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Role of Structure of the Pp/Magnetite Nanocomposites on Their Thermal Properties

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The thermal degradation behaviour of polypropylene and its magnetite composites have been investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Distribution of magnetite nanoparticles in a polymer matrix has been studied by scanning and transmission electron microscopy and also atomic force microscopy. The thermal and mechanical properties of nanocomposites based on polypropylene and magnetite nanoparticles have also been investigated. It has shown that, the introduction of Fe_3O_4 nanoparticles in polypropylene increases its thermal stability of about 100^0C. The maximum increase in the thermal stability of PP was observed in the case of a 20% weight content of Fe_3O_4 nanoparticles in polypropylene.

1. Introduction

In recent years there has been increasing interest to the composites based on thermoplastic polymers, filled with homogenous nanoparticles. The properties of composites polymers with inorganic nanoparticles have been determined by the properties of the mixed components and structure of derived composites [A.M.Magerramov 2013]. For use of polymer nanocomposites at a relatively high temperature conditions, their thermal stability is of great importance. Materials with additive polymer nanocomposites on the one hand have enhanced thermal stability which may exhibit resistance to combustion; even impart fireproofing properties to the product, and on the other hand- the freezing resistance. Polypropylene is a polycrystalline polymer having attractive mechanical properties such as strength and elasticity at ambient temperature. PP with fillers is considered to be one of best thermoplastic materials. At high temperatures, the polypropylene with embedded nanoparticles may reveal even more interesting and meaningful properties. Modification of polypropylene (PP) leads to creating a variety of composite materials and allows to solve the problem of obtaining materials with desired properties and expand the area of their use[A.M. Maharramov 2012].
Fe_3O_4 nanoparticles are of great practical application in microelectronics for the creation of unique miniaturized sensors; in biomedicine - to develop drug delivery systems; in obtaining of nanocomposites that can find its application as effective catalysts in various chemical processes as well as in various fields of science and technology. Therefore, the study of physical and chemical properties of magnetic polymer nanocomposite based on PP+Fe_3O_4, including its thermal and mechanical properties is an urgent problem.In this work we have studied the role of the structure of nanocomposites based on polypropylene and magnetite Fe_3O_4 nanoparticleson the thermal properties of nanocomposites, as well as the relation between the structure and properties of nanocomposites[M.A. Ramazanov 2016].

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2. Materials and Methods

2.1 Materials

Isotactic polypropylene (PP grade Moplen HF500N, homopolymer); density - 0,92g/cm^3 at 25^{0}C, Mw = 250000, Mn = 67000, Melt Mass-Flow Rate- MFR = 11,5g /10 min (230^{0}C, 2.16 kg), melting T = 162^{0}C. Fe_3O_4 nanopowder with size 7-15nm .

2.2. Synthesis of magnetic polymeric nanocomposites.

The polymer nanocomposite materials were prepared as follows: isotactic polypropylene was solved in toluene solvent, at a temperature 120^{0}C. Magnetite nanoparticles were added to the polymer solution at different weight contents (1%, 5%, 7%, 10%) and stirred for two hours in order to prepare a homogeneous mixture. The mixture was transferred to a Petri dish and dried in a vacuum oven during the day. From these samples by hot-pressing at the melting temperature of polypropylene and a pressure of 10 MPa were obtained 100 micron thin film. Cooling the films after hot pressing was carried out in water at the cooling rate 20grad/min [Shirinova.H.A. 2016].

2.3 Methods of analysis

2.3.1. Scanning electron microscopy (SEM)

Distribution of magnetite nanoparticles in polymer matrix was studied using scanning electron microscopy (SEM, JEOL JSM-7600 F). Scanning was carried out at an accelerating voltage of 15 kV and a working distance of 4.5 mm. In order to avoid the chargingof the surface of polymeric nanocomposite thin film, the sample was covered by 10 nm thick layer of platinum.

