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The effect of ormosil nano-particles on the toughness of a polyester resin

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Abstract Organic–inorganic hybrid nano-particles have been synthesized via a modified Stöber method. Nano-particles have been prepared from silica precursors with different organic functionalities. Methyl, ethyl, vinyl and phenyl modified silicas have been synthesized with a view to using these particles as modifiers for polymers and polymer matrix composites. Nano-composites have been produced using polyester as a matrix. The effect of the nano-particles on the toughness of the polyester has been investigated and it is shown that the incorporation of nano-particles leads to an improvement in toughness. For the methyl, ethyl and vinyl ormosils (organically modified silicas) the improvement is minor. The phenyl ormosil gives a greater improvement. This is attributed to different toughening mechanisms.

Introduction

Matrix cracking within and, in particular, between plies is a limiting feature of composite materials in service. Within the polymer composites literature there are many papers concerned with the selection or modification of the matrix in order to optimise the toughness of the composite. The development of intrinsically tough matrices (thermoplastics and modified thermosets), the use of resin interleaves between plies and the addition of secondary reinforcement, such as silicon carbide whisker or carbon beads are examples of methods investigated for the toughening of polymer matrix composites [1–10].

In recent years, organic–inorganic hybrids have been developed with potential applications in a range of technologies including sensors [11] and lasers [12, 13]. Organically modified silicas (ormosils) are one type of organic–inorganic hybrid [11]. The present work is part of a programme to investigate the efficacy of a range of ormosils (in nano-particulate form) as modifiers for polymers and polymer matrix composites [14–18]. This paper considers the effects of these particles on the toughness of a polyester resin. To understand the effect that the ormosils have on the matrix system it is important to appreciate the interaction between the ormosils and the matrix. This has been investigated in an associated paper [18] in which it has been shown that:

- the organic functionality replaces some of the silanol functionality at the surface of the silica particles
- the methyl, ethyl and vinyl functionalities are sufficiently densely packed that they can be considered as a monolayer that prevents the retained silanol groups from interacting with chemical probes or the polymer matrix
- the larger phenyl groups are less densely packed and allow retained silanol groups to interact
- the organic functionalities interact only weakly, if at all, with the resin system

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- with the exception of the phenyl modified silica, the ormosils are likely to act essentially as voids in the matrix
- the phenyl ormosil is more strongly bonded to the matrix, but the overall bonding is weak when compared to an unmodified silica.

In another paper [17] the dispersion of the particles into the polyester matrix was discussed together with some preliminary mechanical property data from Charpy impact testing and compact tension (CT) testing. The Charpy test was shown to be inconclusive in this instance. The CT test showed that there was a significant difference between the modified and unmodified silicas, but the data could not be used to quantify toughness properties as it was evident that the modification of the polyester had led to a greater degree of plastic deformation, in all systems, than is permissible for an LEFM test. In this current paper the *J*-integral has been used to evaluate the toughness behaviour, and the results presented are taken in the context of the surface analysis of the particles from the previous work such that candidate toughening mechanisms are considered.

Experimental

Materials

Methyl, ethyl, vinyl and phenyl modified silica nanoparticles (diameters are presented in Table 1) were produced using a modified Stöber (hydrolytic) route [14]. These were used as modifiers for a polyester matrix. The polyester normally contains HDK N20 (Wacker), which is a commercial fumed silica, used as a thixotropic agent. However, samples of this resin, Crystic 2-406PA (Scott-Bader), an unsaturated polyester resin, were made available without the fumed silica addition (designated PEs in this work) and it is this resin that is used as the baseline for this investigation. The polyester is cured with Catalyst M (Scott-Bader), a trade name for the initiator methyl ethyl ketone peroxide. All the samples described here were cured with 1 vol% initiator and were post-cured at 80 °C for 3 h.

