

EFFECT OF SMALL ADDITIVES OF POLYAMIDE MODIFIED BY POLYVINYLPIRROLIDONE AND MONTMORILLONITE ON POLYPROPYLENE TECHNOLOGICAL PROPERTIES AND HEAT RESISTANCE

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ABSTRACT

The effect of small polyamide additives modified with polyvinylpyrrolidone and montmorillonite on polypropylene technological properties and heat resistance has been researched in the work. It has been determined that the melt flow index of the obtained composites increases by more than 2 times in comparing with pure PP. It has been shown that adding a small amount of polyamide modified by montmorillonite-polyvinylpyrrolidone mixture to polypropylene significantly increases heat resistance of the material. The displacement of the beginning of thermal-oxidation destruction and burning samples into the range of higher temperatures on 114-123°C, dependently on the modified polyamide content has been observed.

Keywords: polypropylene, polyamide, montmorillonite, polyvinylpyrrolidone, mixture, nanocomposite, modification, thermal analysis.

INTRODUCTION

The first attempts to create composites based on polymers and aluminosilicates were made in the 1950's [20]. However, adding up to 40-50 wt % of clays (bentonite, hector, etc.) did not improve the properties of the polymer material primarily owing to unsatisfactory dispersion of the silicate filler [18]. Substantial progress in the creation of polymer-silicate nanocomposites of increased physical and mechanical properties in comparison with the basic polymer and traditional dispersive-filled composites was achieved only in the 90's [14]. Currently, the market of layered-silicate polymer nanocomposites is developing most intensively [13].

In order to reach a significant increase of polymer material properties, a uniform distribution of silicate nanoparticles in the polymer ma-

trix needs to be achieved. The greatest changes in physical and chemical properties could be expected while adding anisometric nanosized filler into a polymer matrix [1]. The particles of layered aluminosilicates have considerable anisometry, in particular, montmorillonite (MMT) and its forms which are intercalated by the low molecular weight substances [15].

ANALYSIS OF RECENT RESEARCH

At present, researchers are greatly focused on obtaining nanocomposites based on thermoplastic polymer matrices and mineral high polar aluminosilicate – montmorillonite [1, 3, 12, 16].

In presented work [2] the polypropylene/montmorillonite nanocomposites are obtained by melt intercalation with two-pin extruder application. With the use of a scanning electron mi-

roscope, the authors have proved that MMT is uniformly dispersed into nano-levels. The tests results of mechanical properties of the above composites showed that the bending strength of the composites with a low MMT content (2 wt %) was higher than that of pure polypropylene (PP).

The nanocomposites of PP and layered silicate Na⁺-montmorillonite (3 wt % and 7 wt %) with a polar compatibilizer, which is maleated PP of two types differing in the molecular weight and the content of polar groups were obtained via the method of intercalation from the melt [8]. The compatibilizer of the low molecular weight and high content of polar groups (4 wt %) promotes intercalation of PP, but poorly combines with it and impairs its thermal properties in nanocomposite. The maximum difference between a dynamic module of a nanocomposite with 3 wt % of clay and PP modulus is observed at 80°C and consists about 65%. It is shown, [8] that the compatibility of non-polar and polar polymers determines the crystalline structure and thermal properties of the composite.

In described work [19] the montmorillonite surface before being mixed with PP was modified by a high molecular weight dispersing agent (DAG). It has been shown, that DAG significantly affects the mechanical properties of the composite. The results of scanning electron microscopy show MMT dispersion into PP in the form of non-dislayered particles.

In most cases the mixing of PE and MMT leads to a decrease of the composite's mechanical strength. Although, the increase of strength and thermal characteristics during adding 3 wt % of MMT, modified by maleated PP to the PP is observed [8].

At the same time, the mixing of polar polyamide (PA) with polar MMT ensures an increase of rigidity and mechanical strength of the composite [7] as well as a significant rise in the temperature of destruction beginning [1].

The authors of the work [17] have shown that intercalated nanocomposite is formed upon the modification of polyamide-6 with nanosilicate.

