IPPI

Polyolefins Journal, Vol. 11, No. 4 (2024)
DOI: 10.22063/poj.2024.35560.1326

ORIGINAL PAPER

Structure and kinetic regulations of PP-R/PPH-*g*-MAH/ $Al(OH)_3$ based nanocomposites crystallization

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Received: 30 September 2024, Accepted: 30 October 2024

ABSTRACT

The article presents the results of studies of the influence of aluminum hydroxide concentration on the crystallization process regularities of nanocomposites based on compatibilized polypropylene random copolymer and aluminum hydroxide (PP-R/PPH-*g*-MAH/$Al(OH)_3$). The isothermal crystallization kinetics of compatibilized polypropylene random copolymer composites containing 1, 3, 5, 10, 20, 30 and 50 wt.% of aluminum hydroxide was determined by the stepwise dilatometry method using the Kolmogorov-Avrami equation. The crystallization behaviors of composites were investigated on an IIRT-1 device converted into a dilatometer, in the process of stepwise cooling of samples under a load of 5.3 kg. In this study, maleic anhydride functionalized homopolypropylene (PPH-*g*-MAH) was employed as a compatibilizer to enhance the compatibility between the PP-R and $Al(OH)_3$. Considering the dependence of specific volume and free specific volume on temperature, the first-order phase transition was established, and the glass transition temperature values of the composites were determined. The mechanism of formation and development of crystallization centers in the region of the first-order phase transition was investigated. The obtained values of "n" prove that the mechanism or nature of the growth of crystallization centers changes into three-dimensional spherulitic-two-dimensional disc-shaped-one-dimensional rod-shaped with an increase in the amount of aluminum hydroxide in composite. The study of the temperature dependence of the specific volume for the studied samples showed that the first order phase transition occurs at a temperature of 125°C. It was determined that the second order phase transition temperature (the glass transition temperature determined by the dilatometric method) increases with the increase in the amount of filler. **Polyolefins J (2024) 11: 243-253**

Keywords: Polypropylene random copolymer; aluminum hydroxide; crystallization; specific volume; free specific volume; flame retardant; compatibilizer; density; glass transition temperature; compatibilization.

INTRODUCTION

Polypropylene (PP), polypropylene random copolymer (PP-R) and block copolymer of propylene with ethylene belong to the class of semi-crystalline polyolefins, which are widely used in various industrial fields. This paper focuses on the study of kinetic regularities of crystallization and the mechanism of crystal growth. The crystallization regularities of polymer composites are closely related to their microstructure. Semi-crystalline polyolefins are characterized by the coexistence of amorphous and crystalline phases, the ratio of which largely determines their final properties [1, 2]. In filled composites, the regularity of changes in the crystallization process largely depends on the type and content of the filler.

Composites based on PP-R/aluminum hydroxide are of great interest [3-10] for the production of low-flammability materials for use in construction and other areas of technology. On the other hand, the advantage of this material is also manifested in the fact that during the combustion process no toxic products hazardous to

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human health are released. Thus, the low cost of the composite, ease of use and non-toxicity of aluminum hydroxide compared to other flame retardants open up a promising opportunity for their practical use in special areas of industry. It is characteristic that the efficiency of aluminum hydroxide is directly proportional to its content in the polymer composite. To achieve good fire resistant properties of the material, it is necessary to use aluminum hydroxide in an amount of approximately 50-60 wt.%. However, such a high degree of filling has a negative impact on the change in the physical and mechanical properties of composites.

In the development of polymer composites, problems associated with improving the compatibility of the mixed components of the blend are of great importance. This circumstance is related to the fact that compatibility promotes an increase in the adhesive contact of filler particles with the polymer matrix [11, 12]. The compatibility effect is most effective when using filler nanoparticles. This is due to the fact that the smaller the particle size, the larger their specific surface area becomes and, accordingly, the adhesive contact surface increases. The most effective compatibilizers are graft copolymers of polyolefins with acrylic monomers or maleic anhydride. This is explained by the structural features of the graft copolymer macrochain: the main polyolefin macrochain can participate in the formation of the crystalline phase of the nanocomposite, and the polar grafted chain improves the adhesive contact with the surface of the nanoparticles.

In the process of processing nanocomposites into products using injection molding and extrusion methods, the polymer material goes through the following stages: melting, mixing of the mixture components, cooling (crystallization) and obtaining the product in a mold or calibrating nozzle. Therefore, the problems associated with the study of the behavior of the material during the cooling and molding of a product of complex configuration are of primary importance. In this regard, stepwise dilatometry is the most informative method for studying the crystallization regularities of polymeric materials of nanocomposites. A method for studying the crystallization of polymeric materials using scanning calorimetry is also known. However, this method cannot provide as much information as stepwise dilatometry. This is due to the fact that, unlike scanning calorimetry, dilatometry allows one to determine the dependence of specific volume, free specific volume, and occupied volume on temperature. To study the kinetics of crystallization and the mechanism of crystal growth in Kolmogorov-Avrami coordinates. The ease of use of the dilatometric method and its high information content on the structural features of nanocomposites make it possible to consider it as an effective way to study the crystallization regularities of polymeric materials [13]. Taking into account the above, as well as the high demand of the industry for fire-resistant composite materials, the aim of this work was to study the crystallization process and the growth mechanism of crystalline formations using the dilatometric method in a nanocomposite based on PP-R/PPH-g-MAH/Al(OH)$_3$.

