Industrial waste treatment and application in rubber production

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Abstract. The paper provides for the relevance of various industrial waste treatment and application, as well as their secondary commercialization. It considers treatment of secondary polymer materials turning to additives applied in rubber production, in particular, in production of conveyor and V-type belts used in mechanical engineering. It is found that oligomers obtained from petroleum by-products can be used as an impregnating compound for fiber materials. Such adhesive treatment prior to introduction of impregnating compounds into elastomeric materials improves adhesion and complements performance of obtained composites.

1. Introduction
At present, mechanical engineering is one of the leading industries around the world. In this regard, mechanical engineering also acts as a consumer of enormous amount of various materials, including polymers. In fact, polymers are versatile synthetic materials with different properties. Some of them are as strong as steel, others are more flexible. After these materials appeared, it became almost impossible to replace them. Modern polymers strongly rely on materials modified by various additives, and their application is more advantageous since they improve operating parameters and cost of products. One of the main objectives of introducing different additives into polymers is the improvement of mechanical or other functional properties.

At the same time, a large number of by-products and wastes is formed and collected at food enterprises, chemical and petrochemical industrial plants [1]. Their secondary commercialization could reduce huge losses of material and raw resources, as well as fuel and energy resources and, most importantly, high environmental pollution, alienation of critical territories for landfills, dumps and other waste disposal sites. For example, it is suggested to use an advanced method for application of oil and fat by-products as components of vulcanization activators used in rubber compound production for conveyer covers [2].

Literature sources refer to the use of oligomers obtained from petrochemical by-products and wastes as additives in synthetic rubber production [3]. There are also data on textile waste processing into fiber additives with their subsequent use in rubber production, such as V-type belts, conveyor belts, etc. [4]. Prior to their introduction into rubber compounds, it is advisable to treat fibrous materials with various compositions. Such treatment improves adhesion between elastomers and fibers, makes the introduction of fiber into rubber mixes less complicated, enhances their distribution in elastomer medium, and contributes to further increase in operational properties of rubber products.
Methods to increase adhesion between fibers and elastomers mainly include treatment of textile materials with impregnating compounds. Solutions, dispersions and melts of thermoplastic and thermosetting materials, latex and elastomer solutions, as well as some monomers and oligomers are used for impregnation. This formed the basis for the application of such petrochemical by-products as impregnating compounds. Such approach will improve the efficiency of emulsion rubber production and at the same time it is reasonable to utilize recycled polymer materials and reduce environmental pollution.

This paper studies possible applications of various industrial wastes and by-products to make rubber for the production of engineering and technical items.

2. Materials and methods

Commercial styrene/butadiene rubber SKS-30 ARK is chosen as the subject of study. The study focuses on fiber wastes of textile industry (viscose rayon and capron fiber), petrochemical by-products (low-molecular styrenated copolymer (LMSC) synthesized from polybutadiene by-products and LMSC exposed to high-temperature treatment over pinane hydrogen peroxide (LMSC PHP)).

LMSC synthesized from polybutadiene by-products and containing styrene units, 4-vinylcyclohexene, cyclododecatriene-1,5,9, n-dodecatriene-2,4,6,10 (bound styrene content 75-80%) was used to make high-performance impregnating compounds. However, IR spectroscopy of its composition showed that it contains active oxygen functional groups. In order to increase LMSC reaction capacity, functional groups were additionally introduced into its composition via high-temperature treatment into pinane hydrogen peroxide (PHP).

High-temperature exposure of LMSC PHP leads to the decrease in molecular weight within the first 15-18 hours, which indicates oxidizing destruction resulting in the formation of oxygen functional groups and acid index increase from 0.4-0.6 to 2.3-3.0 mg/100 g with further increase in its dosage. The obtained experimental data demonstrates that the temperature of 100 °C, duration of 15 - 18 h, and 3% PHP dosage serve the best conditions for LMSC modification with PHP. According to gel-permeation chromatography, molecular-mass characteristics of unmodified and modified LMSC equal:

- LMSC $\bar{M}_n = 1200; \bar{M}_w = 6830; \bar{M}_v = 4420;
- LMSC PHP $\bar{M}_n = 720; \bar{M}_w = 890; \bar{M}_v = 850;$

LMSC modification with pinane hydrogen peroxide allows receiving oligomers with lower viscosity and hyperactivity that makes them compatible with elastomers.

Since LMSC and LMSC PHP represent viscous liquids, in order to make the impregnation of fibrous materials easier and further introduce them into elastomer compositions, it is advisable to obtain water dispersions on their basis. Preliminary study showed that unmodified LMSC without solvent dispersed in aqueous phase failed to result in stable dispersion. This is caused by the fact that this product had higher viscosity, and to ensure its proper dispersion there is a need to use more specific equipment. To obtain stable dispersion, 20% toluene solvent was introduced into unmodified LMSC. Dispersion of LMSC PHP in aqueous phase does not require additional hydrocarbon solvent.

Later this followed the development of the efficient method used to collect impregnation of LMSC and LMSC PHP fiber materials, which included generation of aqueous fiber copolymer dispersion (FCD) on their basis. LMSC or LMSC PHP were loaded into the dispersion tank together with antioxidant, and then mixed at 50-60°C until a smooth solution was obtained. Then, fiber material (viscose or capron fiber) was introduced and mixed within 20-30 minutes. The obtained dispersion was filled with 50g of aqueous phase containing rosin oil and leikanol (6.0% and 0.5% for copolymers respectively). The dispersion lasted 3-4 hours. Fiber additive was introduced with the length of 2-5 mm and the dosage of 0.5% for synthetic rubber.

