THE DERIVATIVE-GRAPHICAL INVESTIGATIONS OF THE POLYETHYLENE SYSTEM OF THE LOW DENSITY AND $TlInSe_2$

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The results of the differential-thermal and thermogravimetric analysis of the PELD + *x* weigh % $TlInSe_2$ (*x*=0; 1; 3; 5; 10; 40) system in the interval from 20°C till 500°C are presented in the paper. It has been revealed, that at the $TlInSe_2$ filling PELD the thermal stability increases till 5 weigh% and mass loss for the given composition in the comparison with the initial PELD increases till 93%, proving the full saturation. The two peaks of melting are observed on the DTA curves, the process of the thermal-oxidative breakdown takes place at 330°C and 440°C temperatures.

At high concentrations of the filler till 40 weigh % the changes of the enthalpy law is observed on DTA curves in temperature region 210-218°C.

Introduction

Nowadays the direction, connected with the modified electroactive properties of the polymers by the way of the leading of the different fillers, creating of the polymeric impurities or by the influence of the different ionizing radiations, is quickly developing [1-10].

The leading of the fillers of the inorganic nature in the polymeric matrix is the universal method of the polymer modification. The three-component semiconductor compound $TlInSe_2$ was led in the capacity of the fillers into polyethylene of the high density (PELD) in this aspect. This is caused by the fact, that the given phase has peculiar crystalline and band structures and is the perspective material in the visual and infrared regions of the spectrum, having the record strain-sensitivity and switching properties with memory. The unique properties of the given phase are the fact, that the parameters of the photo- and strain-elements, switches are ruled in the needed direction under influence of the electromagnetic and acoustic waves in the dependence on the mechanical deformation, contact materials, the temperature of the surroundings [11-18]. The composites with the $TlInSe_2$ fillers can have physico-mechanical (elasticity, facility, anti-heat and e.t.c.) [19], electrophysical (electroconductivity with switching, dielectric (ε, $tg\delta$) and additive properties), electroactive (strain-, pyro-sensitive), electroluminescent and other properties. Besides, the study of such compositions is important for the understanding of the mechanism of charge transfer, dissipations of the energies in polymer-semiconductor, polymer-metal heterogeneous systems for the study of the interphase phenomena, and also in processes of structure modification and properties of polymers themselves at their radiation and other types of the influence. In this connection we were carrying out the derivatographical investigations of PELD +*x* weigh % $TlInSe_2$ (*x*=0; 1; 3; 5; 10; 40) system.

Experimental part

The samples of the composition PELD +*x* weigh % $TlInSe_2$ (*x*=0; 1; 3; 5; 10; 40) were investigated on the Q-derivatograph of the MOM firm (Hungary) in the temperature interval 20-500°C. [20]. The heating rate is 5 grad/min. The dry Al_2O_3 was taken in the capacity of the standard. The samples by the type of the connection 0,3 and thickness 80-100 mkm had been obtained by the way of the dry shifting of the powders of the filler and polymer with the following thermopressing at pressure 150 MPa and temperature 200°C, and further, the melt was hardened with the help of the impurity ice-water with the velocity ~2000°C/min [21]. The pressing time was 15 minutes.

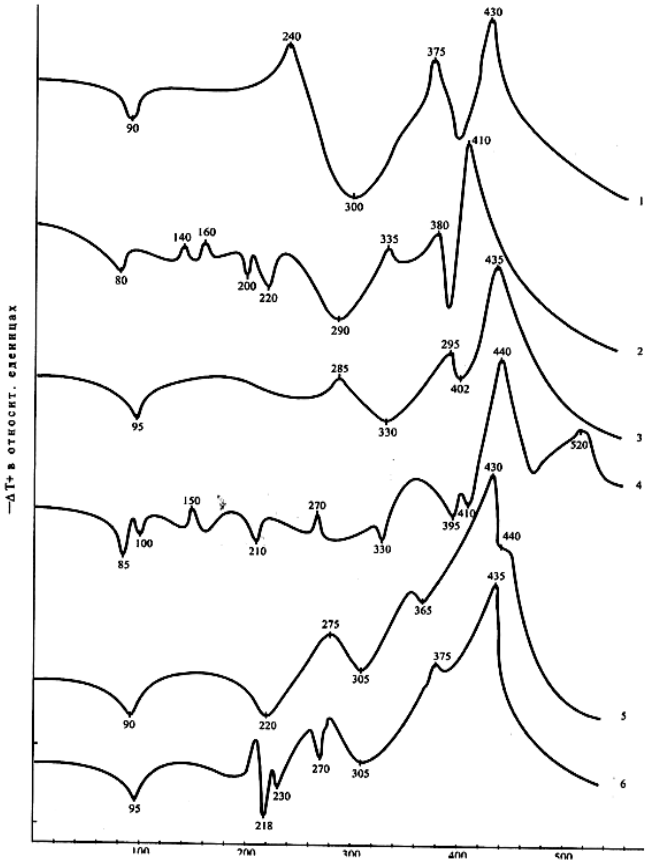

Fig.1. The differentially-thermal curves of the stoichiometric compounds of PELD + *x* weigh % $TlInSe_2$, where 1-*x*=0, 2-*x*=1;,3-*x*=-3; 4-*x*=5; 5-*x*=10; 6-*x*=40 weigh %.

