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Thermal properties and changes in phase structure of PP+ MnO_2- based compositions

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By derivatographic method polypropylene films (PP) exposed to electrothermoplarization filled by MnO_2 to the extent of 0.5 and 1vol.% have been investigated. By electrothermoplarization $E=7\cdot10^6$V/m as a result of ageing PP matrix crystals part amorphism is taken place and thermal stability through it decreases by 40 ^{0}C comparing with PP not exposed to electrothermoplarization effect. It is established that electric intensity leads as to the complete amorphism of PP+0.5vol.%MnO_2 composition so the complete depolymerization followed by volatilization of formed intermediate products to the extent of 100%. Thermal stability of PP+1,0vol.%MnO_2 composition comparing with initial PP under the effect of electrothermoplarization $E=7\cdot10^6$V/m decreases by 65 ^{0}C.

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1. Introduction

It is known that polymer and polymer composite ageing relate to the high local anisotropy of force field due to sharp difference of intramolecular and intermolecular interaction forces. From the theory of thermal property of polymer and composites on their base it follows that the presence of local anisotropy and conservation by macromolecules of their individuality in the polymer composite systems is capable of leading to the appearance of specific regularities of thermal capacity, negative coefficients of thermal expansion and number of other peculiarities.

By modification of electret and electrophysical properties two-phase polymer systems with different solid fillings are of great importance. Under the effect of strong electric field or discharges in polymer the ageing processes covers increasingly deep layers, as a result polymer structure changes associated with the relationship between crystalline and amorphous parts [1] in it, formation of interlayer crystal phase of polymer and etc. can be taken place. Study of thermal and physical properties of polymer composite materials makes it possible to evaluate the quantity of filled material and draw up certain recommendations on their use and production technology [2-3].

With the aim of investigation of electric field influence on the process of ageing, melting temperature, crystallinity degree and depolymerization processes of polypropylene films filled by MnO_2 0.5% and 1.0 vol.% we investigate filled compositions of polypropylene [PP] films exposed to electrothermopolarization by derivatographic method.

2. Methods of sample production and measures

By hot pressing PP samples including additions of MnO_2 low-molecular colorant to the extent of 0,5 and 1,0 vol.% at melting temperature of polymer matrix under the pressure 15MPa for 3 min. with subsequent quick cooling at the rate 2000deg/min. have been made. Obtained samples have been preliminarily exposed to the electrothermopolarization at T_i=335K under the electric intensity $E_i=5\times10^6$ V/m, $E_i=7\times10^6$V/m for t_i=1haur.

Derivatograms have been taken on Q-derivatograph of MOM-typed Paulink-Paulink Erdey system (HUNGAPY) within T 20÷450°C. Weighted amount of films under the investigation depending on thickness is from 70 up to 180 mkm. Channel sensitivity is mg-200; DTA-1/5; DTG-1/15. Rate of heating is 10% min; as a standard Al_2O_3 roasted at T 1000 °C for 12 hours has been used.

Polyolefin samples modified by additions of PP+0,5vol.o%MnO_2, PP+1,0vol.%MnO_2 low-molecular colorants have been investigated on the atomic power microscope of INIEGRA PRIMA model NT-MDT Company at room temperature before and after electrothermopolarization.

3. Experimental results and discussion

In PP derivatogram at E=0 (Fig. 1) on DTA curve there has been observed endothermal effect at T 170°C due to the PP matrix crystal phase melting but exothermal effect at T 300 °C is in agreement with PP thermal destruction that on DTG curve appears as an endothermal effect at 290 °C accompanying by volatilization of formed gases as a result of thermal destruction. From TG curve

course it follows that the amount of formed gases is 12%. Further on DTA curve the wide blurred endothermal effect at T 390° appropriate to PP depolymerization has been observed. During the process of depolymerization attended by deep endothermal effect at T 380°C on DTG curve the volatilization of formed gases to the extent of 63% has been taken place.

