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POLYMER BASED NANOCOMPOSITES

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Abstract

Dispersions consisting of spherical CdS and α-Fe$_2$O$_3$ particles in the nanometer and sub-micron size range, as well as β-FeOOH nanorods with three different aspect ratios were prepared using colloidal chemistry methods. After incorporation of filler particles into polystyrene and poly(methyl methacrylate) matrices influence of filler particles on the thermal stability and the glass transition temperature of polymer matrices was studied in details. Significant influence of content, size and shape of filler particles on thermal properties of polymer matrices was found.

Introduction

Nowadays, polymer composites are widely used in many fields of technology [1,2]. The properties of composites mostly depend on size and shape of filler particles, their concentration, as well as the type of interaction with polymer matrix. Also, polymer composites take advantage of desired properties of host polymers such as possibility to be designed in various shapes, long-term stability and reprocess ability.

Polystyrene (PS) and poly(methyl methacrylate) (PMMA) are important thermoplastic materials with excellent transparency. However, their lower thermal stability restrains them from applications in higher temperature region. To improve the thermal properties of PS and PMMA, fillers such as oxides [3-5], metal chalcogenides [6-8], metals [9,10], organoclays [11] and graphite [12] were incorporated into PS and PMMA.

In this work, we present synthetic procedures for preparation of colloidal dispersions consisting of spherical CdS and α-Fe$_2$O$_3$ particles in the size range from a few nanometers up to a several hundreds of nanometers, as well as β-FeOOH nanorods (NRs) with three different aspect ratios. Also, we present synthetic methodology for incorporation of filler particles into polymer matrices. The prepared nanocomposites were characterized using structural and thermal techniques and influence of concentration, size and shape of fillers on the thermal properties of polymer matrices was discussed in details.

Experimental

Detailed information about preparation of colloidal dispersions consisting of spherical 5 nm CdS [13], 0.2-0.35 μm CdS [7], 5-10 nm α-Fe$_2$O$_3$ [14], and 0.2-0.5 μm α-Fe$_2$O$_3$ [3] particles can be found elsewhere. Dispersions consisting of β-FeOOH NRs with different aspect ratios (4, 80 and 130) were prepared by "forced hydrolysis", i.e., thermal hydrolysis of iron (III) chloride solution similar to the method described in literature [15]. Dispersions in organic solvents were obtained using phase transfer

from water after proper surface modification of above mentioned particles with am-phiphilic molecules such as: sodium dodecyl sulfate, oleic acid, olayamine, etc.

The polymer based nanocomposites were prepared by combining proper amount of organic dispersion with organic solution of PS (Edistir or Glaskar 143 E) or PMMA (Diakon CMG 314V). After evaporation of solvent, content of inorganic phase in PS or PMMA was determined by measuring atomic emission (ICP-AS Perkin-Elmer 6500 instrument) for Cd or Fe.

Microstructural characterization of synthesized particles was carried out on a transmission electron microscope (TEM) Philips EM-400 operated at 120 kV. Samples for microscopy analysis were deposited on C-coated Cu grids.

The differential scanning calorimetry (DSC) measurements of the pure PS and PMMA, as well as nanocomposites were performed on a Perkin-Elmer DSC-2 instru-ment in the temperature range from 50 to 130 °C, while the thermogravimetric analy-sis (Perkin-Elmer model TGS-2) was carried out under a nitrogen atmosphere in the temperature range from 30 to 550 °C.

