UDC 541.68

EFFECT OF ALUMINUM HYDROXIDE CONCENTRATION ON PROPERTIES AND CRYSTALLIZATION REGULARITIES OF COMPOSITE MATERIALS BASED ON HIGH AND LOW DENSITY POLYETHYLENE MIXTURES

F.A. Mustafayeva

Institute of Polymer Materials. ANAS
S. Vurgun str.124, Sumgayit, Azerbaijan AZ5004, e-mail: mustafayevafatima@mail.ru

Received 01.08.2019

Abstract: *The article presents results of research into the influence of aluminum hydroxide concentration on properties and crystallization regularities of composite materials based on mixtures of high and low density polyethylene. Studies were carried out with samples containing 1, 3, 5 and 10 % wt. aluminum hydroxide. All composite materials were based on mixtures of high and low density polyethylene, taken in 50/50 ratio. Dilatometric studies were carried out on an IIRT-1 device in the course of stepwise cooling of samples with a load of 5.3 kg. Temperature dependence of the specific volume, density and free volume of composite materials established. Also, density of compositions at a temperature of 190°C was identified on a capillary rheometer of CEAST MF50 brand. Onset temperature of crystallization and approximate glass transition temperature of composite materials were determined. Physical-mechanical properties of composites, such as ultimate tensile stress and elongation at break, were studied.*
Keywords: *crystallization, dilatometry, specific volume, mixture of polymers, high-density polyethylene*

Introduction

At present, polymer composites are increasingly attracting attention of scientists and experimenters to obtain on their basis the high-quality structural materials with high strength, lightness, resistance to aggressive media, low cost, etc. These materials are available in the form of physical mixtures of polymers filled with mineral fillers of polymer composites, which are distinguished by high technology and ability to be processed in various plastics processing equipment. Through varying the concentration or ratio of mixture components, it is possible to vary properties of composite polymeric materials in a fairly wide range. It is these features of polymer composites that make it possible to obtain materials on their basis that can be widely used in engineering, aircraft engineering, auto industry, ship-building, as well as in space and military equipment. Interest in these materials has increased mainly due to the ability to change mechanical properties and adapt them to specific operating conditions. The process of mixing polymer with polymer has always been one of effective methods for producing compositions with predetermined properties [1-3].

In recent years, polyethylene-polyethylene mixture has been the subject of great scientific and practical interest, in which not only quality problems were solved, but also the cost of products derived from them [4,5]. Scientific and technical progress requires a constant expansion of the range and applications of polymers. In particular, one of the most important requirements for polymeric materials is fire safety. Given that polyethylene is the largest and most widespread polymer, the development of ways to increase its fire resistance is one of the most important tasks requiring special attention. Metal hydroxides have long been considered cheap fillers for the development on their basis of fire-resistant polyolefins [6-8]. At the same time, great attention is paid to composite materials characterized by minimal shrinkage in the course of the molding machine injection. This circumstance makes it possible to select the composition of the composite material in such a way that it is possible to significantly reduce changes in its volume in the process of structural product casting. To control the crystallization process and change the volume of the material in the process of closed volume cooling, the most effective method is the method of dilatometric measurements [9].

In this regard, the purpose of this study was to determine the effect of the concentration of aluminum hydroxide (AH) on the crystallization regularity of composite materials based on mixtures of high and low density polyethylene.

Experimental part

Industrial samples of high-density polyethylene (HDPE) of HD 52518 brand, low-density polyethylene (LDPE) of 17703-01 brand, and filler - aluminum hydroxide (GOST 11841-76, OKP 631887 repacked by VEKTON) were used as the object of research.

LDPE– density- 912 kg/m^3, ultimate tensile stress- 10.3 MPa, elongation at break- 250%. HDPE – density- kg/m^3, ultimate tensile stress- 25.0 MPa, elongation at break- 500%.

Aluminum hydroxide $Al(OH)_3$ – a colorless solid, insoluble in water, has amphoteric properties, is a part of many bauxite. Amorphous aluminum hydroxide has a variable composition $Al_2O_3 \cdot nH_2O$. When heated above 180-200°C it decomposes depending on the size of particles.

Composite materials based on HDPE and LDPE mixture in a 50/50 ratio and with different concentrations of AH (1, 3, 5, 10 % wt.) were obtained by mixing the components on laboratory rollers at a temperature of 150°C within 8-10 minutes. Then, at a pressing temperature of 170-180°C, the plates were molded to cut down appropriate samples for testing.