2.3.2. TEM analysis

Transmission electron microscopyanalyses of nanocomposites were taken on Transmission Electron Microscope of model JEM-1400 plus at the accelerating voltage 50 kV. Samples of nanocomposites were previously sonificated. For this study toluene was chosen as the solvent, because it was identified as one of the best solvents in this experiment. The sonification power was varied from 0 to 30% of the maximum power (130 W) and sonication time was 15 min.

2.3.3. Atomic force microscopy

The morphology of the nanocomposites was studied by using atomic force microscopy NTegra Micro40 2011 (NT-MDT, Zelenograd). For the scan, special silicon cantilevers fabricated by plasma etching method with a radius of curvature of the needle 20 nm and the resonance frequency of 1-5 Hz wereused. Scan size was 3 × 3 microns. The measurements were performed in the semicontact microscopy mode in air, fixed needle change of the cantilever oscillation amplitude, which determines the surface topography. The scanning speed and the number of scanned lines of the image were 256 and 1,969 Hz, respectively.

2.3.4.Thermogravimetric analysis (TGA).

Thermogravimetric analysis of samples was conducted in a thermogravimetric analyze [Fayçal Dergal2013]. (TGA) Model Seiko Exstar 6000 TG / DTA 6300. Nanocomposites samples were heated from 30 ° C to 650 ° C with a heating rate of 10^{0}C / min in a nitrogen atmosphere.

2.3.5.Differential scanning calorimetry (DSC)

Differential scanning calorimetric analysis of nanocomposites was performed on nanocomposites by usingDSC 6100 (Seiko Instruments Japan) model Differential Scanning Calorimeter (DSC). Samples were placed into aluminium sample pans and experiments were carried out under nitrogen atmosphere with a purge rate of 20 ml/min. Samples were heated from 20°C to 250°C then cooled to 25 °C. [Sébastien Leveneur 2014].

3. Results and discussion

Figure 1 presents the TEM image of Fe_3O_4 nanoparticles in the polypropylene matrix obtained by introducing of Fe_3O_4 nanoparticles into the PP solution. Analysis of the micrographs revealed that, the spherical nanoparticles are distributed uniformly in the volume of the stabilizing matrix. As it can be seen from a comparison of the obtained data, the proposed techniques of the introduction of nanoparticles into a polymer matrix does not affect the shape of nanoparticles and the agglomeration of particles does not occur. However, on the TEM images of PP+Fe_3O_4 nanocomposite, there is some broadening of the size distribution, caused by small amounts of aggregated nanoparticles with diameter of 8 nm. Probably, this effect is due to the high temperature at the stage of introduction of Fe_3O_4 nanoparticles in a polymer matrix, which can lead to partial agglomeration of particles and a corresponding increase of their share in the size distribution.

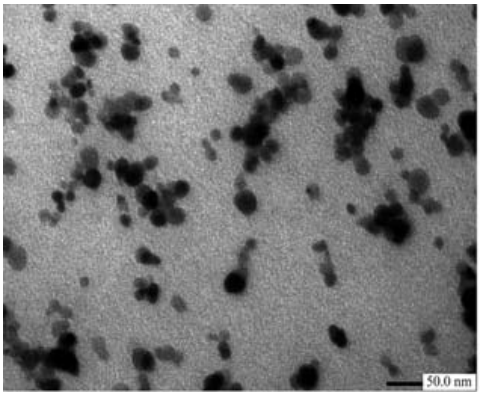

Figure 1.TEM image of PP+10%Fe_3O_4.

