JOURNAL OF
Materials
CHEMISTRY

Curing and morphology of epoxy resin–silica hybrids

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Received 3rd July 1998, Accepted 25th August, 1998

Hybrids of epoxy resin and silica cured respectively with methyl nadic anhydride (MNA) and 4,4′-diaminodiphenyl sulfone (DDS) were prepared. Control of the morphology was achieved through functionalisation of a diglycidyl ether resin respectively with monofunctional and difunctional secondary amine trialkoxysilanes prior to being mixed with a solution of tetraethoxysilane (TEOS) and hardener. Scanning and transmission electron microscopy examinations (SEM and TEM) were carried out to study the morphology of the samples. The results have shown that the preparation conditions and nature of solvent play a vital role in the compatibilisation of the final hybrid. The addition of a hydrolysed TEOS solution into the epoxy resin to produce the corresponding hybrid was found to interfere with the cross-linking reactions with the hardener, inevitably resulting in a reduction in the T_g of the epoxy resin component. This was attributed to side reactions of MNA with the ethanol released from hydrolysis and condensation of the TEOS, producing monofunctional and difunctional esters which act as plasticisers and to decreased functionality of the epoxy resin from the reaction with the HCl used for the hydrolysis of TEOS.

Introduction

Prevention of phase separation and morphology control are crucial factors in the preparation of organic–inorganic hybrid materials (also known as ceramers or nanocomposites) produced by the *in situ* polymerisation of a hydrolysed metal alkoxide within the bulk of an organic component.

It has been shown that highly transparent hybrid materials, with phase domains <100 nm, can be produced by a variety of compatibilisation techniques. *e.g.* (1) Through functionalisation of the polymer or polymerisable oligomer with a trialkoxysilane.[1–4] (2) By adding a functional trialkoxysilane, as a coupling agent, to the precursor mixture to chemically link or provide strong physical interactions between the organic and inorganic domains.[5] (3) By using another polymer as compatibiliser, which is miscible with the primary polymer component and is capable of producing strong interactions with the siloxane component.[6]

Homogeneous hybrids have been prepared also without the use of coupling agents from solutions of polymers containing pendant carbonyl groups along the chains, such as polyvinyl acetate (PVAc) and poly(methyl methacrylate) (PMMA).[7,8]

David and Scherer[9] have shown that hybrids of poly(ethyloxazoline) and silica form a molecular semi-interpenetrating network, as a result of extensive hydrogen bonding being formed between the silanol groups of the siloxane network and the carbonyl groups in the polymer.

Very little has been reported on the preparation of epoxy resin/silica hybrid. Landry *et al.*[4] have prepared a hybrid material from a very high molecular weight epoxy resin ($M_w = 47000$), functionalised with γ-aminopropyltriethoxysilane and silica. A dioxane solution of the reactants catalysed by 0.15 M HCl was cast in open air and subsequently allowed to gel and the solvent to evaporate over a period of two days. This was followed by further drying at 60 °C for 2 h and a curing step at 150 °C for 15 h. No specific mention was made, however, of any likely crosslinking reaction taking place within the organic polymer phase.

Recently, Nishijima *et al.*[10,11] have reported the preparation of a hybrid material based on an epoxy resin/silica system, using tetraglycidyl-*meta*-xylenediamine (TGMXDA) as the resin and 1,2-cyclohexanedicarboxylic anhydride (HHPA) as curing agent. In this case, the hybrid was prepared by producing first a silica filler by the sol–gel method, containing *N*-β-aminoethyl-γ-aminopropylmethyldimethoxysilane as a coupling agent which was subsequently incorporated in the epoxy resin mixture.

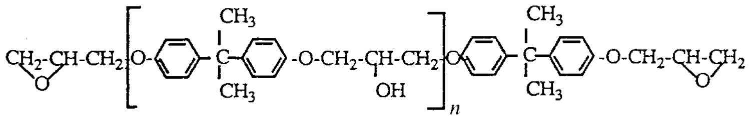
Several workers have used the intercalation process to produce an epoxy resin–clay hybrid[12–15] utilising the well defined dimensions of the structure layers of the chosen clay (*i.e.* montmorillonite). Other workers have shown that the important factor in controlling the dimensions of the inorganic phase is the nature of the intercalating agent.[16]

In this work the possibility of producing hybrids of a cured epoxy resin with silica is being investigated with the scope of determining the influence of curing agents and reaction conditions. Although the occurrence of some adverse reactions between the components of the alkoxysilane precursor for the inorganic phase and either the hardener or the epoxy resin can be anticipated, the extent to which they will affect both the compatibilisation mechanism and the final properties cannot be predicted. This work seeks to identify the major difficulties that are likely to be encountered in attempting to produce epoxy–silica hybrids.

