

SURFACE MODIFICATION OF NANOSILICA FILLERS FOR THE PREPARATION OF SILICA/EPOXY NANOCOMPOSITES

POVRŠINSKA MODIFIKACIJA NANODELCEV SILICIJEVEGA DIOKSIDA ZA PRIPRAVO NANOKOMPOZITOV SiO₂-EPOKSI

Aleksandra Kocijan¹, Marjetka Conradi¹, Milena Zorko²

¹Institute of Metals and Technology, Lepi pot 11, 1000 Ljubljana, Slovenia

²National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
aleksandra.kocijan@imt.si

Prejem rokopisa – received: 2012-09-14; sprejem za objavo – accepted for publication: 2012-09-19

In this paper we focus on the preparation of the epoxy resin Epikote 828LVEL reinforced with nanosilica. Epoxy composites containing 130-nm spherical silica nanoparticles were prepared at a fixed volume fraction ($\varphi = 0.5\%$). To prevent agglomeration the silica fillers were initially pre-treated with diglycidyl ether of bisphenol A. Due to the low content of silica fillers their inclusion in the matrix was confirmed by the increased roughness of the fracture surface compared to the smooth surface of the neat epoxy. Fourier-transform infrared spectroscopy (FTIR) was employed to confirm the changes in the functional groups on the surface of the unmodified and modified silica.

Keywords: epoxy composite, silica, nanotechnology, FTIR, SEM

V tem članku smo se osredinili na pripravo epoksidne smole Epikote 828LVEL z dodatkom silicijevega dioksida. Pripravili smo epoksidkompozite, ki so vsebovali sferične nanodelce silicijevega dioksida velikosti 130 nm z volumenskim deležem $\varphi = 0,5\%$. Da bi preprečili aglomeracijo, smo silicijev dioksid predhodno modificirali z diglicidil etrom bisfenola A. Zaradi majhne vsebnosti polnila smo njihovo vključitev v osnovo potrdili s povečano hrapavostjo na mestu preloma v primerjavi z gladko površino čistega epoksidkompozita. Z infrardečo spektroskopijo s Fourierjevo transformacijo (FTIR) smo potrdili spremembe funkcionalnih skupin na površini nemedificiranega in modificiranega silicijevega dioksida.

Ključne besede: epoksidkompozit, silicijev dioksid, nanotehnologije, FTIR, SEM

1 INTRODUCTION

Polymer-matrix coatings are of particular significance in reducing friction and wear as well as extending the service life of facilities involving surface contact and relative motion due to their low shear strength and good toughness¹. Epoxy-resin coatings with good mechanical, electrical and thermal properties have been widely used in many fields, including mechanical engineering, chemical engineering, electronic engineering and aerospace¹. However, its applications are seriously limited by a poor impact resistance and stress-cracking resistance. To overcome this disadvantage, numerous attempts have been made to modify epoxy resin by introducing various reinforcing agents and fillers²⁻¹¹.

Silica/epoxy composites are some of the most widely used structural materials, appropriate for electronics, automotive and aerospace, due to their ability to sustain mechanical and thermal loading¹², as well as due to its structure with silanol and siloxane groups covering the silica surface. The interaction between the organic and the inorganic phase and the dispersibility of the filler in organic media affect the properties of the composite. This is normally achieved by the application of surface-modified silica, which prevents agglomeration of the nanosilica in the matrix.

In this paper we focus on the surface modification of 130-nm silica particles to prevent agglomeration in the epoxy composite, using silica particles that were pre-treated with the bisphenol-A-type surfactant that is compatible with the Epikote 828LVEL epoxy resin. The chemical analyses of the modified and unmodified specimens were performed in order to identify the chemical interaction during the modification stage. Changes in the surface morphology were observed with a scanning electron microscope (SEM).

