

ORGANIC-INORGANIC HYBRID NANO-PARTICLES AS MODIFIERS FOR POLYMER COMPOSITE MATRICES

David A. Jesson¹, Anna Arkhireeva², John N. Hay², Paul A. Smith¹ and John F. Watts¹

¹ School of Engineering, University of Surrey, Guildford, GU2 7XH, UK

² Chemistry Division, SBMS, University of Surrey, Guildford, GU2 7XH, UK

ABSTRACT

Organically modified silica (ormosil) nano-particles have been prepared with phenyl group functionality and have been incorporated into a polyester resin at loadings of up to 10 volume percent, using various processing routes to disperse the nano-particles. The phenyl ormosil nano-particle modified resins have been characterised mechanically utilising Charpy and fracture mechanics (compact tension) tests and the results have been compared with corresponding data from unmodified resin. The effects of the ormosil nano-particles and the solvents utilised in the effective dispersion of the nano-particles on the morphology and properties of the modified resin systems are discussed.

1. INTRODUCTION

One of the limiting features of composite materials in service is their tendency for matrix cracking within and, in particular, between plies. There is a large body of research in the polymer composites literature concerned with the selection or modification of the matrix in order to optimise the toughness in the composite, in particular with regard to delamination resistance. Amongst the methods, which have been used, are 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. The present work is concerned with matrix modification by incorporation of organically modified silicate nano-particles.

Considerable interest has been shown recently in organically modified silicates (ormosils) because of the wide range of possible applications for such organic-inorganic hybrids [1-4]. These applications include the use of the hybrids to improve a range of bulk polymer properties. The ormosils can be synthesised by the conventional hydrolytic sol-gel process [5], as well as by the non-hydrolytic sol-gel route. Nanoparticulate technology represents another area of interest in current research [6-10] and although research is carried out in fields such as carbon nanotubes [11], the majority of research relates to the use of silicates such as clay.

This project brings together the two areas of organic-inorganic hybrids and nanoparticulates in a piece of work concerned with the production of a range of ormosil nano-particles and their subsequent incorporation into polymers and polymer composites, with the intention of comparing the properties of modified systems with previously tested unmodified systems. An associated area of interest is the nature of the interface between the ormosil nano-particles and the polymer into which they are dispersed, for which initial work was reported in [12].

In the part of the work reported here, a range of hybrid nano-particles has been prepared from corresponding organoalkoxysilane precursors using the hydrolytic sol-gel process. Samples have also been prepared using the non-hydrolytic sol-gel process. The morphology of the particles depends on the type of organic group present in the ormosil and the specific reaction conditions. These particles have then been incorporated into a polyester matrix (at volume fractions of up to around 10 %), using a number of processing routes. The effect of the nano-particles and the processing route on the mechanical properties, in particular toughness, has then been determined. The results have been compared with those from the unmodified polyester, both with and without the commercial thixotropic agent (1% fumed silica) present.

2. EXPERIMENTAL

2.1 Materials

The standard polymer system used was Crystic 2-406PA (Scott-Bader), referred to as PE+1 vol% HDK N20; this is cured at room temperature with Catalyst M (Scott-Bader), a trade name for the initiator methyl ethyl ketone peroxide (also referred to as MEKP or MEK peroxide). All the samples described here were cured with 1 vol% initiator and were post-cured at 80°C for 3 hours. HDK N20 (Wacker, a commercial fumed silica) is used as a thixotropic agent in quantities of approximately 1 vol%. HDK N20 has a particle size of approximately 10 nm, forms aggregates of approximately 100-500 nm and flocculates to form agglomerates of approximately 10-50 µm.

Further samples of this resin were supplied without the fumed silica addition and these are referred to as PE. This was cured and post-cured in the same way as the resin with the thixotropic agent. Fig. 1 shows a schematic of a possible structure of the polyester resin - the structure is based on statistical probability rather than a rigorous chemical analysis.

