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ROAD CONSTRUCTION EQUIPMENT RECOVERING WITH THE COMPOSITE MATERIALS BASED ON REGENERATED POLYOLEFINS

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Abstract

In the nomenclature of functional composite materials based on regenerated polyolefins, a special place belongs to tribotechnical and protective composites used in various branches of mechanical engineering, in the production of non-ferrous metal products by injection molding, in tribosystems operated in road construction technological equipment and mining. Taking into account the variety of structural design of metal-polymer systems and their exploitation conditions, it is necessary to develop a range of means for increasing the maintenance life. Optimal compositions are selected and parameters of their process characteristics are estimated in this work.

Keywords: Metal-polymer rollers, extrusion technologies, rheological characteristics, strain-strength characteristics, deformation-strength characteristics, twin-screw extruders, polymer-polymer systems.

1. Introduction

Composite materials based on mixtures of polymers and oligomers of different composition, structure, parameters of strain-strength, thermophysical, rheological and other characteristics occupy a special place in the brand assortment of materials used for manufacture of articles of metal-polymer static (adhesive, structural, sealing) and dynamic (tribotechnical) systems.

The several operating conditions of thermoplastic material products in the construction and friction units of machines, mechanisms and process equipment make it necessary to specifically modify commercially available polymer binders, which reduce the characteristic disadvantages of thermoplastics due to their composition and structure, and enhance their advantages, determining technical, economic and technological advantages. Characteristic disadvantages of structural multi-tonnage thermoplastic polymers are a sufficiently high coefficient of friction, equal to about 0.6-0.8 at friction without supply of lubricant, relatively low thermal and heat resistance, dependence of parameters of deformation-strength characteristics on temperature and operating conditions of articles.

These features of polymer binders do not allow them to be used in the original unmodified form to obtain structural and tribotechnical self-lubricating composite materials, the products of which are operated at ambient temperatures above 100 °C, are exposed to impact loads, abrasive media and other adverse factors. Not less essential, but often decisive, is the insufficiently high resistance of articles from industrial thermoplastic materials to external factors of the operating environment (action of ultraviolet radiation, ozone, air oxygen, thermo-oxidizing and lubricating media). Macromolecules of structural thermoplastic materials of any composition contain active centers due to features of molecular chain structure or features of synthesis.

These centers are able to interact with various reagents of the operating medium, for example, with air oxygen, lubricant components, etc. As a result, the performance parameters of thermoplastic articles are significantly reduced due to aging and degradation processes. This fact is of particular importance with mechanical and tribotechnical effects on polymer products, in which the number of active centers in macromolecules of surface layers of products increases sharply and mechanochemical, tribochemical and other reactions are initiated, leading to changes in composition, structure, parameters of deformation-strength and other characteristics.

In this regard, one of the priority areas of modern tribotechnical materials science is the development of methods for modifying structural thermoplastic materials, which are multi-tonnage produced at domestic enterprises, with targeted additives that would eliminate or contribute to reducing the initial prerequisites for the destruction of their macromolecules under the influence of operational factors, primarily tribochemical wear.

One of the most readily available and simple methods of making polymer-polymer mixture composites is to mix melts in various process equipment. This direction contributes to a significant expansion of the brand range of structural materials by combining different characteristics of polymers in composition, structure and parameters. Thermodynamic compatibility is important for such mixtures, determined by chain structure, polarity, solubility, chain flexibility, rheological and other characteristics. There are great prospects for a method of producing polymer mixtures in the process of mechanical (mechanochemical) influence on components in the form of a melt or in a solid aggregate state - rolling, crushing, screw extrusion, mixing in high-energy mixers. With this combination, as a result of recombination of macroradicals that are formed during mechanocracking, it is possible to synthesize new grafted and block copolymers, which are quite difficult to obtain by conventional methods.

2. Methods

Literature, patent and commercial sources analysis showed that the most effective modifiers of polymer matrices, from the point of view of increasing their parameters of strain-strength and tribotechnical characteristics, are components that prevent the development of processes of thermal oxidative destruction and tribocracking. In this aspect, modifiers are of particular interests which actively influence the performance parameters of polymer composites by operating factors over a long period of time. One promising type of modifier is highly dispersed particles of oxides, silicates of metals obtained by thermolysis of organic and inorganic compounds.

It seems to us that the proposed methods of modification are effective not only in the creation of tribotechnical ("antifriction" according to [2]) materials, but also in other types of composites for the manufacture of products with given performance parameters.

