METHOD FOR INCREASING THE BOND STRENGTH OF RUBBERS WITH TEXTILE CORDS FROM SYNTHETIC FIBERS

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ABSTRACT

The article discusses the results of studies on the possibility of increasing the adhesion of rubber to textile kapron cord. A rubberized kapron cord is used for tire production as a carcass and has a number of advantages compared to a cotton cord, but kapron a cord has low adhesion to rubber.

To improve the bond strength of rubber with a kapron cord, it is proposed to use a new water-soluble by polyacrylonitrile modified monoethanolamine (MEPAN) polymer with high surface activity obtained from nitron fiber wastes in an impregnating composition. The experimental results showed that the bonding strength of rubbers with a kapron cord treated with an impregnating composition with MEPAN at 110 °C is 27% higher than with a kapron cord treated with a conventional impregnating composition.

In addition to increasing fatigue properties, the positive side of the heat treatment process with an impregnating composition containing MEPAN is the fixation of the elongation of this fiber with a simultaneous increase in strength, processed by the proposed method, this change is only 3.4. The use of this cord in rubber products will significantly extend the life of these products.

Key words: tires, impregnating compounds, kapron cord, rubber cord parts, functional groups, rubber, adhesion, elastomeric matrix.

INTRODUCTION

Currently, the social and economic achievements of any country are largely determined by the development of polymer production. However, their production is associated with a large number of energy, material and labor costs. At the same time, the need to improve the quality of products requires the creation of new composite materials and the improvement of existing ones. Properties of polymer composite materials (PCM) can be significantly improved, and products based on them are more economical when various modifiers are introduced into them. Natural fibers, paper materials, woodworking and pulp production are currently the objects of increased attention of PCM developers. To a large extent this applies to cork chips, which is a waste of construction, prosthetic production. Existing material based on polyurethane (PU) and crushed bark of cork oak PROBKUR-N does not have sufficient chemical resistance and economy, which limits the scope of its use. To expand the scope of its application and reduce the cost allows the use of a mixture of urethane and nitrile butadiene rubbers (PROBKUR-N).

Fiber-reinforced PCMs are widely used in the tire industry. Polyamide (PA) and polyester (PE) cords are used to create a tire carcass. Their main disadvantage is poor adhesion to rubber. The increase in adhesive strength is achieved due to their chemical or physical processing. Despite a large number of works in this area, optimum processing conditions have not yet been found that increase the adhesion of the cord to rubber. In this regard, it is promising to use in the impregnating composition of the new water-soluble polymer MEPAN with high surface activity obtained from nitron fiber waste.

Various types of modifiers are known to improve the adhesion properties of rubbers. Modifiers, diffusing from rubber to the boundary areas of adhesives, can affect their properties. Therefore, the use of new modifiers in lining rubbers may require new approaches to the formulation of adhesives. This necessitates the further development of ideas about the properties of boundary regions.

Today rubber-textile products are a wide class of the most necessary products in our life and technology. They include a large number of different species, including the following:

- automobile, aviation and other types of tires;
- transmission elements of devices for moving various materials (conveyor belts, sleeves, hoses);
- flexible traction links of gears (drive belts, caterpillar tracks, etc.);
- air and water craft (aerostats, inflatable boats, rafts, pontoons, etc.);
- safety devices in auto and air transport (inflatable ramps, airbags, etc.);
- pneumatic building structures (collapsible industrial, agricultural, public and residential buildings and structures, etc.), as well as inflatable furniture;
- personal protective equipment (suits, aprons) and many others.

A feature of rubber-textile products is that they are almost always created as structures and in most cases they are obtained by combining textile reinforcing filler and rubber blanks with subsequent vulcanization [1].

Rubber-textile products mainly work under conditions of the predominant effect of tensile loads; they are also easily deformed when subjected to bending or compressive loads. In rubber-textile materials, the main structural element is yarns or yarn systems. The threads may consist of fibers (yarn) or be continuous chemical threads. Their fibers or filaments (filaments) are combined into a single structural element by obligatory twisting and impregnated with a bonding rubber component. The most important condition for reinforcing rubber-textile materials and products is the low value of the deformation modulus of the matrix (rubber) in comparison with the threads $E_M << E_N$.

