UV absorption by cerium oxide nanoparticles/epoxy composite thin films

Ngoc Nhiem Dao¹, Minh Dai Luu¹, Quang Khuyen Nguyen² and Byung Sun Kim³

¹ Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay District, Hanoi, Vietnam
² Department of Technology Applied Science, Ton Duc Thang University, 98 Ngo Tat To, Binh Thanh District, Vietnam
³ Composite Lab. Korea Institute of Materials Science (IMS), 66 Sangnam-dong, Changwon, Gyeongnam, 641-010, Korea

E-mail: nhiemdn@ims.vast.ac.vn

Received 10 June 2011
Accepted for publication 1 November 2011
Published 19 December 2011

Abstract
Cerium oxide (CeO₂) nanoparticles have been used to modify properties of an epoxy matrix in order to improve the ultra-violet (UV) absorption property of epoxy thin films. The interdependence of mechanical properties, UV absorption property and the dispersed concentration of CeO₂ nanoparticles was investigated. Results showed that, by increasing the dispersed concentration of CeO₂ nanoparticles up to 3 wt%, tensile modulus increases while two other mechanical properties, namely tensile strength and elongation, decrease. The UV absorption peak and the absorption edges of the studied thin films were observed in the UV-Vis absorption spectra. By incorporating CeO₂ nanoparticles into the epoxy matrix, an absorption peak appears at around 318 nm in UV-Vis spectra with increasing CeO₂ concentration from 0.1 to 1.0 wt%. Scanning electron microscopy (SEM) images revealed that a good dispersion of nanoparticles in the epoxy matrix by an ultrasonic method was achieved.

Keywords: epoxy, cerium oxide nanoparticles, dispersion, reduction thin films, mechanical properties

Classification numbers: 4.02, 5.11

1. Introduction
Polymer nanocomposite is a relatively new class of material. Incorporation of inorganic nanoparticles into a polymer matrix can significantly influence the properties of the matrix. The obtained composite might exhibit improved thermal, mechanical or optical properties. The properties of polymer composites depend on the type of incorporated nanoparticles, their size, shape, concentration and interactions with the polymer matrix [1, 2]. Epoxy resin has developed rapidly since it was invented, and has been widely used in practical applications. The most important and industrialized epoxy is bisphenol A, which is derived from epichlorohydrin and consists of glycidol and hydroxyl groups with ether bond on the main chain. It is widely used in adhesive, electronic and coating industries due to the small volume shrinkage in curing and outstanding electrical performance. In the aerospace industry bisphenol A is commonly used as a primer matrix on aluminum alloy 2024-T3 for protecting the surface of aircraft [3]. The incorporation of various reinforced nanosized phases into the epoxy, such as graphite nanofiber, carbon nanotubes, nanoclays, cellulose nanofiber and nanoalumina resin, is one of the most effective ways to improve the properties of the epoxy [3–5].

A wide range of organic and inorganic UV (λ < 365 nm) absorbers are used in the coatings industry to minimize the destructive effect of sunlight on coated items designed for outdoor applications. Organic absorbers include aromatic hydroxyl triazoles, hydroxyl triazines and hydroxyl ketenes, which function as pure UV light absorbers or light stabilizers [6]. Some inorganic oxides have been found to noticeably absorb UV light, such as zinc oxide, cerium oxide, titanium dioxide and iron oxide. Due to its optical, magnetic and electronic properties, CeO₂ is widely used in various
applications, such as catalysis, optical materials, abrasives and ultraviolet absorbents [6–8]. CeO$_2$ possesses many attractive properties which make it highly promising for a wide range of applications such as UV blockers and filters.

Previous investigations have shown that the efficiency of nano additives for UV protection is dependent upon a number of parameters. Particles size is the most important factor. For incorporation of inorganic oxides into the epoxy matrix, the UV absorption of nanosized particles was reported to be much stronger than that of microsized ones. In addition, nanoparticles with smaller size lead to higher transparency and better UV protection. A reduction of the refractive index is also beneficial to UV protection. While concentration and film thickness also affect the transparency, the UV protection qualities of a number of nanosized additive absorbers were compared [9].

The aim of the present work is to investigate the mechanical properties and UV absorption property of CeO$_2$/epoxy thin films. It is expected that the CeO$_2$ nanoparticles would enhance the UV absorption properties of the resulting nanocomposite thin films. The thin film was coated on the surface of thin glass with a thickness of 100 µm using a spiral bar coater.

2. Experimental

2.1. Materials

2.1.1. Epoxy and curing agent. The epoxy used is diglycidyl ether of bisphenol A (epoxy YD-128, Kukdo chemical), which is a standard epoxy with epoxide equivalent weight equal to 190 g eq$^{-1}$. After being cured with an appropriate curing agent, it demonstrates excellent mechanical, chemical, electrical and adhesive properties in a cured state. CeO$_2$ nanoparticles were applied to the epoxy system and processed with the anhydride curing agent MTHPA (methyl tetra hydro phthalic anhydride, KBH-1089, Kukdo chemical). The mixing ratio of epoxy and curing agent was 100/90.

