

THE THERMOMECHANICAL PROPERTIES OF COMPOSITES AND THEIR VULCANIZATES BASED ON HIGH DENSITY POLYETHYLENE AND COPPER

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Abstract. The results of a study of the effect of the concentration of finely dispersed copper and crosslinking agents on the thermomechanical properties of composite materials based on high density polyethylene are presented. It is shown that the loading of copper increases the softening temperature of composite materials. At the same time, depending on the test temperature, two physical conditions were recorded: solid and viscous. To improve the compatibility of the mixed components, maleized polyethylene was used as a compatibilizer. Dicumyl peroxide and sulfur were used as crosslinking agents. It was found that at a concentration of dicumyl peroxide of 1.0 - 2.0 wt. %, composites from a highly elastic state pass into an irreversible glassy state and lose their ability to viscous melt flow. During sulfuric vulcanization, composites filled with copper powder are characterized by three physical states: solid, highly elastic, and viscous. The optimal concentrations of reacting components are shown, and the temperature ranges of the corresponding physical states for various composite materials are predetermined. Comparative data of derivatographic analysis and thermomechanical tests are presented.

Keywords: composite, peroxide, sulfur, thermomechanical properties, highly elastic state, crosslinking agent.

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1. Introduction

As the industrial production of polyolefins increased, it became increasingly important to develop new types of polymer materials on their basis, designed to produce structural products with improved performance properties (Berlin *et al.*, 1990; Ermakov *et al.*, 2007; Pomogajlo, 2002). This is achieved in the process of modifying polyolefins by the load of fillers, plasticizers, stabilizers, polymers, etc. The most effective way to expand the areas of their practical use is the loading of various finely divided fillers. From this point of view, the most promising direction is the load of finely divided metal particles into the composition of polyethylene of varying degrees of crystallinity. The most commonly used dispersed fillers are copper, aluminum, iron, bronze, tin, silver, lead, zinc, etc. (Ol'hov *et al.*, 2013; Osama *et al.*, 2009).

The use of filler particles in the composition of polyethylene can significantly improve the strength, heat capacity, thermal conductivity and electrical conductivity of the composite. Along with this, metal-filled composites acquire completely new properties, such as protection against electronic and penetrating radiation, changes in

fire-retardant properties, etc. All these features of metal-filled composites open up new and promising opportunities for their practical application in various fields of modern engineering and technology (Kakhramanov *et al.*, 2016; Kakhramonov *et al.*, 2018b; Cherdynceva *et al.*, 2013).

In connection with the foregoing, in this paper, the main focus is on establishing the effect of the concentration of metal particles on the nature of changes in the thermomechanical characteristics of polymer composites. Such studies will make it possible to obtain accessible information about the processes taking place in the field of phase transitions and, thus, take a reasonable approach to choosing the polymer processing mode.

2. Experimental part

2.1. Materials

As the polymer matrix used high density polyethylene (HDPE) with the following properties: ultimate tensile strength- 31.3 MPa, bending modulus - 753 MPa, elongation at break - 435%, density 946 kg / m³, melt flow index (MFI) equal to 5.6 g / 10 min., heat resistance -119°C, melting point - 131°C, crystallinity 80%.

The compatibilizer is high density polyethylene functionalized with maleic anhydride (MA) - PEMA. The degree of MA grafting in HDPE is 5.6 wt. %.

Dicumyl peroxide (DP) is a cross-linking agent, light yellow powder, with T_m=40°C, designed to produce cross-linked structures in polymer compositions.

Sulfur is a chemical element with atomic number 16. It is widespread, multivalent. Elemental sulfur is a bright yellow crystalline solid at room temperature. Under normal conditions, sulfur atoms form cyclic eight-atom molecules with the chemical formula S₈. Used as a curing agent polymers.

Finely dispersed copper particles with a particle size of 1.0 -2.0 microns were used as a metal filler.

2.2. Preparation of composites

Mixtures based on HDPE, copper and PEMA were prepared on hot rollers at a temperature of 160°C by loading a filler into the polymer melt within 8-10 minutes. And in this case, first PEMA was loaded into the composition of HDPE, and then filler.

In order to modify the properties of HDPE, finely dispersed copper powder with a size of 1.0–2.0 μm was loaded into its composition. The amount of copper in the composition of HDPE varied within 0.5, 1.0, 5.0, 10, 20, 30 wt. %. The components were mixed on hot rollers at a temperature of 150-160°C by loading copper into the HDPE melt within 8 minutes. A crosslinking agent (DP) was introduced into the melt of polymer mixtures in an amount of 0.25-2.0 wt. %. The pressing of plates for testing the physicommechanical properties was carried out under a press at a temperature of 190-200°C and a pressure of 50 tons.