FCD obtained on the basis of LMSC and LMSC PHP was mixed with emulsion rubber latex. To that effect, FCD was mixed with emulsion rubber latex, and the obtained mixture was coagulated with the aqueous solution of magnesium chloride and the aciditating agent of aqueous solution of sulfuric
acid. Coagulation was carried out at a temperature of 60-65°C. The formed rubber crumb was separated from aqueous phase, washed with warm water and dehydrated in a drying furnace at a temperature of 75-80°C until constant weight loss. Copolymer content in rubber matrix was exposed to: 10, 30 and 50 kg/t of rubber; fiber additive - 5 kg/t of rubber; antioxidants - according to standard requirements.

3. Results and discussion
Such impregnation technology of fiber materials and introduction to elastomer compositions fosters their uniform distribution throughout a rubber matrix and increase the adhesion between fibers and polymers, which, in turn, positively affects properties of rubbers and vulcanized stock. Use of copolymers as an impregnating composition improves tear resistance, repeated elongation and thermal-oxidative aging (Tab. 1).

Table 1. FCD impact on properties of synthetic rubbers and vulcanized stock

| Indicator                                      | Additive (fiber content: 5 kg/t of synthetic rubber, FCD content: 30 kg/t of synthetic rubber) |
|------------------------------------------------|---------------------------------------------------------------------------------------------|
|                                                | without additives | viscose rayon | FCD (viscose rayon) | capron fiber | FCD (capron fiber) |
| Mooney viscosity MB 1+4 (100 °C) of synthetic rubber | 55 | 53 | 55 | 55 | 54 |
| Apparent stress at 300% elongation, MPa        | 13.6 | 13.6 | 15.2 | 13.6 | 14.5 |
| Nominal strength under tension, MPa            | 24.1 | 23.8 | 24.4 | 23.6 | 25.8 |
| Breaking elongation, %                         | 520 | 530 | 580 | 530 | 560 |
| Tear resistance, kN/m                          | 53 | 67 | 88 | 72 | 90 |
| Repeated elongation resistance (100%), th. cycles | 70 | 75 | 97 | 78 | 96 |
| Heat aging ratio:                               |                                       |                             |                |                |
| - against strength                             | 0.44 | 0.56 | 0.78 | 0.62 | 0.77 |
| - against tensile strain                       | 0.25 | 0.40 | 0.45 | 0.45 | 0.46 |

Enhanced resistance to thermal-oxidative influence is caused by the reduction of antioxidant losses due to its introduction into elastomer composition together with fiber-polymer additive. The study of vulcanized stock swelling kinetics (Tab. 2) containing fiber-polymer additive showed the reduction in the swelling rate and increase in the crosslinking density, which was not observed with fiber additives without impregnating compound.

Table 2. Impact of fiber copolymer additive content and types of solvents on vulcanized stock swelling kinetics

| Solvent        | Fiber copolymer additive content (kg/t of synthetic rubber): | Viscoose rayon |
|----------------|------------------------------------------------------------|----------------|
|                | Without additives | 10 | 30 | 50                          |                |
| Toluene        | -0.22 | 2.2 | -0.24 | 2.4 | -0.27 | 2.6 | -0.30 | 2.7 |
| Nefras (oil solvent) | -0.20 | 1.8 | -0.25 | 2.0 | -0.27 | 2.2 | -0.30 | 2.4 |
| 1/Q_{max}^{t+10} . 10^{-1} | 2.0 | 3.0 | 3.4 | 3.6 |

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### 4. Conclusions

Thus, the conducted study makes it possible to conclude the following:

- at present, the prevention and reduction of wastes and their secondary commercialization are rather urgent;
- comprehensive petrochemical and textile waste treatment allows obtaining additives for rubbers, which may further be used for the production of engineering and technical goods with enhanced performance properties.

### References

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[2] Karmanova O V, Popova L V, Poymenova O V, Gusev Yu K 2014 *Bulletin of VSUET* 3 126-129

[3] Zhou Y, Fan M, Chen J L 2015 *Composites. Part B.* 76 180-191

[4] Nikulin S S, Pugacheva I N 2008 *Production and application of elastomers.* 1 26-28

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| $1/Q_{\text{max}}^{\text{Nefras}} \cdot 10^{3}$ | 5.8 | 6.6 | 7.0 | 7.2 |
|---|---|---|---|---|
| **Capron fiber** | | | | |
| Toluene | -0.22 | 2.2 | -0.26 | 2.6 | -0.28 | 3.0 | -0.31 | 3.1 |
| Nefras (oil solvent) | -0.20 | 1.8 | -0.28 | 2.2 | -0.33 | 2.3 | -0.35 | 2.5 |
| $1/Q_{\text{max}}^{\text{tl}} \cdot 10^{3}$ | 2.0 | 3.3 | 3.8 | 4.0 |
| $1/Q_{\text{max}}^{\text{m}} \cdot 10^{3}$ | 5.8 | 6.6 | 6.8 | 7.4 |

Note: vulcanized stock swelling kinetics was described by equation $Y = -b\tau + a$, where $\tau$ and $b$ represent swelling duration (h) and speed (h$^{-1}$), $Q_{\text{max}}$ – equilibrium swelling index, %; $1/Q_{\text{max}} \cdot 10^{3}$ – crosslinking density. $Y = \lg (Q_{\text{max}} - Q_{\text{tl}})$, $a = \lg Q_{\text{m}}$. 