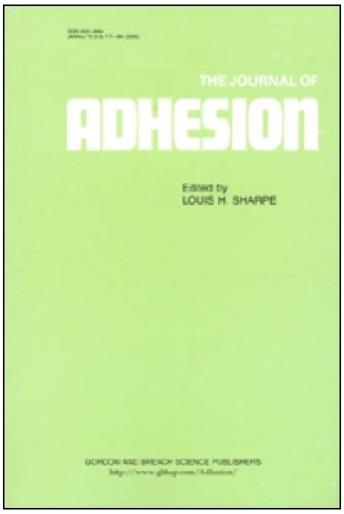

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Toughening structural adhesives via nano- and micro-phase inclusions

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NOTE

TOUGHENING STRUCTURAL ADHESIVES VIA NANO- AND MICRO-PHASE INCLUSIONS

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It has been clearly demonstrated that the addition of low concentrations of nano-silica particles to a typical rubber-toughened adhesive, based upon a two-part epoxy formulation, leads to very significant increases in the toughness of the adhesive and also to increases in the glass transition temperature and the single-lap shear strength. The nano-SiO_2 *particles have an average particle diameter of 20 nm and are very well dispersed in the epoxy adhesive, and only a concentration of about 1% to 8% by mass of such nanoparticles are needed to achieve significant improvements in the mechanical and thermal performance of the rubber-toughened two-part epoxy adhesive.*

Keywords: Epoxy adhesive; Mechanical properties; Nanoparticles; Rubber toughened; Toughness

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INTRODUCTION

There are many advantages that polymeric adhesives can offer compared with the more traditional methods of joining such as bolting, brazing, welding, mechanical fasteners, etc. These include [1, 2] the ability to join dissimilar materials to give lightweight but strong and stiff structures, such as honeycomb sandwich panels. Also, polymeric adhesives may be used to join thin-sheet material efficiently which, due to its low bearing strength, cannot be readily joined by other methods. Further, adhesive bonding frequently represents the most convenient and cost-effective joining technique and, indeed, the bonding operation can often be readily automated. For these reasons, adhesive bonding is widely used in many industries, for example in the automobile, truck, aerospace, railway, and electronic industries. Epoxy adhesives represent the most common type of *structural* adhesive; the term *structural* meaning that the polymerised (*i.e.*, cured or hardened) adhesive possesses a relatively high modulus and strength so that a load-bearing joint is formed.

When polymerised, epoxy adhesives are amorphous and highly crosslinked (*i.e.*, thermosetting) materials. This microstructure results in many useful properties for structural engineering applications, such as a high modulus and failure strength, low creep, and good performance at elevated temperatures. However, the structure of such thermosetting polymers also leads to one highly undesirable property in that they are relatively brittle materials, with a poor resistance to crack initiation and growth. Nevertheless, it has been well established [3–5] for many years that the incorporation of a second microphase of dispersed rubbery particles into epoxy polymers can greatly increase their toughness, without significantly impairing the other desirable engineering properties. Typically the rubber particles are about 1 to 5 μm in diameter with a volume fraction of about 10 to 20%.

More recently there has emerged a new technology which holds great promise for increasing the mechanical performance of structural adhesives. Namely, via the formation of a nanophase structure in the polymeric adhesive, where the nanophase consists of small rigid particles or fibres which have a diameter (or at least one dimension) of about 5 to 50 nm [6, 7].

The present article discusses the effects of combining these two types of approaches to develop improved structural adhesives with the aims of attaining relatively high toughness materials but without significantly compromising the other desirable mechanical and thermal properties of the adhesive.

EXPERIMENTAL

The Materials

The formulations were based upon a two-component epoxy adhesive system, and the recipes are shown in Table 1. The epoxy resin was a standard diglycidyl ether of bis-phenol A (DGEBA) with an epoxy equivalent weight (EEW) of 185 g/mol, (Bakelite EPR 164, supplied by Bakelite AG, Duisberg, Germany). Nanopox 22/0516 (Hanse Chemie, Geesthacht, Germany) is a nanoparticle silica (SiO_2) reinforced bis-phenol A epoxy resin, which consists of surface-modified SiO_2 nanoparticles with an average particle size of about 20 nm, and also with a narrow range of particle-size distribution. This particle size of about 20 nm is created during a sol-gel manufacturing process [6], whereby the silica particles are formed *in situ*, and the particle size and excellent dispersion of these SiO_2 particles remain unchanged during any further mixing and/or blending operations. Further, despite the relatively high SiO_2 content of 40% by mass, the nanofilled resin still has a comparatively low viscosity due to the agglomerate-free colloidal dispersion of the nanoparticles of SiO_2 in the epoxy resin. The small diameter and good dispersion of the nanoparticles of silica are clearly shown in Figure 1. The reactive liquid rubber, which gives rise to the micrometre-sized spherical rubber particles upon curing of the adhesive formulation, was an amine-terminated butadiene-acrylonitrile rubber (ATBN). It was supplied by Noveon (Cleveland, USA) and was Hycar ATBN 1300 × 16 with an amine equivalent weight of 900 g/mol and acrylonitrile content of 18%. The curing agent was a hardener based upon a blend of N,N-dimethyl-1,3-diaminopropane and a polyaminoamide, namely Polypox P502 (UPPC, Baltringen, Germany). The formulations were cured by first mixing together the two different epoxy-resin-based components and, separately, the last two components given in Table 1 in the

