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Nanocomposites with nano-to-sub-micrometer size zinc oxide as an effective UV absorber

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Summary

Zinc (II) oxide micrometer (300 nm) and nano particles (100 nm) were synthesized in different glycols and were used for the preparation of ZnO/poly(methyl methacrylate) nanocomposites. Very low concentrations of zinc oxide quantitatively absorb UV light in the region between 290 and 380 nm. Besides having extraordinary UV absorption properties, nano zinc oxide also substantially enhances the stability towards sunlight as well as thermal stability of resulting nanocomposites. On the other hand, submicrometer ZnO is less effective UV absorber and thermal stabilizer than nano ZnO.

KEY WORDS:
glycols
microparticles
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nanoparticles
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KLJUČNE RIJEČI:
cink (II) oksid
glikoli
mikročestice
nanočestice
nanokompoziti
poliakrilati

Nanokompoziti pripravljeni uz dodatak nano/mikrometarskog cink-oksida za učinkovite UV absorbere

Sažetak

Cink (II) oksidne mikročestice (300 nm) i nanočestice (100 nm) su sintetizirane u različitim glikolima i kasnije upotrijebljene za pripravu ZnO/poli(metil-metakrilatnih) nanokompozita. Vrlo niske koncentracije dodanog cink-oksida potpuno apsorbiraju UV svjetlo u području od 290 do 380 nm. Osim odlične apsorpcije u UV području, nano cink-oksid bitno poboljšava stabilnost nanokompozita na sunčevu svjetlost kao i na toplinsku postojanost, dok je submikrometarski ZnO manje učinkovit UV apsorber i toplinski stabilizator od nanometarskog ZnO.

Introduction

Nano and micro structured materials present one of the most propulsive fields of science today. Zinc oxide, ZnO, is an environmentally friendly and technologically important semi-conductor.[1] Due to a unique combination of electrical and optical properties, it is one of the most attractive semiconductors.[2] It is a wide gap semiconductor having an optical band gap in the UV region that makes it an efficient UV absorber.[2] Besides this, its potential applications are catalysis, optoelectronic devices, sensors and photovoltaic devices. ZnO can be synthesized in a wide range of particle sizes and shapes. The solution phase approach to nano-to-sub-micrometer ZnO particles presents a low cost preparation method which has attracted a lot of interest. Unfortunately, this method resulted either in undefined morphology or in a wide distribution range of particle diameter. For this reason, the preparation of ZnO nanostructures in solution phase still presents a great challenge.

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 favourable processing conditions.[1] The nano ZnO/poly(methyl methacrylate) – (ZnO/PMMA) - composites have potential applications in antireflection coatings, UV protecting sheets and films, transparent barrier/protective layers and as materials with enhanced thermal stability.[3,4] For the preparation of homogeneous ZnO/poly (methyl methacrylate) (ZnO/PMMA) nanocomposites it is crucial to achieve good dispersion stability.[5] 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 compatibilisation with the polymeric matrix has not yet been achieved.[6]

The aim of the present work was: first, to synthesize non-agglomerated ZnO particles in nano-to- sub-micrometer range with narrow particle size distribution by polyol method and second, to use the as-prepared ZnO particles directly without further surface modification for the preparation of UV-absorbing transparent ZnO/PMMA nanocomposite sheets.

Experimental

ZnO was synthesized by the polyol method in di (ethylene glycol) – DEG - and in tetra (ethylene glycol) – TEG.[7,8] Nanocomposites of ZnO and PMMA were synthesized by chain polymerisation between glass plates in bulk. The initiator was dissolved in MMA. Various amounts (0.01, 0.1 and 1.0 wt %) of ZnO powder, synthesized in diols (DEG, TEG), were suspended in that solution. The solution was sonicated and transferred into a glass plate mould. The glass mould was placed into the water bath and methyl methacrylate (MMA) was polymerised for 20 hours at 75 °C. After 20 hours, moulds were taken from the bath and the PMMA sheet was separated from the glass plate mould.

Scanning electron micrographs – SEMs - of gold sputtered samples were taken on a *Zeiss Supra 35 VP* at an acceleration voltage of 3.37 or 5.0 kV, using mixed in-lens and secondary electron detector at a ratio of 0.75/0.25 and working distance between 3-6 mm.

The chemical composition of obtained ZnO particles was studied by the IR spectroscopy using an FTIR spectrometer *Perkin-Elmer 1725 X* in the spectral range between 4,000 and 400 cm^{-1} with a spectral resolution of 4 cm^{-1} in transmittance mode using the KBr pellets technique.

