

# Influence of CdS-filler on the thermal properties of polystyrene

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## Abstract

Influence of CdS-filler particles in the micrometer size range on the properties of the polystyrene (PS) matrix was studied using structural and thermal techniques. Improvement of the thermal stability of the PS matrix for about 50 K was found in the presence of the CdS-filler. Infrared measurements revealed that interaction between the surface of CdS-filler particles and the PS chain is weak. Non-significant changes in the glass transition temperature of the PS matrix upon the incorporation of CdS-filler particles also suggest weak interaction between filler and polymer. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Semiconductor particles; Polystyrene; Filled polymer; Thermal stability; Glass transition temperature

## 1. Introduction

Nowadays, filled polymers 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 filled polymers. The properties of filled polymers mostly depend on size and shape of filler particles, their concentration as well as the type of interaction with polymer matrix.

In the previous study [2] significant improvement of the thermal stability of the polystyrene (PS) matrix filled up with the CdS nanoparticles (the mean particle diameter was 5 nm) was found. 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, in the present study simplified synthetic route for preparation of the PS–CdS filled polymer was developed based on mixing the CdS-filler in micrometer size range with the polymer melt. The influence of particle size of the CdS-filler on the thermal properties of the PS–CdS filled polymer was discussed. Also, our goal was to examine influence of the content of inorganic phase on the thermal stability of the PS–CdS filled polymer.

## 2. Experimental

### 2.1. Sample preparation

The CdS-filler particles were prepared by mixing 500 ml of aqueous solutions at elevated temperature (363 K) containing  $7.0 \times 10^{-2}$  M  $\text{Cd}(\text{NO}_3)_2$  (Merck) and  $1.0 \times 10^{-1}$  M  $\text{Na}_2\text{S}$  (Fluka). Precipitate was washed out several times with water. In order to make surface of CdS-filler particles hydrophobic 150  $\mu\text{l}$  of castor oil (Akzo Chemie) was added. Finally, colloidal dispersion was filtered, and precipitate was dried.

The PS–CdS filled polymers were prepared by mixing in appropriate ratio at 473 K the Edistir PS and the CdS-filler in Haake rheometer. The contents of inorganic phase were chosen to be 1.4, 2.9 and 5.2 vol%. Mixing

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was carried out at 32 rpm rotor speed for about 10 min. After that, the mixture was shaped into sample sheet 0.2 mm thick by compression molding for 5 min at 453 K in Carver laboratory press. The pure PS sheet was prepared in the same manner as the filled polymers in order to obtain the sample with the same thermal history.

## 2.2. Apparatus

The morphology and the mean grain size of the CdS-filler particles were investigated by scanning electron microscopy (SEM JEOL JSM-3T).

The X-ray diffraction (XRD) spectra of the PS–CdS filled polymers were obtained by using Philips PW 1710 diffractometer.

A dispersive spectrophotometer, IR Perkin-Elmer 983 G was used to record IR spectra of the PS–CdS filled polymers and the pure PS matrix.

The differential scanning calorimetry (DSC) measurements of the pure PS and the PS–CdS filled polymers were performed on a Perkin-Elmer DSC-2 instrument in the temperature range from 320 to 400 K. The heating rate was 20 K min<sup>-1</sup>. In order to insure the same thermal history of the samples, prior to measurements they were heated above the glass transition temperature and then cooled down (heating and cooling rate was 20 K min<sup>-1</sup>).

The thermogravimetric analysis (Perkin-Elmer model TGS-2) of the pure PS and the PS–CdS filled polymer samples (7–8 mg) were carried out under a nitrogen or oxygen atmosphere in the temperature range from 310 to 820 K. The heating rate was 10 K min<sup>-1</sup>.