It was determined [6] that nanocomposites based on the PP/PA-6/organic montmorillonite blend obtained via intercalation in the melt have a higher tensile strength and bending strength in comparison to the unfilled PP. Durability decreases with the content of nano-filler increasing. The impact strength of the described nanocomposites is higher than the impact strength of unfilled PP

and reaches 9,61 kJ/m². In the presence of organic montmorillonite, the crystallization rate of PP and PA-6 increases.

Recently, scientists have focused on blends based on polypropylene and polyamide, whose mixing allows reduction of negative properties of the initial polymers [6, 12]. For instance, non-polar polypropylene during the mixing with polar highly hydrophilic polyamide significantly reduces water absorption of the material, as a result, the influence of humidity on strength and heat resistance of the composites is decreased. On the other hand, PP and PA mixing allows expanding the temperature range of the material operation at the negative temperatures – the fragility temperature of the PP is decreased [12].

However, in order to obtain a homogeneous PP/PA blend a compatibilizer usually of a complex chemical structure, in particular, maleated PP needs to be used [2, 6]. But in this case, the probability of chemical cross-linking of PA macromolecules with a partial loss of fluidity increases.

The paper [5] demonstrates the possibility of obtaining a homogeneous mixture of polyamide and polyvinylpyrrolidone (PVP). This mixture is characterized by high crystallinity degree and higher crystallization temperature. At the same time, the mechanical strength of the material after the modification changes slightly. The homogeneity of the mixture is caused by the physical interaction of polyamide and PVP involving hydrogen bonds. Such an interaction reduces the polarity of both polymers, resulting in hydrophobic fragments of chains improving compatibility with non-polar PP without additional compatibilizers.

A new method of montmorillonite intercalation by polyvinylpyrrolidone in water solution in an ultrasonic field has been described [11]. The efficiency of the developed montmorillonite-polyvinylpyrrolidone mixture (MPM) upon the PA-6 modification has been confirmed. Adding of MPM in small quantities to polyamide increases its mechanical, thermal-physical and electrical insulation properties, but reduces induced elasticity at stretching.

Based on the positive effects of PP and PA-6 mixing in the presence of PVP and MMT with PVP on the mechanical and thermal properties of PA-6 we have conducted the research of PP mixtures containing a small amounts of PA-6 modified with MPM.

Thus, the aim of the work is to determine the influence of small additives of polycapromide

which is modified by montmorillonite-polyvinylpyrrolidone mixture on thermal stability and fluidity of the polypropylene.

RESEARCH METHODS

Polypropylene (PP) of the Moplen HF501N (the Netherlands) brand with $MFI_{230/2.16}=9,50$ g/10 min, Vicat softening point of $155^{\circ}C$, $\rho^{20}=0,900$ g/cm³, and tapped density $\rho_t=0,53$ g/cm³ were used in present work.

Also polyamide PA6-210/310 (Belarus) was used with $MFI_{230/2.16}=19$ g/10 min, melting temperature $215^{\circ}C$, density $\rho^{20}=1,12$ g/10 min and viscosity ratio 2,68. Before being used PA-6 was dried in vacuum at $90^{\circ}C$ for 2 hours.

As a modifier for polyamide the montmorillonite-polyvinylpyrrolidone mixture derived from water solution in the ultrasonic field [4, 10, 11] at the MMT:PVP component ratio of 1:5 was used.

Polyvinylpyrrolidone (PVP) with molecular weight 12600 ± 2700 , a softening temperature of $140-160^{\circ}C$, and $1,19$ g/cm³ density at $20^{\circ}C$ was used. Before mixing, PVP was dried in the vacuum at $60-70^{\circ}C$ for 2-3 hours.

Also, montmorillonite Fluka SIGMA-ALDRICH with a surface area of 250 m²/g and pH 4-5 was applied in the work.

The thermal analysis of both basic components and compositions based thereon was carried out on the Q-1500D derivatograph connected to an IBM-compatible PC. The above-mentioned device makes it possible for one sample to simultaneously determine weight loss (thermogravimetry – TG), weight loss rate (differential thermogravimetry – DTG) and thermal peaks (differential-thermal analysis – DTA). The research was carried out in dynamic mode in air. The samples were heated at the rate of $3^{\circ}C/min$. The weight sample was upon the average 200 mg. The model substance was aluminum oxide. Derivatographic studies of the samples were carried out in the temperature range of $20-600^{\circ}C$.