Figure 2 shows SEM images of nanocomposites based on PP + Fe_3O_4 at 5% and 20% weight content of magnetite nanoparticles. As can be seen from the figure, with the increasing nanoparticle weight content up to 20% in a polymer matrix the size of nanoparticles slightly increases. Thus, at 5% concentration of the nanoparticles size is 8-15, and at 20% - 16-30 nm

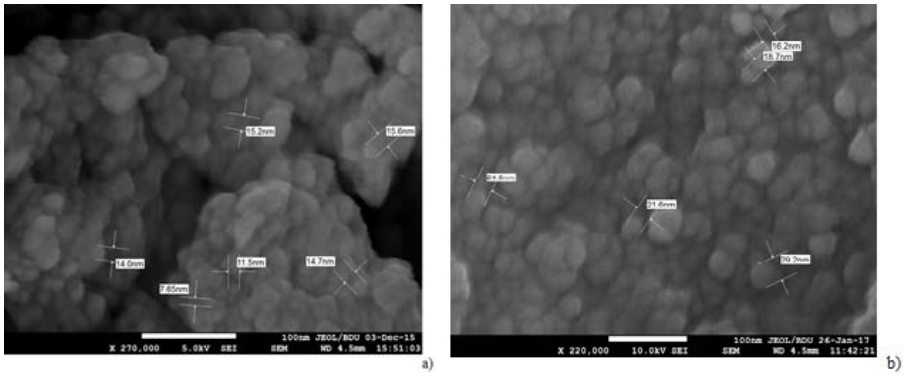

Figure2. SEM images of nanocomposites on the base PP+ Fe_3O_4a) PP+5% Fe_3O_4;b) PP+20% Fe_3O_4

Figure 3 shows AFM images of nanocomposites based on PP + Fe_3O_4 with different weight content of magnetite. As it can be seen from the image, with the addition of magnetite nanoparticles in a matrix, more ordered structure formed. So, at 5% weight content of Fe_3O_4nanoparticles in a polymer the distribution of magnetite is relatively ordered, more perfect structure is formed at 7%. From the AFM image, it is seen that the further increase of the magnetite content in the polymer matrix leads to nanoparticle agglomeration. This correlates well with the values of the average roughness of the surface of the nanocomposites [Saboktakin M.R. 2009].

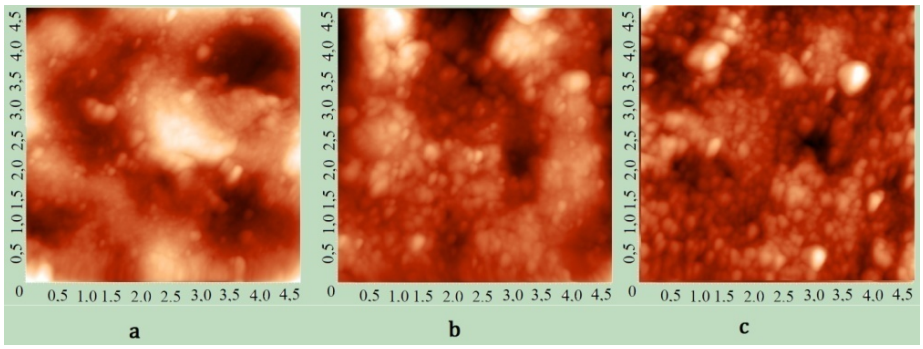

Figure 3. AFM images of nanocomposites PP+Fe_3O_4 a) PP+5%Fe_3O_4, b) PP+7%Fe_3O_4, c) PP+10%Fe_3O_4

Figure 4. shows histograms of the surface roughness of the nanocomposites based on PP+Fe_3O_4. So, the root mean square roughness of the surface of the nanocomposite PP + 5% Fe_3O_4 is 40-50 nm; PP+7%Fe_3O_4 is 30-40 nm; PP+10% Fe_3O_4 is 60-100 nm. From this it may be concluded that the 7%weight contents of Fe_3O_4 nanoparticles in a polymer matrix lead to more perfect supramolecular structure of polypropylene.

