

MECHANICAL PROPERTIES OF PMMA/ZnO NANOCOMPOSITES

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Abstract

Organophilic zinc oxide, ZnO, nanoparticles and nanorods were synthesized in various diols and were used for the preparation of ZnO/poly(methyl methacrylate) nanocomposites. Nano ZnO quantitatively absorbs UV light between 290 and 380 nm in very low concentrations (0.05 – 0.1%). Besides extraordinary UV absorption properties it also increases the storage modulus of resulting nanocomposites by 25% in the temperature region between 35 and 75 °C. Reinforcing effect is dependent on the ZnO particle size and concentration. At low concentrations (up to 0.1 %) nano ZnO increases the modulus while at higher concentrations this effect is deteriorated due to aggregation of nano ZnO. DMA measurements showed that ZnO particle size (specific surface – interface) is the most important factor influencing the storage modulus of nanocomposites, while particle shape (ZnO nanorods) is less important.

1. Introduction

Nanostructured materials constitute one of the most propulsive fields of materials science and have received great attention due to their potential application[1,2] in various fields. Therefore, the research activities on nanoscale particle synthesis and characterization have increased significantly in the last few years. Advanced applications require nanoparticles with narrow particle size distribution and defined particle shape.

Zinc oxide, ZnO, is an environmentally friendly and technologically important semiconductor having an optical bandgap in the UV region, which makes it an efficient UV absorber[2]. Various chemical synthetic approaches to the preparation of ZnO have been reported in the literature. These chemical processes are efficient methods for preparation of nanoparticles and may be scaled up to produce large quantities of material[3,4].

The polyol method is one of the solvothermal methods of ZnO synthesis involving the hydrolysis of ZnO precursors in various diols (polyols)[5]. Diols are solvents with medium polarity, dielectric constants are between 20 and 40, and they have high boiling temperatures[6]. Synthesis of inorganic particles in organic media is attractive because it produces particles with an organophilic surface which need no additional surface

modification for polymer nanocomposite applications.

Poly(methyl methacrylate), PMMA, is an amorphous optically clear thermoplastic material. It is used as a substitute for inorganic glass, because it undergoes ductile rather than brittle fracture, it shows higher impact strength and it has favorable processing conditions[7]. The composites of both ZnO and PMMA have potential applications in antireflection coatings, UV protecting films, transparent barrier/protective layers and as flame retardant materials[8]. For the preparation of homogeneous PMMA/ZnO nanocomposites it is crucial to achieve good dispersion stability[9]. The development of an effective and simple procedure, allowing the production of transparent UV protective coatings on an industrial scale, is still a challenge because full compatibilization with the polymeric matrix has not yet been achieved[10].

Nano ZnO particles of spherical and nanorod shape with organophilic surface have been synthesized from a zincII acetate precursor in various diols, and PMMA/ZnO nanocomposites have been prepared by the radical chain polymerization of methyl methacrylate, MMA, in situ. Besides high UV absorption and high optical transparency, ZnO nanofiller can also enhance the mechanical properties of nanocomposites. The influence of the addition of nano ZnO on the mechanical properties of PMMA/ZnO was studied by dynamic mechanical analysis, DMA.

2. Results

ZnO nanoparticles and nanorods were synthesized from ZnII acetate in various diols with *p*-toluene sulphonic acid, *p*-TSA, as the end-capping agent at high concentration of the precursor (1 mole/L). In di(ethylene glycol), DEG, ZnO nanorods were formed [11] while in other diols (ethylene glycol, EG; 1,2-propane diol, PD) predominantly spherical ZnO particles were produced[12]. HR-TEM micrographs (Fig. 1a) shows spherical ZnO particles (particle size 20 – 40 nm), prepared in EG, while figure 1b shows nano ZnO in the form of rods (diameter 10-50 nm, length 30-150 nm), prepared in DEG. All the particles have narrow particle size distribution.

