UDC 678.7
DOI: 10.15587/2312-8372.2018.152056

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REGULATION OF RHEOLOGICAL AND MECHANICAL PROPERTIES OF POLYPROPYLENE COMPOSITIONS FOR AUTOMOTIVE PARTS

Об'єктом дослідження є технології отримання наповнених ударостійких композицій на основі поліпропілену для виготовлення деталей автомобілів. Головною проблемою є зниження міцності і технічних характеристик зі збільшенням кількості наповнювача в композиціях. Для вирішення цієї проблеми запропоновано введення модифікатору в кількості 5 % мас. до наповнених поліпропіленових композицій.

Вивчено вплив наповнювача та модифікатора на реологічні та механічні властивості композицій на основі поліпропілену. Встановлено, що наявність концентрату кальциту як наповнювача та пропілен-октенового блокспівполімеру як модифікатора в композиції сприяє зниженню її в'язкості, що обумовлено переважним впливом емульгуючої дії стеарата кальцію над загущуючим ефектом мінерального наповнювача. Показано збільшення показника текучості розплаву в композиціях з 5 % пропілен-октенового блокспівполімеру, що пояснюється його пластифікуючою дією та хорошим суміщенням з поліпропіленом. Показано, що введення наповнювача до 10 % мас. підвищує ударну в'язкість у порівнянні з вихідним поліпропіленом. Подальше збільшення вмісту наповнювача до 20 % в композиціях знижує ударну в'язкість майже до значення для вихідного поліпропілену при некритичному зменшенні міцності при розриві. Показано, що наявність 5 % мас. модифікатора в композиціях підвищує значення відносного подовження.

Визначено, що розроблені композиції з 5 % мас. модифікатора та з варіюванням кількості наповнювача можуть використовуватися для виробництва деталей автомобілів різного призначення без суттєвих змін технологічного циклу. Перевагою досліджених композицій є зменшення енерговитрат на переробку високонаповнених композицій. Впровадження розроблених технологій не вимагає додаткових капіталовкладень на переоснащення підприємства, оскільки розроблені композиції можуть перероблятись з використанням звичайного екструзійного обладнання.

Ключові слова: *поліпропілен, концентрат кальциту, пропілен-октеновий блокспівполімер, реологічні властивості, механічні властивості, ударна в'язкість, деталі автомобілів.*

1. Introduction

The steady increase in the use of plastics in the automotive industry over the past decade has led to the fact that from 100 to 120 kg of car weight falls on plastics (for cars) [1]. Most of them are now made up of thermoplastic polymeric materials. Although the use of polyurethane foam and polyester fiberglass is still quite common, but it gradually decreases. Leading position in the exterior and interior of the car wins polypropylene in the form of various modifications. Polypropylene compositions with rubbers and mineral fillers are successfully used for the manufacture of large-sized decorative and structural automotive parts with enhanced scratch resistance (instrument panels, bumpers, etc.) [2, 3]. Expansion of the use of plastics in the design of the car (Fig. 1) is justified by the fact that as a result, the vehicle's own weight decreases, fuel costs and parts wear are reduced, and the payload increases accordingly. The problem of increasing the durability of parts and components due to the corrosion resistance of plastics is largely solved, a reduction in the level of working noise and so on is achieved.

The injection of mineral fillers in polymers allows to create materials with the necessary performance characteristics and helps to reduce the cost of products [4]. For example, polyamides filled with mineral fillers and fiberglass, polypropylene, polycarbonates, etc., are used to make sports car bodies [5].

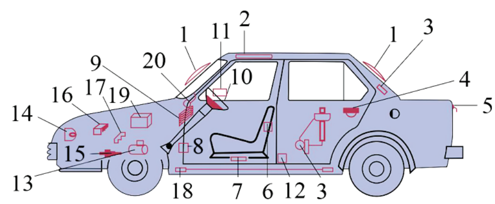

Fig. 1. The use of polymer composite materials for automotive parts: 1 – wiper; 2 – hatch; 3 – motor housing; 4 – door handles; 5 – tail lights; 6 – door locks; 7 – seat control knobs; 8 – fuse panel; 9 – dashboards; 10 – decorative details of the steering wheel; 11 – side mirrors; 12 – seat belt box; 13 – air fan; 14 – headlights; 15 – automatic blocking system; 16 – DIS system; 17 – carburetor parts; 18 – elements of electrical wiring; 19 – central power supply panel; 20 – wiper drive

The main problem, as a rule, is a decrease in strength and technical characteristics with an increase in the amount of filler in the compositions. In this regard, the development of polymeric composite materials with enhanced technical characteristics for car parts is an important task.