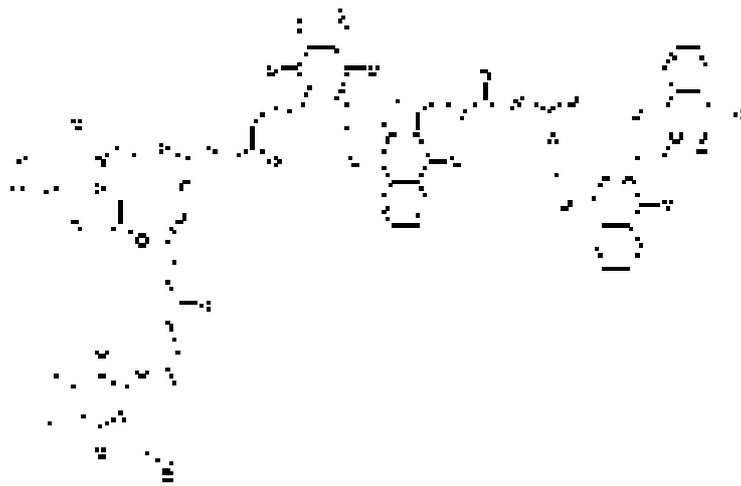


Fig. 1. Theoretical structure of the polyester. This structure is based on statistical probability of components present rather than a fully calculated series of chemical reactions.

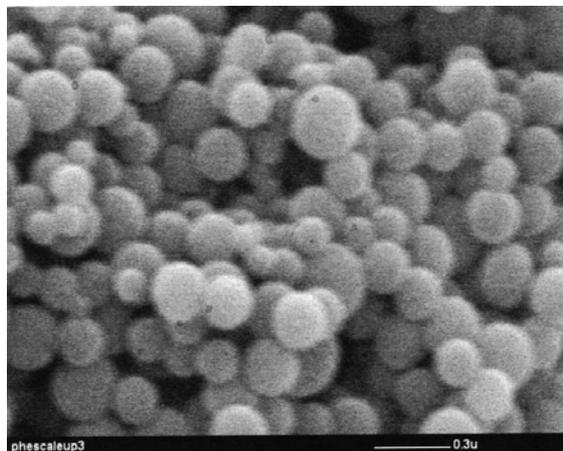


Fig. 2. Phenyl modified silica particles synthesised by the hydrolytic method

Phenyl modified silica nano-particles (~100-160 nm in diameter) produced in two ways were available (i) synthesised using a modified Stöber (hydrolytic) route [7]; these particles were typically 100 – 160 nm in diameter (Fig. 2) and (ii) synthesised using a non-hydrolytic route; these particles were typically 200 – 400 nm in diameter.

Samples of resin with nano-particle additions were prepared using a number of processing routes, described in 2.2, below.

2.2 Processing Routes

Dispersion of the nano-particles into solution is not straightforward because the particles have a tendency to agglomerate when incorporated into the resin. Several methods have been examined to produce adequate dispersion of the particles. Due to the limited quantity of ormosils available, some of the initial trials were carried out using HDK N20 to simulate the ormosils. The methods investigated were manual dispersion of the particles in the resin, high shear dispersion of the particles in the resin and dispersion of the particles in a solvent prior to mixing with the resin. Following dispersion, plaques of 3 mm thickness were cast in an aluminium mould. This gave a good surface finish and no subsequent machining was needed. Table 1 summarises the samples prepared and the associated processing routes. More details are given below.

Table 1. Summary of materials and processing methods investigated

Series	Resin	Dispersion Method	Particles		Notes
			Type	vol %	
1	PE	Manual	N/A		Clear
2	PE+1 vol% HDK N20	Manual			
3	PE	High Shear	HDK N20	1	Visible agglomerations
4	PE	Ethanol	None	0	Clear, no visible particles
5	PE	Ethanol	HDK N20	1	
6	PE	Manual	Phenyl	1	Poorly Dispersed (Fig. 3.)
7	PE	Ethanol	Phenyl	1	Clear, with some visible particles (attributed to post particle production aggregation)
8	PE	Ethanol	Phenyl	8	Agglomerations observed, these are wispiier than those in series 3
9	PE	Ethanol	Phenyl	10	
10	PE	Ethanol	Phenyl	1	Non-hydrolytic phenyl particles, clear, no visible particles