A description of the process used to disperse the particles in the polyester is presented in a previous paper [17]. A range of different methods were trialled. The most effective method found was to disperse the particles in a small quantity of ethanol. The quantity of ormosil used was chosen to give a concentration of 1 vol% in the modified polyester plaque. After dispersion, the ormosil/ethanol mixture is added to a solution of approximately 50 vol% polyester and 50 vol% ethanol (a total of 100 ml of ethanol is normally suitable for 5 g of ormosil) and the solution is then sonicated. Further polyester is added, whilst this solution is still sonicated, until the solution is approximately 90 vol% polyester and 10 vol% ethanol. Finally, this solution is added to the bulk polyester and stirred thoroughly. The ethanol is then removed through a vacuum oven (taking approximately 24 h) and lost styrene is subsequently replaced. The quantity of styrene to be replaced was calculated by weighing the sample before the ethanol was added and after the resin was removed from the vacuum oven, taking into account the mass of the particles added.

Mechanical characterisation

Previous work [17] has shown that there is considerable non-linearity in the load/extension behaviour of these nano-composites. It has therefore been necessary to use *J*-integral methods to assess the toughness of the nano-composites. The test method is outlined in ASTM E1737-96. A double edge notched (DEN) specimen geometry was used with dimensions of $150 \times 20 \times 3\ \text{mm}^3$. Samples were tested in tension using an Instron 1175 (with 5500R upgrade) tensile testing machine under displacement control. The load was measured directly from the 5 kN load cell and displacement was measured using an extensometer of gauge length 50 mm. The test method requires first that the compliance is measured as a function of crack length. The compliance was determined by loading the sample to 0.1% strain at a given crack length, unloading and repeating this cycle twice more for each crack length and then calculating the average value of compliance. The notch was then extended using a jeweller's saw, with a blade width of 0.25 mm. After the compliance calibration was completed, the critical load to fail the samples at a number of crack lengths was measured. For these tests the notch was sharpened and extended to the correct length by 'tapping', using a fresh razor blade. The data are presented in the form of nominal crack length, since the values are an average of several samples. Individual values for the crack length may vary by less than ±0.25 mm. The data reduction method used was the 'single specimen method'. The single specimen method derives two qualities from the test data, the elastic, J_{el}, and the plastic, J_{pl}, contributions to fracture. These two components are dependent upon the test geometry and in the case of a DEN sample J_{el} may be determined from:

$$J_{\mathrm{el}} = \frac{P^2}{4B}\frac{\mathrm{d}C}{\mathrm{d}a} \quad (1)$$

whilst J_{pl} may be determined using:

$$J_{\mathrm{pl}} = \frac{A^*}{B(W-a)} \quad (2)$$

In these expressions P is the maximum experimental load, B is the specimen thickness and $\mathrm{d}C/\mathrm{d}a$ is the differential of the 4th order polynomial that describes the relationship between C, the compliance of the sample, and a, the crack length. A^* is the area described by the relation between stress and strain and a straight line between the origin and the maximum load. W, in the case of a DEN specimen, is half the total width of the specimen. A test rate of 0.5 mm/min was used and the test temperature was 25 °C.

Fractography

The fracture surfaces of the DEN specimens have been investigated using SEM (Hitachi S-4000). The fracture surfaces and supporting material were removed from the bulk of the specimen and mounted on standard stubs. The samples were gold coated. It has proved difficult to focus on individual particles as the sample becomes too highly charged. However, a range of magnifications are presented and these are sufficient to understand the toughening mechanisms and also to indicate the level of dispersion.

Results and discussion

Compliance data and Young's Modulus for the systems tested

Figure 1 shows the experimental data obtained for the relationship between compliance and crack length for the different ormosil containing systems and the unmodified (PEs) resin. The phenyl ormosil has the greatest effect on the compliance with a smaller effect due to the methyl, ethyl and vinyl ormosils; these last three systems are extremely close with little to separate them. From the compliance data for the uncracked samples, it is possible to determine the Young's Modulus of the materials. These moduli are presented in Table 2. It can be seen that there is a reduction in the moduli of the nano-composites compared to the unmodified polyester, with the greatest reduction being observed in the phenyl ormosil modified polyester.

