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DEVELOPMENT OF THERMOPLASTIC COMPOSITE MATERIALS BASED ON MODIFIED POLYPROPYLENE

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To improve the physical-mechanical and thermophysical properties of polypropylene-based thermoplastic composite materials, we performed modification of a polymer matrix by reactive extrusion of polypropylene in the presence of benzoyl peroxide and polysiloxane polyols. Modified polypropylene was compounded with basalt, carbon, and para-aramide reinforcing fillers in a screw-disc extruder. It was established that the reinforcement of modified polypropylene by basalt fibers ensured a 110% increase in tensile strength. The reinforcement of modified polypropylene by carbon fibers allowed fabricating thermoplastic composite materials with tensile strength increased by 14%. The maximum reinforcing effect was observed by using para-aramide fibers as reinforcing fibers for modified polypropylene with tensile strength increased by 30% as compared with initial polypropylene. It was determined that the obtained thermoplastic composite materials based on modified polypropylene can be processed into products by the most productive methods (extrusion and injection molding). The developed materials exhibited improved thermal stability. The proposed ways of modification methods provide substantial improvement in physical-mechanical and thermophysical properties of modified polypropylene-based thermoplastic composite materials as compared with initial polypropylene. In addition, they ensure a significant increase in service properties of the products prepared from thermoplastic composite materials based on modified polypropylene.

Keywords: modified polypropylene, benzoyl peroxide, polysiloxane polyol, thermoplastic composite materials, reinforcing filler.

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Introduction

The development of modern techniques causes the urgent need of constructional materials with improved strength, exploitation safety, thermal stability, low density, etc.

The macromolecule cross-linking is as effective way of improving the properties of polyolefins. This approach can provide the formation of 3D structure due to intermolecular chemical bonds hereby and ensure the enhancement of the following service properties of polyolefins:

– an increase in the maximum operational temperature;

– a decrease in deformation under loading both at normal and increased temperatures;

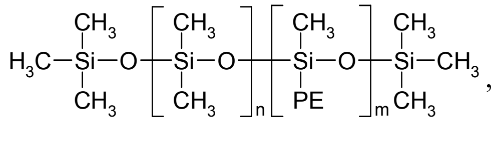
– an improvement in physical-mechanical properties (tensile or bending strengths);

– increased resistance of abrasive wear;

– increased stability under dynamic loads;

– improved chemical resistance.

Earlier [1,2], we conducted the modification of polypropylene (PP) by a mixture of benzoyl peroxide (BP, 0.25 wt.%) and polysiloxane polyols (PSP) having the following structures:



were PE= $C_3H_6-O-(C_2H_4-O)_x-C_3H_6-O-CH_3$ / H

with different content of hydroxyl groups (1,8% and 0,6% for PSP-1 and PSP-2, respectively).

We established that this way of modification allowed us to change purposefully the service properties of polypropylene [2]. It was determined that the PSP type of modifiers with reduced content of hydroxyl group was the most effective one. The optimal quantity of PSP-1 and PSP-2 modifying additives was 1.25 wt.% and 0.75 wt.%, respectively [2].

Table 1 summarizes some properties of polypropylene modified by mixture of 0.25 wt. BP with 1.25 wt.% PSP-1 (MPP-1) and polypropylene modified by mixture of 0.25 wt.% BP with 0.75 wt.% PSP-2 (MPP-2).

Table 1

Properties of polypropylene modified by mixture of 0.25 wt. BP with 1.25 wt.% PSP-1 (MPP-1) and polypropylene modified by mixture of 0.25 wt.% BP with 0.75 wt.% PSP-2 (MPP-2)

Property	PP	MPP-1	MPP-2
Tensile strength, MPa	26.0	54.6	65.8
Elongation at break, %	109.0	12.5	13.3
Melt fluidity index, g/10 min	2.29	3.3	3.1
Young module, GPa	0.3	4.4	4.9

The samples of modified PP (MPP-1 and MPP-2) exhibited enhanced properties as compared with initial polypropylene. Thus, such modification of polypropylene can be used in creation of a polymer matrix for thermoplastic composite materials (TCM).

We conducted the reinforcement of a modified polypropylene with fibers of different nature to improve the physical-mechanical properties of TCM.

