Chemically bonded silica–polymer composites from linear and branched polyamides in a sol–gel process[†]

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A new type of polymer–silica composite based on aramids of either linear or non-linear structure has been prepared successfully *via* the sol–gel process. The linear polyamide chains were prepared by the reaction of a mixture of *m*-phenylene and *p*-phenylene diamines and terephthaloyl chloride in dimethylacetamide. The non-linear (branched) polyamide chains (having an increased number of reactive ends) were synthesized using 1,3,5-benzenetricarbonyl chloride and terephthaloyl chloride to increase the mass average functionality of the monomer. A slight excess of acid chloride was added in both cases to produce amide chains with carbonyl chloride end groups, which permitted the chains to be end-capped with aminophenyltrimethoxysilane. Addition of tetramethoxysilane to a solution of the polymer, and its subsequent hydrolysis and condensation produced a silica network phase chemically bonded to the aramid chains. Films thus produced were yellow, and transparent for concentrations of silica of up to 25 mass%. Tensile strengths increased gradually with increasing silica content up to this same concentration, but then decreased significantly. The overall values of the strength were found to be smaller for the non-linear aramid chains, relative to those of the linear, possibly because of the branches interfering with interchain interactions. Nonetheless, the increases in the tensile strength with increasing inorganic network phase were larger for the non-linear polymer, consistent with the goal of increasing the bonding between the organic and inorganic phases by increasing the number of amidophenyltrimethoxysilane chain ends. Increasing these strengths to values greater than those for the linear chains can probably be achieved by having the branched regions only near the ends of the chains. Since these transparent ceramers were found to withstand tensile stresses of the order of 175 MPa and had thermal decomposition temperatures around 460–475 °C, they may be very useful as matrices for fibre-reinforced composites.

The aromatic polyamides known as aramids play an important role in modern technology based on advanced materials, owing to their high thermal stabilities, strong intermolecular forces, chain rigidity and the inherent stability of the aromatic moiety.[1–3] For example, the fibres produced from Nomex and Kevlar have exceptional strength coupled with excellent high-temperature properties. They are competitive with steel and glass fibres in many applications, in particular in the aerospace industry, where their relatively low densities give them considerable advantages.

In spite of the already excellent properties of this class of polymers, it would nonetheless be useful to try to improve them further. This could perhaps be done by introducing reinforcing ceramic phases generated by the sol–gel technique now being used by ceramists to prepare ceramics by more chemically based routes.[4–14] In this approach, an organometallic compound such as tetramethoxysilane is hydrolysed to silica and, in applications to polymers, this is carried out *in situ* to provide the desired reinforcing filler. Although high-temperature, high-performance polymers are very difficult to treat in the usual sol–gel technique, studies have been carried out on a few aromatic polyamides,[15–19] a number of polyimides[20–35] and several benzoxazole and benzobisthiazole polymers.[36–42] The difficulties result from the fact that many of these polymers already have superb thermal and mechanical properties which are difficult to improve further, and such polymers are relatively resistant to bonding to ceramic reinforcing phases. The bonding problem can be solved, at least in part, by functionalizing the polymer, by adding a bonding agent, or by doing both.

In order to carry out the sol–gel process successfully, a suitable solvent having compatibility with the polymer and the metal alkoxide is necessary. This can be illustrated with poly(phenyleneterephthalamide), which is used to prepare Kevlar fibres. It would have been ideal for use in the preparation of mechanically strong ceramers, if not for the fact that this polymer is not soluble in organic solvents. By introducing 15–20% *meta* linkages into such a resin, however, it is possible to keep the resulting copolymer in solution.[16,18] In these studies, stoichiometric amounts of terephthaloyl chloride were reacted with a mixture consisting of a 35:65 mole ratio of *m*- and *p*-phenylenediamines in dimethylacetamide (DMAC). One advantage of this solvent is its increase in solvating power from the formation of a complex with HCl as the molecular mass increases.[43] By keeping the mass ratio of the monomers to *ca.* 8% of the total reaction mixture it was possible to attain a high molecular mass aramid with good mechanical strength. Using the sol–gel process, a reinforcing silica network was produced *in situ* by the hydrolysis of tetramethoxysilane (TMOS). The mechanical properties of the resulting hybrid material, however, showed no significant improvement in mechanical strength. Various other groups who have used the sol–gel process to synthesize hybrid materials based on high-temperature polymers have reported similar difficulties.[15–42]

