

Dynamic–Mechanical Thermal Analysis of Aramid–Silica Hybrid Composites Prepared in a Sol–Gel Process

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Received 24 July 1996; accepted 11 September 1996

ABSTRACT: Several types of nonbonded and chemically bonded composites of silica with linear and linear–nonlinear aramid polymers were prepared using the sol–gel process. The linear polyamide chains were synthesized by the reaction of a mixture of *m*- and *p*-phenylene diamines and terephthaloyl chloride in dimethyl acetamide. The nonlinear chains were prepared using 1,3,5-benzenetricarbonylchloride along with terephthaloyl chloride, thereby significantly increasing the average functionality of the monomers. These increased functionality chains were then endcapped with aminophenyltrimethoxysilane. Silica networks chemically bonded to the polyamide chains were produced by the addition of tetramethoxysilane to the aramid solution and its subsequent hydrolysis and condensation. The films cast from these solutions were yellow, and those containing up to 25 wt % silica were also transparent. Dynamic–mechanical thermal analysis was carried out to characterize interfacial bonding and interactions, in particular through the use of values of the glass transition temperatures T_g of the polymers. The presence of the silica caused increases in T_g , with the increases being largest for the composites in which there was strong interfacial bonding between the polymer chains and the ceramic silica phase. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1345–1352, 1997

Key words: aramid polymers; nylons; composites; silica; reinforcement; in-situ precipitation; thermal analysis

INTRODUCTION

Polymer–matrix composites have several advantages relative to more conventional structural materials. These include better mechanical properties and good chemical resistance, two highly desirable properties that can be achieved through a judicious choice of components and the appropriate design of the composite structures. In this

way, complex but dimensionally stable high-performance structures can be built from a variety of polymers and reinforcing ceramic phases. Polymers of particular interest in this area are the aromatic polyamides used to prepare aramid fibers (Kevlar®, Nomex®) which exhibit high thermal stability and outstanding strength. For example, the excellent properties of copolymers of these two polymers should make them ideal in the synthesis of inorganic–organic composites. Such polymers can be reinforced by incorporating phases such as silica, titania, alumina, or zirconia (on a highly dispersed level) by means of the sol–gel process.^{1–8} This is a mild chemical method with low processing temperatures and can give

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Contract grant sponsor: Air Force Office of Scientific Research (Directorate of Chemistry and Materials Science)
Contract grant number: F49620-96-1-0052

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nanolevel distributions of the inorganic ceramic particles in the polymeric matrix. The properties of these composites depend primarily on the sizes of the inorganic particles, distribution patterns of the inorganic phase, and the interfacial bonding between the phases.

In recent years, the present authors have synthesized various types of aramid–silica composites using this process.^{9–13} In those aramid–silica hybrid materials in which the aramid chains were not chemically bonded to the silica network, no significant increase in the mechanical strength of the polymer was observed.⁹ In other systems, chemical bonding between the two phases was achieved by endlinking the aramid chains into the silica network, and this gave considerable enhancement in the mechanical strength relative to pure aramid.¹¹ Increase in silica content beyond 10 wt % in the matrix, however, caused decreases in the tensile strength. This may be due to the presence of excess silica particles, some of which may not be linked to aramid chains, and to the inherent brittleness of the silica. Also, at higher silica contents, the inorganic particles increase in size and eventually form clusters. Finally, the porosity of such clusters¹⁴ may also be a factor in the deterioration of the mechanical strength of these hybrid materials.