Manual dispersion was used to prepare the base-line polyester resin, with and without thixotropic agent present (Series 1 and 2). When the particles were included in this process by simply stirring them into the resin in the same way as the initiator (Series 6), the degree of dispersion in the cured resin was inadequate. Fig. 3 shows a photomicrograph of a polished section through a section cut from the Series 6 plaque and the agglomeration of the ormosils is apparent.

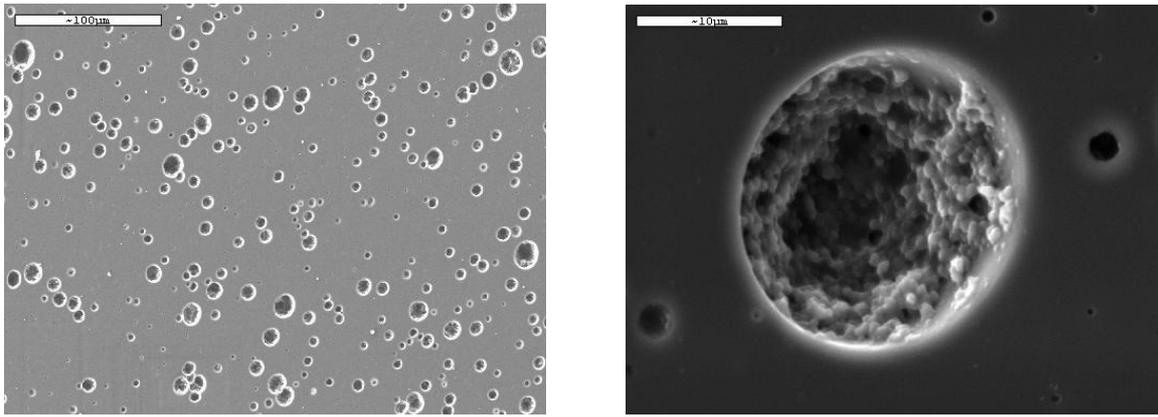


Fig. 3a and b. Digital photomicrographs showing agglomeration of the phenyl ormosils in the polyester matrix.

In an attempt to disperse the particles more effectively, the base-line polyester resin with fumed silica was subjected to high shear mixing using a Cowles blade operating at ~ 8000 rpm. This was developed by adding a stage where a “paste” of fumed silica and polyester was prepared using a pestle and mortar prior to dispersion in the bulk resin (Series 3). Whilst this showed an improved distribution compared to the first attempt, in both samples a discrete phase was visible within the bulk resin, associated with areas where the silica particles were present at higher density.

In view of the difficulties in dispersing the particles effectively in the resin, it was decided to attempt to disperse them in a solvent (ethanol), prior to dispersion in the polymer and the subsequent removal of the ethanol. This route involved the creation of a paste of the ethanol and the nano-particles, the incorporation of polymer into the solvent, the use of an ultra-sonic bath to aid the dispersion of the particles in the ethanol and bubbling an air stream through the polymer to aid in the evaporation of the ethanol and. It has been found also that the removal of the ethanol is accelerated under vacuum. Whilst Crystic 2-406PA is a low-styrene emission resin, some styrene was lost during the removal of the ethanol. The masses of all samples that were prepared with this method were monitored to determine the styrene loss during the removal of the ethanol and this mass was replaced prior to curing. Overall the visual appearance of samples suggests that this method produces samples that are more evenly dispersed (Series 5, 7-10). A control plaque was also produced where the polyester was processed with ethanol, without any particulate additions (Series 4).

2.3 Impact Testing

For impact testing, samples of 12 x 60 mm were machined from each of the 3 mm thick plaques and notched, following ASTM D6110-97. Charpy-type impact testing was carried out using an in-house test facility.