2.1.2. Cerium oxide nanoparticles. Cerium oxide (CeO$_2$) nanoparticles were prepared by an auto combustion process of rare earth nitrate gel/polyvinyl alcohol at low temperature. They were synthesized from rare earth oxides using polyvinyl alcohol as a polymer matrix and obtained by heating the gel precursor from 250 to 800 °C in a muffle. The morphology of CeO$_2$ nanoparticles (figure 1) was studied by transmission electron microscopy (TEM). They have spherical shapes with diameters less than 100 nm. The specific area of CeO$_2$ nanoparticles was determined to be 35.0 m$^2$ g$^{-1}$.

2.2. Fabrication of the CeO$_2$ nanoparticles/epoxy composite

In order to produce the CeO$_2$ nanoparticles/anhydride-cured epoxy composite (up to 3 wt% of nanofibers) by an ultrasonic method, CeO$_2$ nanoparticles were sonicated in ethanol for 30 min using a Sonic Mater sonicator. The solution contained more than 100 ml of ethanol per 1 g of CeO$_2$ nanoparticles. The epoxy was then added and mixed for an additional hour, and the mixture was divided into two layers (with an upper layer of ethanol) after 1 h. The ethanol was decanted and the remaining portion was removed by vacuum extraction at 80 °C for 9 h. The curing agent was blended into the mixture by mechanical stirring for 1 h. The air bubbles were removed under a vacuum at 50 °C for 30 min. The 100 µm thickness thin film was coated by a 24 × 50 mm spiral bar coater (figure 2). The film was kept in the freezer at −26 °C for 36 h (at B-state), and was then cured at 80 °C for 30 min and at 100 °C for 5 h. The specimens for the mechanical test were prepared from the CeO$_2$ nanoparticles/epoxy panels. The epoxy matrix was injected into a metal mold using a vacuum pump. The specimens were cured at 80 °C for 30 min and at 120 °C for 3 h.

2.3. Mechanical test

The specimen was prepared in accordance with ASTM$^4$ D638 standards. The specimen thickness, width, and total length were 3.0, 12.0 and 160.0 mm, respectively. An Instron 5567 was used for the tensile test and the extensometer length was 25.0 mm. The machine was operated under displacement control mode with 2.0 mm min$^{-1}$ of speed and all the tests

$^4$ American Society for Testing and Materials.
were performed at room temperature. Five specimens were prepared from each panel for each condition.

2.4. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM)

The fracture surfaces of the CeO$_2$ nanoparticles/epoxy were observed by SEM after the tensile test. An Au coating with thickness of a few nanometers was applied to the fracture surface. Cerium oxide nanoparticles were observed by TEM. The samples were prepared by ultrasonic dispersion of CeO$_2$ nanoparticles in ethanol before applying a few drops of the solution to a holey carbon copper grid.

2.5. UV absorption

The thickness of the thin film was evaluated before the UV absorption test. UV-Vis spectra of the thin film were measured on a Cary UV-5000 spectrophotometer at room temperature. The optical absorption spectra were measured from 200 to 800 nm with a double-beam optical spectrum analyzer. The measurement error is within ±1%.

3. Results and discussion

3.1. The effect of dispersion by the ultrasonic method

It is well established that the dispersion state of nanoparticles is a crucial factor in determining the final properties of nanocomposites. With conventional processing, mechanical mixing and normal processing, it is usually difficult to achieve very good distribution of nano-structured particles. Moreover, the mechanical properties of CeO$_2$ nanoparticles/epoxy with excellent dispersion increased significantly compared to nanocomposites with somewhat poor dispersion. Significant issues about dispersion and nanocomposite processing need more attention to be solved. The dispersion method has been achieved primarily by sonication of nanoparticles in a solvent followed by dispersion of both the polymer and nanoparticles in solution.

As a result, when using ethanol as a dispersion solution, cerium oxide nanoparticles were well dispersed in ethanol by the ultrasonic method for 30 min. The uniform dispersion of CeO$_2$ nanoparticles was investigated by SEM and showed that CeO$_2$ nanoparticles are well dispersed in the epoxy matrix (figure 3). Furthermore, the ethanol was easily removed after mixing with the epoxy resin and drying.

3.2. Mechanical properties of CeO$_2$ nanoparticles/epoxy composite

The tensile modulus is the slope of tensile strength between 0.1% and 0.3% of strain. The relationship between the tensile modulus of the CeO$_2$ nanoparticles/epoxy composite and the content of the nanoparticles is graphically shown in figure 4. The tensile modulus of the CeO$_2$ nanoparticles/epoxy composite increased with increasing CeO$_2$ nanoparticle concentration up to 3.0 wt%. The tensile modulus of the CeO$_2$ nanoparticles/epoxy composite increased by 2.1, 3.0, 4.3 and 6.3% with the addition of 0.5, 1.0, 2.0 and 3.0 wt% of CeO$_2$ nanoparticles, respectively. The enhancement of the tensile modulus obtained with CeO$_2$ nanoparticles in this study implies that CeO$_2$ nanoparticles are one of the most promising candidates to be used for reinforcing epoxy-nanocomposites.