Rubber-textile products are specially created products - structures with a given location of the fibrous filler in the direction of tensile loads and the rubber layers between them. Layers of rubber due to the small modulus of deformation and high deformability almost do not interfere with bending and compressive loads.

For the manufacture (reinforcement) of rubber-textile products (conveyor belts, drive belts, hoses and others), as well as automobile and aviation tires, textile materials are used - technical threads, belting, cord fabrics. The main types of technical yarns used as starting threads for reinforcing textile structures are viscose (currently their use is small), aliphatic polyamide (polyamide 6-kapron and polyamide 66-anide), polyester. For heavily loaded tires, parapolyamide yarns are used. For special types of tires, carbon, glass and metal threads are sometimes used. For some types of tires and other rubber products, hydrate cellulose (viscose) technical threads are still traditionally used. In very rare cases, cotton yarns are still used.

Mechanical properties of rubber-textile products are determined during half-cycle, single-cycle and multi-cycle tests (a cycle includes the stages of loading, unloading and "rest" of the sample). In half-cycle tests, including only the loading stage, the absolute and relative strength, tensile strength and tensile strength of the reinforcing threads, their elongation and tensile strain modulus, which are conventionally assessed as a load at a given small elongation or elongation at a given small load, are determined.

Endurance of cord yarns during repeated deformations under various conditions is determined using multi-cycle tests. This indicator is estimated by the number of loading cycles before the destruction of the sample or by the relative drop in strength after a given number of cyclones.

In multi-cycle tests, the yarns are repeatedly subjected to various types of deformation: tensile, bending, impact on the copra, compression and bending in rubber-textile samples. In addition, tests are carried out on the resistance to delamination of the rubber-textile system under shear and compression deformations, at which tangential stresses arise at the rubber-thread interface. In this way, the adhesion of the reinforcing threads to the rubber in the multiple loading modes is evaluated.

Moisture resistance or relative loss of strength in the wet state is determined for reinforcing yarns.

The most important conditions for the normal operation of rubber products, especially those subjected to prolonged repeated deformations are the preservation of the long-term adhesive bond of the reinforcing threads to rubber [2].

MATERIALS AND METHODS

Cords in car tires are currently made from various types of artificial and synthetic fibers, which ensure high tire mileage. The greatest effect is the use of synthetic fiber. A cord is the main bearing element, and due to rubber, high adhesion strength of tire parts. When creating packers that accept pressure drops of up to 30 MPa, the elastic chambers are armored along the outer diameter in rows of thin-walled steel tape or wire mesh. The cord is laid in the tire carcass by layers interconnected by rubber layers, which contributes to the strong connection of the individual layers of cord fabric, prevents the threads from rubbing against each other and protects them from moisture. The layers of the cord in the tire are one above the other, the individual threads in these layers are separated by rubber and do not touch each other both in the vertical and horizontal directions. A cord in the tire carcass is always in a tense state, as it perceives the pressure of compressed air. With jolts and bumps that occur during the movement of the car, the cord takes up additional load and experiences additional deformations. If a tire moves on a flat road or with small obstacles and bumps encountered, then deformations and stresses that the cord experiences in the tire are less than the critical deformations and stresses when the cord breaks. When the tire meets an obstacle of great height or with obstacles having sharp protruding corners, stresses and deformations in the cord can reach critical values and then the cord breaks. Tearing of the cord and destruction of rubber in the carcass can also occur under normal conditions due to the fatigue of the material occurring under repeated deformations at small values of deformations and loads compared to critical ones. Therefore quality of the textile cord and adhesion of the cord to rubber, i.e. adhesion of rubber to textile cord are of great importance. A safety and service life of tires depends on these indicators [1].

RESULTS AND DISCUSSION

Studies of interfacial interaction in the contact zone of cord-adhesive and non-impregnated cord-rubber have established the following.

