

# Preparation of TiO<sub>2</sub> Epoxy Nanocomposites by Ultrasonic Dispersion and Resulting Properties

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**ABSTRACT:** Nanocomposites gained more and more importance in the last few years because of their improved performance over the neat polymer matrix, that is, toughness and stiffness can be enhanced simultaneously by the addition of nanoparticles. However, the dispersion of these particles in the matrix remains a big challenge. In this study, two types of TiO<sub>2</sub> nanoparticles were dispersed in two different epoxy resins by means of ultrasound. The particle size development in dependence on the dispersion time was investigated by dynamic light scattering for the

different material systems. Furthermore, the influence of the viscosity on the sonication process' efficiency was analyzed. The resulting nanocomposites were tested for fracture and Charpy toughness. SEM images revealed that the improved fracture toughness properties are correlated to a rougher fracture surface, whose formation dissipates more energy. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1906–1911, 2012

**Key words:** nanocomposites; thermosets; ultrasonic dispersion; toughness

## INTRODUCTION

Nanocomposites enable completely new possibilities for the design of new materials, because they allow the solution of the strength-toughness paradigm. To say that by the insertion of nanoparticles into a polymer matrix, the strength and toughness can be enhanced simultaneously, that is not possible to same degree for composites with microscale reinforcements.<sup>1,2</sup>

However, the dispersion of the nanofillers in the polymer matrix leading to a big particle-matrix interface, which is indispensable for the improvement of the materials properties, remains a big challenge. Usually, this aim is pursued by applying mechanical dispersion techniques such as a dissolver, a torus mill, or a three roll calendar.<sup>3,4</sup> In the last years, sonication proofed to be an adequate alternative technique for the dispersion of nanoparticles.<sup>5,6</sup> However, most studies were carried out in aqueous solutions,<sup>7</sup> and there is only very few experiences for the ultrasonic dispersion of particles in high-viscosity liquids such as epoxy resin.<sup>8,9</sup> As a consequence, the reported processing conditions reported

by different researchers differ very much. Xu et al.<sup>9</sup> observed that 5 min of ultrasonic dispersion of nanoscale graphite in epoxy resin lead to enhanced mechanical properties, whereas 20 min of sonication caused deterioration. Similar results were reported by West and Malhotra,<sup>8</sup> that is, the mechanical properties of Al<sub>2</sub>O<sub>3</sub>-epoxy nanocomposites increased after 5 min of ultrasonic dispersion, whereas only 10 min of sonication were sufficient to initiate degradation of the matrix, resulting in a decrease of the properties profile. Chatterjee and Islam<sup>10</sup> found out that the optimum sonication time of nanoscale TiO<sub>2</sub> in epoxy resin is 30 min. Also Rodgers et al.<sup>11</sup> used this same ultrasonic processing time to disperse SiC nanoparticles. By contrast, Yasmin et al. sonicated expanded graphite in epoxy resin for several hours.<sup>12</sup> Consequently, there is the need for a systematic investigation of the influence of the sonication parameters in the dispersion process. The first results of such an investigation were presented in Refs. 6 and 13.

In this study, titanium dioxide (TiO<sub>2</sub>) nanoparticles were inserted in epoxy resins and dispersed by means of ultrasonic processing. The influence of the viscosity of the prepolymer mixture containing particles and resin on the dispersion quality was evaluated by varying the filler content of the mixture. Furthermore, the dispersion behavior of two different epoxy resins and their influence on the final particle size were investigated. Finally,

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**TABLE I**  
**Characteristics of the Epoxy Resins and the Curing Agent**

Name	Substance	Chemical structure	Ratio
Epilox A19-03	Diglycidyl Ether of Bisphenol A		314 g
Renlam LY 5210	<i>N,N,N',N'</i> -Tetraglycidyl-4,4'-diaminodi-phenyl-methan (70–82%), 1,4-Butandiol-diglycidyl-ether (18–30%)		189 g
Aradur HY 2954	Cyclo-aliphatic amine hardener		100 g

nanocomposite samples with varied particle content were manufactured to perform toughness tests. Fracture surfaces were analyzed by SEM imaging.

