

Effects of SiO₂ Nanoparticles on the Performance of Carboxyl-Randomized Liquid Butadiene–Acrylonitrile Rubber Modified Epoxy Nanocomposites

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ABSTRACT: The effects of SiO₂ nanoparticles on the performance of carboxyl-randomized liquid butadiene–acrylonitrile rubber (CRBN) modified epoxy resin (EP) nanocomposites were studied. With the addition of an appropriate amount of SiO₂ (2%) to EP/CRBN (95/5), the nanocomposites could achieve the desired impact strength and modulus. The morphology of the nanocomposites was studied with scanning electron microscopy and transmission electron microscopy. The nanocomposites showed a three-phase system; both the rubber particles and SiO₂ nanoparticles showed uniform dispersions in the EP matrix, with their phases all nano-sized. A good correlation between the free-volume hole radius and mechanical properties was found. The introduction

of a small amount of nanoparticles (both rubber and SiO₂) into EP led to the formation of interactions between the EP and nanoparticles. The interactions restricted the segment motion and the mobilization of the EP chains and then reduced the free-volume concentration in the amorphous region of EP. The fact that the average free-volume hole radius of EP/CRBN was larger than that of pure EP was mainly attributed to the contribution of the larger size of the free-volume holes within the rubber phase. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1347–1352, 2007

Key words: nanocomposites; structure-property relations; toughness

INTRODUCTION

Epoxy resins (EPs) are used in a variety of applications because their properties, such as the thermal stability, mechanical response, low density, and electrical resistance, can be varied considerably. However, these materials are rather brittle, and for this reason, their toughening has been extensively studied in the last decades. Several methods have been proposed to increase the toughness of EP, and one of the most successful involves the addition of a suitable rubber to uncured EP and then the control of the polymerization reactions to induce phase separation.^{1–6} The great majority of the studies have involved its chemical modification with a reactive elastomer, particularly a carboxyl-terminated butadiene–acrylonitrile copolymer.^{7–9} During the polymerization, the rubber phase-separates because it

becomes less miscible with the matrix, forming tiny particles of rubber that are dispersed in the EP matrix. However, the addition of rubber usually brings a decrease in other properties (mainly the modulus and the thermal properties). Recently,^{10–12} there has emerged a new approach for improving the thermal stability, toughness, and modulus of thermoplastic and thermoset systems through the formation of a nanophase structure in the polymer matrix; the nanophase consists of small, rigid particles, whiskers, or tubes (e.g., layered silicates, silica particles, or carbon nanotubes). The nanophase has at least one dimension of approximately a nanometer length scale.

Both macroscopic and microscopic measurements are normally performed for a newly synthesized composite to achieve an overall understanding. The positron annihilation lifetime spectroscopy (PALS) technique has been widely used in the study of polymeric systems at the molecular level in recent years.^{13,14} A positron can be preferentially localized at a defect or open volume in a solid and annihilated with an electron of atoms of materials. In polymers or porous materials, positronium (Ps), the bound state of a positron and an electron, can be formed and annihilated in the free volume. There are two Ps states: a single state [*para*-positronium (*p*-Ps)] and a triplet state [*ortho*-positronium (*o*-Ps)]. The intrinsic

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lifetime of *p*-Ps is 0.125 ns, whereas that of *o*-Ps is 142 ns *in vacuo*. In a polymer, the *o*-Ps lifetime is shortened to 1–10 ns because of annihilation with an electron of the surrounding molecules. The *o*-Ps annihilation parameters give important information on the chemical environment in which Ps is formed. The hole size and concentration of the free volume of the polymer can be calculated from the *o*-Ps annihilation lifetime and its intensity. Thus, PALS has been developed to characterize the properties of polymers, such as the free-volume hole size, its concentration, and its distribution.

This article discusses the effects of combining the benefits of adding rubber and SiO₂ nanoparticles to epoxy to develop improved matrix materials with the aim of attaining a higher fracture energy without compromising the other desired mechanical and thermal properties of EPs. The main objectives of this study were to (1) determine the morphology and phase distribution of the three-phase system and (2) use PALS as a probe to measure the free-volume properties of the composites and then examine the relationship between the free-volume properties and mechanical properties of the composites.