2.3. Characterization of the composites

The size of the nanoparticles of the composites was determined on an instrument of the STA PT1600 model Linseiz Germany.

Derivatographic analysis was performed on a Paulik, Paulik, and Erdei brand instrument.

The melt flow index (MFI) was determined on a MELT FLOW TESTER, CEAST MF50 (INSTRON, Italy) brand rheometer at a temperature of 190°C and a load of 5 kg. Under these conditions, the MFI of the initial HDPE was 5.8 g / 10 min.

Thermomechanical properties were determined on a Kanavets instrument. The deformation was measured at successively changing temperatures (T) at a load of 0.3 kg/cm² and a heating rate of 50°C/h. When constructing the thermomechanical curve of the polymer $\Delta = f(T)$, it is very important to cover, if possible, the entire temperature range of the polymer's existence - glassy (crystalline), highly elastic and viscous flow conditions. Thermomechanical curves reflect all possible physical, physicochemical and chemical changes that occur in the sample during the change in the temperature of the experiment and, thus, provide reliable information on the temperature transitions that are significant for polymer processing.

3. Results and Discussion

The study of the thermomechanical properties of polymer composites provides a reliable picture of temperature transitions in solid, highly elastic, and viscous flowing states (Kakhramanov *et al.*, 2018a). The results of the studies are fundamental in assessing the processability of composite materials by extrusion and injection molding. Determination of the temperature transitions of composites from one physical state to another allows one to make the right choice of the temperature regime of their operation and processing (Allahverdiyeva *et al.*, 2020). At the same time, special attention was paid to improving the compatibility of the mixed components of the mixture, which was ensured by the use of polyethylene modified with maleic anhydride (PEMA). The use of PEMA as a compatibilizer should help increase the polarity of the polymer base and thereby increase the adhesive strength of macrochains on the surface of copper particles. The latter circumstance will unconditionally contribute to the improvement of the physicomechanical and thermophysical characteristics of composite materials.

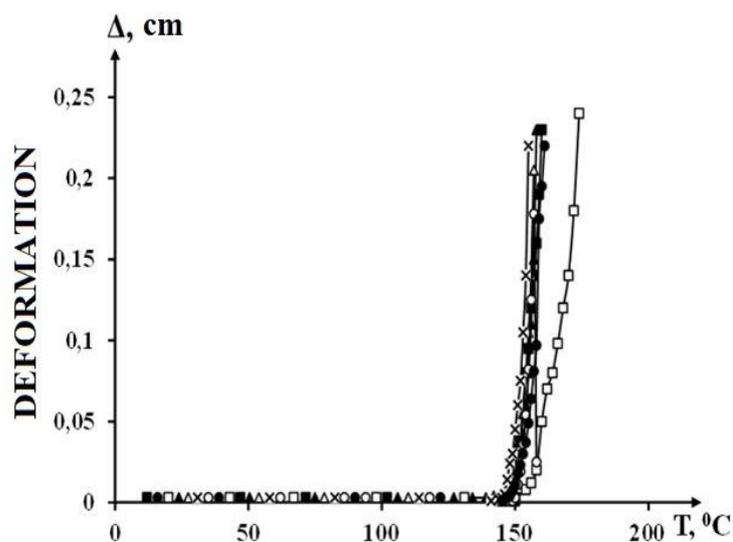


Figure 1. Thermomechanical curves of the dependence of deformation on temperature of composites based on HDPE and copper, in wt. %: □ -the initial HDPE; ■ -0.5; ▲ -1.0; Δ-5.0; x-10; o- 20 and ● - 30.

Figure 1 shows the thermomechanical curves of the temperature dependence of deformation for composites based on HDPE and copper in the range from room temperature to 180°C. By analyzing the curves in this figure, it can be established that in relation to composites, the initial HDPE exhibits a slight increase in the temperature range of the viscous flowing state from 165 to 183°C. The loading of copper contributes to a slightly different character of the change of thermomechanical curves. A common point in the nature of the change in the curves is that HDPE and its composites are presented in two phase states: solid and viscous. At the same time, the softening temperature of the composites, depending on the concentration of copper, changes in the following sequence: initial HDPE - 140; for copper-containing composites: 0.5 wt. % – 142°C; 1.0 wt. % – 143°C; 5.0 wt. % – 148°C; 10 wt. % – 145°C; 20 wt. % – 143°C; 30 wt. % Cu – 140°C. As will be shown below, such an uneven change in the softening temperature of composites with a maximum at 5.0 wt. % copper content may be due to the physical properties of copper. So, for example, the loading of copper in the composition of HDPE leads to a significant increase in the thermal conductivity of the composite: HDPE - 0.38; 0.5 wt. % copper - 0.59; 5.0 wt. % copper - 0.98; 10 wt. % copper - 2.11; 20 wt. % copper - 2.43; 30 wt. % copper - 3.64 W / m K. It is this feature of copper that contributes to the rapid heating of the entire mass of the sample, which is reflected in a decrease in the softening temperature of the composites at 20-30 wt. % of its content.

