DOI 10.1007/s11029-022-10023-4
Mechanics of Composite Materials, Vol. 58, No. 2, May, 2022 (Russian Original Vol. 58, No. 2, March-April, 2022)

INFLUENCE OF FILLER ON THE STRUCTURE, THERMAL STABILITY, AND MECHANICAL PROPERTIES OF COMPOSITIONS BASED ON A MODIFIED POLYPROPYLENE

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Keywords: *polypropylene, calcite concentrate, polyolefin elastomer, thermal stability, mechanical properties*

The effect of a filler on the structure, thermal stability, strength, elongation, and impact strength before and after freezing in compositions based on polypropylene modified with a polyolefin elastomer is considered. It is found that the presence of filler reduces the effective activation energy of the thermooxidative destruction of composites and the technological characteristics of thermal stability, which indicated a decrease in the structuredness of the system. The study showed a tendency to increase the melting and crystallization temperatures of polypropylene with a filler content of up to 20 wt%, as well as to a certain narrowing of the temperature range of melting and crystallization with increasing calcite concentration. This was probably associated with the formation of polymer crystallites more uniform in size. It is found that, at a filler content up to 5 wt%, modified calcite particles can serve as additional nucleators. This was reflected in the increasing strength and impact strength by 5 and 6%, respectively, compared with those of the unfilled one.

Introduction

One of important directions in the creation of polymer composite materials with a given set of properties is combining thermoplastics with elastomers, resulting in thermoplastic elastomers. Such compositions, among other advantages, have an increased impact strength and frost resistance. They can be processed on standard equipment for plastics. Polypropylene

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Translated from Mekhanika Kompozitnykh Materialov, Vol. 58, No. 2, pp. 321-334, March-April, 2022. Russian DOI: 10.22364/mkm.58.2.05. Original article submitted July 1, 2020; revision submitted January 19, 2022.

of various modifications occupies a leading position in the manufacture of functional products for various purposes. With the joint introduction of a filler and an elastomer into polypropylene at certain ratios between the components and the use of a suitable compounding method, composites with a given set of physical and mechanical characteristics can be obtained.

In recent years, a variety of metallocene polyolefin elastomers, with improved structural characteristics compared with those of the traditional rubbers, have been produced commercially. Studying the physical, mechanical, operational, and technological properties of new elastomers in order to clear up the possibility of replacing the traditional elastomers with metallocene ones is an urgent task. It is shown in [1, 2] that the introduction of a metallocene ethylene propylene elastomer into polypropylene at a amounts of 10, 15, 20, and 30 wt% leads to a significant increase in its impact strength and elongation at break. However, this reduces its elastic modulus and tensile yield strength.

Of considerable interest is the modification of polypropylene by adding such elastomers both separately and together with fillers of various nature. To develop filled polymer compositions, it is necessary to determine the effect of each of the components on their technological and operational properties, to choose a rational composition, and to determine the technological parameters for obtaining a polymer material.

The physical and mechanical properties of polymer materials are determined by their structure at the molecular and supramolecular levels [3]. Changes in the molecular structure of polymers lead to a multiphase nature of the system, complications of its crystallization behavior, and a significant change in its properties. The joint introduction of a filler and an elastomer by changing the type of phase separation makes it possible to control the supramolecular structure and, as a consequence, the physicomechanical properties of the composites obtained.

The influence of a modifier on the properties of polymer material manifests itself not only in the solid state, but also in the melt [4], since polymers are able to retain supramolecular formations at temperatures exceeding their melting point. Therefore, topical is studying the effect of filler content on the supramolecular structure of composites, including highly filled compositions based on a modified polypropylene (PP) for various applications. Using the method of differential thermal analysis, it is possible to determine the effect of the content of additives on the thermal characteristics of phase transitions, namely, on the melting and crystallization temperatures associated with the size of crystallites in the temperature range of these transitions, which characterizes the scatter of crystallites in size.

1. Analysis of Investigations and Publications

Combining polymers with fillers makes it possible to obtain materials with completely new properties [5]. Among the large number of mineral fillers, calcium carbonate is used the most, owing to its availability and low cost [6, 7]. However, the incompatibility of its high-energy hydrophilic surface with a low energy surface of such hydrophobic polymers as polyethylene and polypropylene is a problem. In order to increase the efficiency of fillers, their surface is specially treated [8, 9].