Scanning transmission electron micrographs – STEMs - of ultramicrotomed sections of nanocomposites were taken on a *Zeiss Supra 35 VP* at an acceleration voltage of 20.0 kV and working distance of 4.5-5.0 mm using a STEM electron detector. PMMA/ZnO nanocomposites were sectioned on an ultra microtome *Leica Ultra* cut to a thickness between 80 and 250 nm.

The UV – VIS absorption of PMMA/ZnO nanocomposites was measured on a UV-Vis spectrometer *Agilent 8453* in the spectral range between 290 and 380 nm. Sheets of PMMA/ZnO nanocomposites were cut to the width of a quartz quivette. The thickness of specimens was 2.5 mm.

Differential thermogravimetry curves – DTG - were measured in the temperature range between 50-600 °C with a heating rate of 10 °C/min and air flux of 100 ml/min. The quantity of specimens was close to 50 mg.

The size exclusion chromathography system (SEC) composed of an isocratic pump – *Hewlett Packard 1100 Series*, a column - AM polymer GPC gel, linear, mixed with precolumn (1,000 – 5,000,000 g/mol), and a differential refractometer – *Hewlett – Packard Agilent 1160 series*, was used for the molecular weight distribution determination of the PMMA matrix. Experimental conditions for measurements were: solvent - THF, solvent flux – 1 ml/min., injection volume 50 μl and detector temperature = 25 °C. PMMA standards were used for calibration. PMMA specimens were dissolved in THF (conc. = 2 mg/ml) and filtered using *Millipore – Millex PTFE LCR* filters.

Results

Nano and sub-micrometer ZnO particles with the average particle size between 100 and 300 nm with narrow particle size distributions were prepared by the polyol method[7,8] in di (ethylene glycol) – DEG (Figure 1a) and in tetra (ethylene glycol) - TEG (Figure 1b) at 150 – 160 °C. The micrograph (Figure 1b) shows that particles are agglomerates of smaller subunits of the size between 10 and 30 nm, which may have porous structure.

FTIR spectra of these samples show a typical ZnO absorption band[9] at 460 cm^{-1} as well as absorption bands of an organophilic layer at the ZnO surface composed of glycol residues and reaction intermediates at 900, 1,100, 1,410, 1,590 and 3,400 cm^{-1} (Figure 2). Synthesized powders were also characterized by wide angle X-ray diffraction on a *Siemens D-5000* diffractometer with a Cu anode as the X-ray source in the 2Θ range from 2 to 90 °. XRD diffractograms of ZnO samples show characteristic peaks of crystalline ZnO[10] at 2θ values: 31.8; 34.5; 36.2; 47.6; 56.6; 62.9; 66.4; 67.9; 69.1; 72.6; 76.9. Rather broad diffraction maxima indicate very small size of crystallites similar to the size of subunits observed by the SEM microscopy (Figure 1). Since no additional diffraction maxima are observed in diffractograms, we conclude that reaction intermediates, observed in the IR spectra (Figure 2), are amorphous.

The synthesized nano and sub-micrometer ZnO particles were used for the preparation of ZnO/poly (methyl methacrylate) nanocomposites. The advantage of the polyol method is that an organophilic particle surface is formed during the reaction, allowing the preparation of homogenous nanocomposites with organic matrices without additional surface modification. ZnO/PMMA nanocomposites were synthesized by chain polymerisation of MMA in bulk between two glass plates. STEM micrographs of ZnO/poly (methyl methacrylate) nanocomposites, containing 1% of nano ZnO with the particle size of 100 nm and with the particle size of 300 nm (Figure 3), show their homogeneous dispersion in the polymer matrix. Homogeneous dispersion of relatively large sub-micrometer ZnO particles indicates that the organophilic surface layer is an effective dispersion stabiliser.

