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INORGANIC NANOPARTICLES IN POLYMER MATRIX COMPOSITES

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Abstract: Polymer – inorganic nanoparticles composites present an interesting approach, because by combining the attractive functionality of both components result new materials with synergistically improved properties. The objective of this paper was to examine the structure and properties of a new type of composite materials based on thermoplastic polymers and inorganic nanoparticles.

It is very difficult for inorganic nanoparticles to disperse in the polymer matrix through conventional mixing, because the nanoparticles have high surface energy and have tendency to agglomerate during mixing. So, surface of inorganic nanoparticles was modified with a capping agent, who it was used to improve the interface between the organic and inorganic phases. Chemical structure, particle size distribution and surface morphology of the obtained composites were characterized using Fourier infrared spectra (FTIR) and scanning electronic microscopy (SEM).

Keywords: nanoparticles, composites, polymer matrix.

1. INTRODUCTION

For several years, incorporation of different inorganic nanoparticles in polymer matrix is the most interesting approach to synthesize nanocomposites. These materials are of growing interest due to improve properties by combining of both inorganic nanoparticles and organic molecules, and because extensive potential applications in a wide range of industrial fields, such as textile, paints, magnetic fluids, high-quality paper coatings to catalysis, microelectronics and biotechnology [1, 2].

According to the studies, the nanoparticles can be synthesized from a variety of materials with controllable sizes, shapes and composition (semiconductors, oxides, carbon-based materials, nanoparticles, etc.), which can be embedded in various polymeric matrix depending of the potential applications. [3].

The main problem in obtaining nanocomposites is the prevention of particles agglomeration, by modification of the surface of the nanoparticles, in order to improve the compatibility between the inorganic particles and the polymer matrix [4, 5].

In the present work, ZnO nanoparticles were used as inorganic nanoparticles and ZnO-PMMA nanocomposites were obtained by dispersing the ZnO nanoparticles in polymethyl methacrylate (PMMA).

Among inorganic nanoparticles, zinc oxide (ZnO) is one of the most researched, because it can be synthesized in a wide range of particle sizes, shapes, and due to its physical and chemical properties, such as chemical stability, low dielectric constant, high catalysis activity, effective antibacterial and bactericide, intensive ultraviolet and infrared absorption [6].

Polymethyl methacrylate (PMMA) is selected as matrix because is known to be suitable medium to disperse inorganic nanoparticles to improve the dispersion stability. It is also an important polymer with excellent transparency and processability due to its properties and extensive applications [7, 8].

The aim of the present work was to synthesize ZnO nanoparticles by modifying the surface of particles with capping agent, then dispersing in polymer matrix to obtain ZnO-PMMA nanocomposites. It is known that interactions between the nanoparticles and matrix play an important role in determining the quality and properties of the nanocomposites.

The ZnO nanoparticles and ZnO- PMMA nanocomposites were characterized by evaluating their phase analysis through FTIR spectroscopy, and their shape size and distribution in polymer matrix by SEM.

2. EXPERIMENTAL

2.1. Synthesis of ZnO nanoparticles

The ZnO were prepared by adding an amount of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ to ethanol ($\text{C}_2\text{H}_5\text{OH}$) at room temperature and stirred on a magnetic stirrer for 1h. Then, a small amount of glacial acetic acid [CH_3COOH] was added to the mixture and stirred at 60°C for 2h. The addition of NH_3 changed the pH values of the sol from 5 (acidic condition) to 12 (alkaline condition). The resulting white gel was stirred for another 1h. The sample was left alone for 2 days to allow the sol–gel process to finish.

After that, the samples were heat treated at different temperatures 250°C , 350°C , 450°C , 550°C , for 3h with a heating rate of $10^\circ\text{C}/\text{min}$.

2.2. Surface modification of ZnO nanoparticles

Firstly, the surface of ZnO nanoparticles was modified with capping agent (elaidic acid, trans isomer of the oleic acid ($\text{C}_{18}\text{H}_{34}\text{O}_2$)).

The capping agent plays a significant role in improvement the compatibility between inorganic nanoparticles and organic matrix. Also, nanoparticles have the tendency to agglomerate, which makes them lose their specific characteristics.

In our experiments, elaidic acid was solubilized in ethanol solution and an amount of ZnO was introduced into the solution and stirred for a good dispersion. The solution was filtered and the precipitate was washed with the mixture of solvent and deionized water. The precipitate was dried and kept in a vacuum desiccator.