Nowadays, glass fibers are the most common reinforcing filler for polypropylene [3–6]. Application of glass fibers as reinforcing filler provides obtaining TCMs with improved physical-mechanical and thermophysical properties (low shrinkage). However, the reinforcement of polypropylene by glass fibers leads to a significant decrease in the impact strength of TCM [7].

At the same time, basalt fibers (BF) are considered as common fillers for polypropylene [8–12]. They have high strength, thermal stability and relatively low price. As compared with glass, basalt fibers ensure a 10–20% increase in tensile module, tensile strength (especially, after temperature loads) and higher chemical resistance in acid and alkaline media. Reinforcement of PP by basalt fibers allows obtaining TCM with a tensile strength of 37.5 MPa. Increasing adhesion strength in the system «polymer–reinforcing filler» via fiber activation and its dressing by adhesion promoters can provide preparing a thermoplastic composite material with a tensile strength of 67.5 MPa [9].

It is widely known that carbon fibers (CF) are also often used for polypropylene reinforcing Tensile strength of these TCMs can reach 57.2 MPa [13].

The most promising way of fabrication of TCMs based on polypropylene is reinforcing by organic fibers, para-aramide in particular. The use of such reinforcing fibers limits residual stresses in a polymer matrix because their nature is close to the polymer matrix. Para-aramide fibers (PAF) are more elastic than carbon and show good abrasion resistance. Tensile strength of TCMs on their basis is 86.7 MPa [14].

Experimental

For polypropylene reinforcing, we used chopped (with a length of 17.5–20.0 mm) basalt fibers (manufactured by Ltd «Technobasaltinvest», Ukraine), carbon fibers «U-230» (manufactured by Hamwell Composites, Czech Republic), and para-aramide fibers «Arselon» (anufactured by OJSC «SvetlogorskKhimvolokno», Republic of Belarus).

Compounding of modified polypropylene with reinforcing fillers was done in the screw-disc extruder. Injection molding of standard samples was performed by using a molding machine Kuasy 25x32/1. Mechanical and thermophysical properties of prepared TCMs were studied according to ISO standards for plastic materials.

Results and discussions

The tensile strength of TCMs based on both initial (PP) and modified polypropylene (MPP-1, MPP-2) are shown in Fig. 1.

According to results shown in Fig. 1, the application of modified polypropylene as a polymer matrix reinforced by basalt fibers provides the improvement of tensile strength by 110% (from 37.5 MPa to 78.8 MPa). When using MPP usage for the preparation of a carbon fibers reinforced TCM,

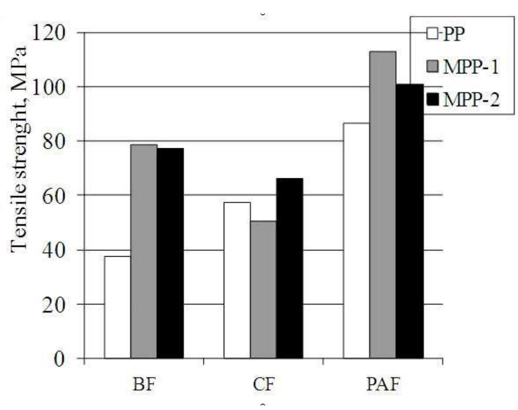


Fig. 1. The tensile strength of TCMs based on initial (PP) and modified polypropylene (MPP-1, MPP-2) reinforced by basalt (BF), carbon (CF) and paraaramide (PAF) fibers (reinforcing degree is 30 wt.%)

the tensile strength is 66.3 MPa, which 14% higher than when using an initial PP. The maximum reinforcing effect was observed by using para-aramide fibers (Armos) as reinforcing fibers for modified polypropylene. The tensile strength of the obtained TCM was 112.9 MPa.

It follows from the analysis of the obtained data that the application of modified polypropylene as a polymer matrix for TCM creation is very effective. Thus, the tensile strength grows by 14–110%, depending on fibers nature. This effect can be caused by the change in the supramolecular structure of a polymer and by an increase in the adhesion interaction in the system «polymer–reinforcing filler».

When determining the loads ratio of a TCM, it is very important to measure the normal stress ratio corresponding to linear deformation under a linear stress state to the limits of proportionality (Young's modulus). The results of the determination of Young modulus are shown in Fig. 2.

