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THERMOMECHANICAL PROPERTIES OF COMPOSITE MATERIALS BASED ON MIXTURES OF HIGH AND LOW DENSITY POLYETHYLENES**F.A. Mustafayeva* , N.T. Kahramanov**

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Abstract: *The results of the research into the influence of polymer components ratio - high density polyethylene and low density polyethylene, into the regularity of changes in thermomechanical properties are presented. The deformation was measured at varying temperatures and at a constant load of 0.5 kg/cm². The concentration of low density polyethylene varied from 10 to 100 wt%. Depending upon the test temperature, two physical states were recorded: solid and viscous-flow. It found that as the concentration of low-density polyethylene in the composition of the polymer mixture rose, the transition temperature in the softened state and the transition temperature in the viscous-flow state dropped. The differential thermal analysis curves showed that at low concentrations of high density polyethylene, two-phase systems were formed in the polymer system. The study of composites based on aluminum hydroxide and a mixture of high and low density polyethylene revealed a wave-like change in softening and viscous-flow temperatures.*

Keywords: *polymer blend, high density polyethylene, low density polyethylene, thermomechanical properties, viscous-flow state.*

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Introduction

At present, polymers and materials based on them have take the place of such basic construction materials as wood, metal, concrete and ferro-concrete. The potentialities of polymer materials are extremely wide due to the variety of polymers and fillers, the inexhaustible variability of mixtures of composites based on them and their modification methods [1]. One such modification method is the polymer blending. Polymer blends are physical mixtures of two or more polymers and are promising for the preparation and development of new materials. By mixing polymers, it is feasible to obtain composite materials with predetermined structural features and properties. Since

polyolefins are the most widely used commercial polymers, the research into the properties of composite materials based on the mixture of polyethylenes is of great interest [2-4].

Having regard to the above, the aim of this work was to study mixtures of low and high density polyethylene and composites based on them by thermo-mechanical analysis that makes it possible to get valuable information on thermal expansion, softening temperatures, composition and phase changes of materials simply by applying a constant force depending on temperature.

Experimental part

Polyethylenes with the following properties were used as the main object of study: low density polyethylene (LDPE) with a

density of 912 kg/m³, ultimate tensile stress 15 MPa, elongation at break 764 %, melt flow rate 8.9 g/10 min. (at 5 kg load and 190°C

temperature); high density polyethylene (HDPE) with a density of 963 kg/m^3 , ultimate tensile stress 30 MPa, elongation at break 50 %, melt flow rate 17 g/10 min. (at 5 kg load and 190°C temperature).

Aluminum hydroxide $\text{Al}(\text{OH})_3$ (GOST 11841-76, OKP 631887 repackaged by ZAO VEKTON) is a colorless solid, insoluble in water. When heated above $180\text{--}200^\circ\text{C}$, it decomposes depending on the particle size.

Polymer blends with various component ratios in blends of 90HDPE/10LDPE, 80HDPE/20LDPE, 70HDPE/30LDPE, 60HDPE/40LDPE, 50HDPE/50LDPE, 40HDPE/60LDPE, 30HDPE/70LDPE, 20HDPE/80LDPE, 10HDPE/90LDPE were made on laboratory rolls at temperatures of $150\text{--}170^\circ\text{C}$ within 8-10 minutes. Furthermore, at a pressing temperature equal to $170\text{--}190^\circ\text{C}$, plates were molded from which appropriate samples were cut out for testing.

Composite materials HDPE/LDPE+ $\text{Al}(\text{OH})_3$ were obtained by the

above method. The concentration of aluminum hydroxide in these composites was 1, 3, 5, 10, 30 and 50 wt%.

The thermal stability test was carried out using a thermogravimetric analysis on a Q-1500 D derivatograph from MOM (Hungary) of the Paulik-Paulik-Erdey system. Sample weight 100 mg, channel sensitivity TG-100, DTG-1mV, DTA-250 μV , T/V-500/5, crucible Pt. Samples were taken on a derivatograph in air flow and heating rate $5^\circ/\text{min}$.

