

## THERMAL AND MECHANICAL PROPERTIES OF PP+Fe AND PVDF+Fe BASED NANOCOMPOSITES

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In this paper, we studied the thermal and mechanical properties of PP + Fe and PVDF + Fe polymer magnetic nanocomposites. It has been found that the thermal stability of polymer nanocomposites with 0.1% volume content of iron nanoparticles increases up to 29<sup>o</sup>C compared to the pure polypropylene. Due to the distribution of iron nanoparticles into the polyvinylidene fluoride polymer matrix, the thermal stability of polyvinylidene fluoride-based nanocomposites decreases. Furthermore, was investigated the dependence of the mechanical properties of PP + Fe and PVDF + Fe nanocomposites on the iron nanoparticles concentration. It has been shown that, for 0,1 % volume content of iron nanoparticles in the polymer matrix the mechanical strength of nanocomposites increases and then decreases. It was pointed out that, Fe nanoparticles play the central role in the structure nucleation in small quantities in polymer matrices, and subsequent increase of nanoparticles content destroys the physical structure of polymers. At lower iron content, a more orderly structure emerges, nanoparticles play a primary role in the formation of the supramolecular structure of the polymer matrix, resulting in stronger interphacial interactions between the matrix and nanoparticles, which leads to the improvement of the nanocomposites properties.

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### 1. Introduction

In recent years, interest to the composites based on thermoplastic polymers filled with homogenous nanoparticles has increased. It is known that, the properties of composites based on polymers and inorganic nanoparticles are determined by the nature of the components influencing on the structure of derived composites and the interphacial interactions between the nanoparticles and the polymer matrix. Their thermal stability of polymer nanocomposites is of great importance while using at conditions of high temperature.

Polymer nanocomposites containing nanoparticles can enhance high thermal stability, i.e. flame retardancy and freezing resistance. It is known that the changes in the physico-chemical and mechanical properties of polymer composite materials are a result of introduction of the filler into the polymer. Some researchers explain this with the conformational flexibility of the macromolecules in the boundary layers and with the influence of the filler surface to the character of interaction between polymer and filler. Of course, this fact also affects to the properties of polymer nanocomposite materials at high temperatures.

Many polymers, including polypropylene, operates at high temperatures in real conditions of operation. The thermal stability of the pristine polymers varies depending on the composition of the polymer material, the bond energy of the atoms in the main chain, cristallinity degree (with increasing cristallinity degree, speed of oxygen absorption decreases), the presence of substituents in the polymer (as the number of substituents increases, the C-C bond energy in the chain decreases).

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The thermal stability of the filled polymers is influenced by the synthesis techniques for polymer nanocomposites, the sizes and distribution of nanoparticles, the presence of additional additives in inorganic fillers and etc.

In addition, the difference between the thermal expansion coefficients of polymer and filler also affect on the durability of the polymer at high temperatures [1-3].

Polymer nanocomposites on the basis of ferromagnetic metal nanoparticles are of great interest because of their application in the high-density information writing, as high sensitive sensors for detecting of weak magnetic fields, spinotronic devices and etc.

Therefore, from the practical point of view, the investigation of the thermal and mechanical properties of magnetic polymer nanocomposites is of great importance.

In this paper we report of the thermal and mechanical properties of PP + Fe and PVDF + Fe magnetic polymer nanocomposites obtained by incorporating of iron nanoparticles into polypropylene (PP) and polyvinylidene fluoride (PVDF).

## **2. Experimental part**

The isotactic polypropylene (PP brand Sigma Aldrich Pcode 1001326963) has a density of 0,9 g/ml at 25<sup>0</sup>C, refractive index- n<sub>20/D</sub> 1.49, transition temp - T<sub>g</sub> -26°C, mol.wt-average M<sub>w</sub> ~ 250000 by GPC, auto-ignition temp -> 674° F, mp - 1890S. PVDF (M<sub>w</sub>~530000, Sigma Aldrich), toluene (chemically pure, 98% PLC), dimetilformamide (chemically pure, 98% PLC).