Results and Discussion

The thermal stability of 5 nm CdS/PS and 5-10 nm α-Fe_2O_3/PS nanocomposites was compared with the thermal stability of the pure PS. The thermograms of the pure PS as well as CdS/PS and α-Fe_2O_3/PS nanocomposites with 4.8 and 3.6 mass% of inorganic phase, respectively, obtained under the atmosphere of nitrogen, are shown in Figure 1.
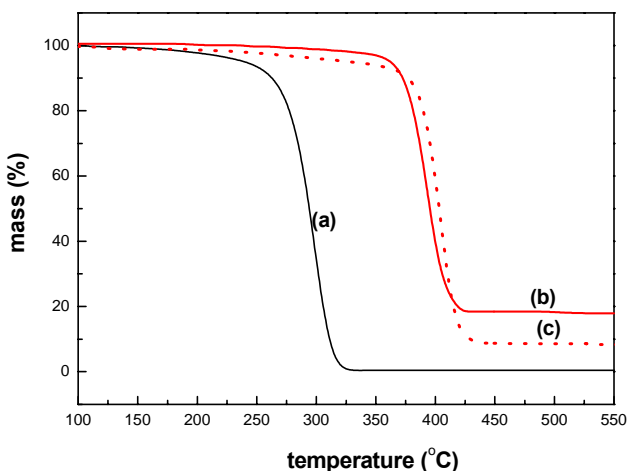

Fig. 1. The thermograms of the pure PS (a), as well as 5 nm CdS/PS (b) and 5-10 nm α-Fe_2O_3/PS (c) nanocomoposites with 4.8 and 3.6 mass% of inorganic phase, respectively, obtained under the atmosphere of nitrogen.

The obtained results indicate that incorporation of nanoparticles (NPs) significantly alters the thermal properties of the PS matrix. The thermal decomposition of PS in the

presence of CdS and α-Fe$_2$O$_3$ NPs is shifted towards higher temperatures by about 100 ^{0}C. Incorporation of other nanofillers such as 5 nm Ni NPs [9], smaller than 10 nm Fe NPs [10], 10-12 nm HgS NPs [8], graphite [12] and clay [11] into the PS matrix induced significantly smaller improvement in its thermal stability. Based on comparison of the obtained results with the above-mentioned literature data we can conclude that the thermal stability of PS is significantly improved in the presence of CdS and α-Fe$_2$O$_3$ NPs.

In order to study influence of size of filler particles on the thermal stability of polymer matrix sub-micron spherical CdS (0.2-0.35 μm) and α-Fe$_2$O$_3$ (0.2-0.5 μm) particles were incorporated into PS. Thermograms of the pure PS and CdS/PS filled polymers with different contents of inorganic phase, obtained under the nitrogen atmosphere, are shown in Figure 2, while the 50% weight loss data concerning α-Fe$_2$O$_3$/PS composites are collected in Table 1. Improvement of the thermal stability of PS matrix can be noticed with the increase of the content of the inorganic phase, but this effect is less pronounced compared to improvement achieved using NPs.
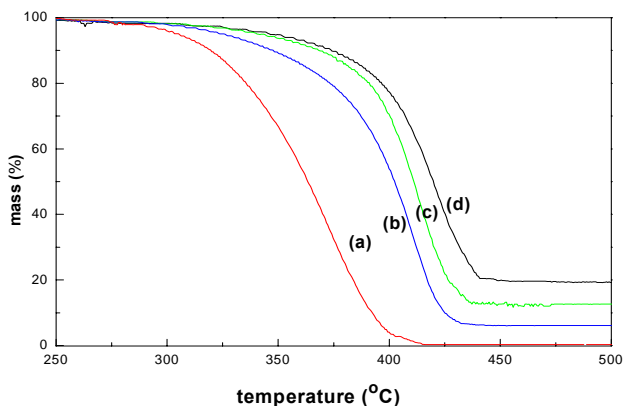

Fig. 2. The thermograms of the pure PS (a) and the 0.2-0.35 μm CdS/PS composites with 6 (b), 12 (c) and 20(d) mass% of inorganic phase, obtained under the atmosphere of nitrogen.

For example, the thermal decomposition of the filled polymer with 17 mass% of 0.2-0.5 μm α-Fe$_2$O$_3$ filler particles is shifted towards higher temperatures for about 70 ^{0}C, while 3.6 mass% of 5-10 nm α-Fe$_2$O$_3$ induced shift of about 100 °C.