The thermomechanical properties of the samples were specified using a Kanavets instrument. The deformation was measured at successively changing temperatures (T) and a load of 0.5 kg/cm^2 with a heating rate of 50°C/h . To carry out research, tablets 24 mm in diameter, 6 mm high, and weighing 3.5–4 gr with a smooth surface were pressed in a special mold. Based on the experimental data obtained, thermomechanical curves of $\Delta = f(T)$ dependence of polymer composites were constructed.

Results and discussion

Fig. 1 shows thermomechanical deformation-temperature curves for HDPE, LDPE, and composites based on HDPE + LDPE blends at different blend ratios. On all the curves shown in this Fig., the structural transition of composite materials from the solid to the viscous-flow state is clearly traced. Comparing the curves in this Fig., it can be established that as the concentration of LDPE in the HDPE + LDPE mixture increases, a regular decrease in the softening temperature and the transition temperature in a viscous-flow state is observed. In the HDPE, 90HDPE/10LDPE, 80HDPE/20LDPE, 70HDPE/30LDPE, 60HDPE/40LDPE, 50HDPE/50LDPE, 40HDPE/60LDPE, 30HDPE/70LDPE, 20HDPE/80LDPE, 10HDPE/90LDPE, LDPE sequence, the transition temperature in the softened state is respectively 145°C , 143°C , 140°C , 140°C , 135°C , 135°C , 135°C , 130°C , 127°C , 113°C , 103°C ; and the transition to a viscous-flow state is respectively 147°C , 145°C , 144°C , 143°C , 143°C , 143°C , 143°C , 139°C , 138°C , 133°C , 118°C . Fig. 1 shows that the thermomechanical curves of polymer mixtures

are located between the curves of the initial HDPE and LDPE. The obtained results are interpreted in such a way that with an increase in the concentration of LDPE in a mixture of HDPE + LDPE, a regular decrease in the density, melting point, and crystallinity of the mixture occurs. The decrease in the temperature of the first-order phase transition together with an increase in the LDPE concentration in the mixture shows an increase in the fraction of the amorphous phase.

In the thermomechanical curves of the initial LDPE and the composite material with the composition 10HDPE/90LDPE, a slightly different regularity is observed in the change of the thermo-mechanical curves. This difference appears itself mainly in the region of deformations and the temperature range from 60°C to 103°C for LDPE and from 61°C to 113°C for the 10HDPE/90LDPE composition, which can be associated with partial amorphization of the mixture structure. This circumstance is especially strongly reflected in the decrease in the physical-mechanical and

thermophysical properties of the compositions. [5].

