; 2) If there is no perfect interphase and fibres and rubbers are not fully bonded, sliding of the rubber matrix along the fibre surface causes additional losses due to friction. There is no general rule that adding fibre increases or decreases the loss angle and it totally depends on the balance of these two factors at different strain, frequency and temperature regimes. The importance of mechanical interaction in short fibre reinforcement was emphasized again to be an important parameter also in determining the viscoelastic properties of the composites.

Section 2: RFL-rubber interaction.

This section consists of two chapters dedicated to the subject of the adhesion mechanism between rubbers and the RFL-layer itself. The effect of RFL-aging, the role of rubber curing systems and inter-diffusion of the latex part of RFL and elastomer are focused upon.

- In chapter five the effect of physical interaction between fibres and rubbers was shown to be minor. Un-aged RFL is able to generate good adhesion to both sulphur and peroxide cured rubbers due to the generation of chemical bonds. As a result of the aging of RFL, ozone is able to decrease the number of 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 was also discussed that, unlike in sulphur vulcanization in which bonding happens only between the latex in the RFL and rubber, peroxide is able to generate bonds also between elastomer and the resin structure of the RFL-coating. It was also shown that mechanical interlocking increases the total interaction between (roughened) fibres and rubbers when the adhesion tests are done in the shear mode, while this effect is not reflected in peeling tests.

- In the sixth chapter the adhesion of aramid fibres after being coated with RFL, in compounds based on NR and in NR blended with a small amount of SBR is investigated. It was shown that though having very similar tensile properties, the latter compound has much better adhesion to RFL which is also less sensitive to RFL aging, compared to the pure NR compound. It is argued that an interphase region is formed between RFL and the elastomer, which is stronger for the compound containing SBR due to its enhanced compatibility with the latex part of the RFL. Even if the RFL-treated fibres are aged, better compatibility causes better mutual diffusion between the latex of the RFL and the elastomer chains and increases the chance of co-vulcanization between rubber and intact latex chains in greater depth from the initial contact zone. This can partly compensate the negative effect of RFL aging.

Section 3: Enhancement of rubber-fibre interaction.

The last section based on the results of the two previous sections, deals with two different approaches for enhancement of the interaction between the aramid fibres and rubber matrices.

- In the appendix, two different methods were employed to enhance the interaction between fibres and rubbers based on the two mentioned mechanisms. Increasing the roughness of the surface of aramid fibres with a laser, and functionalizing the surface of the fibres with chloroformates and isocyanates. Laser irradiation is performed on uncoated fibres (standard fibres) and the SEM pictures showed that roughening was successfully achieved. For chemical modification, fibres with an epoxy sub-coating only, were chosen because of the existence of hydroxyl/amine groups on the surface which provide reactive sites for the reaction with the chemicals mentioned. The presence of bound reactants on the fibre surface was demonstrated using X-ray photoelectron spectroscopy (XPS). Furthermore, the tensile curves showed enhanced properties of the composites reinforced with these modified fibres.

Het voorliggende proefschrift omvat een hoofdstuk literatuurstudie, waarin verschillende wetenschappelijke bronnen en de resultaten van onderscheiden onderzoekers worden besproken, gevolgd door 5 hoofdstukken (2 tot 6) en een bijlage, met betrekking tot de resultaten van uitgevoerd experimenteel werk. De resultaten kunnen worden onderverdeeld in 3 hoofddelen:

Deel 1: rubber composieten met korte vezels

Het eerste deel rubber composieten, versterkt met korte aramide vezels, is gericht op de versterkings-mechanismen waarin de mechanische en visco-elastische eigenschappen van de composieten worden verkend.

- In hoofdstuk 2 zijn NR- en EPDM-rubbers versterkt met korte vezels de onderwerpen van onderzoek. In de verschillende korte vezels-rubber onderzochte systemen, blijkt er chemische hechting op te treden in geval van peroxide-gevulcaniseerde EPDM in combinatie met RFL-behandelde vezels. Dit blijkt uit de trek-rek curves voor dit systeem. Naast chemische binding speelt mechanische interactie tussen vezels en matrix rubber een belangrijke rol. Oppervlakte verschijnselen op de vezels zoals buigen/knikken, dog-bone vormige vezeluiteinden en ruwheid van het oppervlak als gevolg van de RFL-coating veroorzaken mechanische verankering. Dus zelfs in afwezigheid van chemische hechting, verbeteren korte aramidevezels de mechanische eigenschappen van rubber door de mechanische interactie.

