

PREPARATION AND CHARACTERISATION OF EPOXY/ALUMINA POLYMER NANOCOMPOSITES

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Abstract

The effect of adding nanosized alumina fillers of both fibrous and spherical shapes to an epoxy polymer has been investigated. The alumina was dispersed in the epoxy hardener using a sonication technique. A high degree of dispersion could not be obtained and agglomerates were observed in the nanocomposites. Still, mechanical testing revealed that the stiffness of the epoxy polymer could be significantly improved using only small amounts of alumina, even when a significant part of the filler was in an agglomerated state.

1 Introduction

Extensive research is being conducted on polymer composites reinforced with rigid nanoparticles. Engineering polymers, such as epoxy, have many excellent material properties but they are, however, generally brittle materials. Therefore, to fully exploit the properties, epoxy polymers often need to be reinforced by adding either micro- or nanosized particles. Inorganic particles have a much higher stiffness than the polymer matrix and may improve the stiffness, and other properties of the materials [1]. A range of inorganic nanoparticles may be used as reinforcements, including carbon nanotubes [2-4], nanofibres [4], clay [4;5], and silica [6;7]. According to Fu *et al.* [1], the inorganic fillers can modify the stiffness, strength and toughness of polymers. In general, the mechanical properties of particulate-polymer composites depend primarily on the particle size, the particle/matrix interface adhesion and the particle loading. The stiffness depends significantly on particle loading, not particle/matrix adhesion, while the strength and toughness are strongly affected by all three factors, particularly the particle/matrix adhesion and thus the stress transfer between the particles and the matrix.

The main difference between using nanosized fillers, compared to microsized fillers, is the much higher specific surface area of the nanomaterials. Below a critical particle size, the composite stiffness is greatly enhanced due to the effect of the particle size, probably caused by the much larger surface areas imparting a “nano-effect” [1;4;5]. Here, the polymer interphase surrounding the particles gradually dominate the material properties leading to, for example, changes in the glass transition temperature of the polymer [5;8].

Nevertheless, a good dispersion of the nanoparticles in the polymer is usually regarded as a prerequisite to fully exploit their potential benefits. The presence of agglomerates will limit

the effect of adding the nano-filler. Also, Nairn [9] suggests that the interface may be more important for nano-sized fillers than for larger fillers, and that effective reinforcement is dependent on interfacial compatibility. Nairn also suggests that only modest reinforcement effects can be expected at low volume fractions.

The use of nanosized alumina (Al_2O_3) to improve the mechanical properties of epoxy polymers has to some extent been studied [10-15]. Alumina has a tensile modulus of 386 GPa, and should therefore have the potential to significantly stiffen epoxy polymers, which typically have a tensile modulus of around 2.5-3.5 GPa. Brown and Ellyin [10;11] investigated the mechanical behaviour of epoxy reinforced with alumina nanofillers of different shapes. The alumina was dispersed into the polymer by mixing it into the hardener using sonication. Both the tensile stiffness and strength of the epoxy was improved by adding small volume fractions of nanofiller. The reinforcing effect was highest for nanofibres, compared to spherical nanoparticles, and the tensile stiffness increased by up to 19% by adding less than 1.5% by volume of the nanofibre. Similar studies were conducted by Miyagawa *et al.* [12] and Yang *et al.* [14], yielding similar conclusions. The tensile strength and elastic modulus was increased by up to 37% and 60%, respectively, by adding 1 wt% of fibrous alumina. Positive effects on the composite tensile strength after silane surface modification of the alumina has also been observed [10;11].

In this study, we have investigated the dispersion and reinforcing effect of fibrous (whiskers) and spherical nanosized alumina on an epoxy polymer. The alumina is originally in a highly agglomerated state, and a sonication technique was used for dispersion. Both fibrous and spherical alumina was investigated to see if there was any effect of the shape of the filler on the properties of the nanocomposites. The mechanical and thermal properties were determined using tensile testing and dynamic mechanical analysis (DMA). Electron microscopy was conducted to investigate the microstructure of the materials, and to be able to correlate the microstructure to the mechanical properties. The alumina was also surface modified using a silane to investigate whether this could improve the strength of the alumina/polymer interface and thereby improve the properties of the composites.