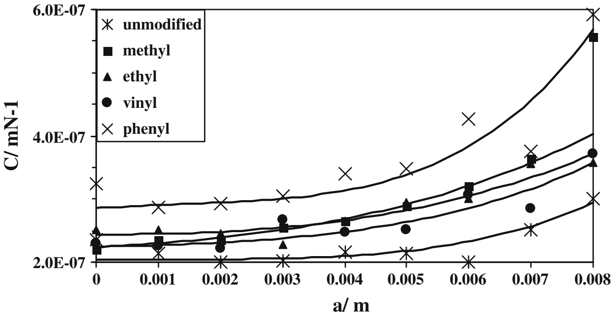

Fig. 1 The relationship between compliance and crack length

From particulate theory it might be expected that the addition of a stiffer particulate phase would lead to an increase in the Young's Modulus of the composite compared to the bulk polymer. However, we must consider that we are dealing not with a 'conventional' filler but with a nano-particle. Hence even a comparatively nominal loading may be expected significantly to disrupt the matrix, due to the much greater number of particles than in a conventional filler system at the same volume fraction. Further, when a particle interacts with the matrix an interphase is produced of polymer affected by the particle. Whilst this interaction may have little or no effect, it is also possible that the self-interaction of the polymer may be affected. It is therefore possible that the matrix is no longer the polyester per se, but rather a phase produced from the overlapping of the interphases associated with each particle. Under these circumstances the properties of the material may be expected to be different from the unmodified material. In the case of the methyl, ethyl and vinyl ormosils this interphase is likely to be limited or, possibly, effectively non-existent. In the case of the phenyl ormosil which has been shown to interact more strongly with the resin, it is suggested that this interphase is likely to be not only present but of a significant size.

The above arguments can be explored quantitatively in a simple way. If we consider a unit cell, a cube, with particles placed at each corner such that the volume of

Table 1 Diameters of ormosil particles

Modified silica	Average particle diameter/nm	
	TEM	SEM
Methyl	85 ± 10	78 ± 9
Ethyl	65 ± 14	65 ± 7
Vinyl	106 ± 19	165 ± 18
Phenyl	148 ± 21	76 ± 9

From Ref. [14]

Table 2 E derived from compliance data (average of five samples)

Resin	Compliance, C ($\times 10^{-7}$ m N^{-1})	Young's Modulus, E (GPa)	J/J m^{-2}
Unmodified	2.04	4.08	130
Methyl modified	2.24	3.72	180
Ethyl modified	2.44	3.42	160
Vinyl modified	2.24	3.72	180
Phenyl modified	2.85	2.92	540

Compliance and Young's Modulus derived from an average of five samples, J values are derived from Fig. 4 and are an average of three values

one particle is contained within the cube then the spacing between the centre of two particles, C, will equal the diameter, $2r$, of one particle plus the inter-particle spacing, i:

$$C = 2r + i \tag{3}$$

The volume fraction of the particles, V_f, will therefore equal the volume of a particle divided by the volume of one unit cell:

$$V_f = \frac{4\pi r^3}{3C^3} \tag{4}$$

Rearranging for C:

$$C = r \cdot \sqrt[3]{\frac{4\pi}{3V_f}} \tag{5}$$

Since V_f in the case of these nano-composites is 0.01, we can estimate that C is approximately $7.5r$ and therefore that i is approximately $5.5r$. Since the average particle size is 140 nm in diameter [14], i is, by calculation, around 380 nm (These calculations are consistent with features that could be identified on one of the fracture surfaces shown later).

Interphases may range in size, with the norm lying in the range 20–200 nm [19]. In the case of the phenyl modified silica the interphase may be expected to lie at the top end of this range, or perhaps even outside. Hence the argument regarding a modified interphase affecting large portions of the matrix appears reasonable.

