

# Polyimide–silica hybrids derived from an isoimide oligomer precursor

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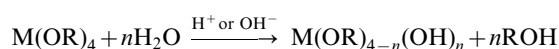
Organic–inorganic hybrids of a cross-linked polyimide and silica were prepared *via* the sol–gel route using an acetylene-terminated oligomeric isoimide and tetraethoxysilane (TEOS) precursors. Two coupling agents,  $\gamma$ -mercaptopropyltrimethoxysilane (MPTMS), and triethoxysilane were employed to compatibilise the organic and inorganic components of the precursor solution mixture. Homogeneous co-continuous phase morphologies could be produced with the use of MPTMS and their properties were evaluated by rheological and analytical techniques. Dynamic mechanical tests were carried out on unidirectional carbon fibre composites based on a polyimide–silica hybrid matrix. The results indicate that the thermooxidative stability of the hybrids at high temperatures is improved considerably over that of the base polyimide. However, the compatibilisation reactions of the coupling agent with the organic precursor, prior to the isomerisation–curing stages, causes a reduction in cross-linking density and a concomitant reduction in the glass transition temperature.

## Introduction

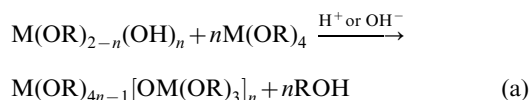
In recent years there has been notable interest in the development of hybrid materials that comprise organic and inorganic components intimately dispersed on the nanometre scale. The prime target in the development of such systems is to improve the mechanical and barrier properties of the corresponding organic materials.

The main method used for combining the inorganic and the organic components into a hybrid material is the sol–gel method. This provides a useful low-temperature route for generating *in situ* a metal oxide phase from an alkoxide precursor, through hydrolysis and condensation reactions, as shown below:

(i) Example of the hydrolysis reaction of a metal alkoxide:



(ii) Example of the condensation reactions leading to the formation of a metal oxide:

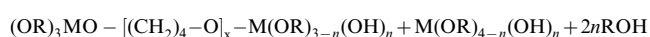


Ideally the hydrolysis and condensation reactions proceed to completion, until all organic (R) components are expelled from the supramolecular inorganic network.

Early studies were carried out on systems where the silica was generated within a poly(dimethylsiloxane) phase.<sup>1,2</sup> The properties of these concept materials were optimised by enhancing the interconnectivity of the constituent domains through the use of a reactive alkoxy-functionalised tetramethylene oxide oligomer as the precursor component.<sup>3</sup>

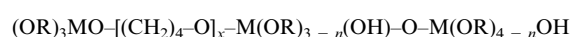
Examples of reactions leading to the formation of organic–inorganic hybrids are:

(a) Hydrolysis of precursors:



(b) Co-condensation of the hydrolysed precursors:

These reactions produce species of the type



and will continue until all the alkyl groups are expelled from the supramolecular oxide hybrid. Acrylic–silica hybrids were later produced by mixing PMMA solutions with TEOS, followed by hydrolysis and condensation reactions.<sup>4,5</sup> H-Bonding between silanol groups of the silica phase and pendant carbonyl groups from the PMMA was found to contribute to the homogeneous dispersion of silica in the organic matrix. Further improvements in phase compatibility have more recently been obtained by the formation of covalent bonds between the two phases with the use of trialkoxysilyl functionalities on the PMMA chains through co-polymerisation with  $\gamma$ -methacryloxypropyltrimethoxysilane.<sup>4,5</sup>

The type of organic polymers that are most suitable for this type of technology are those polymers that are processed from solutions, such as polyamic acids. Typical benefits accrued from the production of hybrids for such systems are thermooxidative stability, reduction of thermal expansion and increased modulus,<sup>6</sup> as well as reduced moisture uptake.<sup>7</sup> The prevention of phase separation in polyimide–silica systems has been achieved by the introduction of connective sites at pendant groups attached to the polyamic acid.<sup>8</sup>

Compatibility of the polyimide matrix and the silica phase was also achieved by pre-reacting aminophenyltrimethoxysilane with the polyamic acid,<sup>9,10</sup> and the introduction of an

epoxy silane coupling agent,  $\gamma$ -glycidyoxypropyltrimethoxysilane in pre-hydrolysed solutions of TEOS.<sup>11</sup> The storage modulus and the  $T_g$  of the compatibilised hybrids were increased considerably relative to the pure polyimide. Dynamic mechanical analysis supported the concept of polyimide chains being entrapped within the silica network.<sup>12,13</sup>

Hybrids from low molecular weight polyamic acids and acid-catalysed TEOS solutions were used as matrices for carbon fibre composites<sup>14,15</sup> and have demonstrated the benefits derived from the inclusion of the co-continuous nanoscale domains of silica.

