

CRYSTALLIZATION REGULARITIES OF A HIGH AND LOW DENSITY POLYETHYLENE BLEND AND COMPOSITE MATERIALS ON ITS BASIS

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Abstract: The results of studies of the regularities and mechanism of crystallization of polymer mixtures of high and low-density polyethylene in various proportions and composite materials based on blends of high and low density polyethylene taken in a 50/50 ratio are given. In filled composites, aluminum hydroxide was used in concentrations of 1, 3, 5, 10% wt. and bentonite in concentrations of 1, 3, 5, 10, 20, 30% wt. Dilatometric studies were carried out on an IIRT-1 device, in the process of stepwise cooling of samples with a load of 5.3 kg.

Keywords: CRYSTALLIZATION, DILATOMETRY, LOW DENSITY POLYETHYLENE, HIGH DENSITY POLYETHYLENE, POLYMER BLEND, BENTONITE, ALUMINUM HYDROXIDE.

1. Introduction

As the engineering, aviation, shipbuilding, and automotive industries developed and improved, increasingly stringent requirements began to be placed on the quality of polymeric materials. It is clear that, according to their characteristics, base polymers produced in the polymer industry are not always able to meet the increased requirements of modern technology. In this regard, the modification methods undertaken in the direction of improving the structure and complex of the properties of polymers allow one to come closer to the accomplishment of the task to one degree or another. One of the most common methods for modifying polymers is blending a polymer with a polymer [1, 2]. 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 [3, 4]. By varying the ratio of high density polyethylene / low density polyethylene (HDPE / LDPE), it is possible to obtain relatively strong and flexible polymeric materials. Along with this, the loading of fillers into their composition actually allows to obtain relatively new types of polymer composites with improved deformation and strength properties, in which the filler plays the role of an amplifier of polymers.

The research task was to study by dilatometry method the regularities and mechanism of crystallization of polymer mixtures of HDPE / LDPE (at 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10 ratios) and composite materials based on HDPE + 50% wt. LDPE and fillers, differing in their nature and particle size.

2. Results and discussion

Industrial objects of HDPE, LDPE, fillers — aluminum hydroxide and bentonite — were used as an object of research. The choice of these fillers in the composition of polymer mixtures was due, above all, the need to obtain fire-resistant composite materials. The HDPE / LDPE ratio in the filled composite materials was 50/50. The choice of this ratio was due to the fact that it is by using an equal amount of HDPE and LDPE in the mixture that their best technological miscibility and mutual dispersibility is achieved.

Composite materials 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, plates were molded from which the corresponding samples were cut down for testing.

Dilatometric studies were carried out on an IIRT-1 instrument during stepwise cooling with a load of 5.3 kg and in the temperature range from 180°C to room temperature.

Studies of the influence of the ratio of the considered polymer components on the density and crystallization onset temperature, which characterizes the first-order phase transition, showed that up to 50% wt. content of LDPE in the composition, the crystallization onset temperature does not undergo any changes and remains within

114°C. At the same time, as expected, there is a regular decrease in the density of samples with increasing concentration of LDPE in the composition. When the concentration of LDPE in a mixture of more than 50% wt. the crystallization onset temperature of the polymer composition begins to decrease. The latter circumstance confirms our understanding of phase inversion at 50% wt. content of LDPE in the composition. The results of studies of the kinetic regularities of crystallization of the original LDPE, HDPE and their mixtures at various ratios showed that all changes in the dilatometric curves of polymer mixtures are concentrated between the curves of the initial components of the mixture (Figure 1).