Secondly, ZnO nanoparticles were dispersed in polymethyl methacrylate (PMMA) matrix under ultrasonic stirring condition at room temperature until a stable suspension was obtained.

2.3. Characterization methods

The chemical compositions of the synthesized ZnO nanoparticles and ZnO–PMMA composites were analyzed by Fourier Transform Infrared (FTIR) spectrometry at room temperature using a Bruker Tensor 27 spectrometer, in the spectral range of $4000 - 400\text{cm}^{-1}$. The spectral resolution was 4cm^{-1} and 64 scans were averaged and KBr pellet technique was used. The discs were prepared by compressing a mixture, formatted from the samples powder and KBr, at pressure of 10 tons for 5 min. in a hydraulic press, and then the discs were scanned to obtain FTIR spectra.

The morphology and the distribution of the ZnO particles in PMMA matrix were studied by Scanning Electron Microscopy (SEM - VEGA II LMU).

3. RESULTS

3.1. Phase analysis of the samples

Figure 1 shows the spectra of zinc oxide sample obtained in the first part of our study. Using FTIR spectrometry we studied the sintering process evolution at different temperatures of the ZnO powder. Spectrum from figure 1(a) is mainly characterized of bands attributable to organic groups. At 250°C it is not noticeable any characteristic band to carboxylic group, which indicates decomposition of acetate, used as raw material. Further increase of the temperature showed major spectral changes (figure 1 (b) and (c)). With the disappearance of the absorption bands characteristic to organic bonds can be seen a better definition of the absorption band attributed to Zn-O bond, and at the end (figure 1 (d)) we can speak of a single Zn-O bond characteristic absorption band that can be observed at 420cm^{-1} .

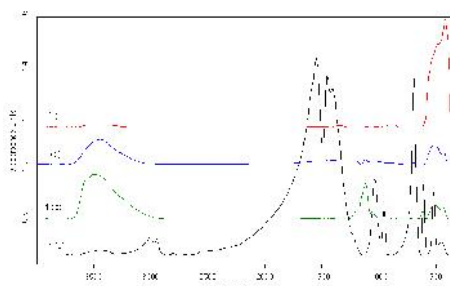


Figure 1: FTIR spectra of ZnO sample sintered at: (a) 250°C , (b) 350°C , (c) 450°C , (d) 550°C

FTIR spectrum of pure elaidic acid (Figure 2 (a)) is characterized by the bands attributed to stretching vibration of C=O mode (1711 cm^{-1}) and C-H (2923 and 2854 cm^{-1}). Figure 2(b) presents the FTIR spectrum of ZnO modified with elaidic acid. FTIR spectra of this sample show a typical Zn-O absorption band at 480 cm^{-1} , as well as the absorption bands of elaidic acid onto the ZnO nanoparticles surface. Formation of a complex between elaidic acid and ZnO is emphasized by comparing the spectra of 2(a) and 2(b). It can be observed the complete disappearance of the band at 1711 cm^{-1} and the appearance of a new broad band at about 1550 cm^{-1} attributed to stretching vibration of COO-.

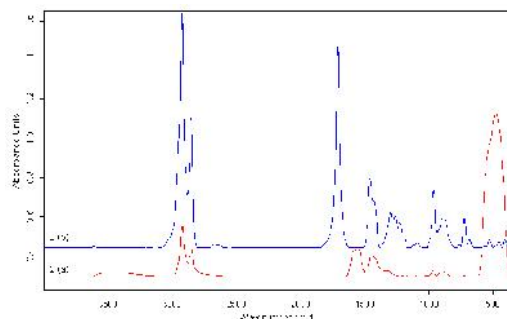


Figure 2: FTIR spectra of (a) elaidic acid and (b) elaidic acid - ZnO samples

FTIR spectra of the sample of pure polymethyl methacrylate (PMMA) (Figure 3(a)) is characterized by absorption bands appearing in the range $1940\text{-}1730\text{ cm}^{-1}$ which can be assigned to the vibration mode of C=O bond and bands in the range $3000 - 2900\text{ cm}^{-1}$ that can be attributed to the stretching mode of C-H bond. The bands in the range $1445\text{-}1370\text{ cm}^{-1}$ can also be attributed to the vibration mode of C-H bond and the band centered at 1271 cm^{-1} can be attributed to the group C-H deformation and the last peak at 736 cm^{-1} corresponds to the vibration out of plane of C-H bond. The band at 1151 cm^{-1} can be attributed to the group C-O from the ester, the band centered at 1236 cm^{-1} can be associated with vibration mode of the group O-CH₃. The absorption band centered at 902 cm^{-1} is correlated to C-C bond vibration mode. FTIR spectra of the samples of ZnO - PMMA (Figure 3(b)) didn't show any spectral band characteristic to metal-oxygen bond of zinc oxide. Finally, the disappearance of the band Zn-O indicates total embedding of the ZnO particles in the polymer matrix of PMMA.s.