Chemical bonding between the aramid matrix and the inorganic network was achieved in some studies¹¹ by endlinking the polymer chains to the ceramic phase. Because of the limited number of chain ends available in a linear aramid, however, interfacial bonding can be achieved only up to a limit. More specifically, the higher the molecular weight of the polymer, the fewer the chain ends and the more limited the bonding capabilities of the chain. In some related materials, the average functionality of the monomer was increased in the synthesis of simultaneously linear–nonlinear polyaramid chains, which could be bonded into the inorganic network at more than just the two ends. Such chains were prepared by the addition of benzenetricarbonylchloride (BTCC) and terephthaloyl chloride (TPC) in a two-step process in which the TPC was first reacted with the diamines, with addition of the trifunctional monomer delayed until near the end of the reaction. The linear parts of the chains give the desired strong intermolecular bonding, while the nonlinear chain ends provide more bonding points (and, thus, better adhesion with the inorganic network). The tensile properties of such systems are under investigation.

The present investigation characterizes such materials using dynamic mechanical–thermal analysis (DMTA), a refined form of thermomechanical analysis primarily employed to study miscibility^{15–18} in various types of polymeric blends and composites. In the present context, it can give important information about interphase interactions in organic–inorganic hybrid composite systems. More specifically, DMTA techniques were used to study such interactions through measurements of storage and loss moduli and the related quantity loss $\tan \delta$. Of particular interest were changes in the glass transition temperature in such matrices as a function of their inorganic content and the type of interphase bonding. The results will be discussed in term of increased adhesion between the phases achieved through chemical bonding and, hence, possible enhancement in the mechanical strengths of these materials.

EXPERIMENTAL

Materials

The monomers employed were 1,4-phenylenediamine, 1,3-phenylenediamine, BTCC, and terephthaloyl chloride TPC. They were all of analytical grade and were obtained from Aldrich, as was anhydrous dimethylacetamide (DMAC) of 99% purity. Aminophenyltrimethoxysilane (APTMS, 97% pure), and tetramethoxysilane (TMOS, 99% pure), were obtained from Huls America Inc. All materials were used as received.

Preparation of Nonbonded Linear Aramid–Silica Hybrid Materials

The required reaction was carried out in a 250 mL conical flask provided with a stirrer. A mixture of 1,4- and 1,3-phenylenediamines, 0.050 mol in a 35 : 65 ratio, was placed into the flask, and 150 g of the DMAC solvent was added. After complete mixing, the amine solution was cooled to 0°C, and TPC (0.050 mol) was added under completely anhydrous conditions. Stirring was continued for an hour, the temperature of the flask was then raised to 25°C, and the reaction was assumed to be complete after 24 h. The resulting materials are essentially Nomex®-Kevlar® copolymers.

For the *in-situ* generation of the inorganic networks, different proportions of TMOS were added

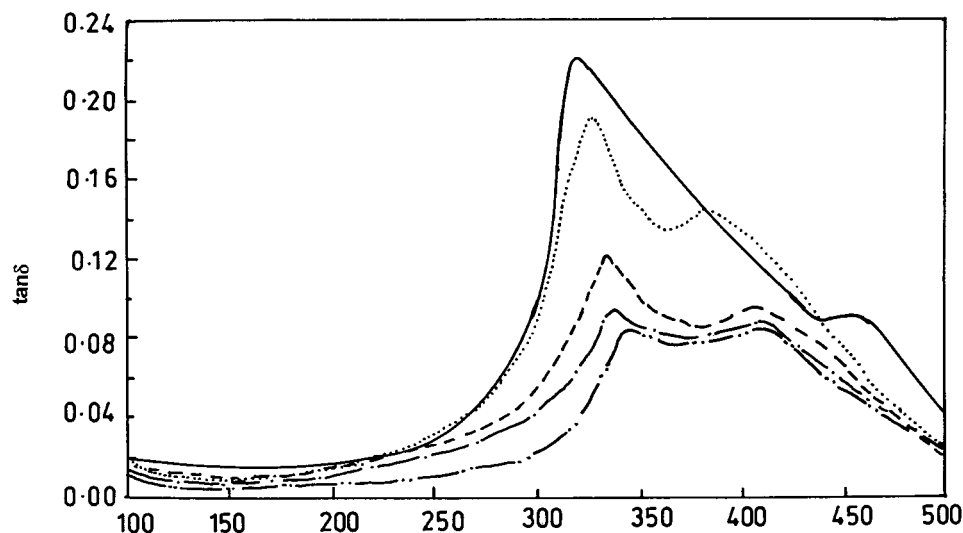


Figure 1 Variation of the loss tangent ($\tan \delta$) with temperature for non-bonded linear aramid-silica composites at 5 MHz. Wt % silica in the composite: 0 (—), 5 (·····), 10 (---), 15 (- · - ·), and 20 (- - - -).