EXPERIMENTAL

Materials

The object of the study was polypropylene random copolymer (PP-R). It is a random copolymer characterized by excellent long-term hydrostatic pressure resistance and thermal stability.

For the compatibilization of PP-R/Al(OH)$_3$ blend the maleic anhydride functionalized homopolypropylene (PPH-*g*-MAH) were used. Maleic anhydride level in PPH-*g*-MAH was in the range of 0.5 to 1.0 wt.%. This grade is designed to function as a coupling agent between reinforcing materials, such as inorganic fillers and polypropylene. The dosage of a compatibilizer (PPH-*g*-MAH) is based on the results of our previous research results [14, 15]. The characteristics of the PP-R and compatibilizer are presented in Table 1.

Aluminum hydroxide (GOST 11841-76, repackaged by ZAO VEKTON) was used as a filler. The average particle size of aluminum hydroxide was 56 nm: Dv

Table 1. Data and properties of the polymeric ingredients.

Sample code	Grade name and manufacturer	MFI	Density	T$_m$
PP-R	Topilene® R200P Hyosung Chemical Corporation	0.2 g/10 min (230°C, 2.16 kg) ASTM D1238	0.9 g/cm^3 ASTM D792	145°C
PPC-*g*-MAH	Exxelor™ PO 1020 ExxonMobil Chemical Company	430 g/10 min (230°C, 2.16 kg) ASTM D1238	0.9 g/cm^3 ASTM D792	162°C

Table 2. Particle size of aluminum hydroxide.

Size µm	Volume %	Size µm	Volume %	Size µm	Volume %	Size µm	Volume %	Size µm	Volume %	Size µm	Volume %
0.0100	0.61	0.0876	5.15	0.77	0.15	6.72	0.00	58.9	0.00	516	0.00
0.0114	1.22	0.0995	4.78	0.872	0.07	7.64	0.00	66.9	0.00	586	0.00
0.0129	1.81	0.113	4.34	0.991	0.00	8.68	0.00	76.0	0.00	666	0.00
0.0147	2.39	0.128	3.83	1.13	0.00	9.86	0.00	86.4	0.00	756	0.00
0.0167	2.94	0.146	3.26	1.28	0.00	11.2	0.00	98.1	0.00	859	0.00
0.0189	3.45	0.166	2.66	1.45	0.00	12.7	0.00	111	0.00	976	0.00
0.0215	3.93	0.188	2.06	1.65	0.00	14.5	0.00	127	0.00	1,110	0.00
0.0244	4.37	0.214	1.49	1.88	0.00	16.4	0.00	144	0.00	1,260	0.00
0.0278	4.76	0.243	0.99	2.13	0.00	18.7	0.00	163	0.00	1,430	0.00
0.0315	5.09	0.276	0.58	2.42	0.00	21.2	0.00	186	0.00	1,630	0.00
0.0358	5.37	0.314	0.28	2.75	0.00	24.1	0.00	211	0.00	1,850	0.00
0.0407	5.57	0.36	0.10	3.12	0.00	27.4	0.00	240	0.00	2,100	0.00
0.0463	5.70	0.41	0.00	3.55	0.00	31.1	0.00	272	0.00	2,390	0.00
0.0526	5.76	0.46	0.00	4.03	0.00	35.3	0.00	310	0.00	2,710	0.00
0.0597	5.73	0.52	0.12	4.58	0.00	40.1	0.00	352	0.00	3,080	0.00
0.0679	5.63	0.59	0.18	5.21	0.00	45.6	0.00	400	0.00	3,500	0.00
0.0771	5.43	0.68	0.19	5.92	0.00	51.8	0.00	454	0.00		

(10) = 20 nm, Dv (50) = 56 nm, Dv (90) = 159 nm. The particle size of aluminum hydroxide was assessed using a laser particle size analyzer Mastersizer 3000 (Malvern Instruments, England) with a measurement range from 0.01 to 3500 µm (Table 2).

Preparation and composition of the studied composites PP-R/PPH-g-MAH/$Al(OH)_3$-based polymer composite materials were obtained by mixing the components on laboratory rollers at a temperature of 170°C within 8-10 minutes. The mixing of the components was carried out in stages. The compatibilizer was added to the melt of the polymer, and then the filler. At a pressing temperature of 190°C, plates were molded, from which the corresponding samples were cut out for testing. Table 3 lists the amounts of components in each sample.

Characterization

Dilatometric study of composites

The study of the dilatometric characteristics of composites was carried out using the IIRT-1 device, converted into a dilatometer (Figure 1). The measurements were carried out during stepwise cooling in the temperature range from 180°C to room temperature and under a load of 5.3 kg. The principle

Table 3. Identification and formulations of all prepared samples.