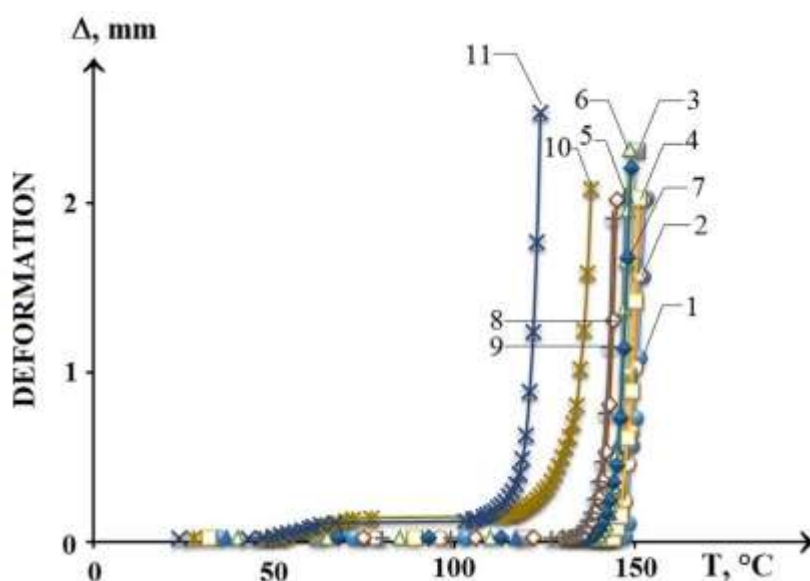


Fig. 1. Influence of the concentration of LDPE + HDPE mixture components (wt%) on the nature of the change in thermomechanical curves: 1(●)–HDPE; 2(○)–90HDPE/10LDPE; 3(■)–80HDPE/20LDPE; 4(□)–70HDPE/30LDPE; 5(▲)–60HDPE/40LDPE; 6(Δ)–50HDPE/50LDPE; 7(◆)–40HDPE/60LDPE; 8(◇)–30HDPE/70LDPE; 9(+)-20HDPE/80LDPE; 10(*)–10HDPE/90LDPE; 11(x)–ASPE.

A comparative analysis of the results of thermo-mechanical tests and differential thermal analysis once again proves our assumption on the appearance of "concentration compatibility" of the mixture components in the range of ratios 40/60 - 60/40 [6]. According to the data of differential thermal analysis (Fig. 2), the melting temperature of the studied samples changed in the following sequence: HDPE-125°C, 90HDPE/10LDPE-125°C, 80HDPE/20LDPE-125°C, 50HDPE/50LDPE-120°C, 20HDPE/80LDPE-105°C and 125°C, 10HDPE/90LDPE-100°C и 120°C, LDPE-95°C. Analyzing the curves in this Fig., it can be seen that at a concentration of LDPE in the mixture below 50 wt%, only one endothermic melting peak appears, and above 50 wt%, 2 endothermic melting peaks appear. This fact is interpreted, first of all, by the insufficient compatibility of HDPE with LDPE at its low concentrations, a relatively large difference in the melting point [6]. The existence of two melting peaks indicates the formation of a two-phase system, or rather, it can be associated with phase inversion, according to which, with an excess of LDPE, it becomes a dispersed

medium, and HDPE becomes a dispersed phase.

It should also be noted that there is a discrepancy between the melting point values determined by the DTA method and the thermomechanical method. This is interpreted by the fact that the thermomechanical analysis estimates the softening temperature of the polymer, and DTA the melting process itself, which usually takes place in a certain temperature range, which can vary between 8 and 12°C [7, 8].

It was of interest to investigate the effect of aluminum hydroxide flame retardant filler on the thermomechanical properties of HDPE/LDPE blends. To this end, composites based on 50 wt% HDPE/50 wt% LDPE and aluminum hydroxide were obtained. The concentration of aluminum hydroxide varied in the range of 1-50 wt%. The choice of the HDPE/LDPE =50/50 mixture ratio came from the fact that, according to the results of the study of the physical-mechanical [6] and rheological [9] properties of composite materials based on mixtures of high and low density polyethylene, it was confirmed that the best technological miscibility and mutual

dispersibility were achieved when using an equal amount of components of the mixture.

