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Effect of electrothermopolarization on thermal properties of compositions based on polypropylene and MnO_2

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Abstract

Information about the internal structure can also be obtained by studying the thermal properties of composites with low molecular weight additives in the low and high temperature range.In this work, by studying the thermophysical properties of PP-based MnO_2 composites after exposure to an electric field, we will look at how the additive changes the properties and determine the processes of thermal degradation after aging. Differential thermal analysis (DTA) or thermospectroscopy method is based on measuring the thermal effect when heating or cooling the test substance depending on the temperature. This method makes it possible to quantify the temperature of various transitions with high accuracy. Also that polymer and polymer composite aging relate to the high local anisotropy of force field due to sharp difference of intramolecular and intermolecular interaction forces. 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 aging PP matrix crystals part amorphism is taken place and thermal stability. 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%.

***Keywords*:** composites, polypropylene, mangan oxide, additions, electrothermopolarization.

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1. Introduction

Derivatographic analysis can be a rapid method of organic synthesis, which gives the possibility to observe the behavior of materials in a wide temperature range using their minimum weighted portions and the possibility to determine the optimum temperature range of the process in the case of intra or intermolecular interactions in the materials. 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.

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 of polymer [1-4,8-10]. In addition, a targeted change in the structure and properties of polymers is implemented either during

synthesis or through the introduction of fragments of another chemical nature into the macromolecule of the finished product. In designing polymer materials with desired properties, particular attention has been recently given to the modification of their surface, because it is the structure of the surface layer that largely determines their behavior under operation conditions [5–7, 11-14].

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

Obtaining a sample of the nanocomposite is carried out by hot pressing at a polymer melting temperature and a pressure of 15 MPa for 10 minutes, followed by cooling to room temperature under pressure. Obtained samples have been preliminarily exposed to the electrothermopolarization at T=100°C under the electric intensity $E=7\cdot10^6$V/m for t=1hour.

Derivatograms have been taken on Q-derivatograph of MOM-typed Paulink-Paulink Erdey system (HUNGAPY) within temperature 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 temperature 500°C for 12 hours has been used.

3. Results and discussion

In PP derivatogram at E=0 (Figure 1.a) on DTA curve there has been observed endothermal effect at temperature 170°C due to the PP matrix crystal phase melting but exothermal effect at temperature 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°C 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.

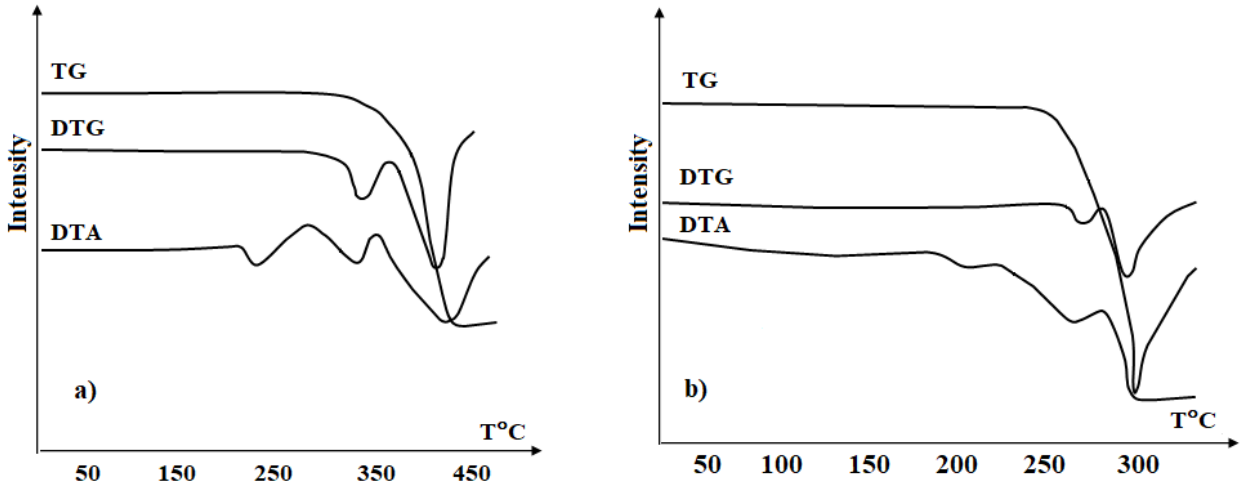


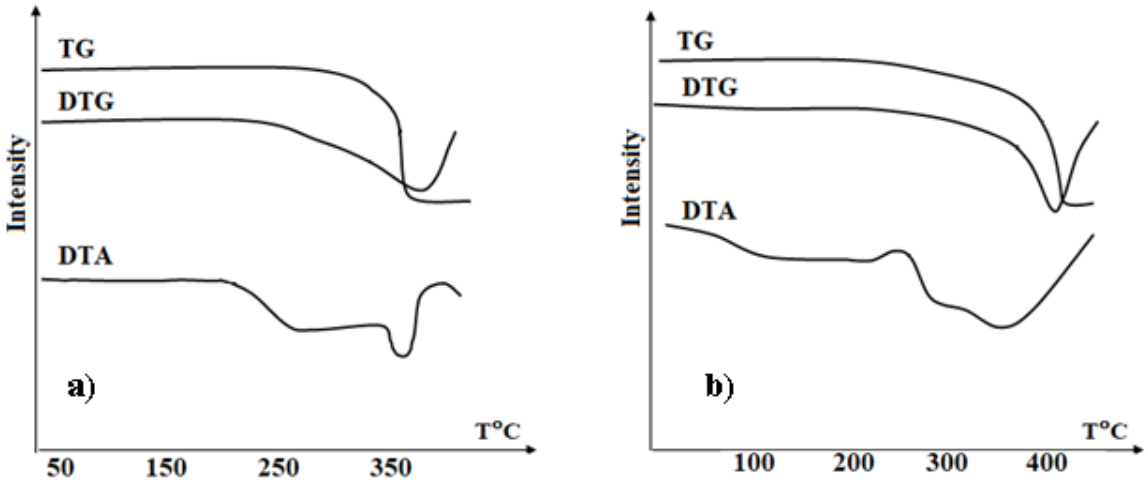
Figure 1. Derivatography of PP films before (a) and after (b) ETP