2 EXPERIMENTAL

Commercial high-purity epoxy resin (Epikote 828LVEL, Momentive Specialty Chemicals B.V.) was mixed with a hardener 1,2-Diaminocyclohexane (Dytek DCH-99, Invista Nederland B.V.) in the proportions of mass fractions 100 : 15.2 % and used as the matrix in the composite. Silica (SiO₂) nanoparticles with a size of 130 nm were used as the reinforcement. The 130-nm silica particles were synthesized following the Stöber-Fink-Bohn method¹³ and their surface was modified to prevent agglomeration using diglycidyl ether of bisphenol A (Sigma-Aldrich) as a surface modifier and imidazole (Sigma-Aldrich) as a reaction catalyst.

The surface was modified by blending a silica mass fraction of 40 % in diglycidyl ether of bisphenol A (modifying agent). The blend was further dispersed in 50 ml of toluene in the presence of imidazole (25 % in mass fraction). The mixture was then refluxed at 100 °C for 2 h. To remove the by-product (imidazole) acentrifuging technique was employed three times using acetone as the solvent. The residual product was dispersed in acetone and stirred at room temperature for 2–3 h. The surface-modified silica was dried in an oven at 110 °C for a few hours.

Epoxy-based composites were prepared by blending with $\varphi = 0.5$ % of 130-nm surface-modified SiO₂ particles. The silica particles were initially dispersed in epoxy resin using ultrasonification for 20–30 min at approximately 40 °C. After adding the hardener in the next step, the mixture was manually stirred and then degassed under vacuum for 10–15 min. Finally, the mixture was poured into a closed vertical mould made of aluminium with an inner-cavity thickness of 3 mm. The curing was performed in two steps. The composites were first pre-cured at 70 °C for 1 h and then post-cured at 150 °C for another hour. For comparison, neat epoxy without silica fillers was also prepared and cured in the same process as the composites.

Fourier-transform infrared spectroscopy (FTIR) measurements were performed using a Thermo Nicolet FT-IR Nexus instrument in the 4000–700 cm⁻¹ region with a 4 cm⁻¹ resolution. The sample was mixed with KBr and dried to obtain a transparent disc, which was then analysed in the instrument.

Scanning electron microscopy using a FE-SEM Zeiss SUPRA 35VP was employed to investigate the morphology and the size of the synthesized and modified silica and examine the interfacial properties in the epoxy composite matrix on fracture surfaces.

3 RESULTS AND DISCUSSION

The FTIR analysis was performed in order to establish the changes in the functional groups on the surface of the unmodified (**Figure 1**) and modified silica (**Figure**

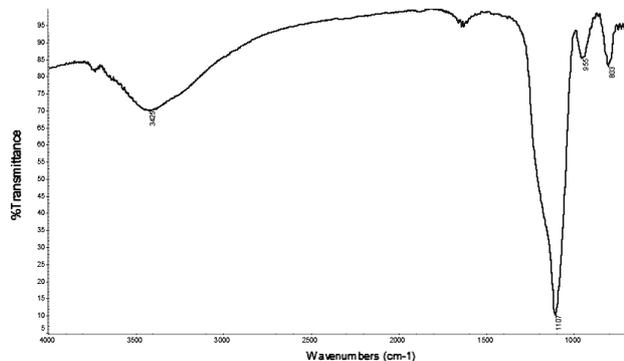


Figure 1: FTIR spectrum of unmodified silica
Slika 1: FTIR-spekter nemodificiranega silicijevega dioksida

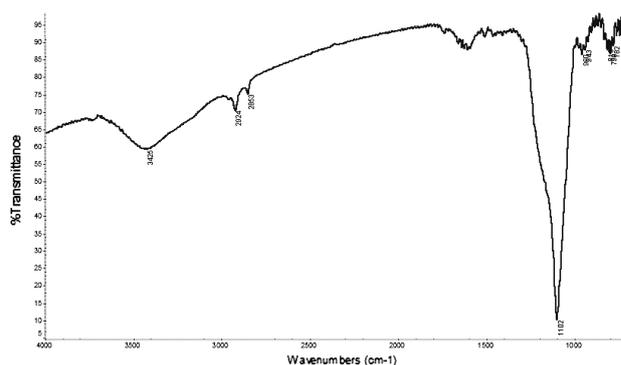


Figure 2: FTIR spectrum of modified silica
Slika 2: FTIR-spekter modificiranega silicijevega dioksida

