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Polymer composite materials based on a mixture of recycled polyolefins and polystyrene plastics

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A series of investigations of the polymer composite materials (PCM) based on recycled polyolefins and polystyrene plastics in different polyolefins-to-polystyrene plastics ratios is presented. The specific features of the interaction of recycled polyolefins and polystyrene plastics were established relating to the change in chemical structure and polarity during aging. It is shown that the presence of oxidized functional groups contributes to an increased thermodynamic affinity of PCM components and improved operational and strength properties during the aging process. The effect of various modifiers on the PCM properties has been investigated. A wide range of PCM compositions was studied to identify the contribution of each component to the PCM properties and the specificity of their interaction. It has been established that the best results are achieved by combining modifiers of different functional purposes.

Keywords: polyolefins, polyethylene, polystyrene plastics, recycled polymers, polymer composite materials, modifying additives, and the polymer aging

Полімерні композитні матеріали на основі суміші перероблених поліолефінів та полістиролпластиків. *В.Л. Авраменко., Л.П. Підгорна, О.Г. Карандашов*

В роботі проведений комплекс досліджень полімерних композиційних матеріалів (ПКМ) на основі вторинних поліолефінів і полістирольних пластиків у різних співвідношеннях поліолефіни : полістирольні пластики. Встановлені особливості взаємодії вторинної поліолефін – полістирольної пластики, що пов’язані зі зміною хімічної структури і полярності в процесі старіння. Показано, що наявність окиснених функціональних груп в процесі старіння сприяє підвищенню термодинамічної спорідненості компонентів ПКМ, покращенню експлуатаційних і міцнісних властивостей. Досліджено вплив різних модифікаторів на властивості ПКМ. Проведені дослідження широкого спектру складів ПКМ з метою виявлення внеску кожного компонента на властивості ПКМ і специфіку їх взаємодії. Встановлено, що найкращі результати досягнуті шляхом поєднання модифікаторів з різним функціональним призначенням.

1. Introduction

Rational use of recycled polymers in the production and consumption of plastics is a pressing issue today [1]. The main types of recycled polymer materials include the technological waste of the production and processing of plastics, defective products, and worn-out products for various purposes that have lost their consumer properties [2, 3]. One of the rational ways to use recycled polymers is to process them to get useful materials and products. Currently, recycled polymers find only limited application and, when accumulated, create many serious environmental problems [4, 5]. An insufficient number of investigations carried out to study recycled polymers, technological processes for their processing and ways to improve their quality hamper an efficient use of these materials and their return to the production cycle.

Table 1 - Properties of the original recycled polymers

Indices	Mixture of recycled polyolefins	Mixture of recycled polystyrene plastics
Breaking tensile stress σ_t, MPa	9.8–13.0	14–20
Relative elongation at break, ε, %	10-14	2-20
Melt flow index (MFI) (g/10 minutes)	0.1-1.2	0.1–6

Many problems can be solved when creating polymer composite materials (PCMs) based on recycled polymers, in particular, creating their mixtures. Imparting specified properties to secondary material based on polymer mixtures is today one of the promising areas for returning secondary polymers to the production cycle. When preparing mixtures, any combination of polymers (two or more) can be used under conditions where the mixed components can be irreversibly deformed [6, 7].

The process of obtaining PCMs using the mixtures of recycled polymers is based on the thermodynamic theory of polymer mixing that makes it possible to determine the limits of mutual solubility of polymers and parameters characterizing the thermodynamic affinity of the components [8]. The lack of thermodynamic compatibility results in the fact that in most cases polymer mixtures are two-phase microheterogeneous systems and it can be fully applied to the mixtures based on polyolefin and polystyrene plastics. Moreover, it has been established that the best strength and performance indices can also be obtained for the mixtures of incompatible or limitedly compatible polymers.

The purpose of this research is to study the mixtures of recycled polymers, in particular polyolefin and polystyrene plastics and to create on their basis PCMs with a broad range of mechanical, technological and operational properties.

2. Experimental

Technological waste, in particular sprues and defective products as well as operational waste i.e. products with expired service life were used as original materials for the study. Polyolefins are a mixture of high- and low-density polyethylenes of various grades and modifications. Polystyrene plastics are a mixture of polystyrenes, in particular block-type polystyrenes (BTPS), as well as impact-resistant polystyrenes of various brands.

The original materials were crushed using an IPR-450M plastic shredder with a calibrating grid diameter of 6-8 mm. The properties of the original recycled polymers are given in Table 1.