In a related attempt, aramid chains having carbonyl chloride end-groups were prepared and then end-capped with aminophenyltrimethoxysilane (APTMOS). The polymer thus prepared was chemically end-linked to a silica network produced *in situ*, again by the hydrolysis of TMOS. The transparency of the films and the tensile strength were improved considerably[17] relative to the corresponding system in which an inorganic network was not bonded to the organic phase. The increase in the mechanical strength was attributed to increased adhesion between the organic and inorganic phases due to bonding

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between the aramid chains and the ceramic reinforcing phase.

This chemical bonding between the aramid chains and the inorganic network was, however, limited, because of the small number of chain ends available from a linear polymer chain. The higher the molecular mass of the polymer, of course, the fewer the chain ends. The purpose of the present study, therefore, was to increase the number of reactive chain ends in the aramid chains without an undesirable decrease in the molecular mass of the polymer. This was done by increasing the mass-average functionality of the monomer, thereby yielding a non-linear polymer chain which could be linked with the inorganic network at more than two points. More specifically, 1,3,5-benzenetricarbonyl chloride (BTCC) was used in the appropriate ratio with terephthaloyl chloride to react with phenylenediamines. Non-linear aramid chains with carbonyl chloride end-groups were thus produced and end-capped with APTMOS. A silica network was then developed by the addition of TMOS in aramid solution and carrying out its hydrolysis and condensation together with that of the APTMOS groups attached to the polymer chains. The mechanical strengths of these ceramers derived from the non-linear aramid chain were then compared with those obtained from the corresponding linear polymer.

Experimental

Chemicals

The monomers, specifically 1,4-phenylenediamine, 1,3-phenylenediamine and terephthaloyl chloride (TPC), were all of analytical grade. They were obtained from Fluka, and dried under vacuum at 55 °C before use. Both AR-grade 1,3,5-benzenetricarbonyl chloride (BTCC) and anhydrous DMAC (99% pure) were obtained from Fluka and used as received. Aminophenyltrimethoxysilane (97% pure) and tetramethoxysilane (99% pure) were obtained from Huls America Inc., and also used as received.

Preparation of linear and non-linear aramids

A mixture of 1,4- and 1,3-phenylenediamines, 5.4460 g (0.05 mol) in a mole ratio of 35:65 was placed into a 250 ml conical flask under completely anhydrous conditions. DMAC (150.00 ml) was added to the flask and the solution was stirred for 30 min. The contents of the flask were then cooled to 0 °C and 10.1510 g (0.05 mol) of TPC added, still under anhydrous conditions. After *ca.* 30 min reaction time the temperature of the mixture was allowed to rise to room temperature, and the stirring was continued for 24 h.

The same mixture of 1,4- and 1,3-phenylenediamines was used for the preparation of the non-linear aramid. DMAC (75.00 ml) was added to this mixture, and the resulting solution was stirred for 30 min. In a separate flask, 9.9480 g (0.049 mol) of TPC and 0.1789 g (0.0006 mol) of BTCC were mixed under anhydrous conditions, followed by the addition of 75.00 ml of DMAC, with stirring for 30 min. The contents of both the flasks were cooled to 0 °C, and the monomers mixed with continuous stirring. After *ca.* 30 min reaction time, the temperature of the reaction mixture was allowed to rise to room temperature; the stirring was then continued for 24 h, after which the reaction was assumed to be complete.

Preparation and characterization of ceramers

A slight excess (0.0005 mol) of TPC was added to both the linear and non-linear polyamides in order to attach carbonyl chloride groups to the chain ends. The reaction mixture was stirred for 6 h. A stoichiometric amount of APTMOS was then added to react with these end-groups, and the stirring continued for a further 6 h at room temperature. The polymer solution thus prepared served as a stock solution to which various amounts of TMOS in DMAC were added. Each system was then stirred for 4 h at 40 °C, after which a measured amount of water in DMAC was added to carry out the hydrolysis and condensation required to produce the silica network. Films of the resulting composite having uniform thickness and containing various amounts of silica were prepared by baking out the solvent from a known amount of silica–aramid composite solution at 55–60 °C. The films were kept in distilled water for 24 h to remove any HCl produced during the polymerization reaction, and were then washed repeatedly with water. They were then dried under vacuum at 80 °C for 96 h.