2. The object of research and its technological audit

The object of research is the technology of producing filled impact-resistant compositions based on polypropylene (PP) for the manufacture of automotive parts.

ISSN 2226-3780

Polypropylene is one of the main materials for the production of polymeric automotive parts due to a wide range of properties and the ability to be processed in almost all ways [6]. The main requirements for bumper systems of automobiles are high impact strength and rigidity [7].

The research results [8] of the effect of varying degrees of filling with nano-clay, talc and calcium carbonate in polypropylene (PP) filled with wood flour are known. It is shown that samples containing 7 mass % calcium carbonate is distinguished by good physico-mechanical properties, but additionally it is supposed to use polypropylene with graft maleic anhydride. One of the directions in the creation of materials with increased impact resistance is the modification of filled polymers with elastomers [9]. The authors of [10] show that modifying PP by the metallocene ethylene-propylene elastomer leads to a significant increase in impact strength and elongation at break. At the same time, the disadvantage is a decrease in the elastic modulus and yield strength. On this basis, one of the most problematic places is the choice of the optimal composition of the composition to ensure the necessary operational properties of the material.

3. The aim and objectives of research

The aim of research is development of new polymeric composite materials based on polypropylene to obtain materials with desired properties for automobile parts by determining the effect of the modifier and the concentration of mineral filler on the rheological and mechanical characteristics.

To achieve this aim it is necessary to perform the following tasks:

1. To determine the effect of the content of calcite concentrate on the rheological properties of a polypropylene melt.
2. To determine the effect of the content of the modifier on the rheological properties of the filled compositions.
3. To determine the dependence of impact strength on the composition of the compositions.
4. To determine the effect of the composition of the compositions on the strength and elongation.

4. Research of existing solutions of the problem

The injection of fillers and elastomers affects the performance properties of the polymer material and the ability of the material to be processed. The main technological factor determining the method of processing is the fluidity of the composition [11]. Filling always leads to complications in the formation of products due to an increase in melt viscosity [12, 13]. Known compositions [14] based on PP and ethylene-propylene rubber, which correspond to the technical characteristics of bumpers and other parts of some cars with a high level of impact strength. But despite this, the melt flow rate (MFR) of such mixtures reaches only 3–6 g/10 min. The authors of [15] show that the addition of natural rubber or ethylene-propylene-diene monomeric rubber to polypropylene significantly increases the impact strength at a rubber content of more than 20 %. However, the strength decreases with increasing rubber content. The authors of [16] investigated the modification of PP epoxidized with natural rubber by compounding in the melt and vulcanization. It is shown that a mixture of 40/60 PP/epoxidized rubber has high rates of relative elongation and impact strength compared to unfilled polypropylene, up to 68 and 56 %, respectively. But the use of sulfur for vulcanization will increase the cost of the final product. In [17], a polypropylene composite filled with wollastonite is investigated with the addition of silicone rubber and maleic anhydride. It is shown that the addition of 5 % rubber to compositions with a wollastonite content of 10–40 % provided increased notch impact strength and bending strength, but reduced non-notched impact strength and strength.

Rheological studies allow to determine the influence of the components of the composition on the properties of the polymer melt [18]. Melts of filled polymers can be considered as concentrated suspensions. For such systems, the possibility of interaction between particles, which affects the character of the flow, should be taken into account. It is known that the properties of such polymer compositions are determined by the content of the filler, the size and degree of aggregation of the particles, as well as the surface characteristics of the filler [4].

In order to increase the efficiency of fillers, a special surface treatment is used [19]. For example, without processing the proportion of calcium carbonate (chalk), the most commonly used filler, large aggregates are formed, which are extremely difficult to evenly distribute in the polymer matrix, which leads to a sharp drop in the physico-mechanical characteristics [20]. Another important aspect is the adsorption capacity of the filler. Fatty acids make the surface of the filler hydrophobic, which, firstly, increases the compatibility of the filler with a non-polar polymer, and secondly, significantly reduces water absorption during storage of the filler. It also has a positive effect on the physico-mechanical characteristics, since water weakens the interaction at the interface.

