

## Review Article

# A Review on Surface Modification of Textile Substrate Using Plasma to Improve Interfacial Bonding with Rubber Matrix

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## Abstract

In the composite, the adhesion between the reinforcement and the rubber matrix plays an important role in ensuring the serviceability of the composite under adverse environmental conditions. The adhesion strength between the reinforcement and matrix is not just for holding the materials together, which should also for providing the capacity to withstand the operating load, transfer the load stress from the rubber matrix to the reinforcing fibre materials. Hence, the adhesion properties of reinforcements with the rubber matrix are always preferred to be high. Synthetic fibre like PET, Nylon and aramid fibre are generally used as reinforcing materials for rubber composite. As such Synthetic fibre does not direct adhere with rubber, to overcome this limitations chemical pre-treatment was used. This article delineates a review on the surface modification of reinforcing material using the plasma treatment to improve the surface roughness and its interfacial bonding with rubber composite through diffusion and mechanical interlocking.

**Keywords:** Plasma, Surface roughening, Interfacial Bonding, Rubber Composite, Polyester, Nylon and Aramid

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## Introduction

Textile reinforced rubber composites are unique in their properties wherein there would be good flexibility, pliability, extensibility, elasticity, compressibility along with the retention of the other important properties of composites such as thermal, mechanical and chemical properties. In order to obtain the unique properties of the composite, both the reinforcement and the matrix are carefully selected based on the end use. Textile materials which have specific properties like high tenacity, high modulus, low shrinkage, optimum elongation, abrasion resistance, temperature and chemical resistance, are being used as reinforcing materials. However, all these properties may not be required for all the applications and hence based on the requirement of end-use applications, type of fibres such as natural or synthetics; construction, such as knitted, woven, braided and nonwoven forms can be used.

Among the choice for reinforcement, natural fibres were previously used as reinforcing material. However, one of the limiting factor related to the use of natural fibres is poor mechanical properties. Due to this synthetic fibres started replacing natural fibres as a reinforcement material. One of the demerits of synthetic fibres for using as reinforcement in rubber composites is their poor adhesion property with rubber. In order to overcome limitations, industries are using, RFL (resorcinol formaldehyde latex) as well as isocyanates pretreatments on reinforcement material.

There are two types of rubber matrices namely, natural and synthetic rubber. Natural rubber has excellent stretch and flexibility and moderate resistance to sunlight, solvents and oil resistances [1]. The Synthetic rubbers, like natural rubbers, can be toughened by vulcanization and improved and modified for special purposes with improved properties like resistance to extreme temperatures and corrosive environments. The synthetic rubbers such as SBR (StyreneButadiene Rubber), Nitrile rubber (acrylonitrile/butadiene) NBR, BR (Butyl rubber), Polychloroprene (Neoprene- DuPont), Chlorosulphonated (Hypalon-DuPont) and Fluroelastomer (Viton-DuPont) are also used as matrix for composites. Both type of rubbers have their own merits and demerits.

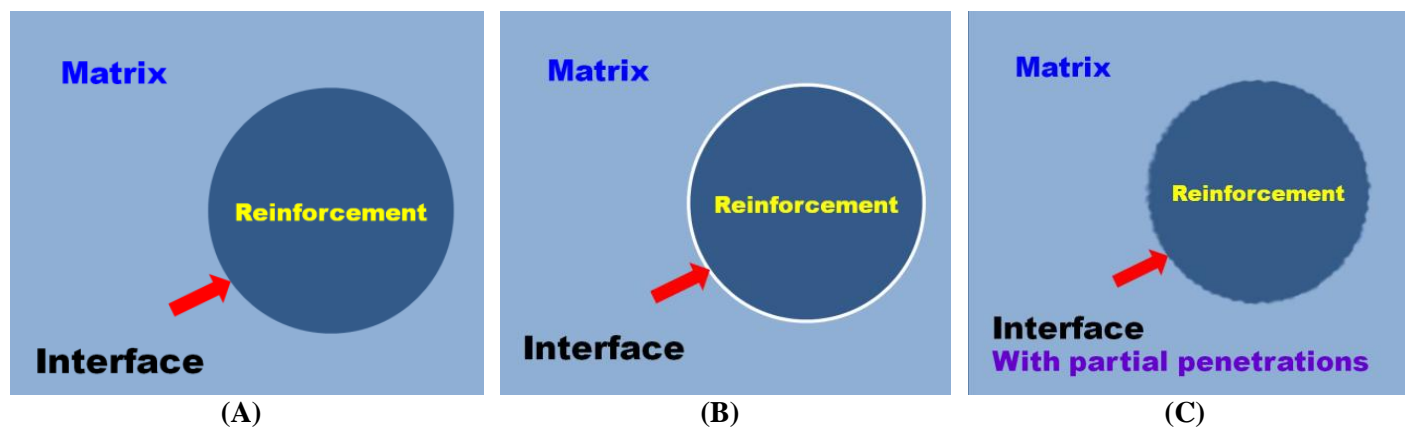
The textile rubber composites find many applications each with some common and different requirements. For examples, for belts applications it requires, the flexibility, pliability, elasticity along with high load bearing and load transfer mechanical properties, heat stability and heat transfer properties along with less weight, no lubrication, compact design, etc. In the case of tire-cord applications almost the similar properties to that of the belt but with specific additional requirements of cyclic load bearing capacity, abrasion resistance, low shrinkage and heat stability, etc. The rubber composite materials used in the inflatable structures like Inflatable Boats, Oil Booms, Inflatable Dams, Inflatable Buildings and Dunnage Bags should withstand the inflation pressure (air or water used for inflation), abrasion resistance, radiation, extensibility and good puncture resistance along with the general load bearing capacity.