Table 1. The 50 % weight loss temperature ($T_{50\%}$) of α-Fe$_2$O$_3$/PS composite

Content of inorganic phase (mass %)	0	5	10	17
$T_{50\%}$ (^{o}C)	354.6	405.4	421.4	432.9

Although the origin of the enhanced stability as a result of adding CdS or α-Fe$_2$O$_3$ to PS is open to debate, we believe that the possible reason for it can be assigned to

reduced molecular mobility of the polymer chains. It is well-known that the changes in molecular weight during thermal degradation of PS are induced by scission of weak peroxide bonds formed by incorporation of oxygen during the polymerization, and due to intermolecular chain transfer reactions, which follow the initial step of the formation of primary free radicals [16]. The reduced molecular mobility induced by the presence of filler suppresses chain transfer reactions and consequently improves the polymer thermal stability. Off course, this effect is more pronounced with the decrease of the size of filler particles.
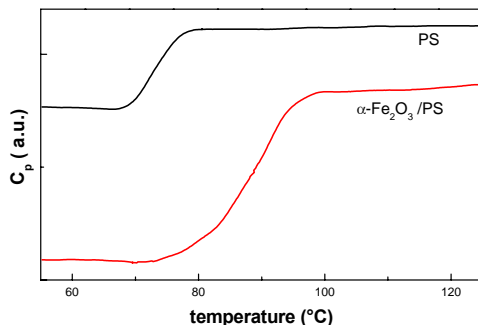

Fig. 3. The heat capacity curves of the pure PS and 5-10 nm α-Fe$_2$O$_3$/PS nanocomposite with 3.25 mass% of inorganic phase.

The heat capacity curves of the pure PS and α-Fe$_2$O$_3$/PS nanocomposite with 3.25 mass% of inorganic phase are shown in Figure 3. A shift in the slope of the heat capacity curves towards higher temperatures was observed after incorporation of α-Fe$_2$O$_3$ NPs into the PS matrix. This slope corresponds to the glass transition temperature of the polymer. It should be emphasized that the glass transition is not a true phase transition since the derivative of the heat capacity can be a continuous function of temperature. The different segmental motions lead to the glass transition spectrum. Therefore, the midpoint of the slope will be treated as the glass transition temperature, e.g., the glass transition temperature is taken to be at the maximum of the heat capacity derivative. Accordingly, a significant shift in the glass transition temperature of PS for 17 ^{0}C was observed after incorporation of α-Fe$_2$O$_3$ NPs. The observed effect can be explained as a consequence of decreased molecular mobility of the polymer chains due to adsorption of polymer segments onto the surface of nanofiller particles. It is obvious that the inter-particle distance of spherical fillers in composites with constant content of inorganic phase is proportional to the particle size. Consequently, there is much higher probability that the polymer segments will interact with nanofillers than with fillers in the sub-micron size range. For example, after incorporation of 0.2-0.5 μm α-Fe$_2$O$_3$ particles in the PS matrix, the shift in the glass transition temperature was about 2.5 °C for the content of inorganic phase of 17 mass%.

In order to study influence of the shape of filler particles on the thermal properties of polymer matrix β-FeOOH NRs with three different aspect ratios were incorporated into the PMMA. Typical TEM images of the β-FeOOH NRs prepared on three differ-