5. Methods of research

Filled compositions based on polypropylene brand 21030 are used, containing (5–50) mass % of mineral filler. As a modifier, propylene-octenoic block copolymer (POBC) «Vistamaxx 6202» (ExxonMobil, USA) are used. Calcite concentrate (CC) of the 1TK brand (Technokom LLC, Ukraine) with a particle size of 2.5 μm (max 20 μm – 1.5 %) is used as a filler, due to its prevalence, accessibility and low cost [21]. The composition of calcite concentrate includes polyolefin and calcium carbonate treated with stearic acid. Polymer compositions are obtained by mechanical mixing of the starting components on an extruder PP-27x30 (USSR). The temperature in the zones of the extruder is 155–210–200–200 °C, the screw rotation speed of 30 rpm. Viscosity (η) of the melts was determined using a MV-2 (USSR) capillary viscometer in the range of shear stresses $(0.1 \div 5.7) \cdot 10^4$ Pa at a temperature of 230 °C. Melt flow rate (MFR) are examined according to GOST 11645-73 on the «IIRT» device (USSR) at a temperature of 230 °C and a load of 2.16 kgf. The flow pattern n is determined from the tangent angle at this point of the flow curve. The impact strength of the composites is determined according to GOST 4647-80. Determination of strength and relative elongation of composites is carried out according to GOST 11262-80.

6. Research results

As a research result, it is established that with CC increase, the viscosity of the composition decreases over the entire range of concentrations and shear stresses (Fig. 2). This contradicts the traditional laws of the flow of melts filled with solid additives, for which an increase in viscosity is typical.

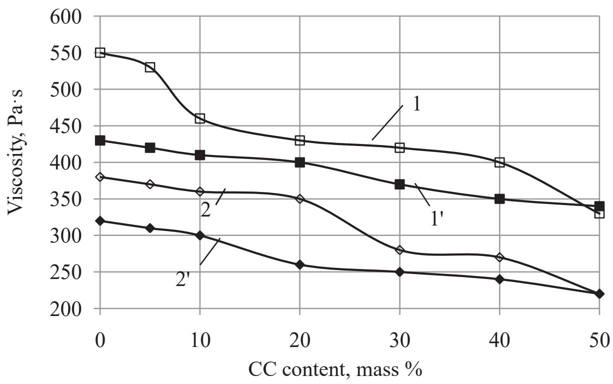

Fig. 2. The effect of the calcite concentrate (CC) content on the viscosity for compositions: curves 1, 2 – PP+CC; curves 1′, 2′ – PP+5 % POBC+CC; for shear stresses $\tau\cdot10^{-4}$ Pa: 1, 1′ – 4.2; 2, 2′– 5.69

This phenomenon may be due to the fact that, in order to improve the rheological properties and wetting of the surface, the CCs are often treated with stearic acid or coupling agents in the amount of 0.5–3 % [22]. Processing improves the compatibility of the filler with a hydrophobic polymer, reduces water absorption during storage, which has a positive effect on the physico-mechanical characteristics [4, 23]. As a result, calcium stearate is formed, in the molecule of which the non-polar «tail» (Fig. 3) in the form of a chain of stearic acid, the Ca–Ca compound consists of molecules of stearate and calcium carbonate, respectively. At the same time, the acid chain is located on the surface of the molecule [24]. The presence on the surface of the used filler of long hydrocarbon chains that have an affinity for PP macromolecules ensures its uniform dispersion in the melt, and also contributes to a sharp decrease in the abrasive effect of the filler on the extrusion equipment.

The viscosity of melts of polymer suspensions PP/CC is determined by two competing factors: the emulsifying action of non-polar «tails» of the acid leads to a decrease in the melt viscosity, and the solid mineral additive contributes to its increase for the formation of aggregates. The predominant influence of the compatibilizing action of stearic acid chains on the surface of calcium carbonate molecules leads to a decrease in the melt viscosity of the system.

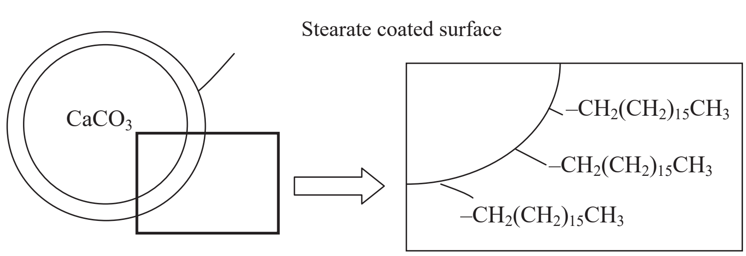

Fig. 3. Diagram of the structure of calcium carbonate surface

A similar effect of a significant reduction in viscosity is also described for compositions consisting of polyvinyl chloride with water-repellent additives based on stearic acid, which activity increases in the series: zinc stearate, calcium stearate, stearic acid [24].