- Hoofdstuk 3 beschrijft de resultaten van onderzoek aan de morfologie van de samengestelde systemen en de interactie van twee verschillende korte aramide-vezels in een EPDM radiatorslang mengsel en het bijbehorende modelsysteem. PPTA-vezels met RFL-dip worden niet volledig verdeeld tot op filament-niveau als gevolg van het lijm-effect van de dip. Ongeacht de mengtijd zijn PP / ODPTA vezels beter bestand tegen de toegepaste schuifspanningen tijdens het mengen. Dat resulteert in betere mechanische eigenschappen in composieten versterkt met deze vezels, ten opzichte van die versterkt met PPTA vezels. Aan de andere kant fungeert de RFL-dip als beschermende laag en belet het overmatig breken van de vezels, met name in het geval voor PPTA. Er wordt aangetoond, dat voor RFL-behandelde vezels chemische binding optreedt tussen een deel van de RFL-behandelde filamenten en EPDM rubber. De composieten met deze vezels hebben betere mechanische eigenschappen vergeleken met die versterkt met standaard spin-coating. De reden voor deze superioriteit is niet alleen de chemische bindingen, maar twee additionele factoren: betere mechanische verankering tussen de RFL-behandelde vezels en de omringende matrix (vanwege de ruwheid van de coating) en de hogere uiteindelijke lengte van deze vezels na mengen.

- Vanwege het belang van de visco-elastische eigenschappen voor de functie van veel rubberen onderdelen, in het bijzonder banden, zijn de dynamische eigenschappen van korte vezels versterkte mengsels onderwerp van het vierde hoofdstuk. Er wordt aangetoond, dat de mechanische en chemische wisselwerkingen tussen de korte vezels en een rubber matrix, reden voor een verhoogde opslagmodulus, op verschillende manieren invloed kunnen hebben op de eigenschappen, afhankelijk van het type matrix, temperatuur, dynamische belasting en de mogelijke toepassing van een constante statische voor-rek. Daarbij dienen twee belangrijkste factoren in beschouwing te worden genomen: 1) Versterking als gevolg van de interactie tussen vezels en rubber, hetgeen resulteert in een toename van de opslagmodulus; 2) als er geen perfecte interfase is en vezels en rubbers niet volledig gebonden zijn, het afglijden van de rubber matrix langs het vezeloppervlak, hetgeen extra verliezen door wrijving veroorzaakt. Er blijkt geen algemene regel te gelden, dat het toevoegen van vezels ertoe leidt dat de verlies-hoek afneemt. Dit hangt af van de resultante van deze twee factoren in de spannings-, frequentie- en temperatuur-regimes. Het belang van mechanische interactie bij korte vezel-versterking wordt nogmaals benadrukt, ook als een belangrijke parameter welke de visco-elastische eigenschappen van de composieten bepaalt.

Sectie 2: RFL-rubber interactie

Dit onderdeel bestaat uit twee hoofdstukken gewijd aan het hechtmechanisme tussen rubbers en de RFL-laag zelf. Het effect van RFL-veroudering en de rol van rubber-uithardende systemen op de onderlinge diffusie van de latex in de RFL-laag en het elastomeer zijn het onderwerp.

- In hoofdstuk 5 wordt aangetoond dat de fysieke interactie tussen vezels en rubbers gering is. On-verouderde RFL kan een goede hechting aangaan met zowel zwavel- als peroxide-vernette rubbers door de vorming van chemische bindingen. Als gevolg van ozon-veroudering van de RFL vermindert het aantal dubbele bindingen van de latex-component in de RFL-coating, hetgeen een negatieve invloed heeft op de RFL-rubber hechting van zwavel-gevulcaniseerde systemen, terwijl vrijwel geen effect wordt waargenomen voor peroxide-systemen. Tevens wordt besproken, dat peroxide in tegenstelling tot zwavel ook verbindingen kan vormen tussen elastomeer en de hars-fase van de RFL-coating. Er wordt ook aangetoond dat mechanische verankering de totale interactie verhoogt tussen de vezels en rubber als de hechtings-tests in afschuif-modus wordt uitgevoerd, terwijl dit effect niet optreedt in peeling testen.

- In het 6e hoofdstuk worden de hechting van aramidevezels voorzien van RFL onderzocht in mengsels op basis van NR en NR gemengd met een kleine hoeveelheid SBR. Er wordt aangetoond dat, terwijl ze vergelijkbaar treksterkte-eigenschappen hebben, de laatste een betere hechting aan RFL geeft en ook minder gevoelig is voor RFL-veroudering. Er wordt gesteld dat een interphase gebied ontstaat tussen RFL en het elastomeer, die sterker is in aanwezigheid van SBR vanwege de verbeterde compatibiliteit met de latex van de RFL. Zelfs als de RFL-behandelde vezels worden verouderd, geeft de betere compatibiliteit betere wederzijdse diffusie tussen de latex van de RFL en de elastomeer-ketens, en vergroot de kans op co-vulcanisatie van rubber en intacte latex ketens verder buiten de primaire contactzone. Dit kan het negatieve effect van RFL veroudering gedeeltelijk compenseren.