In addition, there is reason to believe that copper particles during the rolling process create heterogeneous nucleation centers in the polymer matrix melt, which, when cooling the composite as a whole, affect the mechanism of their crystallization and the formation of a supramolecular structure. The simultaneous formation of crystalline formations at homogeneous and heterogeneous crystallization centers contributes to the formation of fine spherulite crystalline structures (Allahverdiyeva *et al.*, 2020). Moreover, if one part of copper is involved in the formation of crystalline formations, then another part of it is displaced into the interspherulite amorphous region during the growth of spherulites. At a certain concentration of copper particles, the latter contribute to a noticeable increase in the thermal conductivity of composites in the inter-spherical space with subsequent influence on the rapid heating of the polymer matrix with a subsequent decrease in the softening temperature of crystalline structures. In the case under consideration, this fact was established when the copper concentration in the HDPE composition exceeds 5.0 wt. %.

As a result of the derivatographic analysis of the composites, we found that their melting temperature was slightly lower than the softening temperature found from the results of thermomechanical studies. For example, the melting peak of the initial HDPE and composites with 0.5 – 10 wt. % Cu was 137 ° C, and for samples with 20-30 wt. % content the value of this indicator slightly increased to 139°C. It would seem that conflicting data were obtained, since the melting temperature cannot be lower than the softening temperature of the composites. It should be noted that the derivatographic method of polymer analysis shows that the endothermic melting peak of HDPE and its composites varies in a certain range, in the range 125-170°C. The endothermic peak is a thermodynamic indicator characterizing the melting temperature of the sample. Phase temperature transitions, determined by the Kanavets method, are estimated by the deformation method, by pressing a rod with a flat round surface with a diameter of 8 mm into the polymer volume of a composite made in the form of a tablet with a diameter of 16 mm and a thickness of 5 mm (Kakhramanov *et al.*, 2018a; Lyamkin *et*

al., 2012). It becomes obvious that the thermomechanical method for determining the softening temperature of plastics compared with the derivatographic method of analysis is less sensitive to fixing thermal changes in the polymer mass. As a result, the thermomechanical method for estimating the softening temperature of composites according to the Kanavets method has values slightly higher in magnitude than their melting temperature found by derivatography.

Similar changes in thermophysical features were also established in the study of composites based on HDPE+PEMA+copper. We experimentally found that the optimal concentration of PEMA at which the best properties are achieved is its 2.0 wt. % content in the composition of the HDPE + copper composite. The role of the compatibilizer is manifested not only in improving the miscibility and technological compatibility of the mixture components, but also in the ability to influence the formation of heterogeneous nucleation centers in the polymer matrix. There is reason to believe that the load of PEMA in HDPE will generally contribute to an increase in the polarity of the polymer matrix. This circumstance, in turn, will contribute to a significant improvement in the adhesion of the polymer matrix to the surface of copper particles. In addition, it is possible that when mixing on hot rollers as a result of the simultaneous action of thermal and shear stresses, the probability of partial oxidation of the polymer mixture increases with the simultaneous appearance of macroradicals that can recombine with each other to form interchain bridges or interact with maleic anhydride. The thermomechanical curves of the dependences of HDPE + PEMA + copper composites depending on the filler concentration are shown in Fig. 2 below. By identifying the curves in this figure, it can be established that, in contrast to composites not modified by PEMA, the phase transition from solid to viscous flows occurs in a