As a result of the interaction of resorcinol-formaldehyde resin with OH groups of viscose, NH-CO, and terminal NH2 and COOH-groups of the cord, covalent and hydrogen bonds arise, which was shown on model systems using IR spectroscopy and labeled atoms. In the interaction of adhesive polymers containing O, N, COOH groups, 2-vinylpyridine units, with functional groups of viscose and kapron cord, hydrogen and other physical bonds arise, respectively. In the contact area of adhesive-rubber as a result of the interaction of the active groups of the adhesive polymer and resorcinol-formaldehyde resin with the rubber rubber base, covalent, onium, hydrogen bonds in various concentrations can occur. Thus, in the contact zone of the rubber-cord system, interfacial bonds of various nature arise:

- covalent bonds with binding energies of more than 100 kJ/mol, the so-called strong bonds;
- labile hydrogen and onium bonds, the energy of which is on average from 20 to 45 kJ/mol.

These bonds are inferior in strength to covalent bonds, but differ from them in the low activation energy of formation (from 2.0 to several tens of kJ/mol) and therefore are capable of recombination. In addition, between the adhesive and the substrate in the rubber-cord system, the weakest molecular physical bonds with energy of 2.0–8.0 kJ/mol can arise, due to the action of the Vander-Waals forces. The highest strength of adhesive joints was achieved in the presence in the contact region of strong interfacial bonds of high concentration in combination with labile ones [2, 3].

Formation of an adhesive compound begins with the bringing into contact of its elements, with the wetting and spreading of the adhesive on the surface of the substrate, which contributes to the formation of molecular contact. In the contact zone between the adhesive and substrate molecules, dispersion forces act with the formation of other molecular bonds. Due to molecular contact under the action of heat, in the presence of functional groups in the elastomeric adhesive matrix capable of reactions with the functional groups of the substrate, chemical bonds are formed. The resulting adhesive joint is characterized by a certain strength (static and dynamic or fatigue), depending on the mechanical and fatigue properties of the boundary (transition) layers. To ensure high adhesion strength, it is necessary that the mechanical and fatigue properties of the transition layers approach the corresponding characteristics of monolithic rubber. The elastic-liquid properties of the transition layers must be intermediate between the corresponding characteristics of the adhesive and the substrate in order to minimize their deformation. Under these conditions, the destruction of the composite will pass through an array of adhesive or substrate (cohesive nature of the destruction). If the substrate has a much dissected surface, such as cord thread, twisted from many thin threads (rods) or wires, then rheological properties are very important to achieve high strength of the composite. To achieve molecular contact, it is necessary that the rubber mixture in a short period of time when passing the cord fabric, the calender gap passes inside the cord and displace air and moisture from there [4].

Kapron cord is a class of textile materials that are obtained from artificial fibers. Kapron is obtained from oil - the product of the polycondensation of caprolactam. A chemical formula of kapron from which kapron fibers are obtained is [—HN (CH2) 5CO—] n. The physical -mechanical properties of kapron cord are much higher than cotton. Kapron fiber is a white-transparent, very durable substance. Elasticity of kapron is much higher than silk. The strength of kapron depends on the technology and thoroughness of production. A nylon thread with a diameter of 0.1 mm can withstand 0.55 kilograms. Along with high strength, kapron fibers are characterized by resistance to abrasion, the action of repeated deformation (bending). Nylon fibers do not absorb moisture, so they do not lose strength when wet. But kapron fiber also has disadvantages. It is unstable to the action of acids - kapron macromolecules undergo hydrolysis at the site of amide bonds. The kapron is also relatively small in heat resistance. Its strength decreases at 215°C, melting occurs. But compared to cotton, kapron cord has a greater uniformity of thread, less decrease in strength with increasing temperature, less hysteresis loss, better resistance to repeated deformations, less heat generation during tire operation. The mileage of tires made from kapron cord is much (60–70%) higher than that of tires made from cotton cord. Due to these advantages, kapron cord is used in the manufacture of tires, especially when using synthetic rubber. Depending on the purpose, the kapron cord is produced in various thicknesses, strengths, elongation and number of twists. Increasing the number of twists to known limits increases the fatigue strength of the cord. Disadvantages of kapron cord include poor adhesion to rubber, a tendency to residual elongation, and a significant loss of strength with increasing temperature [5]. A process of impregnation and thermo mechanical processing is used to eliminate these shortcomings. In the manufacture of tires, various impregnating compounds are used (table 1), which in the process of thermomechanical processing envelops the fibers from kapron, forming active functional groups on their surface, which then, when rubberizing the cord, create chemical bonds between the rubber matrix, thereby increasing the adhesion of rubber to textile cord [6].