It is known that elastomers, in addition to imparting certain operational properties, act as compatibilizers that enhance the specific intermolecular interaction of the polymer matrix and filler, i.e., improve their compatibility [10, 11]. It is shown in [12] that the introduction of 30 wt% modified kaolin increases the thermal stability of compositions by about 20°C compared with that of pure polymer. Rheological studies of such compositions have shown that the surface treatment of kaolin with polyhedral oligomeric silsesquioxane decreases its viscosity, which can facilitate their processing.

It is shown in [13] that, to improve the mechanical and thermal properties of polypropylene composites with a grafted maleic anhydride, kaolin modified with 3-aminopropyltriethoxysilane can be added as a filler. The addition of the filler in an amount of 2 wt% contributed to an increase in the thermal stability of the composites, with an increase in the impact strength by 30%, strength and the relative elongation at break by 12 and 14%, respectively, compared with those of an unfilled composite.

The amount of filler directly affects the physical and mechanical properties of the composite. In [14], the effect of different degrees of filling with a nanoclay, talc, and calcium carbonate on recycled polypropylene filled with wood flour was studied. Polypropylene with grafted maleic anhydride was used as a binder in the composites, and paraffin wax — as a softening agent. Samples containing 7 wt% calcium carbonate showed the highest strength. The addition of 3 wt% of talc increased the cooling and crystallization temperature. As a result of a thermal analysis, it was found that each of the fillers increased the melting, enthalpy, and crystallization temperatures compared with those of unfilled samples. This indicated an improvement in the interaction at the interface between the ingredients of the composite, which increased the compatibility of the fillers and polymer matrix.

According to the results of [15], PP samples containing more than 8 wt% of a high-molecular-weight polyoctene had a higher Izod impact strength than the original PP. The modification of PP with polyoctene significantly increased in the melt flow index, which is explained by the good compatibility with PP and a strong plasticizing effect of the modifier. With increasing content of polyoctene, the melting and crystallization temperatures of the modified PP did not change, from which it can be concluded that the modifying additive does not affect the structure of PP. The presence of a modifier also makes it possible to reduce the processing temperature of PP and to increase the productivity of extrusion equipment at the stage of obtaining products.

The peroxide treatment of PP [16] at low concentrations of additives makes it possible to regulate the melt flow index in a wide range and to obtain a PP for casting thin-walled products. A study of the thermophysical properties of PP samples modified with peroxides showed that their introduction decreased the melting temperature (from 176 to 168°C) and increased the crystallization temperature (from 105 to 111-112°C). In this case, the crystallinity of the polymer did not undergo significant changes.

Formulation of the problem. Thus, investigating the relationship between the molecular structure of a composite based on polypropylene, modified with a metallocene propyleneethylene elastomer and filled with a chalk concentrate, with desirable physical and mechanical characteristics is topical for the development of materials with desired technological and operational properties.

According to the results of [17], upon increasing the amount of filler from 5 to 50 wt%, the viscosity of the composition decreased on the entire range of concentrations and shear stresses, which contradicts the traditional patterns of flow of melts filled with solid additives, for which an increase in viscosity is typical. Its extraordinary rheological behavior is associated with the presence of long hydrocarbon chains of calcium stearate on the surface of the filler particles and is due to the fact that the emulsifying effect of calcium stearate prevails over the thickening effect of the solid filler. However, the effect of filling with calcite concentrate, in a wide range of concentrations, on the process of thermooxidative degradation and the structure of polypropylene modified with polyolefin elastomer, as well as their relationship with the physicomechanical properties of composites, remains unexplored.

The novelty of the work is the synergistic effect of using a propyleneethylene elastomer synthesized according to the modern technology on metallocene catalysts [18] and a specially treated mineral filler, which has an additional plasticizing effect on polypropylene. This effect makes it possible to obtain highly filled polymer materials with the ability to control their physical, mechanical, rheological properties, and thermal stability.

The purpose of this work is to establish the effect of calcite concentrate on the structure and thermal stability of composites based on polypropylene modified with a propyleneethylene elastomer using the method of differential thermal analysis (DTA) and differential thermogravimetry (DTG) and to determine the relationship between the thermal characteristics of composites and their physical and mechanical properties.

