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Materials Science and Engineering B 146 (2008) 54–58

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Quantitative description of the microstructure of polyurethane nanocomposites with YAG including Tb^{3+}

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Abstract

This paper presents the application of quantitative image analysis for the description of morphological properties of nanocomposites with YAG:Tb. Fracture images of YAG:Tb and nanocomposites were obtained using a high-resolution scanning electron microscope (HR-SEM) and atomic force microscopy (AFM). Quantitative analysis of the images obtained provided an explanation of the mechanism for changes in optical properties of polyurethane (PUR) nanocomposites. It also enabled the determination of the relationship between the structural characteristics and the properties of materials.

Keywords: Nanocomposites; Polyurethane; YAG; Luminescence; Image analysis

1. Introduction

Nanocomposites with polymer matrices that emit light have commanded increasing attention in the last decade as potential materials for photonic applications [1–5]. The matrix of nanocomposites for photonics can be a polymer with high optical properties, with transmission for visible light higher up to 85%. Poly(methyl methacrylate) is one of the best polymers exhibiting high stiffness and high transparency with 92% transmission for visible light. Elastic polyurethanes with luminescence properties have attracted increasing attention, as a subject for both fundamental and applied research [6,7]. An earlier investigation demonstrated that polyurethanes can be made transparent [8,9], with 86% transmission for visible light [7]. Components like nanofillers with rare earth elements added to polymeric matrices give high luminescence properties in nanocomposites. The efficiency and monochromaticity of nanocomposite emissions for use in photoluminescent applications is dependent on the degree of dispersion of nanofillers in the polymer matrix [9]. Optical properties of polymers depend on their molecular structure, crystal structure and morphology. In organic–inorganic combined nanosystems, interfaces between both materials play very important roles [9]. Observations of nanocomposite structures can be made using high resolution scanning electron microscopy (HRSEM) and atomic force microscopy (AFM) and quantitative image analysis. Quantitative analysis of the structure is one method to describe the morphological characteristics of nanocomposites and a good technique to explain the change in properties of materials [10–13].

This paper presents the application of quantitative image analysis to the description of morphological properties of polyurethane nanocomposites with YAG:Tb. A study of the structure of obtained materials by HRSEM and AFM was performed. Optical properties, transparency and luminescence, of obtained materials will be characterized. In this paper the relationships between morphological characteristics of nanocomposites and its properties were analysed.

2. Experimental

2.1. Materials

Components used for PUR synthesis were polycaprolactone diol (PCL) $M_W = 2000$, 4,4′-dicyclohexymethane diisocyanate (HMDI), chains extenders (DIOL A, DIOL B). As a nanofiller yttrium aluminium garnet, $Y_3Al_5O_{12}$ (YAG) doped with 10% molar ratio Tb^{3+} (YAG:Tb) was used [11]. The filler was added to the chosen polyurethane matrix in 0.05, 0.1 and 0.2 wt%, respectively to the whole weight of the polymer [12]. Polyurethane/YAG:Tb nanocomposites were prepared by *in situ* polymerisation. Synthesis was performed by the prepolymer method. Polyurethanes composed of PCL:HMDI:DIOL with a

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doi:10.1016/j.mseb.2007.07.044

molar ratio of 1:5:4 and a constant isocyanate index (1.00) were synthesised.

2.2. Characterisation

The morphology of a microsection of nanocomposites with YAG:Tb was characterised by high resolution scanning electron microscopy (HRSEM) LEO 1530. Surface images were subjected to graphic treatment by scuffing the particle contour. Afterwards, the obtained contour was transferred to a MicroMeter program and the quantitative analysis was performed. The domain structure of PUR matrix was characterized by atomic force microscopy, and topographic images were obtained using a Multimode Nanoscope IIIa (Digital Instrument Inc., USA) with a tapping mode. The microstructure of polyurethane was investigated on a microsection surface. In order to determine the area of particles on the surface obtained using AFM (Digital Instruments Nanoscope Atomic Force Microscope) at the beginning of analysis WSxM 4.0 Develop 10.1 program was used. In this software, contour plot function was adjusted to find the same range of height of the microstructure's elements. After that, background was deleted automatically, so the resulting image was only the outline of the elements characterized by similar height. Picture was saved and loaded into software for stereology called MicroMeter. Using MicroMeter volume part of particles were calculated.

The emission spectra were measured at room temperature using a Jobin-Yvon THR 1000 spectrophotometer equipped with a photomultiplier detector (Hamamatsu R928). As an excitation source we used a 308 nm line of a Lambda Physics excimer laser. All the recorded spectra were corrected for the spectrophotometer response. The emission lifetimes were measured with a Le Croy Wave Surfer 452. The transmittance spectrum was measured at room temperature with a Cary 5E spectrophotometer (Varian).