Toughness data

Having determined the compliance of a material at a number of different crack lengths, it becomes possible to determine J for a specimen. Figures 2 and 3 consider the component elastic and plastic parts of J, J_{el} and J_{pl}, respectively. As can be seen both J_{el} and J_{pl} are approximately double for the phenyl modified resin system compared to both the other modified resin systems and the unmodified system. The relationship between J ($=J_{el} + J_{pl}$) and crack length based on the single specimen method is presented in Fig. 4. This is presented with the addition of horizontal lines of best fit, indicating the values of J that have been determined and assuming that there is no dependence on initial crack length. These values are presented in Table 2.

The value of the critical strain energy release rate, G_C, was determined using compact tension type testing, before it was shown that there was significant non-linearity for the nano-composites. The measured value of polyester G_C for the unmodified system was 140 ± 70 J m^{-2}, which agrees well with the value of J determined for the unmodified polyester and provides confidence in the methodology.

It is apparent that none of the relationships in Fig. 2 is entirely linear although the values should, in prin-

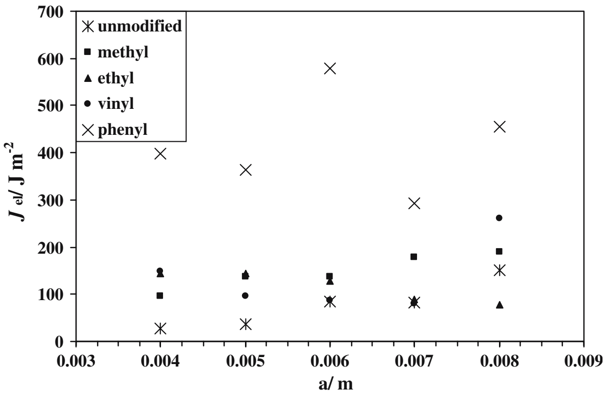

Fig. 2 The relationship between J_{el} and crack length, single specimen method

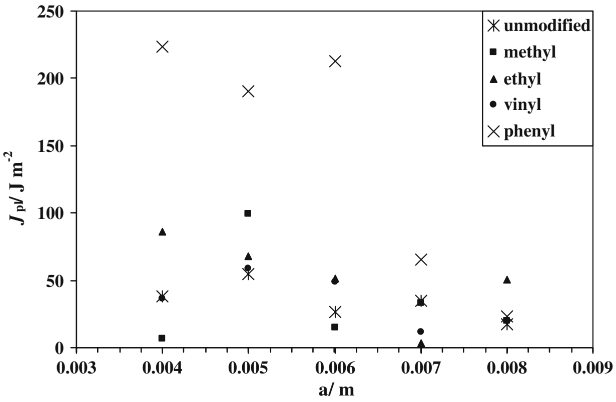

Fig. 3 The relationship between J_{pl} and crack length, single specimen method

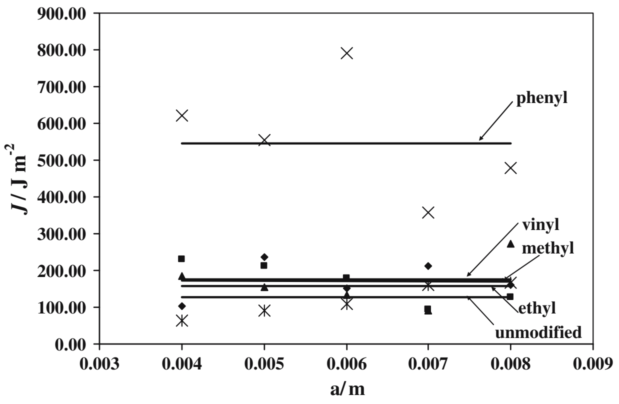

Fig. 4 The relationship between J and crack length with lines of best fit, single specimen method

ciple, be constant with crack length. A slight increase in J is observed with increasing crack length for the unmodified resin which cannot be accounted for. The data for the modified resin systems do not show any systematic trend, however. A possible explanation for the variation in toughness in the nano-composites is that whilst the dispersion is good it is not entirely uniform. A heterogeneous dispersion in a cured sample would lead to localised differences in the material properties. In these circumstances a particular sample might in reality represent a significantly lower loading of ormosil, whilst another might represent a significantly larger loading of ormosil.