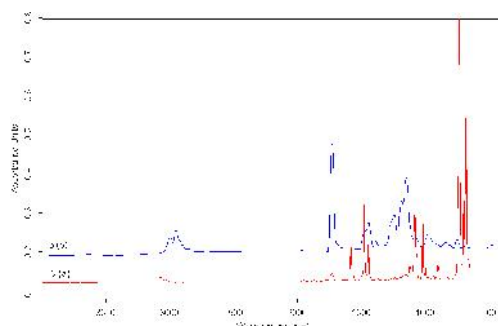


Figure 3: FTIR spectra of (a) polymethyl methacrylate (PMMA) and (b) ZnO-PMMA samples

3.2. Morphological characterizations of the samples

Scanning electron micrographs (SEM) of the ZnO particles, elaidic acid modified ZnO nanoparticles and ZnO - PMMA composites are showed in Figure 4 (a) - (c), respectively.

In Figure 4 (a), we can easily observed that the particles are granular and have a slight tendency of agglomeration. The size of ZnO nanoparticles is in the range from 20 nm to 100 nm.

It is observed in Fig. 4 (b) that elaidic acid modified ZnO nanoparticles consists of particles irregular in shape and presents a good distribution and homogeneity.

In Figure 4 (c), the ZnO nanoparticles are seen as white regions in the darkness PMMA matrix. Also, it is observed that the nanoparticles are non-agglomerated and well dispersed in PMMA matrix.

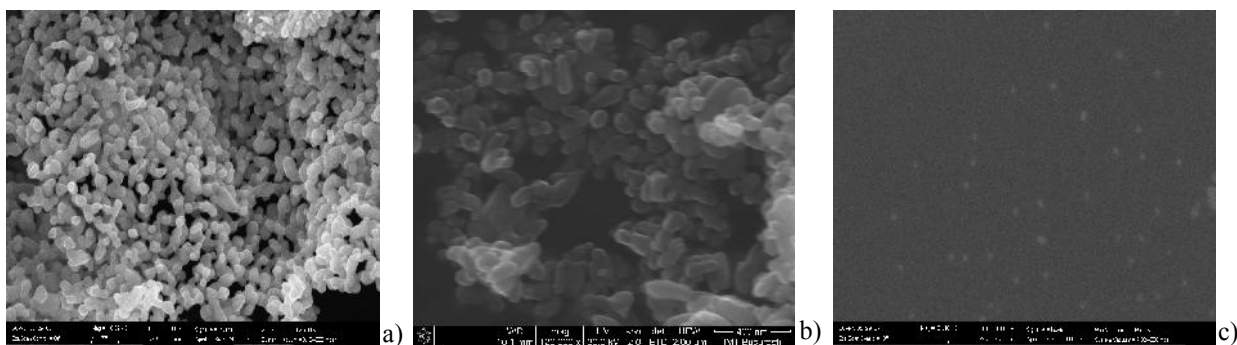


Figure 4: SEM images of the a) ZnO nanoparticles; b) elaidic acid-ZnO; c) ZnO - PMMA

4. CONCLUSION

The ZnO nanoparticles were synthesized by sol-gel method. The nanoparticles were modified with the capping agent (elaidic acid) and then dispersed in organic matrix of PMMA.

FTIR spectra show that 550°C is the optimal sintering temperature for obtaining of ZnO nanopowder. Formation of a complex between elaidic acid and ZnO was emphasized by the disappearance of C=O absorption band and the appearance of a new band attributed to COO- group from COO-Zn. Based on the FTIR spectra, elaidic acid covers the surface of the ZnO particles and is totally embedded in the matrix of PMMA.

From the results obtained, it was concluded that the surface modification of ZnO nanoparticles improves the dispersability in different matrices and also reduces the tendency of agglomeration of the nanoparticles.

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