2. Research Methodology

Modified filled mixtures based on an isotactic polypropylene (PP) of grade 21030 (density 921 kg/m^3, MFR = 2.5-4 g/10 min) were used as objects of our study. The modifier was a Vistamaxx 6202 polyolefin elastomer (EP) (ExxonMobil, United States), which is a block copolymer consisting of repeating blocks of isotactic propylene with an irregular distribution of ethylene (15%). The polyolefin elastomer is characterized by good elastic properties, the ease of processing, and compatibility with a wide range of materials. This elastomer is suitable for compounding with polyolefins to create materials with a balance of operational properties, as well as for thermoplastic compounding, requiring a good distribution and dispersion of filler [19]. A calcite concentrate (CC) of grade 1TK (Ltd Tekhnokom, Ukraine), with an average particle size of 2.5 μm, was used as a filler (the content of particles with a maximum size of 20 μm was 1.5%). CC includes a stearic acid-treated calcium carbonate and polyolefin (with 24 wt% organic part). As a result of the treatment of calcium carbonate, calcium stearate is formed, in whose molecule is a nonpolar "tail" in the form of a stearic acid chain on the surface of the molecule. This treatment improves the compatibility of the filler with the hydrophobic polymer, which has a positive effect on the physical and mechanical characteristics of the material [20, 21].

Mixing the components, followed by strand granulation, was carried out using a ChP 27x30 extruder at temperatures in its zones of 155–210–200–200°C and a screw speed of 45 rpm. The content of CC in the resulting composites was 5–50 wt%.

The tensile strength and elongation were determined according to ISO 527-2:2012 and the impact strength — according to ISO 179-1:2010. The frost resistance of the compositions was determined as an indicator of impact strength after freezing material samples for 30 days at a temperature of –18°C. The accuracy of the methods for determining the mechanical characteristics was ± 5%.

In order to assess the effect of CC on the phase transitions of PP in composites based on it on their thermal stability, the DTA and DTG methods were used. Thermograms were recorded using a Q 1500 D derivatograph (MOM, Budapest). Platinum crucibles were employed for the study, and an Al_2O_3 powder was used as the reference. Thermograms of the extrudate melting process were recorded at a heating rate of 5°C/min from room temperature to 225°C (within the temperature scale of 250°C), after which the melt crystallization curves were recorded at a cooling rate of 1.5°C/min. The sample weight was about 350 mg. The thermograms were used to determine the temperatures of beginning of polymer melting, T_{mo}, melting, T_{m}, and the end of melting, T_{mf}, as well as the temperatures of the beginning of crystallization, T_{co}, crystallization, T_{c}, and the temperature of the end of crystallization of PP, T_{cf}.

The enthalpy of melting, ΔH, was determined by the method described in [22]. To calculate it, the peak area was calibrated for an n-aminobenzoic acid, whose melting enthalpy was 36.3 cal/g. The degree of crystallinity X_{c} (%) was calculated from the enthalpy of fusion of a fully crystalline polymer by the formula

$$X_{\mathrm{c}} = \frac{\Delta H_{\mathrm{m}}}{\Delta H_{\mathrm{ref}}} \cdot 100, \tag{1}$$

where ΔH_{ref} is the heat of fusion of a fully crystalline polymer (for PP, it was 62 cal/g) and ΔH_{m} is the heat of fusion of the given sample.

The resistance of composites to the thermal oxidative degradation was evaluated from the thermal oxidative degradation energy E_a. The activation energy of thermooxidative degradation was determined by the method described in [23]. To calculate E_a and to determine the thermal characteristics of heat resistance, derivatograms were recorded within the temperature scale of 500°C at a heating rate of 5 deg/min. The quantity E_a was calculated by mathematically processing the thermogram curve using Broido's double logarithm method [24] according to the formula

$$\ln(\ln\frac{100}{100-\Delta m}) = -\frac{E_a}{RT} + \mathrm{const} \tag{2}$$

at temperatures within the decomposition interval of the substance, where R is the universal gas constant equal to 8.31 10^3 kJ/mol K.

3. Results and Discussion

The calculated values of activation energy of the extrudates and initial components are presented in Table 1.