To prevent the negative effect of delamination of the mixture, components that increase compatibility in the boundary layers of the two phases are often used.

The characteristics of the polymer polymer system composite material and its ability to form using conventional techniques depend on the quality of the mixing process. Therefore, understanding the mixing processes helps to optimize the processing conditions and improve the parameters determining the quality of composites and, accordingly, products from them, to consider that the mixing can be distributive or dispersive. For example, the morphology (structure) of a mixture is associated with three simultaneously competing processes: distributive mixing, dispersion mixing and coalescence. Depending on the type of prevailing process, it is possible to form three types of mixtures:

- Homogeneous mixture of compatible polymers;
- Single phase mixture of partially incompatible polymers;
- Multiphase mixture of incompatible polymers.

Table 1 shows examples of each type of mixture.

Distributive or laminar mixing characterizes the quality of the alloying phase distribution in the matrix. Homogeneous distribution by applying large shear deformations that increase the contact surface of the phases and reduce the thickness of the layers. At the same time, the use of large shear deformations is not always a sufficient condition for obtaining a homogeneous mixture.

A significant role as the final mixture is played by the type of agitator, the initial orientation and the mutual position of the two or more liquid components.

Table 1. Main types of polymer mixtures

Blend Type	**Mixture components**
Compatible polymer blends	Natural rubber and polybutadiene Polyamides (PA 6 and PA 66) Polypropylene ether and polystyrene
Partially incompatible blends	Polyethylene and polyisobutylene Polyethylene and polypropylene (5% PE in PP) Polycarbonate and polyethylene terephthalate
Incompatible blends	Polystyrene/Polyethylene Polyamide/Polyethylene Polypropylene/polystyrene

Polymer-polymer compositions are usually divided into two main classes - polymer mixtures and polymer alloys. The criterion for their difference from the point of view of colloidal chemistry is preferential heterogeneity for the former and homogeneity for the latter. From the point of view of thermodynamics, the first class includes mechanical systems of various types, in which each component forms its own phase, which under certain conditions (ratios of components) can manifest itself as a polymer filler, and the second class of materials consists of solutions that are formed with a decrease in the total free energy of the system.

Two-phase composites based on polymer mixtures can be divided into two types in structure: ordinary dispersions (or emulsions) and mixtures with two continuous phases (matrix structure) (Figure 1).

a) b)

Figure 1. Phase structure diagrams of two-phase polymer mixtures: a) a conventional dispersion; b) - structure with two continuous phases

Conventional dispersions are characterized by the formation of one of the components of the dispersion medium, and the second component is the dispersed phase (Figure 1, a). The matrix structure is characterized in that both phases of the mixture are continuous and "interwoven" (Figure 1, b). The continuity of both phases is characteristic only for high molecular weight emulsions and is due to their high viscosity.

A characteristic feature of composite materials based on mixtures of polymers (PA and ABS, cellulose acetobutyrate and copolymers of ABS, PA 6 and PA 12, etc.) is the formation in the contact zone of a layer of elements of both components. Similar structures of PA - SFD, DST - SFD, TPU - SFD mixtures are fixed in (Figure 2).

For mixtures of polymers similar in structure and nature (PA 6 - PA 66, PA 6 - PA 12, PE - SEVA), their mutual influence was revealed. For polyamide-based composites, this is manifested in the appearance of additional γ-modification in PA 6 under the influence of additives P 66 and P 12. Thus, the mixing of components close in chemical composition and structure is accompanied by structural changes at the level of structural organization. The effects observed when mixing polymers of different molecular chain structure and chemical nature are not due to intra-phase conversions at the level of elementary cells for crystalline and near-order for amorphous polymers, but at the interfacial level. Nature of changes is determined by size and perfection of structural elements, phase interaction at interface, and for crystallizing polymers - phase correlation within components.


a)

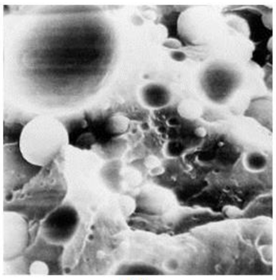
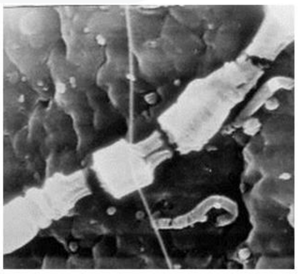

b)

Figure 2. Characteristic view of chips in nitrogen of samples from mixed compositions: a) - PA 6 + 5 wt% SPD; b) - PA 6 + 50 wt% SFD