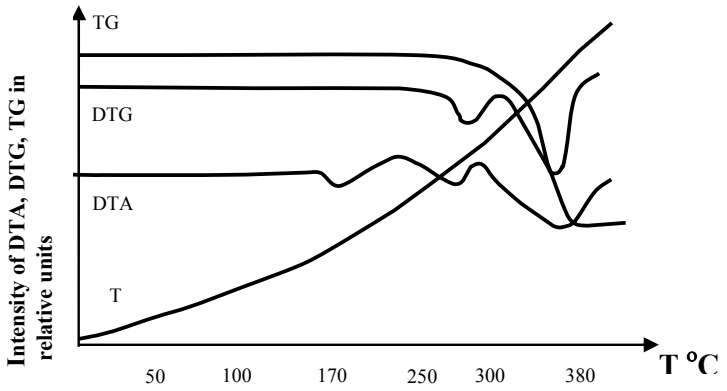


Fig. 1. Derivatogram of PP films obtained by quenching minus water treatment in constant electric field.

By the effect of electrothermopolarization $E_i=7\cdot10^6$V/m on PP (Fig. 2) melting temperature of matrix crystal phase shifts to low temperatures and comes to be equal to T 135°C. At the same time the area of endothermal effect on DTA curve at 135°C the associated melting decreases by 2.5 times and it indicates that under the effect of electrothermopolarization $E_i=7\times10^6$V/m there has been occurred the process of ageing and transition of PP matrix crystal phase into amorphous one. PP thermal destruction on both DTA and DTG curves appears as an endothermal effect at T 250 °C followed by volatilization of formed gases to the extent of 2.99%. PP depolymerization process appears as an endothermal effect at T 300 °C on both DTA and DTG curves, amount of formed volatile gases is 77.2% (by TG curve calculation). Under the effect of electrothermopolarization $E_i=7\times10^6$ V/m there has been taken place ageing, amorphism of PP matrix crystal phase and thermal stability by 40 °C comparing with PP not exposed to electrothermo-polarization has been decreased.

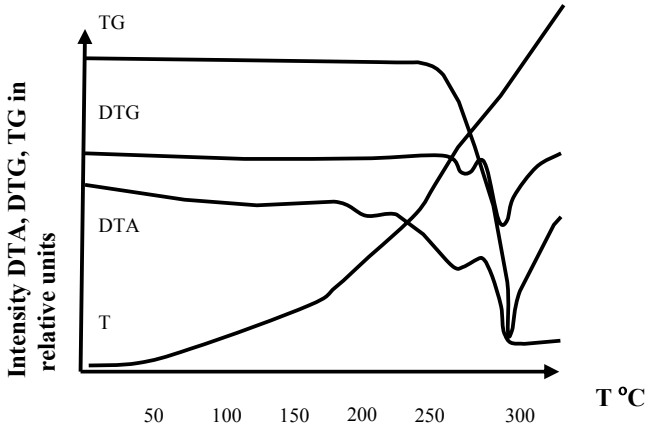


Fig. 2. Derivatogram of PP films obtained by quenching in water processed by constant electric field at $E=7\cdot10^6$V/m.

Derivatographic investigation result of PP filled by MnO_2 to the extent of 015 and 1.0 vol.% and also the films exposed to electrothermopolarization effect are brought to table.

According to the data of Table 1 in PP+0.5vol.%MnO_2 melting temperature of PP matrix crystal phase conforms to 148 °C that is below 12 °C than for initial PP. Amount of formed gases as a result of thermal destruction and depolymerization at E=0 in initial PP and to the extent of PP+0,5 vol.%MnO_2 composition are 20% and 69%, respectively. Filling of PP+0.5 vol.%MnO_2 leads to the partial amorphism of PP matrix