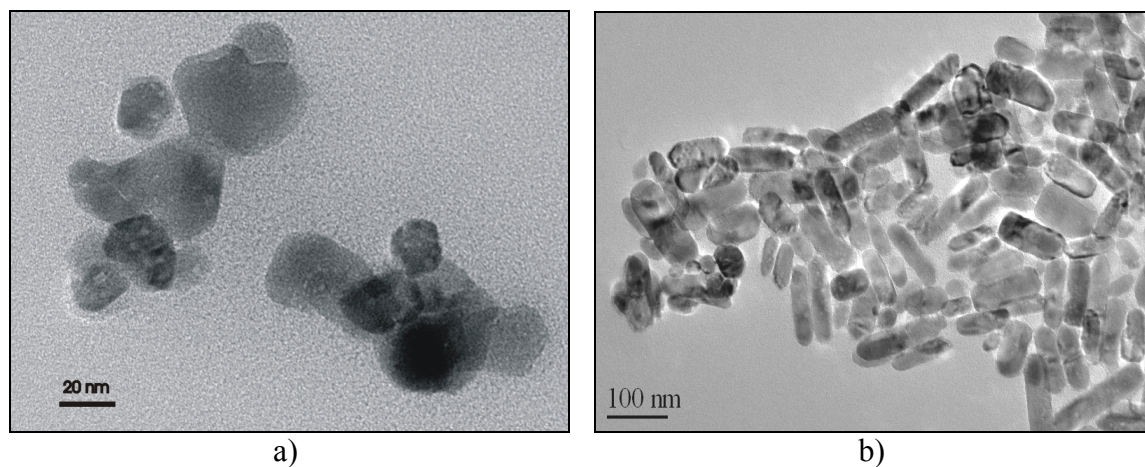


Figure 1. HRTEM micrographs of nano ZnO particles, synthesized with *p*-TSA in various diols: a) EG, b) DEG

The distribution of ZnO nanoparticles and nanorods in the PMMA nanocomposites, prepared by procedure A, was studied by STEM microscopy of their ultra microtomed sections. STEM micrographs in Figure 2 show cross-sections of PMMA/ZnO nanoparticle and nanorod composites containing 1 wt.% of ZnO. The distribution of nano ZnO in PMMA is homogeneous with a few agglomerates. The ZnO nanorod structure can be observed only for some of the particles, because the nanorods are statistically oriented in the three dimensional space (Fig. 2b).

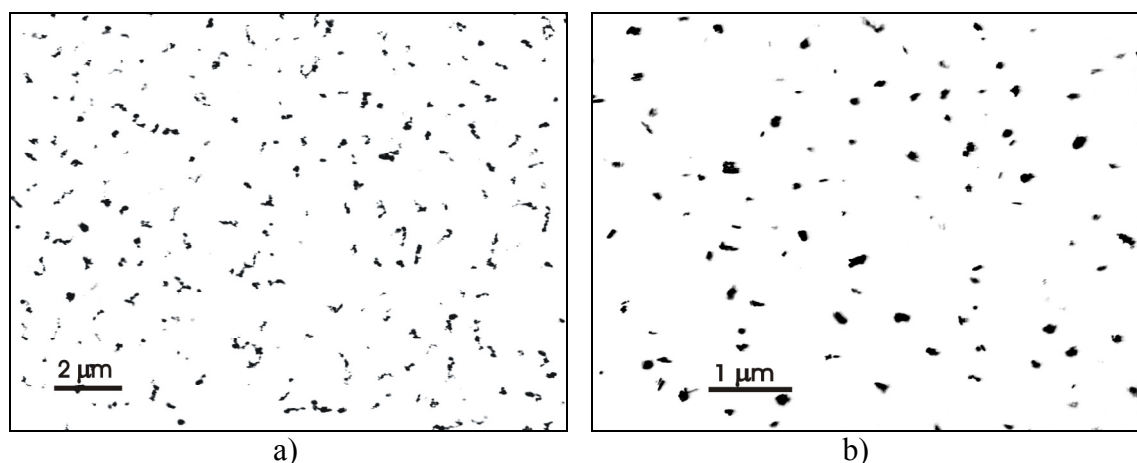


Figure 2. STEM micrographs of nanocomposites PMMA/ZnO – ZnO synthesized in various diols (nano ZnO concentration = 1 wt.%): a) EG, b) DEG.

