International Journal of Advanced Research and Development
ISSN: 2455-4030; Impact Factor: RJIF 5.24
Received: 11-04-2019; Accepted: 17-05-2019
www.advancedjournal.com
Volume 4; Issue 4; July 2019; Page No. 13-17

Kinetic regularities of crystallization of high-filled nanocomposite materials based on high density polyethylene and inorganic substances

Rena Vagif Kurbanova[1], Reykhan Sharkhmardan Gadjiyeva[2], Elmira Iskander Suleymanova[3]
[1, 3] Ph.D., Department of Chemistry, University of Oil and Industry, Azerbaijan
[2] University of Oil and Industry, Azerbaijan

Abstract

Influence of type of inorganic fillers nanoparticles on regularity of changing of special volume depending on temperature for nanocomposites of high density polyethylene is researched. Kinetic regularities and crystallization mechanism of polymer nanocomposites are determined according to Avrami equation.

Keywords: dilatometry, specific volume, crystallization, free volume, occupied volume, nanocomposite, inter spherulitic structure, supramolecular structure, first-order phase transition

---

Introduction

Throughout the world, the problem of developing and researching of nanocomposites for structural purposes is becoming increasingly important. It is interpreted that the nanocomposites, in fact, opens up new possibilities of industrial polymers in the direction of obtaining on their basis of new types of structural materials with improved mechanical and operational properties. A great need arises in the production of nanomaterials intended for use in electronic engineering, machine engineering, space technology, military equipment, etc. [1-5].

At the same time, theoretical studies of the regularities of the crystallization of nanocomposites, which provide answers to many questions on their practical implementation under real conditions of processing by injection molding and extrusion, acquire considerable importance. Thus, for example, in the process of processing by the above methods, the paramount importance is given to research relating to the process of cooling and crystallization of the melt of composites in calibration nozzles or molds of processing equipment. For a qualified approach to the selection of the optimal processing regime for highly filled composite materials based on crystalline polymers, it is necessary to have sufficiently convincing data on the behavior of the polymer melt when passing from a viscous-flowing state to a solid [6- 8].

It is also known that the method of dilatometric studies gives a fairly clear idea of the cooling process and the kinetics of crystallization of polymer composite materials [9]. This circumstance, in turn, makes it possible to implement a systematic approach for the correct selection of the cooling and molding mode of polymer composites during their processing by injection molding and extrusion methods. It is the systematic approach to the analysis of the structure and properties of polymer composites that allows us to obtain sufficiently complete information on the regularities of the crystallization process in the forming part of the equipment. The use of nanoparticles as a filler of plastics introduces quite serious adjustments for establishing the relationship at the "filler-polymer matrix" interface [1].

In this case, very important is the study of the influence of the method of introducing filler on the structure and properties of the polymer matrix. The use of various methods for the modification of polymers with mineral fillers allows for the correct approach to the establishment and study of the interaction at the polymer- filler interface.

In this regard, the purpose of the studies is to determine the effect of the method of introducing nanoparticles of various types on the variation in the regularity and mechanism of crystallization of nanocomposite materials.

Experimental part

As the object of research has been used high-density polyethylene (HDPE) grade mark of HD5218 with the following properties:

Breaking stress:	29.0 MPa
Elongation at break:	30%
Melt index:	24.0 g/10min
Vicat softening temperature:	125°C

As fillers of plastics have been used nanoparticles with a size of up to 110 nm:

- Aluminum oxide Al2O3 is a binary compound of aluminum and oxygen. In nature it is distributed as the main constituent of alumina;
- Silicon dioxide (silica, SiO2) is crystalline silicon dioxide. Silicon dioxide is the main component of almost all terrestrial rocks. 87% of the mass of the lithosphere consists of silica and silicates.
- Synthetic silica (amorphous silica) is an environmentally friendly product with a wide range of applications. According to its characteristics and properties, it is close to or similar to foreign synthetic silica such trade names as aerosil, orisil, asyl, gasil, sorbosil, tixosil, etc.
- Perlite is a rock of volcanic origin. Perlite is characterized by a fine concentric- shell-like

individuality (perlite structure), along which it breaks down into rounded cores (pearls) resembling pearls with a characteristic luster. Among other volcanic rocks, perlite is distinguished by the presence of constitutional water (more than 1%). The porosity can be 8-40%.

