A PLASMA TREATMENT OF SURFACE OF SYNTHETIC TEXTILE FABRICS, USED FOR REINFORCEMENT OF CAR TIRES

František Krčma¹, Jan Janěa², Pavel Šabel², Jiří Buchta², Deepak Subedi², Jana Pryěková¹

¹ Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic
² Department of Physical Electronics, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

Abstract

The surface of the polyester multicord sewing fibers was modified by low temperature plasma at the atmospheric pressure. The surface was treated with various non-equilibrium discharges. The treated polymeric fibers were used in the same form as in industry, i.e. with protecting oil films on their surface. Thus, the first effect of the discharge plasma on the cord during the plasma treatment is the removal of the oil film; the second effect is the actual fiber surface modification. The surface properties were investigated by electron spin resonance spectroscopy and by measuring their contact angle with various liquids. Finally, standard H-tests and peel-tests at industrial conditions were used to characterize the fiber adhesion to commonly used testing rubbers.

1. Introduction

The quality of tires depends considerably on the character of the interface of the reinforcing fiber with the rubber matrix, especially on the rubber adhesivity to the multicord sewing threads. To increase the interfacial strength, the fiber surface is treated by special techniques. The classical system applied in industry is an impregnation of cords in various types of special liquids, usually in more than one dip. Some of the dipping liquids can be also rather hazardous from the environmental point of view.

The surface activation of polymeric fiber materials by low temperature plasmas has been introduced during the last years. The majority of plasma applications in the surface modification field focus on the pure polymeric materials, such as polyethylene and polypropylene. These methods were applied widely at reduced pressures in the range of 1 – 20 Pa [1, 2, 3]. The significant increase of wettability and adhesivity of materials treated by this method has been observed.

The application of low-pressure plasma treatment in industry brings numerous disadvantages, mainly the necessary vacuum systems, long processing times and higher energy consumption. The additional significant problem is that an oil film necessary for the cord fabrication is on the surface of the single fibers of the multicord sewing threads. This film completely changes the mechanisms during the plasma treatment and thus makes these technologies even more complicated.
In our study, we have focused on the plasma surface activation of polymeric fibers at atmospheric pressure, mainly on fibers containing thin oil layers on their surface. The developed technologies could thus be used for a wide range of other industrial applications. New plasma sources were developed and applied in the process of the surface treatment of polymeric fibers. Recently, interesting results have been obtained by using the surface discharge [4] as well as by applying the gliding electrical discharge (Gladarc) in flowing regime at a constant gas flow rate [5]. Some studies have been focused on the use of pulsed electrical microdischarges parallel with the surface to obtain the uniform surface treatment of large-scale samples [6, 7].

The subject of our study is the application of barrier discharges in the activation of oiled polyester (PES) multicord fabrics. The first experiments have been provided also with the aramide fibers.

2. Experimental setup

In our experiment, we have varied the frequency of the dielectric barrier discharges to obtain the optimal plasma properties for the effective plasma removal of the oil film from the cord surface, followed by plasma activation of PES cord with the same type of plasma. Except the experiments with PES the first experiments have been done with aramide cord fibers, too. Polyester multicord sewing threads for tire reinforcement (PES – Trevira 144/420, type 793, produced by KoSa GmbH, Germany; PES – SKL 144x1x2 380/370, produced by Slovkord, Slovakia) and aramide tire cord fibers (Twaron, type 110/1000, produced by Akzo Nobel, Germany) were used in this study. Each thread is composed of more than 300 single thin polymeric fibers screwed together. The fibers were exposed to reactive discharge plasmas from various plasma sources for different exposition times. The details about the plasma treatment can be found in [8].

![Diagram](image)

**Figure 1:** The block scheme of the experiment with diagnostic methods marked with arrows. 1 – non-treated fibers; 2 – plasma treatment; 3 – first dipping and drying; 4 – second dipping and drying; 5 – final product; 6 – ESR spectroscopy; 7 – wettability measurements; 8 – peel – tests; 9 – H – tests.

Dielectric barrier discharges (DBD) were created between two metal electrodes covered with insulating layers (glass, ceramic and polycarbonate) with discharge gap of a few mm. Thanks to the special shape of the metal electrodes, the microdischarges can be observed with the same density around the barrier surface.

Gliding discharges at 50 Hz were produced between two electrodes diverging from each other and placed in the relatively fast parallel gas flow [5], during our experiments in the range of 5 – 10 l min⁻¹. Plasma created in the space between the electrodes is drifted by the gas flow into
the conic space toward the treated fiber material [4]. Dry air and nitrogen were used as the reacting gases in both discharge configurations mentioned above.