In recognising the potential of hybrids in fibre-reinforced composites, the present authors have now extended their investigations to include the use of an addition-type oligomeric resin, traditionally the material of choice for high performance composites for the aerospace industry. The chemistry of the oligoisimide acetylene-terminated precursor selected for this study fulfils the necessary requirements for the use of reactive precursors for the formation of homogeneous continuous morphologies of polyimide and silica.

## Experimental

### Materials

Tetraethoxysilane (TEOS), 98% pure from Acros, was used as the silica precursor. The isoimide oligomer, Thermid IP-600, was supplied by National Starch as a fine powder. The chemical structure of this compound is shown in Table 1.

HPLC grade ethanol, obtained from Fluka, was used as a co-solvent for the production of the precursor solutions from TEOS.

The coupling agents used to compatibilise the organic and inorganic components of the hybrids were respectively  $\gamma$ -mercaptopropyltrimethoxysilane (MPTMS) and triethoxysilane (TES), both supplied by Acros. Their chemical structures are shown in Table 1.

HPLC grade hydrochloric acid at 35% concentration, obtained from Fluka and subsequently diluted down to 2% in distilled water, was used as catalyst in the preparation of the alkoxy silane precursors.

*N*-Methyl-2-pyrrolidone (NMP), from Fluka, was used as solvent for the isoimide oligomer.

TENAX HTA 5131 epoxy-sized carbon fibres were supplied by Tenax Fibres GmbH. The yarn consists of 3000 filaments with a diameter of 7  $\mu\text{m}$ , possessing a typical density of 1.77  $\text{g m}^{-3}$ .

### Preparation of precursor solutions

**Alkoxy silane solutions.** Solutions were prepared by adding ethanol to TEOS at a molar ratio of 1.13 : 1. The molar ratio of water added for hydrolysis with respect to TEOS, including the amount present in the 2% w/w HCl catalyst solution, was 3.12 : 1, using the conditions that have already been reported in the literature.<sup>11–16</sup> The coupling agent was added in varying

amounts relative to the TEOS content. All the ingredients were mixed in a glass container at room temperature until the solutions became transparent and homogeneous, using an amount of acid to give a pH equal to 2.

**Hybrid solution mixtures of alkoxy silane and polyimide precursor.** These systems were obtained by mixing 33.3% solutions of Thermid IP-600 in NMP and alkoxy silane solutions at 80 °C for 10 minutes. The solution mixtures became water-clear within this period. The relative amounts of TEOS used was calculated to give a  $\text{SiO}_2$  content varying between 22 and 30 wt%, including the theoretical amount derived from the siloxane content of the coupling agent. The 'M' notation in the code for the hybrid formulations (denoted by the letter 'H') indicates that MPTMS was used, while the digit denotes the molar ratio relative to TEOS.

**Binary solution mixtures of coupling agent and polyimide precursor.** Binary solution mixtures were prepared in the same manner as for the hybrid precursor solutions by mixing the isoimide oligomer with pre-hydrolysed MPTMS. The relative amounts of water, ethanol and catalyst used to hydrolyse the mercaptosilane coupling agent were the same as those used for the alkoxy silane solution, described above.

The notation 'M', which appears alongside the letter 'B', to identify binary mixtures, refers to the presence of MPTM, while the digit denotes the molar amount of MPTMS relative to TEOS. The latter corresponds exactly to the amount of the coupling agent used in the hybrid (ternary) mixtures.

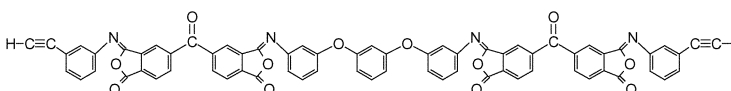
### Preparation of carbon fibre composites

Epoxy-sized carbon fibres were wound on a steel frame and impregnated layer-by-layer with the precursor hybrid solution mixture. The tensioned prepregs were then dried at 80 °C for 1 hour and subsequently transferred to an open-end (leaky) mould. The mould was placed between the platens of a press set at 150 °C and heated under contact pressure for 5 minutes. The pressure was increased to 40 MPa and the matrix was allowed to cure for 1 hour. The pressure was subsequently reduced to 8 MPa and the temperature was increased at 8  $\text{K min}^{-1}$  to 300 °C and was maintained constant for 30 minutes. After cooling to 30 °C, the specimens were cut to the required length for subsequent testing.