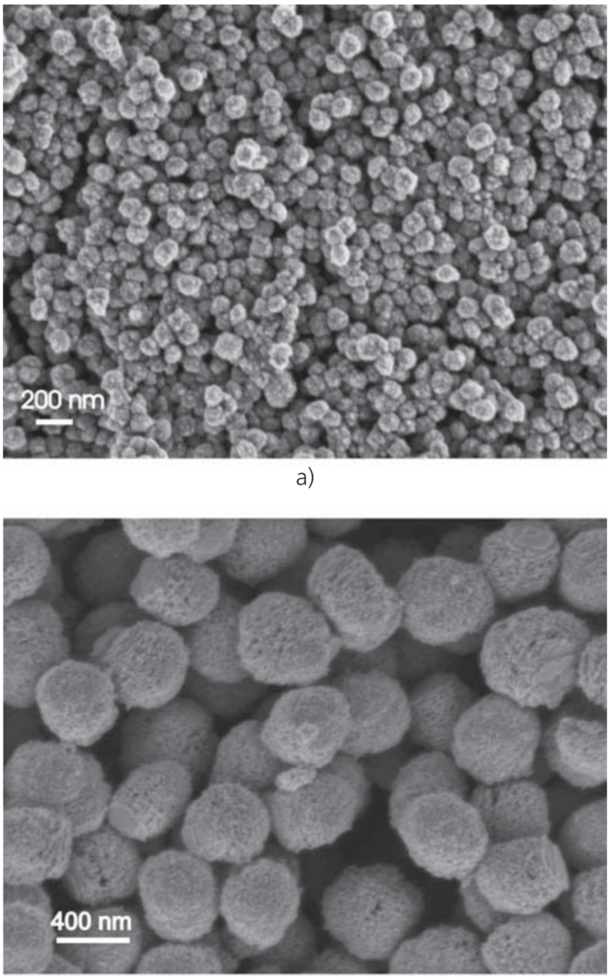
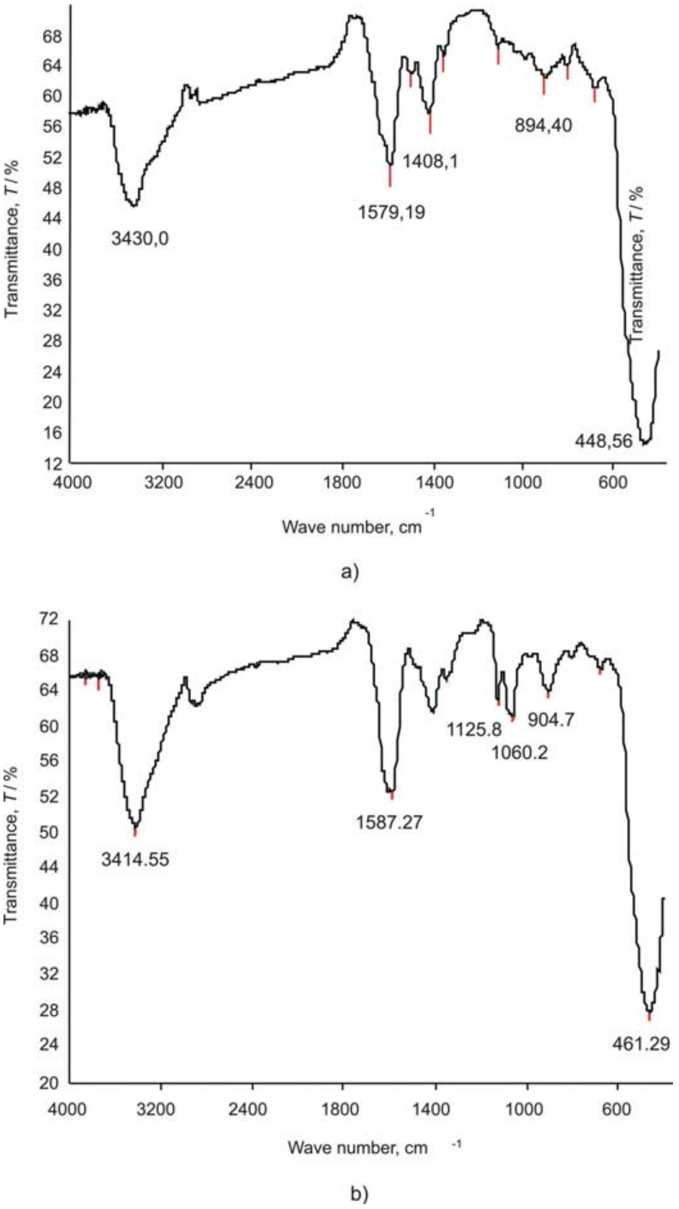


FIGURE 1 - SEM micrographs of nano ZnO (a) – 100 nm, and of submicrometer ZnO (b) – 300 nm

ZnO is well known for its excellent UV absorption.[6,11] UV- VIS spectroscopy showed that 0.1% of nano ZnO (particle size of 100 nm) absorbs more than 99% of the incident UV light (Figure 4). At lower concentrations (0.01 and 0.001%) ZnO nanoparticles absorb from 80 to 90% of UV light indicating that synthesized ZnO nanoparticles are very efficient UV light absorbers. Sub-micrometer ZnO particles are less efficient UV absorbers because quantitative absorbance is achieved by adding 1.0% of ZnO while at lower concentrations absorbance is reduced to 60%. The UV absorption efficiency of ZnO particles is therefore significantly dependent on the particle size.