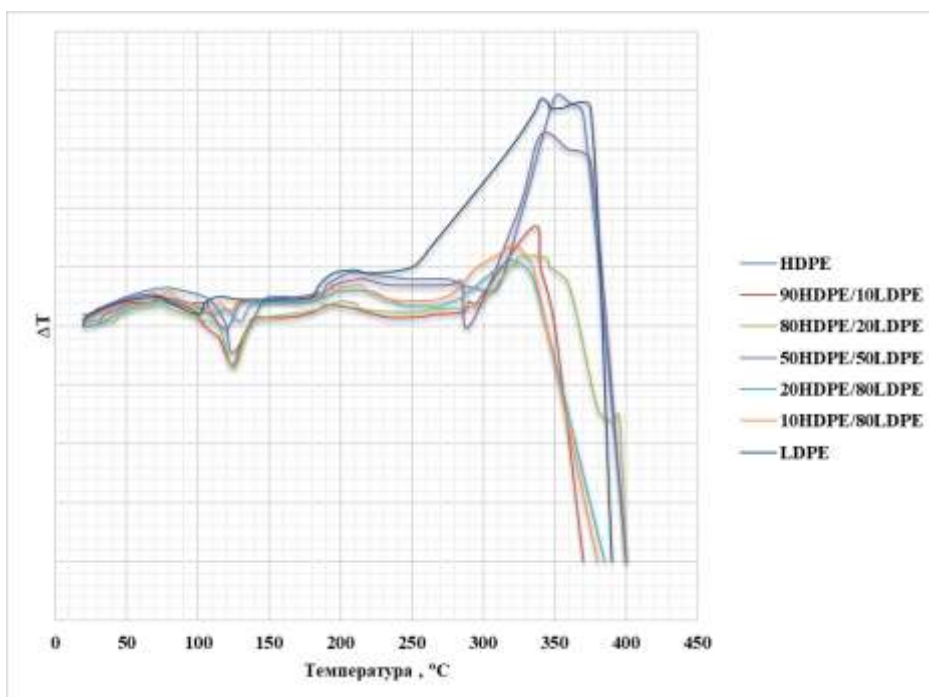


Fig. 2. Differential thermal analysis curves

Fig.3 shows the thermomechanical curves of HDPE/LDPE+Al(OH)₃ composites. As can be seen from this Fig., the test samples do not undergo deformation over a wide temperature range. Only after a temperature of 136°C does the process of softening of the composites begin. A comparative analysis of the curves

reveals that with an increase in the concentration of aluminum hydroxide, the transition temperatures in the softened state and the transition temperatures in the viscous-flow state of composites with 0, 1, 3, 5, 10, 30, and 50 wt% Al(OH)₃ compositions changed, respectively, in the following sequence:

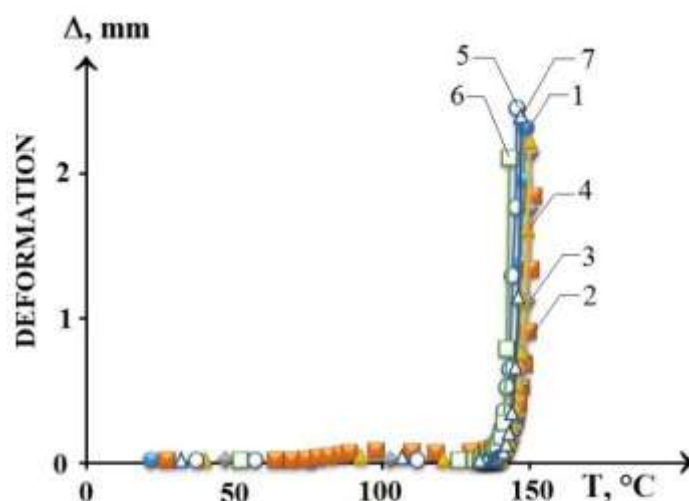


Fig. 3. Influence of aluminum hydroxide concentration (wt%) on the nature of the change in thermomechanical curves of compositions based on HDPE/LDPE + Al(OH)₃: 1(●)–initial HDPE/LDPE; 2(■)–1% Al(OH)₃; 3(◆)–5% Al(OH)₃; 4(▲)–10% Al(OH)₃; 5(○)–30% Al(OH)₃; 6(□)–50% Al(OH)₃.

135°C, 135°C, 137°C, 134°C, 133°C, 126°C, 133°C and 143°C, 145°C, 145°C, 144°C, 141°C, 141°C, 144°C.

As can be seen from the data obtained, a maximum was observed in the change in both indices. A drop in the temperature of the viscous-flowing state of composites at a

relatively high concentration of flame retardant can be associated with loosening of the crystal structure and accumulation of filler particles in the interspherulitic region. The results of our dilatometric studies of HDPE/LDPE+Al(OH)₃ composites confirm this hypothesis [10].