Experimental

Materials

(a) Resin components. The resins used were all bisphenol-A types, namely Epikote 828, Epikote 1001 and Epikote 1009 (manufactured by Shell Chemicals). These have a number average molecular weight of *ca.* 370, 880 and 5000, corresponding to an average degree of polymerisation of 0.1, 2 and 16, expressed in terms of central $CH_2CHOHCH_2$ units per molecule. Their general structure is as shown below:



Two hardeners were used, respectively methyl nadic anhydride (MNA), corresponding to methyl 4-*endo*-methylene-tetrahydrophthalic anhydride, in conjunction with *N*-benzyldimethylamine (BDMA) as catalyst, and 4,4′-diaminodiphenyl sulfone (DDS).

(b) Alkoxysilanes. Tetraethoxysilane (TEOS) (purity> 95%), obtained from Fluka, was used as the precursor for the formation of the silica phase. The compatibilising agents were trialkoxysilanes types, *N*-phenylaminopropyltrimethoxysilane (Y-9669) (purity>98.5) and bis(γ-trimethoxysilylpropyl)amine (A-1170) (purity>95%), both obtained from OSI Specialities.

(c) Auxiliaries. A 32 wt.% solution of HCl in water was used as catalyst for the hydrolysis of the TEOS component. Dimethylformamide (DMF) and tetrahydrofuran (THF) were used as solvents.

Functionalisation of the epoxy resin

Preliminary attempts to functionalise the epoxy resin with either a primary amine silane (*i.e.* γ-aminopropyltriethoxysilane) or with an isocyanate silane (*i.e.* γ-isocyanatopropyltriethoxysilane), from reactions in bulk at 90 °C produced rapid gelation and, therefore, were not studied further.

Aliphatic primary amines are known to react very rapidly with epoxy groups and, despite their bifunctionality, they can promote the formation of highly branched species by catalysing the internal condensation reactions *via* the newly formed hydroxyl groups.

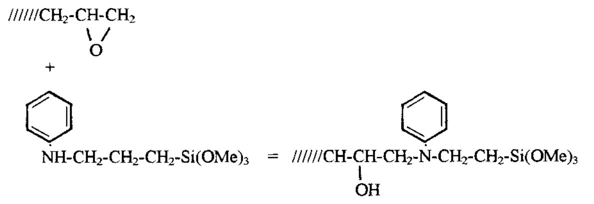
The gelation resulting from the reaction with the isocyanate silane is due to the very rapid reaction of –CNO with the pendant hydroxyl groups in the $-CH_2CH(OH)CH_2O$ segment in the epoxy oligomer, and the subsequent reaction of the urethane groups so formed with the epoxy groups, and with itself, to produce the corresponding allophonate groups.

Subsequent preliminary experiments have identified secondary amines to be suitable for the functionalisation of the chosen epoxy resin. The chemical structure of the silanes used is described in the materials section above.

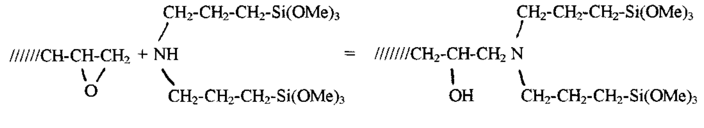
In a round bottom flask was added the epoxy resin and the secondary amine coupling agent at different molar ratios. The mixture was stirred for 2 h at 90 °C and the progress of the reaction was followed by FTIR analysis and by observing qualitatively any increase in viscosity. ^{1}H NMR measurements were used to determine the reaction yield using a 300 MHz equipment.