The results of studies of the morphology features of various heterogeneous polymer mixed compositions (PE - PS, PE - POM, PS - POM, PE - PA 6,) indicate that at the initial moment of formation they have a rather clear interface between the components, the size of which lies in the range of 300-600 Å. During the heat treatment process, the interface between the components becomes fuzzy and a layer having morphological features characteristic of both polymers occurs in its place.
Presence of disperse phase of modifier in matrix polymer leads to change of parameters of deformation-strength, tribotechnical and other characteristics. As shown in , the alloying phase components are capable of being reformed as a reinforcing filler (Figure 3).


a)

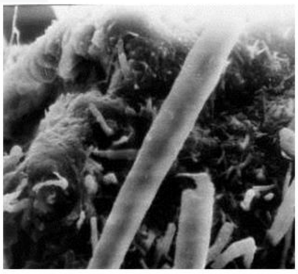

b)

Figure 3. Dependence of tensile strength of polyamide 6 modified with mixture of mechanically activated particles of polyamide 6 - kaolinite on concentration of modifier

It is considered that limit dispersion of heterogeneous mixed compositions is mainly determined by thermodynamic processes at intermolecular interaction of components, and kinetic factors such as method, duration, shear stresses and mixing gradients only contribute to its achievement. However, shows the possibility of

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copolymerization processes in the interaction of radicals formed by mechanical degradation of matrix macromolecules and filler.

Stability of parameters of strain-strength characteristics of polymer-polymer systems is mainly determined by thermodynamic compatibility of components, by which their ability to mutual solubility is usually understood. In order to create this kind of multicomponent system more efficiently, it is necessary to analyze not only thermodynamic miscibility, but also chemical or physical compatibility.

So, improved compatibility in polymer mixtures can be achieved by several methods:

- Selecting polymer pairs or modifying components to enhance intermolecular interaction (e.g. hydrogen bonding);
- Conducting chemical reactions between the components of the mixture in the process of combining to produce an interpolymer;
- Introduction into the system of compactibilizers - low-molecular or high-molecular compounds enhancing specific intermolecular interaction between chains of matrix and alloying components. The compactibilizers may be graph- and block copolymers.

A very effective technique for improving the compatibility of thermodynamically incompatible polymers is to modify polymer mixtures using various active components, or compactibilizers. In this case, compatibility increases due to ion-ion, dipole-dipole interactions or hydrogen bonds, which make it possible to significantly improve parameters of physical and mechanical characteristics of polymer mixtures.

For the manufacture of coatings and sliding bearings for heavy-loaded friction units, aliphatic polyamides are of particular interest, combining a set of parameters of unique characteristics. The materials used to make the friction assembly parts shall have a low friction coefficient and high wear resistance.

Most aliphatic polyamides are characterized by an optimal combination of parameters of these characteristics.

Aliphatic polyamides, including PA 6, PA 66, PA 11, due to the specificity of the structure of macromolecules and the combination of parameters of physical, mechanical and thermophysical characteristics, are widely used to create mixed polymer-polymer systems. In mixed compositions, it is possible to increase impact strength and elasticity, chemical and atmospheric resistance, wear resistance and other characteristics.

Polyamide mixture systems are characterized by an advantageous relationship between cost and technical characteristics, their composition can be easily modified depending on the specifics of the operation of the products.

Using of Polyamides

Nowadays polyamides are widely used for manufacture of wear-resistant parts of bearings, such as smooth journals, axial friction supports, collars of ball and roller bearings.

For production of elements of the pressurizing and sealing systems and also for tribosystems with extreme service conditions of fluorine composite - the materials on the basis of polytetrafluoroethylene (PTFE) modified by coke, graphite, the carbon fibers (CF), oxides of metals, nanoscale particles of carbon of detonation synthesis (UDA, UDG, nanotubes), natural disperse particles - shungits, clays, zeolites, etc. became widespread.

Composite materials based on polymer-polymer systems are obtained by chemical synthesis or mechanical mixing of components in melt, solution or solid phase.

A promising method of preparing mixed compositions with a high degree of dispersion of polymer components is the sequential polymerization of the corresponding monomers on a single catalyst system.

A universal method of creating polymer-polymer mixtures with a high level of dispersion of components obtained by drawing polymers in adsorption-active liquid media using a craising mechanism based on nanoscopic porosity of the composites has been developed.

Polymer mixtures based on primary and regenerated thermoplastics are most often obtained by mechanical mixing of melts on rollers, in closed mixers or extruders.