Deel 3: Versterking van de rubber-vezel interactie

Het laatste gedeelte op basis van de resultaten van de twee voorgaande secties, introduceert twee verschillende benaderingen voor het verbeteren van de interactie tussen aramidevezels en rubber matrices.

- In de bijlage worden twee verschillende methoden voorgesteld om de interactie tussen vezels en rubbers te verbeteren. Het verhogen van de ruwheid van het oppervlak van aramide vezels met een laser, en functionaliseren van het oppervlak van de vezels met chloorformiaten en isocyanaten. Laser-behandeling wordt uitgevoerd op maagdelijke onbehandelde vezels (standaard vezels) en uit SEM-opnamen blijkt dat op-ruwen met succes is bereikt. Voor chemische modificatie werden vezels met een epoxy sub-coating gekozen, omdat de aanwezigheid van hydroxyl / aminegroepen op het oppervlak reactieve plaatsen aanbiedt voor reactie met de genoemde chemicaliën. De aanwezigheid van gebonden reactanten op het vezeloppervlak wordt aangetoond met röntgen foto-elektron spectroscopie (XPS). Bovendien tonen de treksterkte-curves verbetering aan van de eigenschappen van de composietmaterialen verstevigd met vezels op deze wijze gemodificeerd.

Appendix

Enhanced Rubber-Fibre Interaction: Aramid Surface Modification

Based on the invention disclosures DPI-11.011 and 12.011

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ABSTRACT

In the previous chapters the different reinforcement mechanisms of the short aramid fibres have been investigated. It was shown that among different mechanisms, mechanical interlocking and chemical bonding are of significant importance. In the current chapter, two different methods have been employed to enhance the interaction between fibres and rubbers based on the two mentioned mechanisms. Increasing the roughness of the surface of aramid fibres with a laser, and functionalizing the surface of the fibres with chloroformates and isocyanates.

Laser irradiation was performed on uncoated fibres (standard fibres). The SEM pictures showed that roughening was successfully achieved. For chemical modification, fibres with epoxy sub-coating only were chosen because of the existence of hydroxyl groups on the surface which provides reactive sites for the reaction with the chemicals mentioned. The presence of bound reactants on the fibre surface was demonstrated using X-ray photoelectron spectroscopy (XPS). The tensile curves showed enhanced properties of composites reinforced with these modified fibres.

INTRODUCTION

Fibre-elastomer composite are an important class of materials because they combine the strength of the fibres with the unique properties of elastomers. There are different parameters influencing the degree of reinforcement in such composites, among them the adhesion between fibres and elastomers is of great importance.

The strength of the interfacial region between fibres and the matrix determines the stress-transfer length. Stronger, tougher interface regions lead to higher interfacial shear strength and shorter stress transfer length. Thus more of the fibre will carry the applied load. The result is a substantial increase in the tensile strength and modulus. A weaker or more brittle interface has a longer stress transfer length, and relatively less of the fibre will carry the applied load [1, 2, 3]. The nature of the interfacial contact has a large influence on the mode of failure and the toughness of the composite too. A strong interfacial region promotes crack propagation across the fibres, whilst a weak interface causes failure by fibre debonding and pull-out [4].

There are two well-known methods to increase the adhesion between fibres and rubber matrix [5, 6]:

1. By the use of the hexamethylenetetramine, resorcinol, and a high-surface-area hydrated silica (HRH) system which is incorporated in the rubber mix.

2. By fibre surface treatments using for example Resorcinol Formaldehyde Latex system(RFL). The specific adhesive treatments for various types of fibres differ. The adhesive layer is applied on a cord (a bundle of continuous fibres) by a so-called dipping process. A schematic view of this process can be seen in figure 1.

For fibre reinforcement of elastomers the most common method to increase the adhesion is by fibre surface treatment with RFL. Aramid fibres in particular are normally coated with an epoxy sub-coating and an RFL-layer on top. The latex used in an RFL formulation in many cases consists of polymerized styrene (about 15%), butadiene (about 70%) and vinyl pyridine (about 15%) monomers.