Research into dilatometric characteristics of the composites was carried out on IIRT-1 device during stepwise cooling in the temperature range of 25–180°C, with a load of 5.3 kg.

The density and melt flow index (MFI) of the compositions at a temperature of 190°C and a load of 5 kg were determined on a capillary rheometer of MELT FLOW TESTER, CEAST MF50 (INSTRON brand, Italy).

The melting point was determined on a Q-1500 D derivatograph of the MOM company (Hungary) of Paulik, Paulik, and Erdei systems.

Ultimate tensile stress (σ, MPa) and elongation at break (ε, %) were determined in accordance with GOST 11262-80.

Results and discussion

In our previous works, the results of studies of physicomechanical, thermophysical, rheological properties, kinetic regularities of crystallization of composite materials based on mixtures of high and low density polyethylene in various ratios were published [10,11]. As is known, a feature of the polyethylene structure is a combination of crystalline and amorphous phases there in. Many of its physicochemical and mechanical properties depend on their quantitative ratio in polyethylene. But it will be shown below that they also have a significant impact on regularities of changes in the specific volume of composites depending on temperature and filler's quantitative ratio. The filler' particles can increase or reduce the crystallization rate of the semi-crystalline polymer, affect the growth of polymer matrix crystals, as well as the nucleation effect in the melt [12]. It was interesting to study the effect of AH concentration in the properties and crystallization regularities of composite materials based on mixtures with high and low density polyethylene.

The practical application of polymers is determined by the state in which the polymer (viscous, highly elastic, glassy) is in operating conditions.The temperature regions of existence of various physical states of polymers are determined by the dependence of the specific volume on temperature.

. Figure 1 shows the crystallization isotherms, the initial mixture of LDPE and HDPE in a 50/50 ratio, and composite materials based on it at various concentrations of AH. The analysis of dilatometric curves in this figure shows that with increasing AH concentration, the specific volume of composite materials decreases, that is, material compaction is observed, the results of which are summarized in table1.

Table 1 presents the results of research into the effect of AH concentration at a temperature of crystallization which characterizes a first-order phase transition. Loading of 1% wt. AH has almost no effect on the crystallization temperature of the initial LDPE / HDPE mixture and is equal to 114°C.

Table 1. Effect of AH concentration on the density and crystallization onset temperature of composites based on high and low density polyethylene mixture

№	Composition formulation, % wt.	Crystallization onset temperature, ^{o}C	Density, g / sm^3	
			At 25°C	At 190°C
1	HDPE / LDPE	114	0.941	0.730
2	HDPE / LDPE +1 AH	114	0.945	0.766
3	HDPE / LDPE +3 AH	110	0.954	0.782
4	HDPE / LDPE +5 AH	110	0.962	0.790
5	HDPE / LDPE +10 AH	110	1.053	0.801

* *a mixture of HDPE and LDPE were taken in a 50/50 ratio, AH - aluminum hydroxide*

With an increase in AH concentration to10%, the temperature at which the composites begin to crystallize does not undergo any changes and corresponds to a value of 110°C.. Phase transitions of the first kind arecharacterized by constancy of temperature and volume changes. A comparison of maximum and minimum specific volume of samples under study at the phase transition temperature (Fig. 1) says that as AH concentration in composites rises, the difference between these values first increases, and for samples containing 5% and 10% wt. AH decreases at index rate.

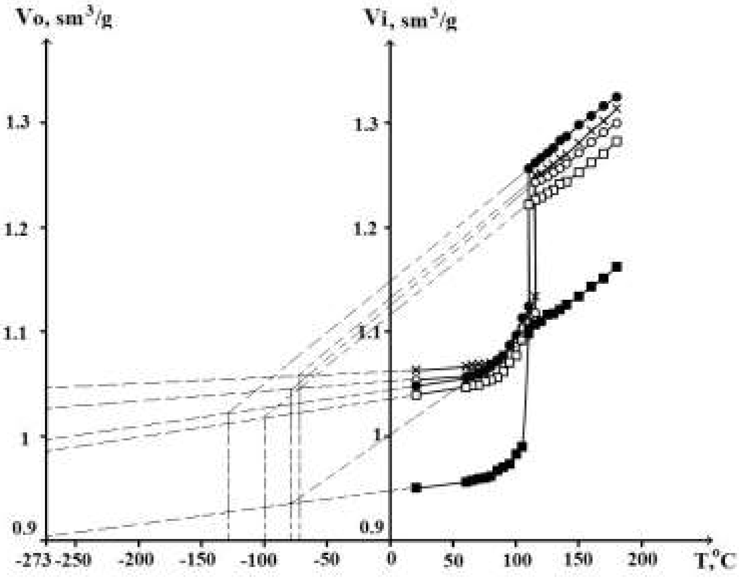

Figure 1. Graphic dependence of specific volume on temperature: ×– initial mixture of 50 % wt. HDPE + 50 % wt. LDPE, ○– HDPE / LDPE + 1% wt. AH, ● – HDPE / LDPE + 3% wt. AH, □– HDPE / LDPE + 5% wt. AH, ■– HDPE / LDPE + 10% wt. AH