The distribution of components in this case is determined by the capacity of the equipment, the mixing mode, the ratio of the viscosities of the polymers and the chemical nature of the components themselves.

One of the main ways to improve the thermodynamic compatibility of polymers and improve the quality parameters of polymer mixed compositions is to improve the mixing processes of the mixture components. Various types of mixers, single screw and multi screw extruders are widely used for mixing components of polymer mixtures.

Currently used in the industry mixers for polymer materials can be classified as follows:

1) According to the physical state of the initial components - mixers for bulk materials (without changing the physical state), low-viscosity and high-viscosity liquids, viscoelastic liquids (with a change in the aggregate state of the mixture during mixing);

2) By the nature of the mixing process - mixers of periodic and continuous action;

3) By the mechanism of the mixing process - mixers of convective, diffusion and convective-diffusion mixing;
4) According to the mixing process mode - turbulent and laminar mixing mixers;
5) According to the method of acting on the mixture - gravitational, centrifugal, shear mixers;
6) In terms of design - drum mixers (without mixing and with mixing devices), with fast, slow-moving, planetary, oval, Z-shaped, worm rotors, disk rotors, etc.

When making composite materials based on mixed polymer-polymer systems, it is preferable to use twin-screw extruders than single-screw extruders due to more efficient mixing and heat removal processes.

The mixing effect in the extruder is provided by two screws arranged in parallel in the cylinder and rotating towards each other or in the same direction.

When the screws rotate towards, they work as rollers, while the material is also supplied along the screws.

The material is shifted and rubbed both between the auger turns and in the gap between the augers and the cylinder body. The amount of backflow of the material increases as the distance between the screws increases and enhances the mixing effect.

A special place in the brand assortment of polymer composites is occupied by materials with increased resistance to thermo-oxidizing media and combustion.

Material with high resistance to combustion is used for production of special-purpose products, household appliances and technological installations with extreme operating conditions.

In the development of belt conveyors for mineral extraction and processing technologies, non-combustible polymer materials are used to make conveyor belt rollers.

For the development of composite material compositions in accordance with their applications (belt conveyor rollers, identification and limiting elements used in the construction industry and road construction), components were selected that provide the necessary combination of deformation-strength, rheological, thermophysical characteristics in combination with technological and economic, which determine the economic efficiency of using products from developed materials in practice.

3. Results and Discussion

The regenerated polypropylene almost completely retains the basic characteristics of the feedstock. Main parameters of physical, mechanical and chemical characteristics of regenerated polypropylene:

- Tensile strength - 23-40 MPa;

- Melt flow index - 1.5-20 g/10 min;
- Density - 0.90-0.91 g/cm³;
- Melting point - 160-168 °C.

For comparative tests, primary polypropylene, regenerated imported polypropylene, crushed semi-finished product obtained by grinding dampened products used in industrial enterprises, a composite material based on polypropylene and high pressure polyethylene were used.

For modifying the matrix polymers, ultra-dispersed polytetrafluoroethylene (UDPTFE) was used thermoplastic (TP), phosphogypsum (PG) is a highly dispersed product formed during the production of phosphorus-containing fertilizers, containing components of various compositions.

Following compositions were developed for analyzing the characteristics of composites:

PP (P) + 0.5-1.0 wt% UP, PP (BP) + 0.5-1.0 wt% UP, PP (SP) + 0.5-10 wt% UP, PP (PN) + 0.5-5 wt% UP, compositions containing 1.0 to 10.0 wt% phosphogypsum (PG), compositions containing 1-30 wt% thermoelastoplastic (TEP) and compositions with complex combination of modifiers: PP + 1-20 wt% TEP + 1-10 wt% PG and PP + 10-20 wt% TEP + 5-10 wt% PG + 1-3 wt% PP.

The composites were prepared by mechanically mixing the components in drum-type mixers, followed by the production of standard test pieces on specialized injection molding equipment on a screw thermoplastic.

Analysis of test results of composite materials by parameters of deformation-strength characteristics (Table 2) indicates achievement of a combination sufficient for the use of composites for the manufacture of articles of various functional purposes, including elements of metal-polymer rollers of belt conveyors, identification and limiting columns for road construction.