#### PRINCIPLES OF ULTRASONIC DISPERSION

Ultrasound has various applications in materials processing. It can be used for the aggregation of particles,<sup>14,15</sup> the separation of particle agglomerates,<sup>16</sup> and for the polymerization of thermoplastic polymers.<sup>17,18</sup> All these effects are enabled by the phenomenon of cavitation. During the propagation of ultrasonic waves in a liquid, a periodic change of positive and negative pressure cycles (relative to the equilibrium hydrostatic pressure of the liquid) takes place. In the high pressure phase, the liquid is compressed, and in the low pressure, phase the local pressure can decrease below the vapor pressure of the fluid and, thus, cavitation occurs. Transient cavitation bubbles can grow during several cycles until reaching a critical size leading to their collapse, which is accompanied by locally extreme conditions such as very high pressure and temperatures.<sup>19</sup> These so-called hot spots can induce splitting up of nanoparticle agglomerates.<sup>20</sup> Gradients near to the collapse may result in different forces on particle agglomerates, such as tensile and shear forces, leading to a separation of the nanoparticles.

#### EXPERIMENTAL APPROACH

In the frame of this study, nanocomposites containing epoxy resin reinforced by titanium dioxide (TiO<sub>2</sub>) nanoparticles with various filler contents were manufactured.

As matrix material, the commercially available bisphenole-A epoxy resin Epilox A 19-03 provided by the company Leuna Harze GmbH and referred to as epoxy resin 1 and the multifunctional resin Renlam

LY5210 provided by Huntsman Advanced Materials BVBA and referred to as epoxy resin 2 were used. The characteristics for the two epoxy resins as well as for the curing agent Aradur HY2954 from Huntsman Advanced Materials BVBA are listed in Table I.

TiO<sub>2</sub> nanoparticles Hombitec RM300 and RM400 with particle diameters of about 15 and 10 nm, respectively, from Sachtleben Chemie GmbH were added to the liquid epoxy resin. For the preparation of nanocomposite samples, the curing agent was added to the prepolymer of particles and resin. The weight mixing ratio of resin and hardener was 100 : 32 for epoxy resin 1 and 100 : 53 for epoxy resin 2 as can be seen from Table I.

Premixing of nanoparticles (between 7 and 14 vol %) and 400-mL epoxy resin was done with a laboratory mixing device (IKA-Agitator, RW20) until a homogeneous suspension was achieved. Before dispersion, the mixture was degassed by means of a dissolver (VMA Getzmann, AE01-10M) to remove entrapped air. The dispersion process was carried out as described in Refs. 6 and 13 using a high intensity sonotrode from Branson PG with a frequency of 20 kHz and a maximum amplitude (from tip to tip) of 130 nm. The ultrasonic horn was immersed into a vessel containing the liquid prepolymer, which, on its part, was immersed in an ice water bath for cooling. Because of the limited efficiency of this cooling method, pauses for sample taking for particle size measurements were extended to cool down the mixture again below 70°C before continuation of dispersion.

Dispersion quality of the prepolymer was examined by dynamic light scattering using a particle size analyzer (Nanotracs). Therefore, samples of the liquid mixture for different dispersion times and conditions were taken and diluted in dichloromethane before the particle size analysis. In the diagrams, the value  $x_{50}$  of the volume distribution of the particles is displayed, indicating that 50% by volume (50 vol %) of

the particles in the mixture are smaller or equal to the displayed value.

The viscosity of the prepolymer containing TiO<sub>2</sub> nanoparticles and epoxy resin was measured by means of a plate rheometer (Rheometric Scientific). The following measuring conditions were applied: torsion of 20% with frequency 10 rad/s, heating from 27 to 120°C with a rate of 5 K/min, and data capture for every 10 s.