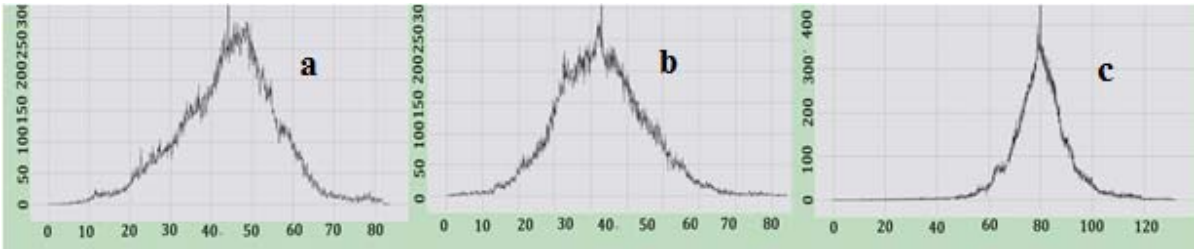

Figure 4. Histogram image of nanocomposites surface roughness a) PP+5%Fe_3O_4, b)PP+7%Fe_3O_4,c)PP+10%Fe_3O_4

As it can be seen from the figure 5, the decomposition occurs at one-stage step. From the TGA curve, it is clear that the PP begins to decompose at temperatures 237,04^0 C with a continuous weight loss up to 475,64^{0}C.After the temperature 475,64^{0}C, the area on TGA curve corresponds to the constant weight. After the addition of 5%weight content of magnetite nanoparticles, the starting temperature of thermo-oxidative degradation of nanocomposites shifted to higher temperatures, that is 306,47^{0}C with a continuous weight loss of up to 477,65^0 C.

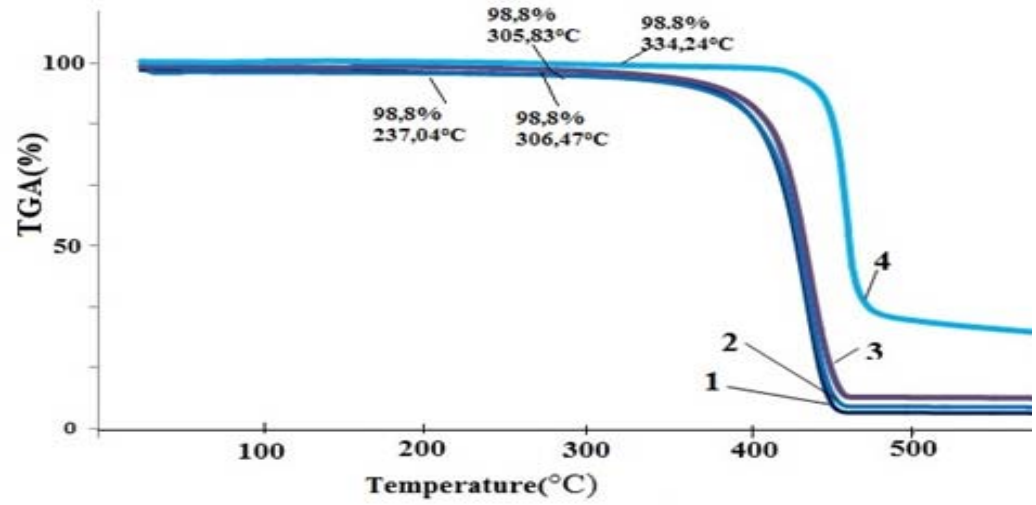

Figure 5. TGA curves of pure polypropylene and nanocomposites on the base PP+ $Fe_3O_4$1)PP; 2)PP+5%Fe_3O_4; 3)PP+10%Fe_3O_4; 4)PP+20%Fe_3O_4

Further increase of Fe_3O_4weight content in the polypropylene matrix leads to further shifts of the decomposition temperature to higher temperatures. So, at 20% weight content of $Fe_3O_4$the decomposition temperature for nanocomposite is 334,24^0 C with a continuous weight loss of up to 495,6^0 C.