The data obtained show that AH smaller concentrations contribute to fuller crystallization process; however, at concentrations of 5-10% wt. the crystallization process in filled composites is somewhat constrained.

It has to be kept in mind that the method of dilatometric measurements makes it possible to approximate estimate a crystallization temperature of composite materials. Approximate values of the glass transition temperature of the studied samples were found at the intersection point of the upper and lower branches of the dilatometric curves (Fig. 1). The glass transition temperature of the initial HDPE / LDPE and composites thereon containing 1, 3, 5, 10% wt. AH is equal respectively to -73, -84, -128, -100, -84°C. From the data obtained, it follows that with AH loading to 3% wt. there is reduction in the negative area glass transition temperature. When the AH concentration is over 3% wt. the glass transition temperature rises. All the data above suggest that at AH low concentrations, the latter in the material melt exhibits properties of nucleating agents thereby obtaining samples with a fine-spherical structure that favorably affect the improvement of these properties. At higher temperatures, the filler particles are accumulated in the amorphous regions impeding the conformational mobility of passing chains and increasing the fragility of the material and, accordingly, decreasing the glass transition temperature of composite materials.

According to the derivographic analysis data, the melting point of the composites under consideration changed as follows: HDPE / LDPE – 120°C; HDPE / LDPE + 1% AH – 120°C; HDPE / LDPE + 3% AH –120°C; HDPE / LDPE + 5% AH– 120°C; HDPE / LDPE +10% AH – 125°C. In this case, a decrease in conformational mobility of highly filled composites is due to a certain increase in their melting point.

Since the experimental determination of free specific volume is a difficult task, it is usually calculated using the graphical dependence of the specific volume of the polymer on temperature.As the temperature of absolute zero (0 K) is approached, the free volume becomes zero, therefore the value of the occupied volume (V_o) is obtained by extrapolation to the ordinate axis (Figure 1).Using the specific volume (V_i) at a given temperature, the free specific volume (V_f) of the test samples was calculated from the difference (V_i–V_o).Figure 2 shows the dependence of the free specific volume on the absolute temperature at various concentrations of AH.

A comparative analysis of the dependency curves shows that the value of the free specific volume for AH-filled composites is higher than in case with the initial HDPE / LDPE blend. This can be explained as being due to the fact that AH particles can create steric hindrances for complete crystallization of macromolecules in the phase transition thereby facilitating the loosening of the material and reducing its density. Due to the incompatibility of the polymer mixture of polyethylene with AH, their contact in the interfacial layer becomes weak. AH reducing the packing density of macromoleculescontributes to the loosening of its structure.To this can also be attributed to a decrease in the ultimate tensile stress of composites with a relatively high content of AH, the results of which are summarized in table 2.

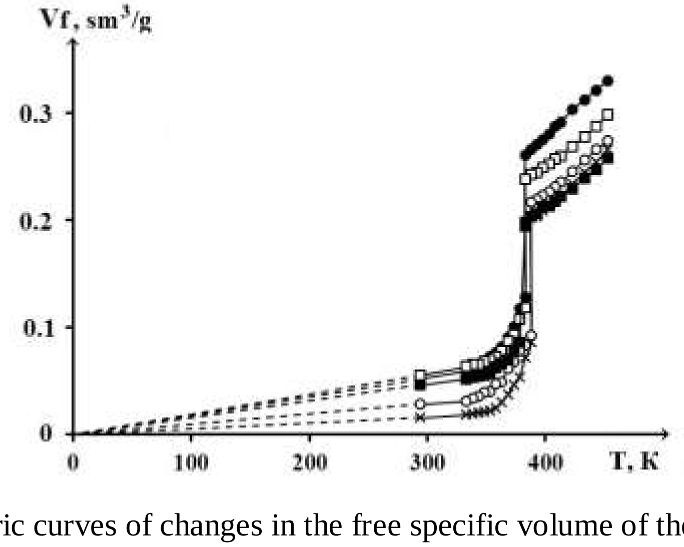

Figure 2. Dilatometric curves of changes in the free specific volume of the absolute temperature: ×– initial mixture of 50 % wt. HDPE + 50 % wt. LDPE, ○– HDPE / LDPE + 1% wt. AH, ● – HDPE / LDPE + 3% wt. AH, □– HDPE / LDPE + 5% wt. AH, ■– HDPE / LDPE + 10% wt. AH