## 3. Results and discussion

The SEM micrograph (Fig. 1) shows the microstructure of the CdS-filler particles used for preparation of

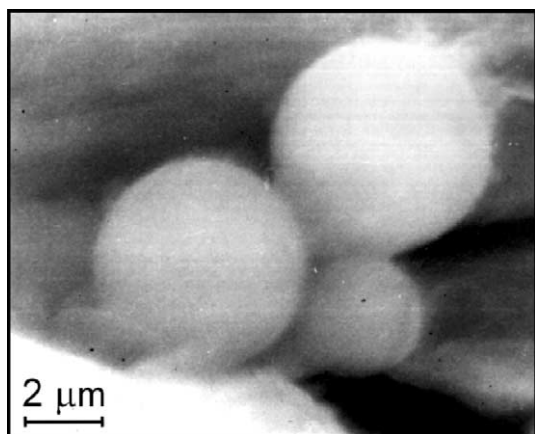


Fig. 1. Typical SEM micrograph of the CdS-filler particles.

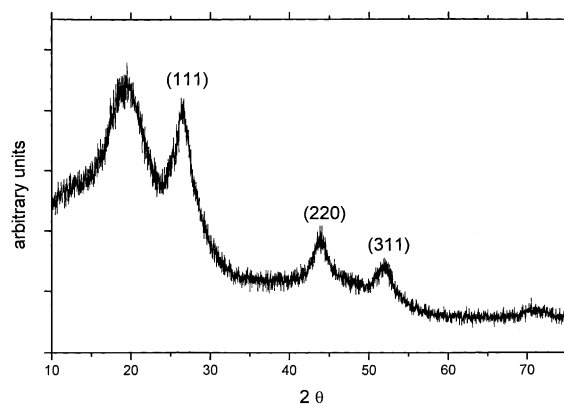


Fig. 2. Typical XRD spectrum of the PS–CdS filled polymer.

the PS–CdS filled polymers. The micrograph was taken at 0° tilt angle, thus making the topography contrast and shape of the particles irrelevant. Ideally spherical CdS particles were observed, as shown in Fig. 1. Also, the analysis indicates that the size of the particles is in the range from 2–4 μm.

A typical XRD spectrum of the PS–CdS filled polymer is shown in Fig. 2. The very broad XRD peak at low diffraction angle indicates the amorphous PS; while slightly sharper peaks corresponding to 111, 220, 311 and 331 planes indicate that CdS is in a cubic phase [3]. The CdS XRD peaks are relatively broad due to the small crystalline domain in the particles. The Scherrer diffraction formula was used to estimate the crystalline domain size ( $D$ ):

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

where  $k = 1$  for the CdS cubic structure,  $\lambda = 1.541 \text{ \AA}$  is the X-ray wavelength,  $\beta$  is the peak angular width and  $\theta$  is the diffraction angle. The crystalline domain size was found to be  $D = 50 \text{ \AA}$ . The large difference between the size of CdS particles (2–4 μm) and the size of crystalline domains (50 Å) indicates that most likely the CdS particles consist of small CdS crystallites.

In order to determine if chemical bonding between the PS matrix and the CdS-filler particles takes place, IR measurements were performed. No difference between the IR spectra of the unfilled and filled PS was observed. Therefore, the chemical composition of the PS matrix is not changed in the presence of the CdS-filler particles in micrometer size range indicating weak interaction between phases, most likely adsorption. On the other hand, it has been shown that incorporation of CdS particles with the mean diameter of 5 nm in the PS matrix lead to the formation of chemical bonds between the surface of nanoparticles and polymer chains [2]. This result is a consequence of large surface to bulk ratio in

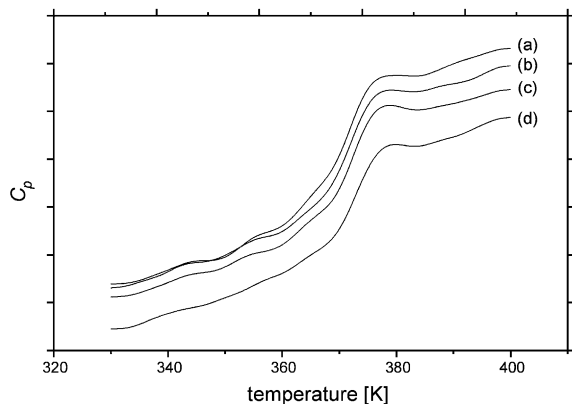


Fig. 3. The heat capacity curves of the pure PS (a) and the PS–CdS filled polymers with 1.4 (b), 2.9 (c) and 5.2 vol% (d) of inorganic phase.