The reaction scheme for the functionalisation of the epoxy resin is as shown below:

(a) Reaction with *N*-phenylaminopropyltrimethoxysilane



(b) Reaction with bis(trimethoxysilylpropyl)amine



It is important to note that only partial functionalisation of the epoxy resin is being considered in these studies so that the composition of the organic phase will remain essentially similar to that of a cured epoxy resin. This confers to the resulting hybrids features that are substantially different from earlier systems in which the difunctional organic oligomer was part of the siloxane network, forming a separate phase from the pure silica network.

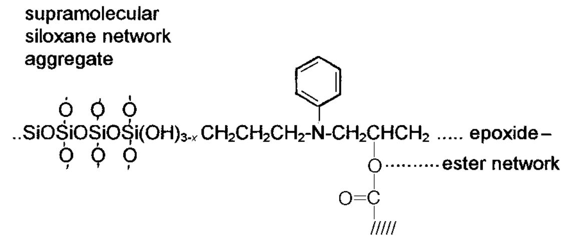
The expected advantages of using the epoxy functionality to produce a network with conventional hardeners for epoxy resins are twofold: (a) it makes it possible to produce hybrid materials in which the organic component predominates so that the inorganic phase acts primarily as a reinforcing component. (b) The formation of a purely organic network would make it possible to produce larger organic domains, thereby reducing the level of brittleness normally experienced with conventional oligomer based organic inorganic hybrids.[1,2]

Preparation of epoxy resin ceramers

The trimethoxysilane functionalised epoxy resin was dissolved in an anhydrous solvent, either DMF or THF, at *ca.* 25 wt.% concentration and measured amounts of water and TEOS at molar ratio of 3–4:1 were added. This was followed by the addition of the HCl solution to bring the pH in the range of 2–3. The reactants were stirred until the mixture became clear (*ca.* 12 h) and finally the resin and the MNA hardener were added. The ceramer solutions were cast in PTFE moulds and the solvent allowed to evaporate slowly at room temperature for *ca.* 24 h to induce gelation and then cured at 80 °C for 48 h. Further curing was carried out in several steps, *i.e.* 24 h at 120 °C, 5 h at 150 °C and 3 h at 180 °C.

The above reactions involve the formation of two primary networks, an epoxide–ester network and a high density siloxane network (silica), each forming two separate phases. The two main phases are linked by species consisting of a network containing the two components.

A schematic example of this type of network is shown below:



Characterisation of the hybrids

(a) The compatibility of hybrids was first assessed from a visual inspection of the state of cast films in order to obtain a qualitative assessment of the dimensions of the phases. Cloudiness and opacity was taken to indicate the presence of heterogeneous structures of the order of *ca.* 0.5 µm or larger.

(b) The morphology of the cured resins was characterised by examining fractured surfaces using a Cambridge stereoscan electron microscope (360 Model). Some samples were etched with a 10 wt.% aqueous HF solution to enhance the contrast between the two phases. Examinations were also made by

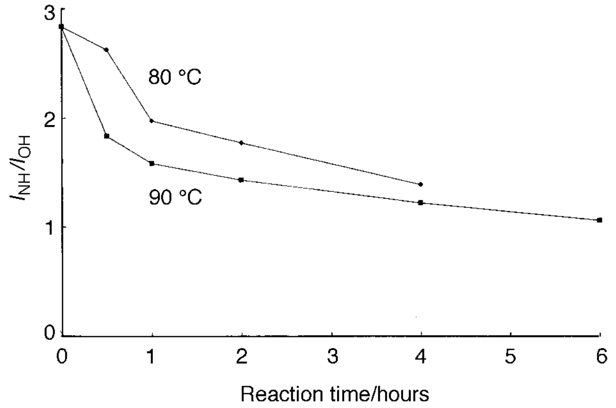


Fig. 1 Conversion of NH groups in the secondary amine silane (Y-9669) in the reaction with Epikote 828 at a molar ratio of 2:1.

transmission electron microscopy (TEM-100CX apparatus manufactured by JEOL Ltd) on thin slices microtomed from cast films cast in epoxy resin.

(c) The curing reactions of the functionalised epoxy resin with hardener were followed by FTIR analysis (Mattson 3000 FTIR spectrometer) and the glass transition temperature (T_g) of the epoxide network in the ceramers was measured using a Dupont DSC 9000 apparatus.