2 Experimental

2.1 Materials

The epoxy polymer investigated in this work was Araldite LY 556/Aradur 917/Accelerator DY 070 from Huntsman. LY 556 is a bisphenol A based epoxy resin, Aradur 917 is an anhydride hardener and DY 070 is an imidazole accelerator.

Two different types of nanosized alumina (aluminium oxide, Al_2O_3) fillers were employed: (1) Fibrous whiskers and (2) spherical particles. The whiskers had a diameter of 2-4 nm and a length of 200-400 nm. The supplier estimated the aspect ratio to be >100. The spherical particles had a diameter of <50 nm and a surface area of >40 m²/g. Pure alumina has a density of 3.96 g/cm³ [16]. Both types of alumina were delivered as dry powders by Sigma Aldrich. Furthermore, γ -glycidyoxypropyltrimethoxysilane (GPS) was used for surface modification of the alumina, and was delivered by Sigma Aldrich.

2.2 Nanocomposite preparation

Neat epoxy polymer specimens were prepared by first mixing the epoxy resin, the anhydride hardener and imidazole accelerator at the ratio 100:90:1 by weight. The blend was stirred manually, and then cast in metal moulds that had been coated with a release agent. The processing schedule was gelation for 4 hours at 80°C and post-curing for 8 hours at 140°C.

The alumina was dispersed in the anhydride hardener of the epoxy polymer by sonication [17]. A bath sonicator, Sonorex Digital 10 P, Bandelin, was run at maximum power, and the temperature of the water bath was kept constant at 50°C. Epoxy and accelerator were then added, the mixture was rigorously stirred, and finally cast in metal moulds and cured. Two different sets of nanocomposite specimens were prepared: (1) Nanocomposites reinforced with whiskers were prepared for tensile testing by casting in cylindrical moulds. The sonication time was 1 hour. Sediments of agglomerated alumina were observed at the bottom of the moulds. (2) Nanocomposites reinforced with whiskers or spherical particles were prepared for DMA analysis by casting in rectangular moulds. The sonication time here was 5 hours. Also, only the fraction of the alumina/hardener mixture that did not contain sedimented alumina agglomerates was used to prepare the nanocomposites.

The alumina fillers were surface modified using GPS [18-20]. This was done by first adding 10 g of alumina filler to 100 ml toluene. The mixture was sonicated for 5 hours, after which the GPS was added at a ratio of 1:1.5 with respect to the amount of alumina. The solution was refluxed for 15 hours, and the filler was repeatedly centrifuged and washed with fresh toluene, before drying in an oven at 110°C for 3 hours. Nanocomposites reinforced with the surface modified alumina fillers were prepared.

2.3 Characterisation

Scanning electron microscopy (SEM) was performed on a Hitachi SU6600 Schottky Field Emission Analytical SEM. The specimens were not coated prior to imaging. The secondary electrons detector was employed to obtain the micrographs.

Tensile testing was conducted on rod-type specimens, as illustrated in Figure 1, employing a MTS Material Testing Systems 810 testing machine. The specimens were prepared by machining of cylindrical rods of the nanocomposites, and tested at a crosshead speed of 5.0 mm/min. A clip-gage extensometer was used for recording the strain.

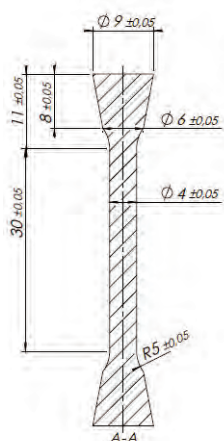


Figure 1. The cylindrical shaped test specimen used for tensile testing of the nanocomposites.

DMA was performed on a DMA 2980 Dynamic Mechanical Analyzer from TA Instruments. Rectangular specimens with the approximate dimensions 60 mm × 10 mm × 3 mm were employed. The analysis was conducted with a low friction 3-point bending clamp, which had a specimen free length of 50 mm. The oscillation frequency was 1 Hz, and the heating rate was 5°C/min. The value of the storage modulus, E' , was measured at a temperature of 30°C,

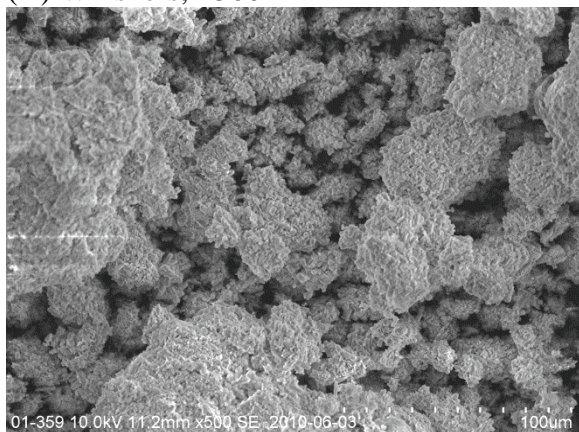
and the value of the glass transition temperature, T_g , of the epoxy polymer is reported as the peak value of the loss modulus, E'' .