Nano ZnO is a highly efficient absorber in the UV region from 32 to 400 nm due to its wide direct band gap of 3.37 eV. Consequently, the addition of nano ZnO into the PMMA matrix significantly enhances UV absorption and UV resistance of nanocomposite materials[13,14]. By modifying the MMA polymerization process (Procedure B) the transparency of composites for visible light was improved (Fig. 3aA and bA). The prepolymer procedure significantly reduces the shrinking of PMMA and consequently reduces the cavity formation, thus enhancing the visible transparency of nanocomposites[15]. By reducing the concentration of ZnO, the aggregation of ZnO is substantially reduced and therefore visible transparency has been additionally improved (Fig. 3aB and bB). The modification of the nanocomposite preparation procedure by the introduction of the sonication through the complete prepolymer synthesis (Procedure C) additionally reduced ZnO agglomeration, enhancing its visible transparency (Fig. 3aC). Nanocomposites with spherical ZnO particles (Fig. 3aC) show unchanged UV absorption at ZnO concentration of 0.01 wt.% while for nanocomposites with ZnO nanorods reduced UV absorption was observed (Fig. 3bC).

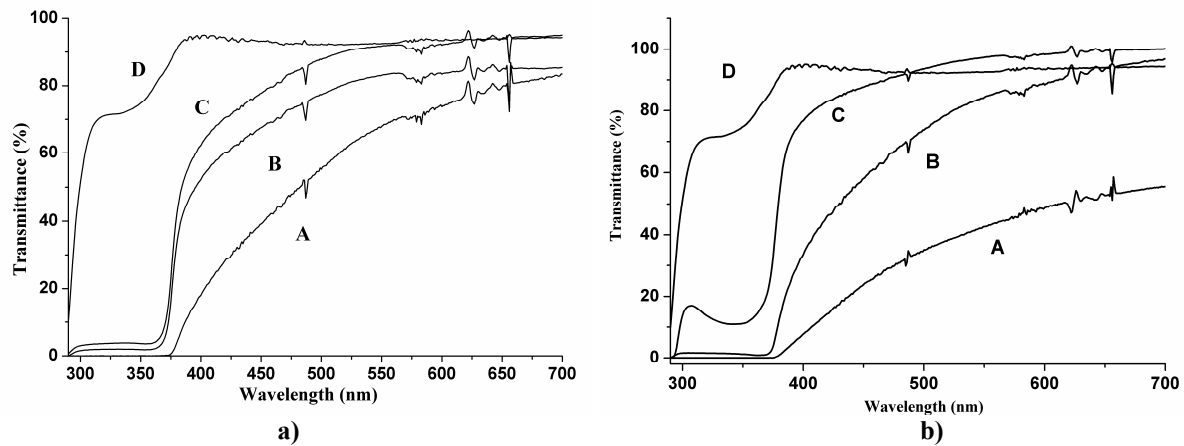


Figure 3. UV-VIS spectra of PMMA/ZnO nanocomposites in dependence on ZnO concentration and nanocomposite preparation procedure: **a)** ZnO synthesized in EG A) 0.1% - proc. B, B) 0.05% - proc. B, C) 0.05% - proc. C, D) pure PMMA; **b)** ZnO synthesized in DEG A) 0.1% - proc. B, B) 0.05% - proc. B, C) 0.05% - proc. C, D) pure PMMA.

The influence of the addition of ZnO nanoparticles and nanorods on the mechanical properties of PMMA nanocomposites was studied by dynamic mechanical analysis, DMA[11]. The storage modulus of nanocomposites is decreasing with temperature due to softening, but it increases with the addition of small amounts of ZnO nanorods (0.01 and 0.1 wt.%), while at higher concentrations (1 wt.%) the reinforcing effect is not intensified (Fig. 4a). This can be explained by the increased aggregation of ZnO nanorods at higher concentrations, leading to a decrease of the interfacial surface. Similar effects were observed also by other authors[16]. The increase of the storage modulus in the glassy state (up to 75°C) is approximately 25 %, while in the intermediate temperature region (from 75°C to 95°C) it is increased by 50 to 100 %. Comparison of the storage modulus of PMMA/ZnO nanorods (length 30–150 nm) composites with those of PMMA composites with spherical ZnO nanoparticles (size 20–50 nm, Fig. 4b) reveals that the latter show a higher increase of the modulus. Therefore ZnO particle size (specific surface - interface) is a more important factor influencing the storage modulus of PMMA/ZnO nanocomposites than is the shape (length) of the particle.