2.4 Compact Tension Testing

Compact tension specimens were prepared from 3 mm thick plaques. Sample dimensions were 46 mm x 50 mm with 10 mm diameter holes drilled at the appropriate points according to ASTM D5045-96. Notching and the production of a sharp crack were carried out following standard method. The sharp pre-crack was produced using a razor blade. Compact tension testing was carried out using an Instron 1175 (100 kN load frame) testing machine with 5500R upgrade. A 5 kN load cell and a dynamic extensometer of 25 mm gauge length (with 5 mm travel) was used; data collection was through the Instron Merlin software. Values of stress intensity factor K and energy release rate G at crack propagation were obtained. For

the latter, load-displacement curves were needed from specimens before and after notching. The crosshead displacement rate used for all testing was 0.1 mm/min. With the exception of specimens from series 8 and 10 plaques, all specimens displayed unstable crack growth. Series 8 and 10, upon reaching maximum load displayed stable crack growth with clear signs of plastic deformation around the crack tip; after removal of the extensometer, the crack growth remained stable until the sample was fractured completely, with an associated extension of approximately 10 mm.

3. RESULTS

3.1 Material Quality

Achieving a reasonable dispersion of the ormosils in the resin has been a key aim of the present work. As mentioned in 2.2 above, series 6 represented the first attempt to produce a resin with ormosils; the particles were difficult to disperse by the manual method and remained agglomerated. Series 3 samples (which were prepared by high shear mixing) also showed regions of poor dispersion. Better results were achieved by the solvent route. Series 7-9 are representative of a series of experiments designed to identify the levels of particle loading for which a reasonable dispersion might be achieved. Loadings of 1 - 6 vol% dispersed well, but at higher loadings the particles had a tendency to agglomerate. The agglomerations in series 8 were dispersed randomly throughout the whole plaque, whereas in the 10 vol% plaque the majority of these agglomerates were situated in the bottom half of the plaque. Samples for mechanical testing were produced from both halves, but the data from the two halves were sufficiently similar that the data were amalgamated and taken as representative of 10 vol% loading.