3 Results and discussion

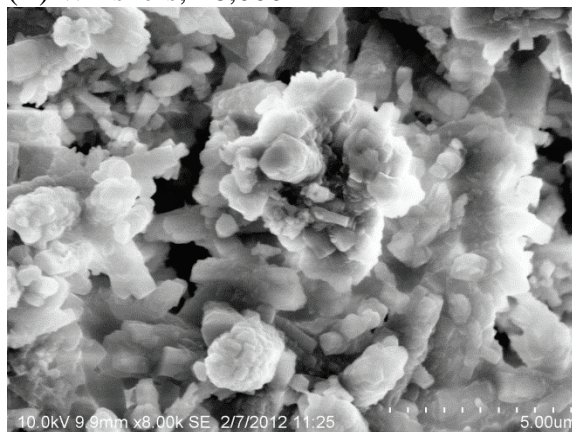
3.1 Alumina nanofillers

Scanning electron micrographs of the two as-received alumina fillers employed in this study are shown in Figure 2, revealing that the fillers reside in a highly agglomerated state. The resolution of the micrographs is too low to detect individual whiskers or particles, but the agglomeration indicates that relatively strong intermolecular forces are acting between the whiskers/particles. This will represent a challenge with respect to the dispersion process of the alumina, both with respect to dispersion into a given solvent and into a polymer matrix, as high forces are required to separate the particles from each another. In fact, difficulties to obtain a high degree of dispersion were observed in this study, as will be explained in more detail below.

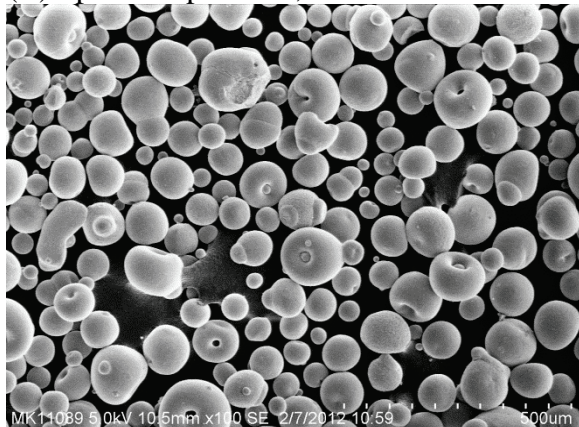
(A) Whiskers, $\times 500$



(B) Whiskers, $\times 8,000$



(C) Spherical particles, $\times 100$



(D) Spherical particles, $\times 10,000$

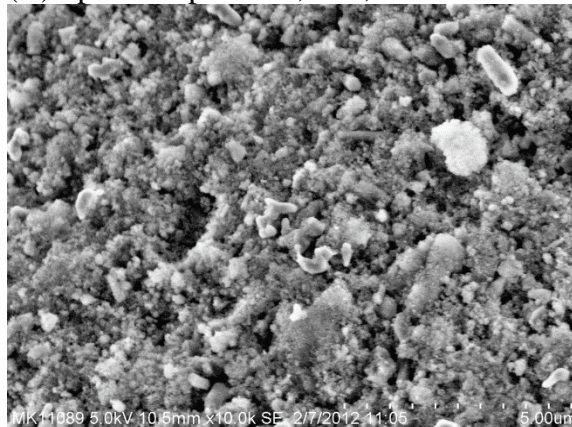


Figure 2. Scanning electron micrographs of the as-received, agglomerated alumina nanofillers.