In the case of hoses application, the requirements are moisture resistance, oil resistance, temperature resistance and chemical resistance, dimensional stability, strength and good adhesion to the rubber [2]. Likewise, for different end-use applications, different properties are required. Hence, based on the property requirements for a particular application, the choice of reinforcement (fibre or yarn or fabric) and the rubber matrix may be preferred.

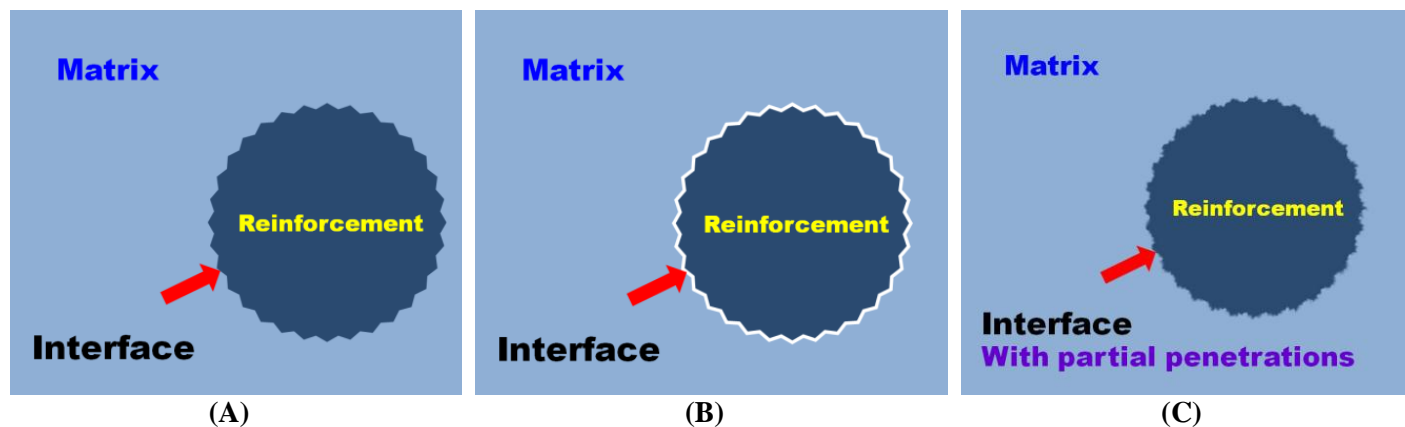
The final properties of the composites are; of course, depending on the blend of the properties of the reinforcement and the matrix. In order to obtain the best properties, particularly for the mechanical properties, of the two components, i.e. the rubber matrix and the textile reinforcement, the adhesion between the rubber and the reinforcement structure must be very strong. Such interfacial bonding between the rubber and the reinforcement play a vital role in the performance and durability of the composites.