Fracture surfaces

The fracture surfaces of DEN specimens have been examined using scanning electron microscopy and representative digital photomicrographs from areas on the fracture surface ahead of the pre-crack are presented in Figs. 5–7. The unmodified and modified resins are compared in Fig. 6 and some particular features are highlighted in Figs. 6 and 7. The micrographs selected are those that best display the features discussed below: at lower magnifications it is difficult to make out the features discussed; whilst at higher magnifications context is lost. The unmodified resin (Fig. 5a) presents a typical smooth fracture surface, consistent with a brittle failure. The surface features of the modified resins (with the exception of the phenyl modified silica, Fig. 5b–d) are reminiscent of the pattern observed following crack pinning by an inclusion or inhomogeneity. This is consistent with the hypothesis that the particles are extremely weakly bonded, if at all, to the matrix, such that a likely toughening mechanism is that of crack pinning [3, 8].

A geometric consideration of the particles with relationship to the crack and crack tip presents some conceptual problems with the hypothesis that toughening is due to crack pinning. This is also true of a number of other toughening mechanisms. The actual toughening mechanism is of comparatively minor importance. Of more interest is the observation that whatever the mechanism, it has only a modest effect on the toughness of the nano-composites produced using ethyl or vinyl ormosils compared to the unmodified resins. Crack pinning is consistent with the moderate toughening effect observed from the incorporation of the methyl, ethyl and vinyl modified silicas, together with photo-micrographs which show a different surface feature to the hackling observed in the unmodified polyester (Fig. 5a). The phenyl ormosil modified resin (Fig. 5e) presents a surface with more crater-like surface features than are observed in the other samples. This rougher fracture surface is indicative of a different toughening mechanism, one in which the available evidence points to a degree of plastic deformation. Some of this plastic deformation would be accounted for in the debonding of the particle from the matrix, a process in which it is likely that the matrix around the particle becomes deformed. In Fig. 6 a surface feature is identified which has only been seen in the methyl and ethyl modified silicas. This type of feature may be due to poor dispersion of the ormosils. It is clearly different to the problematic air bubbles encountered during the initial dispersion trials [17]. It is possible that this feature represents agglomerates that have been interpenetrated by the polyester resin, but without sufficient agitation to break the agglomerate and hence this feature may be analogous to intercalation of clay platelets. At this time this can only be considered as a possibility since it has proven difficult to distinguish particles from the matrix. In Fig. 7b a digital photo-micrograph is presented and it is believed that this shows particles within the matrix and that the dispersion of the particles is quasi-homogenous throughout the matrix. The spacing of the features is consistent with the mean particle size and volume fraction. However, it has not been possible to produce high quality digital photo-micrographs of individual particles in any of the modified resins.

Mechanisms of fracture: the effect of surface chemistry

Conclusions, from another paper [18] regarding the surface chemistry of the ormosils and their interac-