3. Results and discussion

The results of the optical properties analysis of the nanocomposites are presented in Figs. 1–3. The transparency of nanocomposites decreases when the quantity of YAG:Tb is higher. This is due to the difference in the refractive index of the surrounding nanocrystal and the tendency for the nanofiller to agglomerate in the polymer matrix. This might be due to an increase in the volume of the hard domain. The results indicate a significant decrease in luminescence lifetime, by about 50% compared to Tb^{3+} ions, after the addition of nanocrystals into the polyurethane. In order to explain the reason for changes in the optical properties, an analysis of the structures of nanocomposites was performed.

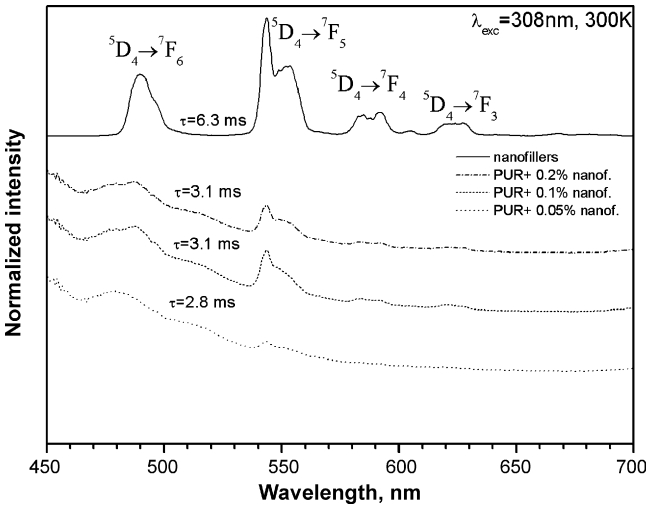

Fig. 2. Luminescence of nanofillers and nanocomposites.

Example SEM images of nanocomposites are shown in Fig. 4. Quantitative analysis of prepared images was carried out. The pattern for performing the image analysis is presented in Fig. 5a. During the analysis, a histogram of the analysed images was prepared, and also the equivalent diameter was measured (example image is show in Fig. 5b). The results of the performed analysis of equivalent diameter sizes are presented in Table 1. The analysis showed that the average equivalent diameter of YAG:Tb in the polyurethane matrix is greater than twice that of the YAG:Tb powder. The biggest equivalent diameter of agglomerates in nanocomposites with 0.05 wt% is greater than three-fold higher, in nanocomposites with 0.1 wt% and 0.2 wt% is above five-fold higher than the YAG:Tb powder.

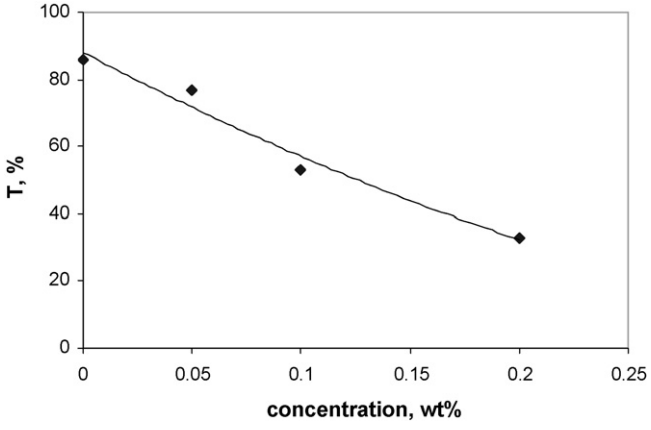

Fig. 1. Transparency (T) of polyurethane matrix and nanocomposites with YAG:Tb by $\lambda = 400$ nm.

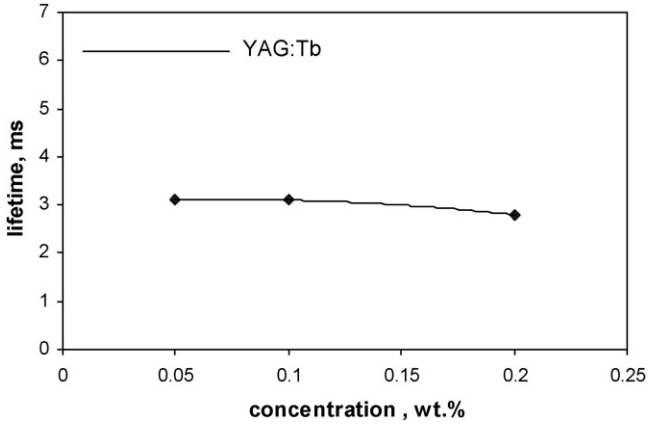

Fig. 3. Luminescence lifetime of nanocomposites in comparison to YAG:Tb.