3. Wettabillity measurements

The chemical changes of the plasma treated fibers were studied mainly by electron spin resonance (ESR) spectroscopy that has been used recently for the study of similar subject concerning the wool plasma treatment [5]. Of course, this method is not only surface sensitive but due to the structure of the fabrics (see above) the ratio between the surface area and the volume is very high and thus the measured signal can give significant information about the radicals at the individual cord surface. All the methods that can be used for surface properties characterization are significantly distorted by the undefined observed structure because it depends on factors such as the single fibers space orientation. In case of ESR this problem can be partially solved when the larger volume samples are used. The changes of the surface energy that represent the indicator of the adhesion force were observed via changes of the fiber wettability. Since there is no equipment for estimation of dynamical contact angle available in our laboratory, we applied two different simplified methods for the characterization of the relative changes concerning the wettability.

The first of our methods uses the rate of liquid penetration into a vertical fiber with a fixed tension. The vertical fiber is assumed to fit to a model of a bundle of parallel capillaries, according to Washburn's [9] equation

\[ t = \frac{r \gamma \cos \theta t}{2 \eta} \]

where \( t \) is the distance of penetration by the liquid at a time \( t \), \( r \) is the radius of each of parallel capillaries, \( \gamma \) is the liquid surface tension, \( \eta \) is the liquid viscosity, and \( \theta \) is the contact angle.

A comparison of a perfectly wetting liquid (a zero contact angle) and a liquid of finite contact angle allow the value of \( r \) to be cancelled from the equation.

We have also studied the time taken by a fixed volume of liquid to spread completely in a horizontally oriented fiber. Although there is no generally accepted method of determining the contact angle and surface energy of fibers precisely, this method can indirectly give the relative change in surface energy of the treated material compared with the untreated material. Liquid drops of fixed volume (5 μl in our experiment) were applied to a horizontally suspended fiber and the time required for the complete infiltration was measured by following the image of the drop on a projector.

The spreading coefficient of a system may be expressed in terms of the difference between the works of adhesion and cohesion according to

\[ s_c = W_a - W_c = W_a - \sigma \]

where \( s_c \) is a spreading coefficient, \( W_a \) and \( W_c \) is work of adhesion and cohesion, \( W_a \) is wetting energy and \( \sigma \) is the surface tension of the liquid. The relation of the spreading coefficient to the volume of the liquid and spreading time is still under investigation.

The adhesion of plasma treated cord fibers onto the standard tire rubber was tested by fifteen standard H-tests and by three peel tests during each experiment. Both of these industrial tests have been carried out at Kordárm Velká nad Veličkou, Ltd., Czech Republic. The multicord sewing threads used in our experiments have been exposed just after the plasma treatment to an adhesive impregnation in various RFL solutions (RFL = resorcinol + formaldehyde + latex, exact composition is under trade secret).
The H-tests were made with a cord thread 15 mm long. This thread was vulcanized to the testing rubber of size 5 x 25 mm on both sides. During the test, the force parallel to the thread was slowly increased and as H-test result the force needed to tear out the thread from rubber was estimated.

In the case of peel tests, two plates of cord fabric (size 25 x 100 mm) were vulcanized together with testing rubber. The force needed to tear the vulcanized plates was measured and the appearance of the peel tests was examined. If the fabric was completely uncovered after the tear, the peel test was graded as 0 i.e. the adhesion between the rubber and the fabric was poor. On the other hand, with improvement of covering of rubber (i.e. with increase of the adhesion between rubber and the fabric) the grade increase.

4. Results and discussion

The experimental results obtained by electron spin resonance (ESR) spectroscopy have been presented recently [8, 10] and thus here they are given only briefly. The decrease of ESR signal of PES and aramide fibers chemically cleaned in acetone with respect of unwashed samples has been observed. This signal has no finer structure and due to the fact that it is significantly less when the fiber was cleaned in acetone and it is more or less the same for both materials, we suppose that this signal must correspond to the protecting oil layer. No other influence of cleaning has been observed. In the case of the aramide fiber the narrow ESR peak at 340 mT was observed and this peak reflects the aramide structure. An increase in the ESR signal is observed after the plasma treatment. This augmentation is related to the increase of the concentration of free radicals created on the surface of the fiber material. Except the increase of the oil signals the small another peak at higher magnetic field can be observed by non-symmetry of ESR peak. This additional peak can correspond to own polymer surface activation.