Consequently, it was found that the addition of magnetite nanoparticles in polypropylene matrix increases the thermal stability and heat resistance, and this observed up to 20% of weight content of Fe_3O_4. This fact is associated with the inorganic nature of magnetite with uniform distribution, which supplies the superior interference of heat sources, thus, improves the thermal stability [M.A. Ramazanov 2009]. Subsequently, the 20% weight content of magnetite in the polymer increases the thermal stability of polypropylene by almost 100° C, which is very high for such an industrial polymer as PP.

The results of TGA analysis of the samples of pure PP and PP + Fe_3O_4 are given in Table 1.

Table 1. Influence of magnetite nanoparticles weight content on the thermal stability of polypropylene

Sample	Initial decomposition temperature(°C)	Half decomposition temperature (°C)	Final decomposition temperature (°C)
PP	237,0	458,37	475,64
PP +5%Fe3O4	306.4	455.74	477.65
PP +10%Fe3O4	305.83	458.67	480.89
PP +20%Fe3O4	334.24	488.44	495.6

To study the thermal phase transitions of polymeric nanocomposites based on PP and Fe_3O_4, the differential scanning calorimetry (DSC)measurementswere carried, which allows to define the degree of crystallinity, glass transition temperature, melting and crystallinity temperatures. Figure 7 shows curves of the melting temperature of polymer PP+Fe_3O_4nanocomposites. Defining the heat of fusion, the degree of crystallinity of the polymer can be calculated which can be investigated by the following relationship:

$$degreecrystallinity(\%) = \frac{H}{H_0} \cdot 100\%$$

H – melting heat, determined by the area ofpeak responsible for the melting of the polymer, H_0 - the heat released at the melting of 100% crystalline polymer, for polypropylene, it is H_0 = 207 mJ/mg

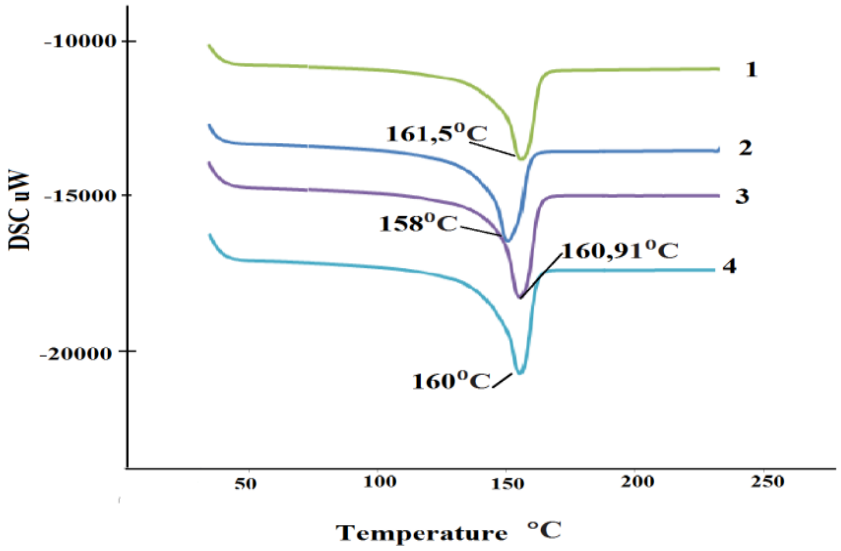

Figure 7. The melting temperature for the PP+Fe_3O_4nanocomposites, derived from DSC analysis 1)PP+5%Fe_3O_4; 2)PP; 3)PP+7%Fe_3O_4; 4)PP+10%Fe_3O_4

Table 2. data obtained by differential scanning calorimetry for pure PP and PP+Fe_3O_4 nanocomposites.