The results of the thermogravimetric (TG) and differential-thermal analysis (DTA) of the studied

compositions PELD +*x* weigh % $TlInSe_2$ are presented on the figures 1 and 2.

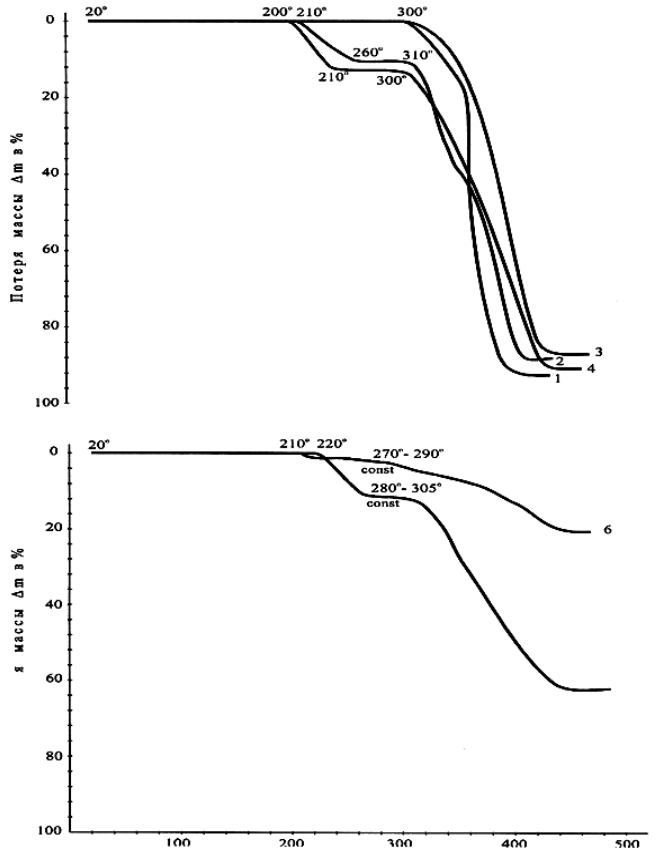

Fig.2. The thermogravimetric curves of the stoichiometric compositions of PELD + *x* weigh % $TlInSe_2$, where 1-*x*=0, 2-*x*=1, 3-*x*=3; 4-*x*=5; 5-*x*=10; 6-*x*=40 weigh %.

The derivatogramm of the pure PELD had also fixed (Fig.1, curve 1 and curve 2) for the comparison of the changes , carrying out in PELD after the addition of формула filler. As it is seen from the fig. 1 (curve 1) the three clearly expressed endothermic effects at 90°C, 300°C, 402°C and two exothermic peaks at 240°C and 430°C are situated on DTA curve correspondingly. The second exothermic effect at 240°C is connected with the beginning of the thermal oxidation of ПЭ film. Probably, the decomposition of the transversal connection takes place on the initial thermal-oxidation. The second exothermic effect at 430°C corresponds to the second step of the thermal-oxidation and to the beginning of the process of the polymer depolymerization [21-24].

According to TG curve (curve 1) in the temperature interval 20-300°C the weight loss isn't observed, i.e. the polymer is stable till 300°C. Further, the mass loss begins from the 300°C (the disconnection of the weak connections, the endoeffect is on DTA at 300°C) and the mass loss, thermal destruction is~ 45%. The maximum of the mass loss is observed in region 365-400°C. The bulk loss of the mass is 92%, and the residual is ashes 8%.

