**PROCESSABILITY STUDIES
OF SILICA - THERMOSET POLYMER MATRIX NANOCOMPOSITES**

**C.Lekakou, I.Kontodimopoulos, A.K.Murugesh, Y.L.Chen, D.A.Jesson, J.Watts
and P.A.Smith**

**Center for Materials, Surfaces and Structural Systems
School of Engineering
University of Surrey
Guildford, Surrey GU2 7XH**

ABSTRACT

The aim of this study is to investigate the processability of silica-thermoset polymer matrix nanocomposites in terms of dispersion of silica nanoparticles and their effect on curing. Two thermosetting resins were considered, an epoxy and a polyester resin, with 5 % silica, although 1% silica was also used in preliminary studies in the polyester system. Various combinations of mechanical mixing and sonication were investigated for the dispersion of silica nanoparticles under different processing conditions and times in solvent-free and solvent-containing systems. It was found that the best dispersion route involved a solvent-aided dispersion technique. Consequently, different procedures for the solvent removal were investigated. Optical microscopy and SEM were used to characterize the resulting nanocomposites. DSC and rheological DMTA tests demonstrated that the silica nanoparticles shorten the gel time and promote curing in these thermosetting systems.

1. INTRODUCTION

Silicate and silica nanocomposites form two types of dispersed phase: (a) Clays form layered silicates consisting of micro-platelets of nanometers thickness; (b) silica nanocomposites contain dispersed silica nanoparticles. Clay nanocomposites have been investigated to improve certain polymer properties, such as thermal stability [1], fire retardancy [2-3], barrier properties [4-6] which might improve hydrothermal aging [6], flexural modulus, strength and toughness [1,5] and lower shrinkage [7]. Nanodispersion maintains the transparency of a transparent polymer matrix whereas microcomposites are not transparent. Nanocomposites with silica nanoparticles have been reported to display increased mechanical properties [8,9] such as modulus, tensile, flexural and impact strength up to a certain silica content (e.g. 2.5% [10]) and decreased mechanical properties thereafter, improved fracture toughness [11] and better thermal stability [12,13].

In order to obtain the beneficial properties of the large surface area of the dispersed phase in nanocomposites, clay platelets must be exfoliated [14] and the silica particulates must be fully dispersed at nanolevel. Exfoliation and nanodispersion are by no means trivial and should not be taken for granted. Various techniques have been used to effect dispersion, either on their own or combined: mechanical mixing [5, 15, 16], sonication [17, 18] and solvent-aided mixing [5, 12]. Nanoparticles may also be produced in-situ in the polymer matrix [13, 19].

Silica nanoparticles consist of SiO_2 crosslinked structures with a few silanol, $-\text{SiOH}$, terminating groups, which might interact with the polymer matrix. Ragosta et al [11]

detected a reaction between the epoxy groups and silanol groups present on the surface of silica nanoparticles, leading to increased interfacial adhesion. Dispersed silica nanoparticles have been used as a curing agent in an epoxy system in the presence of magnesium chloride, acting as a catalyst, to yield a silica-epoxy nanocomposite [20]. Incorporation of silica nanoparticles and silicates has been reported to raise the glass transition temperature, T_g , of the resulting nanocomposite (cyanate ester composites [9], vinyl ester composites [1], epoxy composites [13, 21]) but also to reduce T_g (clay-biobased epoxy nanocomposites [18]).

This study focuses on the processability of silica-epoxy and silica-polyester nanocomposites in terms of dispersion of silica nanoparticles and their effect on the curing of the thermosetting resins. The first stage involved the investigation of processing with different particle dispersion techniques. While a combination of solvent-aided mixing and sonication was found to be the best route, the technique has been used in the past only for epoxy systems [5] and needed further development and refinement for polyester systems. The processing studies were complimented with DSC (differential scanning calorimetry) and rheological DMTA (dynamic mechanical testing) studies during resin curing to investigate the effect of nanoparticles on curing and rheology. Microstructural studies were performed on fractured surfaces.

2. MATERIALS

A silica powder, WACKER HDK N20, was used in this study as the source of hydrophilic nanoparticles. The powder has been produced by WACKER SILICONES in the following process [22]: primary silica nanoparticles of about 10 nm (see Figure 1(a)) are produced during the hydrolysis of trichlorosilane in a hydrogen/oxygen

flame at about 1200 °C; in the flame the primary particles fuse into aggregates of about 100 to 500 nm and of irregular shape; on cooling, the aggregates flocculate to form agglomerates of about 10-50 µm, also called tertiary structures. Figure 1(b) presents what is probably a small agglomerate of these silica particles dispersed in ethanol by sonication in an ultrasonic bath for 30 min. Whereas the agglomerates are loosely connected and may be broken down, the aggregates consist of primary particles that have fused to form a face-to-face sintered structure and, hence, cannot be dissociated by physical means.