To modify polyethylene (PE) and polystyrene (PS)-based compositions the following additives were used: calcium stearate (CaSt), polybutadiene rubber (PBR), dicumyl peroxide (DCP), thermoplastic elastomer DST-30, surfactants of the following groups: alkylamides, ethoxylated alcohol phosphates, alkylaryl sulfonic acids, chloroxyl (hexachloroparaxylene), phenosan 23 (ester of 3,5-di-tert-butyl-4-hydroxyphenylpropionic acid and pentaerythritol), ferrocene (iron dicyclopentadienide), quinol D (oligomer of 2,2,4 trimethyl-1,2-dihydroquinoline), and powdered coal.

The PE and PS-based mixtures were prepared for 4 to 5 minutes in the rotary agglomerator. When obtaining modified compositions, modifying additives were added to the agglomerate. To prepare compositions using the roller method, laboratory L-16M rollers with a friction of 1:1.2 and a drive shaft rotation speed of 30 rpm were used. The mixture was rolled at 150-170 °C until the components melted and then for 30 minutes in accordance with the specified mode. To press the compositions, a laboratory press equipped with electrical heating was used (force of 300 kN and the table plate size of 400×400 mm). The holding time at a temperature of 160–170 °C was 3 to 5 minutes per 1 cm of thickness; specific pressure was of 20 to 30 MPa. For PCM granulation, an extruder with a screw diameter of 38 mm, an L/D ratio of 17, and a screw rotation speed of 120 rpm was used. Temperature in extruder zones was as follows: zone 1 − 120 to 130 °C; zone 2 − 130 to 150 °C; zone 3 − 160 to 190 °C, and the head temperature varied in the range of 170 to 190 °C. The temperature control accuracy in the zones was ± 5 °C. The die casting was carried out using a Plastinjector V-60 injection molding machine (Bresso, Italy) under the following modes: pressurized injection and holding time was 20 s, total cast cooling time varied in the range of 60 to 80 s (at a casting temperature of 190 to 230 °C), the casting pressure was of

80 to100 MPa, and the mold temperature was 30 ± 2 °C.

Physical and mechanical properties were determined using standard methods, in particular, tensile failure stress and relative elongation according to ISO 5272, impact strength according to ISO 0160, Brinell hardness according to ISO 2039-1, density according to ISO 1183-2, and the degree of crystallinity was determined by the X-ray diffraction method using an URS 50 IM system with a copper anode and a nickel filter [9].

The structure of polymer specimens was studied using sections of 20 µm thick in transmitted and reflected light under an MBI-6 microscope. Thermomechanical studies were carried out on an automatic Kargin-Teitelbaum machine at compressive loads of 0.354, 0.674 and 2.66 MPa. Differential thermal analysis was carried out using a Paulik-Paulik-Erdei-system derivatograph. The specimen heating rate was 5°C/minute and the specimen weight was 200 mg [10]. The melt flow index (MFI) was determined using the IIRT-M system under loads of 21.6, 50.0 and 100 N. Weather resistance was determined on a bench according to ISO 18225. Light resistance was also determined on a bench according to ISO 4892-3 (a mercury quartz lamp PRK-2 was used).

3. Results and discussion

The stability of a material consisting of a mixture of various components was characterized by so-called "operational stability", i.e. the time during which the change in the indices of the properties of the system due to its transition from a thermodynamically nonequilibrium state to the equilibrium state remains within the limits of values acceptable under operating conditions.

The long-term photo-aging of polymers and the impact of mechanical loads on them lead to significant structural and chemical changes causing the formation of peroxide, hydroperoxide, carboxyl, ether and other polar functional groups, which, unlike primary polymers, will contribute to the thermodynamic compatibility of polymer waste [11], including PE and PS. However, it has not yet been possible to achieve a significant increase in thermodynamic compatibility due to the fact that the chemical reactions that occur during aging are topographic in nature, and polar functional groups are concentrated mainly in the surface layer, while the bulk of the sample is subject to oxidative stress to a lesser extent. Hence, it is not enough to use only a thermodynamic approach to determine the optimal PCM composition. In this case, not only the composition, but also the structure of the PCM, which is formed both in the process of preparing the composition and in the process of transition from the composition to the material, may be decisive. Under intense mechanical and thermal effects during mixing, the physical and chemical properties of various ingredients of compositions can cause them to interact with each other, and as a consequence, the properties of the PCM can differ significantly from the properties of the original materials.

We have searched for modifying additives that contribute not only to increasing the adhesive interaction at the phase boundary, but also to increasing the operational stability and durability of the products made of the composite materials under study, as well as to improving the technological PCM properties. We studied the effect of such modifying additives as calcium stearate, dicumyl peroxide, polybutadiene rubber, as well as such mixtures of modifying additives as polybutadiene rubber and dicumyl peroxide, butadiene styrene thermoplastic elastomer and surfactant, coal and surfactant, as well as such stabilizing additives as phenozan-23, quinol-D, chloroxyl, and ferrocene on the properties of mixtures based on recycled PE and PS.