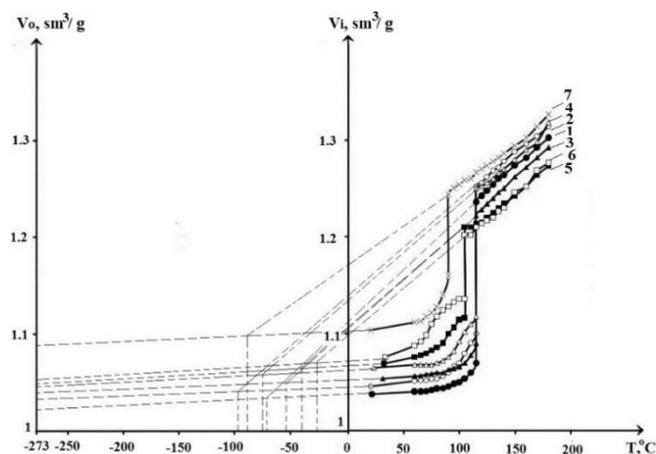


Fig. 1. Kinetic regularities of crystallization of the original LDPE, HDPE and their mixtures at different ratios: 1 (●) – 100% wt. HDPE, 2 (○) – 10% wt. LDPE + 90% wt. HDPE, 3 (▲) – 20% wt. LDPE + 80% wt. HDPE, 4 (Δ) – 50% wt. LDPE + 50% wt. HDPE, 5 (■) – 80% wt. LDPE + 20% wt. HDPE, 6 (□) – 90% wt. LDPE + 10% wt. HDPE, 7 (×) – 100% wt. LDPE

It should be noted that the melting point of HDPE is 125°C and that of LDPE is 95°C. This means that in the process of cooling samples of polymer mixtures, the HDPE macromolecules will first crystallize at 110 - 114°C, and then LDPE. The development of the crystallization process is promoted by such factors as the flexibility of the polymer chains, the symmetry of the molecular structure, the absence of bulky side substituents in the polymer chain, the presence of potential possibilities for fixing orderly arranged macromolecules. It can be assumed that in the process of cooling the samples, the crystallization of HDPE macromolecules and the growth of spherulite formations is accompanied by the displacement of relatively branched LDPE macromolecules into amorphous regions. It is not excluded that, depending on the amount loaded into the composition of the LDPE, the mechanism of crystallization and the packing of its macromolecules may change significantly. Apparently, at low concentrations of LDPE (up to 20% wt.), the crystallization process of the HDPE macromolecules is

accompanied by the formation and growth of its own spherulite formations, which push the LDPE macromolecules into the amorphous regions. Compaction and concentration of LDPE macromolecules in the amorphous regions of the crystalline phase of HDPE create certain steric difficulties for crystallization and folding of branched macrochains into more ordered and perfect crystalline formations. The further crystallization process of LDPE macromolecules in the cramped conditions of the amorphous regions of HDPE becomes excessively difficult. That is why, the process of crystallization of compositions up to 50% wt. LDPE content proceeds at the same temperature close to the crystallization temperature of HDPE, i.e. 114°C. There is reason to believe that the process of melting and crystallization for each of the components of the mixture proceeds independently of each other. Only, in this case, distortions or shifts in the temperature ranges of melting and crystallization are possible. It is possible that with a ratio of components (HDPE / LDPE) within 40-60 / 60-40, the process of formation of crystalline formations under phase inversion proceeds in a slightly different way. It can be assumed that with such a ratio of mixture components a certain parity is achieved, in which the formation and growth of spherulite formations of HDPE and then LDPE are not accompanied by interference in the placement of macromolecules in ordered regions. In addition, we can assume the appearance of "concentration compatibility" of the components of the mixture in the range of 40/60 - 60/40 ratios.

Crystallization of polymers is a spontaneous process. This process is reflected in the change in the characteristic properties of polymers: its density increases, the modulus of elasticity increases, i.e. polymer stiffness, other characteristics change. The filler particles can increase or decrease the crystallization rate of the semi-crystalline polymer, affect the growth of polymer matrix crystals, and the effect of nucleation in the melt. It was interesting to study the effect of aluminum hydroxide and bentonite on the regularities of crystallization of composite materials based on mixtures of high and low density polyethylene.

Studies based on a mixture of HDPE / LDPE (50/50) and bentonite were carried out with different concentrations (1, 3, 5, 10, 20 and 30% wt.) of bentonite. 1% wt. the content of bentonite in a mixture of LDPE / HDPE does not have any change on the temperature of the beginning of the crystallization process, and is equal to 114°C. For composite materials with a concentration of bentonite in the range of 3–30% wt. phase transition of the first kind occurs at 110-113°C. The density corresponding to room temperature for these materials naturally increases. The upper branches of the isotherm (Figure 2) directly reflect a decrease in the specific volume and, accordingly, an increase in the melt density of the composites with an increase in the amount of bentonite in the composition. The loading of bentonite in the composition of the polymer mixture helps to reduce the free specific volume. This fact suggests that the filler particles are mainly embedded in the free volume of the polymers.