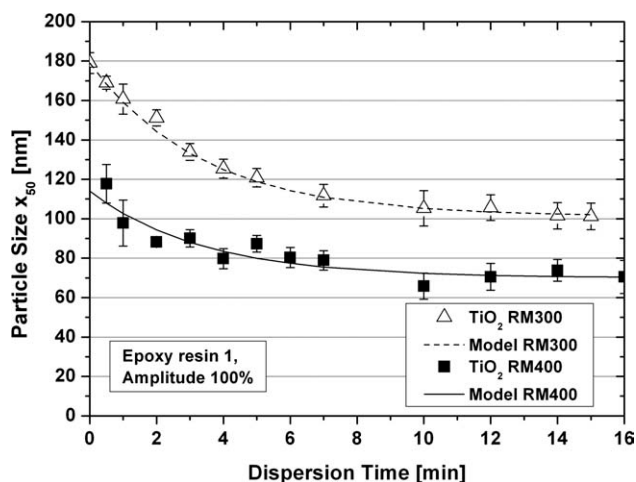
Nanocomposite specimens with varied filler content were manufactured from mixtures sonicated for 15 min at amplitude 100%, because these are the optimum processing parameters leading to good dispersion results without degradation of the resin as shown in Ref. 13. Samples were prepared by adding epoxy resin to dilute the prepolymer to the desired particle content. After degassing this mixture by the dissolver, the curing agent was stirred in for about 15 min by means of the laboratory agitator, and the mass was cast into moulds and cured thermally for 16 h at 70°C and subsequently for 8 h at 120°C.

For fracture toughness and Charpy toughness tests samples with TiO<sub>2</sub> nanoparticles of 0 (neat epoxy resin), 2, 5, and 10 vol % were used. Charpy impact test was done according to DIN EN ISO 179-1, and compact tension specimens for fracture toughness analysis were tested as specified in the ASTM E 399 testing standard. Neat epoxy samples for comparison were without sonication treatment.

SEM pictures of the fracture surfaces of fracture toughness samples were carried out using a Zeiss device. To avoid charging of the surfaces, the samples were preliminary evaporated with carbon.

## RESULTS

A good dispersion of the nanoparticles in the polymer matrix is an important prerequisite for obtaining an improved properties profile of the resulting nanocomposites. Therefore, the influence of the application of two different nanoscale TiO<sub>2</sub> fillers RM300 and RM400 with slightly different primary particle sizes of 15 and 10 nm, respectively, on the dispersion quality was investigated. Figure 1 shows the development of the particle size  $x_{50}$  in dependence on the ultrasonic dispersion time. The dispersion behavior reveals to be the same for both fillers and the final particle size, which can not be undercut with these dispersion conditions, is reached between 10 and 15 min of sonication. However, for TiO<sub>2</sub> RM400, a final particle size  $x_{50}$  of about 70 nm could be reached, whereas the attained  $x_{50}$  value for TiO<sub>2</sub> RM300 was only about 100 nm. In both the cases, the power input of the sonotrode was insufficient to break up all particle agglomerates, and thus, the primary particle size provided by the manufacturer could not be attained. In addition, a previous study



**Figure 1** Development of the particle size  $x_{50}$  during dispersion in epoxy resin 1 for the two different nanoparticles RM300 and RM400.

revealed that there are also crystal bonded aggregates bigger than the primary particles, which cannot be broken up by conventional dispersion techniques.<sup>13</sup>

The sonication induced particle size reduction can be described in both the cases by the model developed in Ref. 6:

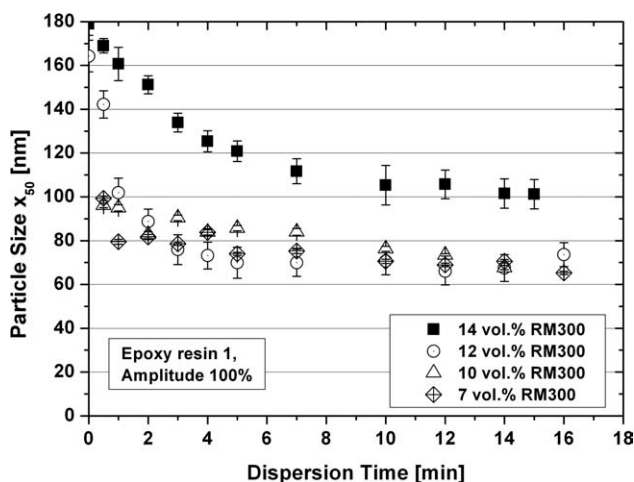
$$X(t) = \left[ X_A - e^{-\frac{a^* \times P}{s \times V_T}} - X_P \right] \times e^{-\frac{k \times V_{\text{eff}} \times t}{V_T}} + e^{-\frac{a^* \times P}{s \times V_T}} + X_P \quad (1)$$