Table 2. Parameters of deformation-strength characteristics of composite materials based on regenerated thermoplastics

Sample No.	Composition of composite sample	Property Parameters					
		Physical yield strength, MPa	Deformation at physical yield strength,%	Strength at maximum force, MPa	Deformation at maximum force,%	Breaking strength, MPa	Fracture deformation,%
1	2	3	4	5	6	7	8
1	SP+UP 5%	25,525	3,98	25,525	3,98	23,425	7,89
2	SP+UP 1%	25,400	3,64	25,400	3,64	23,375	9,56

3	SP+UP 0,5%	26,825	3,73	26,825	3,73	25,050	7,98
4	PN+TEP10%+FG5%	25,025	16,92	25,025	16,92	21,800	36,00
5	PN+TEP10%+FG 10%	17,100	1,87	25,850	9,95	25,850	9,95
6	PN+TEP20%+FG 10%	19,425	18,56	19,425	18,56	15,625	64,81
7	PN+TEP20%+FG 5%	20,950	15,93	20,950	15,93	17,100	203,09
8	PN+TEP20%+FG+UP	19,775	15,09	19,775	15,09	15,875	118,66
9	PN+TEP10%+FG+UP	23,200	12,66	23,200	12,66	19,700	36,62
10	PN+FG5%	22,675	14,11	22,675	14,11	20,550	25,02
11	PN+FG 10%	23,375	10,94	23,375	10,94	21,725	22,58
12	P+TEP10%+FG5%	23,025	15,92	23,025	15,92	14,025	190,36
13	P+TEP10%+FG10%	19,225	17,26	19,225	17,26	16,300	226,55
14	P+TEP20%+FG5%	17,050	21,45	17,050	21,45	15,525	201,43
15	P+TEP20%+FG10%	16,825	21,30	16,825	21,30	14,500	160,49

Conducted studies of parameters of strain-strength characteristics of composite materials of different composition on the basis of primary and regenerated polypropylene made it possible to make selection of optimal composite with parameters of characteristics sufficient for manufacture of structural elements of selected functional purpose. At the same time, it was necessary to evaluate the parameters of rheological characteristics for a reasonable choice of the technology for processing composites into products by injection molding or extrusion. The results of evaluation of rheological characteristics parameters according to the melt flow index (MFI) criterion under standard test conditions are presented in Table 3.

Table 3. Rheological characteristics of polypropylene-based composite materials

Sample No.	**Composition of composite material, wt%**	**MFI, g/10 min**	**T, °C**
1	**2**	**3**	**4**
1	PP (P)+UP 0,5%	2,88	200
2	PP (P)+UP 1%	2,80	200
3	PP (BP)+UP 0,5%	3,58	200
4	PP (BP)+UP 0,5%	3,80	200
5	PP (SP)+UP 0,5%	7,55	250
6	PP (SP)+UP 1%	17,10	250
7	PP (SP)+UP 5%	16,85	250
8	PP (PN)+UP 0,5%	4,85	200
9	PP (PN)+UP 1%	5,53	200
10	PP (PN)+UP 5%	5,00	200

The results of the studies show that, according to the melt flow rate (MFI) parameter in the processing temperature region of 200-250 °C, composites of various compositions have significant differences that determine the choice of their processing technology into an article. Thus, modification of matrix polypropylene of

various kinds with phosphogypsum in an amount of 1-10 wt% does not significantly affect the initial fluidity of the polymer and allows processing of composites by injection molding.
When a thermoplastic elastomer (TPE) with high melt viscosity is introduced into polypropylene, a significant decrease in this value for the composite compared to the original thermoplastic is observed. For such composites, it is advantageous to use extrusion technology in the manufacture of products of a given functional purpose or the use of increased melt injection pressures in injection molding.

4. Conclusion

Complex modification of polypropylene with thermoelastoplast (TEP) and phosphogypsum (PG) leads to a decrease in the PTP parameter, which is in the range of 2.78-6.15 g/10 min and depends on the selected matrix polymer (P, BP, PN, SP). Attention is drawn to the effect of the modifying additive of ultra-dispersed polytetrafluoroethylene (UPTFE), the introduction of which into the composition in an amount of 0.5-5.0 wt% contributes to an increase in the parameter of fluidity of polypropylene (P, BP, PN, SP) up to values from 2.8 to 17.1 g/10 min. The probable mechanism of action of UPTFE on parameters of rheological characteristics of polypropylene-based composites is plasticisation of melt with oligomeric component having temperature range of transition to flowing state 60-90 °C.
Compositions of composite materials have various parameters of rheological and structural characteristics, which affect quality parameters of articles obtained by injection molding and extrusion technologies, estimated by the structure of the surface layer.
Designs of functional equipment, such as belt conveyor rollers, identification and limiting elements, in which components made from composite materials based on regenerated polyolefins are developed.

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