As can be seen from data in the table, the effective activation energy of the thermooxidative degradation of EP was slightly lower than that of PP (80.8 and 87.3 kJ/mol, respectively), which may be due to the violation of microtactic-

TABLE 1. Activation Energy of Thermooxidative Destruction and Thermal Characteristics of the Thermal Stability of Compositions and Individual Components

Composition, wt%			Activation energy E_a, kJ/mol	Weight loss onset temperature, °C	Loss temperature of 5% mass, °C
PP	EP	CC			
100	-	-	87.3	255	295
-	100	-	80.8	230	290
-	-	100	62.2	240	295
95	5	-	77.9	235	285
90	5	5	76.4	237	280
65	5	30	76.2	237	280
45	5	50	75.8	240	285

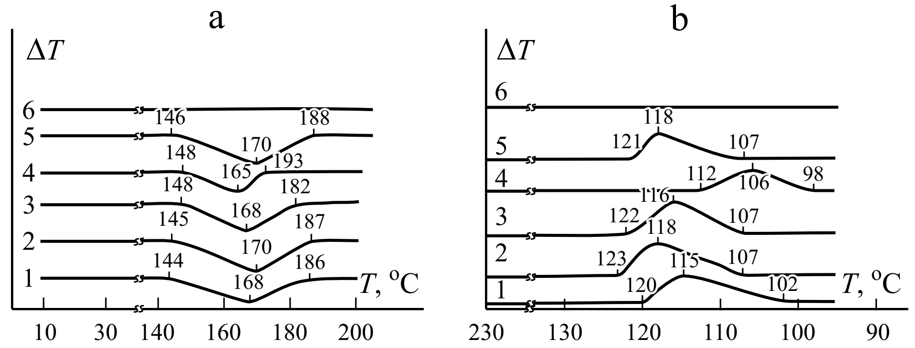

Fig. 1. Thermograms of (a) melting and (b) crystallization for composites based on PP: 1 — PP; 2 — PP + 5 wt% CC; 3 — PP + 50 wt% CC; 4 — CC; 5 — PP + 5 wt% EP; 6 — EP.

ity of the PP chain and the amorphous state of EP. With increasing amount of filler in the PP+EP+CC compositions, the effective activation energy slightly decreased. This indicated that, in the presence of the modifier and filler, the cohesion in the system decreased.

For a more complete characterization of the thermal stability of the compositions, the temperature indicators of thermal stability were determined (see Table 1). It can be seen from the above data that the introduction of EP, as well as simultaneously CC and EP, somewhat lowed the thermal stability of the composites.

To study the effect of content of the filler and modifier on the temperature characteristics of phase transitions based on PP, thermograms of melting and crystallization were recorded within the temperature scale of 250°C (Fig. 1).

On the DTA curve of EP heating (curve 6 in Fig. 1a), there is no thermal effect of melting, and on the DTA cooling curve (curve 6 in Fig. 1b), there was no thermal effect of crystallization, which indicated that the initial EP was amorphous under these heating conditions and cooling. The absence of thermal effects of melting and crystallization indicated that they cannot directly affect ΔH of the PP phase transition.

The introduction of a modifier can have an effect indirectly through changes in the structure at the molecular and supramolecular levels. The degree of crystallinity X_c was calculated on the assumption that the content of PP as the base polymer in CC was 20 wt%. Therefore, the calculated values of X_c were relative and could only indicate a trend towards an increase or decrease in this indicator caused the introduction of CC (Table 2).

It can be seen from the data in the table that, depending on its content, CC affects the processes of melting and crystallization of PP in composites based on it. At the simultaneous presence of CC and EP, the tendency to an increase in the values T_m and T_c of polypropylene at a low (5 wt%) and medium (10–20 wt%) CC content, as well as to some narrowing of the ranges of melting and crystallization temperature range with increasing CC content, remained the same.

TABLE 2. Influence of Calcite Concentrate on the Temperature Characteristics of Phase Transitions and the Degree of Crystallinity of PP for Composites Based on It

Composition of the polymer material, wt%			Thermal characteristics of phase transitions									
			Melting (T, °C)				X_c,%	Crystallization (T, °C)				X_c,%
PP	EP	CC	T_{mo}	T_m	T_{mf}	ΔT_m		T_{co}	T_c	T_{cf}	ΔT_m	
100	-	-	144	168	186	42	12.3	120	115	102	18	31.9
-	-	100	148	165	173	25	-	110	106	98	12	-
95	5	-	146	170	188	42	12.0	121	117	105	16	28.8
90	5	5	146	170	190	44	13.1	122	117	106	16	31.3
85	5	10	146	171	187	41	12.9	122	117	106	16	31.3
75	5	20	145	170	187	42	12.2	121	116	105	16	32.5
65	5	30	143	168	183	40	12.5	122	117	106	16	28.9
55	5	40	142	168	181	39	12.5	121	116	106	15	31.7
45	5	50	141	168	180	39	14.3	121	116	106	15	37.2

The narrowing of the temperature range of phase transitions is associated with the formation of polymer crystallites with more uniform sizes [25]. With an increase in the content of CC in the composition, the content of grafted calcium stearate chains also increases [17]; therefore, their plasticizing effect also increases. At a low content of CC, modified calcite particles can probably serve as additional nucleators—substances capable of changing the supramolecular structure.