Characterizing the influence of each of the studied additives on the entire range of properties of the mixtures of recycled polymers, we note that the most important parameter determining the behavior of a polymer material during its operation is its strength. In this case, to achieve high target strength parameters, the chemical modification (structuring) is used [12]. Dicumyl peroxide (DCP) was used as a structuring agent promoting the formation of a spatially cross-linked material and, to a certain extent, eliminates the defective space at the interface, which is characteristic of composite materials.

Table 2 shows the values of σ_t and MFI depending on the PCM composition and the amount of DCP introduced into their composition. The given data are indicative of wide possibilities for regulating the strength properties of the mixtures of recycled PE and PS. However, for compositions with a predominant content of the PE component, it is preferable to crosslink the PCM by introducing DCP. For example, when using dicumyl peroxide for compositions

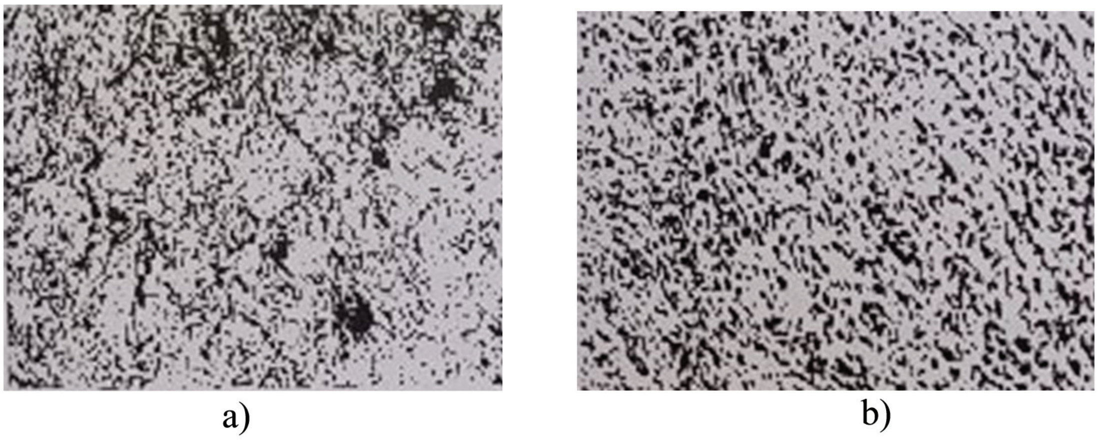


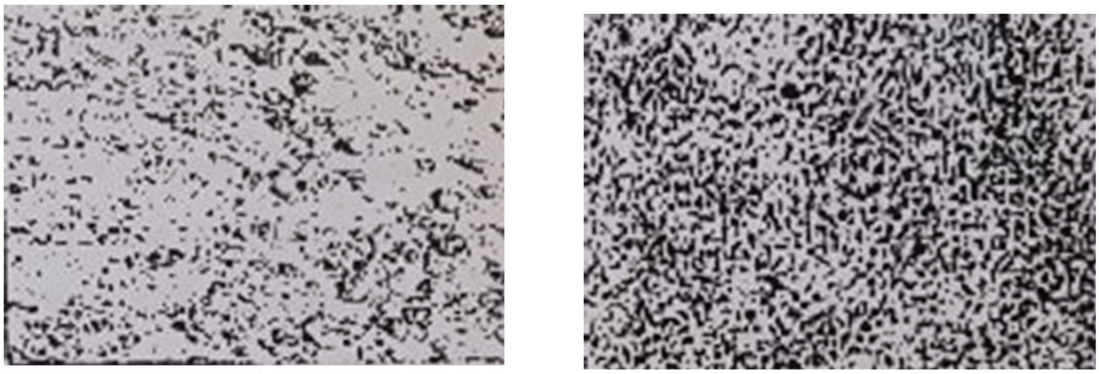
Figure 1 - Microphotographs of the films of the rolled mixture composition of 80 % PE + 20 % PS with magnification (×65): a) 80 % PE + 20 % PS, b) 80 % PE + 20 % PS + 0,5 % DCP

with a predominant PE content, an increase in physical and mechanical properties is achieved with an optimal DCP content of 0.5%. Thus, σ_t = 8.0 MPa for compositions of 80% PE + 20% PS, and σ_t = 9.8 MPa for compositions of 80% PE + 20% PS + 0.5% MAC.