EXPERIMENTAL

Materials

The bisphenol A type EP (E-51) used for this experiment was purchased from Wuxi Huili Resin Factory (Wuxi, China). Its number-average molecular weight was 370. The curing agent 4,4-diamino diphenyl methane (DDM) was obtained from Jiangying Hui-feng Chemical (Jiang Ying, China). Carboxyl-randomized liquid butadiene-acrylonitrile rubber (CRBN; acrylonitrile content (AN) = 22–25%, molecular weight = 3000–5000 g/mol) was supplied by Lanzhou Chemical Co. (Lanzhou, China). The SiO₂ nanoparticles (mean size = 50 nm) were obtained from Zhejiang Zhoushan Mingri Nanomaterials Co. (Zhoushan, China).

Preparation of the composites

First, EP and CRBN in a certain mass ratio were mixed via stirring in a 90°C oil bath for 2 h. Then, the mixture was dispersed with ultrasonic equipment (KQ-50DZ, Kunshan Ultrasonic Equipment Co., Ltd., Kunshan, China) for another 0.5 h. Second, an alcohol/SiO₂/coupling agent mixture (mass ratio = 100/10/1) was stirred for 0.5 h and then dispersed with ultrasonic equipment for another 0.5 h. Third, the alcohol/SiO₂/coupling agent mixture was added to the other EP/CRBN premixture. Afterward, the mixture obtained in the third step was stirred in a 90°C oil bath for 2 h to remove the sol-

vent (alcohol) and then dispersed with ultrasonic equipment for another 0.5 h. At last, an appropriate amount of DDM (curing agent) was added to the mixture, which was stirred for several minutes. The mixture was quickly poured into a preheated steel mold coated with a mold release agent. After degasification for about 0.5 h at 90°C, the mold was kept at 90°C for 2 h and then at 150°C for 5 h to form the specimens.

Characterization of the composites

The impact tests were performed with an impact tester (XCJ-5, Chengde Testing Machine Co., Ltd., Chengde, China) according to ASTM D 256. The flexural experiments were carried out with a universal material testing machine (SANS Testing Machine Co., Ltd., Shenzheng, China) according to ASTM D 790. Five specimens of each sample were tested, and the mean values and standard deviations were calculated.

The morphology of the composites was examined with a JEM 6360 scanning electron microscope (Japan). All the samples were coated with gold to improve the scanning electron microscopy (SEM) imaging. To view phase-separated rubber particles with transmission electron microscopy (TEM), ultra-thin sample films were first treated with osmium tetroxide (OsO₄) and then observed with a JEM 1200EX transmission electron microscope (Japan).

PALS measurements

PALS was measured with an EG&ORTEC (Tennessee) fast-fast lifetime spectrometer with an FWHM191Ps for a ⁶⁰Co prompt peak of 1.18 Mequiv of γ rays. A 6×10^5 Bq positron source (²²Na) was deposited in a piece of Kapton, which was sandwiched between two films of the same sample in a chamber together. All PALS measurements were performed at room temperature. Every spectrum contained about 10⁶ counts. The resulting spectra were consistently modeled with a three-component fit with the computer program PATFIT88.¹⁴

RESULTS AND DISCUSSION

Mechanical properties

The impact strength of the cured EP samples containing different amounts of the rubber agent is summarized in Figure 1. The best performance was achieved with 5% rubber. Above this optimum rubber content, a fall in the impact strength was observed. Similar behavior has been reported for other rubber-modified EP systems and attributed to the agglomeration of rubber particles with an increase in the rubber concentration.¹⁵ Agglomerates

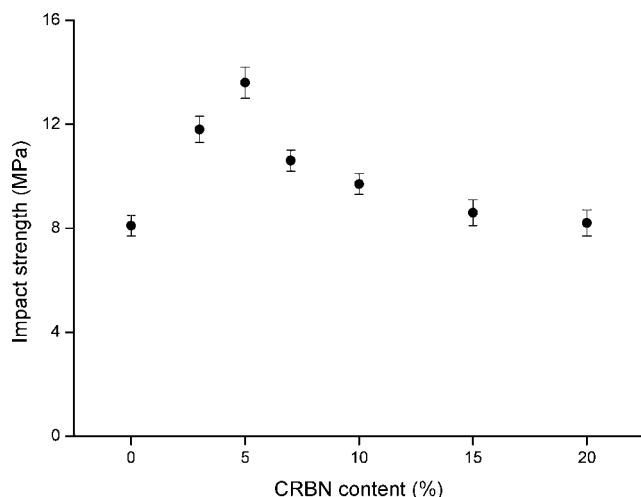


Figure 1 Impact strength of EP/CRBN.