3.2 Tensile testing

The results of the tensile testing of the nanocomposite reinforced with whiskers are given in Table 1. In this case, the whiskers were not surface modified and the specimens were cast in cylindrical moulds. There is a significant increase in the elastic modulus as the alumina content in the nanocomposite is increased. The value is increased from 3123 MPa for the neat epoxy polymer, to 3541 MPa for the specimen containing 4.10 wt% alumina. This is an increase of around 13%, and comparable to what was observed by Brown and Ellyin [10;11]. Also, upon addition of only 0.08 wt% alumina, which corresponds to 0.026 vol%, the elastic

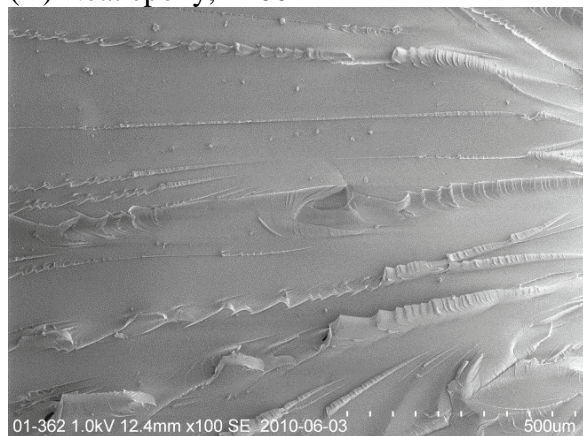
modulus is increased to 3308 MPa. For comparison, a simple rule of mixtures analysis [21] anticipates an elastic modulus of 3223 MPa.

Scanning electron micrographs of fracture surfaces of the tensile test specimens are shown in Figure 3. The fracture surface of the neat epoxy polymer is relatively smooth, which is indicative of a relatively brittle epoxy polymer. However, the fracture surface of the nanocomposite with 4.10 wt% alumina has a much more rough appearance, which is similar to what would be expected for a filled, more tough epoxy polymer. Also, a significant amount of alumina agglomerates can be observed. This shows that the dispersion method used in this study was not sufficient to break up the agglomerates shown in Figure 2, and that they are acting as obstacles for the propagation of cracks. On the other side, the tensile strength is reduced upon addition of alumina. This could be explained by the agglomerates creating defects which act as initiation sites for crack propagation.

Type of reinforcement	Content of alumina [wt%]	Elastic modulus [MPa]	Tensile strength [MPa]
Neat epoxy	0	3123 (105)	89 (1)
NT-whiskers	0.08	3308 (138)	91 (1)
	0.41	3384 (119)	90 (1)
	0.82	3357 (110)	89 (1)
	2.46	3453 (174)	80 (7)
	4.10	3541 (126)	81 (3)

Table 1. Results from the tensile testing of nanocomposites reinforced with non-treated alumina whiskers (NT-whiskers). Average values of five replicate specimens. The standard deviation is given in brackets.

(A) Neat epoxy, $\times 100$



(B) NT-whiskers, 4.10 wt%, $\times 500$

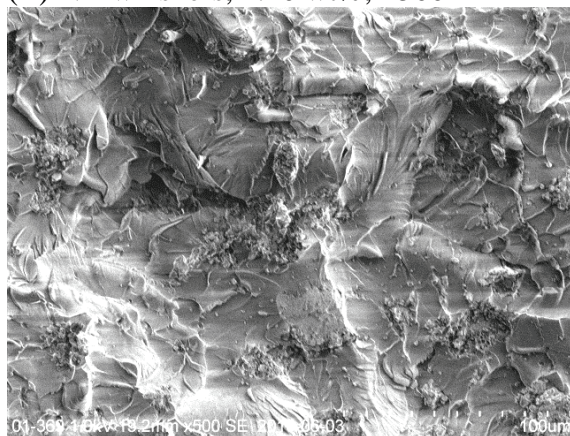


Figure 3. Scanning electron micrographs of fracture surfaces from the tensile testing of nanocomposites reinforced with non-treated alumina whiskers (NT-whiskers).