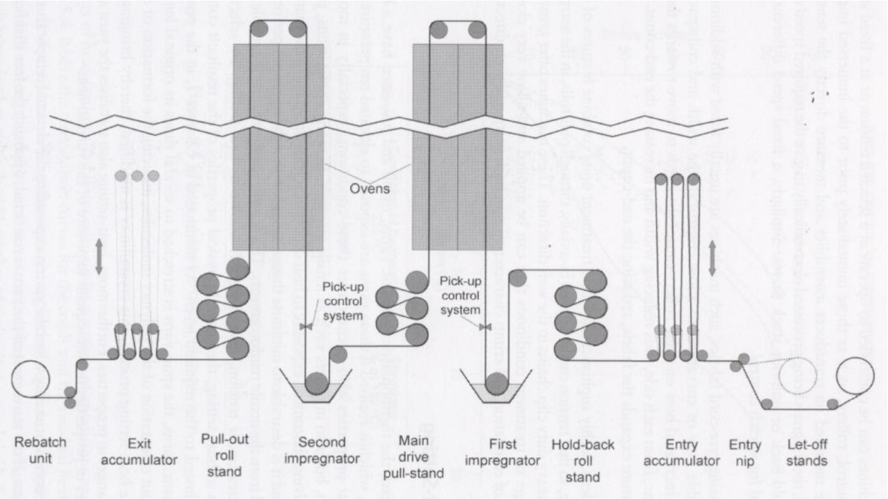


Figure 1: Schematic view of a dipping process [7].

Though RFL is in use as an adhesion promoter for fibre-elastomer systems for already a long time, there are drawbacks in its applications which has left an open outlook to search for alternative treatments. One of the main disadvantages of the RFL treatment is its sensitivity to light and air [8, 9]. RFL-treated fibres are widely used in sulphur-cured compounds, in which the 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 the rubber matrix and so form bridging sulphur cross-links [10]. Exposing RFL to ozone causes reduction of the number of double bonds in the latex part and results in restricted ability of RFL to co-vulcanize with the elastomer. Another disadvantage of RFL is that it does not work as effective with short fibres as with cords [11, 12]. Various alternative methods have been developed so far for treatment of different sorts of fibres to be used in polymer matrices [13], among those for example plasma treatment has abtained a lot of attention [14-16].

In the current appendix, based on the previous research results [11, 12, 17], two different approaches have been applied to enhance adhesion between fibres and rubbers. The first method is to roughen the surface of untreated fibres to enhance mechanical interaction between fibres and the surrounding matrix with the application of laser pulses; the second method is to functionalise the surface of the fibres with an epoxy sizing with different chemicals, namely isocyanates and chloroformates.

EXPERIMENTAL

Laser Treatment*:* The treatment was performed with ultra-short laser pulses with an temporal pulse width of 6.7 picoseconds Full-Duration Half- Maximum (FDHM). The wavelength used was 343 nanometres. The average influence obtained by overlapping pulses should be above a minimum threshold and below a maximum in order to increase the surface roughness without degradation of the material below the surface region. Table I shows the experimental setup elements in details and Table II shows the laser conditions employed during the surface modification phase of the process. The type of fibres used were poly (para-phenylene terephtalamide) (PPTA), Twaron ® type 1000, 1680 dtex produced by Teijin Aramid B.V. Scanning electron microscopy (SEM) was performed on the samples, using a bench-top NeoScope JCM-500 device, after coating the samples with a very thin layer of platinum.

Table I

Experimental setup Trumpf TruMicro 5050 laser	
Pulse duration	≈ 6.7 ps
Wavelength	1030 nm
Max Power	50 W
Max repetition rate	400 kHz
Max pulse energy	125 µJ
Trumpf Third Harmonic Generator (THG)	
Wavelength in	1030 nm
Wavelength out	343 nm
Conversion Efficiency	≈ 30 %
X-Y stage Aerotech	
Accuracy	0.001 mm
Z stage Aerotech	
Accuracy	0.002 µm
Scanner Scanlab Intelliscan 14	
Design wavelength	355 nm
Serial number	91381
Linos F/theta-Ronar lens	
Focal length	103 mm
Design wavelength	355 nm
Options	Telecentric
Serial number	102516
Correction file	D2_041.ctb
Scanlab camera adaptor	
Laser wavelength	343 – 355 nm
Observation wavelength	510 – 680 nm
Product number	113848

Table II: Experimental settings.