Samples thus obtained were characterized with regard to their thermal and mechanical properties. Thermogravimetry (TG) studies on the samples were performed under a nitrogen atmosphere with a Perkin Elmer TAS-7 system, using a heating rate of 20 °C min^{-1}. Tensile properties were measured at room temperature, by means of an Instron Universal Testing Instrument (Model TM-SM 1102 U.K.). The sample lengths were 3.5 cm and the drawing rate was 0.5 cm min^{-1}.

Results and Discussion

Thin films cast from the linear and non-linear polyamides were yellow, were transparent for silica contents up to 25 mass%, and were very tough. This toughness was demonstrated by the relatively large areas under their stress–strain isotherms up to their maximum extensions, which correspond to the energy or work required for rupture. The films containing 30% silica were only semi-transparent, and those containing more than 40% silica were opaque and brittle. Partial phase separations appeared to occur for the systems with higher silica contents. The transparency in the present systems in which the inorganic and organic phases were chemically bonded appeared to be much better than the system reported previously[16,18] which did not have any interphase bonding. It seems that as the inorganic network structure becomes extensive there is an increasing tendency towards particle size growth. These particles agglomerate and their distribution becomes irregular; this tendency is apparently much stronger in the unbonded system and this increases the magnitude of the scattering and the associated opaqueness.

The thermal stability of these linear ceramers, as measured by TG, is described in Fig. 1. Both the linear and non-linear polyamides had thermal decomposition temperatures in the range 440–480 °C. No significant change was found relative to the decomposition temperature for the unbonded system.[16,18] For poly(1,4-phenyleneterephthalamide) this temperature has

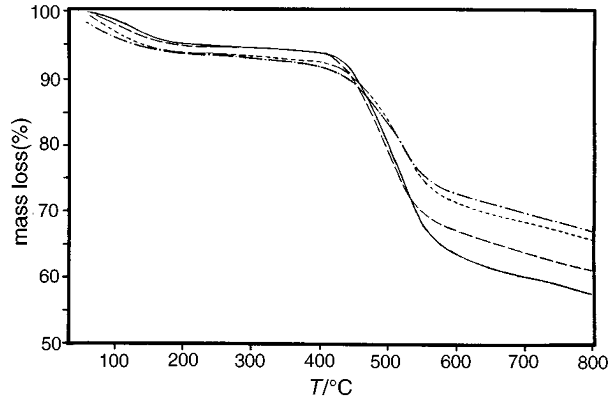

Fig. 1 Thermogravimetry curves for aramid–silica hybrid films with various silica contents [(—), 0%; (– – –), 5%; (---), 15%; (–·–), 25%] obtained at a heating rate of 20 °C min^{-1} in nitrogen

been reported[44] to be around 500 °C. *meta* Linkages introduced into the aramid chains reduced this temperature slightly, as expected. The network structure introduced was expected to increase this temperature. No significant increase in thermal stability was observed, however, presumably because the network was not very extensively cross-linked (of the required carbonyl chloride groups, only 2% were derived from the trifunctional monomer). As expected, the mass of residue obtained at 800 °C was almost proportional to the silica content in the composite.

The stress–strain curves for the composites in which there was no bonding agent present are shown in Fig. 2. The ultimate stress at rupture is seen to decrease with increasing silica content; the elongation at break behaves similarly, after a very slight increase. The stress–strain curves for linear polyamides chemically bonded to the silica network with APTMOS, however, show considerable increases in the tensile strength. These results, and their comparison with those for the pure polyamide, are shown in Fig. 3. The increase in the ultimate strength, however, is seen to decrease slightly for silica contents greater than 20%, as does the length at rupture. Comparing this system with the unbonded one described in Fig. 2 shows that end-linking the aramid chain with the inorganic network does result in some enhancement in tensile strength. Specifically, a tensile strength of 175 MPa at room temperature was achieved with 10% silica.

It was hoped that greater binding could be achieved between the organic and inorganic phases by using the non-linear polyamide with a larger number of chain ends for end-linking with the inorganic network. Unfortunately, as is clear from Fig. 4, the tensile strength of the pure aramid has decreased.