The objects of the research were: sample 1 – pure PP, sample 2 – blend composition of PP:(PA-6/MPM) is 95:5, sample 3 – blend composition of PP:(PA-6/MPM) = 85:15, sample 4 – blend composition of PP:(PA-6/MPM) = 70:30.

The melt flow index (MFI) of the initial polymers and their mixtures was determined applying the capillary viscosimeter of IIRT [9].

The samples for studies were obtained as follows: a mixture based on polyamide and MPM

was initially obtained at the ratio of 90:10 wt % [9]. The derived agglomerate was dried in vacuum at $80^{\circ}C$ and mechanically mixed with polypropylene at ratios of 5:95, 15:85, 30:70 wt %. The blends obtained were plasticized by the method described in literature [9]. The last stage was obtaining samples by the injection molding under investigation in the form of standard blades applying the Kuasy 32/25 injection molding machine following the optimal technological parameters: temperatures in zones of the injector's heating cylinder – $170, 195, 235^{\circ}C$; temperature of the injection mould – $68-70^{\circ}C$; injection pressure – 100 MPa; injection boost time – 6 s; cooling time – 25 s.

RESULTS AND DISCUSSION

In order to determine the processability of polymer materials and identify the technological parameters of the process the rheological characteristics are required to be known. Therefore, it was primarily determined how the composition of polypropylene-based composites obtained in the work affects MFI. The results of the studies are presented in Table 1.

Adding polyamide-6 modified by MPM into polypropylene causes the increase of MFI composites, with the content of modified polyamide 15 and 30 wt %. MFI of the composites are higher than MFI of initial PP and PA-6. Adding 5 wt % modified polyamide-6 into polypropylene causes an increase of MFI by almost in 2 times in comparison with PP. The above mentioned confirms the formation of an inverse mixture in melt with a lower viscosity. Accordingly, the described changes have been taken into account during the processing of developed composites by injection molding. The obtained samples were applied for thermal research.

Table 1. Melt flow index of composites based on modified polypropylene

Composition	Mass fraction, wt %	MFI, g/10 min
PP (pure)	-	9,50
PA-6 (pure)	-	19,0
PP: (PA6/MPM)	95:5	17,85
	85:15	22,92
	70:30	23,1

The results of thermal analysis for the samples of composites are presented in Figure 1, while comparison of the DTA curves in Figure 2.

The thermolysis of sample of pure PP occurs within 3 stages (Figure 1a, Table 2). At the first stage, the melting process of the sample takes place in the temperature range of 140-170°C without weight loss. The DTA curve shows an endothermic peak with a maximum at the temperature of 157°C. At the second stage of thermolysis a thermal oxidative degradation of the sample occurs followed by intense weight loss in the temperature range of 230 to 400°C (Table 2). In the DTA curve appears an exothermic peak with a maximum at the temperature of 386°C. At the third stage of PP thermolysis in the temperature range of 400-600°C, the carbonaceous residue burns out as the exothermic peak manifests itself in the DTA curve at the temperature maximum of 422°C.

The DTA curves of the modified PP samples are significantly different in comparison with pure PP (Figure 1b-d, Figure 2). The appearance of shallow endothermic effects on the DTA curves of samples 2 and 4 at the first stage of thermolysis in the temperature range at 80-110°C, corresponded to the emission of physically-bound water. The endothermic effects which are observed on the DTA curves of samples 2-4 in the temperature range of 140-165°C at the second stage of thermolysis correspond to melting of the material. The exothermic effect revealed at the third stage of thermolysis of sample 2 within the temperature range of 165-230°C corresponds to its thermal oxidative destruction similarly for the sample of pure PP (sample 1). The exothermic effects at the third stage of thermolysis of samples 3 and 4 at 160 to 225°C correspond to the PP thermal oxidative destruction, which proceeds simultaneously with recrystallization of polyamide modified with MPM [9].