Experimental setup Trumpf TruMicro 5050 laser	
Wavelength [λ]	343 nm
Average Power [P_{avg}]	355 mW
repetition rate	200 kHz
pulse energy [E_{pulse}]	1,775μJ
Scan speed [v_{scan}]	2 m/s
Spotsize [d_{spot}]	15 µm
Interpulse displacement [x_{pulse}]	10 µm
Pulse overlap	33%
Number of over scans [OS]	10
Line separation [x_{line}]	15 µm

Chemical Modification: All chemicals were obtained from Sigma Aldrich. In the first step 3-Chloropropyl isocyanate and 2-Chloroethyl chloroformate were used for model reactions. The set up was as follows:

<u>3-Chloropropyl isocyanate:</u> A round bottom flask fitted with a reflux condenser was filled with 200 ml THF and 10 grams of dry epoxy treated aramid fibres. The content was refluxed at 66°C during 1 hour. Subsequently 1.7 ml of 3-Chloropropyl Isocyanate and 0.24 ml Dibutyltin diacetate (DBTDA) was added to start the coupling reaction. The mixture was refluxed at 66°C for 2 hours and allowed to cool down to room temperature during another 2 hours. The fibres were removed from the flask and filtered over a redband paper filter (Fisher) to remove the solvent. They were washed with 100 ml of ultrapure water and 100 ml of pure ethanol to remove catalyst and other by-products and finally they were dried for 48 hours in air and stored in a dry and dark place.

<u>2-Chloroethyl chloroformate:</u> A round bottom flask fitted with a reflux condenser was filled with 200 ml Tetrahydrofuran (THF) and 10 grams of dry epoxy-treated aramid fibres. The content was refluxed at 66°C during 1 hour. Subsequently 1.0 ml of 2-Chloroethyl chloroformate and 1.0 ml triethylamine were added to start the coupling. The mixture was refluxed at 66°C for 2 hours and allowed to cool down to room temperature during another 2 hours. Filtering was performed like for 3-chloropropyl isocyanate. The fibres were washed

with 100 ml of ultrapure water and 100 ml of pure ethanol to remove catalyst and other by-products and finally they were dried for 48 hours in air and stored in a dry and dark place.

The XPS used to quantify the level of surface grafting was a Quantera SXM (scanning XPS microprobe) from Physical Electronics.

In the second step, grafting was performed on fibres with epoxy pre-coating, using allyl-chloroformate and allyl-isocyanate. The procedures were identical to those for 3-Chloropropyl isocyanate and 2-Chloroethyl chloroformate.

To evaluate composites with the treated fibres, an EPDM compound was prepared with the formulation according to Table III. The EPDM type was Keltan 8340A from DSM Elastomers BV and carbon black N-550 from Evonik GmbH.

Table III: Evaluation recipe

Ingredient	EPDM	Carbon Black	Oil	Stearic Acid	PEG 2000	Perkadox 14/40	TRIM
phr	100	105	8	1	2.5	7.5	4

The masterbaches were made in an industrial scale internal mixer and the curatives and 5phr short fibres were added on a two-roll mill. The milling direction was considered as longitudinal direction of fibre orientation. After determining the cure characteristics with a Rubber Process Analyzer (RPA2000) of Alpha Technologies the compounds were cured at 170°C for their t_{90}+2 mins. Tensile tests were performed with a Zwick Z1.0/TH1S tensile tester, speed 200 mm/min, in the longitudinal direction of fiber orientation in the samples.

RESULTS AND DISCUSSION

Laser Treatment: Change in the topography of polyester and polyamide fibres, using laser pulses has been reported by several researchers [18, 19, 20]. Watanabe and Takata [21] applied laser pulses on the surface of epoxy-coated aramid fibres to enhance the adhesion between an RFL top-layer with the epoxy sub-coating. Considering the importance of mechanical interlocking specially in short fibre reinforcement [11], in this study the laser was applied to increase this sort of mechanical interaction between aramid fibres and rubber. Figure 2 shows SEM pictures of the treated fibres. It can be seen that the surface of the fibres is successfully roughened without severe damage to their bulk. The depth of the treated area can be estimated to be between 1 to 2 microns and the thickness of the fibres are around 12 microns. It should be noticed that because of the huge difference between the modulus of the aramid fibres and the rubber compound, even a decrease in the fibres properties can be accepted to some extent without a negative effect on the final composite properties.

The treated materials unfortunately could not be tested in a real composite made with the roughened fibres due to lack of facilities needed to make the set up for an adhesion test. Due to time limitations, this approach was not further pursued.

