The treatment of fibrous fillers with low-temperature plasma and their application in polychloroprene-based adhesive compositions

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It is well known that filled polymer composites possess improved properties. This is due to their increased activity. Possessing a large free surface, the fillers enter into contact with the functional groups of the polymers. Here, adhesion forces appear that ensure strong bonding of the filler with the polymer [1].

Reinforced materials frequently possess anisotropy of properties, which most often depends on the distribution of the reinforcing component in the composite and the anisotropy of the fibres themselves. The best properties are possessed by chaotically filled composite materials [2].

Without activation of the fibres, their cohesion with the matrix in the composite materials is weak. The surface energy of the fibres must be increased. Activation of the fibres can be done by treatment with a non-equilibrium low-temperature plasma, which increases the surface energy and thereby activates the fibre [3].

Change in the surface and physicomechanical properties of the fibres may be due both to the removal of impurities (the creation of a surface relief), ordering of the amorphous phase, and additional structure formation and to the formation of crosslinks and smoothing of the surface.

Furthermore, it is known that fibres treated with non-equilibrium low-temperature plasma that are fillers for adhesive composites can improve their adhesion properties by the formation of active functional groups on the fibres [4].

The aim of this work was to investigate the effect of the treatment of fibrous fillers with low-temperature plasma and their application in polychloroprene-based adhesive composites in the bonding of elastomeric materials.

The bond strength to vulcanisates based on isoprene (SKI-3), ethylene propylene (SKEPT-40), nitrile butadiene (SKN-18), and chloroprene (KhK) rubbers was assessed using adhesive compositions based on polychloroprene of the 88 series [5, 6].

As fillers for investigating the adhesion properties of adhesive composites, use was made of three types of ground fibre: polyamide fibres (23 KNTS – 187 tex) of 1–3 mm size, carbon fibres (based on polyvinyl alcohol fibres) of 2–3 mm size, and basalt fibres (TU 5769-001-14361167-2006) of 5–10 µm size.

The bond strength of the adhesive joint was determined by the shear method according to GOST 14759-69 on strips of vulcanisates of 10 ± 1 mm width and 2 ± 0.1 mm thickness.

Modification of ground polycaproamide fibres of grade 23 KNTS was carried out by their preliminary treatment in a non-equilibrium low-temperature plasma – in ac low-frequency (50 Hz) glow discharge. A special Teflon electrode holder was placed in a vacuum reaction chamber, and metal electrodes were fastened in it. A special metal frame was placed in direct contact with the lower electrode, on which the fibres to be treated were placed. The unit was evacuated to a pressure of 10⁻² Pa by means of a roughing pump, and the pressure in the reaction chamber was monitored using a vacuum gauge. Then, purified air was introduced through a bleed-in system to a pressure of 15–20 Pa, and a voltage was
supplied to the electrodes from an ac source. Power was supplied from the grid via a step-up transformer, with current of 50 Hz frequency, and a 100 mA current was measured by an ammeter. The fibre treatment time was 2 min [7].

In determining the effect of laser modification of fibrous fillers on the adhesion properties of adhesives of the 88 series, the following relationships were established. The introduction into the indicated adhesive composites of fibrous fillers modified with plasma in quantities of 0.1–0.5% leads to an increase in strength of adhesive bonding of the vulcanisates.

Assessment of the effect of plasma modification of carbon fibres on the adhesion properties of adhesive 88NT in the bonding of vulcanisates based on SKN-18 and KhK is presented in Figure 1.

It was established (Figure 1) that modification of the adhesive composition of grade 88NT with carbon fibres pretreated with plasma leads to an increase in bond strength with vulcanisates based on SKN-18 and KhK on average by a factor of 1.5.

In the case of using plasma-treated basalt fibres for the modification of adhesive 88NT (Figure 2), the adhesion properties of the given composition in the bonding of vulcanisates based on SKN-18 and KhK increase by 30–40%.

In assessment of the influence of the content of plasma-modified polyamide fibres on the adhesion properties of adhesive 88SA in the bonding of vulcanisates based on SKI-3 and SKEPT-40, it was established that the strength of adhesive bonding likewise increases significantly (Figure 3).

From Figure 4 it can be seen that the modification of elastomer adhesive compositions of grade 88SA with plasma-treated carbon fibres leads to an increase in shear strength on average by a factor of 2.
Analysis of experimental investigations of the effect of plasma modification of fibrous fillers makes it possible to state that plasma modification in bonding technology increases significantly the adhesion strength of the adhesive joint, which is due primarily to the more uniform distribution of the fibrous filler in the adhesive film on account of increase in the wettability of the modified fibres. Furthermore, there is an increase in the contact surface between the filled adhesive and substrate, and also enhanced interaction with the substrate on account of the formation on the fibres of active functional groups [8].

Thus, low-temperature plasma treatment is one of the most promising and modern methods of surface modification of materials, including fibrous fillers, which makes it possible to vary the surface properties considerably in a wide range and to expand significantly the areas of application of such fillers [9].

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REFERENCES