act as defects and initiate catastrophic failure. Therefore, in this study, the CRBN content was fixed at 5%, and we mainly discuss the influences of different SiO₂ contents on the EP/CRBN (95/5) base.

The mechanical properties of EP/CRBN (95/5) containing different SiO₂ nanoparticle contents are summarized in Table I. The impact strength dropped with the further addition of SiO₂ nanoparticles in comparison with that of EP/CRBN (95/5). However, all the specimens showed a higher impact strength than pure EP. The modulus increased with the addition of SiO₂. In particular, in comparison with pure EP, EP/CRBN showed a lower flexural modulus, whereas the further addition of SiO₂ was very useful in upgrading the flexural modulus. With the addition of an appropriate amount of SiO₂ (2%), the nanocomposites could achieve the desired impact strength and modulus.

Morphology

To understand how the nanoparticles and rubber particles impacted the fracture behavior, an SEM examination of fractured EP/CRBN and EP/CRBN/SiO₂ was performed. Figure 2(a) shows a micrograph of a fractured unmodified EP sample. EP exhibited a smooth fracture surface. EP modified with CRBN showed a much rougher fracture surface. Furthermore, the micrograph did not show distinct separated particles of rubber, indicating good compatibility and strong interfacial adhesion between EP and CRBN. For the EP/CRBN/SiO₂ system, the fracture surface was rougher than that of pure EP too. There was no visible SiO₂ aggregate on the fracture surface. This means that nano-SiO₂ was well-dispersed in the composites.

To further confirm the phase behavior of the nanocomposites, the ultrathin film samples were first

treated with OsO₄. The double bond within the rubber phase could be dyed, and the rubber phase exhibited a gray zone in the TEM photographs. The SiO₂ nanoparticles exhibited a black zone in the TEM photographs. As shown in Figure 3, the nanocomposites showed a distinct three-phase system. The rubber particle size of the EP/CRBN system was less than 200 nm. The addition of SiO₂ did not have a significant effect on the phase dispersion of rubber particles in the EP matrix. The SiO₂ nanoparticles dispersed satisfactorily, with the size ranging from 50 to 300 nm.

The addition of SiO₂ nanoparticles did not have a synergism effect with CRBN on increasing the impact strength of the EP matrix. This result was different from the result reported by Balakrishnan et al.¹¹ They found a good synergism of a clay and an elastomer to the toughness of the EP matrix because the clay was easily absorbed to the rubber interface. In this study, as shown in Figure 3, the particles of SiO₂ and rubber dispersed in the EP matrix individually, and there was little interaction between them. Therefore, the addition of nano-SiO₂ mainly accomplished the function of reinforcing the EP matrix.

PALS analysis

Each spectrum was resolved into three components with the computer program PATFIT88. After the background and source correction were subtracted, the variance of fit was less than 1.2. The average radius (R) of the free-volume holes in a quantum mechanical model developed by Tao and Eldrup^{16,17} can be proposed as follows:

$$1/\tau_3 = 2\{1 - R/(R + 0.1656) + \sin[2\pi R/(R + 0.1656)]/2\pi\}$$

where τ_3 is O-Ps life time.

Figure 4 shows the curves of τ_3 for *o*-Ps as a function of the rubber content in the composites. The R values of the mean free-volume holes in these composites were calculated with the equation and are shown in Figure 5. The R value of EP/CRBN was a

TABLE I
Mechanical Properties of the Nanocomposites

EP/CRBN/SiO ₂	Impact strength (MPa)	Flexural modulus (MPa)
100/0/0	8.1 ± 0.4	2754
95/5/0	13.6 ± 0.6	2348
95/5/1	11.3 ± 0.2	3668
95/5/2	12.6 ± 0.4	3726
95/5/3	11.2 ± 0.3	3907
95/5/4	9.1 ± 0.2	3825
95/5/5	8.3 ± 0.4	3683