At the same time, the physical structure is also changed significantly. It can be seen in Fig. 1 that the original PE-PS composition has a complicated defect structure with the defects of different sizes and localization. When DCP is introduced into the mixture, defects are "healed", the structure of the material becomes more homogeneous, resembling the structure of interpenetrating polymer networks. This figure clearly shows that cross-linking has little effect on the deformation and strength properties of the mixture, which may indicate the high molecular weight of recycled PE and PS. Cross-linking of a mixture of recycled PE and PS with a prevailing content of PE has a greater effect on the orientation of crystallites, contributes to the reduction of their defectiveness, as well

Table 2 - Tensile strength and melt flow index of PE-PS compositions modified by DCP

Components of the compound, %		MPC, %	σ_t, MPa	MFI, g/10 min (T = 190 °C)	
PE	PS			21.6 H	50.0 H
100	-	-	9.8	1.38	6.8
100	-	0.3	10.0	0.23	2.40
100	-	0.5	10.2	Not flow	Not flow
100	-	0.7	9.6	Not flow	Not flow
80	20	-	8.0	1.04	5.80
80	20	0.3	8.8	0.62	1.40
80	20	0.5	9.8	0.02	0.21
80	20	0.7	10.0	Not flow	0.08
50	50	-	17.8	0.96	5.10
50	50	0.3	17.0	0.61	1.40
50	50	0.5	16.2	0.01	0.17
50	50	0.7	14.8	Not flow	Not flow
20	80	-	28.0	0.91	4.68
20	80	0.3	23.0	0.40	1.20
20	80	0.5	21.4	0.20	1.60
20	80	0.7	20.0	0.03	0.20
-	100	-	35.1	1.60	5.10
-	100	0.3	24.1	2.40	6.20
-	100	0.5	18.0	4.97	16.70
-	100	0.7	16.2	6.10	18.30



a) b)

Figure 2 – Microphotographs of the films of the rolled mixture composition of 20 % PE + 80 % PS with magnification (x65) *a*) 20 % PE + 80 % PS, b) 20 % PE + 80 % PC + 0,5 % *StCa*

as to the orientation of polymer chains and the leveling of "stress concentrators".

For PE-PS compositions with a predominant content of the PS component, a good dispersing effect is achieved by introducing calcium stearate (*StCa*) into the composition. As can be seen from Fig. 2, the composition of 20% PE + 80% PS represents droplets of one phase in another. The droplets are not uniform in size. Small droplets coalesce, forming clusters. This results in the system instability, which, in turn, degrades performance properties and leads to delamination of materials in finished products. The introduction of 0.5% *StCa* into the composition results in a finely dispersed homogeneous structure (Fig. 2b).

In addition to improving homogeneity, the presence of *StCa* in the composition can cause other effects associated with changes in the conformations of macromolecules and depending on the magnitude of the thermodynamic affinity of *StCa* to the components of the polymer mixture. The micrograph (Fig. 2b) indicates that the introduction of *StCa* results in an increased ordering of the supramolecular structure of the mixture and an improved homogeneity due to the formation of a finer ferolite structure and the elimination of defective areas.

An effective method of modifying PCM is the introduction of elastomeric additives such as rubber into the composition [13]. In some respects, the modification of plastics with rubbers competes with some chemical methods for increasing impact strength, elongation at break, ductility or increasing the tendency to fluidity. Table 3 shows the physical and mechanical characteristics of PE-PS compositions modified with PBR. As can be seen from the data presented in Table 3, the strengthening effect of PE-PS compositions is increased with an increase in the content of the PS component.

The effect of strengthening the compositions with rubber can be explained by the fact that dispersed rubber particles located in both phas-

Table 3 - Physico-mechanical characteristics of PE-PS compositions modified with polybutadiene rubber

Compound components, %		PBR, %	σ_t, MPa	ε, %	*a*, kJ/m^2
PE	PS				
80	20	-	8.0	25	not destroyed
75	20	5	7.4	40	HP
70	20	10	6.5	58	HP
60	20	20	5.8	70	HP
50	50	-	20.0	10,0	10,0
45	50	5	18.0	30	HP
40	50	10	17.2	36	12.6
30	50	20	16.8	36	14.0
20	80	-	28.0	10	8
20	75	5	14.8	18	16
20	70	10	22.2	26	20
20	60	20	24.3	30	22