Sample	Melting temperature (°C)	Crystallisation temperature (°C)	Melting enthalpy (mJ/mg)	Degree of crystallinity (%)
PP	158	113,3	91,9	42,39
PP +5%Fe3O4	161,5	114	88,3	44,65
PP +7%Fe3O4	160,9	115	99	47,82
PP +10%Fe3O4	160,9	117,3	96	46,37

In accordance with the table that the pure PP melts at 158°C and with the formula (1), the calculated degree of crystallinity of the PP is 44.39%. As it can be seen from the figure 7, the addition of fillers does not lead to a significant change in the melting temperature. The degree of crystallinity is increased at 7% weight content of Fe_3O_4 and then slightly decreases [M.A.Ramazanov 2003].Further decrease of crystallinity degree is due to the destruction of the crystalline phase with increasing of filler concentration towards the polymer matrix.

4. Conclusion

The thermal degradation behaviour of polypropylene and its magnetite composites have been investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Distribution of magnetite nanoparticles in a polymer matrix has been studied by scanning and transmission electron microscopy and also atomic force microscopy. The thermal and mechanical properties of nanocomposites based on polypropylene and magnetite nanoparticles have also been investigated. It has shown that, the introduction of Fe_3O_4 nanoparticles in polypropylene increases its thermal stability of about 100^0C. The maximum increase in the thermal stability of PP was observed in the case of a 20% weight content of Fe_3O_4 nanoparticles in polypropylene.

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Reference

Fayçal Dergal, Ali Mansri , Laurent Billon. Characterization by Tga and Uv-visible of New Pigment Materials Containing Mica, P4VP and D&C Red 6 Dye. J.Chemical engineering transactions. VOL. 32,2013,2131-2136

Maharramov A.M., M.A. Ramazanov*, F.V. Hajiyeva and S.Q.Aliyeva Formation of Nanoporous Structures of Polypropylene Irradiated by High Energy Heavy Ions j. Nanomedicine& Nanotechnology, 2012, 3:5

Maharramov A.M M.A.Ramazanov, F.V.Hajiyeva, V.M.Guliyeva Investigation of structure and electrophysical properties of nanocomposite materials on the basis of zirconium dioxiden in isotactic polypropylene matrix Journal of Ovonic Research v.9, . 5, 2013, p. 133

Ramazanov M.A.,, S.J.Kerimli, S.A.Abasov, R.Z.Sadykov The Crystallization Mode Influence and Magnetic Field action upon the Mechanical and Thermal Properties of Composite materials on the Basis of polymers and Magnetic Additives, Surface Engineering and Applied Electrochemistry, v.45,№2,2009, p. 136

Ramazanov M.A.,, A.S.Huseynova, N.A.Eyubova, S.A.Abasov Thermal properties and changes in phase structure of PP+MnO2 based composites j. Optoelectronics and Advanced MaterialsRapid communications (OAM-RC) v.4, ISS.12 2010, p. 2003

Ramazanov M.A., Maharramov A.M., Hajiyeva F.V., Kirac F., Guven O., 2016. Morphology, mechanical and thermal properties of nanocomposites based on isotactic polypropylene and zirconium dioxide nanoparticles,RevistaRomână de Materiale / Romanian Journal of Materials, 46 (3), 375 – 382

Saboktakin M.R., Maharramov A.M., Ramazanov M.A., 2009. Microwave Absorption Studies on SuperparamagneticConductingNanocomposites as Signal Coating Materials, Polymer-Plastics Technology and Engineering, 48, 1–5

Sébastien Leveneur, France Delannoy , Yoann Levesqueau, Jean-Pierre Hébert , Lionel Estel , Bechara Taouk, Tapio Salmi. The Limit of DSC as a Preliminary Tool to Determine the Safety Parameters. 2014. Chemical engineering transactions,vol 36,139-144, DOI: 10.3303/CET1436024

Shirinova.H.A., Luca. Di Palma., Sarasini.F., Tirillò.J., Ramazanov.M. A., Hajiyeva.F., Sannino.D., Polichetti.M., Galluzzi.A., 2016. Synthesis and characterization of magnetic nanocomposites for environmental remediation Chemical Engineering Transactions, 47, 103-108 DOI: 10.3303/CET1647018.