From table 2 it can be seen that the loading of AH does not lead to a noticeable change in melt flow.Basically, the effect of AH appears on the change in mechanical properties.The results of the study are in good agreement with the data of dilatometric measurements,according to which AH contributes to loosening the structure of the composite, which in acertain way affects the deterioration of the ultimate tensile stress and the elongation at break of the composites.

Table 2. The effect of the AH concentration on physical-mechanical properties of composites based on high and low density polyethylene mixture

№	Composition formulation, % wt.	Ultimate tensile stress, MPa	Elongation at break, %	MFI, g /10 min
1	HDPE / LDPE	22.2	56	11.784
2	HDPE / LDPE +1 AH	20.0	37	11.300
3	HDPE / LDPE +3 AH	20.1	36	10.387
4	HDPE / LDPE +5 AH	18.5	36	10.222
5	HDPE / LDPE +10 AH	18.7	28	11.733

** a mixture of HDPE and LDPE were taken in a 50/50 ratio, AH - aluminum hydroxide*

Thus, the method of dilatometric measurements makes it possible to obtain sufficiently complete clarity for determination of the influence of filler particles on the nature of changes in the structure and properties of composites. On the basis of the data obtained, it is possible to evaluate the regularity of cooling of the polymer composite into the product in the mold and thereby predetermine the main trends affecting their quality. Therefore, quantifying these properties through the use of dilatometry is crucial. By dilatometry, it was found that as AH concentration rises, the specific volume of composites decreases and a regular increase in density is observed. The lower and upper limits of the temperature used in these samples were determined.

REFERENCES

1. Mishra J., Tiwari S.K., Abolhasani M.M., Azimi S., Nayak G.C. The book "Micro and Nano Fibrillar Composites (MFCs and NFCs) from Polymer Blends". Chapter 2. Fundamental of polymer blends and its thermodynamics. *Woodhead Publishing Series in Composites Science and Engineering*. 2017, pp. 27-55.
2. Runt J., Huang J. Chapter 8- Polymer blends and copolymers. *Handbook of thermal analysis and calorimetry*. 2002, vol. 3, pp. 273-294.
3. Kahramanov N.T., Huseynova Z.N., Hasanova A.A., Mustafayeva F.A., Allahverdiyeva Kh.V. Influence of technological parameters of injection moulding on physico-mechanical properties of dynamic elastoplasts based on polyolephines and nitrile-rubber. *Chemical Problems*. 2018, no. 3(16), pp. 420-428. (In Azerbaijan).
4. Nabeela A.M. Studing the mechanical properties and morphology of ternary blends of polyethylene. *Ebg.&Tech. Journal*. 2009, vol. 27, no. 6, pp. 1197-1202.
5. Anour S., Abdalah K., Rabea E., Shalh A., Hassan E., Wael E. The influence of LDPE content on the mechanical properties of HDPE/LDPE blends. *Res. & Dev. Material Sci.* 2018, vol. 7, no. 5, pp. 791-797.
6. Glikshtern M.V. Flame retardants. *Polimernyie Materialyi – Polymer Materials*. 2003, no. 5, pp. 15-18. (In Russian).
7. Xu Z., Yan L., Chen L. Synergistic flame retardant effects between aluminum hydroxide and halogen-free flame-retardants in high-density polyethylene composites. *Procedia Engineering*. 2016, vol. 135, pp. 631-636.

8. Han Z., Wang Y., Dong W., Wang P. Enhanced fire retardancy of polyethylene/alumina trihydrate composites by graphene nanoplatelets. *Materials Letters*. 2014, vol. 128, pp. 275-278.
9. Maurice H.E. van der Beek. Specific volume of polymers: influence of the thermomechanical history. Eindhoven Technische Universiteit. 2005, 113 p.
10. Kakhramanov N.T., Mustafaeva F.A., Arzumanova N.B., Guliev A.D. Kinetic regularities of the crystallization of composite materials based on a mixture of polyethylene of high and low density. *Materialovedenie – Materials Science*. 2019, no. 5, pp. 43-48. (In Russian).
11. Kakhramanov N.T., Mustafaeva F.A., Osipchik V.S., Arzumanova N.B., Khamedova L.H., Lyalyaeva R.N. Rheological properties of polymer blends based on low and high density polyethylene. *Kompozity i nanostruktury – Composites & nanostructures*. 2018, vol. 10, no. 4(40), pp. 166-170. (In Russian)
12. Das S., Samal S.K., Mohanty S., Nayak S.K. In the book "Crystallization in multiphase polymer systems", chapter 11 - Crystallization of polymer blend nanocomposites. 2018, pp. 313-339.