Figure 5a shows the dependence of $\tan \delta$ on the concentration of ZnO nanorods as a function of temperature, showing relaxation peaks corresponding to glass transition of the amorphous phase. The dependence reveals that glass transition is shifted to higher temperatures when a low concentration of ZnO nanorods is added (0.01 and 0.1 wt.%), while at higher concentrations no additional shift was observed, which is consistent with the results in figure 4a. It is interesting that the shift of glass transition temperature to higher temperatures (Fig. 5a and b) and the increase of storage modulus (Fig. 4a and b) both show similar trends.

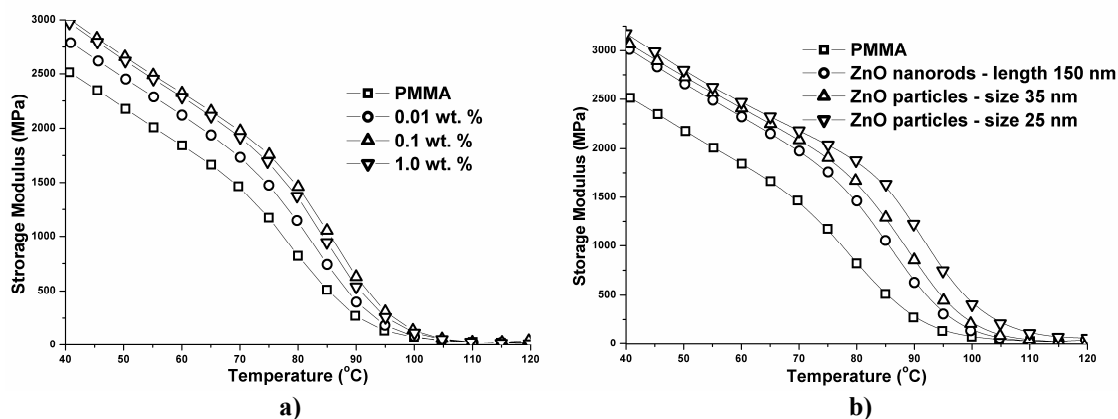


Figure 4. Storage modulus of PMMA/ZnO nanorod composites: (a) as a function of the ZnO nanorods concentration, (b) as a function of the ZnO particle size and shape – concentration of ZnO is 0.1 wt.%.

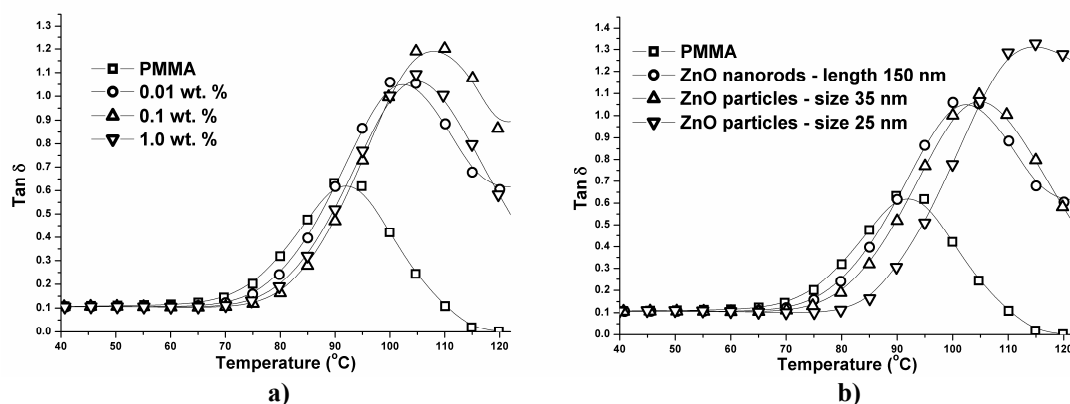


Figure 5. Tan δ of PMMA/ZnO nanorod composites: (a) as a function of the ZnO nanorods concentration, (b) as a function of the ZnO particle size and shape – concentration of ZnO is 0.1 wt.%.