Iron nanoparticles prepared by electro-exploding wire techniques.

### **2.1. Synthesis of polymer nanocomposites**

PP+Fe based polymer nanocomposite materials were prepared as follows: isotactic polypropylene powder with particles of 0.5-1.0 micron size was solved in toluene, at a temperature 120<sup>0</sup> C. Magnetite nanoparticles of 0,5-1.0 nm were added to the polymer solution and stirred for two hours in order to prepare a homogeneous mixture. In order to remove solvent, the samples were vacuum dried for 1 day. From these samples by hot-pressing at the melting temperature of polypropylene and a pressure of 10 MPa were obtained thin films with different film thickness. Thus, nanocomposites containing 0.1, 0.5, 1, 2, 5, and 10 % of the Fe filler were prepared. Cooling the films after hot pressing was carried out in water at the cooling rate 200 K/min [4,5].

### **2.2. Methods of research**

#### ***Atomic force microscopy***

The morphology of the nanocomposites was studied using atomic force microscopy NTegra Micro40 2011 (NT-MDT, Zelenograd). For the scan used 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. Scan size was 5×5 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, respectively 256 and 1,969 Hz.

#### ***Thermogravimetric analysis (TGA).***

Thermogravimetric analysis of samples was conducted in a thermogravimetric analyser (TGA) Model Seiko Exstar 6000 TG /-DTA 6300. Nanocomposites samples were heated from 30 ° C to 650 ° C with a heating rate of 10<sup>0</sup>C / min in a nitrogen atmosphere.

#### ***Differential scanning calorimetric analysis(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 aluminum 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.

Technique to study the mechanical durability of the nanocomposites based on was described in work

### 3. Results and discussion

Fig. 1 shows 2D AFM image for PP+Fe based nanocomposites. As it is clear from 2D AFM image, the change occurs in the supramolecular structure of polymer as the iron content increases in the polymer matrix. The fig.2 shows the histograms of the surface roughness for PP and PP+Fe based nanocomposites. As it is clear from Fig. 2, the average surface roughness for pure PP is 80-120 nm, for the PP+5%Fe based nanocomposite it is 40-80 nm.. From this it can be concluded that, changes in upper molecular structure of polymer and the chipping of structure elements of surface morphology of polymer occur with addition nanoparticles to the polymer matrix [6-9].

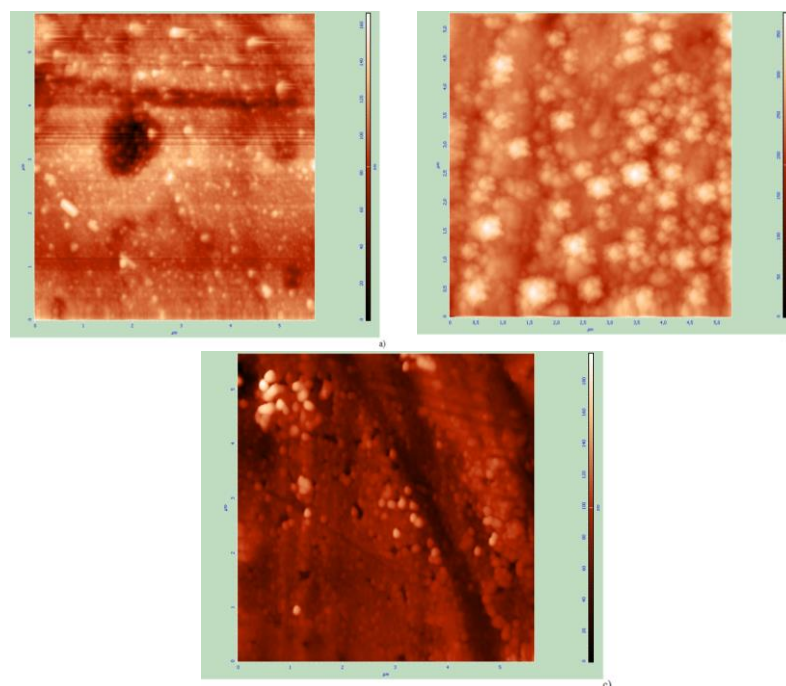


Fig. 1. AFM 2 D images of nanocomposites PP+Fe depending on the volume content of iron nanoparticles: a) PP+0,1%Fe; b) PP+0,3%Fe; c) PP+5%Fe