In [26], the effect of a nucleator (salt of an organic acid) on the thermophysical and physicomechanical properties of PP was studied. The authors believed that the microstructure of PP does not change, since the melting temperature did not vary. Changes in the supramolecular structure of PP samples under the action of artificial nuclei of structure formation were manifested as changes in the strength, hardness, stiffness, and other properties of the polymer. The ordering of the supramolecular structures of PP appeared in DSC curves as an increased thermal effect of melting. In this work, it is likely that calcium stearate molecules had a plasticizing effect at the interface, which partially neutralized the effect of the nucleator, due to which the effect on the crystal structure was minimal.

The mild effect of SS and EP on the formation of the PP crystal structure in composites was apparently due to the plasticizing effect of the SS and elastomer components on PP crystallization with the formation of core–shell structures in the PP matrix.

In the range of medium and high concentrations of CC in the composition, when a spatial network of filler particles modified with stearic acid can be formed, the plasticizing effect of calcium stearate and PP as the base of CC can be predominant.

The process of structure formation is affected by an increase in the ability of the modified calcite to disperse, i.e., to make a uniform distribution of particles in the polymer medium even at a high CC content. The uniform distribution of the particles was ensured by a thorough mixing in a twin screw extruder.

The introduction of a filler can indirectly influence the properties of PP by changing its structure at the molecular and supramolecular levels [27]. The data in Fig. 1 and Table. 2 shows that the modifier and filler as a whole have a little effect on its degree of crystallinity, probably due to the influence of factors that can act in opposite directions in different concentration ranges.

In this work, a calcite concentrate treated with the stearic acid was used as a filler. This obviously led to the β-nucleation of PP, which agrees with the opinion of the authors of [28]. The fixation of stearic acid residues on the surface of $CaCO_3$ particles is evidenced by the decrease in the surface energy of calcite particles from 70–100 to 20–30 mJ/m^2 [8], which is commensurate with the PP surface energy of 31 mJ/m^2 [29]. Due to the decrease in the surface energy of calcite particles, the interaction between them is weakened, which means that the dispersion improves and the aggregation of particles in the composition decreases [13]. In boundary layers of the polymer, which are formed around the filler particles,

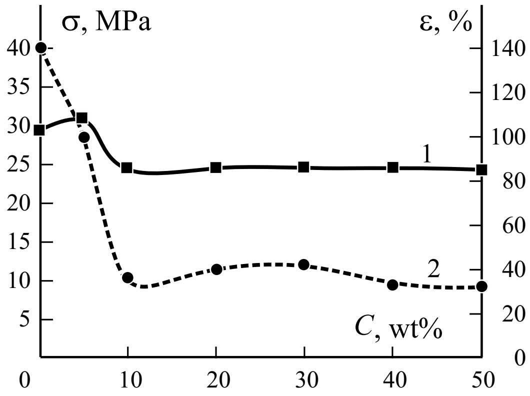

Fig. 2. The tensile strength σ (1) and relative elongation ε (2) vs. the content of calcite concentrate C in compositions based on PP modified with 5 wt% EP.

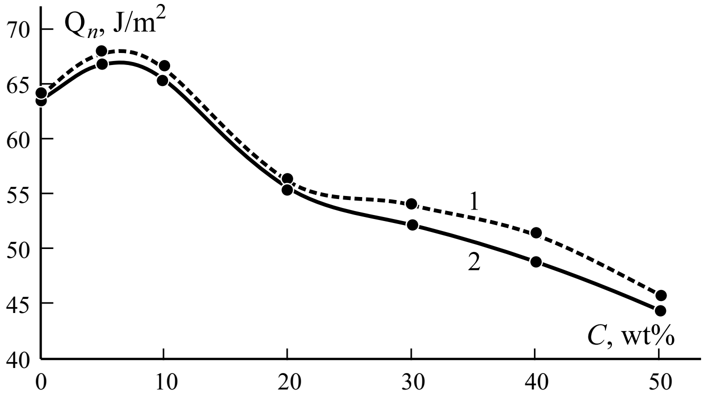

Fig. 3. The impact strength Q_n before (1) and after (2) freezing vs. the content of calcite concentrate in compositions based on PP modified with 5 wt% of EP.

the appearance of a free volume is possible, which increases the mobility of macromolecular regions. At the same time, calcite concentrate particles can better fill cracks and voids due to their round shape, in contrast to clay fillers and talc [14], which leads to an improvement in the physicomechanical properties of composites.