CdS nanoparticles and presence of large number of dangling bonds on the surface.

The heat capacity curves of the pure PS and the PS–CdS filled polymer are shown in Fig. 3. It can be noticed that the midpoint of the slope on the heat capacity curve, i.e. the glass transition temperature ( $T_g$ ), is shifted towards higher temperature upon incorporation of the filler into the polymer matrix. The maximal shift of the  $T_g$  for about 2 K, suggests weak interaction between the CdS-filler particles and the PS matrix. This result is in agreement with above mentioned IR measurements. Also, it should be pointed out that increase of the  $T_g$  with the increase of filler content indicates that the mobility of the matrix is altered due to decrease of the interparticle distance. This result is in agreement with previous DSC measurements of Bergeret and Alberola [4]. These authors also did not observe significant changes in the  $T_g$  of the PS matrix filled with 50 vol% of glass beads with the mean diameter of 5  $\mu\text{m}$ . On the other hand, dramatic increase in the  $T_g$  for 17 K was observed in the case of the PS matrix filled with 1 vol% of hematite particles with the mean diameter of 5 nm [5]. Obviously interaction between inorganic and organic phases grows stronger with the increase of surface to bulk ratio of the filler.

Thermograms of the pure PS and the PS–CdS filled polymers with different contents of inorganic phase, obtained under the nitrogen atmosphere, are shown in Fig. 4. An improved thermal stability of the PS–CdS filled polymers with respect to the pure PS matrix can be noticed. For example, the thermal decomposition of the filled polymer with 5.2 vol% of the CdS-filler particles is shifted towards higher temperature for about 50 K compared to the unfilled PS. Possible reason for the increased thermal stability of the filled polymers is partially altered molecular mobility of polymer chains

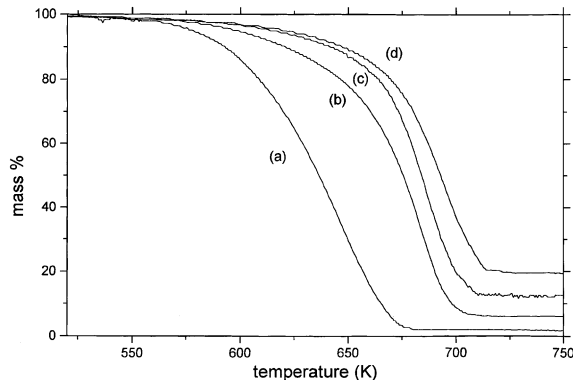


Fig. 4. The thermograms of the pure PS (a) and the PS–CdS filled polymers with 1.4 (b), 2.9 (c) and 5.2 vol% (d) of inorganic phase, obtained under an atmosphere of nitrogen.

due to their adsorption on the surface of the CdS-filler particles. It is well known that the molecular weight changes in thermal degradation of the PS are connected to the effects of scission of weak bonds as well as the intermolecular chain transfer reactions which follow the initial step of formation of primary free radicals at the chain ends [6]. Therefore, restricted motions of polymer segments attached to the particle surfaces can suppress chain transfer reactions and produce better stability of the filled polymer. Schnabel et al. [7] have shown that chemical alteration induced by  $\gamma$ -radiation can improve thermal stability of both crosslinked and uncrosslinked PS. Thus, new chemical bonds probably act twofold: first they additionally improve the interaction between the phases, and second they can change the decomposition route during thermal treatment. This observation is supported with results on thermal degradation of PS–CdS nanocomposite (the mean particle diameter was 5 nm) [2]. In this case, chemical bonding between inorganic and organic phases takes place and thermal degradation was shifted for about 100 K towards higher temperature for the composite with 1 vol% of inorganic phase. It should be emphasized that the substantial increase of the thermal stability of PS–CdS filled polymers should be accompanied with larger shift in the glass transition temperature if this effect is solely due to restriction of molecular mobility of polymer chains, leaving space for additional study.

To conclude, improvement of the thermal stability of the PS matrix with the usage of the CdS-filler particles in the micrometer size range 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 filled polymer, is currently underway in our laboratory.

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