Compositions filled with calcite concentrate, as well as the initial polypropylene, have been investigated to reveal an anomaly of viscosity, that is, with an increase in stress or shear rate, the viscosity decreases.

The behavior of such liquids is described by a step equation:

$$\tau=\eta\cdot\gamma^{n},$$

where n – the flow index. It is found that in compositions based on polypropylene filled with CC, the deviation degree from the Newtonian flow regime is complex (Table 1). The described dependence is due to the fact that the index n, like viscosity, depends on many factors with the predominant action of one of them in each specific case.

Table 1

The effect of calcite concentrate content on the flow regime of n filled compositions

CC content, mass %	For compositions PP+CC		For compositions PP+5 % POBC+CC	
	n, at $\tau\cdot10^{-4}$ Pa		n, at $\tau\cdot10^{-4}$ Pa	
	5.69	1.61	5.69	1.61
0	2	1.5	2	1.5
5	2	1.5	2	1.3
10	1.6	1.2	1.9	1.5
20	1.9	1.3	2	1.4
30	2	1.4	1.9	1.2
40	2.1	1.5	2	1.4
50	2.3	1.5	1.9	1.5

It is established that with an increase in the CC content to 50 mass %, MFR in the composition increases from 3.1 g/10 min without CC to 6.6 g/10 min at 50 mass % of filler. At the POBC injection as an elastomer in the composition in the amount of 5 mass %, the curves of the MFR dependence on the CC content are of a similar nature ranging from 3.4 g/10 min without CC to 6.9 g/10 min at 50 mass % (Fig. 4). This is due to a good combination of POBC with PP and its plasticizing effect. The plasticizing effect of the composition, modified by elastomer, compared with PP filled with 50 mass % of CC, is 4.3 %.

The impact strength indicator characterizes the strength of the material under impact loads. The elastic modifier phase, coupled to the polymer, ensures uniform distribution and damping of the impact energy, whereby the modified polymeric materials withstand a higher shock load.

When the CC content 5–10 mass %, the impact strength rises somewhat (Fig. 5), which may be due to the effect of nucleation of polypropylene by the calcite concentrate. This effect is enhanced in the POBC presence, as a plasticizer. The increase in the CC content from 20 to 50 mass % leads to increased fragility of the material.

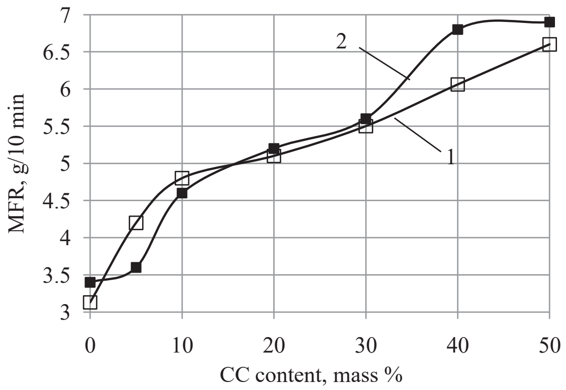

Fig. 4. The effect of the CC content on the MFR of the compositions: 1 – PP+CC; 2 – PP+5 % POBC+CC

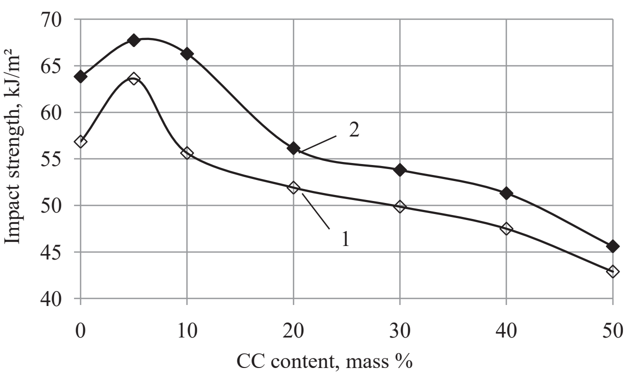

Fig. 5. The effect of the CC content on the impact strength of the compositions: 1 – PP+CC; 2 – PP+5 % POBC+CC

At the injection of 5 % CC in the composition, the strength at break increases (Fig. 6). The strength of the PP+CC compositions with an increase in the CC content from 10 to 50 mass % reduces by 39 %. While the strength of the compositions containing 5 mass % of POBC, with a content of 10–50 mass % of CC almost does not change.