### Gelation studies

Alkoxy silane solutions, prepared as described above, were kept under quiescent conditions at 60 °C in small glass flasks, 6 mm in diameter, filled to nearly full volumetric capacity and sealed to prevent the escape of volatiles, particularly HCl and ethanol, during storage. The state of gelation of the reaction products was assessed by monitoring their viscoelastic characteristics. The Haake CV 20 cone-and-plate viscometer was used for this purpose and was operated at room temperature with a frequency of 4.63 Hz and a strain amplitude set at 5%, recording the storage shear modulus,  $G'$ , and the loss modulus,  $G''$ . The point at which the  $G'$  and  $G''$  curves intersected was taken as the "gel time". The gel time of both alkoxy silane

**Table 1** Names and structures of the polyimide precursor and coupling agent

Name	Code	Chemical structure
Thermid IP-600 <sup>®</sup>	PI	
$\gamma$ -Mercaptopropyltrimethoxysilane (MPTMS) Triethoxysilane	M	HS-(CH <sub>2</sub> ) <sub>3</sub> -Si(OCH <sub>3</sub> ) <sub>3</sub> H-Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>

solutions and the corresponding hybrid mixtures was also determined by a manual method as follows: flasks 25 mm in diameter were filled to about 10% of their capacity and solutions were matured at 60 °C and periodically shaken to judge their level of fluidity. The gelation point was taken to be the time at which upon tilting the flask no flow could be observed over a period of 1 minute.

### Infrared spectroscopy

Binary mixtures of the Thermid isoimide oligomer and MPTMS at two different concentrations were cast as films between KBr disks firmly pressed together and placed inside a Specac 20.100 temperature controlling device. A heating ramp of 4 K min<sup>-1</sup> was used to raise the temperature from 60 to 150 °C in order to partially cure the samples. To achieve full cure the samples were subsequently heated to 300 °C in a Carbolite oven at a heating rate of 28 K min<sup>-1</sup>. Infrared spectra were obtained using a Unicam FTIR Spectrometer, model Mattson 3000.

### Differential scanning calorimetry

The same binary mixtures examined by infrared spectroscopy were also analysed by DSC. Films dried under vacuum at 80 °C for 2 hours were compacted and hermetically sealed in aluminium pans. These samples were tested through the temperature range of interest, typically from 30 °C to 350 °C under a nitrogen atmosphere at a heating rate of 20 K min<sup>-1</sup>, using a TA Instruments Thermal Analyst 2000 DSC.

### Thermogravimetric analysis

**Hybrid films.** The thermal stability of films produced from hybrid solution mixtures was assessed on a TA Instruments Hi-Res Modulated TGA 2950 Thermogravimetric Analyser. The curing steps for small amounts (4–7 mg) of pre-dried films were carried out inside the TGA instrument with a steady flow atmospheric air, first from 80 to 300 °C at 50 K min<sup>-1</sup> and then to 400 °C after a 5 minute isotherm. The weight loss was then recorded for further heating from 400 to 700 °C, where the samples were held for 5 minutes.

**Binary films.** Pre-dried films produced from binary mixtures of the isoimide oligomer and MPTMS were subjected to TGA runs consisting of a steady ramp of 10 K min<sup>-1</sup> from room temperature to 700 °C in an inert nitrogen atmosphere.