By the effect of electrothermopolarization $E=7\cdot10^6$V/m on PP (Figure 1b) melting temperature of matrix crystal phase shifts to low temperatures and comes to be equal to

temperature 135ºC. At the same time the area of endothermal effect on DTA curve at 135ºC the associated melting decreases by 2,5 times and it indicates that under the effect of electrothermopolarization $E=7\cdot10^6$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=250ºC followed by volatilization of formed gases to the extent of 2,99%. PP depolymerization process appears as an endothermal effect at T=300ºC on both DTA and DTG curves, amount of formed volatile gases is 77,2% (by TG curve calculation).

Under the effect of electrothermopolarization $E=7\cdot10^6$V/m there has been taken place ageing, amorphism of PP matrix crystal phase and thermal stability by 40ºC comparing with PP not exposed to electrothermopolarization has been decreased.

Derivatographic investigation result of PP filled by MnO_2 to the extent of 0,5 and 1,0 vol.% and also the films exposed to electrothermopolarization effect are brought to table. According to the data of Table in PP+0,5vol.%MnO_2 melting temperature of PP matrix crystal phase conforms to 148ºC that is below 12ºC 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+0,5vol.%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 28ºC in comparison with initial PP. By electrothermopolarization $E=7\cdot10^6$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).



a) b)

Figure 2. Derivatogramof PP+1% MnO_2 films before (a) and after (b) ETP

Thermal destruction of composition PP+0,5vol.%MnO_2 exposed tob electrothermopolarization has been taken place in wide temperature range 225-370ºC with the peak on DTA curve at temperature 280ºC. There has been simultaneously taken place depolymerization followed by intensive endothermal effect at 280-410ºC. At temperature 215-225ºC according to the course of TG curve the loss of volatilizing gases is 8,6%, then at temperature 225-270ºC 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 270ºC up to 370ºC and 370-410ºC 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 temperature 225-270ºC indicates the presence of forming new interlayer crystal phase of matrix which thermal decomposition comes about at 221-225ºC to the extent of 8,6%.

Thus the effect of electric field brings about as the complete amorphism of PP+0,5vol.%MnO_2 composition so the complete depolymerization 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 temperature 256^{o}C accompanying by volatilization of light-weight components to the extent of 8,5% on TG curve (Figure 2a).

Content of composition on PP base	**Differential-thermal analysis - DTA**		**Differential-thermo gravimeter analysis - DTG , TG**			
	endoeffective T ^{o}C	**exoeffective T ^{o}C**	**endothermic eff. T ^{o}C**	**Temperature range of gas volatilization on TG curve at T ^{o}C, %**		**Residue %**
PP, E=0	170-melting 390-depolymerization	300-thermodestruction	290, 380	240-300 12	300-390 63	25
PP, E=7·10^{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=7·10^{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=7·10^{6}V/m	60-melting 235- weak 298-depolymerization	205-intensive	362	175-235 6	235-298 12 298-362 82	0

Table. Results of DTA, DTG and TG stidies of polymer nanocomposite PP+MnO_2

Depolymerization on DTA curve accompanies by endothermal effect at temperature 350^{o}C that on DTG curve appears as a wide blurred endoeffect at temperature 380^{o}C. According to TG curve calculations within temperature 205-256^{o}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^{o}C in comparison with initial PP. In PP+1,0vol.%MnO_2 composition polarized at E=7·10^{6}V/mon DTA curve there has been revealed weak endothermal effect at temperature 60^{o}C due to the PP matrix crystal phase melting (Figure 2b). Exothermal effect at temperature 225^{o}C is in agreement with thermal destruction but depolymerization of PP+1,0vol.%MnO_2 by electrothermopolarization E=7·10^{6}V/m has been occurred within temperature 235-362^{o}C with the endoeffect maximum at temperature 298^{o}C. Processes of thermal destruction and depolymerization on DTG curve appears as one intensive endoeffect at temperature 175-362^{o}C with the peak at temperature 362^{o}C. At temperature 175-235^{o}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 235-298^{o}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%.

Thus by electrothermopolarization E=7·10^{6}V/minPP+1,0vol.%MnO_2 on DTA curve

there has been observed endothermal effect at 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=7·10^{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 1,0vol.%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=7·10^{6}V/mon initial PP there has been reduced as the melting temperature of polymer matrix phase by 35°C as the thermal stability by 40°C comparing with PP not exposed to the electrothermopolarization effect.

4. Conclusion

The observed changes of spectra for compositions due to MnO_2 concentration are related to the changes of supramolecular structure of polymers, the conditions of ETP with the change of interaction degree between phases of polymer with the filler at the expense of charges accumulated att the phase boundary. Thus, by electrothermopolarization E=7·10^{6}V/m in PP+1%MnO_2 on DTA curve there has been observed endothermal effect at 60°C appropriate to PP matrix crystal phase melting formed as a result of polarization. Thermal stability of PP+1%MnO_2 composition by electrothermopolarization E=7·10^{6}V/m decreases by 65°C comparing with PP not exposed to the effectt of electrothermopolarization. Proceeding from the a bovementioned of a Table filling of PP by 0,5 and 1% MnO_2 by electrothermopolarization leads to the decrease of crystallinity degree and reduction of thermal stability by 28% and 65% respectively.

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