Dilatometric studies of the kinetic regularities of the stepwise crystallization of polymer nanocomposites were carried out in accordance with the procedure given in [9].

Nano-fillers were introduced into the melt of HDPE on rollers at a temperature of 190°C. To study the physico-mechanical properties of polymer composites, they were pressed at a temperature of 210°C. From the pressed plates, samples were cut to determine the Breaking stress and the elongation at break of the filled composites. Nano-fillers were introduced into the composition of polyethylene by the method given in [10].

Breaking stress and elongation at break were determined in accordance with GOST 11262-80.

Results and Discussion

There are two main ways of introducing the filler into the polymer: 1 - mixing the filler in the polymer melt during processing or granulation, 2 - during the synthesis of polymers, i.e. polymerization filling. Both of these methods have their advantages and disadvantages. The introduction of mineral filler in the process of mechanical mixing is simple, but at the same time it does not allow uniform dispersion of the filler in the polymer volume. The introduction of the mineral filler at the stage of polymer synthesis (polymerization filling) provides not only its uniform dispersion in the bulk of the polymer matrix, but also contributes to a significant increase in the complex of its physico-mechanical properties [10].

Figure 1 shows the curves of the specific volume versus temperature $Vi = f(T)$ for HDPE compositions with different chalk content introduced in the ethylene polymerization stage (curves 1-3) and in the process of mechanical mixing on rolls (curves 4, 5). From the presented dilatometric curves, it can be established that with an increase in the content of chalk in the polymerization-filled compositions from 13.5 to 62 wt %, the specific volume (Vi) decreases sharply. Similarly, an increase in the concentration of chalk introduced into HDPE by a mechanical method leads to a regular decrease in the specific volume. It is characteristic that irrespective of the concentration of the filler and the method of its introduction into the polymer in a narrow temperature range of 398-403 K, crystallization from the melt of composites or a first-order phase transition is observed. Thus, if the sharp change in Vi in the temperature transition region for HDPE + 13.5 wt % chalk is 0.14 cm3/g, for HDPE+20 wt % - 0.125 cm3/g, HDPE+44 wt % - 0.07 cm3/g, HDPE+50 wt % - 0.075 cm3/g, HDPE+62 wt % - 0.065 cm3/g. Consequently, with an increase in the filler concentration, the values of Vi in the region of the phase transition decrease substantially and simultaneously this shift shifts to a region of comparatively high temperatures from 398 to 403 K. Slow cooling of the melt in the presence of the filler leads to the fact that the phase transition begins at a relatively higher temperature. This is interpreted by the fact that in the case under conside-ration, the filler nanoparticles simultaneously act as a structurant, forming in the melt heterogeneous crystallization centers that accelerate the crystallization process of HDPE [1].