(d) Various model experiments were carried out to elucidate the mechanism of the reactions involved in the curing process. (These are outlined in the next section.)

Results and discussion

Functionalisation of epoxy resins

The reaction of the low molecular weight resin, Epikote 828, with the secondary aromatic amine silane (Y-9669) was monitored by FTIR analysis, measuring the intensity ratio of the NH peak at 3396 cm^{-1} for the silane component to the OH peak at *ca.* 3500 cm^{-1} formed in the epoxide network.

Plots of the NH/OH absorbance peak ratio against reaction time at 80 and 90 °C are shown in Fig. 1. From these it is evident that the reaction is not complete, and that it reaches about 50% conversion after 1–2 h. Since the reaction yield, even at 90 °C, did not increase appreciably after 2 h, this condition was chosen for the final preparation of the telechelic functionalised epoxy resin. For the same system, *i.e.* Epikote 828/Y-9669 at molar ratio of 2:1, ^{1}H NMR measurements revealed a 44% conversion of the Y-9669. When the epoxy resin was reacted with bis(γ-trimethoxysilylpropyl)amine (A-1170) at molar ratio of 3:1, FTIR measurements showed that the conversion of A-1170 was much higher than with Y-9669 and NMR data confirmed that the conversion was 85% after only 1 h at 90 °C. In both cases the unreacted aminosilane was not removed from the functionalised oligomer as this would participate in the subsequent reactions with the hydrolysed TEOS in the sol mixture and in the post curing reactions of the epoxy resin.

Effect of preparation conditions on the compatibility† of epoxy-silica hybrids

The results have shown that for the low molecular weight resin (*i.e.*, Epikote 828), the amount of secondary difunctional aliphatic aminosilane A-1170 required in functionalised epoxy resin in order to obtain a compatible hybrid was much lower than for the monofunctional aromatic aminosilane (Y-9669). A molar ratio of epoxy resin to silane A1170 of 10:1 was found to be sufficient to achieve compatibility as compared to a molar ratio of 4:1 for the monofunctional aminosilane Y9669. It is not known, however, to what extent, the higher degree of conversion in the functionalisation reaction is responsible for the above behaviour relative to the bifunctionality resulting from the use of silane A1170. The enormous effect that an increase in the molecular weight of the epoxy resin has on the compatibility of the hybrid is very clearly demonstrated from the data in Table 1, which shows that the amount of Y-9669 is reduced by a factor of seven when the molecular weight of the epoxy resin is increased from 370 to 5000. This is expected to result from the increased number of pendant hydroxyl groups along the chains of the epoxide oligomer which provide stronger H-bonding interactions with the silanol groups of the silica phase, thereby reducing the rate of phase separation and subsequent growth during the drying stage of the preparation of the ceramer films.

For ceramers based on Epikote 1001 ($M=880$) using THF as solvent an appreciable effect was observed for the stirring time after adding the hardener, *i.e.*, the longer the stirring time the higher is the compatibility of the hybrids. This effect is shown in the SEM micrographs in Fig. 2 and TEM micrographs in Fig. 3.

No effect was observed on the compatibility of the cast films when THF was used to replace DMF as the solvent for the ceramer solution. However, the stirring time needed to compatibilise the ceramer increased considerably. Replacing DMF with methyl ethyl ketone (MEK) produced opaque systems even after prolonged stirring, *e.g.* 6 h at room temperature.

This solvent related kinetic effect for the compatibilisation of the ceramer is related to the solubility of the products of the reaction in the precursor ceramer solution. In other words, a more advanced stage of reaction between the functionalised epoxy resin and the hydrolysed TEOS is required when the H-bonding power of the solvent is reduced.

Curing reactions of the epoxy resin in the corresponding silica ceramers

Effects on glass transition temperature. It was observed that ceramers based on the epoxy resin functionalised with the aromatic amine silane (Y-9669) containing 25 wt.% of silica, and cured with MNA under standard conditions, *i.e.* 24 hours at 120 °C, 5 hours at 150 °C and 3 hours at 180 °C, displayed a glass transition (T_g) of *ca.* 75 °C, as compared with the value of 106 °C for the pure epoxy resin system.