$X_A$  is the initial and  $X_P$  is the primary particle size,  $V_{\text{eff}}$  is the effective volume of dispersion,  $V_T$  is the total sonicated volume of the mixture,  $P$  is the power input into the mixture,  $\sigma$  is the strength of the nanoparticle agglomerates,  $a^*$  is a transference constant describing the transfer of the power to the agglomerates, and  $k$  is a (reciprocal) time constant, which describes the circulation in the mixture. As described in Ref. 6, the maximum power input at amplitude 100% was determined calorimetrically to be 219 W. By the help of the ultrasonic dispersion model (1), it can be calculated that the power input necessary for reaching the primary particle size  $X_P$  would be:

$$P_{X_P} = 315 \text{ W.}$$

This required power input is about 44% higher as the one that could be realized by the sonotrode used in this study. However, the requirement therefore is that all agglomerates are solely bonded by van der Waals forces. As shown in Ref. 13, this is not always true. In the nanocomposite, crystal bonded aggregates are also encountered, which cannot be broken up by conventional dispersion techniques.

As the viscosity of a liquid affects the cavitation threshold during sonication, the influence of the viscosity on the dispersion quality was evaluated.



**Figure 2** Dependence of the particle size  $x_{50}$  on the filler content/viscosity for RM300 in epoxy resin 1.

Different viscosities of prepolymers containing TiO<sub>2</sub> RM300 and epoxy resin 1 were obtained by varying the particle content from 7 to 14 vol %. Figure 2 shows the development of the particle size  $x_{50}$  in dependence on the sonication time for nanoparticle contents between 7 and 14 vol %. The corresponding viscosities at 80°C (as this is the average temperature during our ultrasonic dispersion process) are listed in Table II, together with the final achieved particle sizes. (For comparison, the viscosity of the neat epoxy resin was measured as well.) It can be seen that by reducing the viscosity from 1.14 Pa s (14 vol % RM300) to 0.50 Pa s (12 vol % RM300), the ultrasonic dispersion process seems to be more efficient, because the final particle size is reduced by about 30 nm. This could be explained by a reduction of cavitation threshold due to the viscosity decrease. Thus, more cavitation bubbles can form, which results in a better dispersion.

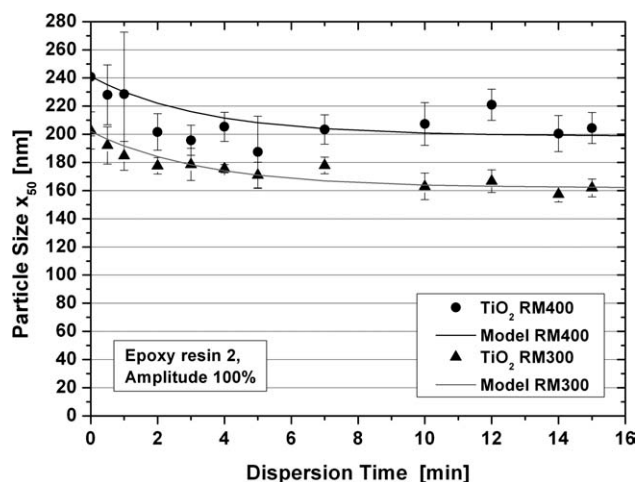
When reducing the viscosity further up to 0.11 Pa s (7 vol % RM300), there is no significant improvement in the dispersion quality. This could be ascribed to the fact that with decreasing viscosity there are less shear forces in a liquid. Thus, agglomerate breakage due to shear forces is less efficient. This negative effect seems to superimpose the positive effect of the reduced cavitation threshold.

