Multifunctional Nanostructured Composites Based on TiO_2 Nanoparticles

J. Gutierrez, I. Mondragon, A. Tercjak*

Summary: Inorganic-organic nanostructured thermosetting composites based on poly(styrene-*block*-ethylene oxide) (SEO) block copolymer used as templating agent and titanium dioxide (TiO_2) nanoparticles synthesized via sol-gel were prepared. The morphologies generated in the binary and ternary epoxy-based systems were studied using atomic force microscopy (AFM). Ternary systems showed good dispersion of synthesized nanoparticles and simultaneously maintained nanostructure order of the cured block copolymer/epoxy-based system due to self-assembly of SEO block copolymer. Transparent multifunctional advanced thermosetting materials with tuneable properties controlled varying the ratio between inorganic and organic components was successfully designed.

Keywords: atomic force microscopy (AFM); block copolymers; epoxy; nanoparticles

Introduction

The ability to control both the length scale and the spatial organization of the block copolymer at the nanoscale makes them particularly attractive candidates for use as templates for the dispersion and selective location of inorganic nanofillers.[1–7] One feasible pathway for generating self-assembled thermosetting nanostructures is the use of amphiphilic block copolymers consisting of thermoset-miscible and thermoset-immiscible blocks. As it is well known, nanostructured materials based on thermosetting matrices can find application in many different fields of nanotechnology, such as nanostructured functional surfaces, nanolithography, or building of nanostructured inorganic/organic hybrid composites. In this case, block copolymers lead to a selective dispersion of nanoparticles obtaining advanced multifunctional nanostructured thermosetting materials.[8–11]

Group 'Materials + Technologieś, Department of Chemical and Environmental Engineering, Polytechnic School, University of the Basque Country, Pza Europa 1, 20018 Donostia/San Sebastián, Spain
E-mail: juncal.gutierrez@ehu.es

In the present work, hybrid inorganic/organic bisphenol-A type epoxy matrix composites have been prepared. This study discussed the influence of the ratio between blocks of the poly(styrene-*b*-ethylene oxide) (SEO) block copolymer on the final morphology of the thermosetting systems using two different molecular weight SEO block copolymers. Moreover, TiO_2 nanoparticles were used in order to develop inorganic/organic nanostructured epoxy based systems with well-dispersed inorganic nanoparticles.

Experimental Part

A diglicydylether of bisphenol A epoxy monomer (DGEBA) (DER 332, purchased from Dow Chemical) was used. This epoxy resin was cured with a stoichiometric amount of an aminic hardener, 4,4́-methylenebis(3-chloro 2,6-diethylaniline) (MCDEA), supplied by Lonza. Two amphiphilic SEO block copolymers with high (HSEO) and low (LSEO) PS block contents ($M_n^{PS} = 125\ 000$ g/mol, $M_n^{PEO} = 16\ 100$ g/mol, Mw/Mn = 1.4 for HSEO; $M_n^{PS} = 58\ 600$ g/mol, $M_n^{PEO} = 31\ 000$ g/mol, $M_w/M_n = 1.03$ for LSEO) were purchased from Polymer

Source, Inc. Titanium dioxide nanoparticles were synthetized via sol-gel synthesis using titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$, TTIP) as precursor.

Scheme 1 shows the generation of TiO_2 nanoparticles using sol-gel technique. TiO_2 nanoparticles were synthesized according to the preparation method published by Gutierrez et al.[12–14] The reaction start from a precursor and after a series of hydrolysis and condensation the network formation takes place in acidic medium. Finally, hydrophilic TiO_2 nanoparticles with surface hydroxyl groups are obtained.