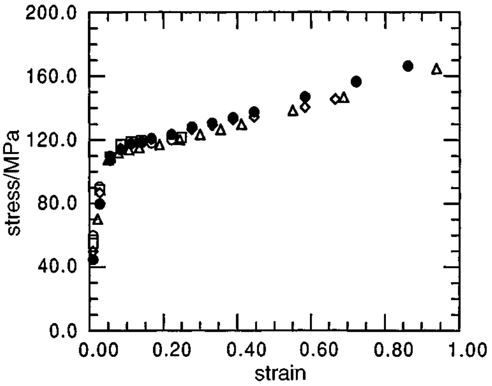

Fig. 2 Stress–strain isotherms for linear aramid–silica films without interphase bonding. Silica content: (●), 0%; (△), 5%; (◇), 10%; (□), 15%; (○), 20%.

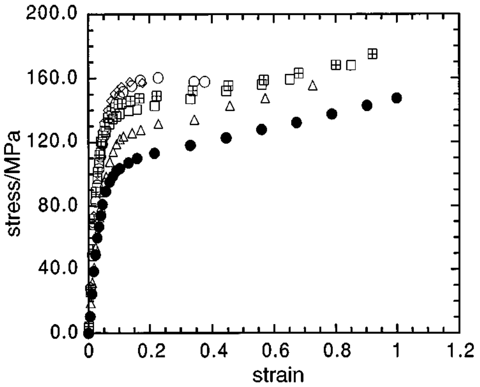

Fig. 3 Stress–strain isotherms for linear aramid–silica films with interphase bonding. Silica content: (●), 0%; (△), 3%; (□), 6%; (⊞), 10%; (○), 20%; (◇), 25%.

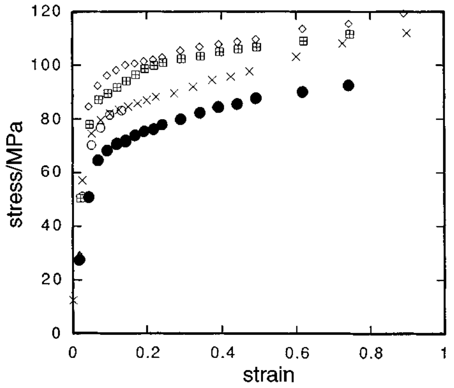

Fig. 4 Stress–strain isotherms for non-linear aramid–silica films with interphase bonding. Silica content: (●), 0%; (×), 5%; (◇), 10%; (⊞), 15%; (○), 25%.

This is possibly due to the non-linear structure of the chains hindering the development of secondary interactions between the chains. However, the increases in tensile strength from the introduction of silica into the non-linear polyamide is much larger than those obtained similarly with the linear polymer. This may be due to the large number of reactive ends which were created in the non-linear chains and which became chemically bonded with the inorganic network. Thus, the results do support the concept of improving interphase bonding by the use of polyamide chains having more than two reactive ends.

The randomness in the non-linear structure which gives rise to the overall decrease in strength is shown schematically in Fig. 5(*a*). The structures shown suggest replacing the present non-linear chains with others synthesized to be primarily linear, except for non-linear regions at the ends which bear the additional functional groups. Such chains can be prepared by replacing the addition of BTCC to the TPC with a two-step process in which the TPC is first reacted with the diamines, with addition of the trifunctional monomer postponed until near the end of the reaction. There would thus be the usual linear part of the chain for developing strong intermolecular bonding, while the chain ends still provide the desired bonding with the inorganic network, as shown in Fig. 5(*b*). Such work is in progress.

Conclusions

Several types of poly(phenyleneterephthalamide) chains were used to prepare organic–inorganic composites by chemically bonding these chains to a silica network generated *in situ* by the sol–gel process. Some enhancement in tensile strength was observed in the case of the linear polyamide–silica chemically bonded system. The non-linear polyamide system showed decreasing strength relative to those obtained with the linear polymer, presumably due to the irregularity of the polyamide structure. There were, nonetheless, even larger increases in tensile strength on addition of silica to the non-linear chains, presumably because of their larger number of reactive groups. A 'linear–non-linear' polyamide chain structure having long linear chains but branched structures near to or at the chain ends is suggested for further improvements in the mechanical strength of these types of composites.