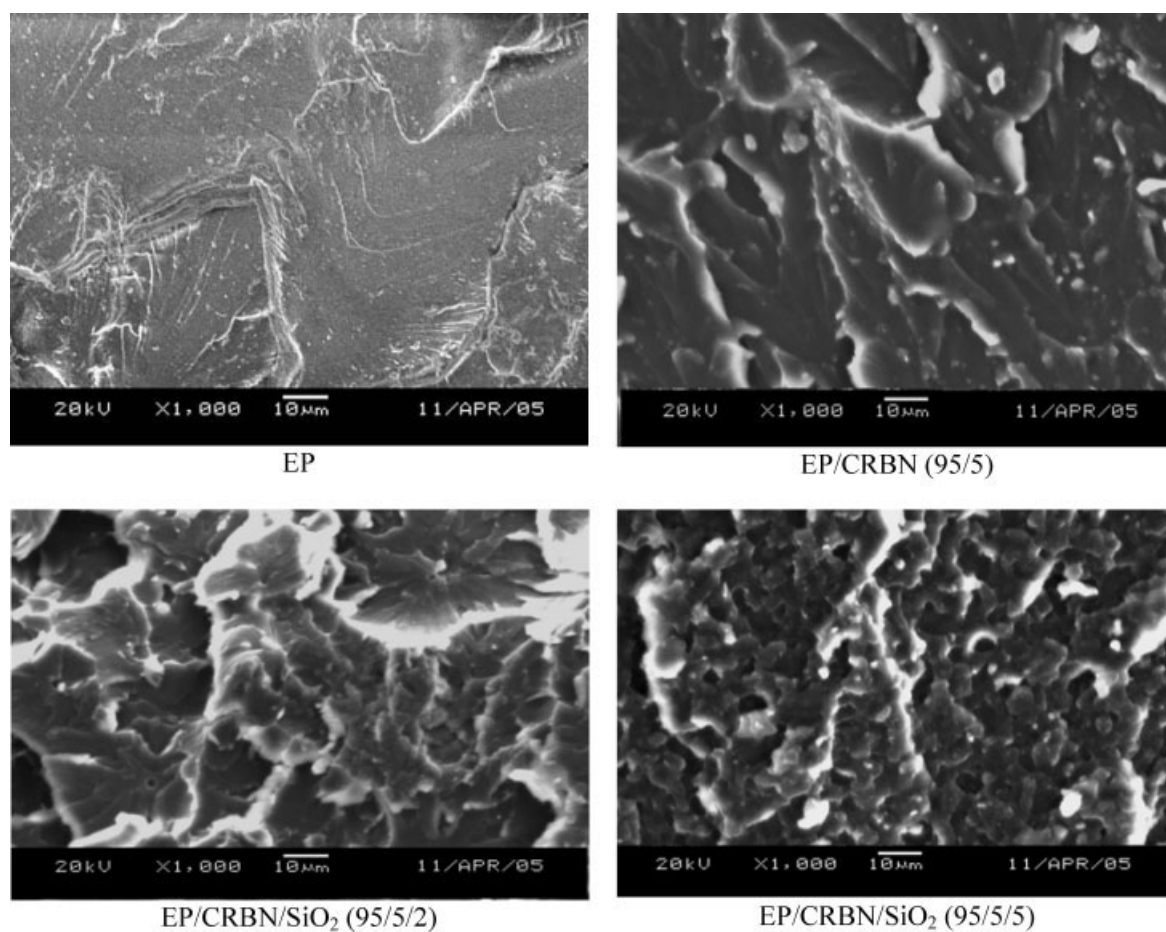


Figure 2 SEM images of the impact fracture surface.

bit larger than that of pure EP. Then, the R value of the nanocomposites dropped slowly with the addition of the SiO_2 nanoparticles. Previous studies^{12,18–20}

employing PALS to study polymer composites have found that the mean free-volume size of composites often decreases with respect to that of the unmodi-