Table 1 - Impregnating compositions

Name of materials	**For 100 mass. parts of rubber, mass. parts**	**Mass concentration of solids, %**	**Weight of sample, kg**	
			Per 1000 kg of the composition ± 2%	**Solids ± 2%**
Rubber in the form of latex DMVP-IOX (100%)	50.0	40.2	-	-
Rubber in the form of latex SKD-I or SKD-IC (100%)	50.0	40.2	-	-
Resin SF-282 (100%)	16.5	13.3	-	-
Formaldehyde (100%)	6.6	5.3	-	-
Sodium hydroxide (100%)	1.2	1.0	-	-
Ammonia water (25%)	3.82	-	-	-
Softened water	828.03	-	-	-
Latex DMVP-IOX (26%)	-	-	201.2	52.3
Latex SKD-I or SKD-IC (28%)	-	-	186.8	52.3
Polycondensed solution of resin SF-282 (5%)	-	-	508.0	25.4
Ammonia water (25%)	-	-	4.0	-
Softened water	-	-	100.0	-
TOTAL:	956.15	100.00	1000.0	130.00

SF-282 resin used in the impregnating composition is toxic and difficult to access, therefore, we propose to replace the resin with a new water-soluble polymer obtained from their waste nitron fibers and having high surface-active properties [7, 8]. This polymer MEPAN synthesized at the Department of PR and PCh SKSU named after M. Auyezov and in its surface-active properties significantly exceeds the resin SF-282. Tests on the use of a water-soluble polymer in an impregnating composition have shown that the fatigue strength of kapron fiber increases by more than 3 times. An ordinary kapron cord that is unstabilized, subjected to repeated deformations at 130°C has 5 thousand cycles to failure, a regular stabilized cord has 36 thousand cycles to failure, and in a stabilized cord, the resistance to repeated deformations increases to 540 thousand cycles.

In addition to increasing fatigue properties, the positive side of the heat treatment process with an impregnating composition with MEPAN is the fixation of the elongation of this fiber with a simultaneous increase in strength, processed by the proposed method, this change is only 3.4. The use of such a cord in rubber products will significantly extend the life of these products.

In addition, the processed cord with higher mechanical properties, processed by the method proposed above, can be used in the tire industry due to its high fatigue properties and stabilization of elongation.

In studies, impregnating compositions with different concentrations of MEPAN were used. MEPAN contains a large number of methylol groups capable of interacting with capron hydroxyl groups. In addition, it can form hydrogen bonds with the amide groups of capron fibers. A pronounced extreme dependence is observed between the MEPAN concentration and adhesive strength (Fig. 1).

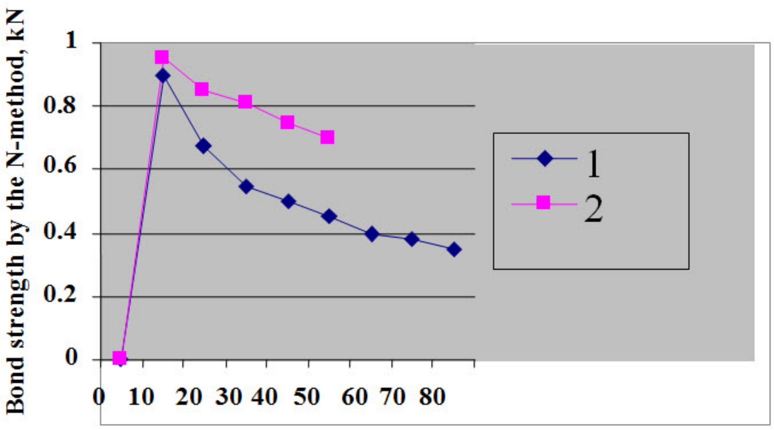

Fig. 1. Dependence of strength of rubber based on SRI-3 with viscose (1) and kapron (2) cords on the concentration of MEPAN