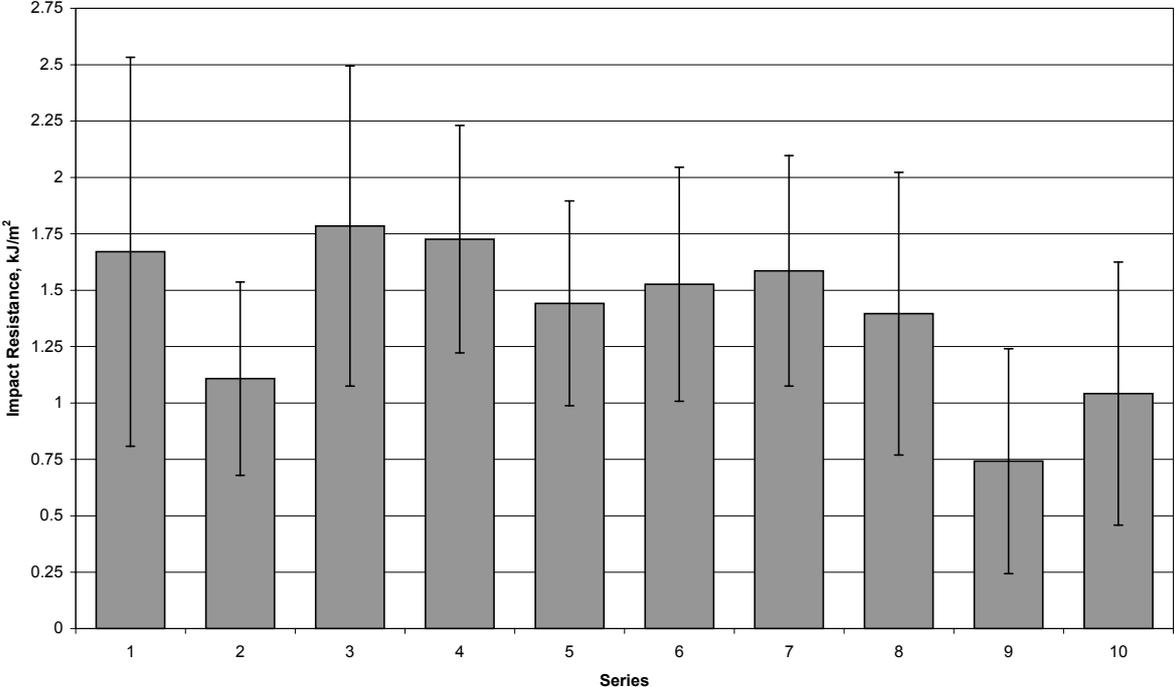


Fig. 4. Charpy impact test results for a number of series of samples as outlined in Table 1.

3.2 Impact Testing

The results from the impact tests on samples cut from the series of plaques presented in Table 1 are shown in Fig. 4. As is often the case with Charpy testing of this type, the variation (standard deviation) is large and it can be seen that all the data overlap within one standard deviation.

3.3 Compact Tension Testing

Compact tension testing was carried out on samples from series 1, 2, 4, 5, 8 and 10. Load-displacement data are presented in Fig. 5 and 6, while values for K are presented in Fig.7. Series 8 and 10 data are included in these figures, although it is recognised that the load-displacement data from these series display an unacceptable degree of plastic deformation in the context of LEFM property measurements. Fig. 5 shows an indicative load-displacement curve from a series 10 sample, compared to similar samples from Series 2 and 4. Fig. 6 presents data for the average value of the maximum load plotted against the average value of the maximum displacement during the compact tension tests, i.e. a number of tests (three in the cases of series 8 and 10 samples, six in the cases of 4 and 5 and more in the cases of 5 and 7) have been analysed to provide maximum values, which have then been averaged. The data need to be viewed with some caution, since samples had different thicknesses and different starter crack lengths. The greater ductility of samples from series 8 and 10 is clearly apparent from the larger displacement values. Fig. 7 presents the K data for all of the compact tension samples. The G values are not shown, but it should be noted that the values for series 8 and 10 were significantly enhanced, compared to those from series 4.