In [30], when elastomers of different polarity were introduced into a PP/untreated $CaCO_3$ mixture, it was established that the use of a nonpolar ethylene-octene copolymer leads to the formation of a structure with a separate dispersion of elastomer and filler particles in the polypropylene matrix. At the same time, the use of the polar savilene instead of ethylene-octene copolymer led to the encapsulation of $CaCO_3$ particles by the elastomer. It should be noted that the glass-transition temperature of composites with a nonpolar copolymer increase with increasing amount of filler, which points to the interaction of the filler and the polypropylene matrix. In the triple heterogeneous PP/elastomer/filler system, three interfaces can simultaneously exist: PP/elastomer, PP/filler, and elastomer/filler.

In connection with the above-mentioned, it can be assumed that a mixed structure was formed in the studied PP/EP/CC composites studied, in which the core–shell structures and separately dispersed particles of the modifier and filler were simultaneously present in the polypropylene matrix. The morphology of the composite may be a PP matrix with incorporated filler particles, EP particles, and boundary layers of PP at the CC/PP and CC/EP interfaces. The ratio between these structures can be different depending on the CC content and mixing conditions.

The results of studies on the strength and relative elongation are shown in Fig. 2. When filling the composition with 5 wt% of CC, the strength index was at the initial level. In this case, the relative elongation index slightly decreased, probably due to the nucleation of filler particles. On increasing the filler content to 10 wt%, the strength and elongation somewhat decrease, but remain constant with further filling up to 50 wt%. This behavior was associated with the presence of calcium stearate on the surface of filler particles and the amorphous nature of EP, which was confirmed by DTA results.

A similar behavior of the compositions was observed when determining the impact strength before and after freezing (Fig. 3). At the filler content of 5-10 wt% in the compositions, their impact strength index increases. This may also be due to the effect of the nucleative activity of CC particles during PP crystallization, which was confirmed by the results of thermal analysis.

Investigation results showed that the impact strength of compositions filled with CC practically did not decrease after freezing. This effect was enhanced by the plasticizing action of EP and the formation of an elastomeric phase, probably due to a change in the particle size of the elastomeric modifier [1]. This increased the ability of the composition to dissipate the impact energy, which reduced the brittlness of the original polymer. A further increase in the CC content from 20 to 50 wt% increased the brittleness of the material. Thus, the optimal amount of filler was 5–20 wt%.

Conclusions

As a result of the research conducted, the following conclusions can be drawn.

1) The presence of calcite concentrate does not significantly affect the crystal structure of polypropylene modified with a polyolefin elastomer synthesized on metallocene catalysts by using a new technology.

2) It was shown that the presence of polyolefin elastomer and calcite concentrate reduced the effective activation energy of oxidative thermal degradation of composites and the technological characteristics of thermal stability by 12%. This indicated that, in the presence of additives, the structuring in the system decreased, which manifested itself in a decrease in the viscosity of the compositions.

3) It was found that the calcite concentrate at a low (5 wt%) and medium (10-20 wt%) content increased the melting and crystallization temperatures by 2°C. When the content of calcite concentrate was 20-50 wt%, the intervals of phase transitions of melting and crystallization narrowed by 3 and 1°C, respectively.

4) At a low content of calcite concentrate filler of up to 5 wt%, the modified calcite particles can serve as additional nucleators, which was reflected in an increasing strength and impact strength by 5 and 6%, respectively, compared with those the unfilled composition. At the same time, calcium stearate molecules had a plasticizing effect at the interface, which partially neutralized the action of the nucleator, due to which their effect on the crystal structure was minimal.

Thus, the extraordinary decrease in the viscosity of melts of filled modified polypropylene compositions in a wide range of concentrations, the “soft” effect on the crystal structure of composites even at a high filler content were probably associated with good wetting of the surface of modified calcite concentrate particles by the PP melt, the uniform distribution of the filler in the mixture of polymers, and the plasticizing effect of polyolefin elastomer molecules and calcium stearate on the surface of the filler.

The use of the latest polyolefin elastomer as a modifier and calcite concentrate as a filler makes it possible to control the technological and physicomechanical properties of PP-based polymer compositions intended for the manufacture of vehicle parts for various purposes.

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