ent ways are shown in Figure 4. The first dispersion (see Figure 4A) consists of 75-125 nm in length and 23-27 nm in diameter β-FeOOH NRs (aspect ratio of about 4). The second dispersion (see Figure 4B) consists of 250-350 nm in length and 3-5 nm in diameter β-FeOOH NRs (aspect ratio of about 80), while the third dispersion (see Figure 4C) consists of 550-1000 nm in length and 5-8 nm in diameter β-FeOOH NRs (aspect ratio of about 130). It is clear that it is more difficult to control length then the diameter of β-FeOOH NRs. Ability to control length of β-FeOOH NRs decreases with the increase of aspect ratio. Also, β-FeOOH NRs have tendency to array parallel to each other and to form bundle-like aggregates.
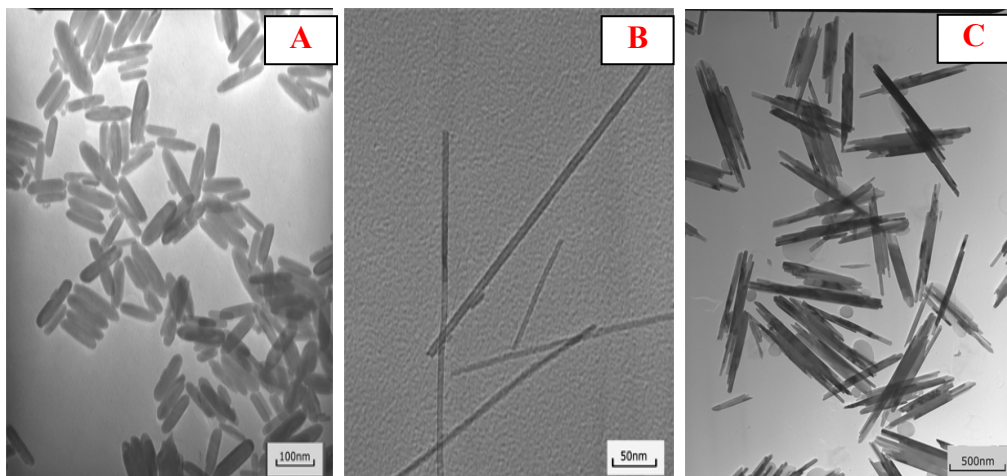

Fig. 4. Typical TEM images of β-FeOOH NR$_s$ with different aspect ratios: (A) 4, (B) 80 and (C) 130.

Data concerning the glass transition temperature of the pure PMMA and β-FeOOH/PMMA nanocomposites (aspect ratio 4, 80 and 130) with 1.5, 3.5 and 6.5 mass% of inorganic phase are collected in Table 2. Significant shift in the glass transition temperature of PMMA towards higher temperatures (20-30 °C) was observed after incorporation of β-FeOOH NRs. The increase of the glass transition temperature of more than 20 °C was observed when content of β-FeOOH NRs (all aspect ratios) was as low as 1.5 mass%.

Table 2. Glass transition temperature (°C) of β-FeOOH/PMMA nanocomposite

Content of inorganic phase (mass %)	Aspect ratio of β-FeOOH NRs		
	4	80	130
0	93.3	93.3	93.3
1.5	116. 4	118.8	122.3
3.5	120. 5	120.9	123.1
6.5	121. 1	122.4	124.3

Further increase of the content of inorganic phase led to additional increase of the glass transition temperature. Also, for nanocomposites with the same content of inorganic phase increase of the glass transition temperature was observed with the increase of the aspect ratio of β-FeOOH NRs. Various nanofillers have sometimes completely opposite effects on the glass transition temperature of the PMMA. For example, the presence of 4 mass% of commercially available modified silica (AEROSIL[®] R805, R812 and R972) induced shift of the glass transition temperature for 18 °C towards higher temperature [17,18], while the presence of 6 mass% of poly(dimethylsiloxane) surfactant-modified clay increased the glass transition temperature of PMMA for 3 °C [19]. On the other hand, the presence of 0.5 mass% of 39 nm in diameter alumina particles decreased the glass transition temperature of PMMA for 25 °C [20]. Based on this, it seems that β-FeOOH NRs have pronounced effect on the glass transition temperature of the PMMA matrix. The observed effect can be again explained as a consequence of decreased molecular mobility of the PMMA chains due to adhesion of polymer segments onto the surface of β-FeOOH NRs.

Conclusion

Significant influence of filler particles (CdS, α-Fe_2O_3 and β-FeOOH) on the thermal stability and glass transition temperature of polymer matrices (PS and PMMA) was found. Basically, the thermal stability and glass transition temperature of polymer matrices is function of concentration, size and shape of filler particles. The increase of content of inorganic phase, the decrease of size of filler particles, i.e. increase of specific surface area and the increase of aspect ratio of rod-shaped filler particles induced improvement of thermal stability of polymer matrices and the increase of the glass transition temperature.

Acknowledgements

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