to the polyamide solutions. After complete mixing, a measured amount of water in DMAC was added to carry out the hydrolysis and condensation required to form a silica network in each sample. Stirring of the reaction mixture was continued for an additional 6 h at 60°C. Films of uniform thickness were obtained from the samples containing various amounts of silica by casting onto a plate and then baking out the solvent in an oven at 75–80°C. After drying, they were soaked in water to leach out any HCl produced during the polymerization. The films were then dried at 80°C under vacuum for 96 hrs.

Preparation of Bonded Linear Aramid-Silica Hybrid Materials

The same mixture of 1,4- and 1,3-phenylenediamines and DMAC, and the same preparative conditions, were used for this material. In this

case, however, a slight excess (0.0005 mol) of the TPC was added to the polyamide solution in order to produce carbonyl chloride chain ends. The stirring was continued for 6 hrs, a stoichiometric amount of APTMOS was added to this reaction mixture under complete anhydrous conditions, and the stirring continued for about 6 hrs at 60°C. This permitted reaction of the amino groups on the APTMOS bonding agent with the carbonyl chloride end groups of the polymer.

The polymer solution thus prepared served as a stock solution into which various amounts of TMOS in DMAC were thoroughly mixed under completely anhydrous conditions. A measured amount of water in DMAC was added, and the stirring at 60°C was carried out for 6 h for the *in-situ* hydrolyses and condensations used to produce chemically linked silica networks. Composite films containing various amounts of silica were obtained as described above.

Table I Glass Transition Temperatures of the Nonbonded Linear Aramid-Silica Hybrid Materials

Sample	Silica Contents (wt %)	T_g (°C)
1	0.0	320
2	5.0	325
3	10.0	333
4	15.0	337
5	20.0	344

Preparation of Chemically Bonded Linear-Nonlinear Aramid-Silica Hybrid Materials

These materials were prepared to increase the limited number of chain ends available for chemical bonding with the inorganic network in the above system. This was done by increasing the average functionality of the monomer by first preparing linear aramid chains, but then making them non-linear at their ends. BTCC was used in appropriate ratio with TPC to react with the phenylenedi-