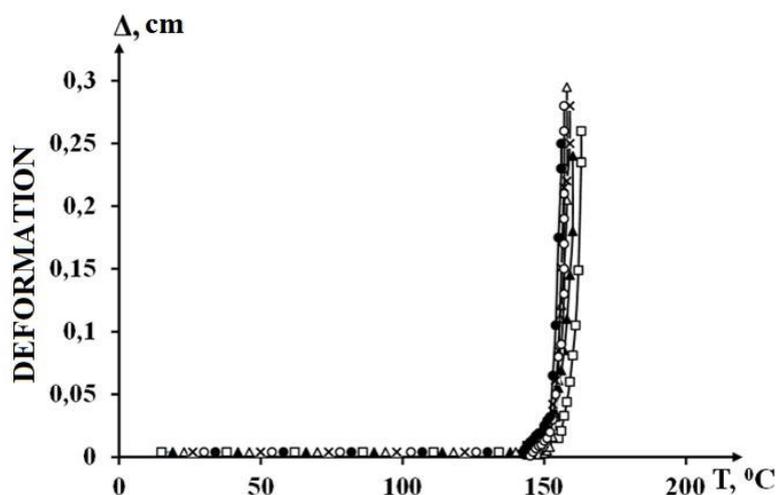


Figure 2. Thermomechanical curves of the dependence of deformation on temperature of composites based on HDPE + PEMA and copper, in wt. %: □ -the initial HDPE + PEMA; □ -0.5; ▲ -1.0; Δ-5.0; x-10; o- 20 and ● - 30.

narrow temperature range. Moreover, the maximum temperature of the viscous flow state does not exceed 163°C. The softening temperature of the HDPE + PEMA + copper composites varies as follows: the initial HDPE + PEMA – 142°C; composites – 0.5 wt. % – 144°C; 1.0 wt. % – 146°C; 5.0 wt. % – 148°C; 10 wt. % – 146°C; 20 wt. % – 145°C and 30 wt. % – 142°C. And in this case, the maximum temperature of the first-

order phase transition is 148°C for a composite with 5.0 wt. % copper. A further increase in copper concentration is also accompanied by a decrease in the phase transition temperature of highly filled composites. For a comparative assessment, we determined the melting temperature of the considered composites by derivatographic analysis, the values of which depending on the copper concentration varied as follows: for the initial HDPE + PEMA and for composites with 0.5-10 wt. % copper content – 139°C, and with 20-30 wt. % copper – 140°C. Based on the obtained experimental data, it can be noted that in this case, while derivatographic data show a slight increase in the melting temperature of composites at a copper concentration of 20-30 wt. %, in the case of thermomechanical studies, on the contrary, there is a slight decrease in the softening temperature of composites from 148 to 142°C. As we noted above, this becomes possible due to the ability of copper to provide high thermal conductivity and the heating rate of a highly filled composite. It should be noted that in the literature issues related to the vulcanization of metal-polymer systems are extremely poorly covered, despite the fact that in this case it seems possible to significantly expand the scope of their practical use. This is interpreted in that as a result of the vulcanization of the composites, it seems possible to further increase their softening temperature and strength. In this regard, we used dicumyl peroxide (DP) and sulfur as vulcanization agents. It was important to establish how significant the contribution of each vulcanization agent to the regularity of changes in thermomechanical curves can be. In this case, using the example of a composite with 5.0% copper content in the composition of the HDPE + PEMA polymer mixture, the task of the study was to fix the temperature phase transitions from a solid state to a highly elastic, viscous, or glassy state.

Figure 3 shows the thermomechanical curves of vulcanized composites depending on the concentration of DP. Analyzing the curves in this figure, it can be noted that even with the loading of the minimum amount of DP (0.25 wt. %), a characteristic change is observed with the formation of a highly elastic plateau in the region of 160-167°C. A further increase in temperature leads to a transition from a highly elastic state to a viscous fluid. The viscous state region covers the temperature range 167 - 173°C.

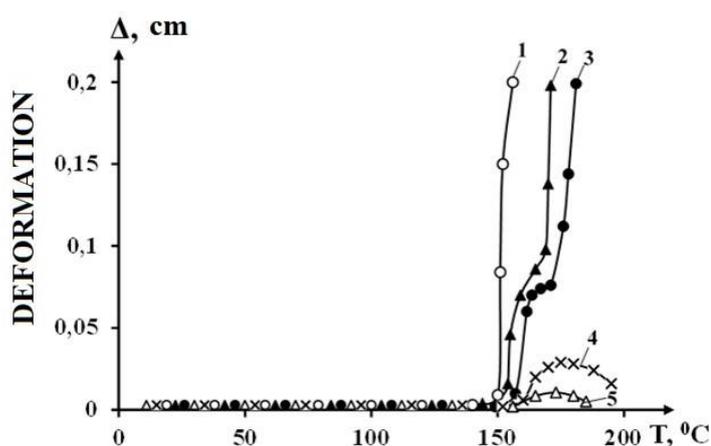


Figure 3. Effect of DP concentration on the regularity of thermomechanical curves of a composite based on 1 (○) - HDPE + PEMA + 5.0 wt. % copper; 2 (▲) - 0.25; 3 (●) - 0.5; 4 (x) - 1.0; 5 (Δ) - 2.0 wt. % DP