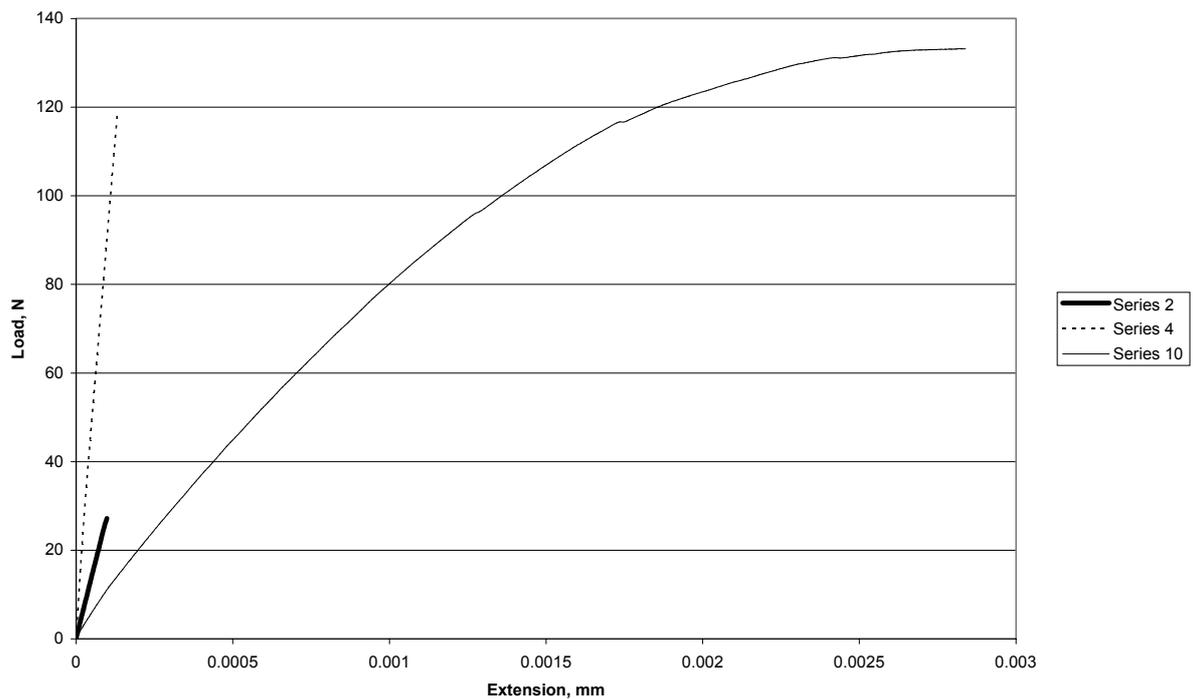


Fig. 5. Typical load-extension data during compact tension tests on three of the resin series (details of the series are given in Table 1)

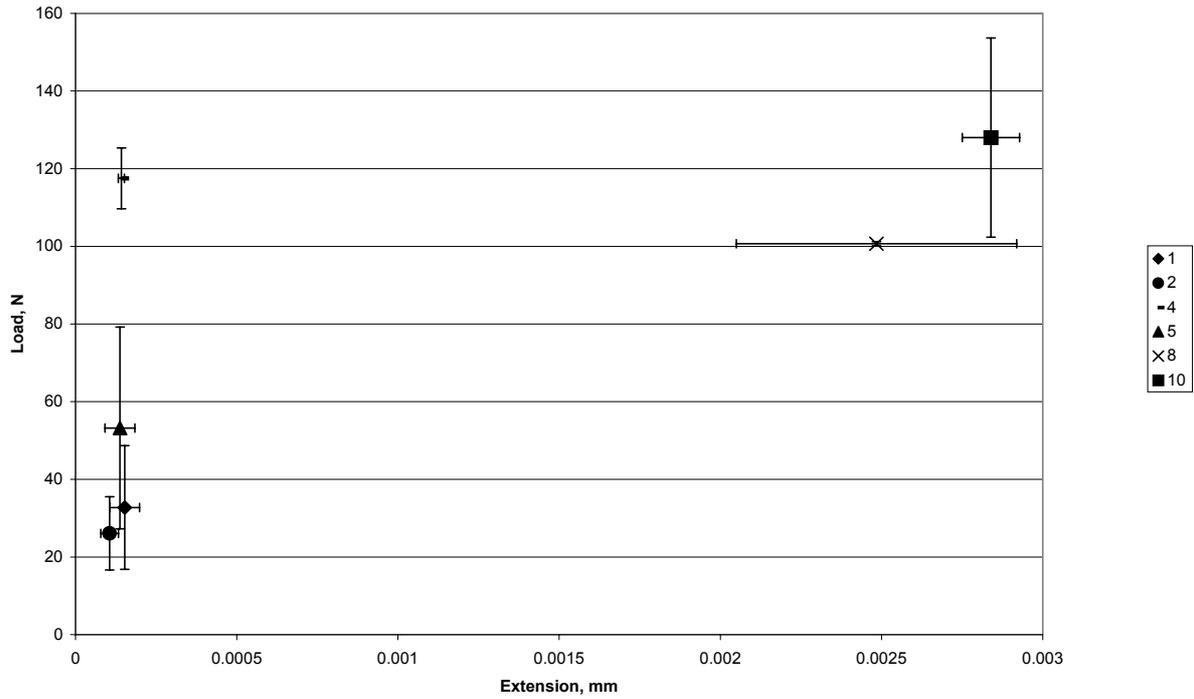


Fig. 6. Mean value of maximum load plotted against mean value of maximum extension from compact tension tests on a range of resins (details of series are given in Table 1). Error bars show $\pm 1\sigma$.