According to obtained data, we can make a conclusion that TCMs based on modified polypropylene (MPP-1, MPP-2) and reinforced with basalt fibers are more «rigid». Thus, these materials are less able to «cold flow» under static loads and more stable towards crack formation. Kaushal and Singh [15] showed that the obtained TCM can resist under static and dynamic loads within increasing energy that is spent on TCM destruction.

The TCMs based on modified PP can be processed into wares by the most productive ways (extrusion and injection molding). The melt fluidity index (MFI) of MPP-1 with 30 wt.% degree of reinforcing is as follows: 1.3 g/10 min, 1.6 g/10 min, and 2.0 g/10 min for basalt fibers, carbon fibers, and para-aramide fibers, respectively. MFI for MPP-2 with 30 wt.% degree of reinforcing is as follows: 1.7 g/10 min, 1.8 g/10 min, and 2.2 g/10 for basalt fibers, carbon fibers, and para-aramide fibers, respectively.

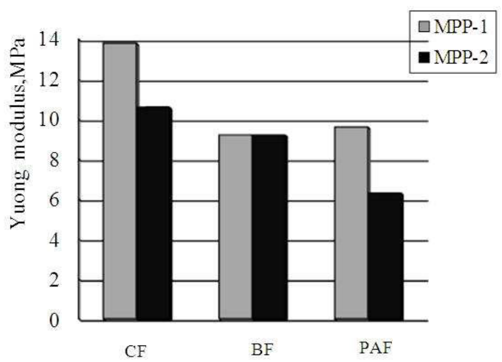


Fig. 2. The Young modulus of TCMs based on modified polypropylene (MPP-1, MPP-2) reinforced with basalt (BF), carbon (CF) and paraaramide (PAF) fibers (reinforcing degree is 30 wt.%)

According to ISO 3451 standard, there is a need to know the real and theoretical fibers content in the polymer matrix.

To determine a real reinforcing degree of MPP, a pyrolysis analysis of the obtained TCMs was conducted (Table 2).

Table 2

Theoretical (T) and real (R) reinforcing degree of modified polypropylene (wt.%)

Fibers nature	T	R
Carbon fibers	30	22
Basalt fibers	30	24
Para-aramide fibers	30	28

From the analysis of data given in Table 2, we can observe that real and theoretical reinforcing degrees are not the same. This can be a result of «specific» compounding of reinforcing fillers with polymer matrix, which depends on the screw-disc operation and construction.

To determine the temperature operation range and processing parameters for the production of ready-to-use wares based on modified polypropylene, we conducted the investigation of thermal stability by the TGA method (thermogravimetric analysis) (Fig. 3).

It follows from the analysis of TGA data that

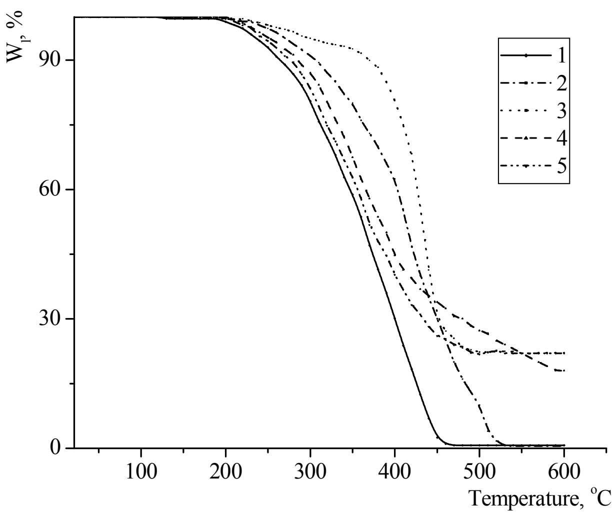


Fig. 3. The TGA data of initial and modified polypropylene and TCM reinforced with different fibers:
1 – initial polypropylene; 2 – modified polypropylene (MPP-1); 3 – MPP-1 reinforced by basalt fibers; 4 – MPP-1 reinforced by para-aramide fibers; 5 – MPP-1 reinforced by carbon fibers (reinforcing degree is 30 wt.%)

the nature of reinforcing filler have a significant influence on the thermal stability of the obtained TCM. Thus, the composite materials reinforced by basalt fibers exhibited an active destruction temperature of 340^{0}C, which is much higher than for similar compositions based on initial polypropylene [8], where an active destruction temperature was approximately 265^{0}C. An increase in thermal stability can be caused by more intensive interaction at the phase boundary «polymer–fiber» and by appearance of additional thermal-stable bounds between polypropylene macromolecules due to the «peroxide crosslink» process. However, the change of an active destruction temperature was not observed for the modified polypropylene reinforced by CF and PAF [13,15], which, probably, results from the absence of any interactions at the phase boundary «polymer–fiber» due to specific features of a filler surface.