crystal phase, increase of volatile gases and as a result to the thermal destruction by 6-8% and decrease of thermal stability by 28°C in comparison with initial PP. By electrothermopolarization $E_i=7\cdot10^6$V/m effect on the same composition of PP+0,5vol.%MnO_2 there has been observed complete amorphism of matrix crystal phase (on DTA curve endoeffect appropriate to melting of PP matrix crystal phase is not revealed). Thermal destruction of composition PP+0,5vol.%MnO_2 exposed to electrothermo-polarization has been taken place in wide temperature range 225-370°C with the peak on DTA curve at T 280 °C. There has been simultaneously taken place depolymerization followed by intensive endothermal effect at T 280-410°C. At T 215-225°C according to the course of TG curve the loss of volatilizing gases is 8,6%, then at T 225-270 °C there has been observed direct line with respect to the course of TG curve that corresponds to the composition constancy, i.e. volatilization of formed gases is not taken place. Further beginning from 270°C up to 370 °C and 370-410 °C there has been proceeded the process of weak bond breakage and volatilization of formed intermediate gases to the extent of 18,5% and 73%, respectively. Composition constancy of TG curve within T 225-270 °C indicates the presence of forming new interlayer crystal phase of matrix which thermal decomposition comes about at 221-225°C to the extent of 8,6%.

Table 1.

Content of composition on PP base	Differential-thermal analysis - DTA		Differential-thermo gravimeter analysis - DTG , TG			
	endoeffective T°C	exoeffective T°C	endothermic eff. T°C	Temperature range of gas volatilization on TG curve at T°C, %		Residue %
PP, E=0	170-melting 390-depolymerization	300-thermodestruction	290, 380	240-300 12	300-390 63	25
PP, $E=7\times10^6$ V/m	135-melting 250-destruction 300-depolymerization		250, 300	200-250 22,9	250-300 77.2	0
PP+0.5%MnO_2 E=0	148- melting 400- depolymerization		400	212-320 20	320-400 69	11
PP+0.5%MnO_2 $E=7\times10^6$ V/m	280- destruction 410- depolymerization	215-weak	410	215-225 8,6 225-290 const	290-370 185 370-410 73	0
PP+1.0%MnO_2 E=0	256- destruction 350- depolymerization	205 -weak	380	205-300 8,5	300-350 53.5 360-380 38	0
PP+1.0%MnO_2 $E=7\times10^6$ V/m	60- melting 235- weak 298- depolymerization	205-intensive	362	175-235 6	235-298 12 298-362 82	0

Thus the effect of electric field brings about as the complete amorphism of PP+0.5vol.%MnO_2 composition so the complete depolymerization (Fig. 3) following by volatilization of depolymerization formed intermediate products to the extent of 100%.

In PP+1,0vol.%MnO_2 composition not exposed to electrothermopolarization (E=0) on DTA curve there has been found out blurred endothermal effect at T 256°C accompanying by volatilization of light-weight components to the extent of 8.5% on TG curve.

Depolymerization on DTA curve accompanies by endothermal effect at T 350°C that on DTG curve appears as a wide blurred endoeffect at T 380°C. According to TG curve calculations within T 205-256°C there has been proceeded thermal destruction process (breakage of weak bonds) accompanying by volatilization of formed gases to the extent of 2.5%. Thermal stability decreases by 35°C in comparison with initial PP.

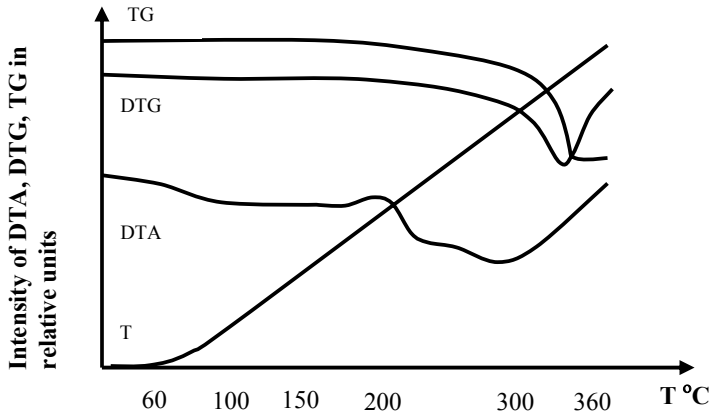


Fig. 3. Derivatogram of PP+0.5 vol.% MnO_2 films obtained by quenching in water processed by constant electric field at $E=7\times10^6$ V /m.