The four endothermic effects at 80; 200; 220 and 390°C and four exothermic effects at 140; 160; 368 and 410°C have been observed on the derivatogramm of the stoichiometric composition 1 weigh% $TlInSe_2$+99 weigh % PELD. From the comparison of these data with data on the fig.1 (curve 1) we can conclude, that the first endothermic effect at 90C corresponds to the melting of PELD.besides, here the two new endothermic effects at 200°C, 220°C (curve 2), accompanying by the mass loss on TG curve till 12%, appear in the samples of the compositions PELD/формула, the last probably is caused by the decomposition of the weak connections and the beginning of the oxidative processes in the filled part of PELD. The confirmation of the above mentioned are exothermic effects on curve DTA with maximums at 140 and 160°C. The exothermic effect at 140°C corresponds to the first stage of the oxidation of PELD part, filled by $TlInSe_2$ and the second exoeffect at 160°C corresponds to the modified pert of PELD. The endothermic effect at 290°C corresponds to the depolymerization of PELD part, as filled by $TlInSe_2$, so unadulterated by $TlInSe_2$. The exoeffect at 368°C corresponds to thermal-oxidative destruction of the filled $TlInSe_2$ part of PELD and at 410°C corresponds to unaltered part of unaltered part of PELD

From the comparison of DTA curves of the pure PELD and samples of the composition 1 weigh% $TlInSe_2$+99weigh% PELD (fig. 1. curves 1,2 and 2. curves 1,2) is seen, that the introduction into PELD of $TlInSe_2$, the new peaks are observed on DTA curve: (exoeffect) at 140°C and endothermic effects at 200 and 220°C, that proves about partial modifying of the polyethylene. That's why at the low content of $TlInSe_2$ the coexistence of the two different parts of the polymers – main and modified are observed in the composition content.

The partial filling of PELD, totally coinciding with the fig. 1.1, is also observed in the compound 3 weigh % $TlInSe_2$+97% PELD (fig.1. curve 3). The comparison of DTAcurves of these samples shows, that the decomposition of the weak connections in both parts of the investigated composition takes place at 330°C, and depolymerization process begins to carry out also at the one temperature 345°C, though the continuance of the oxidation of the depolymerization by the filled part takes place at 395°C, and by the unaltered part at 435°C. According to TG in this compound 3 weigh% $TlInSe_2$ +97 weigh % PELD (fig. 2. curve 3) the constancy of the compound, characterizing the thermostability of the filled part is observed in the temperature region 300-330°C, and the destruction of the weak connections of both parts of polymer is observed from 330°C, accompanying by the mass loss of the quantity 14,7%. The thermostability of the filled part of PELD with the addition 3 weigh % $TlInSe_2$ increases on 50-60°C and corresponds to 300-305°C.

From the derivatogramm of the compound 5 weigh % $TlInSe_2$ +95 weigh % PELD (fig. 1.4 and 2.4) is followed, that the two endothermic effects at 85 and 100°C, characterizing the melting of the crystals of the investigated compound, are observed on the curve DTA. The appearance of these endothermic peaks (fig.1, curve 4) can be connected with the creation of new crystal formation of the polyethylene on the surface of the particles $TlInSe_2$, which melt at 100°C. It is need to note, that the increase of the crystallinity of the polyethylene is observed at the addition of other types of the fillers [21]. Thus, from these data is

followed, that at the definite ratio of the components in PELD/$TlInSe_2$ system the semiconductor fillers are the crystallization centers, moreover new-formated crystallites have the increased melting point (second melting peak at 100°C).The exoeffect at 150°C corresponds to I stage of the oxidation of the filled part of PELD. The endoeffect at 210°C corresponds to the disconnection of the weak connections of this filled part of PELD. According to trend of curve TG (fig. 2.4) the weight constancy, characterizing the thermostability of the filled part of polymer, is observed in the temperature region 20-210°C. In the temperature region 210-260°C the change of the trend of curve TG in the direction of the mass loss in the quantity 12,4% , caused by the disconnection of the weak connections of the filled part is observed. The exoeffect at 270°C is caused by the first stage of the oxidation of the unaltered part of the polyethylene. The endoeffect at 330°C corresponds to the disconnection of the weak connections of the unaltered part of the polyethylene in the quantity 18,6%, the endoeffect at 395°C is probably caused by the oxidative depolymerization of the filled part, and endoeffect at 410°C is caused by the unaltered part of PELD. The exoeffect at 440°C is connected with depolymerization process. Thus the filler leads to the temperature increase of PELD depolarization.

As it is seen from the calculations of the thermogravimetric curves (fig. 2 curve 4), the most effectibe structure of PELD is carried out at 5 weigh % concentration of $TlInSe_2$ in the comparison with (fig. 2).

From the comparison of DTA curves for the different compositions of PELD/$TlInSe_2$ is followed, that (fig.1 and 2) the observable first endothermic effect at 80-95°C is caused by the melting point of the unaltered part of PELD for all investigated compositions on DTA curve, the endothermic effect at 100°C corresponds to the melting point of the filled part, which has own specific thermal effects, connected with processes on the borders of phase division.