Sample code	PP-R (wt.%)	$Al(OH)_3$ (wt.%)	PPH-*g*-MAH (wt.%)
PH	98	–	2
PHA_1	97	1	2
PHA_3	95	3	2
PHA_5	93	5	2
PHA_{10}	88	10	2
PHA_{20}	78	20	2
PHA_{30}	68	30	2
PHA_{50}	48	50	2

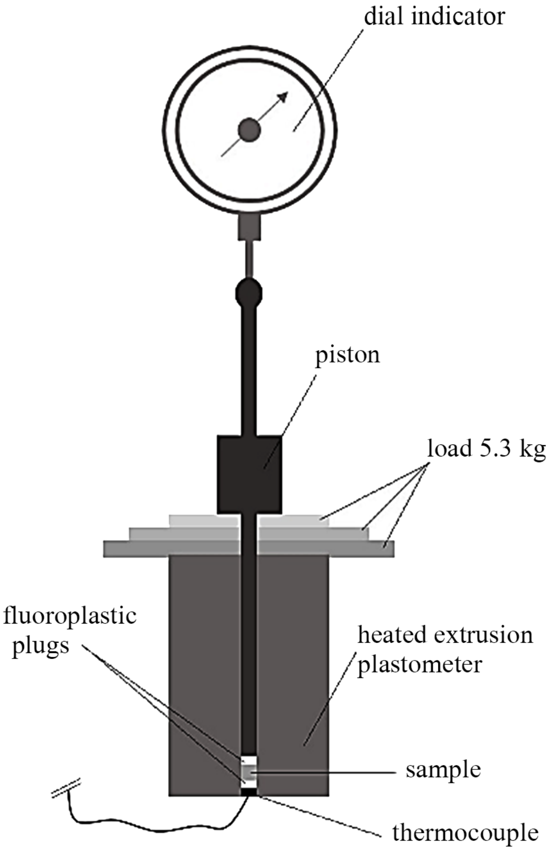


Figure 1. Diagram of a dilatometer for studying the dependence of specific volume on temperature.

of the method is to measure the change in the specific volume of materials depending on temperature. The dilatometric method of analysis is a highly accurate and sensitive method for assessing the first-order phase transition and the kinetic regularities of crystallization in the Kolmagorov-Avrami coordinates. Analysis of crystallization kinetics was carried out based on the methods proposed in the work of [16].

Scanning Electron Microscopy (SEM)
The morphology of the mixture was characterized using a JEOL scanning electron microscope, model JSM-6610 (Japan).

Thermogravimetric Analysis (TGA)
Thermogravimetric analysis (TGA) of the samples was carried out using a STA 6000 Simultaneous Thermal Analyzer, by Perkin Elmer in the temperature range of 25-700°C, heating rate 10°C/min.

RESULTS AND DISCUSSION

The nucleation process in the initial semi-crystalline polyolefin occurs only at homogeneous nucleation centers, which ultimately contribute to the formation of relatively large crystalline formations. The introduction of even 0.5-1.0 wt.% filler, as a rule, leads to the fact that the growth process of crystalline formations proceeds from two nucleation centers: homogeneous and heterogeneous. In this case, the formation of fine spherulitic crystalline formations occurs. A further increase in the filler nanoparticle content will lead to the fact that during the process of crystallization and crystal growth, most of the filler will be pushed out into the interspherulitic amorphous space. There is reason to believe that the interspherulitic region will concentrate in its space foreign substances that do not participate in the process of formation and growth of crystalline formations. As for the compatibilizer, the segments of the PPH-*g*-MAH macrochain containing polar MAH groups will also be pushed into the interfacial amorphous region. The majority of the PPH-g-MAH macrochain that does not contain polar groups will directly participate in the formation of crystalline formations. Thus, the accumulation of polar groups of MAH and nanoparticles in the amorphous region will contribute to improve the compatibility of the mixed components of the mixture and increasing the adhesive contact of the polar groups of the graft copolymer segments with the specific surface area of the nanoparticles. The interaction of polymer segments of macrochains containing polar groups of MAH with the surface of nanoparticles is accompanied by a slowdown in their segmental mobility, which in a certain way affected the change in the temperature dependence of the specific volume of the nanocomposite. Besides, as shown in Figure 2, the filler content has a significant effect on the regularities of changes in dilatometric curves. If at low nanoparticle contents (1.0 wt.%) the structure-forming effect is noticeably felt in the nature of the change in the dilatometric curves, then at higher contents the increase in melt viscosity has a significant effect.