Conclusions

The reinforcement of modified polypropylene with mineral and synthetic fibers is a promising way to obtain thermoplastic composite materials. The application of proposed modification methods can provide a significant increase in physical-mechanical and thermophysical properties of TCMs based on MPP, as compared with polypropylene, which will improve the service properties of wares.

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РОЗРОБКА ТЕРМОПЛАСТИЧНИХ КОМПОЗИЦІЙНИХ МАТЕРІАЛІВ НА ОСНОВІ МОДИФІКОВАНОГО ПОЛІПРОПІЛЕНУ

Д.О. Червяков, О.С. Свердліковська, О.В. Червяков

Для покращення фізико-механічних і теплофізичних властивостей термопластичних композиційних матеріалів на основі поліпропілену, було здійснено модифікацію полімерної матриці шляхом реакційної екструзії поліпропілену у присутності пероксиду бензоїлу та полісилоксанполіолів. Модифікований поліпропілен суміщали з базальтовими, вуглецевими та параарамідними армуючими наповнювачами у черв'ячно-дисковому екструдері. Встановлено, що при армуванні модифікованого поліпропілену базальтовим волокном рівень міцності при розтягу збільшується на 110%. Армування модифікованого поліпропілену вуглецевим волокном дозволяє отримати термопластичні композиційні матеріали з міцністю при розтягу, збільшеною вище на 14%. Максимальний армуючий ефект спостерігався при армуванні модифікованого поліпропілену параарамідними волокнами, міцність при розтязі отриманого органопластику була вище на 30% у порівнянні з вихідним поліпропіленом. Встановлено, що отримані термопластичні композиційні матеріали

на основі модифікованого поліпропілену можуть перероблюватися у вироби найбільш продуктивними методами – екструзією та литтям під тиском. Розроблені матеріали мають підвищений рівень термічної стабільності. Визначено, що застосування запропонованих методів модифікації значно покращує низку фізико-механічних та теплофізичних властивостей термопластичних композиційних матеріалів на основі модифікованого поліпропілену у порівнянні з вихідним поліпропіленом та дозволяє значно збільшити рівень експлуатаційних властивостей виробів на їх основі.

Ключові слова: модифікований поліпропілен, пероксид бензоїлу, полісилоксанполіол, термопластичні композиційні матеріали, армуючий наповнювач.

DEVELOPMENT OF THERMOPLASTIC COMPOSITE MATERIALS BASED ON MODIFIED POLYPROPYLENE

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To improve the physical-mechanical and thermophysical properties of polypropylene-based thermoplastic composite materials, we performed modification of a polymer matrix by reactive extrusion of polypropylene in the presence of benzoyl peroxide and polysiloxane polyols. Modified polypropylene was compounded with basalt, carbon, and para-aramide reinforcing fillers in a screw-disc extruder. It was established that the reinforcement of modified polypropylene by basalt fibers ensured a 110% increase in tensile strength. The reinforcement of modified polypropylene by carbon fibers allowed fabricating thermoplastic composite materials with tensile strength increased by 14%. The maximum reinforcing effect was observed by using para-aramide fibers as reinforcing fibers for modified polypropylene with tensile strength increased by 30% as compared with initial polypropylene. It was determined that the obtained thermoplastic composite materials based on modified polypropylene can be processed into products by the most productive methods (extrusion and injection molding). The developed materials exhibited improved thermal stability. The proposed ways of modification methods provide substantial improvement in physical-mechanical and thermophysical properties of modified polypropylene-based thermoplastic composite materials as compared with initial polypropylene. In addition, they ensure a significant increase in service properties of the products prepared from thermoplastic composite materials based on modified polypropylene.

Keywords: modified polypropylene; benzoyl peroxide; polysiloxane polyol; thermoplastic composite materials; reinforcing filler.

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