Table 2 lists T_g values for the two modified epoxy resins, one with silane A-1170 and the other with dibutylamine (DBA) at various molar ratios. These show that systems containing DBA displayed an increase in T_g from 96 to 125 °C and remained constant even after increasing the level of modification from 10:1 to 10:2 molar ratio of epoxy to amine groups. The equivalent ceramer system also displayed a small increase in T_g at 10:1 molar ratio functionalisation, but the T_g dropped to 62 °C when the molar ratio of the epoxy to amine groups was increased to 10:2.

FTIR analysis showed, however, that when a TEOS solution in THF was mixed and heated for 2 h at 80 °C with MNA, there was no change in the anhydride absorption band at 1780 cm^{-1}. When, however, this was carried out with a TEOS

Table 1 Effect of molecular weight of bisphenol-A epoxy resins on the amount of Y-9669 (50% conversion) for compatibilization of epoxy resin/silica hybrids at room temperature

Molecular weight of epoxy resin	370	880	5000
Molar ratio of Y-9669 to epoxy resin	0.50	0.17	0.07

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†The term compatible is used to indicate that the morphological structure consists of domains considerably less than the wavelength of visible light.

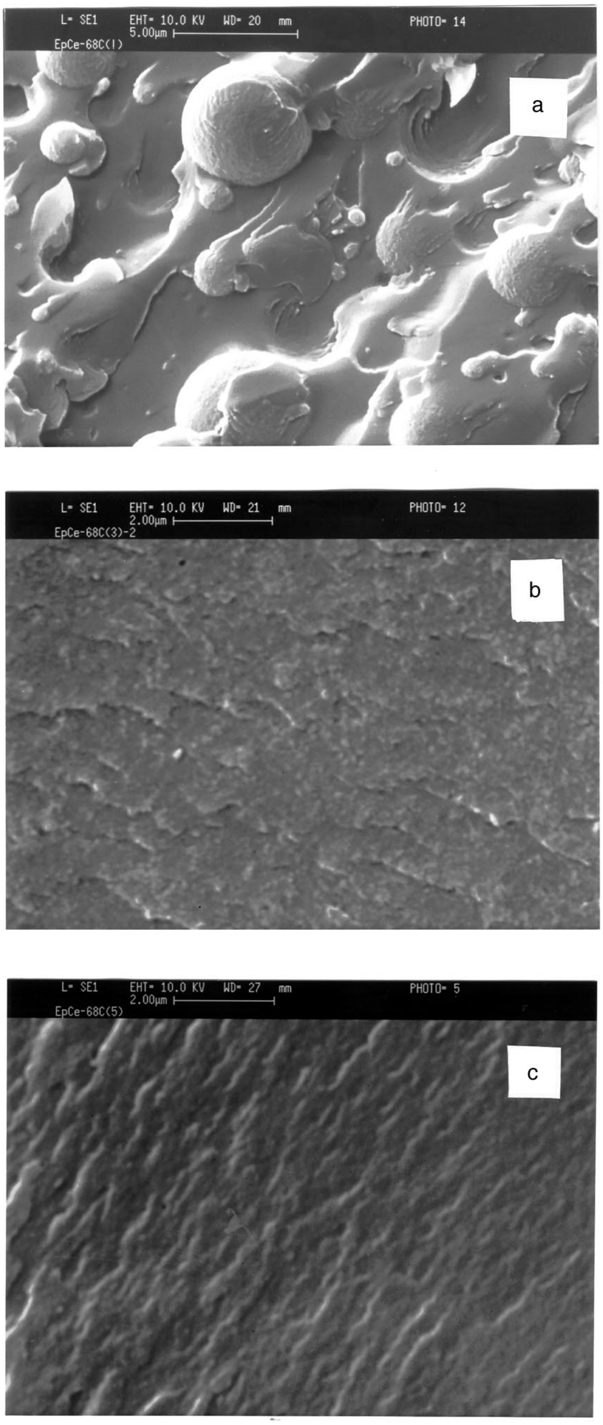
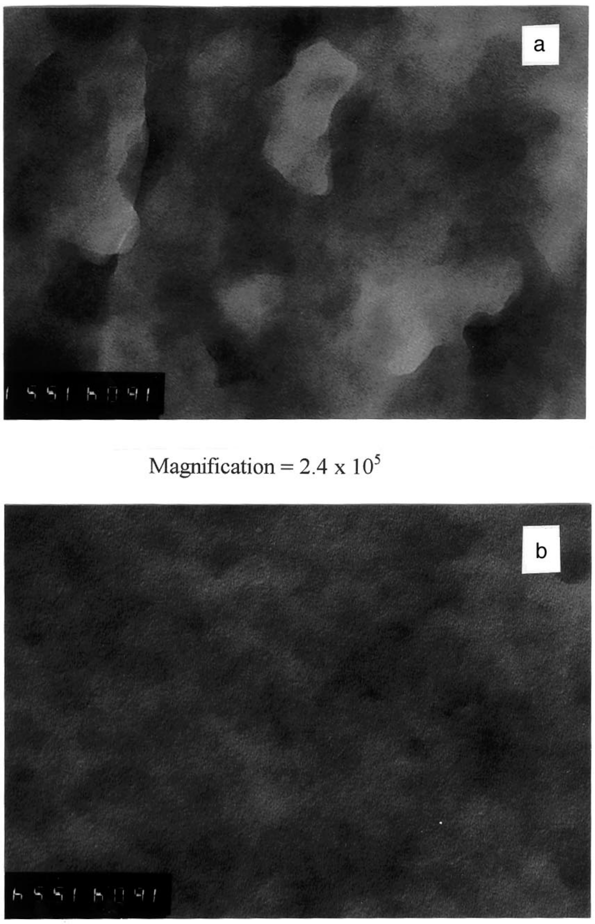