3.3 Dynamic mechanical analysis

The results of the DMA experiments are given in Table 2. Nanocomposites of non-treated and surface modified whiskers and spherical particles were prepared and cast in rectangular moulds. There is no indication of a significantly increased storage modulus of the reinforced nanocomposites. One exception may, however, be the nanocomposite containing surface treated spherical particles (specimen "NT-50nm"), where the value of the storage modulus was increased from 3057 MPa to 3247 MPa. FT-IR analysis (not shown here) indicated the presence of GPS on the surface of the spherical particles, which could result in the formation

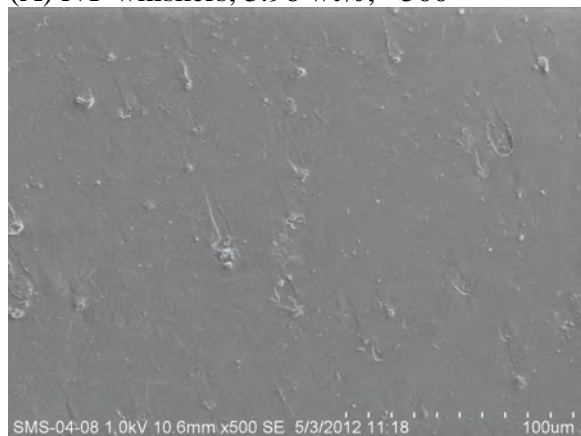
of a stronger particle/polymer interface. SEM showed a very smooth fracture surface of these nanocomposites, and few agglomerates were observed, see Figure 4.

The glass transition temperature of the epoxy polymer is not negatively affected by the addition of the alumina nanofiller. One indication, however, is that the glass transition temperature may be slightly increased upon addition of the whiskers.

Type of reinforcement	Content of alumina [wt%]	Storage modulus [MPa]	Glass transition temperature [°C]
Neat epoxy	0	3057	151
NT-50nm	3.39	2987	150
GPS-50nm	2.82	3247	154
NT-whiskers	3.96	3118	157
GPS-whiskers	3.84	3039	160

Table 2. Results from DMA of nanocomposites reinforced with alumina; non-treated spherical particles (NT-50nm), surface modified spherical particles (GPS-50nm), non-treated whiskers (NT-whiskers) and surface modified whiskers (GPS-whiskers).

(A) NT-whiskers, 3.96 wt%, ×500



(B) GPS-50nm, 3.84 wt%, ×500

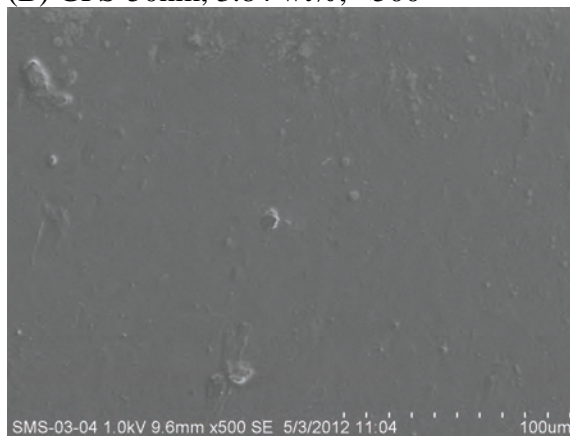


Figure 4. Scanning electron micrographs of fracture surfaces of nanocomposite specimens that were tested using the DMA. The specimens were fractured after the DMA test.

3.4 Discussion

As can be seen from Tables 1 and 2, there is a discrepancy between the results of the stiffness of the nanocomposites containing non-treated alumina whiskers (specimen “NT-whiskers”). That is, an increased stiffness was observed in the tensile tests, but not in the DMA experiments. The explanation for this could lie in the difficulty of obtaining a high degree of dispersion with the sonication technique that was used here, and the resulting sedimentation of alumina agglomerates. Slightly different preparation procedures were used, resulting in different contents of agglomerated alumina in the nanocomposites. The tensile specimens contained relatively high amounts of agglomerates, while few agglomerates were observed in the DMA specimens. The relative amounts of dispersed and agglomerated whiskers in the composites have not been quantified, but the result is nevertheless an increase in stiffness when agglomerates are present. The sedimentation of large agglomerates was difficult to control, and the alumina content of the DMA specimens may therefore be lower than what is indicated in Table 2. However, there are indications that the surface modification procedure

had a positive influence on the material properties of the nanocomposites reinforced with spherical alumina fillers.

4 Conclusions

A low degree of dispersion was obtained when employing a bath sonicator to disperse alumina nanofillers in the anhydride hardener. Agglomerates were observed in the epoxy polymer nanocomposites. Nevertheless, small amounts of alumina whiskers seemed to significantly improve the stiffness of the epoxy polymer, even when a significant part of them, if not most, were in an agglomerated state. The improved stiffness is likely to be an effect of the agglomerates, and not dispersed alumina whiskers.

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