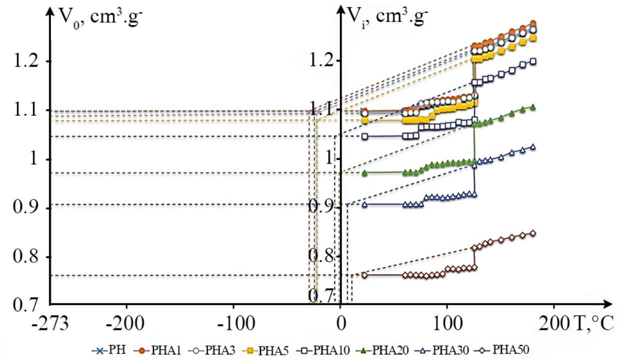


Figure 2. Dependence of specific volume on temperature for composites based on PP-R/ PPH-*g*-MAH /Al(OH)$_3$.

As can be seen from Figure 2, with an increase in the concentration of Al(OH)$_3$, the specific volume of nanocomposites decreases, which indicates their compaction. The results of the study of the nanocomposite density at different filler contents are summarized in Table 4. With an increase in the Al(OH)$_3$ content in the order of 1, 3, 5, 10, 20, 30 and 50 wt.%, the specific volume of nanocomposites at room temperature changes accordingly in the following sequence: 1.0976, 1.0870, 1.0794, 1.0462, 0.9713, 0.9063 and 0.7607 cm^3.g^{-1}. It should be noted that the specific volume of the PH composite, i.e. the unfilled, initial compatibilized PP-R at room temperature was 1.0981 cm^3.g^{-1}. Such a noticeable change in the specific volume of the samples indicates that Al(OH)$_3$ particles and their content influence the processes of crystallization and nucleation.

As can be seen from Figure 2, as the temperature decreases, the value of the specific volume decreases. And only at the temperature of the first-order phase transition does a sharp jump in the change in specific volume occur. This jump corresponds to the moment when the transition from a viscous flow state to a solid state occurs. According to the obtained data, the crystallization onset temperature for all studied composites remains unchanged and is 125°C. If

Table 4. Some crystallization parameters of PP-R/PPH-*g*-MAH/$Al(OH)_3$-based composites.

Sample code	Crystallization onset temperature,°C	Glass transition temperature, °C	Density at room temperature, g×cm^{-3}
PH	125	-25	0.9107
PHA$_1$	125	-30	0.9111
PHA$_3$	125	-23	0.9199
PHA$_5$	125	-23	0.9264
PHA$_{10}$	125	-6	0.9558
PHA$_{20}$	125	-2	1.0295
PHA$_{30}$	125	6	1.1034
PHA$_{50}$	125	10	1.3146

we compare the maximum and minimum specific volume of the studied samples at the phase transition temperature (crystallization onset temperature), we can see that with an increase in the concentration of $Al(OH)_3$ in the composites, the difference between these values first increases (PHA1), and for samples containing 3-50 wt.% $Al(OH)_3$, a decrease in the value of this indicator is observed. The value of this indicator in PP-R/PPH-g-MAH/$Al(OH)_3$ based composites is in the following sequence: PH-0.0968, PHA1-1.1017, PHA3-0.0915, PHA5-0.0902, PHA10-0.0774, PHA20-0.076, PHA30-0.0593, PHA50-0.0408 cm^3.g^{-1}. It shows that at low concentrations of $Al(OH)_3$, it promotes the complete occurrence of the crystallization process; on the contrary, in composites with a high content of $Al(OH)_3$ the process of crystallization or change in specific volume is reduced. This is due to the fact that with an increase in the filler content, the proportion of the polymer matrix in the nanocomposite decreases accordingly.

The glass transition temperature is one of the characteristic temperatures of polymers. This directly affects the operational and technological characteristics of materials. The method of dilatometric measurements allows for an approximate estimate of the glass transition temperature, i.e. the temperature of the second-order phase transition of the nanocomposites under study. In Figure 2, the glass transition temperature for each nanocomposite is estimated from the intersection point of the upper and lower branches of the dilatometric curves. Table 4 presents the results of the study of the effect of the amount of aluminum hydroxide on the glass transition temperature.

It is known that the glass transition temperature of polymer composites is associated with the mobility of macrosegments, which, as a result of interphase interaction, can change significantly in the presence of rigid filler particles. Comparing the data presented in Table 4, it can be established that with an increase in the filler content, a natural increase in the glass transition temperature of nanocomposites is observed. Such a noticeable increase in the glass transition temperature of the nanocomposite with an increase in the filler content indicates an increase in the adhesive contact in the polymer-filler system and, as a consequence, a decrease in the mobility of the macrosegments.

According to existing concepts, the mobility of macrochains depends on the intensity of intra- and intermolecular interactions, the conformational capabilities of macromolecules and the presence of free volume in the polymer. The minimum glass transition temperature value is observed in the PHA1 composite (at a concentration of 1 wt.% $Al(OH)_3$ in the composite). This dependence indicates the structure-forming effect of 1 wt.% filler and a reduction in the defectiveness of the crystalline phase of the PP-R. A further increase in the amount of $Al(OH)_3$ leads to an increase in the glass transition temperature. In all likelihood, this circumstance is associated with an increase in the degree of adhesive contact in the PP-R-$Al(OH)_3$ system, a decrease in free volume and, accordingly, a decrease in the conformational mobility of the components in the interphase amorphous region. This feature of the behavior of nanocomposites modified with a compatibilizer is confirmed by studying the temperature dependence of the free specific volume (Figure 3).