3. Conclusions

Organophilic ZnO in the form of spherical particles and nanorods was synthesized by hydrolysis of a precursor, ZincII acetate, in various diols as a medium with the addition of p-TSA as an end capping agent. p-TSA reduces the average particle size and increases the ZnO crystallinity. DEG induces the preferential growth of ZnO in c-axis as shown by XRD diffraction and HR TEM microscopy. In other diols ZnO nanoparticles with spherical shape are formed. ZnO nanoparticles and nanorods have been synthesized at high concentration of the precursor (1 mole/L) allowing their preparation in gram quantities, which is beneficial in the preparation of large sheets of PMMA/ZnO nanorods composites.

Unmodified as-synthesized nano ZnO powders were used for the preparation of PMMA nanocomposites. ZnO nanoparticles and nanorods are excellent UV absorbers because they quantitatively absorb UV light in the 290 to 370 nm region at concentrations of 0.1 wt.% of ZnO and above. The optimal concentration of ZnO nanorods is between 0.01 and 0.1 wt.% to obtain materials with high absorption of UV light and high transparency for visible light.

DMA analysis of PMMA/ZnO composites shows that ZnO nanoparticles and nanorods increase the storage modulus of nanocomposites and shift the T_g towards higher temperatures

at low concentrations (0.01 – 0.1 wt.%), while at higher concentrations (1.0 wt.%) the reinforcing effect is deteriorated, which was ascribed to the aggregation of ZnO nanorods. Comparing the reinforcing effects of ZnO nanorods and ZnO nanoparticles it was observed that the latter show a more pronounced effect on the storage modulus and T_g than the former, due to their smaller size and larger specific surface.

4. Materials and Testing Methods

4.1 Materials

4.1.1 Synthesis of ZnO nanoparticles and nanorods

Zinc(II) acetate (1.0 M), *p*-toluene sulphonic acid, *p*-TSA, (0.1 M) and deionised water (2 mol/1 mol Zn) were mixed with 60 ml of diol and sonicated for 10 min. The mixture was transferred into a 250 ml glass reactor equipped with a mixer, condenser and digital thermometer. The temperature was raised for about 10 min to 190°C and kept constant for 50 min. with constant stirring. Between 90°C and 120°C Zn acetate dissolved in the diol, after 20 to 30 minutes at 190°C the solution became white and after 60 min. a white suspension of ZnO was obtained. The suspension was left overnight and centrifuged (8000 rpm, 20 min). The ZnO was washed twice with ethanol and centrifuged (8000 rpm, 20 min.). The obtained ZnO powder was left to air dry. Spherical ZnO nanoparticles were synthesized by the same procedure in ethylene glycol and in 1,2-propane diol.

4.1.2 Synthesis of ZnO/PMMA nanocomposites

Nanocomposites of the synthesized ZnO nanoparticles and nanorods and PMMA matrix were prepared by the radical chain polymerization of MMA monomer in bulk in three variations: radical polymerization between glass plates starting directly from the ZnO dispersion in monomer – MMA (Procedure A); polymerization between glass plates starting from the previously prepared dispersion of ZnO in prepolymer (Procedure B); polymerization between two glass plates starting from ZnO dispersion in prepolymer which was polymerized during constant sonication (Procedure C). The detailed description of all three procedures is given in the previous publication[15]. The nanocomposite plate thickness using procedure A was 1.5 mm, while procedures B and C gave nanocomposite plates with a thickness of 3.5 mm.

4.2 Testing Methods

The morphology of the synthesized ZnO nanorods was studied by HR-TEM electron microscopy (JEM 2000FX microscope, JEOL, acceleration voltage - 200 kV). For HR TEM microscopy, a drop of dispersion of nano ZnO in organic solvent was placed on a Cu grid. The nanocomposite materials were studied by STEM microscopy (Supra 35 VP, Zeiss, acceleration voltage - 20.0 kV, working distance - 4.5-5 mm). Nanocomposites were sectioned on the ultra microtome (Reichert Ultracut, thickness 80 - 250 nm).

UV-VIS spectra of nanocomposites were measured on an Agilent 8453 UV-VIS spectrometer, Agilent Technologies, (spectral range 290 - 380 nm, sample width 12 mm, thickness 1.6 and 3.5 mm).

DMA measurements were performed on DMA Q800, Thermal Analysis, using a single cantilever clamp (temperature range 30 – 150°C, heating rate 5°C/min, amplitude 15 μ m, frequency 10 Hz).

5. References

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