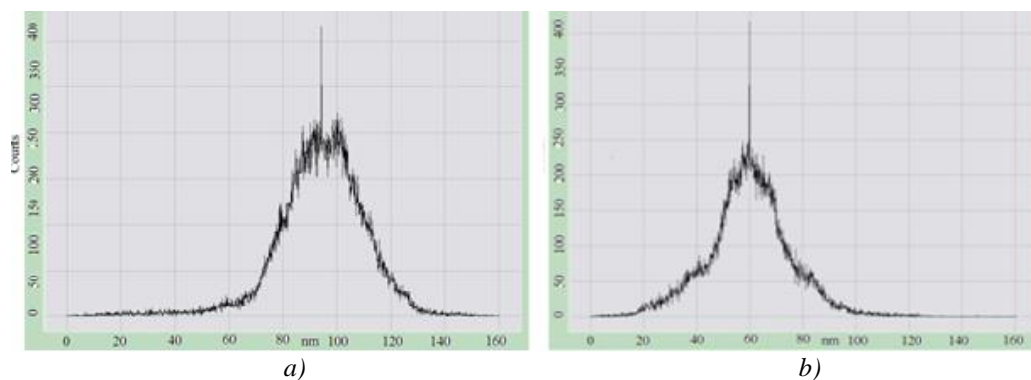


Fig. 2. Histogram of image of nanocomposite roughness PP + Fe:  
a) PP; b) PP+5% Fe

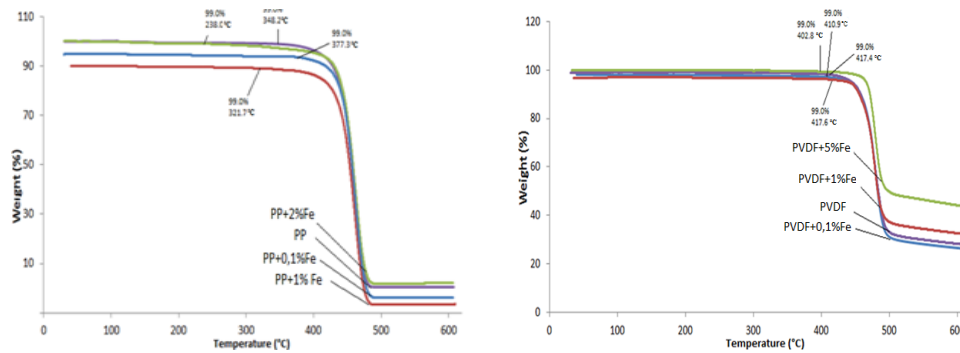


Fig. 3. TGA curves of nanocomposites PP+Fe (a) and PVDF+Fe (b):

The thermogravimetric analysis (TGA) of nanocomposites have been carried out, to determine the thermal stability of PP+Fe and PVDF+Fe nanocomposites.

Fig. 3 shows the results of TGA curves of nanocomposites of PP+Fe and PVDF+Fe. From the Figure 3 (a) it is seen that, thermooxidative decomposition of polymer nanocomposites occurs in a single-step process.

PP begins to decompose at temperature 348,24<sup>0</sup>C, defined as 1% weight loss, with a continuous weight loss up to 472,33<sup>0</sup>C. After the reaching 472,33<sup>0</sup>C, as seen from the TGA curve it reveals the constant weight.