With the load of 0.5 wt. % DP into the composition of this polymer mixture, the region of the highly elastic state is characterized by a more distinct plateau in the temperature range of 163 - 173°C, which characterizes the manifestation of the properties of rubber. The viscous state region covers the temperature range 173-180°C. At a concentration of 0.25–0.5 wt. % DP, the composites retain the melt's ability to flow, which allows us to consider them as a promising structural material with an optimal spatial structure for practical use in special fields of technology. The MFI of vulcanized composites is reduced from 4.8 to 1.02 g / 10 minutes, which fully ensures the possibility of processing them on standard molding equipment and an extruder.

A further increase in the concentration of DP from 1.0 to 2.0 wt. % is accompanied by the fact that, with an increase in temperature, the samples pass from the solid state to the glassy state. This physical state is characterized by a high crosslink density, in which the composite becomes brittle and almost completely loses its ability to melt flow. The absence of melt flow in these composites makes them unsuitable for processing and, therefore, are not of interest for further study (Ulitin *et al.*, 2012). Therefore, the most interesting from a technological point of view are vulcanized composites 0.5 wt. % DP content.

Figure 4 shows the thermomechanical curves of sulfur vulcanized composites. The amount of sulfur was varied from 3.0 to 10 wt. %. As can be seen from this figure, regardless of the concentration of the vulcanizing agent, sulfur contributes to the fact that the samples are characterized by all three physical states characteristic of rubbers.

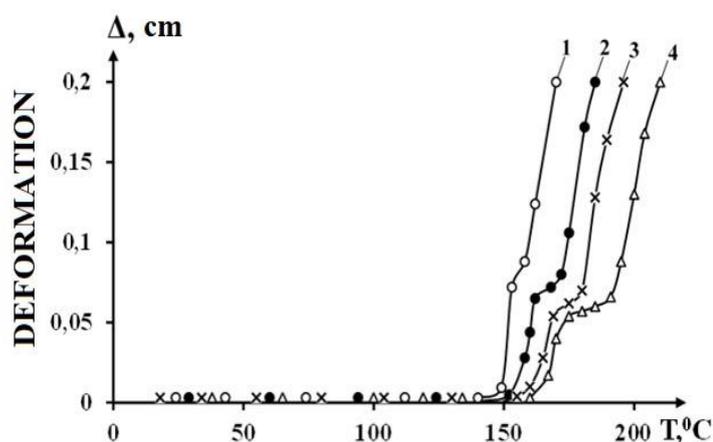


Figure 4. Effect of sulfur concentration on the regularity of changes in the thermomechanical curves of a composite based on HDPE + PEMA + 5.0 wt. % copper: 1 (o) – 3.0; 2 (●) – 5.0; 3 (x) – 7.0; 4 (Δ) – 10 wt. %

With a sulfur content of 3.0; 5.0; 7.0 and 10 wt. % of the composition of the composite, the transition from a solid to a highly elastic state occurred, respectively, at a temperature of 154; 161; 169 and 176°C, and from highly elastic to viscous at a temperature of 160; 174; 180 and 194°C. An increase in the temperature of transitions from one physical state to another with an increase in the concentration of the vulcanizing agent indicates the appearance of crosslinked structures that affect the nature of the changes in the thermomechanical curves (Dyakonov *et al.*, 2020). Moreover, with an increase in sulfur concentration from 3.0 to 10 wt. %, the maximum temperature at which deformation in the samples is reached up to 2 mm in depth

increases from 171 to 212°C. When sulfur is introduced in an amount of 1.0–10 wt. %, the MFI of the samples decreases from 4.8 to 0.98 g/10 min, i.e., it retains the necessary melt flow for processing by injection molding and extrusion.

4. Conclusion

Thus, based on the foregoing, it can be concluded that the loading of a compatibilizer (PEMA) in HDPE helps to improve the miscibility and technological compatibility of the components of the mixture. The use of vulcanizing agents such as DP and sulfur made it possible to obtain composites characterized by a crosslinked spatial structure and high heat resistance. High heat resistance of composites opens up promising possibilities for their practical use in harsh extreme operating conditions.

The most optimal concentration of DP, in which the composite is characterized by high heat resistance and retains the ability to process on traditional equipment is 0.25–0.50 wt. %.

As a result of sulfuric vulcanization, the transition of the composite from a solid to a glassy state does not occur, which is explained by the absence of densely cross-linked crosslinking.

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