2). The spectra for the modified silica showed evidence of additional peaks in the range 2853–2924 cm⁻¹, corresponding to the absorption of C-H aliphatic and aromatic stretching. Additional peaks appearing at 1500–1600 cm⁻¹ and 780 cm⁻¹ were related to aromatic C=C stretching and ortho-disubstituted benzene, respectively. The weak band at approximately 1400 cm⁻¹ corresponded to C-H stretching. The bend at 1100–1300 cm⁻¹ corresponded to C-O stretching and additional weak bands at 850–960 cm⁻¹ to C-H bending. The additional bands for the modified silica were attributed to the modifier molecule, which confirms the successful modification of the silica and was also observed by other authors¹⁴.

The morphology and size of the nanosilica synthesised following the Stöber-Fink-Bohn method and modified using diglycidyl ether of bisphenol A as a surface modifier and imidazole as a reaction catalyst were examined by SEM imaging (**Figure 3**). The results show that the size of the particles is 130 nm; the particles are uniform, round and evenly distributed, without

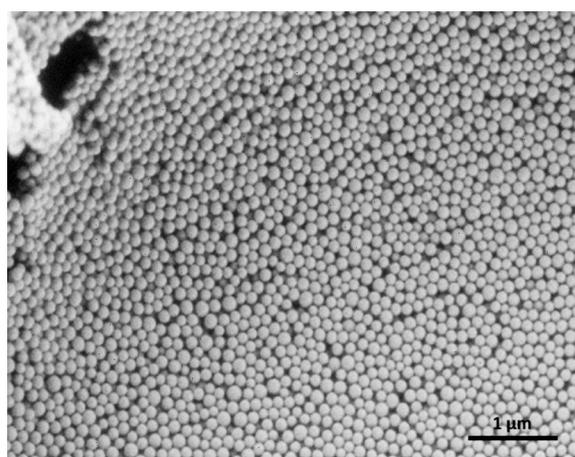


Figure 3: Morphology of the synthesized nanosilica following the Stöber-Fink-Bohn method and modified using diglycidyl ether of bisphenol A as a surface modifier and imidazole as a reaction catalyst
Slika 3: Morfologija nanodelcev silicijevega dioksida, sintetiziranih po Stöber-Fink-Bohnovem postopku in modificiranih s površinskim modifikatorjem diglicidil etrom bisfenola A in reakcijskim katalizatorjem imidazolom

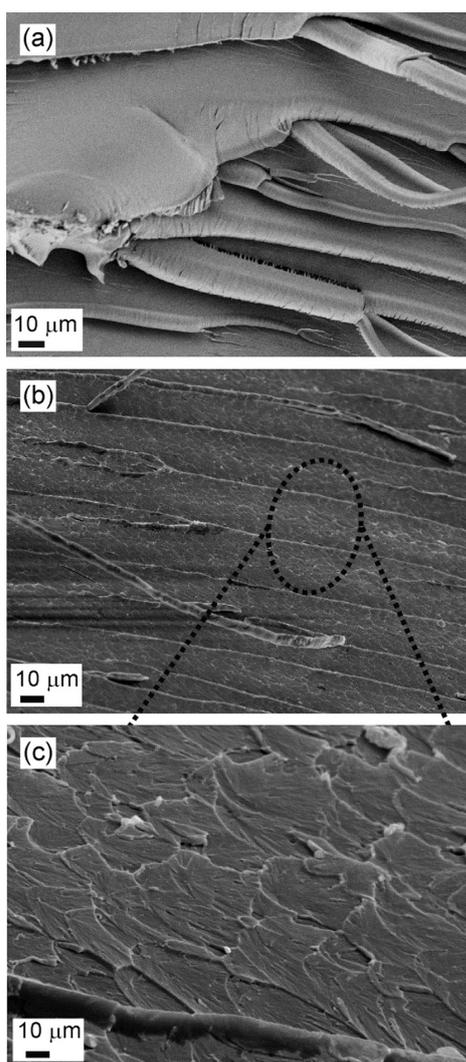


Figure 4: a) Fracture surfaces of pure epoxy, b) composite with $\varphi = 0.5\%$ 130-nm silica fillers and c) fracture surface detail – fish-skin-like microstructure – in 130-nm silica/epoxy composite