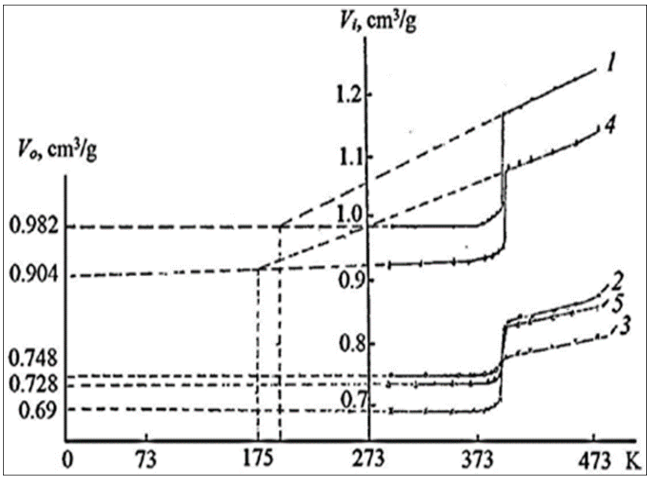

Fig 1: Dependence of specific volume on temperature for polymerization-filled compositions (1-3) and mechanical mixtures (4, 5) with different content of chalk, wt%: 1- 13.5, 2- 44, 3 – 62, 4 – 20, 5 – 50

Analogously, the dependences Vi=f(T) for HDPE compositions with Al2O3 and SiO2 were investigated. It can be established from the data presented in Fig. 2 in the region of the viscous-flowing state that the specific volume decreases with an increase in the Al2O3 content from 13 to 53 wt %. And in this case, regardless of the type of filler, a first-order phase transition occurs in a narrow temperature range of 398-403 K. As the concentration of the filler Vi increases, in the region of the phase transition it also decreases from 0.173 to 0.09 cm3/g. It should be noted that, in contrast to HDPE samples containing Al2O3, the introduction of SiO2 on the contrary promotes a certain increase in Vi in the region of the phase transition. For example, the change in Vi in the region of the phase transition in the HDPE+13 wt% SiO2 composition is 0.116, HDPE+18 wt % 0.154, HDPE+27 wt % 0.134, HDPE+32 wt % 0.144 cm3/g.

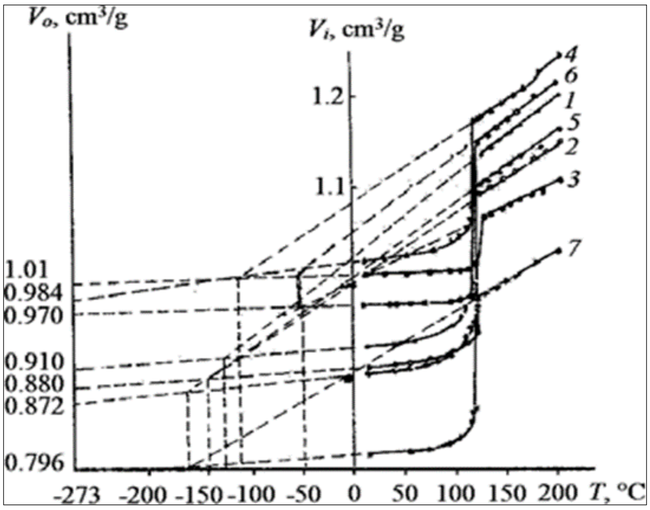

Fig 2: Dependence of specific volume on temperature for various concentrations of Al2O3 (1-3) and SiO2 (4-7), wt%:1- 13, 2- 20, 3 – 53, 4 – 13, 5 – 18, 6 – 27, 7 - 32

In the first case, the decrease in Vi in the region of the phase transition can be interpreted in that the proportion of the polymer in the composition decreases with increasing Al2O3, and in the second case, the increase in Vi is a significant effect from the formation of heterogeneous nucleation centers by SiO2 particles. The filler, depending on its nature, can have a different effect on the character of the crystallization of HDPE in the composition. When studying the regularities of crystallization of filled HDPE compositions, we introduced concepts of "true" and "apparent" crystallization from the melt. This is explained by the fact that, in contrast to polymers, fillers are subjected to a very slight volumetric expansion. Therefore, if we exclude the volume and weight fractions of the filler from the polymer matrix, it is possible to study the "true" change in the regularity of $V_i'=f(T)$ only by the polymer component.

Figure 3 shows the dilatometric curves of the dependence of the true specific volume (V_i') on temperature. Analysis of these curves shows that when the true crystallization of HDPE is determined, the dependence $V_i'=f(T)$ changes according to a certain pattern: if the increase in the concentration of SiO2 did not lead to an additive change in the study of "apparent" crystallization (Fig. 2), *Vi=f(T),* then when considering the "true" crystallization of these same samples, such a regularity is revealed.