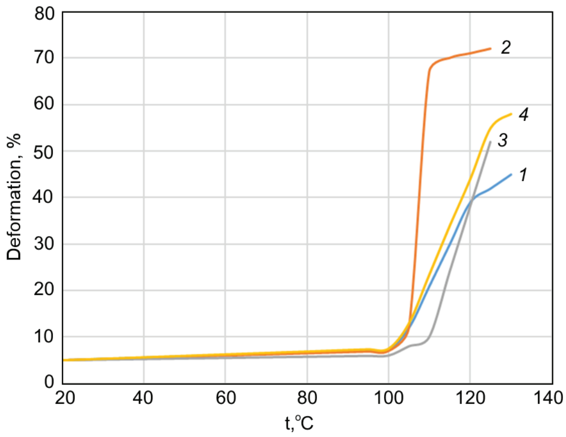


Figure 3 – Thermomechanical curves for compositions 80% PE + 20 % PS with different modifiers at a load of 0.33 MPa and a rate of 2 deg/minute: 1 − 80 % PE + 20 % PS; 2 − 80 % PE + 20 % PS + 0,5 % DCP; 3 − 80 % PE + 20 % PS + 0,5 % *StCa* ; 4 − 80 % PE + 20 % PS + 10 % rubber

es of the mixture components also fill the defective interphase regions, and, during deformation, absorb most of the energy, which leads to an increased elasticity and impact strength of the system. However, modification of the PE-PS composition with polybutadiene rubber leads to a significant decrease in tensile strength. The introduction of flexible PBR elements (structural modification) into a mixture of recycled polymers has a more complicated character in comparison to amorphous polymers (PS), due to the presence of a crystallizable polymer (PE). The effect of structural plasticization turns out to be opposite to the effect of conventional plasticization: the rubber lowers the glass transition temperature (T_c) and the density of the amorphous phase and also slightly reduces the degree of PE crystallinity. As a result, σt decreases, and ε usually increases, which does not contradict the known ideas about the effect of rubbers on the properties of polymers.

The nature of the influence of the studied modifiers, in particular DCP, *StCa*, PBR on the manufacturability of the materials under study is characterized by thermomechanical curves (Fig. 3). The analysis of the curves shows [14]

Table 4 - Strength properties and MFI of PE-PS compositions modified with polybutadiene rubber and dicumyl peroxide

Compound components, %				σ_t, MPa	MFI, g/10 min		ε, %
PE	PS	PBR	DCP		21.6 H	50.0 H	
100	-	-	-	9.8	1.38	6.80	118
95	-	5	-	9.3	0.23	1.20	125
90	-	10	-	8.6	57.00	2.88	115
80	-	20	-	8.0	0.73	3.40	22
50	50	-	-	20.0	1.60	5.90	10
45	50	5	0.1	18.0	2.40	6.50	20
44.9	50	5	0.1	22.1	1.80	5.10	26
44.7	50	5	0.3	24.2	1.20	3.00	29
44.5	50	5	0.5	23.2	0.90	2.80	27
40	50	10	-	17.2	3.80	7.30	26
39.9	50	10	0.1	23.0	3.00	6.70	31
39.7	50	10	0.3	24.9	2.50	4.50	39
39.5	50	10	0.5	23.8	4.30	3.90	37
30	50	20	-	16.8	4.30	8.00	33
29.9	50	20	0.1	22.8	3.30	6.90	37
29.7	50	20	0.3	24.0	3.10	4.00	46
29.5	50	20	0.5	23.0	2.40	3.60	40
20	80	-	-	28.0	0.91	4.60	10
20	69.7	10	0.3	34.8	2.50	3.80	38
10	90	-	-	32.0	0.60	2.80	10
10	79.7	10	0.3	40.0	0.61	1.90	37
10	69.5	20	0.5	37.2	0.40	3.10	39
-	95	5	-	28.3	1.68	5.40	8.9
-	90	10	-	25.8	1.71	5.60	9.4
-	80	20	-	22.3	1.73	6.00	10.4
-	100	-	-	35.1	1.60	5.10	8

Table 5 - Values of density and degree of crystallinity of the modified PE-PS compositions and initial components

Compound components, %					ρ, kg/m^3	H, %
PE	PS	*StCa*	PBR	DCP		
80	20	-	-	-	923	57
79.5	20	0.5	-	-	926	62
79.5	20	-	-	0.5	925	63
75.0	20	-	5	-	921	61
70.0	20	-	10	-	917	59
74.5	20	-	5	0.5	920	63
20	80	-	-	-	1015	<10
20	79.5	0.5	-	-	1010	<10
20	79.5	-	-	0.5	1014	<10
20	75.0	-	5	-	1012	<10
20	70	-	10	-	1005	<10
20	74.5	-	5	0.5	1017	<10
100	-	-	-	-	911	63
99.5	-	0.5	-	-	917.8	70
99.5	-	-	-	0.5	915.5	66
95.0	-	-	5	-	908.,7	68
90.0	-	-	10	-	909.7	67
-	100	-	-	-	1054	0
-	99.5	0.5	-	-	1054	0
-	99.5	-	-	0.5	1062	0
-	95	-	5	-	1056	0
-	90	-	10	-	1060	0

that the introduction of modifiers results in an increase in the level of high elasticity and deformation resistance of the system, and the deformation resistance increases in the following series StCa – PBC – MDC series.