As 0,1% iron nanoparticles content were added into the polypropylene, the decomposition peak shifted to higher temperatures (up to 377,33<sup>0</sup>C). Weight loss of nanocomposite continues up to 474,53<sup>0</sup>C and then remains constant. With the further increase of the iron content in the polypropylene matrix the decomposition temperature shifts back down lower temperatures. So the decomposition temperature for nanocomposites with 1 % iron content, is 321,73<sup>0</sup>C and for nanocomposites with 2 % iron content decomposition temperature is 238,01<sup>0</sup>C.

So as it seen the thermal resistance of prepared nanocomposite is strongly influenced with the introduction of Fe nanoparticles in the polypropylene matrix, the distribution of iron nanoparticles into polypropylene increases the thermal stability of polypropylene and this continues up to 0,1% volume content of iron nanoparticles.

The further increasing of iron nanoparticles content in the polymer matrix, decreases the the thermal stability of nanocomposites. So, at 0,1% content of iron nanoparticles the decomposition temperature of nanocomposite shifts to higher temperatures (up to 29<sup>0</sup>C) compared to the pristine polymer [8-9].

Fig. 3 (b) shows the results of TGA curves of nanocomposites of PVDF+Fe. As it is seen from TGA curves, onset of thermooxidative decomposition for PVDF is 417,42<sup>0</sup>C. With the introduction of 0,1% volume content of nanoparticles into the polymer matrix, the decomposition temperature shift back down to lower temperatures (410,92<sup>0</sup>C). Further rise of the concentration of iron nanoparticles led to the onset temperature of decomposition shifts back down to lower temperatures. i.e, at 1% and 5% Fe content - the onset of decomposition are 409,63<sup>0</sup>C and 402,80<sup>0</sup>C correspondingly.

So, it can be concluded that, the introduction of iron nanoparticles into the polyvinylidene fluoride matrix, decreases the thermal stability of polyvinylidene fluoride based nanocomposites.

Literary analysis reveals that, the stabilizing effect of metal and metal-oxide nanoparticles at high temperatures is explained by the orientation effect of smaller dispersed metal nanoparticles or by as a result of destruction the emergence of new polymeric chains bind to metal atoms. These metal particles play a central role in the formation of secondary structures in the polymer. In some cases the stabilizing properties of some metals is explained by the oxidation-reduction processes [10-13].

Table 1. Effect of iron nanoparticles on polypropylene and polyvinylidene fluoride thermostability

| Samples                               | PP     | PP+0,1%Fe | PP+1%Fe | PP+2%Fe | PVDF   | PVDF+0,1%Fe | PVDF+1%Fe | PVDF+5%Fe |
|---------------------------------------|--------|-----------|---------|---------|--------|-------------|-----------|-----------|
| Initial decomposition temperature(°C) | 348,24 | 377,33    | 321,73  | 238,01  | 417,42 | 410,92      | 409.63    | 402.80    |
| Half decomposition temperature (°C)   | 456,63 | 458,44    | 457,14  | 458,24  | 482,68 | 481,64      | 484.21    | 490,61    |
| Final decomposition temperature (°C)  | 472,33 | 474,33    | 474,53  | 474,69  | 507,99 | 499,92      | 512.77    | 609.32    |

The data of thermal phase transition in PP+Fe and PVDF+Fe nanocomposites was obtained on the basis of the differential scanning calorimetric (DSC) analysis method (Fig. 4 and 5). As the Fe nanoparticles content increases in the polymer matrices the crystallization temperature of nanocomposites increases. With addition of iron nanoparticles to the polymer matrix, crystallization temperature of PP+Fe and PVDF+Fe nanocomposites shifts toward higher temperatures. It is clear from literary analysis that, only strong structurants can affect to the crystallization temperature of nanocomposites. So, it was pointed out that, iron nanoparticles play the role of active structurant and can shift the crystallization peak up to higher temperatures[14-17]. It has also been revealed that, the incorporation of iron nanoparticles into the PP and PVDF polymer matrices can decrease their melting point. Calculated the degree of crystallinity for PP+Fe and PVDF+Fe nanocomposites is given in the Table 2. The equation for calculation the degree of crystallinity, using fusion enthalpy of crystalline polypropylene and polyvinylidene fluoride, that are 165 J/g and 105 J/g respectively, is:

$$\% \text{ Crystallinity} = \frac{\Delta H_{\text{sample}}}{\Delta H_{\text{sample}}^0} \times 100 \quad (1)$$