Fig. 2 SEM micrographs showing the changes in morphology brought about by increasing stirring time. (a) 0 h (opaque), (b) 3 h (translucent), (c) 5 h (transparent).

solution hydrolysed in the presence of HCl and then mixed under the same conditions, a part of the anhydride groups was converted to ethyl carboxylate groups (absorption band at 1737 cm^{-1}) as a result of the reaction with the ethanol formed from the hydrolysis of TEOS (Fig. 4).

It is noted in Fig. 4 that spectra (a) and (b) are similar, whereas spectrum (c) displayed a large reduction in the intensity of the peak at 1780 cm^{-1} and the formation of a large peak at 1737 cm^{-1}. This means that, under the curing conditions used in this work, only ethanol formed from the hydrolysis of TEOS can react with MNA and not the SiOH groups.



Magnification = 2.4 x 10^5

Fig. 3 TEM micrographs of morphology of ceramers with different stirring time after adding hardner. (a) 0 h (opaque), (b) 5 h (transparent).

Table 2 Effect of functionalization of epoxy resin on the T_g (°C) of the resulting network[a]

	Epoxy resin: modifiers (molar ratio)		
	10:0	10:1	10:2
DBA	96	125	125
A-1170	96	100	62

[a]System: MNA hardener and BDMA catalyst. Curing conditions: 120 °C, 5 h; 150 °C, 3 h; 180 °C, 1 h.

Side effects of HCl used as catalyst for the precursor siloxane solution. It is worth noting also that DSC measurements showed that the presence of water did not affect the T_g of epoxy resin cured by MNA. When C_2H_5OH was deliberately added, on the other hand, to the epoxy resin mixture, the T_g of the cured epoxy resin decreased from 119 to 55 °C. When HCl was also added to the epoxy resin mixture containing C_2H_5OH, the T_g of the cured epoxy resin, however, decreased from 119 °C to only 90 °C. This indicates that the reaction between the anhydride and hydroxyl groups proceeds to a lower degree of conversion when HCl is present. It is known, in fact, that esterification reactions occur more readily under basic conditions.[17]

FTIR analysis of the products extracted from films after immersion in THF for 24 h at 60 °C has indicated the presence of ester groups due to formation of monoesters and possibly some biesters from the reaction of MNA with ethanol. The evidence is provided by the appearance of a strong absorption peak at 3500 cm^{-1}, which is attributed to hydroxyl groups in the carboxylic acid produced from the anhydride.