ALÜMİNİUM HİDROKSİDİN MİQDARININ YÜKSƏK VƏ AŞAĞI SIXLIQLI POLİETİLEN QARIŞIĞI ƏSASINDA OLAN KOMPOZİT MATERİALLARIN XÜSUSİYYƏTLƏRİNƏ VƏ KRİSTALLAŞMA QANUNAUYĞUNLUQLARINA TƏSİRİ

F.Ə. Mustafayeva

AMEA Polimer Materialları İnstitutu,
AZ 5004, Sumqayıt ş, S. Vurğun küçəsi, 124
e-mail: mustafayevafatima@mail.ru

Məqalədə alüminium hidroksid miqdarının yüksək və aşağı sıxlıqlı polietilen qarışığı əsasında olan kompozit materialların xüsusiyyətlərinə və kristallaşma qanunauyğunluqlarına təsiri tədqiqatlarının nəticələri təqdim olunmuşdur. Tədqiqatlar təkibində 1, 3, 5 və 10 kütlə % alüminium hidroksid olan nümunələrlə aparılmışdır. Bütün kompozit materiallar 50/50 nisbətində götürülmüş yüksək və aşağı sıxlıqlı polietilen qarışığı əsasında olmuşdur. Dilatometrik tədqiqatlar İİRT-1 qurğusunda, nümunələrin 5.3 kq yük altında pilləli soyutma prosesində aparılmışdır. Kompozit materialların xüsusi həcminin, sıxlığının və sərbəst həcminin temperatur asılılığı müəyyən edimişdir. Kompozitlərin 190℃ uyğun sıxlıqları CEAST MF50 markalı kapilyar reometrdə müəyyən olunmuşdur. Kompozit materialların kristallaşmasının başlanğıc temperaturu və təxmini şüşələşmə temperaturu müəyyən olunmuşdur. Kompozitlərin dartılmada möhkəmlik həddi və nisbi uzanması kimi fiziki-mexaniki xüsusiyyətləri tədqiq edilmişdir.

Açar sözlər: *kristallaşma, dilatometriya, xüsusi həcm, polimer qarışığı, yüskək sıxlıqlı polietilen, aşağı sıxlıqlı polietilen, alüminium hidroksid.*

ВЛИЯНИЕ КОНЦЕНТРАЦИИ ГИДРОКСИДА АЛЮМИНИЯ НА СВОЙСТВА И ЗАКОНОМЕРНОСТЬ КРИСТАЛЛИЗАЦИИ КОМПОЗИТНЫХ МАТЕРИАЛОВ НА ОСНОВЕ СМЕСЕЙ ПОЛИЭТИЛЕНА ВЫСОКОЙ И НИЗКОЙ ПЛОТНОСТИ

Ф.А. Мустафаева

Институт Полимерных Материалов Национальной АН Азербайджана
AZ5004, г. Сумгайыт, улица С.Вургуна, 124; e-mail: mustafayevafatima@mail.ru

В статье приводятся результаты исследований влияния концентрации гидроксида алюминия на свойства и закономерность кристаллизации композитных материалов на основе смесей полиэтилена высокой и низкой плотности. Исследования проводились с образцами, содержащими 1, 3, 5 и 10 % масс. гидроксида алюминия. Все композитные материалы были на основе смесей полиэтилена высокой и низкой плотности, взятых в соотношении 50/50. Дилатометрические исследования проводились на приборе ИИРТ-1, в процессе ступенчатого охлаждения образцов при нагрузке 5.3 кг. Установлена температурная зависимость удельного объёма, плотности и свободного объёма композитных материалов. Плотность композиций при температуре 190°С была идентифицирована на капиллярном реометре марки CEAST MF50. Определены температура начала кристаллизации и приближенные значения температуры стеклования композитных материалов. Исследованы такие физико-механические свойства композитов, как разрушающее напряжение и относительное удлинение.
Ключевые слова: *кристаллизация, дилатометрия, удельный объем, смесь полимеров, полиэтилен высокой плотности, полиэтилен низкой плотности, гидроксид алюминия.*