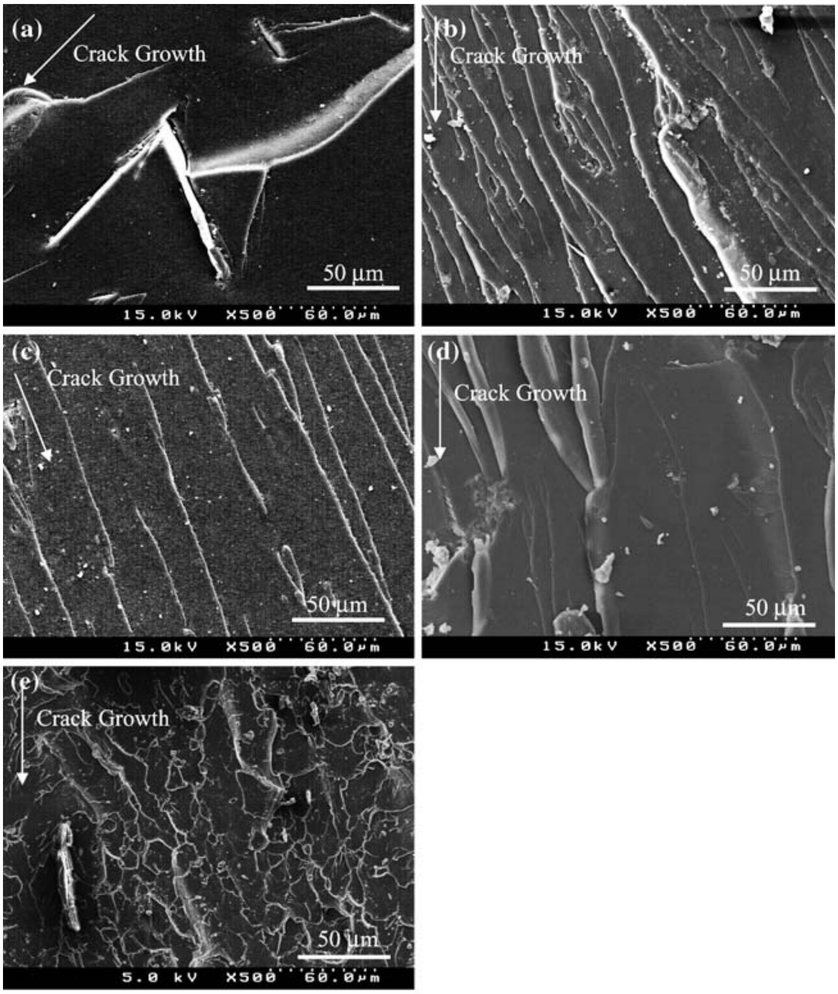

Fig. 5 Digital photomicrographs of the fracture surface of an unmodified polyester resin and ormosil modified polyester resins at similar magnification. (**a**) Unmodified (**b**) methyl modified (**c**) ethyl modified (**d**) vinyl modified and (**e**) phenyl modified

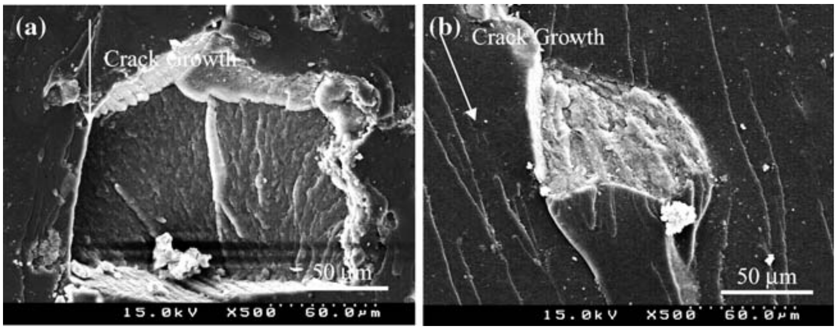

Fig. 6 Digital photomicrographs comparing features on the fracture surface of two ormosil modified polyester resins. (**a**) Methyl modified and (**b**) ethyl modified

tion with a polyester, were presented at the beginning of this paper. In particular, there is a difference between the phenyl ormosil and the other modified silicas. The phenyl ormosil has a surface structure that allows retained silanol groups to interact chemically with the resin system, whilst the surface structure of the methyl, ethyl and vinyl modified silicas do not allow retained silanol groups to interact. In effect, apart from the phenyl modified silica, the surface chemistry of the ormosils is such that there is little if any interaction between the particles and the matrix. Hence, these nano-particles will behave in the manner of voids, as discussed by Lange [20]. These voids act to pin the crack front.