### *Interfacial bonding and performances*

The final properties of the composites not only depend on the properties of the components but also the way in which the interfacial bonding is formed between the components, in the two-component composites, it is between the matrix and the reinforcement. In such bi-component composite, the interfacial bonding is the bond that is formed at the interface of the matrix and the reinforcement while the interface itself is the proximity contact region of the two which is schematically shown in **Figures 1, 2**. Figure 1 schematically represents the bi-component composite with reinforcement having smooth surface while Figure 2 schematically represents the bi-component composite with reinforcement having the rough surface. It can be observed from both the figures Figure 1 (A) and Figure 2 (A) that the matrix is in very close contact with reinforcement when observed macroscopically, wherein the interface region space may not be visible. However, when the same region is viewed microscopically to the order of atomic scale, a region of interaction could be ascertained as shown in Figure 1 (B) and 2 (B), respectively, wherein the specific region of the interface could be visualized. It is this region at which both the mechanical and chemical interactions could take place between the components of the composite [3].



**Figure 1** Schematic representation of the interface between the matrix and reinforcement with smooth surface, (A) the interface intact, (B) the interface magnified and (C) partial penetration of the components



**Figure 2** Schematic representation of the interface between the matrix and reinforcement with rough surface, (A) the interface intact, (B) the interface magnified and (C) partial penetration of the components

Accordingly, the interfacial interactions can be broadly classified as chemical or mechanical. Both types of interactions are initiated during curing reaction of the matrix. For the chemical reactions to take place there should be appropriate functional/reactive groups both in the matrix and also on the reinforcing fibre surface. Such chemical reactions would end up with any one of the four basic types of bonding i.e. covalent, ionic, Hydrogen-bonding and Vander Waals's forces of attractions. Of these four types the last type of chemical bonding, the Vander Waals's forces of attractions would be present in the interface as is common to all materials. Such Vander Waals's forces of attractions with a high degree could also become the source of strong interfacial chemical interaction.

The mechanical bonding between the matrix and reinforcement could take place as a partial penetration effect of the polymeric molecules of both the matrix and reinforcement mutually due to the partial interfacial melting effect as shown in the schematic diagrams (Figure 1 (C) and Figure 2 (C)). This leads to the formation of a sort of mechanical interlocking effect between the matrix and the reinforcement, which would play a major role in transferring the load, applied to the composites, from the matrix to the reinforcement. In such mechanical interaction of the matrix and the reinforcement, the point of surface smoothness and roughness of the reinforcement can influence the degree of interaction as shown in Figure 1 and Figure 2. Figure 1 (A) shows the smooth reinforcing surface while Figure 1 (B) shows the rough reinforcing surface and correspondingly Figure 1 (C) and Figure 1 (C) show the reinforcement effects with partial interfacial melting and interactions. Of the two, it can be visually deduced and also microscopically that a reinforcement with rough surface would have a high degree of mechanical interlocking effect with a high degree of interfacial interaction. Such rough surface coupled with good chemical bonding ability of the components would derive the maximum possible interfacial adhesion in the composite.

Most of the synthetic based fibres remain circular and smooth, by virtue of manufacturing through melt spinning. Hence, the mechanical interlocking effect with the matrix would comparatively remain poor as shown in Figure 1 (C). So, the mechanical interlocking effect can be created between the fibre and matrix by making the fibre surface into rough surface through pre-treatment process. There is some research attempts to increase the surface roughness of fibres and to improve the interfacial bonding of the composites [4-5]. Studies on surface roughening of fibres through mechanical methods such as sandblasting, etching with abrasives; chemical methods such as alkaline and acid treatments; biological treatments such as enzymes and microbes and physical methods such as plasma treatment and combustion have been carried out for improving surface chemical and physical properties [6-9].

In addition, plasma treatments which is a purely a physical treatment finds major interest amongst the researchers. Plasma Treatment has the advantage of being dry and energy efficient processes compared with the wet treatments which involve heating of bulk aqueous treatment solutions, subsequent drying of the treated samples and the effluent handling and treatments [10]. Additionally, the plasma treatment is much appreciated for the submicron level of surface reactions without affecting the bulk properties, which might be happen in the other methods, if the reaction conditions are not maintained within the set limits [10]. The change in the surface energy, contact angle, wettability and also create a new functional group on the surface and contribute for mechanical and chemical bonding at the interface. This review article outlines about the surface modification of different textile substrates using plasma to improve the interfacial bonding with rubber composites.

### *Plasma Technology*

Plasma technology has been used from since 1960s, to improve the surface properties of the substrate in many textile applications and also in fibre reinforced composites. Using the plasma treatment has been well know for surface properties modification without altering bulking properties, and for its ability to change the surface chemistry and topography [11].