Free volume is the space in a total mass of the polymer that is unoccupied by the molecules themselves [17]. Free volume is an internal characteristic of the polymer matrix and is formed due to the gaps between the interweaving of polymer chains. Free volume pores are inherently dynamic and have the ability to move, since the size of an individual free volume depends on the temperature and the movements of the surrounding polymer chains. The simplest and

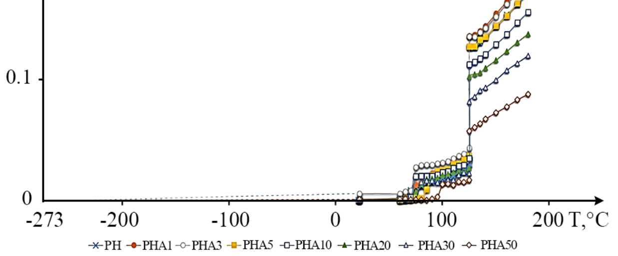


Figure 3. Dependence of free specific volume on temperature for composites based on PP-R/ PPH-*g*-MAH / $Al(OH)_3$.

most accurate method for calculating the specific free volume in a polymer volume can be made from the following relationship [18]: $V_f = V_i - V_o$ (specific free volume = total specific volume – specific occupied volume), where V_i (cm^3.g^{-1}) is the specific volume of the polymer composite at any temperature, V_o - the occupied specific volume, is determined graphically from Figure 2 by extrapolating the lower branch of the dilatometric curve to absolute zero.

Figure 3 shows the dependence of free specific volume on temperature at different degrees of filling of the nanocomposite. As can be seen from the curves presented in this figure, with an increase in the amount of filler in the composites, a natural decrease in free volume is observed, which clearly indicates that nanoparticles are embedded in the free volume. A significant decrease in the specific free volume in the region of the viscous flow state is accompanied by an increase in the effective viscosity of the melt. Minor changes in the solid state region lead to an increase in the strength and rigidity of nanocomposites, up to brittle fracture at high degrees of filling. In semicrystalline polymers, free volume is mainly contained in the amorphous interspherulitic space. In the presence of a compatibilizer, the adhesive contact of the polar macrochains with the filler surface is so strong that it leads to an improvement in the dispersion of the filler in the interspherulitic volume of the polymer matrix and, as a consequence, a decrease in the free specific volume. If we consider the change in free specific volume in the solid state, we can see that, regardless of the filler content, they differ little from each other.

We considered two aspects where semi-crystalline PP-R in molten state is mixed with different amount of Al(OH)$_3$ and then the polymer composite is crystallized. First, what is the role of Al(OH)$_3$ in the crystallization kinetics of PP-R/PPH-*g*-MAH. The second case highlights the role of Al(OH)$_3$ in determining not only the crystallization kinetics, but also the resulting morphology of the Al(OH)$_3$ dispersion.

Table 5. Mass percentage of each element determined by EDS analysis for PHA$_{50}$.

Element	Mass percentage (wt.%)
C	77.33
O	16.62
Al	6.05

EDS analysis (Figure 4) of sample PHA50, which contains the largest amount of filler (50 wt.%) confirmed the presence of the elements carbon (C), oxygen (O) and aluminum (Al), and the absence of any other impurity elements. The obtained results confirm the fact of obtaining a nanocomposite of the composition PP-R, PPH-*g*-MAH, Al(OH)$_3$. In addition, it can be seen that the elements have good dispersion and no obvious aggregation, indicating a distributed structure. The figure shows the distribution of Al(OH)$_3$ in PHA$_{50}$. According to this figure, Al(OH)$_3$ particles are uniformly distributed in the polymer matrix (Figure 4, SEM). Table 5 shows the percentages of these elements found from the EDS analysis. According to the data in Table 5, the Al content in the studied material basically corresponds to the PHA$_{50}$ content. In addition, the distribution of the composite is uniform.

Measuring the filler content by thermal analysis is one of the methods that allows quantitatively assessing the dispersion of the filler in the matrix [19, 20]. Annealing the sample at 700°C and the formation of a solid residue can be used as a method to estimate the actual filler content in the polymer matrix. As can be seen from the TGA curves presented in Figure 5, the 700°C