Slika 4: a) Slika preloma čiste epoksmole, b) kompozit z 0,5 % volumenskim deležem polnila silicijevega dioksida velikosti 130 nm in c) povečava luskinastega dela površine na prelomu v kompozitu z delci silicijevega dioksida velikosti 130 nm

forming clusters, which again confirms the effective modification of silica to prevent agglomeration.

Prior to SEM imaging of the fracture surfaces, the samples were frozen in liquid nitrogen and broken by hand in order to compare the fracture surfaces of the neat epoxy and the 130-nm silica/epoxy composites (**Figure**

4). The inclusion of silica fillers in the epoxy matrix was confirmed by the increased roughness of the composite's fracture surface compared to smooth surface of the pure epoxy. As shown in **Figures 4b** and **4c**, the silica/epoxy composite breaks in characteristic steps decorated with a fish-skin-like microstructure. One should also note that due to the low volume fraction of silica fillers, single particles did not appear to be exposed on any surface of the composite.

4 CONCLUSION

In the present study, 130-nm silica particles were synthesized following the Stöber–Fink–Bohn method and their surfaces were successfully modified in order to prevent agglomeration in the epoxy matrix. The modification was performed using diglycidyl ether of bisphenol A as a surface modifier and imidazole as a reaction catalyst. The efficacious modification was confirmed using FTIR analyses and SEM imaging.

This study was conducted in order to achieve better mechanical and corrosion properties of the composite, which were also investigated and will be published elsewhere.

5 REFERENCES

- ¹ S. Q. Deng, L. Ye, K. Friedrich, *J. Mat. Sci.*, 42 (2007), 2766–2774
- ² A. C. Moloney, H. H. Kausch, T. Kaiser, H. R. Beer, *J. Mat. Sci.*, 22 (1987), 381–393
- ³ J. Spanoudakis, R. J. Young, *J. Mat. Sci.*, 19 (1984), 487–496
- ⁴ M. Hussain, Y. Oku, A. Nakahira, K. Niihara, *Mat. Lett.*, 26 (1996), 177–184
- ⁵ E. P. Giannelis, *Appl. Org. Chem.*, 12 (1998), 675–680
- ⁶ T. Lan, T. J. Pinnavaia, *Chem. Mat.*, 6 (1994), 2216–2219
- ⁷ A. S. Zerda, A. J. Lesser, *J. Polym. Sci. Part B-Polym. Phys.*, 39 (2001), 1137–1146
- ⁸ R. P. Singh, M. Zhang, D. Chan, *J. Mat. Sci.*, 37 (2002), 781–788
- ⁹ R. A. Pearson, A. F. Yee, *J. Mat. Sci.*, 26 (1991), 3828–3844
- ¹⁰ C. B. Bucknall, G. Maistros, C. M. Gomez, I. K. Partridge, *Makromolekulare Chemie-Macromolecular Symposia*, 70 (1993) 1, 255–264
- ¹¹ R. A. Pearson, A. F. Yee, *Polymer*, 34 (1993), 3658–3670
- ¹² A. Moiala, Q. Li, I. A. Kinloch, A. H. Windle, *Composites Sci. Techn.*, 66 (2006), 1285–1288
- ¹³ M. Zorko, S. Novak, M. Gaberscek, *J. Ceramic Proc. Research*, 12 (2011), 654–659
- ¹⁴ C. S. Sipaut, N. Ahmad, R. Adnan, I. Ab. Rahman, M. A. Bakar, J. Ismail, C. K. Chee, *J. Appl. Sci.*, 7 (2007) 1, 27–34