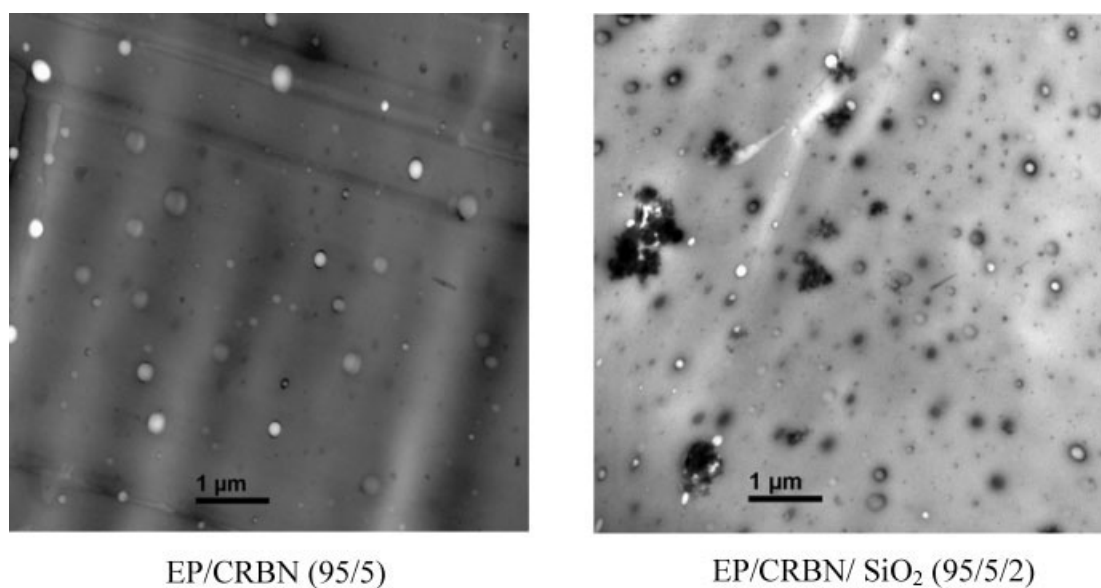


Figure 3 TEM images of the impact fracture surface (20,000 \times).

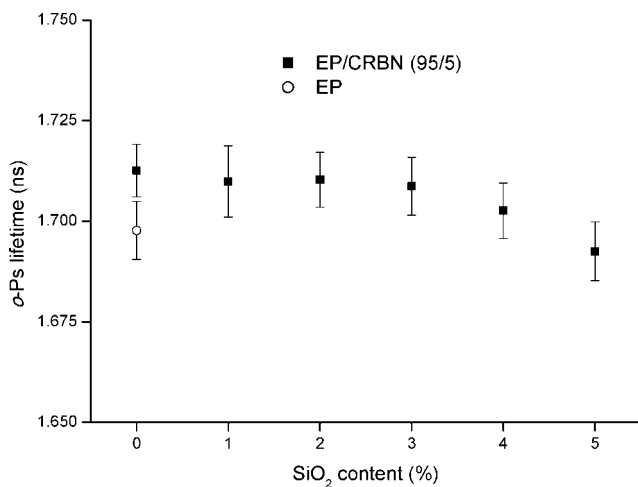


Figure 4 *o*-Ps lifetime of the nanocomposites as a function of the SiO₂ content.

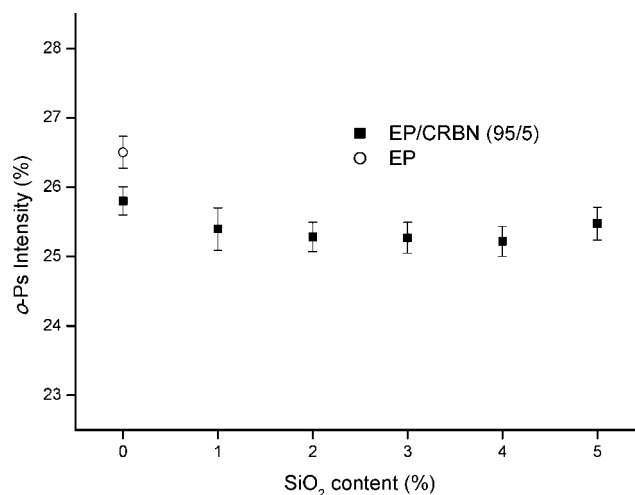


Figure 6 *o*-Ps intensity of the nanocomposites as a function of the SiO₂ content.