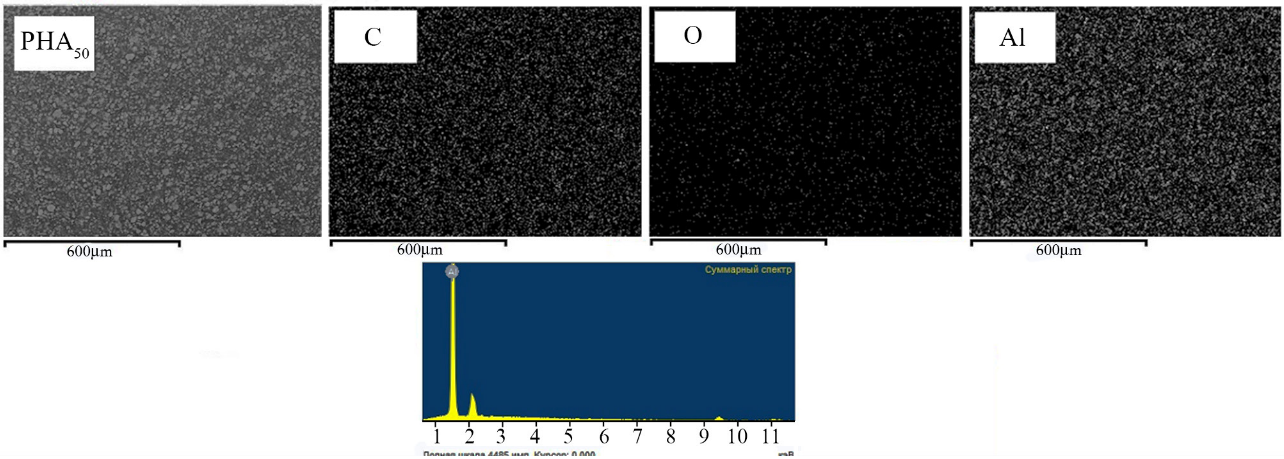
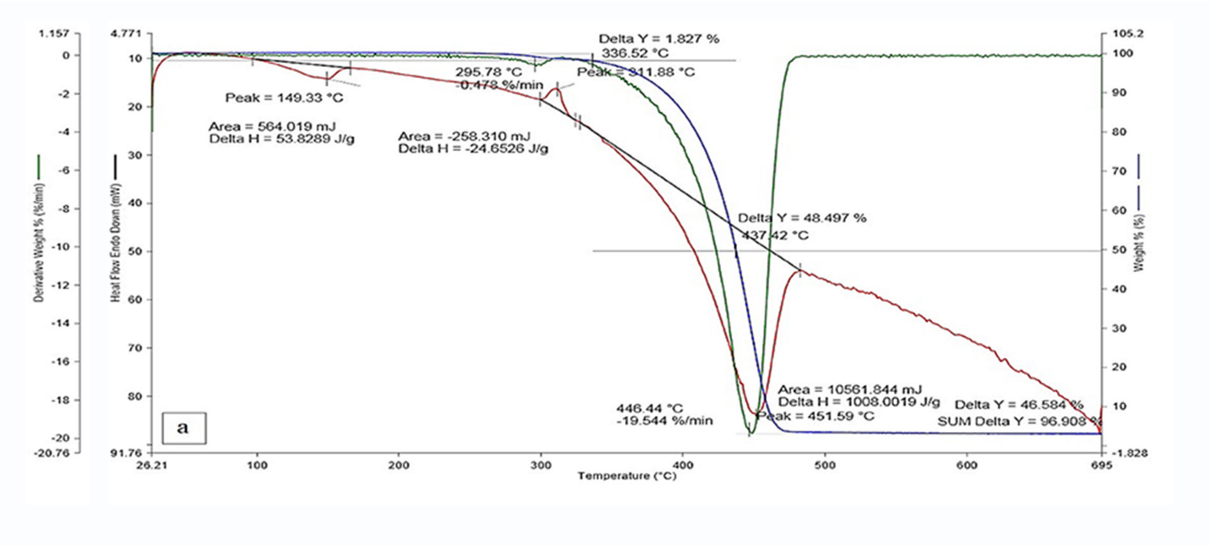
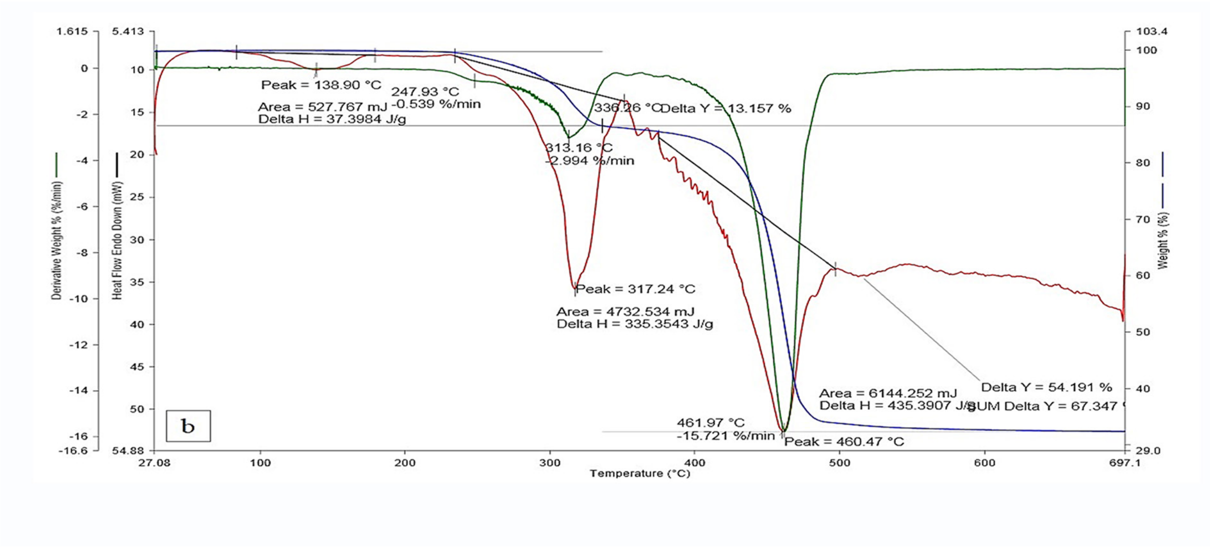