Two alternative polymer resins were used in this study: a polyester and an epoxy resin. Preliminary experiments were carried out using Crystic 471 PALV polyester resin supplied by Scott Bader Co, which already contained 1 wt % WACKER HDK N20 particles as thixotropic aid. The main experiments were carried out using the same polyester resin but without the thixotropic aid, so that the silica powder could be added externally at 5 wt %. Crystic 471 PALV consists of an orthophthalate based, unsaturated polyester and 42 % styrene, which is used as a diluent and crosslinking agent in the subsequent curing of polyester. The system was supplied with cobalt naphthanate as pre-accelerator. Catalyst M, which is methyl ethyl ketone peroxide (MEKP), was used as initiator in the curing of polyester, at a concentration of 1.5 wt % of the polyester system.

The epoxy components were supplied by Ciba Polymers and consisted of Araldite LY564, based on a bisphenol A epoxy resin with a reactive diluent, and Hardener HY 2954, a cycloaliphatic amine. Araldite LY564 was mixed with WACKER HDK N20 powder in a weight ratio of 100:7. After the dispersion of the silica nanoparticles,

Hardener HY 2954 was added at an Araldite LY 564: Hardener HY 2954 weight ratio of 100:35 to effect the curing of epoxy, resulting in composites with about 5 wt % silica.

3. PROCESSING PROCEDURES AND OPTIMISATION

3.1 PRELIMINARY PROCESSING EXPERIMENTS:

POLYESTER WITH 1% WACKER HDK N20 PARTICLES

The preliminary experiments were carried out using Crystic 471 PALV polyester resin, which already contained 1% WACKER HDK N20 particles in the form of aggregates or agglomerates. The purpose of these series of experiments was to investigate the effect of different mixing techniques and conditions on the break up of agglomerates. The resin with the particles was subjected to the following alternative procedures:

- a. Manual mixing.
- b. Mechanical mixing using a mechanical stirrer at 10^4 rpm for 30 min.
- c. Mechanical mixing using a mechanical stirrer at 10^4 rpm for 30 min, followed by degassing under vacuum at room temperature for 30 min.
- d. Mechanical mixing using a mechanical stirrer at 10^4 rpm for 70 min.
- e. Mechanical mixing using a mechanical stirrer at 10^4 rpm for 70 min, followed by degassing under vacuum at room temperature for 30 min.
- f. Mechanical mixing using a mechanical stirrer at 10^4 rpm for 70 min, followed by sonication in an ultrasonic bath for 60 min.

In the case of mechanical mixing, a sawtooth stirrer was used consisting of a disc with teeth at the periphery coming vertically up and down in an alternating manner. After the mixing regime was completed, catalyst M was added and mixed into the resin. The samples were left to cure at room temperature and, after 3 days, they were sectioned and specimens were examined under the optical microscope.

Manual mixing (technique a) was thought insufficient, since agglomerates of 5-10 μm were present in the optical micrographs. In general, it was found that rigorous mechanical mixing (techniques b and d) introduced air bubbles in the mixture which were difficult to remove. Degassing under vacuum (techniques c and e) was tried to remove the bubbles, but this also resulted in the removal of some of the styrene from the polyester resin, yielding an incompletely cured system. The sonication (technique f) helped to remove some but not all of the bubbles.

3.2 SOLVENT-FREE DISPERSION TECHNIQUES

The next step was to use epoxy as the alternative polymer resin, since it would be easily treated under vacuum or higher temperatures without the removal of any active ingredient, such as styrene in the case of polyester resin. To avoid significant air entrapment, a closed mixing vessel filled to the top was used, with a triangular frame stirrer at lower rotation speeds than in section 3.1.

Technique a. Mechanical mixing of Araldite LY564 and silica powder was carried out using a mechanical stirrer at 600 rpm for 30 min. Then the hardener was mixed

mechanically into the epoxy and the mixture was left to cure at room temperature for 3 days.

Technique b. Mechanical mixing of Araldite LY564 and silica powder was carried out using a mechanical stirrer at 600 rpm for 30 min. The mixture was subsequently subjected to sonication in an ultrasonic bath at room temperature for 30 min. Then the hardener was mixed mechanically into the epoxy and the mixture was left to cure at room temperature for 3 days.