In PP+1,0vol.%MnO_2 composition polarized at $E_i=7\cdot10^6$V/m on DTA curve there has been revealed weak endothermal effect at T 60°C due to the PP matrix crystal phase melting (Fig. 4). Exothermal effect at T 225°C is in agreement with thermal destruction but depolymerization of PP+1.0vol.%MnO_2 by electrothermopolarization $E_i=7\times10^6$V/m has been occurred within T 235-362°C with the endoeffect maximum at T 298 °C. Processes of thermal destruction and depolymerization on DTG curve appears as one intensive endoeffect at T 175-362°C with the peak at T 362°C. At T 175-235°C according to TG curve calculations the gas volatilization formed as a result of thermal destruction to the extent of 6% has been taken place. Further at T 235-298°C the rate of gas liberation decreases and reaches 12% but depolymerization process accompanies by intensive volatilization of formed gases to the extent of 82%.

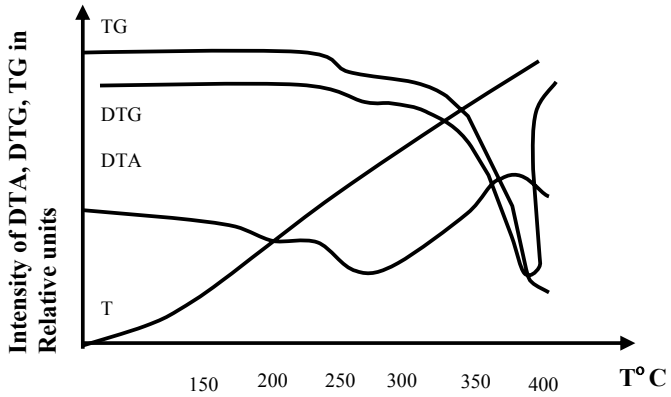


Fig. 4. Derivatogram of PP+1.0 vol.% MnO_2 films obtained by quenching in water processed by constant electric field at $E=7\times10^6$ V /m.

Thus by electrothermopolarization $E_i=7\times10^6$ V/m in PP+1,0 vol.%MnO_2 on DTA curve there has been observed endothermal effect at T 60 °C appropriate to PP matrix crystal phase melting formed as a result of polarization. Thermal stability of PP+1.0vol.%MnO_2 composition by electrothermopolarization $E_i=7\cdot10^6$ V/m decreases by 65°C comparing with PP not exposed to the effect of electrothermopolarization.

Proceeding from the data of above-mentioned Table filling of PP by 0.5 and 1.0 vol.%MnO_2 by electrothermopolarization leads to the decrease of crystallinity degree and reduction of thermal stability by 28% and 65%, respectively. By the effect of electrothermopolarization ($E_i=7\times10^6$ V/m) on initial PP there has been reduced both the melting temperature of polymer matrix phase by 35°C and the thermal stability by 40°C compared to PP not exposed to the electrothermopolarization.

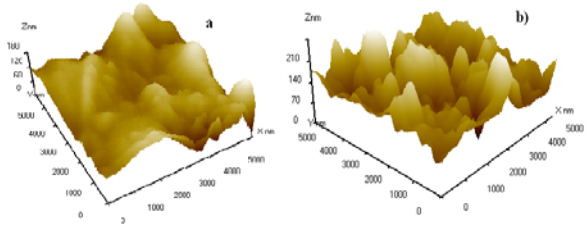


Fig. 5. PP+0.5 vol.% MnO_2 based APM composition image a) no polarized b) polarized.