The stress-strain curves of the CeO$_2$ nanoparticles/epoxy matrix containing 0.5, 1.0, 2.0 and 3.0 wt% of CeO$_2$ are presented in figure 5. It can be seen that the tensile strength of the CeO$_2$ nanoparticles/epoxy composite decreased with increasing the concentration of the CeO$_2$ nanoparticle content up to 3.0 wt%. Indeed, the nanoparticles had no
effect on the tensile strength of polymer-nanocomposites. The decrease of tensile strength is normally achieved in particulate reinforced polymer-nanocomposites. At the maximum point, for 1.0, 2.0 and 3.0 wt% nanoparticle content, the tensile strength of the CeO$_2$ nanoparticles/epoxy decreased by 3.7, 5.2 and 8.1% compared with that of pure epoxy, respectively. The tensile strength of the CeO$_2$ nanoparticles/epoxy matrix showed similar values with 0.5 and 1.0 wt% of CeO$_2$ nanoparticle content. Elongation of the CeO$_2$ nanoparticles/epoxy composite with 0.5, 1.0, 2.0 and 3.0 wt% of nanoparticles decreased by 5.3, 10.5, 15.8 and 21.1% compared with that of pure epoxy, respectively. From those results it can be concluded that the CeO$_2$ nanoparticles have improved the stiffness of epoxy-nanocomposites.

3.3. The effect of CeO$_2$ nanoparticle content on the UV absorption property of thin film

For evaluation of the UV protective quality of the samples, the main measured factors were the reflection coefficient of $R = I_r/I_0$ and transmission coefficient of $T = I_{out}/I_0$, where $I_r$, $I_{out}$ and $I_0$ are the intensities of the reflected, transmitted and initial optical signals, respectively. Each photodetector based on the unit formed an electric signal proportional to the intensity of either reflected or transmitted light with the adjusted wavelength. Calculations of all the main spectral and optical properties of the samples were based on the measured dependencies $R(\lambda)$ and $T(\lambda)$ [10].

The UV absorption coefficient of CeO$_2$ nanoparticles/epoxy thin film containing 0.0, 0.1, 0.25, 0.5, 0.75 and 1.0 wt% of nanoparticles is shown in figure 6. A well-defined sharp and strong absorbance peak located at 318 nm, which is shifted toward the short wavelength, indicates the narrow and uniform particle size distribution obtained via this fabrication route. The UV absorption of the CeO$_2$ nanoparticles/epoxy thin film increased with increasing CeO$_2$ nanoparticle concentration up to 1.0 wt%. The maximum absorption corresponding to the larger nanoparticles is shifted towards the short wavelength region. Those results indicated that the nanoparticle content had a strong effect on the absorption property of the CeO$_2$ nanoparticles/epoxy thin film. With 0.5 and 1.0 wt% of CeO$_2$ nanoparticles, the thin film absorbed more than 48 and 90% of UV light with an absorbance peak at around 318 nm, respectively.

4. Conclusion

CeO$_2$ nanoparticles with an average size of less than 100 nm were synthesized and incorporated into the epoxy matrix. The mechanical properties and UV absorption property were determined for the thin film based on the CeO$_2$ nanoparticles/epoxy. Enhancements of 2.1, 3.0, 4.3 and 6.3% in tensile modulus were obtained after adding 0.5, 1.0, 2.0 and 3.0 wt% CeO$_2$ nanoparticles, respectively. The tensile strength and elongation decreased with increasing CeO$_2$ nanoparticles up to 3.0 wt%. It has been shown that with small CeO$_2$ nanoparticle concentration, the UV absorption property of the thin film was noticeably improved. The epoxy thin films with 1.0 wt% of CeO$_2$ nanoparticles absorbed more than 90% of UV light with an absorbance peak at around 318 nm. The data obtained during the experiments can be used for the fabrication of UV reduction thin films.

References

[1] Džunuzović E, Jeremić K and Nedeljkovic J M 2007 Eur. Polym. J. 43 3719
[2] Rozenberg B A and Tenne R 2008 Prog. Polym. Sci. 33 40
[3] Shi H, Liu F, Yang L and Han E 2008 Prog. Org. Coat. 62 359
[4] Omrani A, Simon L C and Rostami A A 2009 Mater. Chem. Phys. 114 145
[5] Kippax P, Waid-Smith S and Pugh D 2007 Paint Coat. Ind. 23 44
[6] Tao Y, Gong F H, Wang H, Wu H P and Tao G L 2008 Mater. Chem. Phys. 112 973
[7] Ji P, Zhang J, Chen F and Anpo M 2009 Appl. Catal. B: Environ. 85 148
[8] Yu S H, Colfen H and Fischer A 2004 Colloid. Surf. A 243 49
[9] Yin L, Wang Y, Pang G, Koltypin Y I and Gedanken A 2002 J. Colloid Interface Sci. 246 78
[10] Ushakov N M, Yu G Y, Gorobinskii L V, Popkov O V and Korobudskic I D 2008 Acta Mater. 56 2336