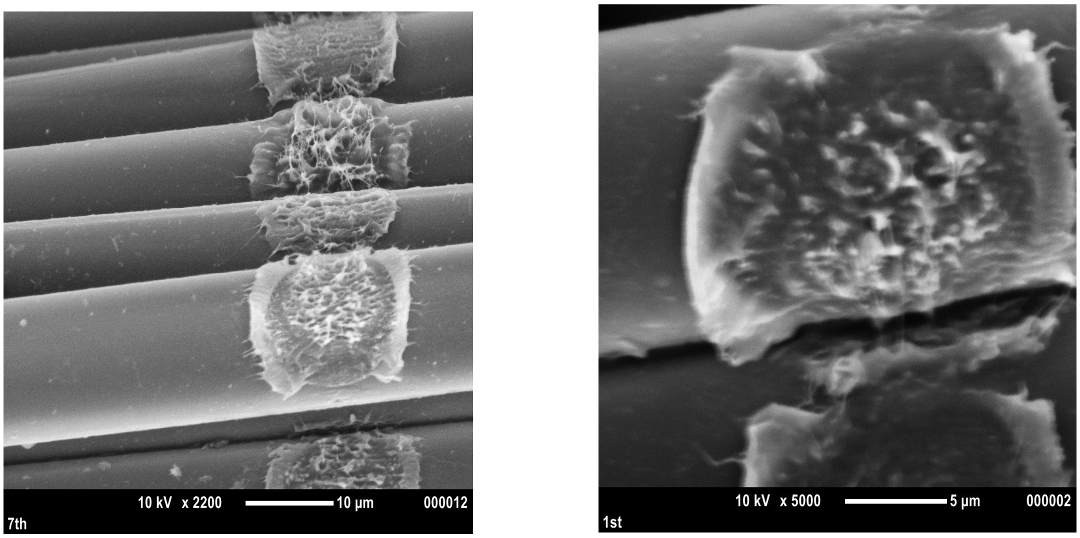


Figure 2: SEM pictures of the laser treated fibres.

Chemical Modification: Aramid fibres are very inert by nature and are not able to create chemical bonds to the surrounding matrix. As described before, a common method to increase the adhesion is by fibre surface treatment, using Resorcinol Formaldehyde Latex (RFL). Aramid fibres in particular are not reactive with RFL either and are normally coated with an epoxy sub-coating and the RFL-layer on top. This epoxy layer provides a lot of hydroxyl and NH groups, depending on the type of the epoxy cure system used. Here, attempts have been made to treat the surface of short-epoxy treated fibres directly with isocyanates and chloroformates as alternatives for the RFL treatment.

The proposed reaction mechanisms between the mentioned chemicals and OH groups on the surface the epoxy-treated fibres can be found in details in references [22,23]. The reactions can be schematically presented as:

$$\mathrm{R\text{-}OH + O{=}C{=}N\text{-}C\text{-}C\text{-}C\text{-}Cl \rightarrow R\text{-}O\text{-}C({=}O)\text{-}N\text{-}C\text{-}C\text{-}C\text{-}Cl}$$

$$\mathrm{R\text{-}OH + Cl\text{-}C({=}O)\text{-}O\text{-}C\text{-}C\text{-}Cl \rightarrow R\text{-}O\text{-}C({=}O)\text{-}O\text{-}C\text{-}C\text{-}Cl}$$

After treatment with 3-Chloropropyl isocyanate and 2-Chloroethyl chloroformate the surfaces of the fibres were then analysed with XPS to detect chlorine on the surface, which for either case is an indication of the modification being successful. The results showed that in both samples a peak related to chlorine was detectable at 200 eV: figure 3.

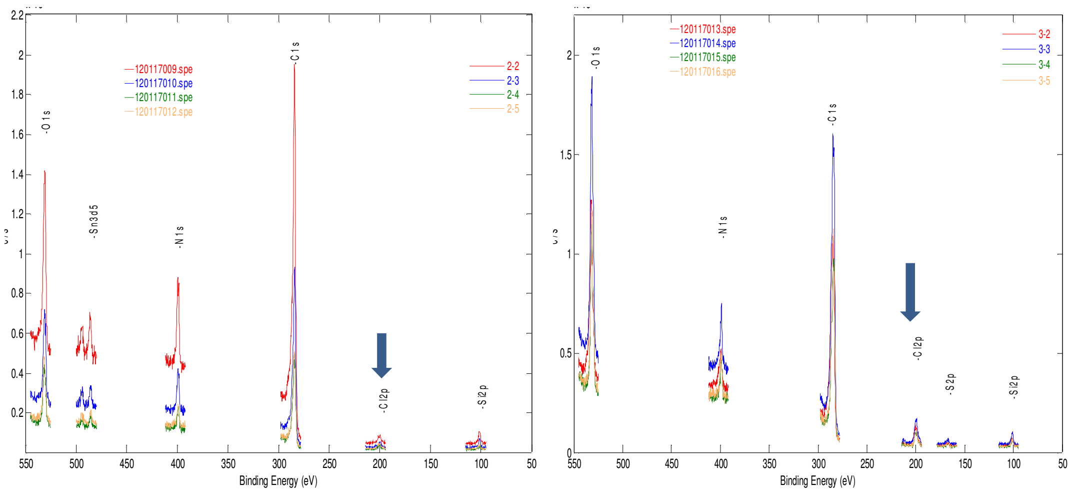


Figure 3: XPS results for fibres treated with left: 3-Chloropropyl isocyanate, right: 2 Chloroethyl chloroformate.