To evaluate the influence of the prepolymer matrix on the ultrasonic dispersion a second multifunc-

**TABLE II**

**Correlation between Particle Content, Viscosity, and Final Particle Size  $x_{50}$  for TiO<sub>2</sub> RM300 in Epoxy Resin 1**

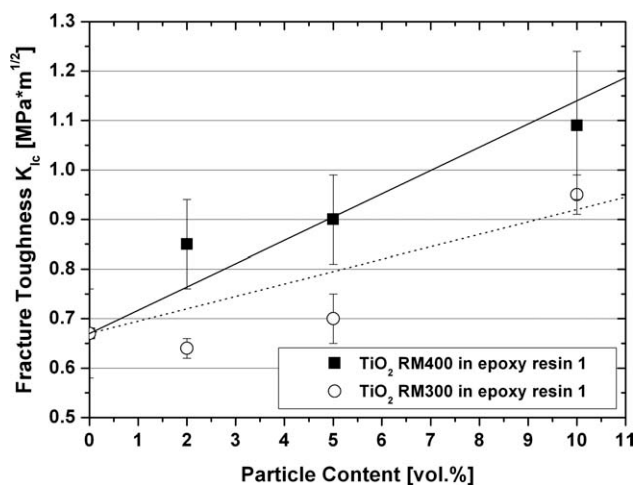
Particle content (vol %)	14	12	10	7	0 (neat resin)
Viscosity at 80 (Pa s)	1.14	0.50	0.42	0.11	0.02
Final particle size $x_{50}$ (nm)	100	70	70	70	-



**Figure 3** Development of the particle size  $x_{50}$  during dispersion in epoxy resin 2 for the two different nanoparticles RM300 and RM400.

tional epoxy resin, but with approximately the same viscosity at 80°C of about 0.02 Pa s was used, referred to here afterward as resin 2. However, when introducing TiO<sub>2</sub> nanoparticles, there was a strong increase in viscosity up to 8 Pa s for RM300 and up to 10 Pa s for RM400, so that only maximum particle contents of 8.5 vol % TiO<sub>2</sub> could be achieved. Figure 3 shows the development of the particle size  $x_{50}$  in dependence on the sonication time for dispersion of the two nanoparticles in epoxy resin 2. For TiO<sub>2</sub> RM300, a final particle size of about 180 nm and for TiO<sub>2</sub> RM400 of about 200 nm could be attained. It reveals that these final achievable particle sizes are much bigger than the ones attained when dispersing in epoxy resin 1. This supports the thesis that up to a certain viscosity ultrasonic dispersion is more efficient for lower viscosities than for high ones. In this context, it has to be noted that the final particle size for RM400 in epoxy resin 2 is higher than the one for RM300, while this was converse for epoxy resin 1. This is another indication for the inferior dispersion quality at higher viscosities. For this dispersion, process the ultrasonic dispersion model also fits, as can be seen from Figure 3.

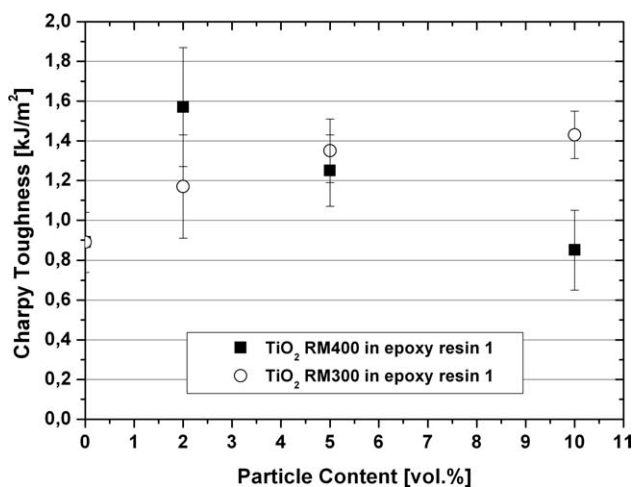
After ultrasonic dispersion of TiO<sub>2</sub> nanoparticles in epoxy resin nanocomposite samples were prepared by adding curing agent as described in the Experimental Approach section. For these samples, fracture and Charpy toughness tests were performed. In Figure 4, the fracture toughness  $K_{Ic}$  in dependence on the particle content for TiO<sub>2</sub> RM300 and RM400 in epoxy resin 1 is displayed. There seems to be a linear increase in toughness with rising filler content. At 10 vol % of TiO<sub>2</sub>, there is an increase in toughness of about 60% for RM400 and of about 40% for RM300. This is consistent with results from Ref. 21, where an increase of fracture toughness of BaSO<sub>4</sub> in epoxy resin with rising particle content up to 1.1 MPa m<sup>1/2</sup> was observed.