Results. The obtained specimens were fractured and their fractured surface was gold-coated. SEM micrographs revealed poor micro-scale mixing in both techniques a and b, with white regions of high particle concentration as is shown in Figures 2(a) and (b). The high particle concentration regions (see Figure 2(c)) contained features of about 100 nm, which was thought to indicate the presence of intercalated agglomerates.

Similar results were expected for the polyester system as well, since it has even higher viscosity than the epoxy system. The conclusion was to introduce a solvent to aid the dispersion of silica nanoparticles. After the nanoparticles were dispersed, the solvent would need to be removed totally from the system before curing to avoid any plasticizing effects in the final composite.

3.3 SOLVENT-AIDED DISPERSION TECHNIQUES

3.3.1 Epoxy nanocomposites

In order to avoid problems of poor micro-scale mixing, ethanol was used as a solvent to lower the viscosity of the epoxy resin and to aid mixing. The first stage involved the manual mixing of 120 ml ethanol with 10 g of WACKER HDK N20 powder, followed by sonication at room temperature for 30 min. 140 ml of Araldite LY564 was added to the mixture and the system was mixed mechanically with a triangular frame stirrer at 1000 rpm for 30 min. The system was left in an oven at 100 °C under vacuum for 5 h to evaporate the ethanol. The hardener was then added and mixed mechanically at 1000 rpm for 5 min. The reacting mixture was left to cure, specimens were fractured, their fractured surface was gold-coated and examined under SEM.

The fractured surface in Figure 3(a) showed river-markings, also observed in previous studies of silica [10] and silicate [4] nanocomposites, whereas the pure epoxy shows a smooth featureless fracture surface [4, 10, 21] indicating brittle failure. No aggregates were observed at micro-level in Figure 2, which means that the solvent-aided processing technique yielded good dispersion of silica particles. There were also no micro-voids, meaning that there was no entrapped air in the produced nanocomposites. Closer examination at higher magnification in Figures 3(b) and (c) revealed features of 50-100 nm in grape-like groups which were thought to correspond to very well dispersed nano-aggregates of WACKER HDK N20 silica particles, which would not be expected to be dispersed to any smaller nanoscale, since the primary silica nanoparticles are fused at that nanolevel. It was considered that these nano-features in the fracture surface would increase the required fracture energy and, hence, the toughness of the polymer resin.

In conclusion, the solvent-aided dispersion process was considered to produce the best dispersion of WACKER HDK N20 particles.

3.3.2 Polyester nanocomposites

The idea of solvent-aided dispersion was also adopted for the processing of polyester nanocomposites, with methanol used as the solvent. In this case 10 g of WACKER HDK N20 powder was mixed with 200 ml methanol, first manually and then by sonication for 30 min. The mixture was placed in a glass flask and 200 ml of Crystic 471 PALV polyester resin (without any particles) was added. The mixture was stirred mechanically at 700 rpm for 30 min. This was followed by the slow distillation of methanol, while the mixture was stirred mechanically. The distillation process ensured the removal only of methanol at 65 °C while the styrene still remained in the mixture due to its much higher boiling point. Catalyst M was added and mixed manually, the mixture was poured into a glass mould and left to cure at room temperature, specimens were obtained and fractured, their fracture surface was gold-coated, and they were examined under SEM.

Figure 4 presents the fracture surface of polyester specimens (Crystic 471 PALV polyester and catalyst M) without any WACKER HDK N20 powder. The surface displays thin hair-like lines (Figure 4(a)), which under closer inspection in Figure 4(b) reveal longitudinal fracture features. It is considered that the SEM micrographs should have a resolution of more than 30 nm, because of the presence of gold particles of that size on the gold-coated fracture surface.

Figure 5 presents the fracture surface of the polyester nanocomposites, prepared following the methanol-aided mixing procedure. The mixing is homogeneous at micro-scale showing no micro-aggregates. Figures 5(b) and 5(c) reveal a cornflake-like fracture surface with circular features of 100 nm covering the whole fracture surface, unlike in the case of polyester in Figure 4(b). We believe that the surface features in Figure 5(c) indicate the presence of highly dispersed WACKER HDK N20 aggregates of fused primary silica nanoparticles.

Since the solvent-aided processing procedures described in section 3.3 proved successful in the dispersion of the silica nanoparticles, they have been selected as the preparation methodology for the silica-epoxy and silica-polyester nanocomposites tested in the rest of this study.