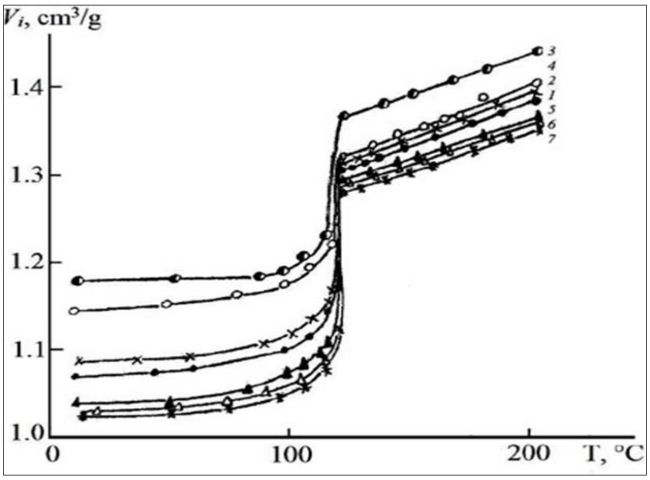

Fig 3: Dependence of "true" specific volume on temperature for compositions with different content of HDPE filler (wt%): Al2O3 (1-3) and SiO2 (4-7):1 – 13, 2 – 20, 3 – 53, 4 – 13, 5 – 18, 6 – 27, 7 – 32.

The glass transition temperature (Tg) was determined by extrapolating the dependence *Vi=f(T)* from the temperature range in which the polymer is in the viscous state to the solid state region [2].

When T_g is determined from the dilatometric curves of the apparent crystallization of polymerization-filled HDPE compositions, it is not possible to trace a clear pattern in the change in the glass transition temperature as a function of the filler concentration. A completely different picture is observed in the determination of T_g from the dilatometric curves of the "true" crystallization of the HDPE composition, according to which the glass transition temperature increases with an increase in the content of these fillers. This circumstance indicates that, depending on the type and concentration of fillers, their effect on the crystallization process and the formation of the supramolecular structure of the polymer are manifested in different ways. Thus, for example, a particle of highly dispersed filler can be either a center of crystallization with the formation of spherulite, or it can be displaced during crystallization into interspherulitic disordered regions, mainly located in defective regions. In this case, if the size of the filler particles exceeds the diameter of the spherulite core, they cannot be centers of formation of crystalline formations [3]. Taking into account that the nanoscale particles of the filler are much smaller in diameter than the growing fine spherulitic structures, a very real possibility is created for the formation on their basis of heterogeneous crystallization centers.

Structural features of polymers, as well as possible phase transitions and the entire complex of relaxation processes are largely determined by the "free" volume and its temperature dependence. Figures 1 and 2 show the extrapolation of the dependence *Vi=f(T)* to absolute zero, with approach to which the free volume becomes zero. With this processing of dilatometric data, it is possible to determine the specific volume of the polymer composition at 0 K, i.e. occupied volume (Vo). And then, knowing *Vi* at any temperature, we can calculate the value of the "free" specific volume using the difference $V_f=V_i-V_o$.

In crystalline polymers, in particular HDPE, the free volume is predominantly composed of defects in crystalline structures and intersherolite space, which is generally generalized under the name "amorphous region" [4]. Therefore, when studying the crystallization of filled polymer systems, it seems interesting to investigate the regularity of the change in the free volume as a function of the temperature and concentration of the filler.

For example, Figures 4 and 5 show the temperature dependences of the free specific volume of chalk and perlite-filled HDPE compositions.

