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$_3$O$_4$ nanoparticles in polypropylene increases its thermal stability of about 100°C. The maximum increase in the thermal stability of PP was observed in the case of a 20% weight content of Fe$_3$O$_4$ 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. Maharramov 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$_3$O$_4$ 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$_3$O$_4$, 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$_3$O$_4$ nanoparticles on the thermal properties of nanocomposites, as well as the relation between the structure and properties of nanocomposites [M.A. Ramazanov 2016].
2. Materials and Methods

2.1 Materials

Isotactic polypropylene (PP grade Moplen HF500N, homopolymer); density - 0.92g/cm³ at 25°C, Mw = 250000, Mn = 67000, Melt Mass-Flow Rate- MFR = 11.5g /10 min (230°C, 2.16 kg), melting T = 162°C. Fe₃O₄ 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°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 charging of 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 microscopy analyses 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 were used. 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 Dergal 2013]. (TGA) Model Seiko Exstar 6000 TG / DTA 6300. Nanocomposites samples were heated from 30 ° C to 650 ° C with a heating rate of 10°C / min in a nitrogen atmosphere.

2.3.5. Differential scanning calorimetry (DSC)

Differential scanning calorimetric analysis of nanocomposites was performed on nanocomposites by using DSC 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 Fe₃O₄ nanoparticles in the polypropylene matrix obtained by introducing of Fe₃O₄ 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+Fe₃O₄ 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 Fe₃O₄ 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%Fe₃O₄.

Figure 2 shows SEM images of nanocomposites based on PP + Fe₃O₄ 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.

Figure 2. SEM images of nanocomposites on the base PP+Fe₃O₄a) PP+5%Fe₃O₄;b) PP+20%Fe₃O₄.

Figure 3 shows AFM images of nanocomposites based on PP + Fe₃O₄ 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 Fe₃O₄ nanoparticles 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 a) PP+Fe₃O₄;b) PP+5%Fe₃O₄;c) PP+20%Fe₃O₄.
Figure 3. AFM images of nanocomposites PP+Fe₃O₄ a) PP+5%Fe₃O₄, b) PP+7%Fe₃O₄, c) PP+10%Fe₃O₄

Figure 4. shows histograms of the surface roughness of the nanocomposites based on PP+Fe₃O₄. So, the root mean square roughness of the surface of the nanocomposite PP + 5% Fe₃O₄ is 40-50 nm; PP+7%Fe₃O₄ is 30-40 nm; PP+10% Fe₃O₄ is 60-100 nm. From this it may be concluded that the 7% weight contents of Fe₃O₄ nanoparticles in a polymer matrix lead to more perfect supramolecular structure of polypropylene.

Figure 4. Histogram image of nanocomposites surface roughness a) PP+5%Fe₃O₄, b)PP+7%Fe₃O₄, c)PP+10%Fe₃O₄

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°C with a continuous weight loss up to 475.64°C. After the temperature 475.64°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°C with a continuous weight loss of up to 477.65°C.

Figure 5. TGA curves of pure polypropylene and nanocomposites on the base PP+ Fe₃O₄ 1)PP; 2)PP+5%Fe₃O₄; 3)PP+10%Fe₃O₄; 4)PP+20%Fe₃O₄

Further increase of Fe₃O₄ weight content in the polypropylene matrix leads to further shifts of the decomposition temperature to higher temperatures. So, at 20% weight content of Fe₃O₄ the decomposition temperature for nanocomposite is 334.24°C with a continuous weight loss of up to 495.6°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 Fe₃O₄. 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 + Fe₃O₄ are given in Table 1.
To study the thermal phase transitions of polymeric nanocomposites based on PP and Fe₃O₄, the differential scanning calorimetry (DSC) measurements were 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+Fe₃O₄ nanocomposites. Defining the heat of fusion, the degree of crystallinity of the polymer can be calculated which can be investigated by the following relationship:

\[
\text{degree of crystallinity} (%) = \frac{H}{H_0} \cdot 100\%
\]

H – melting heat, determined by the area of peak responsible for the melting of the polymer, H₀ - the heat released at the melting of 100% crystalline polymer, for polypropylene, it is H₀ = 207 mJ/mg

Figure 7. The melting temperature for the PP+Fe₃O₄ nanocomposites, derived from DSC analysis
1)PP+5%Fe₃O₄; 2)PP; 3)PP+7%Fe₃O₄; 4)PP+10%Fe₃O₄

Table 2. Data obtained by differential scanning calorimetry for pure PP and PP+Fe₃O₄ nanocomposites.

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

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 Fe₃O₄ 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$_3$O$_4$ nanoparticles in polypropylene increases its thermal stability of about 100°C. The maximum increase in the thermal stability of PP was observed in the case of a 20% weight content of Fe$_3$O$_4$ nanoparticles in polypropylene.

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Reference


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