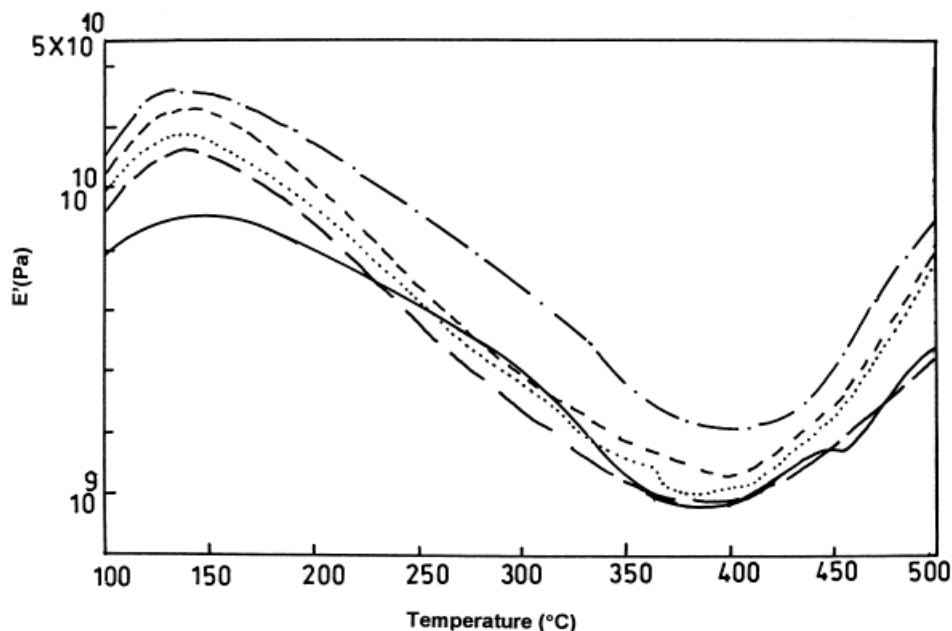


Figure 2 Temperature dependence of the storage modulus for non-bonded linear aramid-silica composites. See the legend to Figure 1.

amines. A mixture of 1,4- and 1,3-phenylenediamines, DMAC, and TPC was used as described above. After about 1 h of reaction time, however, 0.0006 mol of BTCC was added under anhydrous conditions, and the stirring continued for 24 hrs at room temperature. A stoichiometric amount of APTMOS was then added to react with the carbonyl chloride end groups in the reaction mixture, and

the stirring continued for about 6 hrs at room temperature. Various amounts of TMOS in DMAC were added to this polymer solution, with stirring for 6 hrs. Afterward, a measured amount of water in DMAC was added for the hydrolysis-condensation reactions producing the silica networks. Films containing different proportions of silica were prepared as described above.

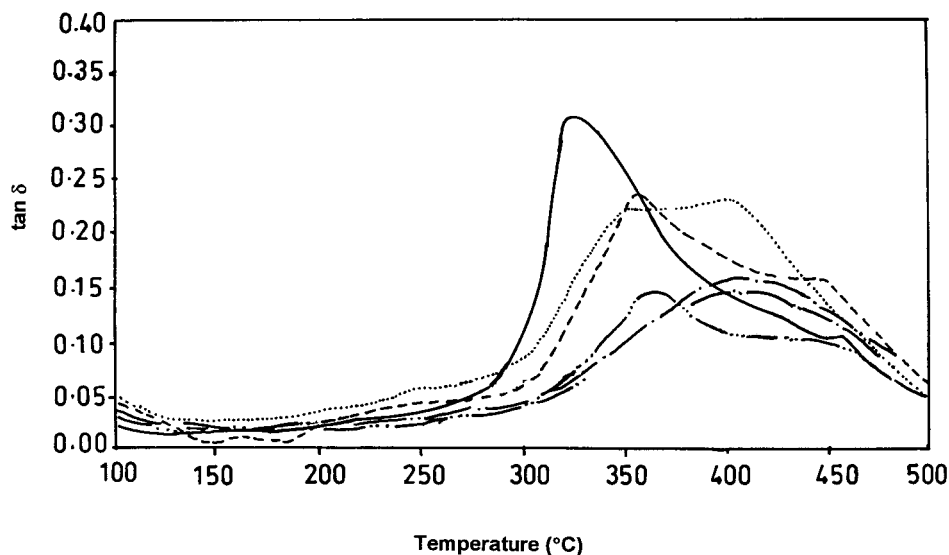


Figure 3 Variation of $\tan \delta$ with temperature for chemically bonded linear aramid-silica composites. % Silica in the composite: 0 (—), 5 (·····), 7.5 (---), 10 (-·-·-), 15 (- - - -), and 20 (- · - · -).

Table II Glass Transition Temperatures of the Chemically Bonded Linear Aramid-Silica Hybrid Materials

Sample	Silica Contents (wt %)	T_g (°C)
1	0.0	320
2	5.0	348
3	7.5	357
4	10.0	407
5	15.0	402
6	20.0	380

Characterization of the Composite Films

Dynamic-mechanical thermal analysis was carried out on the films over the range of 100–500°C, using a frequency of 5 MHz. Different modes of vibration are possible with the Rheometric Scientific DMTA III apparatus that was employed, but the most popular is reversed bending, and this was used in the present work. Films of the composite materials having fixed length (5.00 cm) but varying thicknesses (0.080–0.235 mm) and widths (2.30–6.20 mm) were subjected to the cyclic stress. Of primary interest were the temperature dependences of the loss and storage moduli and $\tan \delta$.