fied polymer as filler particles can occupy small holes of the matrix and then lead to the suppression of the local molecule motions. In this study, to discuss the influence of the rubber particles on the mean free-volume size of the composites, two opposite effect should be considered. On the one hand, the well-dispersed nanosized rubber particles tended to occupy small holes in the EP matrix, resulting in a reduction in the mean free-volume size of the composites. On the other hand, the size of the free-volume holes within the rubber phase could not be ignored. Generally, the rubber phase is much looser than the crosslinked EP matrix. The size of the free-volume holes within the rubber phase is larger than that of EP, and this results in an increasing effect on the mean free-volume size of the composites. The larger R value of EP/CRBN versus that of pure EP was the integrative result of these two effects.

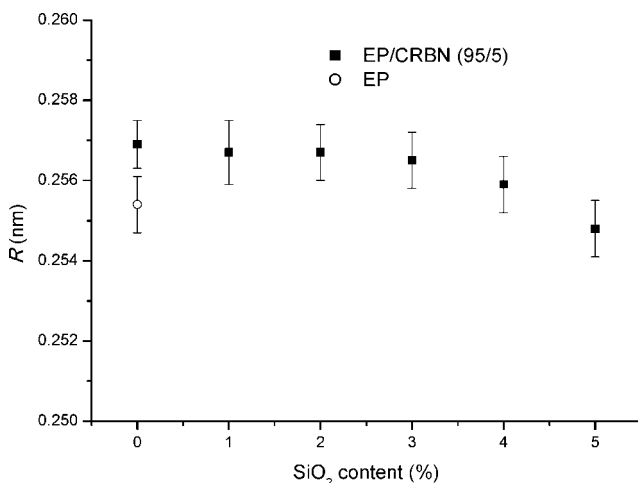


Figure 5 Total free-volume size (R) of the nanocomposites as a function of the SiO₂ content.

Actually, the rubber phase was more precisely a rubber-rich phase that retained some EP molecules. Within the rubber-rich phase, EP molecules could easily enter the free-volume hole of CRBN because the carboxyl groups of CRBN were capable of reacting with EP. This led to a segmentation effect on the free-volume hole of the rubber-rich phase. Thus, this is another factor to be considered when we consider the fact that the changes in the R value between EP/CRBN (95/5) and pure EP were not significant (from 0.2554 to 0.2569 nm). The results showed that strong interfacial interactions between the two phases occurred, and this was necessary for efficient stress transfer between the rubber particles and epoxy matrix.

In the case of the rigid SiO₂ nanoparticles, we could ignore the contribution of the *o*-Ps formation in the filler.²¹ For its uniform dispersion, it occupied small holes in the EP matrix and acted as a bridge to make more molecules interconnected, resulting in a reduction in the total free volume and increase in the rigidity of the composites. Figure 6 shows the *o*-Ps intensity of the composites. The nanocomposites showed lower *o*-Ps intensity than pure EP. The results showed that the free-volume concentration in the nanocomposites was less than that of pure EP. The introduction of a small amount of nanoparticles (both rubber and SiO₂) into EP led to the formation of interactions between the EP and nanoparticles. The interactions restricted the segment motion and the mobilization of EP chains and then reduced the free-volume concentration in the amorphous region of EP.

CONCLUSIONS

The effects of SiO₂ nanoparticles on the performance of CRBN-modified EP nanocomposites were studied.

With the addition of an appropriate amount of SiO₂ (2%) to EP/CRBN (95/5), the nanocomposites could achieve the desired impact strength and modulus. The nanocomposites showed a three-phase system; both the rubber particles and SiO₂ nanoparticles showed a uniform dispersion in the EP matrix, with their phases all nanosized. A good correlation between *R* and the mechanical properties was found. The introduction of a small amount of nanoparticles (both rubber and SiO₂) into EP led to the formation of interactions between the EP and nanoparticles. The interactions restricted the segment motion and the mobilization of EP chains and then reduced the free-volume concentration in the amorphous region of EP. The larger *R* value of EP/CRBN versus that of pure EP was mainly attributed to the contribution of the larger size of the free-volume holes within the rubber phase.

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