The presented curves make it clear that the additives introduced into the composition of polymer mixtures have practically no effect on the T_c of the mixture, but significantly change the deformation properties of the mixtures of the polymers under study.

It was of interest to study the effect of a combination of modifiers of various functional purposes on PCM properties. For example, the use of PBR in combination with DCP does not exclude chemical interaction in the system. The efficient chemical interaction processes are facilitated by the use of recycled polymer materials that are partially oxidized under operating conditions and contain an increased amount of oxygen-containing groups and multiple bonds.

The data presented in Table. 4, allow us to conclude that the use of the complex modifying additive PBR + DCP leads to a significant increase not only in σ_t, but also in ε, which indicates an increase in the compatibility of the components and their adhesion at the phase boundary. The change in σ_t and ε correlates with the content of the compositions and the modifiers present in them. For example, σ_t is the lowest, and ε is the highest in recycled PE-based compositions with a PBR modifier. The introduction of PS (hard polymer) and the cross-linking DCP agent into the composition results in a decrease in ε.

In addition to the effect on strength properties, the content of PE and PS in PCM, as well as modifying PBR and DCP additives also affects the fluidity of the compositions; in particular the compositions containing no cross-linking agent have an increased fluidity. However, the nature of the change in MFI depending on the PCM composition indicates the manifestation of complex physical, physico-mechanical, and chemical processes of interaction of the components.

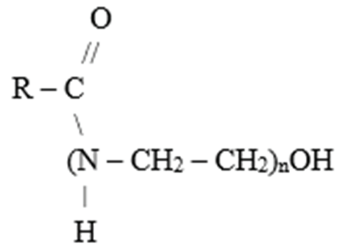
To study the effect of modifying PE and PS mixtures with various additives, the density (ρ) of the composite material and the degree of crystallinity (*H*) were determined by X-ray diffraction. The values of density and degree of crystallinity of compositions with a predominant PE and PS content and other initial components are given in Table 5.

The presented data indicate that for compositions with a predominant content of PE, such modifying additives as DCP and especially the complex modifying DCP + PBR additive act as active structure-forming agents for PE, which leads to a significant increase in the density and degree of crystallinity of the polymer mixture. The introduction of rubber into such systems results in a decrease in density, however, the degree of crystallinity is increased compared to the original composition. This confirms the earlier conclusion that PBR particles promote healing of defects and lead to ordering of the structure as a whole.

For compositions with a predominant content of PS, the introduction of the specified modifying additives (with the exception of the complex additive DCP + PBR) does not lead to an increase in density, which, in principle, does not contradict the concepts of the structure of amorphous polymers. Assessing the crystallinity of the composition in this case is difficult due to a small amount of PE in the composition, and PS is a typically amorphous polymer. It can be assumed that modifiers introduced into compositions with a predominant PS content somewhat worsen the overall molecular order of its structure. It must be emphasized that the action of the complex PBR+DCP additive leads to an increase in the density of the mixture of recycled polymers, regardless of the prevailing content of one or another component.

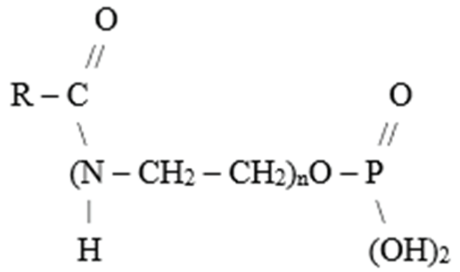
Subsequently, to modify the mixtures based on recycled PE and PS, another complex additive was studied, i.e. the mixture of thermoplastic elastomer DST-30 and surfactants selected from the group of alkylamides, alkylamide phosphates, alkylaryl sulfonic acids, as well as their mixtures. The choice of such a wide range of surfactants is due to the presence of various functional groups in worn polymers and is aimed at ensuring compatibility of the system components. Thermoplastic elastomer DST-30 is a block-copolymer of an A-B-A type and it contains butadiene and styrene elements which are similar to the components of the composition in their kinetic nature. On the other hand, DST-30 is not a mixture of components, it is a chemical compound. Therefore, studying its effect will allow us to draw conclusions on the mechanism of structure formation in polymer mixtures.

Compounds selected from the groups of alkylamides of the general formula (R is an alkyl radical) were used as surfactants:



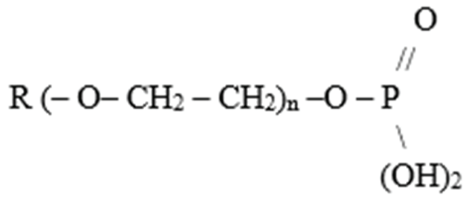
R=10-16, n=5

alkylamide phosphates of the general formula:



R = 10-16, n = 7

ethoxylated alcohol phosphates of the general formula:



R = 10-13, n = 7

alkylarylsulfonic acids of the general formula:

$$R\,Ar - SO_3H$$

R = 10-14

or a surfactant mixture.

