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LETTER

Influence of CdS-filler on the thermal properties of poly(methyl methacrylate)

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Nowadays, polymer composites are widely used in many fields of technology. Among them a significant roles play polymers containing semiconductor particles, especially for the manufacturing of electronic devices [1]. Therefore, it is important to understand the effects of these fillers on the properties of composites. 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.

Poly(methyl methacrylate) (PMMA) is an important thermoplastic material with excellent transparency. However, its lower thermal stability restrains it from applications in higher temperature region. To improve the thermal properties of PMMA, fillers such as silica, titania, zirconia and alumina [2–8], as well as clay [9] were introduced into the PMMA. Recently, we showed significant improvement of the thermal stability of the polystyrene matrix filled up to a few mass% with the CdS nanoparticles (the mean particle diameter was 50 Å) [10]. This effect is a consequence of high surface to bulk ratio of the CdS nanofiller and the presence of large number of dangling bonds that lead to the formation of chemical bonds between surface atoms of the CdS nanoparticles and the polymer chains. However, the synthetic route for preparation of nanocomposites is quite complex involving transfer of nanoparticles from water to organic phase. Because of that, simplified synthetic route for preparation of the polystyrene–CdS composite was developed based on mixing the CdS-filler in micrometer size range with the polymer melt [11].

In the present study, we synthesized new composite using PMMA as a matrix and submicronic CdS particles as a filler. The composite was characterized using structural techniques and the influence of the CdS-filler on the thermal properties of the PMMA–CdS composite was discussed in detail.

The CdS-filler particles were prepared by mixing 500 mL of aqueous solutions containing 7.0×10^{-2} M $Cd(NO_3)_2$ (Merck) and 1.0×10^{-1} M Na_2S (Fluka) at 90 °C. Precipitate was washed out several times with water. In order to make surface of CdS-filler particles hydrophobic 150 (L of castor oil (Akzo Chemie) was added. Finally, colloidal dispersion was filtered, and precipitate was dried. The PMMA–CdS composite was prepared by dissolving appropriate amount of CdS in solution of PMMA (Diakon CMG314V)) in xylene, and consequent evaporation of solvent. The contents of inorganic phase were chosen to be 1.5, 3.0 and 6.0 wt%.

In order to characterize morphology of the PMMA–CdS composite atomic force microscopy (AFM) was performed using Quesant Universal SPM instrument operating in noncontact (intermittent) mode. Measurements were performed in air using Si probes. Typical AFM image of the PMMA–CdS composite is shown in Fig. 1. Non-agglomerated spherical CdS particles in the size range from 0.2 to 0.35 μm in the PMMA matrix can be noticed.

The X-ray diffraction (XRD) spectra of the PMMA–CdS composites were obtained by using Philips PW 1710 diffractometer. A typical XRD spectrum of the PMMA–CdS composite is shown in Fig. 2. The XRD peaks corresponding to 1 1 1, 2 2 0 and 3 1 1 crystallographic planes indicate that CdS is in a cubic phase (12] The CdS XRD peaks are very broad due to the small crystalline domains in the particles. The Scherrer diffraction formula was used to estimate the crystalline domain size (*D*)

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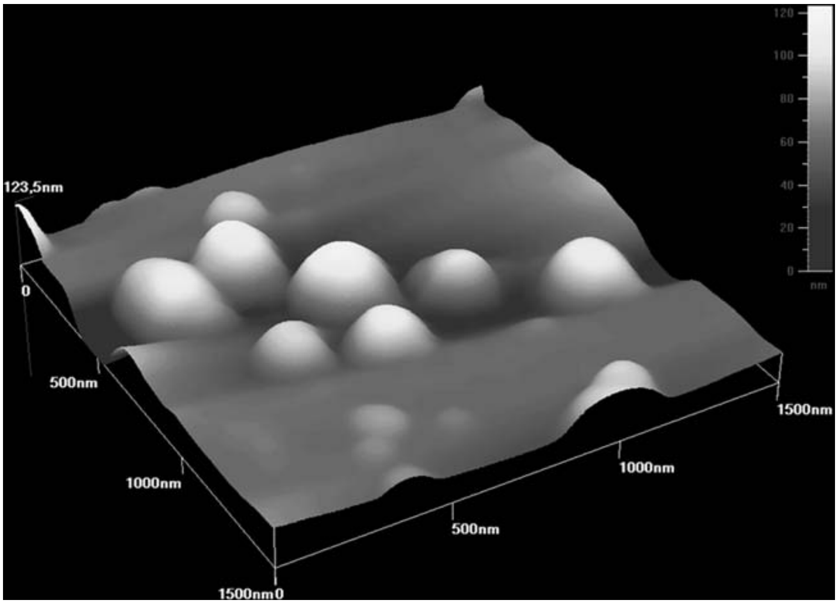