Figure 4. EDS elemental distribution maps and SEM of PHA$_{50}$.



(a)



(b)

Figure 5. TGA of composites based of (a) PHA5 and (b) PHA_{50}.

residues of samples PHA5 and PHA50 containing 5 and 50 wt.% aluminum hydroxide, respectively, are similar in the char wt.% to composition of polymer composites.

$Al(OH)_3$ shows a weight loss of 34.661 wt.% due to decomposition and release of water vapor, leaving approximately 65.339 wt.% inorganic residue in terms of Al_2O_3. On the other hand, PP-R decomposes and evaporates, leaving virtually no residue. The residues of PHA5 and PHA50 composites are 3.092% and 32.653%, after thermal decomposition at 700°C, confirming the original composition of the composite and the fact of uniform distribution of the filler throughout the polymer matrix.

According to DSC (Figure 5), it can be said that with the introduction of 50 wt.% $Al(OH)_3$, a slight shift in the melting onset temperature towards lower temperatures (the melting point of PHA5 is 149.33°C and the melting point of PHA50 is 138.90°C) is observed, which may be associated with the formation of simple rod-shaped crystals, affecting the decrease in their melting temperature.

The study of the kinetics of polymer crystallization is of great importance from both scientific and technological points of view [21-23]. This is explained by the fact that for a long time the method of dilatometry of polymeric materials was considered as a theoretical basis for the process of their processing, especially in terms of cooling the product in the mold of the injection molding unit. The study of the kinetic laws of crystallization at the temperature of the first-order phase transition allows us to estimate the overall growth rate of the crystalline phase and gain an idea of the crystallization mechanism. The kinetics of crystallization can be analyzed using the well-known Kolmogorov-Avrami equation. A number of studies have proven the applicability of Avrami's theory to the study of the crystallization process in polymeric materials in the region of the first-order phase transition and effectiveness of using this equation in assessing the crystallization mechanism [16,24]. For partial analysis of isothermal crystallization growth of polymers, the Avrami equation is usually used, which has the following general form:

$$\varphi = e^{-K\tau^n} \tag{1}$$

where φ is the part of the polymer that has not yet undergone transformation into the crystalline phase; K is the generalized constant of crystal nucleation and growth; and n is a constant in the range from 1-4. It is Avrami exponent whose value is dependent on the mechanism of nucleation and the form of crystal growth [25].

Taking the double logarithm of Avrami's equation gives:

$$\lg(-ln\varphi) = lgK + nlg\tau \tag{2}$$

It is known that the efficiency of fillers in PP-R depends on their specific surface area, particle size and surface properties [26]. The smaller the size of the filler particle, the greater its specific surface area for adhesive contact with the macrochains of the polymer matrix. The use of a compatibilizer helps to increase the adhesive contact of the surface of the filler particles with its polar groups in the interphase amorphous region. The change in the morphology of the PP-R matrix in the presence of Al$(OH)_3$ is associated with the manifestation of the effect of nucleation of filler particles during the crystallization of the polymer. The nucleation activity is determined by the adsorption interaction between the polymer melt and solid particles. The overall rate of crystallization consists of two parts: the rate of nucleation and the rate of crystal growth. Nucleation is the starting point of crystallization. For the studied systems, the introduction of 1-5 wt.% of Al$(OH)_3$ filler accelerates the nucleation process, and with a filling of 10-50 wt. %, this stage slows down. This is due to the fact that at a high concentration of filler in the polymer volume, a regular increase in the effective viscosity of the melt and the rigidity of the polymer-filler bond is observed, which affects the regularity of crystallization of the nanocomposite. An increase in the filler concentration leads to an increase in heterogeneous nucleation centers, which, together with homogeneous centers, contribute to a simultaneous increase in the number of crystalline formations and overloading of the entire crystalline phase with the formation of fine-spherulitic structures.

Figure 6 shows the crystallization kinetic regularities of PP-R/PPH-*g*-MAH/Al$(OH)_3$ nanocomposites. By analyzing the curves in this figure, it can be established that with an increase in the content of Al$(OH)_3$ in the composition of the compatibilized PP-R, a regular decrease in the angle of inclination of the curves to the abscissa axis is observed. The latter circumstance indicates that the filler content has a significant impact on the mechanism of formation of the crystalline structure of nanocomposites. For example, if the value of n for the initial polymer matrix PP-R + compatibilizer (3) and for the sample with 1.0 wt.% Al$(OH)_3$ content (4) is 3.1, then this fact indicates that during the crystallization process, "three-dimensional spherulitic" structures are formed with the continuous formation of nucleation centers.