When a surfactant (surfactant) or a mixture thereof is added to a PE-PS composite, the following is observed: equalization of the melt viscosities of the composite components and a decrease in the surface tension at the phase boundary. Chemical interactions between the composite components may also occur between the chemically active surfactant groups and the double bonds of the DST-30 block copolymer, as well as the oxygen-containing groups that oxidize during the use of the PE and PS composites, resulting in increases in σ_t, ε and a of the PCM by 20–50%. Moreover, the degree of increase in these properties depends on the composition of the initial polymer mixture. For example, for a predominant PE content, an increase in ε is observed to a greater extent, and

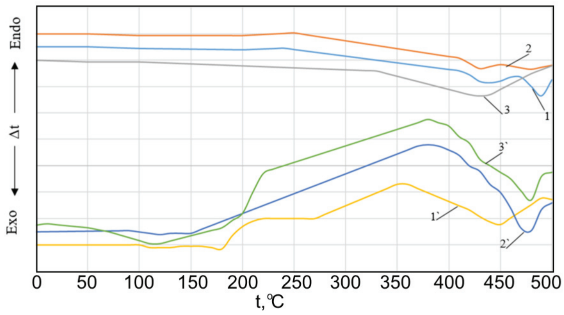


Figure 4 – Derivatograms of compositions: 1,1′ - 70% PE + 30% PS; 2,2′ - 75% PE + 20% PS + 5% DST-30; 3,3′ - 74,7% + 20% PS + 5% DST-30 + 0,3% surfactant. 1-3 are DTA curves; 1′-3′ are TGM curves.

for a predominant PS content an increase in σ_t is observed.

The effect of surfactants and their mixtures on the interaction processes in PCM was studied using thermal analysis (Fig. 4).

The TGM curves (Fig. 4) show two peaks for the compositions 70% PE + 30% PS and 75% PE + 20% PS + 5% DST-30 in the region of polymer destruction, corresponding to the temperatures of a maximum destruction rate of PS and PE. For the composition 64.7% PE + 30% PS + 5% DST-30 + 0.3% surfactant, one broad peak is visible, corresponding to the maximum rate of destruction [9].

On the DTA curves, for the compositions 70% PE + 30% PS and 75% PE + 20% PS + 5% DST-30, only an inflection is observed in the area of PS destruction, and for the composition 64.7% PE + 30% PS + 5% DST-30 + 0.3% surfactant, the inflection is smoothed out and there is one endothermic peak characterizing the destruction of the entire system. Based on this, we can conclude that all components of this composition are chemically interrelated and behave as a single system. In addition, for the modified composition containing a surfactant, the area limited by the oxidation peak is significantly smaller than for the unmodified composition, which also confirms the chemical interaction of the studied modifiers with the components of the composition.

According to a mechanism similar to the previous one, the PE-PS compositions are modified by the mixed waste from the consumption of polyurethane foam (PUF), obtained from worn out shoe soles, and a surfactant selected from the studied group (Table 6).

In order to expand the areas of application of composite materials based on PE and PS of mixed consumer waste and to ensure the possibility of their long-term operation, it is essential to increase the resistance of the compositions to UV irradiation, especially taking into account the presence of PE in PCM. For this purpose, various light-stabilizing additives were introduced into the compositions, in particular phenosan-23, quinol-D, ferrocene and chloroxyl. All of the listed additives are fine powders that mix well with crushed waste and are evenly distributed throughout the mixture during processing. The results of studying the effect of these additives on the properties of the compositions showed that with the introduction of light-stabilizing additives, the value of σ_t remains at the level of the original composition, but at the same time, the value of ε is increased significantly (5-8 times). This may be due to the plasticizing effect of photostabilizing additives, since most of them have an oligomeric structure.

Table 6 – Physical and mechanical properties of PE-PS compositions of the mixed consumer waste, modified with polyurethane waste and surfactant

Compound components, %				σ_t, MPa	ε, %
PE	PS	PUF	Surfactant		
80	20	-	-	8.0	22
75	20	5	-	9.30	8.15
74.9	20	5	0.1	9.61	9.12
74.7	20	5	0.3	10.20	12.40
74.5	20	5	0.5	8.59	10.40
70	20	10	-	9.81	4.95
69.9	20	10	0.1	10.40	8.30
69.7	20	10	0.3	11.30	11.60
69.5	20	10	0.5	11.00	10.20
60	20	20	-	10.90	8.80
59.9	20	20	0.1	11.40	9.40
59.7	20	20	0.3	12.0	10.50
59.5	20	20	0.5	10.50	9.70