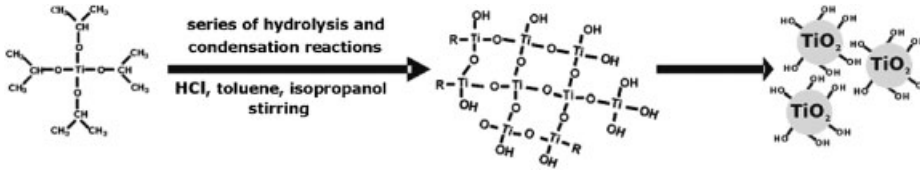
The dispersion of TiO_2 nanoparticles and morphology of investigated binary and ternary thermosetting systems were studied by atomic force microscopy (AFM). AFM measurements were performed in tapping mode using a Nanoscope IIIa (Multimode from Digital Instruments) equipped with an integrated silicon tip/cantilever having a resonance frequency of ~300 kHz. The flat surfaces of the investigated systems were obtained by cutting with a diamond knife using a Leica Ultracut R ultramicrotome.

Results and Discussion

AFM images of HSEO and LSEO based nanostructured thermosetting systems with different block copolymer contents are shown in Figure 1.

Light continuous areas in the AFM phase images correspond to epoxy matrix linked with the PEO block whereas the dark areas correspond to PS block domains.[7,14–15] In the case of thermosetting systems modified with HSEO, microphase separation of PS-block-rich domains occurs up to 30 wt % of HSEO block copolymer content in epoxy system. On the contrary, for the thermosetting systems modified with LSEO block copolymer even 40 wt % of LSEO block copolymer leads to nanostructured thermosetting system. This behavior can be related to the higher amount of epoxy-philic PEO-block in the case of LSEO block copolymer if compared to the HSEO block copolymer content. For both systems (HSEO and LSEO) increasing of the block copolymer content led to changes in the generated morphology. The morphology of thermosetting systems modified with HSEO block copolymer changes from spherical micelles one (5 wt % HSEO) to the long wormlike micelles (20 and 30 wt % HSEO) passing throughout vesicles-like morphology (10 wt % HSEO). Under the same preparation conditions, the morphology of thermosetting systems modified with LSEO block copolymer changes from spherical (5 and 10 wt % LSEO) to hexagonal structure (20, 30 and 40 wt % LSEO) as a consequence of microphase separation of PS block from PEO block/epoxy-rich phase. Comparison between thermosetting systems modified with 40 wt % block copolymer indicates that the epoxy based system modified with HSEO shows phase inversion. Thus, PEO-block/epoxy-rich phase separate in continuous PS-block-rich phase at the macroscale. On the contrary, 40 wt % LSEO thermosetting systems shows hexagonal morphology where PS-block cylinders were located perpendicular and parallel to the cut surface.

The morphology of the hybrid inorganic/organic thermosetting systems were also studied (Figure 2 and 3). TiO_2 nanoparticles are the hardest component of these systems[16] and therefore, in the AFM



Scheme 1.
Preparation of TiO_2 nanoparticles by sol-gel synthesis.