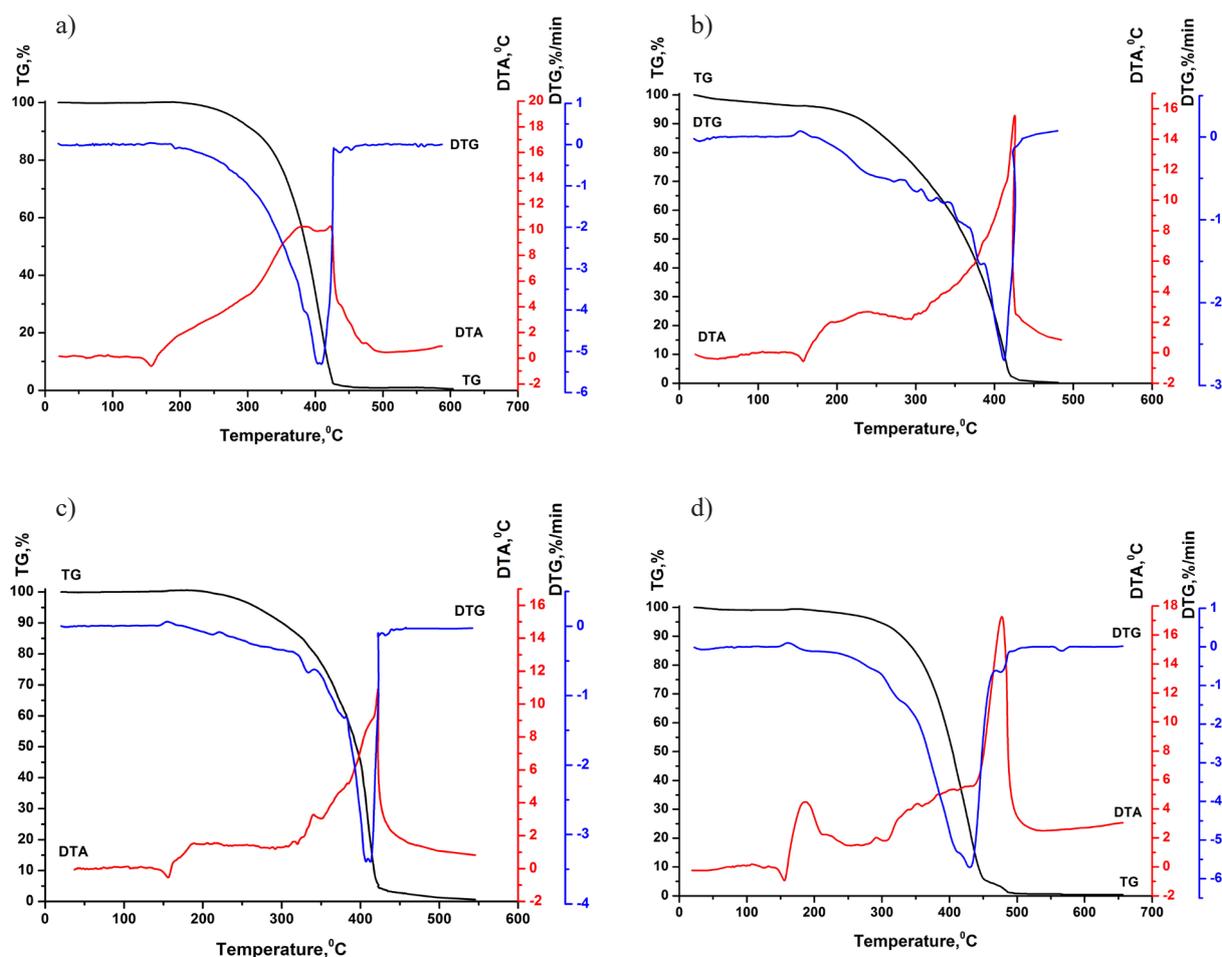


Fig. 1. Thermograms of the composites based on polypropylene and polyamide-6, previously modified with montmorillonite-polyvinylpyrrolidone mixture (MPM): a – sample 1 – PP, b – sample 2 – PP:(PA-6/MPM) = 95:5, c – sample 3 – PP:(PA-6/MPM) = 85:15, d – sample 4 – PP:(PA-6/MPM) = 70:30