4. DSC and DMTA STUDIES OF CURING

Dynamic DSC tests were performed in a Universal V 3.58 TA DSC instrument at 12 °C/min up to 200 °C. Figure 6(a) presents the results for the pure epoxy system and a silica-epoxy curing system with 5% silica nanoparticles. It looks that the silica nanoparticles promote the curing reaction in epoxies, starting and peaking at about 10 °C lower than the pure epoxy system. Furthermore, the area of the exotherm in the silica-epoxy system (see Figure 6(b)) is larger than the corresponding area in the pure epoxy, indicating that the silica-epoxy system has reached more advanced curing. It has been reported [22, 23] that the hydroxyl group acts as a catalyst in the curing reaction between the epoxy and amine groups which might lead to promotion of the curing reaction at the surface of silica nanoparticles that contain hydroxyl groups as part of the silanol groups.

Dynamic DSC experiments were also carried out for the polyester and silica-polyester nanocomposites up to 350 °C. First, polyester and silica-polyester nanocomposite samples were cured in situ in dynamic DSC up to 350 °C. The major curing exotherm peak occurred around 80 °C, whereas degradation occurred after 290 °C. Then other samples of the same composition were cured separately at room temperature for 24 h and subsequently subjected to the same dynamic DSC run, yielding a remaining curing exotherm. Subsequently, the ratio of the measured exotherm areas for the remaining cure and the full in-situ cure would give an estimate of the extent of uncured material (% non-cure) in the samples firstly cured for 24 h at room temperature. The results are presented in Table 1 (% cure = 100 - % non-cure) and show that the addition of 1% silica nanoparticles promotes the curing reaction, possibly by further reaction between the hydroxyl part of the silanol groups and end-carboxylic groups in the polyester resin, chemically strengthening the interface between silica nanoparticles and polyester resin.

Figure 7 presents rheology data during the curing of epoxy systems obtained from DMTA experiments in a Rheometrics RDA II instrument in a dynamic time sweep at a frequency of 1.6 Hz at room temperature. It can be seen that although both epoxy and 5 wt % silica-epoxy systems start from a similarly low viscosity (1.7 Pas), the time for the pure epoxy system to reach a viscosity value of 45 Pas is around 440 min (which has been considered as a nominal gel time in this study) whereas the time to reach the same viscosity for the silica-epoxy system is 324 min at room temperature. The much faster gelling of the silica-epoxy system is thought to be the result of both the presence of the dispersed silica nanoparticles which would eventually raise the

viscosity of the system during curing and also the accelerated curing that occurs in the presence of silica nanoparticles, as was shown in the DSC studies.

5. CONCLUSIONS

The processing of silica-epoxy and silica-polyester nanocomposites has been studied with regards to the dispersion of silica nanoparticles and their effects on the resin curing. Dispersion of silica nanoparticles was achieved by a combination of mechanical mixing and sonication, where care was taken to avoid considerable air entrainment during mixing which would result in air micro-voids in the nanocomposite.

A solvent-aided dispersion procedure is recommended since inhomogeneous dispersion of silica nanoparticles takes place at micro-scale without a solvent. The solvent was removed from the epoxy system under vacuum at elevated temperature in an oven. However, to avoid the evaporation of styrene in the polyester system, the solvent (methanol) aiding the dispersion process of silica was removed by distillation, which means that it can also be recycled.

SEM characterization of the fractured surfaces of the nanocomposites produced via the solvent-aided processing route proved that there are no features at micro-scale, no micro-domains of particles, no mixing in homogeneities and no micro-voids. The fracture surface of the nanocomposites revealed additional features of up to 100 nm, when compared to the fracture surface of the pure resin, which were thought to be related to the presence of nanoparticles and thought beneficial in increasing the required fracture energy and, hence, toughness of the nanocomposite.

DSC studies showed that the silica nanoparticles promoted curing in both epoxy and polyester systems. DMTA studies of curing demonstrated that the presence of silica nanoparticles shortens considerably the gel time and raises the viscosity of the curing system at much faster rate at gelling.