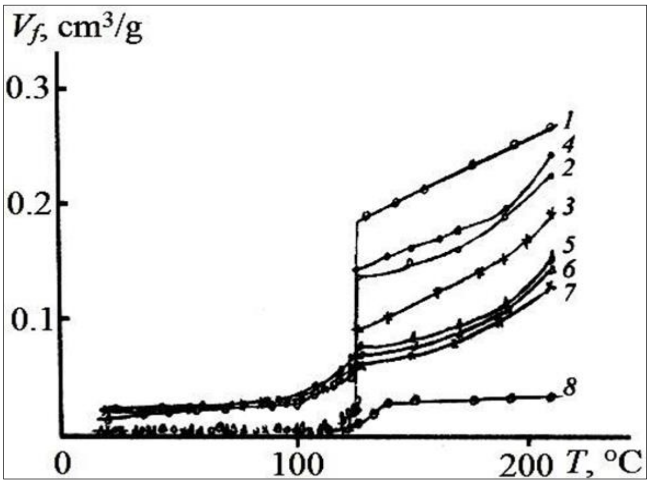

Fig 4: Dependence of the free specific volume on temperature for polymerization-filled HDPE compositions at different perlite concentrations (wt%): 1- 14, 2- 23, 3 – 30, 4 – 34, 5 – 41, 6 – 45, 7 – 50, 8 - 62.

From Fig. 4, it is seen that with increasing perlite concentration in polymerized- filled HDPE compositions in the viscous flow region, a natural decrease in the free specific volume is practically observed. In a solid area, i.e. after a phase transition, a violation of the additivity of the change in the free volume from the perlite concentration is observed. In particular, it was found that the density of the polymer composition increases with increasing perlite concentration to 34 wt%. Further increase of the latter is accompanied by a decrease in density. This circumstance is important, since it once again confirms the opinion that perlite particles fulfill not only the functions of nucleation nuclei. At high perlite concentrations, part of it is displaced into intersherolite regions, thereby filling the voids, and loosening the supramolecular structure of the nanocomposite. Analysis of the dilatometric curves in Fig. 5 shows that during the polymerization filling, an increase in the chalk content from 13.5 to 62 wt% is accompanied by a decrease in the free specific volume, both in the viscous flow region and in the solid phase.

Fig. 5 also shows data on mechanically filled compositions. It can be established from a comparative analysis of curves 4 and 5 that with an increase in the chalk concentration from 20 to 50 wt%, the specific volume decreases substantially both in the region of the viscous-flow and solid states.

For a clearer interpretation of the regularities considered above, it seemed interesting to study the kinetics of crystallization of filled polymer compositions in Avrami coordinates, according to which the crystallization process is described by nexpression: $\varphi = e–k\tau$, where φ is the part of a polymer that has not undergone transformation into a crystalline phase; k is the generalized constant of nucleation and growth of crystals; n is a constant (varies from 1 to 4), its value depends on the nature of the nucleation and growth process [8].

The double logarithm of Avrami equation gives: $\lg(-\ln\varphi)=\lg k +\lg\tau$. This dependence must be a straight line in coordinates $\lg(-\ln\varphi)$-$\lg\tau$. Processing of data on the kinetics of crystallization of polymer compositions showed the applicability of the Avrami theory. Thus, it has been established that the value of n for HDPE and its composition with Al2O3 varies within the limits of 0.72-1.04 (Fig. 6), and for polymer compositions containing SiO_2, as the filler concentration increases from 13 to 32.5 wt%, the value of n increases from 1.0 to 1.38. The latter circumstance indicates that with increasing SiO_2 content in HDPE the rate of crystallization increases. In both cases, the crystallization process proceeds along a single mechanism with the formation of lamellar crystals, for which the value of n varies within 1-2.