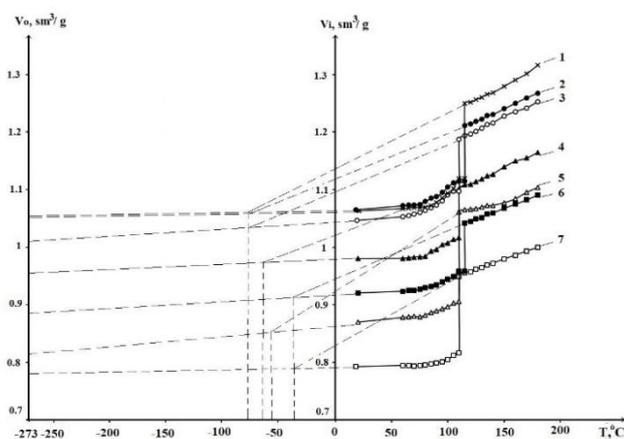


Fig. 2. Regularities of change in specific volume from temperature for nanocomposites based on bentonite / HDPE / LDPE: 1(×)–50% wt. LDPE+ 50% wt. HDPE, 2(●)– HDPE / LDPE+1% wt.

bentonite, 3(○)– HDPE / LDPE+3% wt. bentonite, 4(▲)– HDPE / LDPE+5% wt. bentonite, 5(Δ)– HDPE / LDPE+10% wt. bentonite, 6(■)– HDPE / LDPE+20% wt. bentonite, 7(□)– HDPE / LDPE+30% wt. bentonite

Studies based on a mixture of HDPE / LDPE (50/50) and aluminum hydroxide were carried out with composite materials containing 1, 3, 5, 10% wt. aluminum hydroxide. Loading 1% wt. aluminum hydroxide has almost no effect on the onset temperature of crystallization of the initial LDPE / HDPE mixture and is equal to 114°C. With an increase in the concentration of aluminum hydroxide to 10%, the onset temperature of crystallization of the composites does not undergo any changes and corresponds to a value of 110°C (Figure 3). With an increase in the concentration of aluminum hydroxide, the specific volume of the composite materials decreases, that is, compaction of the material is observed.

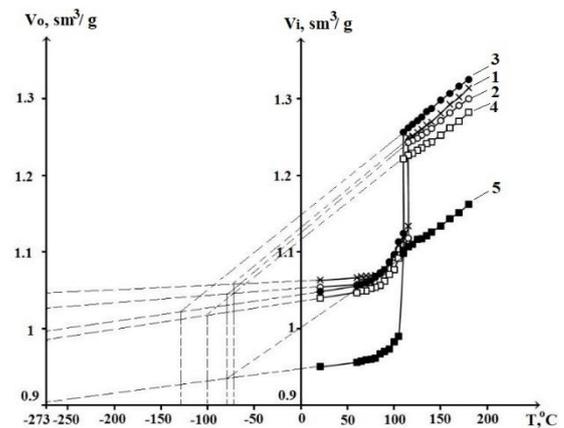


Fig. 3. Graphical dependence of specific volume on temperature for composites based on $Al(OH)_3$ / HDPE / LDPE: 1(×)–50% wt. LDPE+ 50% wt. HDPE, 2(○)– HDPE / LDPE + 1% wt. $Al(OH)_3$, 3(●)– HDPE / LDPE + 3% wt. $Al(OH)_3$, 4(□)– HDPE / LDPE + 5% wt. $Al(OH)_3$, 5(■)– HDPE / LDPE + 10% wt. $Al(OH)_3$

The data obtained showed that at low concentrations of aluminum hydroxide, it contributes to the complete crystallization process, but at concentrations of 5-10% wt. on the contrary, the process of crystallization in filled composites is somewhat more difficult. Comparative analyzes have shown that the value of free specific volume for composites filled with aluminum hydroxide is higher than for the original HDPE / LDPE mixture. This can be explained by the fact that aluminum hydroxide particles, by creating steric hindrances for the complete crystallization of macromolecules in the region of the phase transition, contribute to the loosening of the material.

3. Conclusion

Based on the above, it can be stated that a change in the ratio of components in a mixture of HDPE + LDPE leads to an ambiguous change in the structure and properties of polymer blends. In the ratio 40/60 - 60/40, phase inversion occurs, under which conditions are created for the formation of an optimal crystalline structure. In filled composites, the loading of 1% wt. filler does not affect the crystallization onset temperature of the initial mixture of LDPE / HDPE. With a further increase in the concentration of the filler in the polymer mixture, a decrease in the crystallization onset temperature is observed.

4. References

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