RESULTS AND DISCUSSION

General Observations

The films thus prepared were a transparent yellow and were very tough. The DMTA results gave val-

ues of their storage moduli, loss moduli, and, hence, the glass transition temperatures (T_g). Aramid polymers typically have values of T_g ranging from 250 to >400°C, depending on the proportion of *m*- and *p*-phenylene rings. In addition, the properties of aromatic copolyamides, and polymers in general, should depend not only on structural composition but also on comonomer sequence distribution. In the present investigation, the distribution in the Kevlar® with some metaunits was intentionally random in order to facilitate preparation of solutions for the sol-gel processing.

Nonbonded Linear Aramid-Silica Hybrid Materials

The variations of the loss $\tan \delta$ with temperature for the pure aramid, and for the linear aramid hybrid materials with no chemical bonding to the silica, are shown in Figure 1. These results indicate that with an increase in temperature, onset of segmental motion starts at a particular temperature, with a sharp increase in $\tan \delta$. The pure aramid employed shows a peak at $T_g = 320^\circ\text{C}$. In the case of the hybrid material, however, this peak splits up into two portions, showing a displaced maximum and then a shoulder at higher temperature. These sharp peaks for the hybrid materials are observed at slightly higher temperatures than those for the pure aramid, and the variations in the locations of the maxima with silica content are given in Table I. The addition

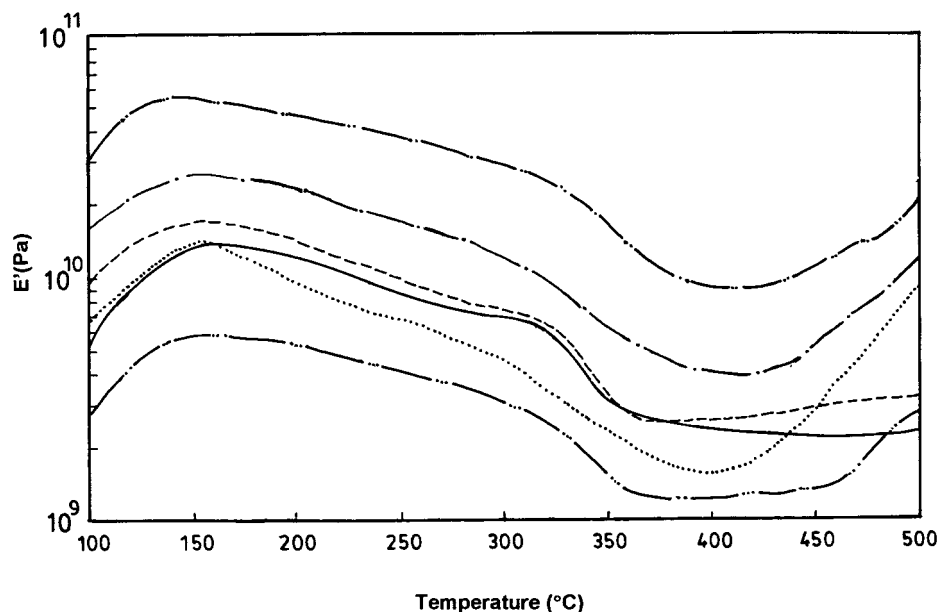


Figure 4 Temperature dependence of the storage modulus for chemically bonded linear aramid-silica composites. See the legend to Figure 3.