In our opinion, the main reason for a significant increase in bond strength in rubber-cord systems with artificial and synthetic fiber cords when MEPAN is introduced into the impregnating composition is the formation of a large number of different physical bonds between the elastomeric matrix of rubber compounds and the impregnated cord.

CONCLUSION

The use of MEPAN in impregnating compounds has a positive effect on the bond strength of rubbers with nylon textile cord. The bonding strength of rubbers with a kapron cord treated with an impregnating composition containing MEPAN at 110 °C is 27% higher than with a kapron cord treated with a conventional impregnating composition. It was noted above that the highest strength properties of rubber-cord systems are achieved with the formation of a spectrum of vulcanization and interfacial bonds of various energies. Apparently, the often observed effect of synergism can be explained in a similar way when using surfactants in impregnating compositions with various types of functional groups, as well as when combining products that improve the wetting of a substrate with a rubber compound and the fluidity of a mixture with compounds that form a large number of different types of physical bonds.

REFERENCES

1 Shmurak, I. L. Shinnyy kord i tekhnologiya yego obrabotki [Tire cord and technology for its processing]. Moscow, Nauch.-tekhn. tsentr «NIISHP», 2007. 220 p.
2 Syritsin L.M., Shmurak I.L. Proizvodstvo shinnogo korda i texnologiya ego obrabotki [Tire cord production and processing technology]. Voronezh: Voronezhskiy gosudarstvennyj universitet, 2006. 400 p.
3 Shmurak I.L. Shinnyj kord i texnologiya ego obrabotki [Tire cord and processing technology]. Moscow, Legprombytizdat, 2004. 334 p.
4 Sakibayeva S.A., Yeskarayeva G.Z., Tasanbayeva N.Ye., Belousov V.A., Sagitova G.F., Pak N.V., Beysenbayev O.K. Rezinovaya smes'. Pred. patent po zayavke № 2000/1309.1 [Rubber compound. Provisional patent. According to the application no. 2000/1309.1].
5 Sakibayeva S.A., Yeskarayeva G.Z., Tasanbayeva N.Ye., Belousov V.A., Sagitova G.F., Pak N.V., Beysenbayev O.K. Rezinovaya smes' // Patent. Po zayavke № 2000/1309.1
6 Satayev I.K., Sakibayeva S.A., Sagitova G.F. O primenenii PAV serii «Uniflok», «EPAN» v rezinovoy promyshlennosti [On the use of surfactants of the Uniflock, EPAN series in the rubber industry]. Nauka i obrazovaniye Yuzhnogo Kazakhstana - Science and Education of South Kazakhstan, 2002, no. 28, pp. 34-36.
7 Myrkhalykov Zh.U., Turebekova G.Z., Sagitova G.F., Sakibayeva S.A. Vozmozhnosti povy`sheniya adgezii reziny` k tekstil'nomu kordu iz iskusstvenny`x volokon [Possibilities of increasing the adhesion of rubber to a textile cord of artificial fibers]. Tekhnologiya tekstil'noy promyshlennosti. Izvestiya vysshykh uchebnykh zavedenij – Texnologiya tekstil`noj promyshlennosti. Izvestiya Vysshikh Uchebnykh Zavedenij, 2015, no. 1 (355), pp. 49-53
8 Turebekova G.Z., Sagitova G.F., Sakibayeva S.A. Puti povysheniya prochnosti svyazi sistemy rezina - viskoznyy tekstil'nyy kord [Ways to increase the bond strength of the rubber - viscose textile cord system]. Texnologiya tekstil`noj promyshlennosti. Izvestiya Vysshikh Uchebnykh Zavedenij, 2016, no. 3 (363), pp. 67-70.