REFERENCES

1. F.Hussain, D.Dean, A.Haque and A.M.Shamsuzzoha, *J.Advanced Materials*, **37**(1), 16 (2005)
2. M.Zammarano, M.Franceschi, S.Bellayer, J.W.Gilman and S.Meriani, *Polymer* **46**(22), 9314 (2005)
3. J.W.Gilman, R.H.Harris, J.R.Shields, T.Kashiwagi and A.B.Morgan, *Polymers for Advanced Technologies* **17**(4), 263 (2006)
4. D.P.R.Kint, G.Seeley, M.Gio-Batta, A.N.Burgess, *J. Macromolecular Sci-Physics* **B44**(6), 1021 (2005)
5. W.P.Liu, S.V.Hoa, M.Pugh, *Comp.Sci.Techn.*, **65** (15-16), 2364 (2005)
6. L.Wang, K.Wang, L.Chen, C.B.He, L.Wang and YW Zhang, *Pol.Eng.Sci.*, **46**(2), 215 (2006)
7. L.Xu and J.L.Lee, *Proc ICCM 14* (2003)
8. Y.P.Zheng, R.C.Ning and Y.Zheng, *J.Reinforced Palstics and Composites*, **24**(3), 223 (2005)
9. K.W.Liang, G.Z.Li, H.Toghiani, J.H.Koo and C.U.Pittman, *Chemistry of Materials*, **18**(2), 301 (2006)
10. P.Singh, A.Kaushik and A.Kirandeep, *J.Reinforced Plastics & Composites*, **25**(2), 119 (2006)
11. G.Ragosta, M.Abbate, P.Musto, G.Scarinzi and L.Mascia, *Polymer*, **46**(23), 10506 (2005)
12. Q.Chen, R.W.Xu, J.Zhang, D.S.Yu, *Macromolecular Rapid Communications*, **26**(23), 1878 (2005)
13. T.M.Lee and C.C.M.Ma, *J.Polymer Science Part A-Polymer Chemistry*, **44**(2) 757 (2006)

14. E.P.Giannelis, *Advanced Materials*, **8**, 29 (1996)
15. R.Velmurugan and T.P.Mohan, *J.Materials Science*, **39**(24), 7333(2004)
16. W.P.Liu, S.V.Hoa and M.Pugh, *Comp.Sci.Technol.*, **65**(2), 307 (2005)
17. S.McIntyre, I.Kaltzakorta, J.J.Liggat, R.A.Penthrick and I.Rhoney, *Industrial & Engineering Chemistry Research*, **44**(23), 8573 (2005)
18. H.Miyagawa, R.J.Jurek, A.K.Mohanty, M.Misra and L.T.Drzal, *Composites Part A-Applied Science & Manufacturing*, **37**(1), 54 (2006)
19. K.A.Carrado, L.Q.Xu, R.Csencsits and J.V.Muntean, *Chemistry of Materials*, **13**(10) 3766 (2001)
20. Y.L.Liu and S.H.Li, *J.Applied Polymer Science*, **95**(5), 1237 (2005)
21. C.Basara, U.Yilmazer and G.Bayram, *J.Applied Polymer Science*, **98**(3), 1081 (2005)
22. WACKER “HDK N20 Pyrogenic Silica- Fumed Silica”,
http://www.wacker.com/internet/webcache/en_US/PTM/TM/HDK_N20.pdf?t_s=1107437644605 (2004)
23. C. Lekakou, A. Hearn, A.K. Muruges and B. Le Page, to be published in
Materials Science and Technology
24. R.Mezzenga, L.Boogh and J-A.E.Manson, *Macromolecules*, **33**, 4373 (2000)
25. R.Mezzenga, S.A.Page and J-A.E.Manson, *J.Colloid & Interface Science*, **250**, 121 (2002)

Table 1. Degree of curing from dynamic DSC experiments during the curing of polyester and polyester with 1 wt % silica nanoparticles

Material	% Catalyst M	% Cure
Polyester	1	71.4
Polyester+silica	1	75.8
Polyester	2	72.7
Polyester+silica	2	77.4

FIGURES

Figure 1. TEM micrographs of WACKER HDK N20 particles in ethanol after the suspension has been subjected to sonication in an ultrasonic bath for 30 min.

(a)

(b)

(c)

Figure 2. Solvent-free dispersion of silica particles in epoxy nanocomposites. SEM micrographs of fracture surface: (a) Technique a; (b) Technique b; (c) Technique b, magnified circled region of (b): a= high particle concentration region, b= region with no particles. Scales: (a) 30 μm (b) 10 μm (c) 1 μm

(a)

(b)

(c)

Figure 3. Solvent-aided processing of epoxy nanocomposites. SEM micrographs of fracture surface. Scales: (a) 10 μm (b) 1 μm (c) 0.3 μm

(a)

(b)

Figure 4. SEM micrographs of fracture surface of polyester without WACKER HDK

N20 particles; scales: (a) 10 μm (b) 1 μm

(a)

(b)

(c)

Figure 5. Solvent-aided processing of polyester nanocomposites. SEM micrographs of fracture surface. Scales: (a) 10 μm (b) 1 μm (c) 0.3 μm

(a)

(b)

Figure 6: Dynamic DSC experiments at 12 °C/min during curing. (a) DSC results during curing (b) a comparison of the DSC exotherms during the curing of pure epoxy and 5 wt% silica-epoxy system.

Figure 7: Rheology results of DMTA during curing