**Figure 4** Fracture toughness in dependence on the particle content for RM300 and RM400 in epoxy resin 1.

In Table III, fracture toughness for nanocomposites with epoxy resin 1 and 2 is compared. For the neat epoxy resin, the fracture toughness is equal and also for the nanocomposite samples with 5 vol % of RM300. For RM400, there is a difference and the nanocomposites based on epoxy resin 1 show a better performance. These results are surprising, because the dispersion quality was much worse for epoxy resin 2. Thus, one would expect considerable inferior mechanical properties for the nanocomposites based on this resin. It seems that the role of dispersion quality is not that important in this case. This might be ascribed to a good adhesion between nanoparticles and epoxy matrix. Thus, agglomerates do not necessarily act as weak points, where crack growing initiates.

Figure 5 shows the Charpy toughness of the nanocomposite samples for different filler contents in epoxy resin 1. For RM400, the Charpy toughness increases for low filler contents up to 76% over the value of the neat epoxy resin. When increasing the particle content up to 10 vol %  $\text{TiO}_2$ , the toughness decreases again to the value of the neat resin. This is a common behavior for nanocomposites and was also observed by Zhang et al.<sup>22</sup> and by Chen et al.,<sup>23</sup> who explain it by the increasing importance of the agglomerates in the material giving rise to high stress concentrations. It seems that this dynamic Charpy test is more sensitive to nanoparticle agglomeration than the  $K_{Ic}$  toughness, which is measured under quasi-static conditions. By contrast, for RM300 the Charpy toughness increases with increasing filler content, as



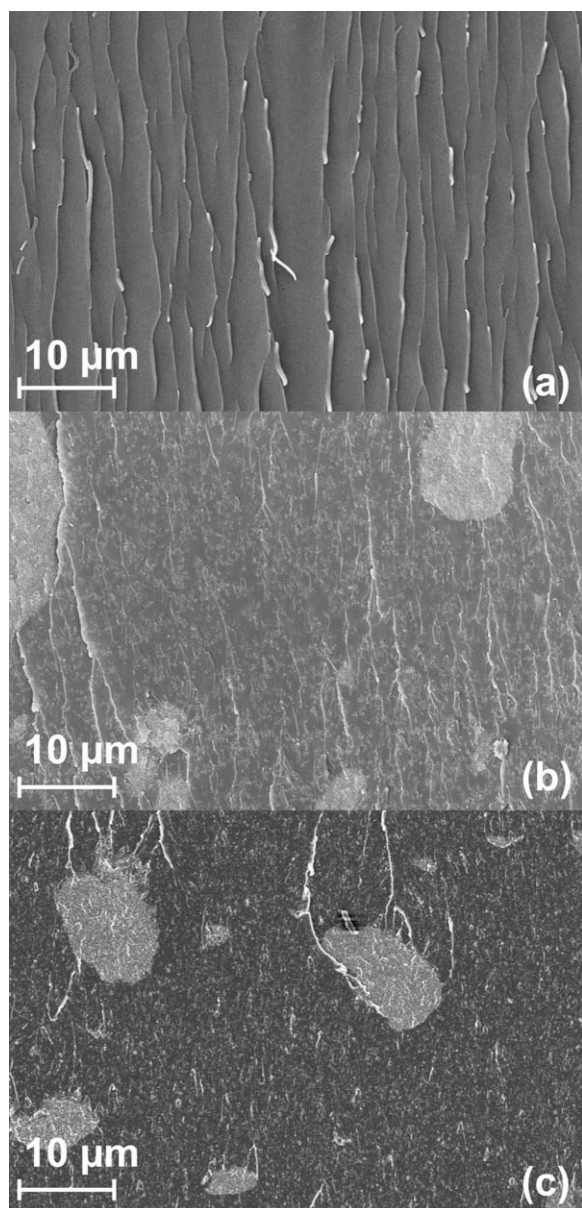
**Figure 5** Charpy toughness in dependence on the particle content for RM300 and RM400 in epoxy resin 1