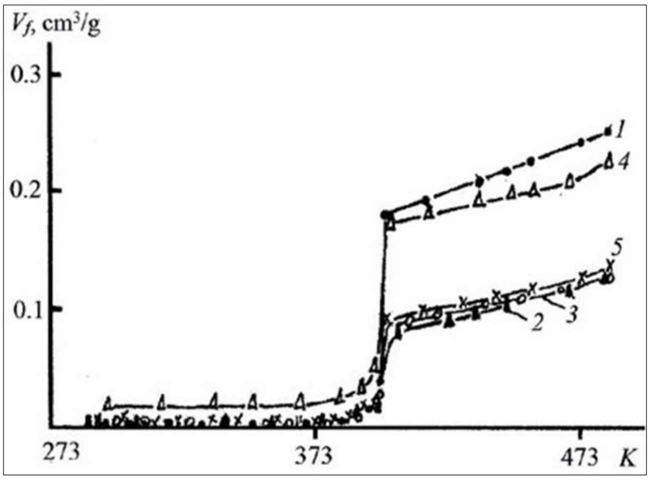

Fig 5: Dependence of the free specific volume on temperature for polymerization-filled HDPE compositions (1-3) and mechanical mixture (4, 5) with different chalk content (wt %): 1 – 13.5, 2 – 44, 3 – 62, 4 – 20, 5 – 50. Vf, cm3/g

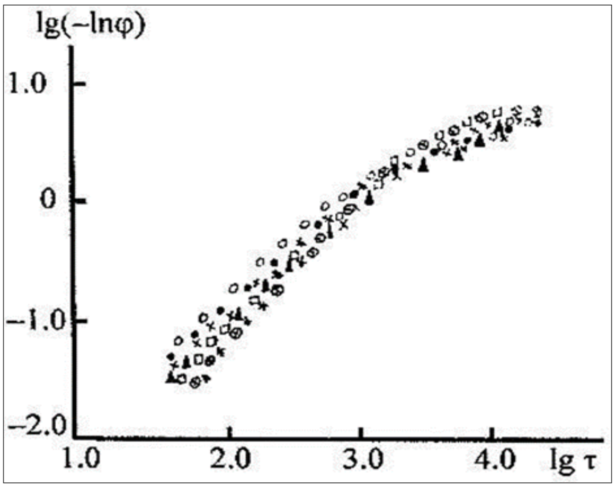

Fig 6: Kinetics of crystallization of HDPE compositions with different contents of Al2O3 (1-3) and SiO2 (4-7) (wt %): 1(o) – 13, 2(•) – 30, 3(×) – 53, 4(▲) – 13, 5(⊗)– 18, 6(ϒ) – 37, 7(☼) – 32.

Analyzing the data presented in Fig. 7, it can be established that with an increase in the aerosol concentration from 13 to 31 wt%, the value of n practically does not change and varies within 1.4-1.6. In any case, an increase in the value of n indicates an increase in the rate of crystallization of HDPE. It should be noted that if in the initial HDPE the proportion of the polymer that undergoes a first-order phase transition φ is 0.9-0.95, then for the filled polymer systems, φ= 0.55-0.75. A small deviation from the linear relationship, especially in the final stage of isothermal crystallization, is explained by the slowing down of the crystallization process.

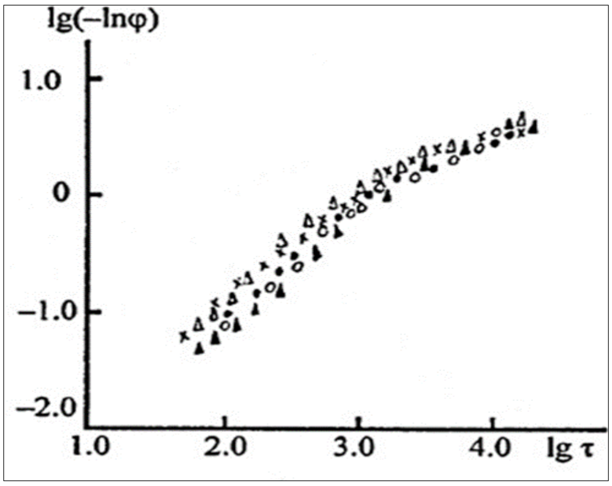

Fig 7: Kinetics of crystallization of HDPE compositions with different content of aerosil (1-4) and Fe2O3 (5) (wt %): 1(×) – 10.5, 2(Δ) – 14.5, 3(▲) – 24, 4(o) – 31, 5(•) – 63.