There are two types of interaction take place with the surface during the plasma treatment [12]. The first type of interaction refers to chain scission, crosslinking, intermolecular and intramolecular reaction of polymer chains themselves. The second type of interaction take in plasma induced polymerization and grafting. The most commonly used non polymerizing gases are argon, helium, oxygen, nitrogen, hydrogen and ammonia. The various polymerizing gases and precursors like hydrocarbon, fluorocarbons and silicone used for grafting on the substrate surface. The inert gas like helium and argon are used as carrier gas for etching and polymerization [13]. Due to high energy metastable state and excellent heat conductivity, helium gas is favored over the other gases [14].

The non-polymerizing gases depends on different parameters like discharge power, exposure time, nature of the substrate and nature of gas which influences the effect of the plasma on the substrate. The generation of free radicals on the surface by means of chain scission is initiated by an inert gas, whereas reactive gases like ammonia and oxygen can integrate the nitrogen or oxygen containing group [13]. Such kind of changes on the surface substrate will improve adhesion, bondability, dyeability and printability etc., in various applications.

Li et al. 1997 [15] stated that the main purpose of plasma surface treatment of textiles used as reinforcements in composite materials was to modify the chemical and physical structures of their surface layer. In order to improve the

fibre matrix adhesion, the plasma treatments are used for imparting polar groups or by changing the surface roughness of the textile substrates [16-18]. The plasma exposure on the polymer surface not only modifies the surface roughness, but it also leaves the active sites at the surface on the polymers which are subjected to post-reactions; this is also called aging [19]. The aging effect is influenced by external factors like adsorption or oxidation, and internal tendency to attain an energetically favorable state by diffusion and restructuring processes. It also lowers the surface energy by adsorbing the contaminants from the atmosphere [20].

## **Plasma Treatment On Textile Fibre To Improve Interfacial Bonding With Rubber**

### ***Polyester***

The Polyethylene terephthalate fibers cord treated using 30 min argon plasma treatment followed by 30 min oxygen plasma treatment, at 75 W power and 40 Pa pressure, without altering the traction strength of the fibers cords [21]. The plasma-treated cords were followed by resorcinol formaldehyde latex and rubber coating. The PET cord showed the increased adhesion of ~ 280% compares to untreated. The shorter treatment times would favour adhesion by the increase in the surface polarity, whereas the longer treatment times would allow a better mechanical anchorage and an easier diffusion of the low molecular weights from the fiber surface to the RFL coating to complete the adhesion.

Shijian et al. (1999) [22], studied the plasma polymerization technique on textile tire cord for the improvement of rubber adhesion. Using semi-continuous reactor operated on a pulsed DC glow discharge, coatings of plasma-polymerized pyrrole or acetylene were deposited on the surface of cords. They concluded that low power and high-pressure condition are better than high power and low-pressure condition for coating plasma polymerization. The plasma polymerization coating shows the significant increase in the pull-out force. They also reported that structure was found to be strongly dependent on the deposition conditions.

Simor et al. (2004) [23] reported that the H<sub>2</sub>O atmosphere plasma treatment on polyester cord threads for the improvement of adhesion without using RFL treatment. The atmospheric-pressure H<sub>2</sub>O plasma was generated in an underwater diaphragm discharge. The plasma-treated polyester cord threads surface become rough, mechanical anchorage from the increased surface roughness contributes significantly to the observed increase in cord/rubber adhesion. The plasma treatment resulted in approximately 100% improvement in the adhesion when compared to the untreated polyester cord threads (RFL treated).

Krump et al. (2005) [24] studied the effect of atmospheric pressure plasma treatment on the adhesion strength between poly(ethylene terephthalate) (PET) fibres and styrene-butadiene rubber (SBR). The main findings of their studies are the lubricants present in the fibre causes the decrease in adhesion strength, if the lubricant is removed from the fibre and treated with plasma shows improved adhesion strength between them.

Jasso et al. (2006) [6] investigated the effect of low-temperature nitrogen plasma treatment and subsequently grafted with maleic acid (MAc), to enhance the adhesion with styrene-butadiene rubber (SBR) blend. Three factors (i.e. time of grafting (min), the speed of movement (m min<sup>-1</sup>) and concentration of MAc (mol dm<sup>-3</sup>) are selected to study the effect on adhesion strength. The morphological changes are observed for Mac grafted PET which forms new polar groups and improved the adhesion strength of the rubber. In the case of mechanical properties like stress at Break; elongation at break; elongation at loading by force, negligible changes were observed.

Jaššo et al. [25] studied the coating of PET cords at atmospheric pressure plasma discharge in the presence of butadiene/nitrogen gas mixtures. The roughness formed on the PET surface about 5 µm to 15.170 µm pores.