In the second step, after the grafting reactions between isocyanates and chloroformates with epoxy-coated aramid fibres has been proved to happen, the fibres were modified using the same method with allyl-chloroformate and allyl-isocyanate to provide reactive sites for peroxide crosslinking:

$$\text{R-OH + O=C=N-C-C=C} \rightarrow \text{R-O-C(=O)-N-C-C=C}$$

$$\text{R-OH + Cl-C(=O)-O-C-C=C} \rightarrow \text{R-O-C(=O)-O-C-C=C}$$

When the treated fibres are added to an EPDM compound containing a peroxide curing systems, peroxide will be able to generate bonds between the elastomer chains and the allyl tails of the grafted molecules. The mechanism of the peroxide reaction is rather simple [24]: as a result of heating, the peroxide molecule splits and generates molecules with oxygen radicals. These radicals are able to abstract allylic hydrogen from the modified surface, generating carbon radicals. Two carbon radicals react with each other and form a carbon-carbon bond. Here the presence of the allyl groups favours the reaction because H-abstraction of such group is easier than even abstraction of a secondary hydrogen from a hydrocarbon which needs more energy. Because the allyl group stabilizes the radical function. Allyl-containing compounds are well-known as co-agents for peroxide vulcanization.

The tensile results are presented in comparison with a compound without fibres, and compounds with standard fibres (treated with standard finish which is an oily substance that facilitates processing), epoxy-treated (EpT) and RFL-coated (with an epoxy subcoating layer): Table IV and figure 4. It can be seen that adding fibres generally results in an increase in the tensile stress. This happens even for Standard fibres which do not generate chemical bonds to rubber, due to the mechanical interlocking mechanism of reinforcement. It is observed that Epoxy-treated fibres offer no advantage over St-fibres and, unless they are coated with an RFL top-coating, good interaction is not generated between the fibres and rubber.

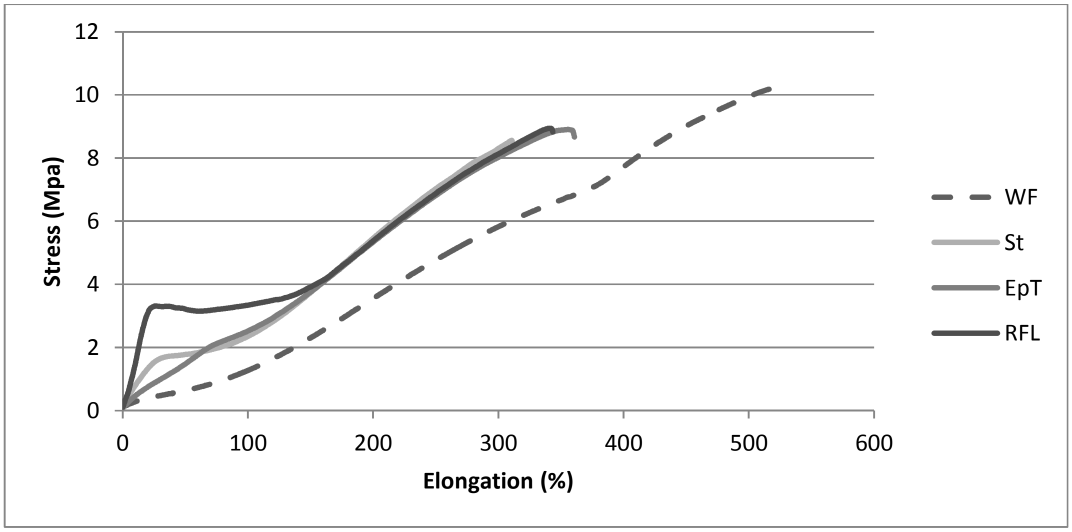
The results of fibre modifications are interesting. It is clear that allyl-isocyanate (IS) and allyl-chloroformate (CH) treated samples are comparable with RFL-coated samples and that the properties have improved considerably over WF and standard fibres. The shape of curves for the IS and CH, similar to that for RFL, is also an indication of chemical bonding [11]. The chemical bonds between the hyrdrocarbon tails of the modifier chemicals and rubber chains, result in a considerabe reinforcement till 10 to 20% elongation.