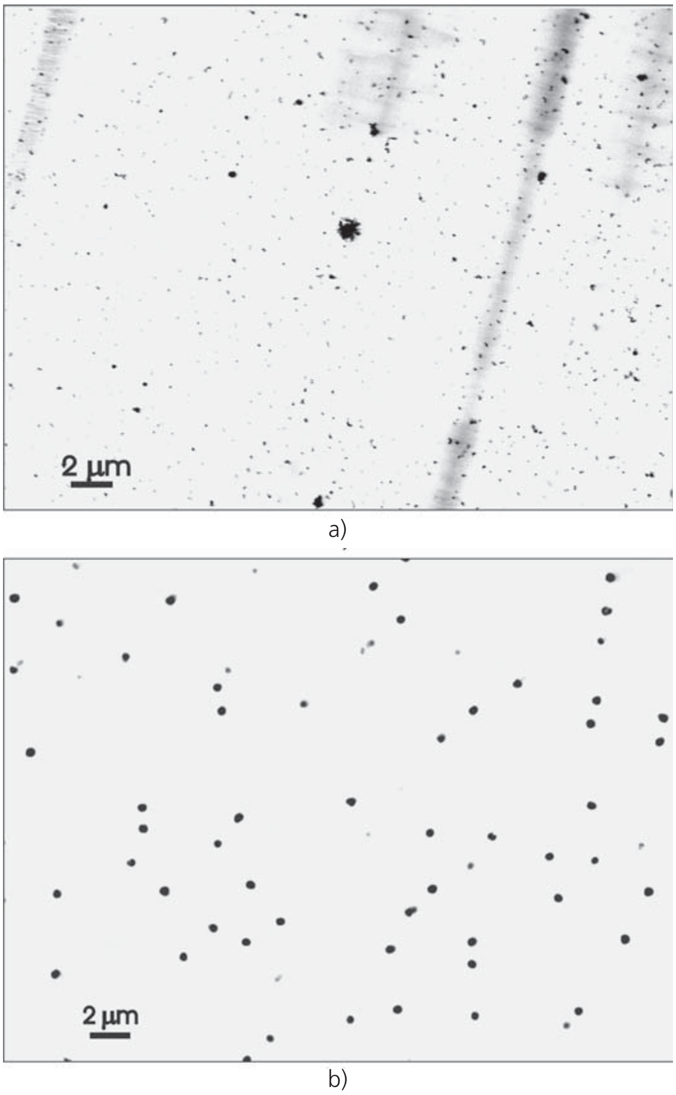


a)

b)

FIGURE 2 - IR spectra of nano (a) and sub-micrometer (b) ZnO

It is also known that ZnO enhances the thermal stability of PMMA/ZnO nanocomposites.[12-14] DTG curves of PMMA/ZnO nanocomposites (Figure 5) show that by adding 0.1 weight % of nano ZnO the decomposition temperature is 30 °C higher than for pure PMMA, while at 1.0% of ZnO the decomposition temperature increases by 40 °C. At lower concentrations (0.01 and 0.001%) the stabilizing effect is less pronounced. Sub-micrometer ZnO particles showed a similar, but weaker, stabilizing effect indicating that the average particle size is also an important parameter in the enhancement of the PMMA thermal stability. One of possible mechanisms of enhancing thermal stabilization is the interaction between the surface of a ZnO particle and segments of the PMMA polymer chain which reduces segmental mobility. The fact that the stabilization effect is enhanced by increasing the ZnO concentration can be explained by the increased interaction surface. The less intense thermal stabilization effect on 300 nm ZnO particles can also be explained by the smaller specific interaction surface. However, ZnO enhances thermal stability only when MMA is polymerised *in situ*, in the presence of ZnO particles, and not in the case when it is mixed with the PMMA polymer. The mechanism responsible for the thermal stabilization of in situ polymerized PMMA has yet to be elucidated.[16]



a)

b)

FIGURE 3 - TEM micrographs of ZnO/poly(methyl methacrylate) nanocomposite containing 1% of ZnO with the average particle size of (a) 100 nm and (b) 300 nm

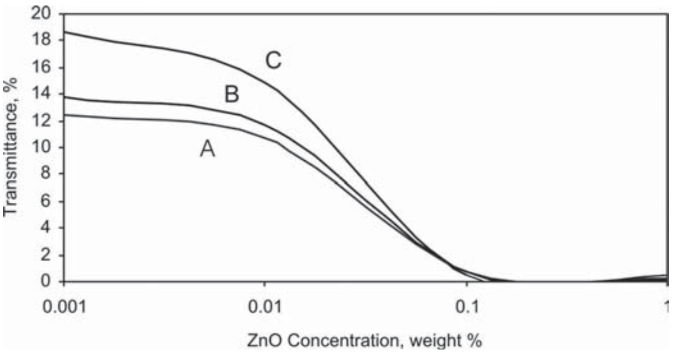


FIGURE 4 - UV transmittance of ZnO/poly (methyl methacrylate) nanocomposites at 290 (A), 320 (B), and 360 nm (C) versus the concentration of ZnO (100 nm)