TABLE 1 Formulations of the Epoxy Adhesives

	Control	2KA	2KB	2KC	2KD	2KE
DGEBA	100	96.25	92.5	85.0	70.0	—
Nanopox XP 22/0516	—	6.25	12.5	25.0	50.0	100
Hycar ATBN 1300 × 16	45.8	45.2	44.5	43.9	43.2	27.8
Polypox P 502	91.6	90.4	88.9	87.9	86.5	55.5
% mass parts SiO_2 (on total)	0	1.05	2.1	4.1	8	21.8

Parts by mass given.

All formulations possess 18.1 ± 1.5% ATBN based on the total mass.

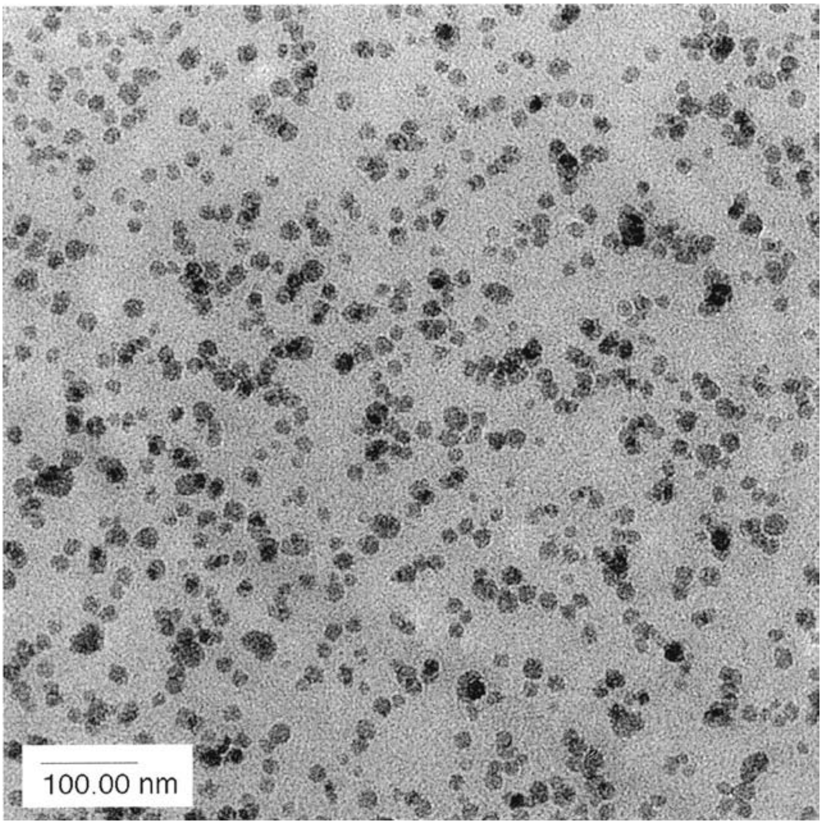

FIGURE 1 Transmission electron micrograph showing the excellent dispersion of the SiO_2 nanoparticles in the epoxy resin ('Nanopox XP 22/0516').

proportions, by mass, stated. Just prior to joint preparation and curing, these two blends were then mixed together, *i.e.*, as Parts "A" and "B", respectively, of the two-component adhesive formulation. The adhesive was cured for 24 h at room temperature followed by 2 h at 60°C.

