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Study on the Adhesive Properties of Polyesters Reinforcing Materials

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ABSTRACT : Polyester cord yarns have been treated in an atmospheric-pressure nitrogen plasma reactor in order to enhance their adhesion to rubber. A thin layer of the plasma was generated in the close vicinity of the yarn surface using various types of surface discharge. To assess the effect of the plasma treatment on fiber surface properties, the cord thread/rubber matrix adhesion values measured using the untreated and treated cord threads were compared. The static and dynamic adhesion of the cord thread to rubber was characterized by using the standard Henley test. The dynamic adhesion values for the reference and plasma treated fiber were 7,3 ± 1,2 N and 83,5 ± 3,5 N. The surface properties were investigated by scanning electron microscopy, infrared spectroscopy and electron spin resonance spectroscopy. It is concluded that both polar group interactions and increased surface area of the fibers are responsible for the improved adhesive strength.

Keywords : plasma, polyester, fibre, adhesion

Ⅰ. Introduction

The high-performance advanced polyester fibres are superior to the conventional rubber reinforcing materials because they have a very high strength, dimensional stability, toughness and fatigue resistance at a much lower specific weight. The stresses acting on the rubber matrix are transmitted to the fibres across the interface. A sufficient interfacial adhesion between the matrix and fibre surface must be much stronger that in the case of the conventional reinforcing, and it is a necessary condition for exploiting fibres full strength and modulus (Figure 1). The key factor is the interactions between the functional groups at the fibre surface and the functional groups of the rubber matrix. The relatively inert chemical structure of polyester which gives many of its desirable properties contributing

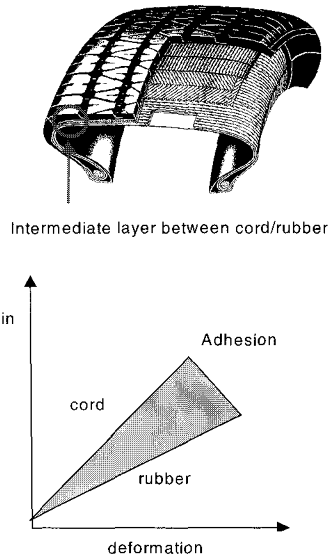

Figure 1. The significance of interfacial adhesion for a rubber/cord composite system in tires.[6]

adversely to its ability to bond to rubber compared with rayon and nylon, gives much lower surface reactivity.[1] The standard method of the improvement of adhesion between the reinforcing polymer fibers and the rubber matrix is based on the surface modification of fibres in the emulsion consisted of resorcinol, formaldehyde and latex (RFL) followed by a thermal treatment at temperatures higher than 200℃. The insufficient polar surface of commonly used synthetic polymer fibres (polyester, aramid, polyethylene) causes little chemical bond between the fiber and the resorcinol resin. The modification using RFL is relatively expensive.

An alternative way for surface activation is the low temperature nitrogen plasma at atmospheric pressure. Our patented device was used for this surface treatment[2] and the information about it was published in more articles on reinforcing materials .[3-5] The device simplifies the surface treatment of reinforcing materials to required improved adhesion levels without RFL.

Ⅱ. Experimental and results

Our patented method appears to be more technically and economically feasible than other known plasma-treatments of the tire reinforcing fibres made at reduced pressures on the order of $10^{-5} \sim 10$ Torr, where batch processing and long processing times were necessary. The plasma reactor (Figure 2) consisted of two on-axis arranged electrodes housed in a glass chamber. Nitrogen of a technical purity was introduced into the chamber with a flow rate on the order of 1 cm^3 per second. The grounded stainless-steel tubular anode was 1 mm in inner diameter. The cathode was a 15 mm diameter hemi-spherically capped brass rod with a 2 mm diameter hole in its axis. The treated cords moved on the axis of the electrode system with a speed from 1.5 to 60 m per minute. The distance between electrodes was adjusted to 15 mm. The cathode was connected with a tyratron source of pulsed high voltage. The HV pulse rate was maintained at 100Hz and the peak voltage was approximately 25 kV. The rise time of the HV pulses was 75 ns and pulse half-width of 400 ns.

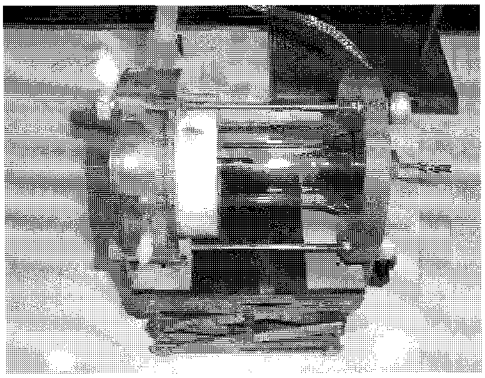

Figure 2. Plasma reactor designed in this study.