### Morphology examinations

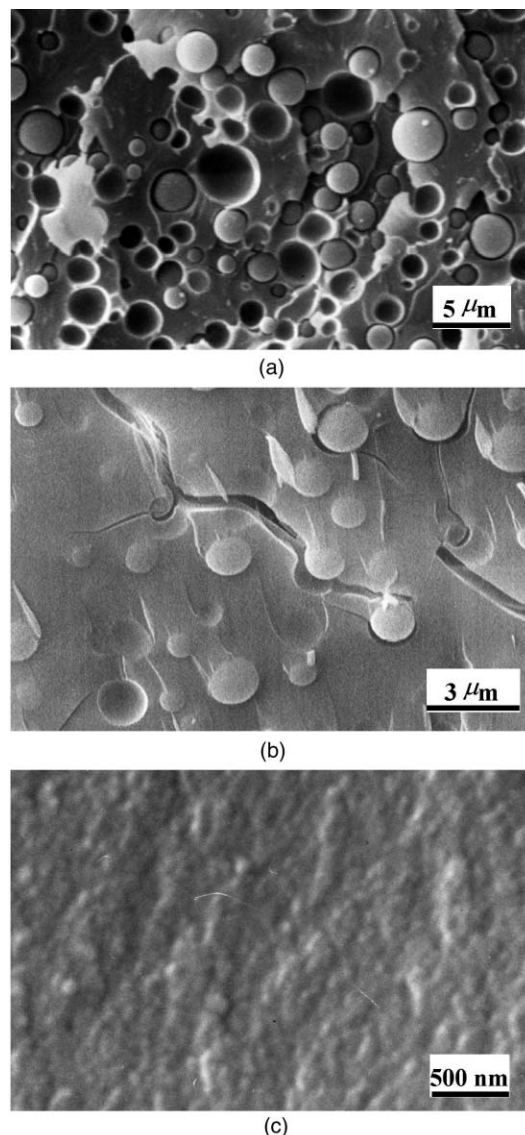
The fractured surface of films was examined on a Cambridge 360 Stereoscan electron microscope to characterise the morphological structure.

### Dynamic mechanical thermal analysis

Dynamic mechanical spectra were obtained on unidirectional fibre composites from 30 to 300 °C. The measurements were made on a Polymer Laboratories DMTA apparatus, model MK II, at a frequency of 1 Hz at a heating rate of 3 K min<sup>-1</sup> using a dual cantilever clamping configuration. The strain level was chosen so that the nominal peak-to-peak displacement did not exceed 23 μm. The specimens, 1.4–1.5 mm thick, 5 mm wide and with a free length of 5 mm, were tested in the transverse direction *i.e.*, with the fibres lying at right angles to the direction of the bending stresses.

## Results and discussion

The micrographs in Fig. 1 show the effects of the two compatibilisers used for the preparation of the precursor mixtures on the morphological structure of the hybrids

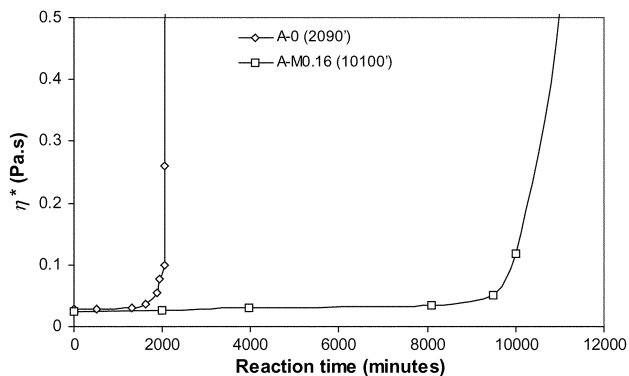


**Fig. 1** Scanning electron micrographs of polyimide-silica mixtures: (a) no coupling agent, (b) triethoxysilane used for compatibilisation, (c) compatibilised with  $\gamma$ -mercaptopropyltrimethoxysilane coupling agent.

produced. It is noted that the micrographs in Fig. 1a and 1b are quite similar, both revealing the presence of fairly large spherical silica particles dispersed in the polyimide matrix. This particulate morphology is indicative of the lack of adequate compatibility for the organic and inorganic components.

The morphology of the sample in Fig. 1c, on the other hand, suggests the presence of very fine interconnected silica domains which are well bonded to the continuous polyimide phase.<sup>16</sup> The high level of phase compatibility, brought about by the use of MPTMS coupling agent, is associated with strong interfacial interactions arising as a result of chemical reactions between the supermolecular species in the mixture. The lack of compatibility for systems containing H-Si(OEt)<sub>3</sub> coupling agent was unexpected as it was assumed that it would undergo similar addition reactions to MPTMS. Steric hindrance around the Si-H bond may have prevented such reactions taking place at the terminal -C=CH groups under these circumstances owing to their proximity to the aromatic nucleus. In other words, the relatively slow reaction rates may have also prevented the formation of sufficient quantities of functional groups to induce the required level of compatibilisation.