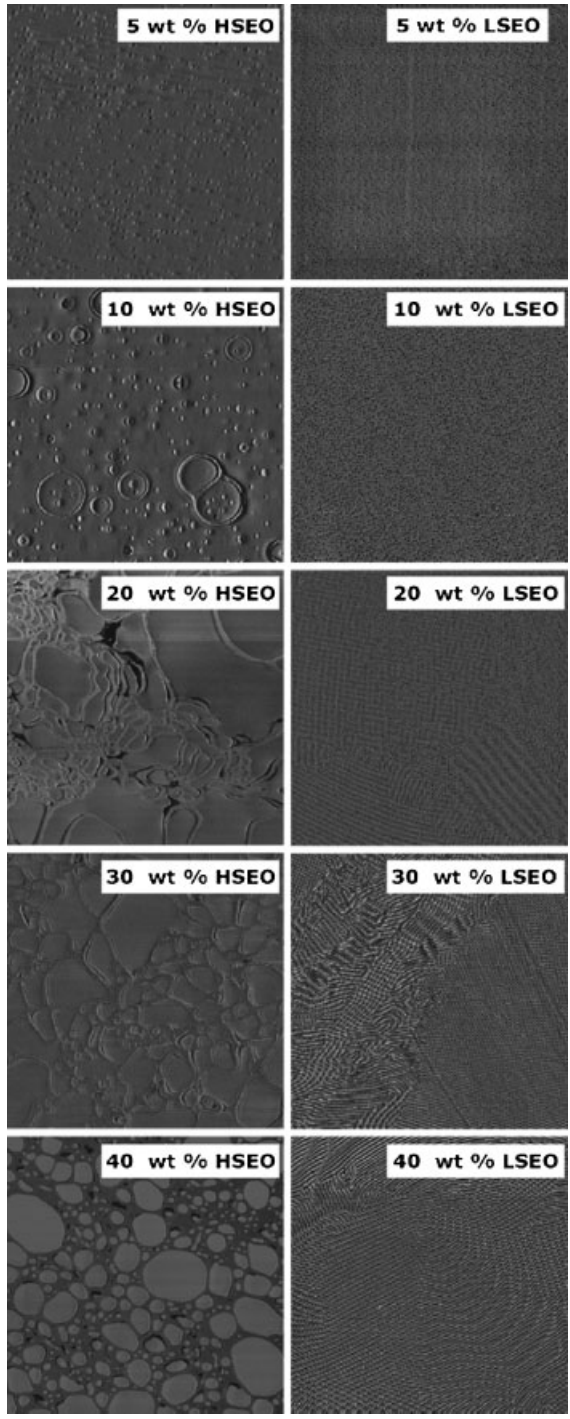


Figure 1.
AFM phase images (5 μm × 5 μm) of HSEO-(DGEBA/MCDEA) and LSEO-(DGEBA/MCDEA) binary systems.

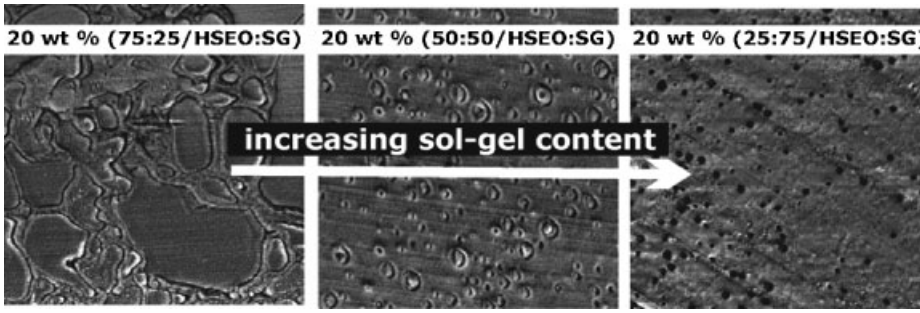


Figure 2.
AFM phase images (3 μm × 3 μm) of epoxy matrix modified with 20 wt % (block copolymer:sol-gel) varying HSEO:SG ratio.

images, their appeared as spherical bright spots. It should be pointed out that for all hybrid systems well dispersed spherical bright TiO_2 nanoparticles appeared along the sample surface (Figure 2 and 3). This good distribution of TiO_2 nanoparticles confirms the strong interactions between the PEO block/epoxy-rich phase and the

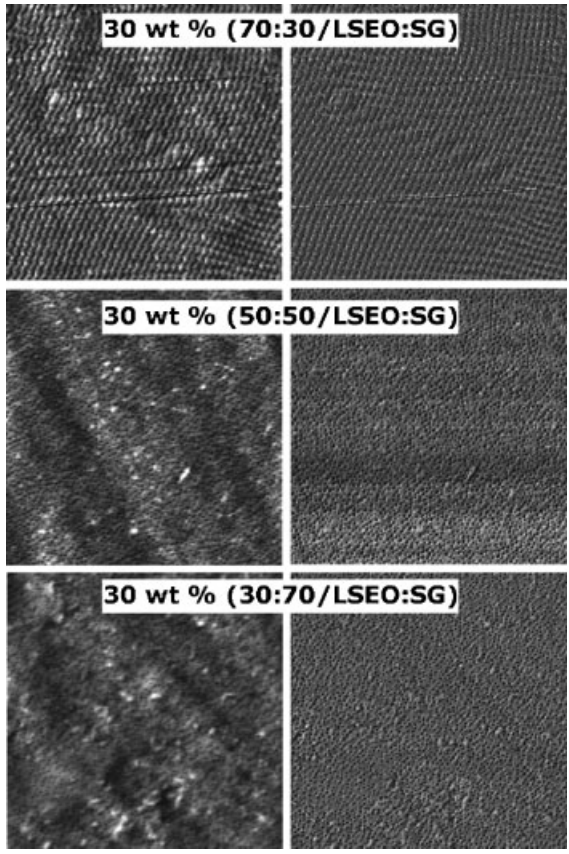


Figure 3.
AFM images (height and phase) (3 μm × 3 μm) of epoxy matrix modified with 30 wt % (block copolymer:sol-gel) varying LSEO:SG ratio.