With the introduction of 5, 10 and 20 wt.% Al$(OH)_3$, the n value changes within 2-3, which corresponds to the formation of "two-dimensional disc-shaped" structures. And finally, with an Al$(OH)_3$ content of 30-50 wt.%, the value of n changes within the

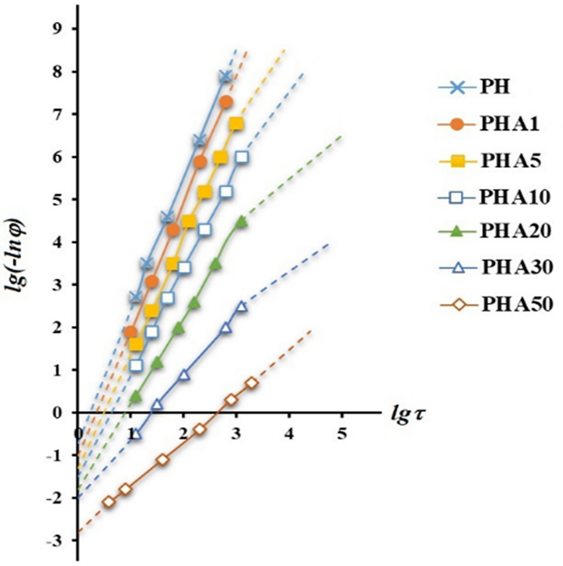


Figure 6. Kinetic regularities of crystallization of PP-R/ PPH-*g*-MAH /Al$(OH)_3$ based composites in logarithmic Avrami coordinates in the region of the first order phase transition.

range of 1-2, which confirms the formation of the simplest "one-dimensional rod-shaped" structures with the continuous formation of heterogeneous and homogeneous nucleation centers.

In this case, the introduction of filler in quantities of 1, 5, 10, 20, 30 and 50 wt.% changes the value of the generalized constant of nucleation and growth of crystalline formations in the following sequence: -0.9; -1.2; -1.5; -1.6; -2.1; -2.2; -2.8. Substituting the obtained values of K and n into the Kolmogorov-Avrami equation (2), we can obtain the following equations for the kinetic regularities of crystallization of nanocomposites:

$$lg(-ln\varphi) = 3.1lg\tau - 0.9 - PH \quad (3)$$

$$lg(-ln\varphi) = 3.1lg\tau - 1.2 - PHA_1 \quad (4)$$

$$lg(-ln\varphi) = 2.5lg\tau - 1.5 - PHA_5 \quad (5)$$

$$lg(-ln\varphi) = 2.3lg\tau - 1.6 - PHA_{10} \quad (6)$$

$$lg(-ln\varphi) = 2.1lg\tau - 2.1 - PHA_{20} \quad (7)$$

$$lg(-ln\varphi) = 1.3lg\tau - 2.2 - PHA_{30} \quad (8)$$

$$lg(-ln\varphi) = 1.1lg\tau - 2.8 - PHA_{50} \quad (9)$$

Thus, by specifying the crystallization time (in seconds), it is possible to determine the proportion of uncrystallized composite (φ) at a given point in time (τ).

The method of dilatometric studies is the theoretical basis for the process of cooling products during the processing of polymeric materials by injection molding and extrusion. Knowing the crystallization regularities, one can roughly estimate the temperature regime for cooling the product in the mold. The holding time under pressure in the mold determines the time required for complete crystallization and cooling of the product in the mold.

CONCLUSION

Thus, based on the above, we can come to the following conclusions:

1. The crystallization process of composites based on PP-R/PPH-*g*-MAH/$Al(OH)_3$ was experimentally studied using the dilatometric method. The effect of the increase in the amount of aluminum hydroxide on the regularity of changes in the dependence of specific volume on temperature and free specific volume on temperature was studied. It has been established that increasing the amount of aluminum hydroxide in composites leads to a significant increase in density.
2. According to the obtained data, regardless of the amount of aluminum hydroxide introduced, the crystallization onset temperature for all the studied composites remains unchanged and is 125°C.
3. An approximate estimate of the glass transition temperatures of the studied samples using the dilatometry method showed that the glass transition temperature increases with an increase in the amount of aluminum hydroxide.
4. Analysis of the crystallization kinetics using the Kolmagorov-Avrami equation showed that, with an increase in the amount of aluminum hydroxide, the growth of crystals changes into three-dimensional spherulitic-two-dimensional disc-shaped-one-dimensional rod-shaped sequences.

ACKNOWLEDGEMENTS

The presented work was carried out in accordance with the work program of the Institute of Polymer Materials of the Ministry of Science and Education of the Republic of Azerbaijan.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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