Conclusions

Based on the foregoing, it can be concluded that with an increase in the concentration of LDPE in the composition of the HDPE + LDPE mixture, a decrease in the softening temperatures and transition temperatures to the viscous-flow state of the composites were observed. Comparative analysis of thermomechanical curves and curves of differential thermal analysis showed that the best technological miscibility and mutual dispersibility was achieved with the ratio of

components HDPE/LDPE=50/50.

Studies of the thermomechanical characteristics of HDPE/LDPE+Al(OH)₃ composites showed that as the concentration of aluminum hydroxide in the composition of the polyethylene mixture increases, a maximum appears, followed by a decrease in the softening temperature and viscous-flow state, due to loosening of the supramolecular structure of the polymer compositions.

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AŞAĞI VƏ YUXARI SİXLİQLİ POLİETİLEN QARIŞIQLARI ƏSASINDA KOMPOZİSİYA MATERİALLARININ TERMOMEXANİKİ XÜSUSİYYƏTLƏRİ

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Xülasə: Məqalədə polimer komponentlərinin - aşağı və yuxarı sıxlıqlı polietilenin nisbətinin termomexaniki xüsusiyyətlərinin dəyişmə qanunauyğunluqlarına təsiri tədqiq olunmuşdur. Deformasiya dəyişən temperatur və 0.5 kq/sm^2 sabit yük altında ölçülmüşdür. Aşağı sıxlıqlı polietilenin miqdarı 10-100 kütlə % aralığında dəyişdirilmişdir. Sınaq temperaturundan asılı olaraq iki fiziki hal qeyd olunmuşdur: bərk və özlüaxıcı. Polimer qarışığın tərkibində aşağı sıxlıqlı polietilenin miqdarının artımı ilə yumşalma temperaturunun və özlüaxıcı temperatura keçid temperaturunun aşağı düşdüyü müəyyən olunmuşdur. Differensial termiki analiz ayrıləri polimer sistemdə aşağı sıxlıqlı polietilenin aşağı miqdarında ikifazalı sistemlərin formalaşdığını göstərmişdir. Aşağı və yuxarı sıxlıqlı polietilen qarışığı və alüminium hidroksid əsasında kompozitlərin tədqiqi yumşalma və özlüaxıcı hala keçid temperaturlarında dalğayabənzər dəyişmənin olduğunu göstərmişdir.

Açar sözlər: polimer qarışığı, yuxarı sıxlıqlı polietilen, aşağı sıxlıqlı polietilen, termomexaniki xüsusiyyət, özlüaxıcı hal.

ТЕРМОМЕХАНИЧЕСКИЕ СВОЙСТВА КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ НА ОСНОВЕ СМЕСЕЙ ПОЛИЭТИЛЕНОВ ВЫСОКОЙ И НИЗКОЙ ПЛОТНОСТИ

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Аннотация: Приводятся результаты исследования влияния соотношения полимерных компонентов – полиэтилена высокой плотности и полиэтилена низкой плотности, на закономерность изменения термомеханических свойств. Деформация измерялась при изменяющихся температурах и при постоянной нагрузке равной 0.5 кг/см^2 . Концентрацию полиэтилена низкой плотности варьировали от 10 до 100% масс. В зависимости от температуры испытания были зафиксированы два физических состояния: твердое и вязкотекучее. Установлено, что с увеличением концентрации полиэтилена

низкой плотности в составе полимерной смеси наблюдается снижение температуры перехода в размягченное состояние и температуры перехода в вязкотекучее состояние. Кривые дифференциально-термического анализа показали, что при низких концентрациях полиэтилена высокой плотности в полимерной системе формируются двухфазные системы. Исследование композитов на основе гидроксида алюминия и смеси полиэтилена высокой и низкой плотности показало волнообразное изменение в температурах размягчения и вязкотекучего состояния.

Ключевые слова: смесь полимеров, полиэтилен высокой плотности, полиэтилен низкой плотности, термомеханические свойства, вязкотекучее состояние.