![Figure 2: The square of the height of the water penetration as a function of the time for the multicord sewing threads after different types of plasma treatment. The error bars of 10 % are not included to keep the clarity of the dependencies in the graph.](image)

![Figure 3: Spreading time measurement made for 5 µL of distilled water put on the surface of the sample. Penetration rate after cleaning in acetone was smaller than that of the untreated sample for the first few minutes (8 – 10 min) and larger after that.](image)

The liquid penetration rate compared with the untreated threads was slower after the plasma treatment in nitrogen atmosphere at the frequencies of 10 and 20 kHz. It is necessary to note that the protecting oil coating placed on the surface of the cord increases the cord wettability with water. This decrease in the penetration rate is in accordance with the observations by ESR spectroscopy and with the results of the removal of the coating oil from the surface of
the material. Partially it can be explained by the activation of the oil residues on the surface of the cords. On the contrary, the plasma treatment at 30 kHz causes an increase in the wettability of the cord with water (see Fig. 2). This result can be attributed to two effects. Cleaning of the sample surface is the first of them; it is supposed to reduce the wettability. The second effect is the modification of the polymer surface itself (it increases the wettability) and in the case of the treatment provided at 30 kHz this plasma activation is predominant. This modification can be seen through the surface energy increase. The fiber sample cleaned in acetone showed quite different tendency in comparison with the others samples given in Fig. 2. It can be seen that the initial wettability rate is significantly slower due to lower surface energy after the removal of the protecting oil film.

In the spreading time measurement described above, the acetone cleaned sample shows the longest (85 s) time for the same volume of liquid which indicates only cleaning of the sample without any further surface modification.

From Fig. 3 it is possible to observe the increase in the spreading time with the increasing frequency of plasma without the sample treated at 30 kHz. It indicates that with the increasing operating frequency the efficiency of the plasma removal of the oil coating from the surface of the cord increases as well. In the case of the treatment made at 30 kHz, there are two effects. The first one is the plasma cleaning as in the case of the samples treated at lower frequencies and the second one is the activation of the material. The result is the decrease in the spreading time. In accordance with the results of wettability measurements the effect of the plasma activation is predominant, which is indicated by a spreading time lower than the spreading time of the untreated sample.

**Table II.** Measurements of wettability. Remarkable differences (of about 40% for RFL and 16% for water) can be observed between the fibers treated and not treated by the means of barrier discharge performed at 30 kHz. The time of the measurements was 15 minutes in all cases. Error of the measurements was 10% for the RFL solution and 5% for water.

<table>
<thead>
<tr>
<th>Height of capillary elevation after 15 min</th>
<th>RFL [mm]</th>
<th>water [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated PES fiber</td>
<td>17</td>
<td>100</td>
</tr>
<tr>
<td>PES fiber treated by the means of SD 50 Hz</td>
<td>16</td>
<td>104</td>
</tr>
<tr>
<td>PES fiber treated by the means of SD 10 kHz</td>
<td>18</td>
<td>103</td>
</tr>
<tr>
<td>PES fiber treated by the means of SD 30 kHz</td>
<td>24</td>
<td>116</td>
</tr>
</tbody>
</table>

It is possible to observe the differences in wettability (of approximately 41% for RFL and 16% for water) between the treated and untreated oiled fibers. The treatment has been made in the barrier discharge plasma created at 30 kHz in N₂ atmosphere. The modifications of wettability of the PES fibers treated by plasma produced at 50 Hz –10 kHz for both solutions are within the order of the experimental error.

These results are also in good accordance with the results obtained by ESR spectroscopy, by measurements of the spreading time, by measurements of the capillary rise dynamics and also by industrial H-tests and peel-tests.

5. Conclusion

We made the first experiments with the plasma treatment of synthetic cord fibers to increase the adhesion of industrial multicord sewing threads to the rubber matrix. Oilig of
The original cord fibers is the main technological problem. The dielectric barrier discharge has been found to be the most effective tool for the treatment of both polyester and aramide cords. The plasma processing can be the most effectively done in the nitrogen at atmospheric pressure. The barrier discharge has been used at various operating frequencies. At low frequencies no significant changes in the fiber surface properties have been observed, although barrier discharge created at higher frequencies can remarkably improve the adhesion of the cord to rubber.

The plasma treatment of the multicord sewing threads has been characterized by different techniques from the physical, structural as well as technological points of view. The experimental results of the used techniques correspond with each other. Except the pure nitrogen buffer gas, some small admixture of other high reacting gases can be used to create the favorable radicals at the polymer surface and/or to increase the plasma reactivity. Due to this fact, further experiments will concentrate on the optimization of the discharge conditions with respect to the use of ammonia or other ecologically acceptable additives in the discharge gas mixtures. Ammonia can be applied for this purpose, the other obviously used additives, namely gases containing fluorine and chlorine, have not been used due to their toxicity and ecological unacceptability in the industrial technology.

The good results obtained at higher discharge frequencies indicate the necessity to develop a new power supply working at higher frequencies up to 100 kHz.

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References