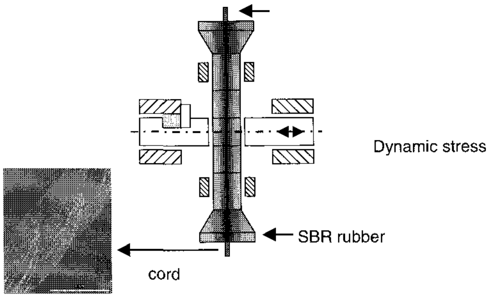

Figure 3. A schematic diagram of Henry test.

To assess the effect of the plasma treatment on fiber surface properties, the cord thread/rubber matrix adhesion values for the untreated and treated cord threads were measured and they are compared. The samples were prepared by pressing the cord thread between two slides from a conventional rubber blend consist of SMR 20, SBR Kralex 1500, PB BR SKD 2 and by subsequent vulcanisation. Adhesion of the cord thread to rubber was characterized using a standard Henley test according to STN 62 1464 illustrated by Figure 3. The dynamic adhesion values for the untreated and plasma treated fibers were 7,3 ± 1,2 N and 83,5 ± 3,5 N, respectively. More than ten times higher adhesion forces were obtained for plasma-treated fiber. In order to explain the improvement the surface pro

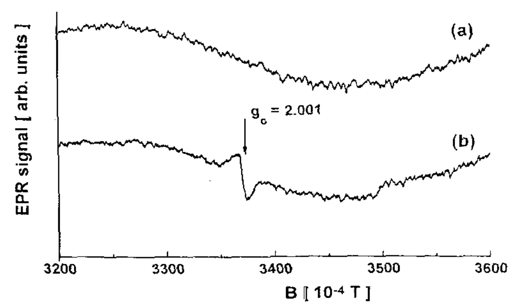

Figure 4. Electron spin resonance spectroscopy (ESR) of (a) untreated and (b) treated cords.

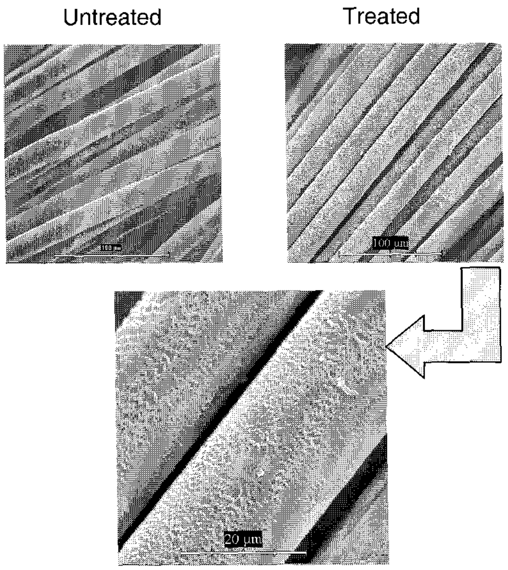

Figure 5. SEM micrographs of untreated and plasma-treated fibers under low temperature and atmospheric pressure.

perties were investigated by electron spin resonance spectroscopy (Figure 4) and scanning electron microscopy (Figure 5). It is concluded that both the polar group interactions and increased surface area of the fibers are responsible for the improved adhesive strength.

Ⅲ. Concluding Remarks

The obtained results of the surface treatment by low temperature nitrogen plasma at atmospheric pressure demonstrate that this method of the surface treatment of polyester cords introduces a suitable and technologically applicable system for the improvement of adhesion of polyester reinforcing materials to rubber. The results confirmed that the treatment using discharge has improved dynamic adhesion between polyester fibre and rubber matrix. In the case of untreated polyester cord, adhesion was measured also after washing of acetone when the pre-adhesion surface treatment applied by the producer of cords was removed from the surface of cords. The values of adhesion confirm increased adhesion to rubber compound after surface activation. The adhesion of polyester cords after treatment by low temperature nitrogen plasma at atmospheric pressure evaluated by standard Henley test is on the 80% level of surface treatment by RFL. The dynamic adhesion values for the reference and plasma treated polyester cord were 7.3±1.2N and 83.5±3.5N.

참고문헌

1. H. Janssen, *Kautschuk Gummi Kunststoffe*, **48**, 622 (1995).
2. M. Cernák, K. Fusek, J. Starigazda, I. Hudec, and P. Janypka, "Device for surface treatment of fibres using a surface electric discharge", Slovak patent application, SK 174/98, 1998.
3. I. Hudec, P. Janypka, M. Cernák, M. Štefecka, and J. Ráhel, "The surface treatment of reinforcing materials by atmospheric - pressure plasma", *Proc. of Slovak Rubber Conference 99*, Puchov, p. 112-115, 1999.
4. M. Štefecka, J. Ráhel, M. Cernák, I. Hudec, M. Mikula, and M. Mazúr, *J. Mater. Sci. Letters*, **18**, 2007 (1999).
5. M. Štefecka, J. Ráhel, I. Hudec, P. Janypka, M. Cernák, and M. Kando, "Atmospheric-pressure plasma treatment of polyester monofilaments for rubber reinforcing", *J. Mater. Sci. Letters*, **19**, 1869 (2000).
6. B. Yilmaz, "Adhesion mechanisms in tyre cord", *Proc. of Slovak Rubber Conference 2000*, Puchov, May 23-24, 2000.