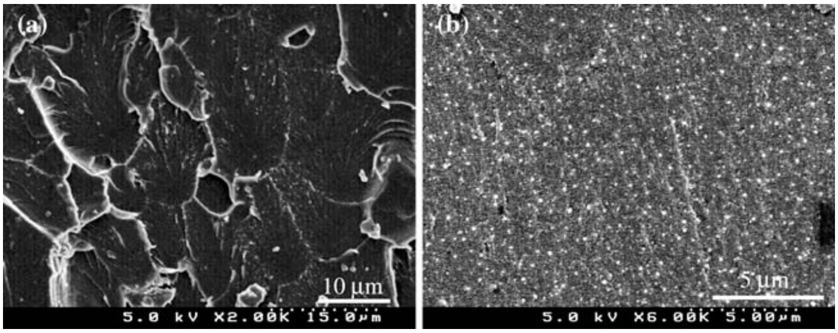

Fig. 7 Digital photomicrographs of the fracture surface of a phenyl ormosil modified polyester resin at two levels of magnification

Should there be any bonding between these ormosil nano-particles and the matrix then this will be beneficial in that it will act to absorb energy, unlike the bonding between the commercial silica and the matrix, which can be considered too strong: if bonding is too strong then a bonded particle would act to deflect the crack front to a *minimally impeded path* [4]. The bonding between the matrix and the phenyl ormosil nano-particles lies between that of the extremely strong bonding of the commercial silica (facilitated by the large numbers of silanol groups) and the extremely weak bonding of the other ormosils. In the case of the phenyl modified silica therefore, it is clear that there is a more complex process at work.

Huang and Kinloch [21] presented a summary of toughening by rubbery particles. Of the mechanisms presented, the bridging mechanism presented is clearly specific to rubbery phases. The cavitation of the rubbery particle would also seem to be a specific mechanism, but this could be deceptive. It has been shown that hard particles can undergo a cavitation-like process that is due to debonding of the particle from the matrix, as well as plastic deformation of the matrix around the particle [22]. Also, a more general form of toughening is localised shear band yielding. This presents a significant option. It is possible that the stronger bonding between the retained silanol groups and the polymer system allows localised shear band yielding to occur, whilst the disruption provided by the phenyl modification prevents the matrix from becoming too strongly bonded to the particle. The weakly bonded particles are not easily fractured, but the dispersed stronger bonds anchor the matrix in place such that the matrix can plastically yield over a much larger volume.

Given the magnitude of improvement in the toughness of the phenyl ormosil modified resin it is probable that more extensive plastic deformation is taking place throughout the matrix, in the form of shear, or dilatational, bands. The inter-particle spacing is an important factor when determining the effectiveness of this type of toughening [19, 22–24]. Whilst a method of determining the critical spacing has not yet been determined, it has been shown that there is an increase in toughness with a decrease in spacing. This is attributed to a change in the stress state within the region of the ligament which changes from plane strain to plane stress, allowing more significant plastic deformation to take place before failure.

Further, as argued above, when considering nanoparticle modified systems, the scale of the particles must be considered. For a constant loading of particulates, the probability that the interphases will interact in this manner increases as the particle size decreases. Hence, when dealing with nano-particles, even a modest volume fraction can lead to a condition where there is interaction between the interphases associated with particles. Under these circumstances the properties of the material may be expected to be different from the unmodified material. In addition, overlapping interphases are likely to carry out the localised shear band yielding, mentioned previously, and hence act on other particles causing them to initiate localised shear bands, in such a manner that the process zone of plastically deformed material may become larger than might at first be expected.

Concluding remarks

By modifying the surface of silica nano-particles with organic functionalities it has been possible to show that there is a potential to tailor the acido-basic functionality to particular needs. In the current research, it has been shown that complete modification of the surface, such that retained silanols are unable to interact with the polyester system leads to a slightly tougher system than the unmodified polyester. A tougher nano-composite is produced, however, if the silanol groups are reduced (compared to an unmodified silica particle) but not entirely eliminated (as is the case with the phenyl modified silica). The difference in toughening mechanism is attributed to a difference in the surface characteristics between the methyl, ethyl and vinyl ormosils (retained silanol groups are unable to interact) and the phenyl ormosil (retained silanol groups are still able to interact).

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