The same system was not explored for sulphur cured elastomers, because considering the sulphur reaction mechanism [25], for such cases different isocyanate and chloroformate chemical treatments were needed containing hydrocarbon tails with unsaturation in the structure and a -CH2- group between the allylic protons and another carbon atom. In other words, though the existence of carbon-carbon double bonds (-CH=CH-) is necessary for sulphur crosslinking, the carbon attom which will become bonded with sulphur is not the unsaturated carbon atom itself but a saturated neighbouring carbon which in turn follows by another saturated carbon atom. The proposed structure for such molecules is (fn)-C-R-C=C-R', in which (fn) is the functional group needed for grafting to the epoxy-coating on the fibre, which here is again isocyanate or chloroformate and R and R'are alkane groups. Such products are not commercially available and should have been syntesized which was not done because of lack of time.

However, it has been proved that the functionalisation has been successful, and the hydrocarbon chains bonded to the epoxy coating of the fibres are available for reaction with the elastomer. It can be concluded that using isocyanates and chloroformates with suitable hydrocarbon tails for sulphur reaction most probably also result in generation of chemical bonds between the fibre-coating and elastomers.

Table IV: Stress values (MPa) at different elongations.

	10%	25%	50%	100%
WF	0,28	0,44	0,63	1,28
St	0,79	1,53	1,87	2,35
EpT	0,47	0,87	1,48	2,52
RFL	1,47	3,3	3,2	3,34
IS	2,94	2,92	2,9	3,22
CH	2,28	2,34	2,41	2,85



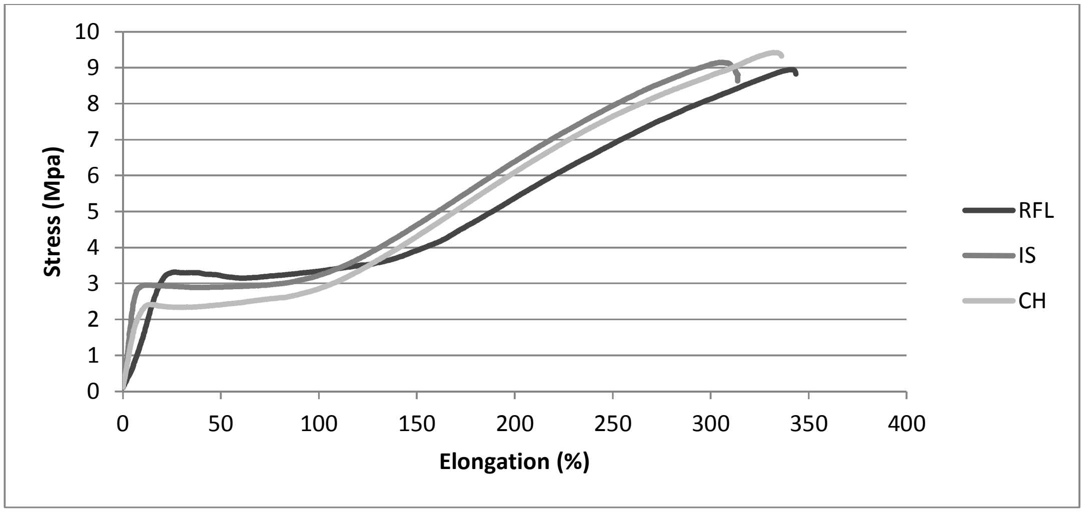


Figure 4: The tensile curves of the compound without fibres (WF) and the compounds containing 5 phr of standard fibres (St), Epoxy treated (EpT), RFL-coated, treated with allyl isocyanate (IS) and allyl chloroformate (CH), in longitudinal direction of fibre orientation.

CONCLUSIONS

Considering the different adhesion mechanisms for short and continuous aramid fibres various approaches can be considered to enhance their interaction with the elastomers. Particulairly for short fibres in which RFL is not as effective as in continuous fibres, treatment with different chemicals which can be bonded to elastomer chains can be an alternative for RFL. In this respect Allyl-Isocyanates and Allyl-Chloroformates are two classes of chemicals which are able to functionalize epoxy pre-coated fibres for make them reactive towards peroxide crosslinking. A similar approach to make these fibres reactive towards sulphur crosslinking could not be explored (yet) by lack of commercial availability and lack of time.

A different approach is to consider methods which can create roughness on the surface of the fibres to improve mechanical interlocking. In this respect laser etching looks to be promising, especially considering its ease of use. In practice a laser machine can be mounted easily on the production line after the spinning process.

Further research is needed to develop the degree of reinforcement as a result of the treatments given.

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Ring the bells that still can ring

Forget your perfect offering

There is a crack in everything

That's how the light gets in.

Leonard Cohen