Mechanical and Thermal Properties

The glass transition temperature, T_g, of the various formulations was measured using the method of dynamic mechanical thermal analysis (DMTA) at a frequency of 10 Hz. The single-overlap shear strengths were determined using either untreated aluminium-alloy substrates (Grade 6016, according to DIN Standard 55-283) or chromic-acid etched aluminium-alloy substrates (Grade 2024 T3, according to ASTM Standard D 1002). The adhesive fracture energy, G_c, was measured using chromic-acid–etched aluminium-alloy substrates and tapered double-cantilever beam (TDCB) specimens (according to BS Standard 7991). The coefficient of variation on the values of G_c was ±12%. Finally, to also indicate the toughness levels of the different formulations, roller-peel tests were conducted employing chromic-acid–etched aluminium-alloy substrates (Grade 2024 T3, according to ASTM Standard D 3167).

RESULTS

The results are given in Table 2. There are several noteworthy points. First, the glass transition temperature, T_g, may be somewhat increased by the presence of the nanosilica particles. It would appear that a concentration of about 8% by mass of nano-SiO_2 particles results in an increase in the T_g by about 5°C, compared with the formulation containing no nano-SiO_2 particles.

However, secondly far more striking is the increase in the value of the adhesive fracture energy, G_c, upon the addition of the nano-SiO_2 particles. The value of G_c increases from 1200 J/m^2 for the control rubber-toughened epoxy up to a maximum of 2300 J/m^2 for the formulation with a concentration of 4.1 mass% of nano-SiO_2 particles. Thus, there is clearly a very significant and substantial additional toughening effect induced by the additional presence of the nanoparticles. Compared with an unmodified epoxy formulation with no dispersed rubbery phase, the rubbery particles are known to increase the toughness of the adhesive via interactions of the stress field ahead of the crack tip and the rubbery particles, which leads to greatly enhanced plastic deformation of the epoxy matrix. It is not

TABLE 2 Mechanical and Thermal Properties

	Control	2KA	2KB	2KC	2KD	2KE
% mass SiO_2	0	1.05	2.1	4.1	8.0	21.8
T_g (°C)	70	67	71	67	75	73
Lap shear (1) (MPa)	13.4	19.2	17.8	16.7	16.2	11.8
Lap shear (2) (MPa)	20.8	20.9	22.0	23.0	23.2	20.3
G_c (J/m^2)	1200	1800	1800	2300	2000	1300
Roller peel (N/mm)	3.1	5.1	5.5	4.6	3.8	2.8

Lap shear (1) tests used untreated aluminium alloy.

Lap shear (2) tests used etched aluminium alloy.

immediately obvious why the additional presence of the nano-SiO_2 particles should further increase the toughness so markedly. Previous work [8] on rigid fillers that were micrometres in size, as opposed to being nanometres in size, has shown that the toughening mechanisms which are induced by the presence of the rigid particles may also involve enhancing the plastic deformation that occurs in the epoxy matrix, but that other mechanisms such as crack deflection and crack twisting [9] around the rigid particles may also be initiated. Future work will explore the detailed mechanisms of toughening which are initiated by the nanoparticles, which may lead to even further increases in the mechanical performance of structural adhesives, containing a complex structure of nano- and microsized phase inclusions.

Thirdly, the increases in toughness indicated by the fracture-mechanics tests described above are also confirmed by the results of the roller-peel tests shown in Table 2. These also reveal that the peel energy of the formulations containing the nanoparticles may be significantly improved, compared with the control formulation.

Finally, the lap-shear strength was measured using single-lap joints loaded in tension. As indicated in Table 2, both untreated and chromic-acid–etched aluminium alloys were used for the substrates. The use of the former type of substrate led to the lap joints failing mainly at the adhesive/substrates interface, while the use of the latter type of etched substrate led to failure occurring cohesively within the adhesive layer. The lap-joint strengths were considered to be of interest since an increase in the toughness of an adhesive material by a formulation change is often accompanied by a decrease in the lap-shear strength. However, clearly this is not the case with the nanosilica rubber-toughened materials. From Table 2 it is evident that the addition of the nano-SiO_2 particles to the rubber-toughened epoxy leads to a significant increase in the strength of the single-lap joints, prepared using either the untreated or the chromic-acid-etched aluminium-alloy substrates.

CONCLUSIONS

It has been clearly demonstrated that the addition of low concentrations of nanosilica particles to a typical rubber-toughened adhesive, based upon a two-part epoxy formulation, leads to very significant increases in the toughness of the adhesive and also to increases in the glass transition temperature and the single-overlap shear strength. The nano-SiO_2 particles have an average particle diameter of 20 nm and are very well dispersed in the epoxy adhesive. A concentration of only about 1% to 8% by mass of such nanoparticles are needed to achieve significant improvements in the mechanical and thermal performance of the rubber-toughened two-part epoxy adhesive.

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