observed for the fracture toughness  $K_{Ic}$ , too. The enhancement for a particle content of 10 vol % is 60% over the value of the neat epoxy resin. This correlates to the results from Table II that the dispersion quality seems to be less important for RM300 and an increasing number of agglomerates with increasing filler content does not affect the mechanical behavior. This behavior might be ascribed to a different chemical surface treatment of the nanoparticles RM300 and RM400 influencing the particle matrix bonding. Unfortunately, there is no information on this difference available from the manufacturer; however, the different color of the particles supports this assumption.

Figure 6 shows SEM pictures of the fracture surfaces after fracture toughness test. The neat epoxy resin in Figure 6(a) possesses a relatively smooth surface indicating brittle fracture. The nanocomposites of epoxy resins 1 and 2 with 5 vol %  $\text{TiO}_2$  RM300 in Figure 6(b,c) show a significantly rougher surface due to the well dispersed reinforcing particles. To create this bigger fracture surface, more energy during fracture is required, which results in improved fracture toughness properties for these composites. However, in both the cases, there are still agglomerates. These agglomerates seem to be larger for the nanocomposites based on epoxy resin 2, which is consistent with particle size analysis, because dispersion quality in epoxy resin 2 was worse than in resin 1. Nevertheless, the bonding between the agglomerates and the matrix seems to be quite well, indicating that the agglomerates are

**TABLE III**  
Fracture Toughness  $K_{Ic}$  for the Two Nanoparticles  $\text{TiO}_2$  RM300 and RM400 in Epoxy ResinS 1 and 2

	RM300 in epoxy resin 1	RM300 in epoxy resin 2	RM400 in epoxy resin 1	RM400 in epoxy resin 2
$K_{Ic}$ for 0 vol % $\text{TiO}_2$ ( $\text{MPa m}^{1/2}$ )	0.67	0.68	0.67	0.68
$K_{Ic}$ for 5 vol % $\text{TiO}_2$ ( $\text{MPa m}^{1/2}$ )	0.70	0.73	0.90	0.80



**Figure 6** SEM pictures of fracture toughness samples' fracture surfaces for (a) neat epoxy resin 2, (b) the nanocomposite with 5 vol % of RM300 in epoxy resin 2 and (c) the nanocomposite with 5 vol % of RM300 in epoxy resin 1

not necessarily acting as weak points in the nanocomposites, because the sensitivity of the mechanical properties also seems to be influenced by the type of loading, that is, static or dynamic.

### CONCLUSIONS

In this study, TiO<sub>2</sub> RM300 and RM400 nanoparticles could be successfully dispersed in epoxy resin by means of ultrasound and the resulting nanocomposites showed an enhanced performance over the neat polymer.

It was shown that decreasing the nanoparticle-polymer mixture's viscosity up to a certain degree

could make the dispersion process more efficient, leading to smaller particle sizes.

Nanocomposite samples manufactured after sonication showed enhanced fracture and Charpy toughness. The fracture toughness increased with increasing nanoparticle content. Even though the dispersion quality was worse for the second employed epoxy resin, fracture toughness values at 5 vol % TiO<sub>2</sub> were nearly the same.

Charpy toughness showed an increase with rising filler content for RM300 and a maximum toughness at small particle contents for RM400.

SEM pictures revealed that the insertion of TiO<sub>2</sub> nanoparticles into the polymer led to a rougher fracture surface, accompanied by higher energy absorption during failure than for the neat epoxy resin.

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