The thermostability for the compounds 1; 3; 5 weigh % $TlInSe_2$ corresponds to 290°C. The thermostability of the polymer increases on 35-45°C because of the no saturation of $TlInSe_2$ with the increase of the percent concentration of $TlInSe_2$ from 10 till 40 weigh %. The two regions of PELD are revealed on the thermogravimetric curve, beginning from 10 weigh % $TlInSe_2$ in PELD: the first region of the mass loss is observed in the temperature region 220-280°C, caused by the filled $TlInSe_2$ part of PELD, further the constancy region is observed on TG curve in the temperature region 280-305°C, characterizing the thermostability of the filled part of the polymer. The small mass loss at 305-345°C characterizes the disconnection of the weak connections of the both parts of PELD, the depolymerization of both parts is also carried out at 345°C, but thermal-oxidative destruction divides into two parts at the temperature 430°C and 440°C.

At high contents of the fillers till 40 weigh% on DTA curve the character peaks at 215-218°C with the change of enthalpy sign are observed, which are character for the crystal transfers by the type crystal-crystal and $TlInSe_2$ filler.

As it is seen from (fig.1, curve 6 and fig.2, curve 6) the derivatogramm consists from two diagrams: low-temperature region characterizes filled part of PELD $TlInSe_2$ (from 205 till 270°C), and high-temperature – from 290 till 435°C of unaltered of PELD. It is need to note, that with the increase of the percent concentration of $TlInSe_2$ the maximal temperature of the decomposition of the compound PELD +x weigh % increases from 380°C for the initial PELD till 410°C for the compound 40 weigh% $TlInSn_2$. The gross mass loss for the initial PELD at the heating from 20°C till 500°C is 92%, at the increase of the concentration $TlInSe_2$ from 1 till 5 weigh % the mass loss decreases till 88-87%, that proves about connection of particles of $TlInSe_2$ by the polyethylene. The mass loss for the compound with 5 weigh % $TlInSe_2$ increases in the comparison with the initial PE till 93% that proves again, that effective filling of the polyethylene is carried out at the concentration 5 weigh % $TlInSe_2$. For the composition 5 weigh % $TlInSe_2$ the mass loss in the comparison with the initial PE increases till 93% that again is proved, that effective modifying of PE structure carries out at the 5 weigh % $TlInSe_2$ concentration.

Conclusion

The derivatographic investigations of PELD +*x* weigh % $TlInSe_2$ system show, that thermal stability of the composition increases at the filling till 5 weigh % of PE. It is obtained the new material, having high work temperature for the creation on it base the more perspective piezo-elements, than initial phase. Each phase at the high percents of $TlInSe_2$ is special, the change of the enthalpy sign is observed on DTA curve at the temperature interval 215-218°C.

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AŞAĞI SIXLIQLI POLİETİLEN VƏ $TlInSe_2$ KOMPOZİSİYALARININ DERİVATOQRAFİK TƏDQİQİ

Təqdim olunmuş işdə ASPE + x çəki % $TlInSe_2$ (x=0; 1; 3; 5; 10; 40) sisteminin 20-500^0 C temperatur intervalında differensial-termik və termoqravimetrik analizlərinin nəticələri verilmişdir. Müəyyən olunmuşdur ki, $TlInSe_2$ ASPE ilə 5 çəki %-ə qədər doldurulması zamanı termik davamlılıq artır və verilmiş tərkib üçün təmiz ASPE ilə müqayisədə kütlə itkisinin 93%-ə qədər artmvsı tam doyma faktını təsdiq edir. DTA əyrilərində iki ərimə pikləri müşahidə edilir, termooksidləşmə destruksiya prosesi 330^0 və 440^{0}C temperaturlarda baş verir.

Doldurucunun 40 çəki.%-ə qədəryüksək konsentrasiyası zamanı DTA əyrilərində 210-218^{0}C temperatur intervalında entalpiyanın işarəsinin dəyişməsi müşahidə olunur.

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ДЕРИВАТОГРАФИЧЕСКИЕ ИССЛЕДОВАНИЯ КОМПОЗИЦИЙ ПОЛИЭТИЛЕН НИЗКОЙ ПЛОТНОСТИ И $TlInSe_2$

В работе излагаются результаты дифференциально-термического и термогравиметри-ческого анализов системы ПЭНП + x вес.% $TlInSe_2$ (x=0; 1; 3; 5; 10; 40) в интервале температур 20-500^{0}C. Выявлено, что при наполнении $TlInSe_2$ ПЭНП до 5 вес.% возрастает термическая устойчивость и для данного состава потеря массы по сравнению с исходным ПЭНП увеличивается до 93%, подтверждающие полное насыщение. На кривых ДТА наблюдается два пика плавления, процесс термоокислительной деструкции проходит при температурах 330 и 440^{0}C.

При высоких концентрации наполнителя до 40 вес.% на кривых ДТА в области температур 210-218^{0}C наблюдается изменения закона энтальпии.

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