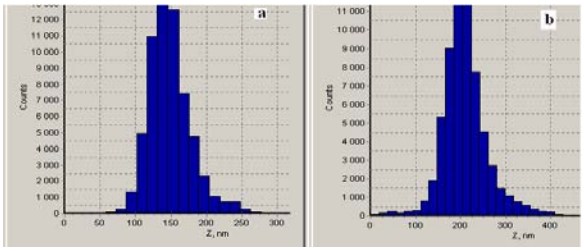


Fig. 6. PP+1.0 vol.% MnO_2 based APM composition image a) no polarized b) polarized.

From microstructure investigation carried out by atomic power microscopy (APM) it is established that the influence of MnO_2 low-molecular addition on the composition (Fig. 5, 7) appears as a change of composition relief after the polarization. Histogram of surface heterogeneity of investigated composition materials shows that (Fig. 6, 8) with MnO_2 concentration increase of composition sample relief changes and becomes rough. We reveal increase of structural element sizes on the surface of PP+0.5vol.% MnO_2 and PP+1.0vol.% MnO_2 composition samples.

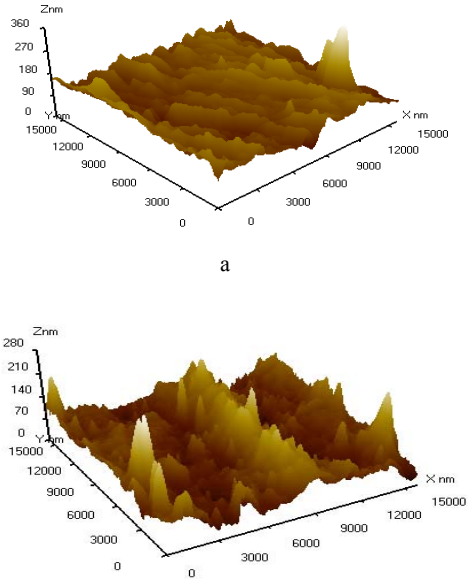
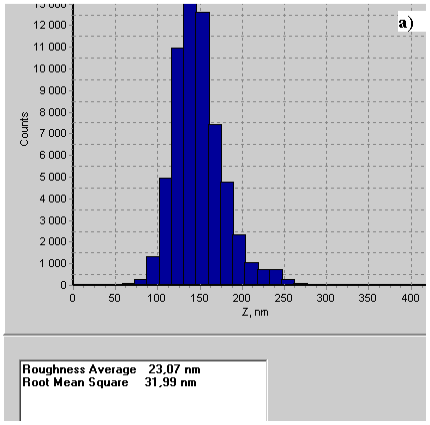


Fig. 7. PP+1.0 vol.% MnO_2 based APM composition image, a) no polarized, b) polarized.



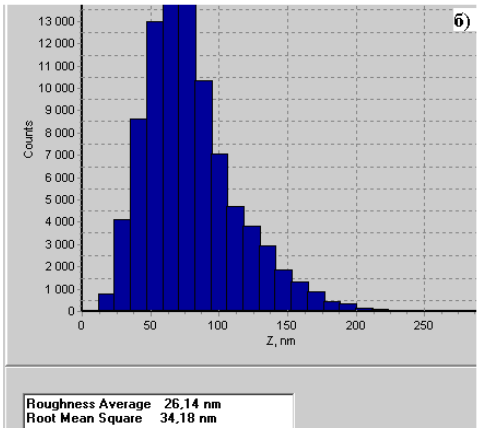


Fig. 8. PP+1.0 vol.% MnO_2 based histogram of composition roughnes,s a) no polarized, b) polarized.

References

[1] N. A. Eyubova, A. M. Magerramov, V. P. Malin, Y. N. Gazaryan, Radiation in physics and chemistry. Collected Volume. Baku, Elm, ed.1, 9-13.

[2] M. A. Bagirov, N. A. Eyubova, V. P. Malin, A. A. Aliyev, A. M. Magerramov, High-molecular compounds. M., **29a**, (5), 917 (1987).

[3] Yu. A. Ferapontov, S. B. Putin, P. Yu. Putin, Transactions TSTU, tom15, 4, pp.826-834 (2009).

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