Table 2. TG analysis results for the samples of composites

Sample	Thermolysis stage	Temperature range, °C	Weight loss, %
1	I	140-198	-
	II	198-400	65.6
	III	400-600	34.4
2	I	20-140	3.6
	II	140-165	-
	III	165-230	4.7
	IV	230-312	20.3
	V	312-480	71.2
3	I	20-140	-
	II	140-163	-
	III	163-225	0.9
	IV	225-321	13.0
	V	321-545	85.5
4	I	20-140	0.9
	II	140-160	-
	III	160-218	0.6
	IV	218-322	7.1
	V	322-439	77.9
	VI	439-600	13.0

In contradistinction to the pure PP sample, at the fourth stage of thermolysis of the modified samples within 218-322°C temperature range in the DTA curves a shallow endothermic effect is appeared. In this range is occurred the weight loss of samples that corresponds to processes of hydrolytic and oxidative destruction of PA-6 and PVP, as well as to processes of PP thermal oxidative destruction. It should be noted that the depth of endothermic effects increases with an increase of the content of modified PA-6 in the composites.

Within the temperature range of 312-545°C the processes of thermal oxidative destruction and combustion of hydrolysis products of the modified samples which are accompanied by intense weight loss as well as appearance of sharp exothermic peaks observed in the DTA curves (Figure 2). It should be noted that with an increasing of the modified PA-6 content the thermal stability of the samples is rising. This is evidenced by decreasing in the intensity of exothermic effects and their displacement to the range of higher temperatures in comparison with the sample of pure PP. Thermooxidative processes proceed in PP at the temperature of 198°C, in sample 2 – at temperatures higher than 312°C, in sample 3 – at temperatures above 321°C, in the sample 4 – at temperatures above 322°C.

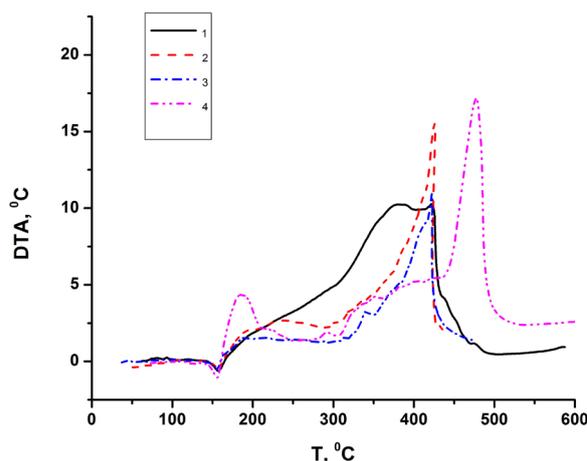


Fig. 2. DTA curves of composites based on polypropylene and polyamide-6, pre-modified MPM: 1 – PP, 2 – PP:(PA-6/MPM) = 95:5, 3 – PP:(PA-6/MPM) = 85:15, 4 – PP:(PA-6/MPM) = 70:30

In contrast to samples 2 and 3 there is a sharp exothermic effect in the DTA curves of sample 4 at 439-600 °C that corresponds to the combustion of the carbonaceous residue which was formed in the presence of significant amount of modified PA-6.

CONCLUSIONS

Consequently, grounding on the studies conducted, it can be argued about the influence of insignificant additives of polyamide, which is modified by intercalated montmorillonite on the technological properties and heat resistance of polypropylene. The MFI of the obtained composites increases by more than 2 times, compared to pure PP, indicating the formation of an inverse mixture in a melt of lower viscosity. The above changes were considered at the selecting of optimal parameters for processing of the developed composites via injection molding.

Thermolysis of samples of modified PP occurs during 5-6 stages, in contrast to the sample of pure PP, the thermolysis of which occurs during 3 stages.

Based on the thermal studies, it can be concluded that adding to polypropylene of 5-15 wt % of polyamide modified by the montmorillonite-polyvinylprolidone mixture significantly increases the thermal stability of material. Above mentioned results are confirmed by the displacement of beginning of processes of thermal oxidative destruction and combustion of samples to higher temperatures on 114-123°C in dependence to the content of modified PA-6.

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