Fig. 1 Typical AFM image of the PMMA–CdS composite

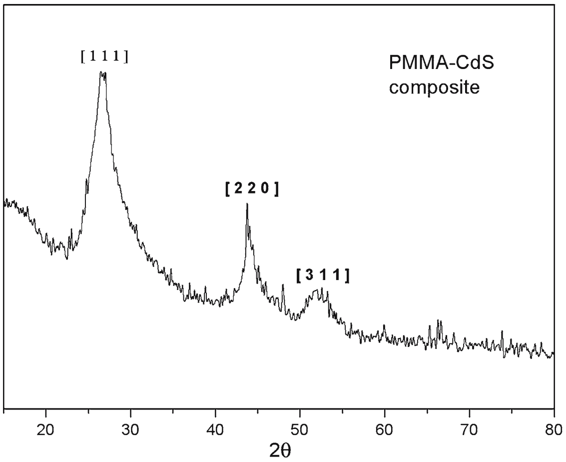

Fig. 2 Typical XRD spectrum of the PMMA–CdS composite

$$D = k\lambda/\beta\cos\theta \qquad (1)$$

where k = 0.9 for the CdS cubic structure, λ = 1.5405 Å is the X-ray wavelength, β is the peak angular width and θ is the diffraction angle. The crystalline domain size was found to be D = 27 Å. Having in mind that the CdS particles are in the size range from 0.2 to 0.35 (m, it can be concluded that the CdS particles are polycrystalline.

In order to determine does chemical bonding between the PMMA matrix and the CdS-filler take place, IR measurements were performed. A disperssive spectrophotometer, IR Perkin–Elmer 983 G was used to record IR spectra of the PMMA–CdS composites and the pure PMMA matrix. No difference between the IR spectra of the unfilled and filled PMMA was observed. Therefore, the chemical composition of the PMMA matrix is not changed in the presence of the submicronic CdS-filler particles indicating weak interaction between phases. Similar result was obtained after incorporation of the 2 μm CdS particles into polystyrene [11]. On the other hand, it has been shown that incorporation of the CdS particles with the mean diameter of 50 Å in the PS matrix lead to the formation of chemical bonds between the surface of nanoparticles and polymer chains [10]. This result is a consequence of large surface to bulk ratio in CdS nanoparticles and presence of large number of dangling bonds on the surface.

The differential scanning calorimetry (DSC) measurements of the pure PMMA and the PMMA–CdS composites were performed on a Perkin–Elmer DSC-2 instrument in the temperature range from 50 to 130 °C. The heating rate was 20 °C min^{-1}. In order to insure the same thermal history of the samples, prior to measurements they were heated above the glass transition temperature (T_g) and then cooled down (heating and cooling rate was 20 °C min^{-1}). The heat capacity curves of the pure PMMA and the PMMA–CdS composite with 1.5 wt% of inorganic phase are shown in Fig. 3. It can be noticed that the midpoint of the slope on the heat capacity curve, i.e. the T_g, is slightly shifted towards higher temperature upon incorporation of the filler into the polymer matrix. The shift of the T_g for about 2 °C suggests weak interaction between the CdS-filler particles and the PMMA matrix. This result is in agreement with above mentioned IR measurements. It seems that influence of the CdS-filler on the T_g is moderate compared to the oxides. For example, at alumina concentration greater than 0.5 wt%, the T_g of PMMA decrease by 25 °C compared to the neat polymer [6]. On the other hand, the T_g of the silica–PMMA composites increases from 113 to 131 °C as the silica loading increases to 4 wt% [7].