The progress of the gelation of alkoxy silane solutions at 60 °C evaluated in terms of viscosity has been described elsewhere.<sup>16</sup> Typically the viscosity increases slowly up to the



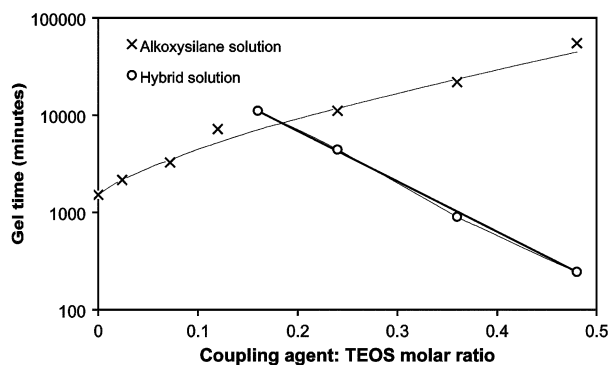
**Fig. 2** Dynamic viscosity curves for TEOS-based alkoxy silane solutions. (A-0: no coupling agent; A-M0.16: molar ratio MPTMS : TEOS = 0.16 : 1. The figures in brackets denote the corresponding gel times in minutes).

onset of gelation, when it rises very rapidly to extremely high values (see Fig. 2). The time to gelation *i.e.* the gel point, increases with the concentration of the MPTMS coupling agent (Fig. 3). Considering the established effect of pH on the reaction rates for hydrolysis and condensation,<sup>17–22</sup> it is reasonable to presume that gelation slows down as a result of the increased concentration of protons in the solution resulting from the presence of MPTMS, which is acidic in nature.

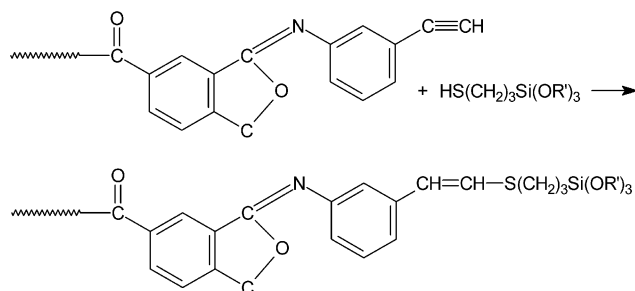
For the case of hybrid mixtures, *i.e.* in the presence of the organic precursor, the reverse trend is observed (see Fig. 3). This suggests that the resulting increase in gelation rate arises from the reactions of coupling agent with the organic component, in addition to the condensation reactions of the methoxy groups of MPTMS with the pre-hydrolysed TEOS. The proposed interaction would involve the linking of the two evolving networks in the inorganic (siloxane) and organic polyisoimide species *via* the reactive groups in the  $\gamma$ -mercaptopropyltrimethoxysilane coupling agent. The most likely reaction that is expected to take place between the mercapto group of the silane coupling agent and the acetylene end groups of the isoimide molecule is shown in Scheme 1.

The effect of the reaction of the mercaptosilane with the isoimide oligomer chains is clearly demonstrated from the changes in the dynamic mechanical spectra in Fig. 4, which reveal a lowering of the temperature at which the  $\tan \delta$  peak is observed, and a concomitant increase in the height of the damping peak. These are obviously associated primarily with a reduction in cross-linking density, even though a possible plasticisation contribution from the aliphatic chains in the coupling agent cannot be excluded.

Infrared spectra for binary polyimide formulations and the polyimide control, both cured at 300 °C, are shown in Fig. 5. To observe the effect of the presence of MPTMS on the extent



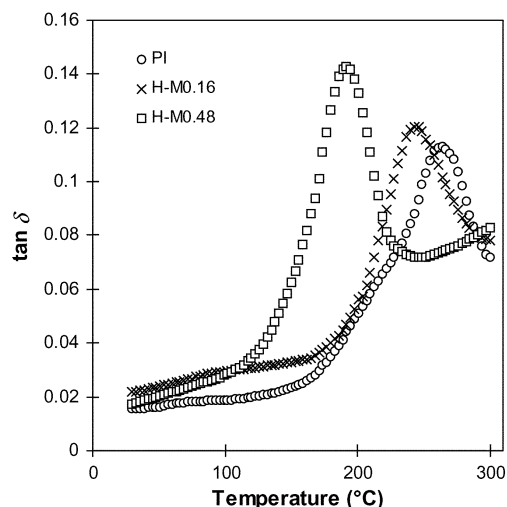
**Fig. 3** Variation of gel time with MPTMS concentration for the alkoxy silane solution and the corresponding hybrid solution mixtures containing the isoimide precursor.