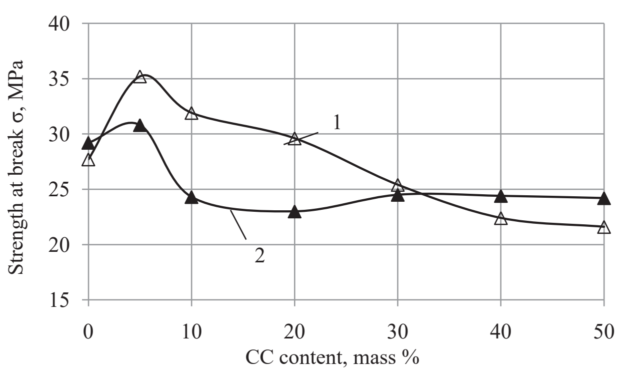

Fig. 6. Dependence of strength at break on the CC content in the compositions: 1 – PP+CC; 2 – PP+5 % POBC+CC

POBC injection in the amount of 5 mass % to PP increases the relative elongation from 112 % to 140 %. When the CC content to 10 mass % in compositions with and without 5 % of POBC, the elongation decreases by 74 and 82 %, respectively. A further increase in the CC content to 50 mass % does not entail a significant change in these indicators.

7. SWOT analysis of research results

Strengths. The advantage of the investigated compositions is the reduction of energy consumption for the processing of highly filled compositions, which is associated with a decrease in their viscosity, compared with the original polypropylene. The use of modified filler ensures its uniform dispersion in the melt and a sharp decrease in its abrasive effect on the extrusion equipment.

Weaknesses. The disadvantage of the compositions is the use of propylene-octenoic block copolymers as a modifier for controlling the properties of the composition, which is not produced by the Ukrainian industry, may lead to an increase in production costs.

Opportunities. Developed compositions based on polypropylene with 5 mass % propylene-octenoic block copolymers with varying content of calcite concentrate can be used to produce parts for automobiles of various purposes without significant changes in the technological cycle.

Threats. The implementation of the developed technologies into production does not require additional capital investments for the re-equipment of the enterprise, since the compositions developed can be processed using conventional extrusion equipment. Adding filler in the composition allows to adjust the necessary rheological and mechanical parameters of the compositions, while the filling will reduce the cost of production, since the cost of the filler is less than the cost of polypropylene, as the main polymer.

8. Conclusions

1. It is established that the injection of 5–20 mass % of calcite concentrate allows to adjust the rheological properties of the melts of compositions based on polypropylene. It is shown that with an increase in the concentration of the filler, the viscosity of the melts decreases in comparison with the initial polymer, which is due to the predominant influence of the emulsifying action of calcium stearate over the thickening effect of the mineral filler. The investigated systems are typical non-Newtonian fluids.

2. The increase in the melt flow index of the compositions with 5 % propylene-octenoic block copolymer is due to its plasticizing effect and good combination with polypropylene.

3. The increase in the CC content to 10 mass % increases the impact strength by 10 % compared to the original polypropylene. A further increase in the content of calcite concentrate to 20 % leads to a decrease in impact strength almost to the value for the output polypropylene with a non-critical decrease in tensile strength.

4. With the injection of 5 mass % of calcite concentrate in the composition of the tensile strength increases. With further increase in the content of the filler from 10 to 50 mass % strength is reduced by 39 %. The strength of the compositions containing 5 mass % of propylene-octenoic block copolymers, with a content of 10–50 mass % of calcite concentrate is almost unchanged. When the CC content to 10 mass % in compositions with and without 5 % propylene-octenoic block copolymers, the elongation decreases by 74 and 82 %, respectively. A further increase in the content of the filler to 50 mass % does not entail a significant change in this indicator.

Developed compositions based on polypropylene with 5 mass % of propylene-octenoic block copolymer with varying content of calcite concentrate can be used for the production of automotive parts for various purposes.

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