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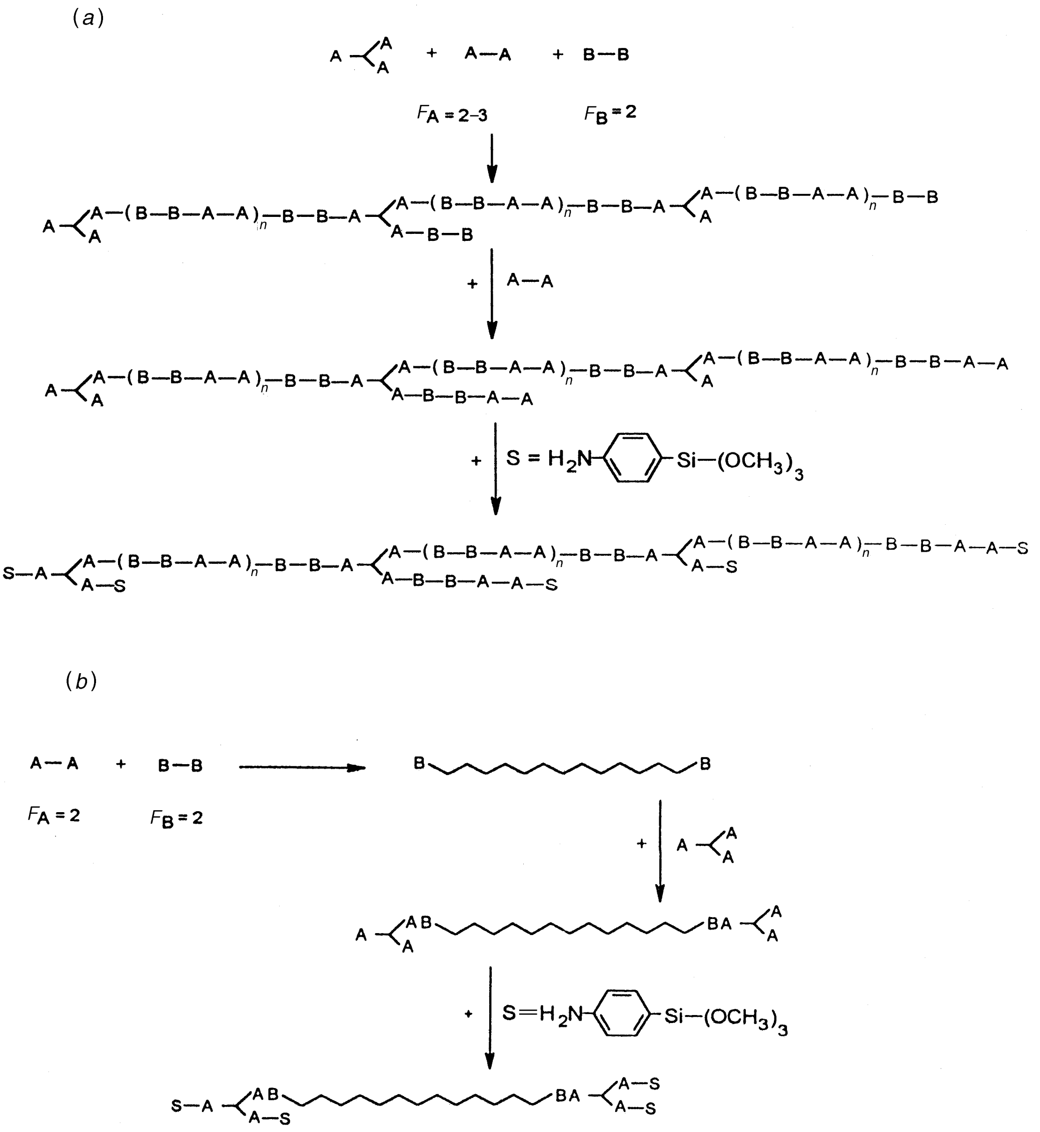

Fig. 5 Aramid network formation using different functionalities of the branch units; the goal is improvement of the interconnectivity of the inorganic domains with the organic structure using aminophenyltrimethoxysilane. A, aromatic di-/tri-acid chloride; B, aromatic diamine; S, aminophenyltrimethoxysilane. (*a*) Random non-linear aramid structure used in this work; (*b*) proposed linear and non-linear aramid structures under investigation (F = functionality).

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