It is assumed that the ZnO surface influences the polymerisation reaction of the MMA monomer.[15] The SEC chromatograms of PMMA polymerised in the absence and in the presence of nano ZnO (Figure 6, curve B) show that nano ZnO increases high molecular weight fractions and reduces lower molecular weight fractions (Figure 6, curve B). Thus, nano ZnO increases the average molecular weight and peak average molecular weight of PMMA, confirming that nano ZnO influences the chain polymerisation reaction of MMA.

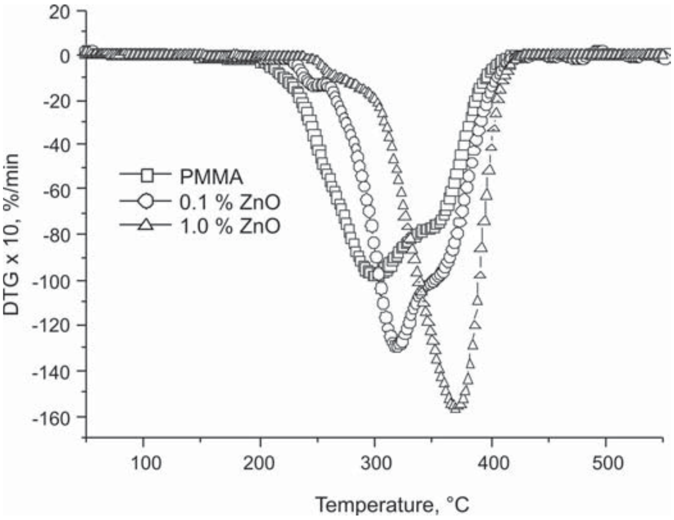


FIGURE 5 - DTG curves of ZnO/poly(methyl methacrylate) nanocomposites with different ZnO content

Conclusion

Nano and sub-micrometer ZnO with an organophilic surface layer were synthesized by the polyol method after which ZnO/poly(methyl methacrylate) nanocomposites were prepared. The particle size of nano ZnO was 100 nm and of sub-micrometer ZnO was 300 nm, both samples having narrow particle size distribution. Particles of both ZnO samples were homogeneously dispersed in the PMMA matrix. Homogeneity of particle dispersion was higher for the sub-micrometer ZnO, indicating that the organophilic layer on the particle surface is a very efficient dispersion stabilizer. Nano ZnO with a 100 nm particle size is a very effective UV absorber; for example, the addition of 0.1 % quantitatively absorbs UV light in the range from 290 to 370 nm. Additionally, it increases the initial decomposition temperature of the PMMA matrix by 30 to 60 °C at concentrations of 0.1% and above. On the other hand, submicrometer ZnO with 300 nm particle size is a less effective UV absorber and thermal stabilizer. It is obvious that the average particle size is an important parameter for optimizing the UV absorption and thermal stabilization of ZnO/PMMA composites. The influence of nano ZnO on the chain polymerization reaction of MMA was confirmed by the SEC chromatography.

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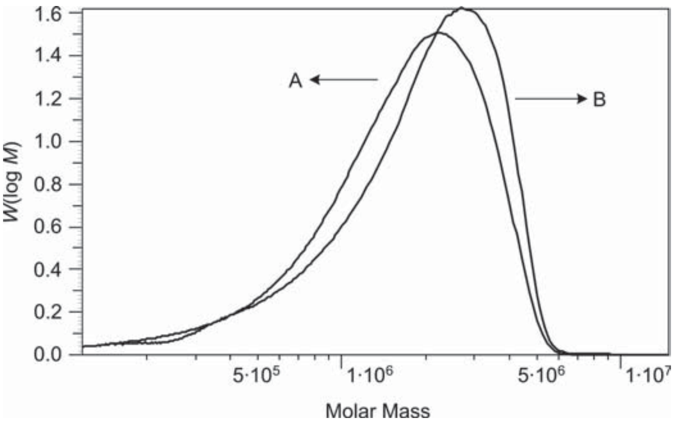

FIGURE 6 - SEC chromatograms of a pure PMMA (A) and of a PMMA polymerized in the presence of 0.1% nano ZnO (B)

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