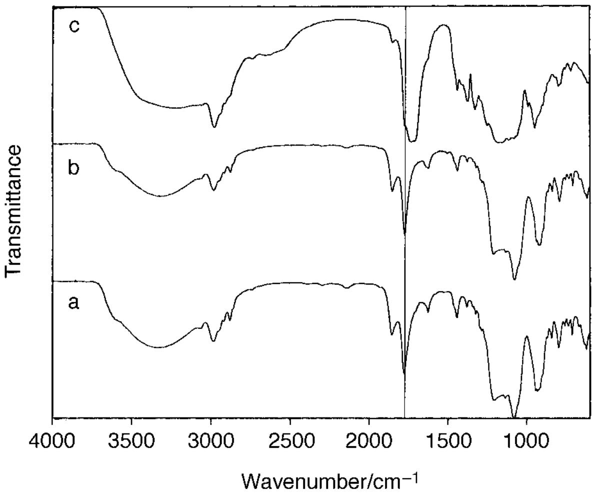


Fig. 4 FTIR spectra for mixtures of MNA and TEOS solution in THF. (a) mixture of MNA and TEOS solution dried at room temperature, (b) mixture of MNA and TEOS in the presence of HCl, dried at room temperature and heated at 80 °C for 2 h, (c) mixture of MNA and TEOS, heated at 80 °C for 2 h, then cast film at room temperature and dried at room temperature under vacuum.

Table 3 Effect of nature of hardner on the T_g of the epoxy network in the ceramer[a]

SiO_2 content (wt.%)	MNA	DDS
0	103	124
2	80	93
10	63	89

[a]Curing conditions: 120 °C, 24 h; 150 °C, 5 h; 180 °C, 3 h.

It was noted that under the same curing conditions, the T_g of the epoxy resin crosslinked with DDS was higher than when MNA was used as hardener (Table 3). The resulting ceramer, however, exhibited a similar reduction in T_g as for the MNA cured system, despite the lack of any possibilities for the formation of network diluents as side products. To verify further that the main cause for the reduction in the T_g of the organic phase is the reaction of the epoxy groups with HCl, an epoxy resin/DDS mixture was prepared with the addition of volumetric amounts of HCl and DMF corresponding to the levels used in the production of the corresponding ceramers and cured under the same conditions.

Thin films were prepared to ensure that there was no residual solvent left in the material after curing. DSC analysis was used to obtain confirmation of the total absence of residual solvent in the film by showing that the T_g of the resin was the same irrespective of the amount of DMF used in the resin mixture, *i.e.* 193 °C.

When both HCl and water were also added to the resin mixture, T_g decreased to 160 °C, irrespective of the water content. The possibility of water reacting with the epoxy groups was also discounted by model experiments in which small amounts were mixed with the epoxy resin in a THF solution and kept at 80 °C for 18 h. FTIR measurements showed that hydroxyl group intensity did not increase in comparison to the pure epoxy resin. Conversely a similar experiment carried out under acidic condition revealed a large increase in the intensity of the hydroxyl groups in the mixture. From this it is deduced that the large reduction in the T_g of the epoxy phase in the ceramer has to be attributed primarily to the reduction in concentration of epoxy groups as a result of the reaction with HCl used for the hydrolysis of TEOS, irrespective of the type of hardener used.

Conclusions

The following conclusions can be drawn: (1) it is possible to produce organic–inorganic hybrid materials based on epoxy resins through the sol–gel method, provided that the epoxy resin is functionalised with an organo trialkoxysilane.

(2) Secondary aliphatic aminosilanes are more effective than aromatic/aliphatic aminosilanes for the compatibilisation of epoxy resin–silica hybrids.

(3) The level of compatibilisation achievable for epoxy resin–silica hybrids can be enhanced by increasing the magnitude of the following parameters: (a) molecular weight of the resin, (b) degree of functionalisation of the epoxy resin, (c) polarity of the solvent and (d) processing temperature.

(4) The glass transition temperature of the epoxy network in a ceramer is lower than the value achievable in the absence of the inorganic phase. This is attributed primarily to the following reasons: (a) side reactions between the hardener and by-products of the hydrolysis of TEOS, and (b) the reduction in effective concentration of epoxy groups as a result of their reaction with the acid catalyst used for the hydrolysis of TEOS.

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Paper 8/05144E