Table 7 - physical and mechanical properties of PE-PS compositions of the mixed consumer waste depending on the atmospheric aging time

Compound components, %	σ_t, MPa				ε, %				σ_i, MPa			
	aging time				aging time				aging time			
	Output	Months			Output	Months			Output	Months		
		1	2	3		1	2	3		1	2	3
80% PE + 20% PS	8.0	8.2	7.9	8.0	22	20	18	18	10.2	10.0	9.8	9.7
79.7% PE+20% PS+0.3% phenosan 23	7.1	7.6	8.0	7.9	190	180	182	186	11.0	11.2	11.0	10.9
79.7% PE+20% PS+0.3% quinol D	7.3	7.7	7.9	7.7	111	110	108	107	11.4	11.6	11.2	11.2
79.5% PE+20% PS+0.5% chloroxyl	8.0	8.2	8.6	8.7	180	172	170	168	10.6	10.7	10.8	10.8
79.7% PE+2 % PS+0.3% ferrocene	8.0	8.1	8.4	8.3	102	98	96	98	10.4	10.3	10.5	10.6

To assess the effect of light-stabilizing additives on the properties of the mixtures of recycled PE and PS during operation over time, studies on the weather resistance of PCM were carried out for 3 months in summer. The data in Table 7 show that the UV-stabilizing additives having large molecules with highly branched groups and a highly conjugated structure are capable of absorbing solar UV radiation or shifting the absorption region towards longer wavelengths due to the formation of intermolecular hydrogen bonds.

The MFI remains practically at the same level, and this indicates that the processes occurring in the composition under the influence of light stabilizers affect only short-range order regions. This table also shows that the properties of the compositions modified with photostabilizers retain their values in comparison with the original composition. In a number of cases, during the aging process, an improvement in the indicators of the properties being studied is observed.

An effective way to reduce the cost of PE-PS compositions and obtain composite materials with increased hardness is to modify polymer mixtures using the powdered coal as filler, which is a technological waste of its mining and processing. Coal, which is a solid form of carbon, contains low molecular weight volatile aromatic compounds, high molecular weight resins and a large number of different oxidation products. In addition, it contains water, sulfur, sulfur-containing compounds, etc. This creates the preconditions for its effective use as a modifying additive, especially for recycled polymers that also contain a significant number of chemically active groups. The effectiveness of the modifying effect of coal can be significantly increased by introducing surfactants, which makes it possible to increase the activity of the filler and improve the physical and mechanical properties of the filled composite materials by improving the interaction at the highly developed interface between the polymer particles and the filler.

When studying the strength properties of the PE and PS -based compositions modified with powdered coal and surfactants, it was established that such a modifying additive makes it possible to obtain PCM with an H_B of 105-128 MPa with a fairly high strength (σ_t = 32.0-36.6 MPa) and thermal stability (241-270 °C).

The proposed modifying additives give an opportunity for obtaining PE and PS-based PCM with an improved set of performance properties. On the other hand, the studied series of additives allows for targeted regulation of the PCM properties in a wide range for various operating conditions, which makes it possible to maintain and, in some cases, improve the properties of compositions based on PE and PS waste. This confirms the previously made conclusion that composite materials based on recycled polymer raw materials are full-fledged polymer materials that can have a wide field of application.

4. Conclusions

The effect of various modifying additives, in particular calcium stearate, dicumyl peroxide, polybutadiene rubber, as well as their mixtures on the properties of polymer composite materials based on the mixtures of recycled polyolefins and polystyrene plastics has been studied. It has been established that the use of mixtures of various modifying additives in combination with photo- and thermal stabilizers can regulate the strength properties and structure of PCM. Studying the properties of various mixtures with a predominant content of polyolefin or polystyrene components makes it possible to form a fine spherulite structure. This is facilitated by the introduction of small amounts of calcium stearate (for compositions with a predominant content of polystyrene plastics) and dicumyl peroxide (for compositions with a predominant content of polyolefins) into polymer mixtures. It has been shown that the studied modifiers improve the elasticity of PCMs and increase strain resistance in the series of calcium stearate – butadiene rubber – dicumyl peroxide. It was established that the introduced additives do not change the glass transition temperature of the mixture.

The efficiency of using powdered coal as a filler in the form of technological waste from its extraction and processing for obtaining PCM with increased hardness and some reduction in their cost has been demonstrated.

Analysis of the DTA data for the studied PCMs does not exclude the possibility of chemical interaction between the components included in their composition.

The studies have established that PCMs obtained on the basis of recycled polyolefins and polystyrene plastics subjected to the three-month atmospheric aging did not change the achieved level of the indicators of their physical and mechanical properties and the products based on them can be used as those based on primary materials.

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