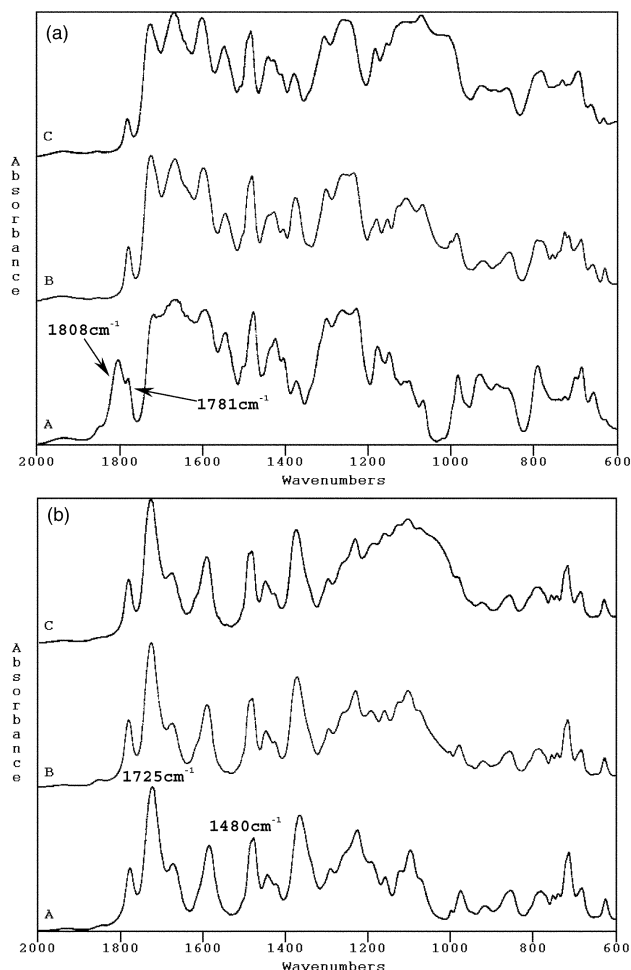
**Scheme 1**

of imidisation after full cure, the absorbance area of the imide band at 1725  $\text{cm}^{-1}$  in the polyimide control was compared to that recorded for the binary samples. Absorbance areas were obtained after subtracting any interference to the imide band and integrating the absorbance from an adjusted baseline. These values were subsequently normalised against the invariant aromatic band at 1480  $\text{cm}^{-1}$ , as an internal standard. The normalised absorbance area ratios in Table 2 indicate a decrease in the extent of imidisation in the presence of MPTMS. This result is confirmed by the decrease and complete disappearance of the peak at 1808  $\text{cm}^{-1}$  (for the C=O stretch of the isoimide carbonyl) from the spectra of samples B-M0.16 and B-M0.48 (Fig. 5(a)), without a corresponding increase in the imide content (*i.e.*, in the peak at 1781  $\text{cm}^{-1}$  for the imide C=O stretch).

DSC thermograms for both the original oligoimide and the films obtained from binary mixtures, all vacuum-dried at 80 °C, are shown in Fig. 6. There are two prominent features in these thermograms: first the endothermic peak at 180 °C, which is attributed to solvent evaporation, and second the broad exothermic peak resulting from a combination of two events, respectively the imide isomerisation within the oligomeric chains and the crosslinking reactions *via* the acetylene endgroups.<sup>23</sup> In the case of films produced from binary solution mixtures, the decrease in the magnitude of both the endotherm and the exotherm is probably attributable to the reaction of the mercaptosilane coupling agent with the isoimide oligomeric chains (see Scheme 2 below). Hence, the observed changes result from two opposite effects, the decrease in endotherm due to the reduction in the amount of residual solvent present, and the decrease in occurrence of the exothermic and/or isomerisation reactions.



**Fig. 4** Loss angle ( $\tan \delta$ ) spectra for unidirectional composites obtained from DMTA measurements, with the fibres lying perpendicular to the bending stresses. The matrices were based on the control polyimide (PI) and two hybrid formulations (H-M0.16 and H-M0.48, *i.e.* with low and high contents of the MPTMS coupling agent, respectively).



**Fig. 5** Infrared spectra of polyimide and binary films (a) vacuum-dried at 80 °C and (b) cured at 300 °C. (A) pure isoimide precursor, PI, (B) binary mixture with low concentration of coupling agent, B-M0.16, (C) binary mixture with high concentration of coupling agent, B-M0.48.