This phenomenon can be caused by the fact that in the presence of the filler, simultaneously with the increase in heterogeneous nucleation centers, the number of crystalline formations rapidly filling up with a free volume in the polymer and increasing the probability of collision of growing structures from each other grows.

The increase in the number of collisions has a certain effect on the slowing of the growth rate of crystals and the formation of fine spherulite structural formations. This circumstance, in turn, entails a deviation of crystallization isotherms from rectilinear dependence. Further growth of crystallinity is already associated with the process of improvement or a kind of "healing" of defects in primary structures, which is not described by the Avrami equation [6].

In comparison with the initial HDPE, composite materials containing mineral fillers have higher values of physico mechanical properties. The maximum strength characteristics are achieved with the introduction of about 30 wt % of the filler.

It has been found that mechanically filled HDPE compositions are substantially inferior in properties to polymerization-filled composites. Thus, for example, if the maximum strength of perlite-filled HDPE compositions (at 30 wt %) at the synthesis stage is 37 MPa, then for mechanical injection it is 19.8 MPa. The latter is explained by the fact that in the case of polymerization filling, the strength of the adhesion of the polymer to the filler particles is significant and plays a dominant role in evaluating the complex of properties of the compositions as a whole.

Thus, based on the foregoing, it can be concluded that the dilatometric characterization of polymer composites provides a fairly complete picture of the crystallization processes of the filled composites. These studies will allow specialists to correctly select the optimal conditions for cooling the melt of the composite in the mold of the injection molding machine and the molding head of the extruder.

References

1. Кахраманов Н.Т., Азизов А.Г., Осипчик В.С., Мамедли У.М., Арзуманова Н.Б. Наноструктурированные композиты и полимерное материаловедение. Пластические массы, 2016, № 1-2, с. 49-57.
2. Берлин А.А., Вольфсон С.А., Ошман В.Г. Принципы создания компози- ционных материалов. М.: Химия, 1990. - С. 240.
3. Шитов Д.Ю., Кравченко Т.П., Осипчик В.С., Раков Э.Г. Композиционные материалы на основе полипропилена с углеродными наполнителями. Пластические массы, 2013, № 5, с. 29-32.
4. Петрюк И.П. Влияние параметров дисперсной структуры на содержание межфазного слоя в наполненных полимерах. Пластические массы, 2014,№ 5-6, с. 7-9.
5. Гордиенко В.П., Сальников В.Г. Влияние диоксида кремния различной природы на структуру и свойства линейного полиэтилена при УФ-облучении. Пластические массы, 2014, № 5-6, с. 9-13.
6. Kakhramanov N.T., Ismailzade A.D., Arzumanova N.B., Mammadli U.M., Martinova Q.S. Filled composites based on polyolefins and clinoptilolite. American Scientific Journal, 2016, №4 (4), p. 60-65.
7. Кахраманов Н.Т., Арзуманова Н.Б., Осипчик В.С., Гулиев А.М. Реоло- гические свойства композитных материалов на основе рандом полипро- пилена и везувиана. Перспективные материалы, 2017, № 4, с. 35-47.
8. Торнер Р.В. Теоретические основы переработки полимеров (механика процессов). М.: Химия, 1977. - С. 252.
9. Буният-заде А.А., Кахраманов Н.Т., Щаринский Е.А. Исследование селек- тивного влияния длины привитых цепей на процесс изотермической кристаллизации несовместимых бикомпонентных систем на основе ПЭВП и акрилонитрила. Высокомолекулярные соединения, 1981, т. 23(А), №5, с.1017-1020.
10. https://www.kazedu.kz/referat/111062.