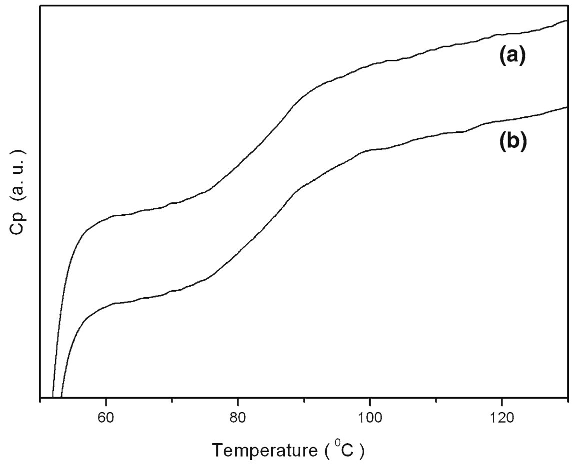

Fig. 3 The heat capacity curves of the pure PMMA (**a**) and the PMMA–CdS composite with 1.5 mass% (**b**) of inorganic phase

The thermogravimetric analysis (Perkin–Elmer model TGS-2) of the pure PMMA and the PMMA–CdS composite samples were carried out under a nitrogen or oxygen atmosphere in the temperature range from 40 to 500 °C. The heating rate was 10 °C min^{-1}. Thermograms of the pure PMMA and the PMMA–CdS composites with different contents of inorganic phase, obtained under the nitrogen atmosphere, are shown in Fig. 4. An improved thermal stability of the PMMA–CdS composites with respect to the pure PMMA matrix can be noticed. For example, the thermal decomposition of the composite with 1.5 wt% of the CdS-filler is shifted towards higher temperature for about 25 °C compared to the unfilled PMMA.

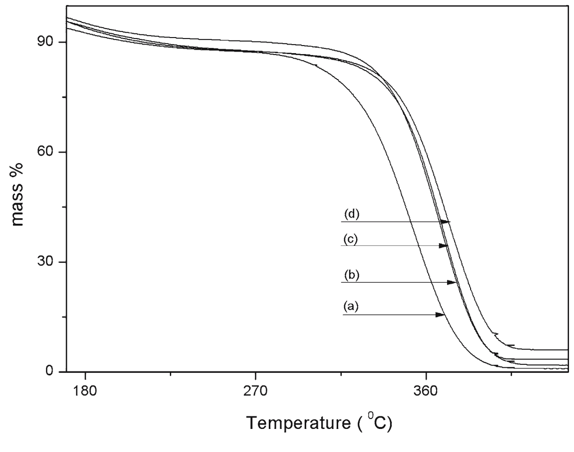

Fig. 4 The thermograms of the pure PMMA (**a**) and the PMMA–CdS composites with 1.5, (**b**) 3 (**c**) and 6 mass% (**d**) of inorganic phase, obtained under an atmosphere of nitrogen

It is interesting to note that additional increase of the content of inorganic phase (up to 6 wt%) did not induce significant improvement of the thermal stability of the composite. The observed effect of the improvement of the thermal stability of PMMA upon incorporation of submicronic CdS particles is similar to literature data concerning influence of silica and zirconia [7, 8], as well clay [9] on the thermal stability of PMMA. Possible reason for the increased thermal stability of the composites is reduced molecular mobility of polymer chains due to the presence of the filler. It is well known that the degradation of PMMA occurs by an efficient chain-transfer process in which the end group reacts with a radical to form an active chain end, which can depolymerize [13, 14]. Therefore, restricted motions of polymer segments attached to the particle surfaces can suppress chain transfer reactions and produce better stability of the composite.

Improvement of the thermal stability of the PMMA matrix with the usage of the CdS-filler particles in the size range from 0.2 to 0.35 μm is demonstrated. Optimization of the synthetic procedure, which is basically the trade off between the size of CdS-filler particles and their content in the composite, is currently underway in our laboratory.

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