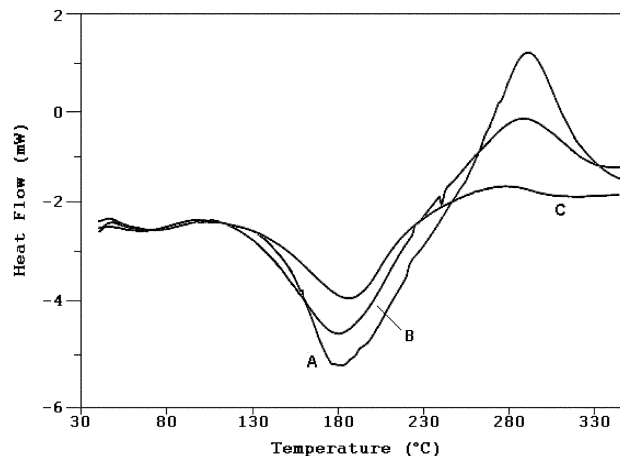
The suggested reaction in Scheme 2 is supported by the infrared spectra on dried non-imidised films (Fig. 5(a)) which display a clear reduction in the concentration of isoimide groups when MPTMS is present in the mixture due to background interference. However, it has not been possible to obtain further evidence for the formation of the proposed thioester

$R(O)C-S-(CH_2)_3-Si(OR')_3$  (for example from the identification of the band for the  $CH_2-S$  group, between 1270 and 1220  $cm^{-1}$ ). It is possible that the reactions of the isoimide with the mercapto groups of MPTMS may contribute to the lowering of the  $T_g$  as a result of internal plasticisation, although a similar effect may also be caused by the reduction in the degree of imidisation.

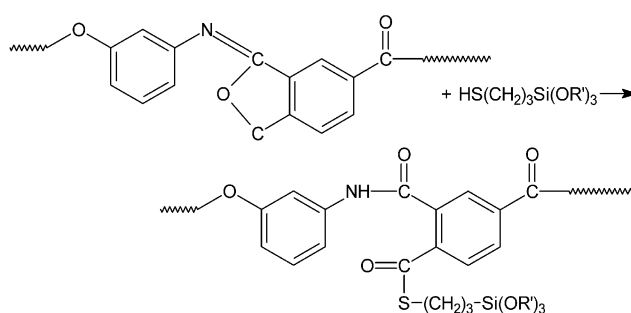
The results of the thermogravimetric analysis, carried out to establish the effect of the presence of the coupling agent on the

**Table 2** Optical density ratios of the Thermid polyimide and binary films cured at 300 °C

Sample	Coupling agent : PI wt ratio	Optical density ratio of IR bands: imide ( $1725\text{ cm}^{-1}$ )/aromatic ( $1480\text{ cm}^{-1}$ )
Isoimide-derived polyimide (PI)	0	0.894
PI-MPTMS binary (B-M0.16)	0.155	0.759
PI-MPTMS binary (B-M0.48)	0.466	0.692



**Fig. 6** DSC thermogram of vacuum-dried isoimide and binary films. (A) pure isoimide precursor, PI, (B) binary mixture with low concentration of coupling agent, B-M0.16, (C) binary mixture with high concentration of coupling agent, B-M0.48.