synthesized hydrophilic SG network. Thus, for all hybrid inorganic/organic ternary composites, TiO_2 nanoparticles were preferentially confined at epoxy-rich matrix, nearby to the interface between the epoxy-rich matrix and microphase separated PS block domain. Moreover the size of the TiO_2 nanoparticles in all ternary epoxy based systems was almost the same, with a diameter around 20–30 nm.

The morphology of ternary thermosetting systems modified with different ratios between HSEO block copolymer and sol-gel was shown in Figure 2. In the case of 20 wt % (75:25/HSEO:SG) thermosetting system, AFM phase image shows almost the same morphology if compared to the corresponding system without TiO_2 nanoparticles (20 wt % HSEO, Figure 1). However, the addition of TiO_2 nanoparticles led to the highest surface roughness. For the thermosetting system with the same ratio of HSEO block copolymer and TiO_2 nanoparticles, 20 wt % (50:50/HSEO:SG), microphase-separated vesicles were detected. Comparing the final morphology of this system to the same system without titanium dioxide nanoparticles (10 wt % HSEO, Figure 1) suggests that TiO_2 nanoparticles were located into the epoxy-rich phase confined between the bilayered PSblock-rich phase formed vesicle structure. Moreover, the average size of the vesicles decreased and became more regular if compared to 10 wt % HSEO thermosetting system. In the case of 20 wt % (25:75/HSEO:SG) thermosetting system the ratio between block copolymer and sol-gel was changed, increasing the inorganic content of the sample. AFM image show spherical PS micelles in the continuous epoxy-rich matrix.

The morphology of ternary thermosetting systems modified with different ratios between LSEO block copolymer and sol-gel was shown in Figure 3. AFM image corresponding to the 30 wt % (70:30/LSEO:SG) system shows, similarly to the system modified only with 30 wt % LSEO block copolymer, hexagonally packed cylinder morphology where PS cylinders are arranged parallel and perpendicular to the cut surface. In the case of 30 wt % (50:50/LSEO:SG) system the ratio between block copolymer and sol-gel was changed, increasing the inorganic content of the sample and higher amount of bright spots (TiO_2 nanoparticles) embedded in the epoxy-rich matrix can be clearly detected. In the case of (70:30/LSEO:SG) system morphology changes from hexagonal to spherical one. Uniformly dispersed spherical PS block domains with an average diameter of $\sim$50 nm in the continuous epoxy-rich matrix were detected. Moreover, AFM image clearly shows well-dispersed individual TiO_2 nanoparticles.

Conclusion

Transparent multiphase nanostructured thermosetting composites with well-dispersed TiO_2 nanoparticles were developed using two different molecular weight SEO block copolymers as a templating agent. Playing with both block copolymer molecular weight and their amount in the thermosetting systems one can generate different desired nanostructured systems. Designed thermosetting composites containing both TiO_2 nanoparticles and SEO block copolymer can open a new strategy for preparation of well-defined transparent multifunctional thermosetting materials which have a large number of applications in variety of fields.

Acknowledgements: Financial support from Basque Country Government in the frame of ETORTEK nanoIKER (IE11–304), Grupos Consolidados (IT-365–07) and NANOTES (S-PE10UN40) and from the Spanish Ministry of Education and Innovation (MAT-2009–06331) is gratefully acknowledged. Additionally, J.G. thanks Eusko Jaurlaritza/Gobierno Vasco (Programas de becas para formación y perfeccionamiento de personal investigador) and A.T. acknowledges MICINN for Ramón y Cajal program. Moreover, we are grateful to SGIker units of the UPV/EHU.

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