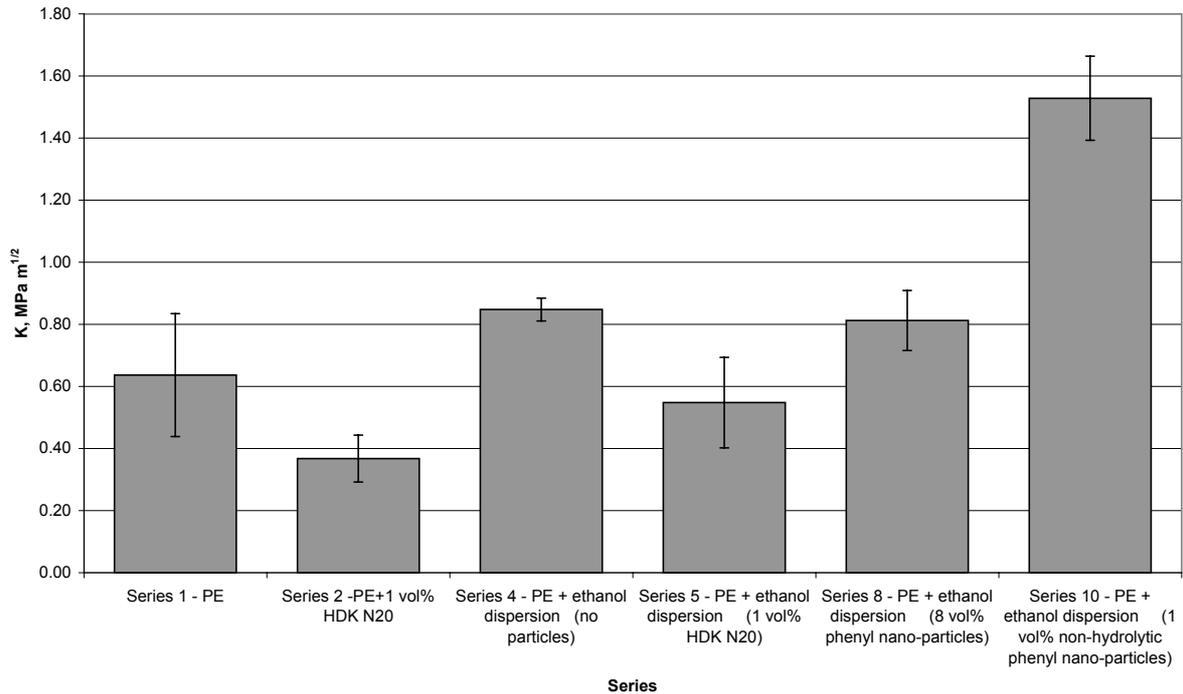


Fig. 7. "Fracture toughness" values for modified and unmodified polyester resins, determined from the peak load in the compact tension tests.

4. DISCUSSION

The Charpy data are inconclusive. Any differences between the materials cannot be discerned clearly within the variability of the results obtained. It may be that higher loadings of ormosil (series 9, 10) give lower impact resistance (Fig. 4).

Some of the trends in the compact tension data are more significant however. The data from series 1, 2, 4 and 5 perhaps suggest first that the presence of the fumed silica reduces the K value compared to that of the base resin without the fumed silica and second that the K values are enhanced to a degree by some effect of the ethanol processing route. On the other hand, the mean values for each set of samples are all fairly close to typical literature values for a polyester. The addition of particles has had a clear effect on the samples tested by compact tension. While the K value derived for series 8 samples is similar to series 4, the dramatic increase in the maximum extension suggests a significant improvement in G (or more appropriately perhaps J) values. The K value (and G value) for samples from series 10 is clearly the highest of all the sets. The slow crack growth in the compact tension samples, together with the Charpy data, suggests that the benefit of the ormosils lies in preventing crack growth at low strain rates rather than providing impact resistance.

5. CONCLUDING REMARKS

Organically modified silica particles have been synthesised, with phenyl groups replacing surface hydroxyl groups, via both the hydrolytic and non-hydrolytic routes. A processing route, in which the nanoparticles are dispersed initially in ethanol, prior to combining with resin, appears to produce a reasonable distribution of nanoparticles in the final plaques. Charpy-type and compact tension specimens have been prepared from cast plaques and tested.