As it can be seen from the table, up to the 1 % nanoparticles content, the degree of crystallinity increases, then decreases.

Has been investigated the dependence of the mechanical properties of PP+Fe and PVDF+Fe nanocomposites from the Fe nanoparticles' concentration (Fig. 6). It was pointed out that, mechanical durability of nanocomposites first increases up to 1 % of volume content of Fe nanoparticles, and then, with further increasing of nanoparticles content, decrease [14].

Table 2. Values of crystallinity degree for the nanocomposites PP+Fe and PVDF+Fe

| Samples          | PP    | PP+1%Fe | PP+5%Fe | PVDF  | PVDF+1%Fe | PVDF+5%Fe |
|------------------|-------|---------|---------|-------|-----------|-----------|
| Crystallinity(%) | 44.39 | 45.07   | 42.56   | 38.57 | 44.28     | 41.61     |

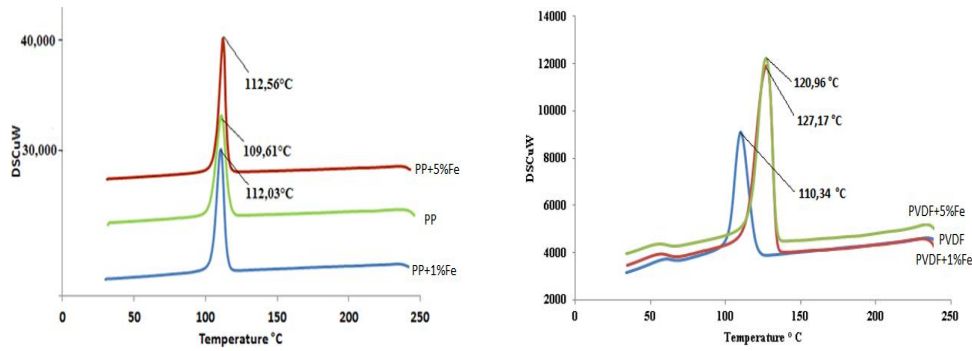


Fig. 4. Data derived from differential scanning calorimetry for PP+Fe (a) and PVDF+Fe(b) nanocomposites

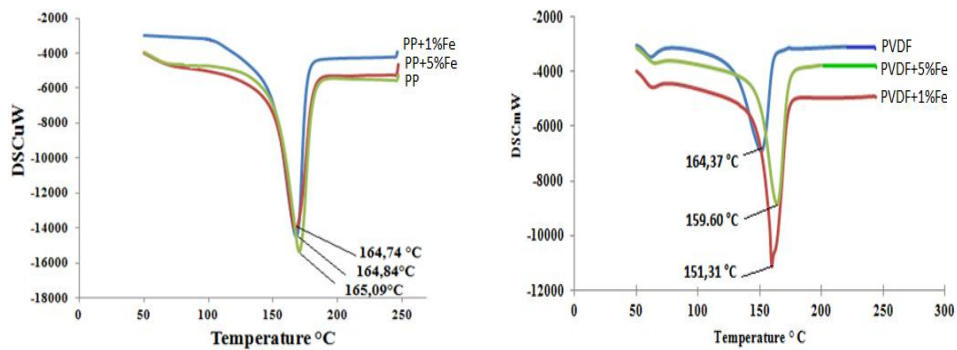


Fig. 5 The melting temperature for the PP+Fe (a) and PVDF+Fe (b) nanocomposites, derived from DSC analysis