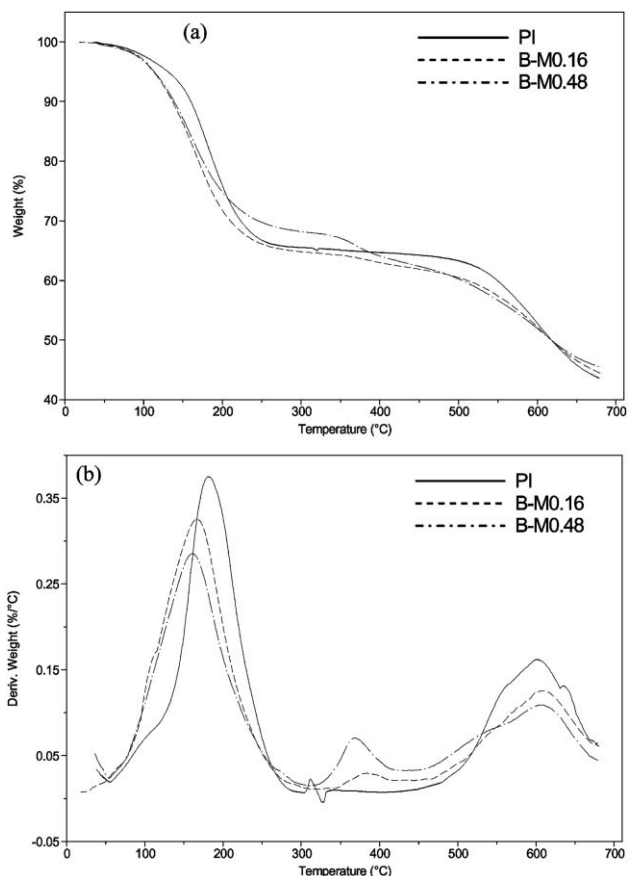


**Scheme 2**

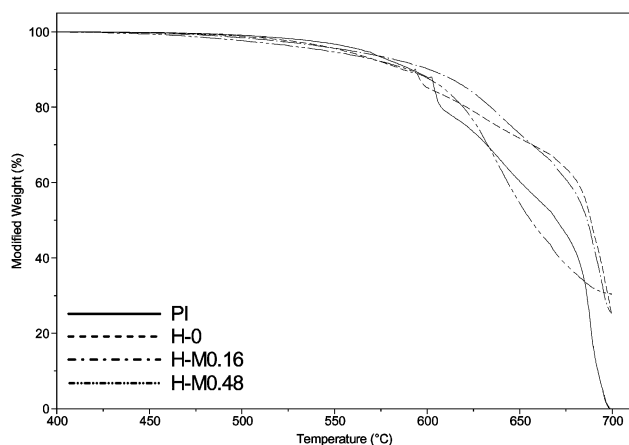
thermal stability of the polyimide component, reveal that for the binary polyimide-MPTMS and the polyimide control there are the two main weight loss steps (Fig. 7). The first step starts at approximately 85 °C and is associated primarily with the loss of solvent. The decrease in the temperature at which the peak for the derivative of weight loss occurs with increasing the amount of coupling agent (Fig. 7b) indicates that the interaction of the coupling agent with the isoimide oligomer facilitates the removal of solvent during the heating cycle. In other words, the H-bonding capability of the NMP solvent with the isoimide is considerably reduced by the predominance of the interactions with the coupling agent.

The second major weight loss step for the binary films B-M0.48 and B-M0.16 and for the pure PI occurs, respectively at approximately 490 °C, 520 °C and 530 °C. This weight loss is associated with the degradation of the organic polymer. Since the decomposition of the aliphatic component of coupling agent is expected to take place between 350 and 400 °C, the reduction in the observed degradation temperature can be taken to result from the decreased level of isomerisation within the oligomer chains, which brings about a deterioration in thermal stability of the polyimide network as a whole.

The above interpretation of the progress of the degradation reactions is also supported by the TGA data for hybrid films (see Fig. 8). Since pyrolysis is carried out in air, the depletion of organic matter is expected to be complete at the end of each run, and the residue will consist entirely of inorganic matter (silica). It is noted that between 600 and 700 °C the polyimide hybrids which were produced with low levels of compatibiliser (and even in the complete absence of compatibiliser) exhibit an appreciably enhanced thermooxidative stability relative to the pure polyimide film. Conversely, the hybrid containing a large amount of MPTMS (*i.e.*, H-M0.48) shows the opposite tendency at temperatures above 625 °C.



**Fig. 7** Thermogravimetric curves of polyimide (PI) and binary films (B-M0.16 and B-M0.48). Pre-dried samples were heated in an inert nitrogen atmosphere at  $10 \text{ K min}^{-1}$  from room temperature to  $700^\circ\text{C}$ .



**Fig. 8** Thermogravimetric curves of polyimide (PI) and hybrid films containing varying amounts of the MPTMS coupling agent (*i.e.* MPTMS : TEOS = 0, 0.16 and 0.48). The samples were cured in air at  $300^\circ\text{C}$  and devolatilised at  $400^\circ\text{C}$  inside the TGA furnace before weight loss data were recorded. The vertical axis scaling is adjusted to allow for this preliminary heat treatment.

## Conclusions

The present study has led to the conclusion that compatibilised hybrid compositions of polyimide from an isoimide

oligomer and silica from tetraethoxysilane can be produced with the use of  $\gamma$ -mercaptopropyltrimethoxysilane coupling agent. The interaction of the organic and inorganic precursors with the coupling agent has an important effect on the gelation behaviour of the precursor solutions, as well as on the properties of the resultant hybrids.

Evidence exists of the interference of the coupling agent with the isomerisation of the oligomer precursor to polyimide, which brings about a reduction in the glass transition temperature of the final cured product, owing to the decrease in crosslinking density.

## Acknowledgement

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