Krump et al. 2006 [26] studied the effect of atmospheric plasma treatment on PET and a rubber matrix. The plasma treatment confirmed the recrystallization of the polymer chains by forming new melting peak, changes in chemical species and surface become more wettability, but in the case of mechanical properties, no significant changes were observed. The adhesion strength between the PET and rubber matrix were improved which also found to be comparable with standard industrial chemical treatment (RFL).

### ***Nylon***

Periyasamy et.al 2018 [27], studied the submicron surface roughening of aliphatic polyamide 6,6 (nylon 6,6) fabric using dielectric barrier discharge-based atmospheric low-temperature plasma for improving the adhesion bonding with rubber. Scanning electron microscope micrographs revealed the presence of submicron roughness on the nylon 6,6 fibre surface with pores of around 100 nm (0.1 µm) for the optimum treatment time of 180 s above which the pore merging effect dominated resulting in the net low surface roughness. The peel strength of the rubber composite, which is a measure of interfacial bonding, increased to 150% as the maximum for the optimum plasma treatment time of 180 s.

### *Steel wire*

Yoon et al. (2001) [28] investigated the zinc-plated steel filaments adhesion to rubber compounds which are coated with RF plasma polymers of acetylene or butadiene. In their study, three carrier gas has been used, where oxygen carrier gas was not as effective as argon or nitrogen for better adhesion strength. By using the plasma-polymerized coating of acetylene in combination with argon plasma etching and a carrier gas, the adhesion of zinc-plated steel filaments to rubber compounds was greatly enhanced. But plasma polymerization alone results in a low pull-out force. In the case of Butadiene plasma-polymerized coating pull-out forces were found to be lower. The presence of C=C enhanced the pull-out forces with acetylene plasma-polymerized coating.

### *Aramid*

Van ooi et al. (2006) [29] studied the adhesion of aramid tire cord through argon plasma etching and acetylene plasma polymerization and compared with RFL treated. In their study, two different plasma reactors are used i.e. DC and RF plasma reactor. Both the RF and DC reactor significantly enhanced the adhesion aramid tire cord, through acetylene plasma polymerization in combination with argon plasma etching [29] which found to be lower than that of RFL-treated aramid cords. They have also reported that RF reactor showed higher adhesion than the results from DC reactor under all the conditions such as argon etching only, acetylene plasma polymerization only, and the combination of acetylene plasma polymerization with argon plasma etching [29]. DC reactor with low pulse rate is more effective for enhancing the adhesion than high pulse rate DC plasma. The enhanced interfacial adhesion of aramid cord to rubber could be related to the presence of C≡C and C=C moieties in plasma polymer films confirmed from ATR-FTIR analysis.

Pieter & Peter (2012) [30] studied the chemical adhesion activation process of aramid and the potential alternative for the epoxy treatment by plasma treatment. The plasma treatment on aramid yarn in the nitrogen atmosphere, the oxygen percentage was increased to a maximum of 17%. The high surface roughness found on the aramid yarn for nitrogen atmosphere compared to air atmosphere plasma treatment. The plasma-treated aramid showed lower adhesion than the chemically treated ones. In the chemical treated aramid, the curing of epoxy based finishing led to high hydroxyl group formation on the surface, which led to the formation of strong interfacial adhesion. The hydroxyl groups could covalently bond with RFL dipping, which led to strong interaction with the rubber matrix [31]. In the case of plasma treated aramids, they showed a limited portion oxygen which contributed to the hydroxyl group. They have confirmed that the mechanical adhesion i.e. interlocking played a minor role.

### **Conclusion**

Plasma treatment for textile reinforcement's materials of rubber composites is an eco-friendly process. Using this method for surface modification for tailoring fibre-matrix bonding strength and controlling interfacial bonding and adhesion, without influencing their bulk mechanical properties. The process parameters for plasma treatment like treatment time, type of gas, power are needed to be carefully selected in order to achieve equilibrium between the control degradation, surface roughness and improvement of the wettability and the polar components. The polar component of the fibre surface energy was sensitive towards the nature of gas and the treatment time which actually helps in interfacial bonding the textile substrate through mechanical interlocking effect and diffusion. Using the Plasma-induced pretreatment, in-situ and post-polymerization grafting techniques on reinforcement fibres need to be further studied through the direct attachment of chemical groups such as sulfur and methyol groups on the reinforcement can be done. This will helps the reinforcement material to direct interact with rubber for improved interfacial bonding.

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