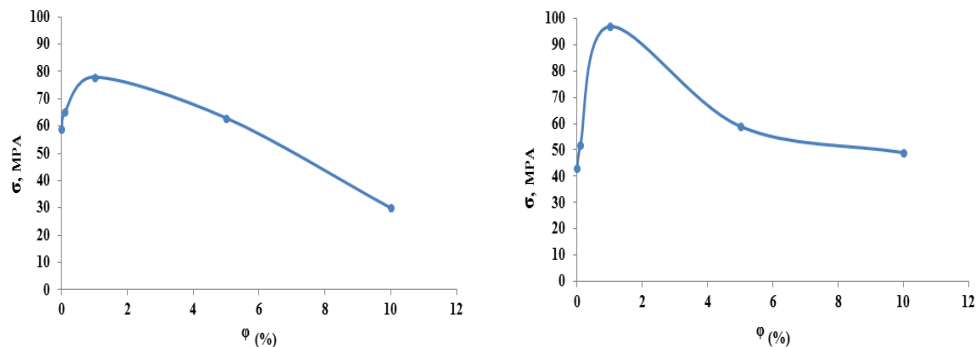


Fig. 6. Dependence of mechanical strength of PP+Fe (a) and PVDF+Fe (b) nanocomposites on the weight content of iron nanoparticles.

It should be noted that, polymer matrix and nanoparticles can actively interact with each other and interaction degree depends on the concentration of main phase, sizes of nanoparticles and preparation condition of nanocomposites. At the interphase between filler and matrix forms an interphase or border layer with properties that differ from matrix properties. In the boundary layer of nanocomposite, while occur nanoparticles structurant activities, formed the crystal polymer structure. It is believed, that nanoparticles structurant activities led to improvement of the thermodynamic conditions of crystallinity of the molecular chains on the boundary layer.

So, we studied the structural, thermal and mechanical properties of PP+Fe and PVDF+Fe nanocomposites. Has been determined that, the properties of polymer nanocomposites is highly dependent on the supramolecular structure of polymer, polarity of polymer, as well as the volume content of nanoparticles. Has been demonstrated that, at low iron concentrations in the polymer

matrix, more ordered supramolecular structure formed in comparison with polymers with high iron concentration. The further rise of Fe volume content results in the formation of more ordered structure and leads to relatively orderly distribution of Fe nanoparticles inside the polymer matrix, whereas Fe nanoparticles behave like filler.

Has been defined that, small amount of iron nanoparticles play the role of structurant in polymer matrix, further increase of iron content in nanocomposites leads to the destruction of the physical structure of polymers. At lower concentrations of nanoparticles leads to the formation of more ordered structure, and in turn, this leads to the enhancement of properties of these nanocomposites[18,19].

#### 4. Conclusions

In this paper, we studied the thermal and mechanical properties of PP + Fe and PVDF + Fe polymer magnetic nanocomposites. It has been found that the thermal stability of polymer nanocomposites with 0.1% volume content of iron nanoparticles increases up to 29<sup>0</sup>C compared to the pure polypropylene. Due to the distribution of iron nanoparticles into the polyvinylidene fluoride polymer matrix, the thermal stability of polyvinylidene fluoride-based nanocomposites decreases. Furthermore, was investigated the dependence of the mechanical properties of PP + Fe and PVDF + Fe nanocomposites on the iron nanoparticles concentration.

It has been shown that, for 0,1 % volume content of iron nanoparticles in the polymer matrix the mechanical strength of nanocomposites increases and then decreases. It was pointed out that, Fe nanoparticles play the central role in the structure nucleation in small quantities in polymer matrices, and subsequent increase of nanoparticles content destroys the physical structure of polymers. At lower iron content, a more orderly structure emerges, nanoparticles play a primary role in the formation of the supramolecular structure of the polymer matrix, resulting in stronger interfacial interactions between the matrix and nanoparticles, which leads to the improvement of the nanocomposites properties.

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