It is clear that the particles are having an effect on crack propagation in the resin. Testing of a greater range of loadings is underway and proper quantification through J-integral methods may well be needed. The effect of using the modified matrix in glass fibre laminates will then be examined.

Other areas of further work will include the testing of other solvents for the dispersion of the ormosil nano-particles in the resin. Non-polar solvents such as toluene may be investigated. Other possibilities include PMA and styrene, which should not disrupt the existing chemistry. This must be considered carefully, however, as increasing the concentration of styrene in the resin system or introducing PMA may lead to differences in the cured structure leading to changes in the material properties. Other ormosils will also be tested for their effects upon the resin system: to date methyl, ethyl and vinyl particles have all been synthesised and the synthesis of ormosils with other functionalities is planned. It is also important to determine if there are differences in the synthesis route (i.e. hydrolytic or non-hydrolytic).

ACKNOWLEDGEMENTS

The authors wish to thank the Engineering and Physical Sciences Research Council (EPSRC) and the MoD (through the Defence Science and Technology Laboratory - dstl) for their joint funding of this project, Scott-Bader for their support of this project, Dr. Brian Le Page for his assistance in the production and testing phases and Mr. Arran Wood for his assistance with the Charpy testing.

References

1. **Kasemann, R., and Schmidt, H.**, "Coatings for Mechanical and Chemical Protection based on Organic-Inorganic Sol-Gel Hybrids", *New Journal of Chemistry*, **18**, (1994), 1117-1123
2. **Mackenzie, J.D.**, Hybrid Organic-Inorganic Materials: The Sol-Gel Approach", *ACS Symposium Series*, **585**, (1995), 226-236

3. **Hou, L., Hoffman, B., Schmidt, H. and Mennig, M.**, "Effect of Heat Treatment and Additives on the Photochromic and Mechanical Properties of Sol-Gel Derived Photochromic Coatings containing Spirooxazine", *Journal of Sol-Gel Science and Technology*, **8**, (1997) 923-926
4. **Lebeau, B. and Sanchez C.**, "Sol-Gel Derived Hybrid Inorganic-Organic Nanocomposites for Optics" *Current Opinion in Solid State Materials Science*, **4**, (1999), 11-23
5. **Arkhireeva, A. and Hay, J.N.**, "Synthesis of sub-200 nm silsesquioxane particles using a modified Stöber sol-gel route", *J. Mater. Chem.*, **13**, (2003), 3122-3127
6. **Nicourd, J.-F.**, "Toward New Multi-Property Materials", *Science*, **263**, (1994), 636-637
7. **Giannelis, E.P.**, "Polymer Layered Silicate Nanocomposites", *Advanced Materials*, **8**, (1996), 29-35
8. **Gilman, J.W.**, "Flammability and Thermal Stability Studies of Polymer Layered-Silicate (Clay) Nanocomposites", *Applied Clay Science*, **15**, (1999), 31-49
9. **Song, J.H., Huh, H. and Hahn, H.T.**, "Stress Evaluation of Nanocomposites with Nanoplatelets", ICCM conference proceedings" (2003)
10. **Lui, W., Hoa, S.V. and Pugh, M.**, "Effects of Morphology of Organoclay modified Epoxy Nanocomposites on Mechanical Performance", ICCM conference proceedings, (2003)
11. **Viculis, L., Mack, J., Ali, A., Luoh, R., Yang, G., Kaner, R., Hahn, T. and Ko, F.**, "Nanocomposite Fibrils from Graphite Nanoplatelets", ICCM conference proceedings, (2003)
12. **Jesson, D.A., Abel, M.-L., Arkhireeva, A., Hay, J.N., Smith, P.A. and Watts, J.F.**, "Organic-Inorganic Hybrid Nanoparticles: Adsorption Characteristics of Polyester Resins", *Surface and Interface Engineering(special edition – papers submitted at ECASIA '03)*, Submitted