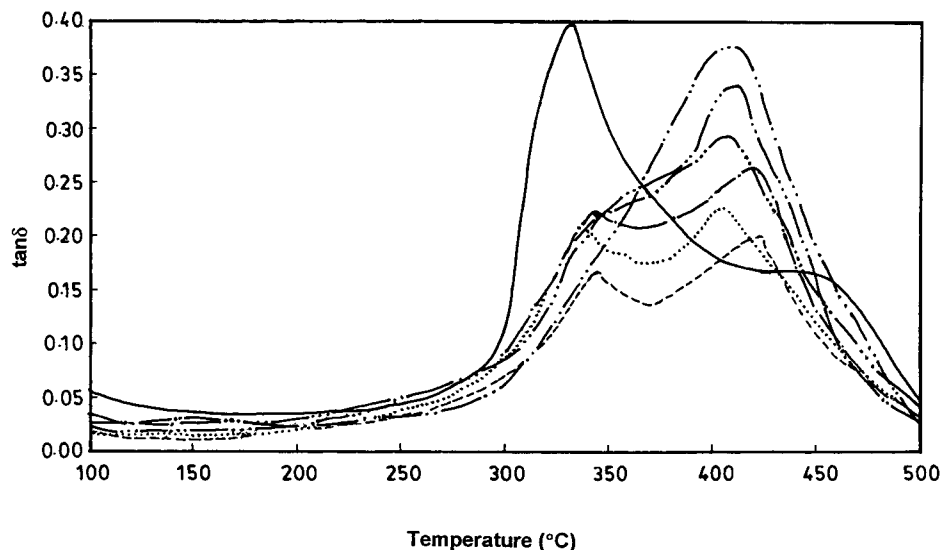


Figure 5 Variation of $\tan \delta$ with temperature for chemically bonded linear–nonlinear aramid–silica composites. See the legend to Figure 3.

of silica shifts the peaks to higher temperatures because the inorganic network hinders segmental motions of the polymer chains. The shoulders at higher temperatures suggest physical interactions between the inorganic phase and parts of the polymer matrix. The peaks generally decrease in intensity and broaden with increase in the amount of silica.

The temperature variation of the storage modulus in bending is given in Figure 2. The storage modulus initially increases with an increase in silica content and then slightly decreases. The silica network is much less flexible than the organic phase, and increased proportions of the silica should thus increase the storage modulus up to a point. Beyond this point, however, the inorganic phase can begin to form agglomerates, which could increase the brittleness to the extent of lowering the modulus.

Table III Glass Transition Temperatures of the Nonbonded Linear–Nonlinear Aramid–Silica Hybrid Materials

Sample	Silica Contents (wt %)	T_g (°C)
1	0.0	332
2	2.5	340
3	5.0	344
4	7.5	344
5	10.0	410
6	15.0	407
7	20.0	406

Bonded Linear Aramid–Silica Hybrid Materials

Figure 3 shows the variation of loss $\tan \delta$ with temperature for the pure aramid and for the linear aramid chains chemically bonded with the silica network. With addition of silica, the single sharp peak of the aramid again splits into a peak and a broad shoulder, with the shoulder shifting to higher temperatures with increase in silica content. A comparison of Figure 3 with Figure 1 indicates that the shifts of $\tan \delta$ to higher temperatures are significantly larger in the chemically bonded system. The difference suggests increased adhesion between the two phases, the polymer and the silica. This is further documented by the values of T_g given in Table II, relative to those in Table I, and by the fact that the composite having 10% silica shows a smooth, broader curve with no shoulder at all. The improved bonding is obviously the reason for the higher values of the tensile strength for films having 7–10% silica, as compared to that of the pure aramid.¹¹ The temperature variation of the storage modulus is given in Figure 4. The storage modulus initially increases with the addition of silica but then decreases around 20% silica content. The sharp decrease in modulus with onset of thermal motions occurs at higher temperatures for the composites containing larger amounts of silica.

Chemically Bonded Linear–Nonlinear Aramid–Silica Hybrid Materials

The variations of $\tan \delta$ with temperature for the pure aramid, and for the chemically-bonded lin-

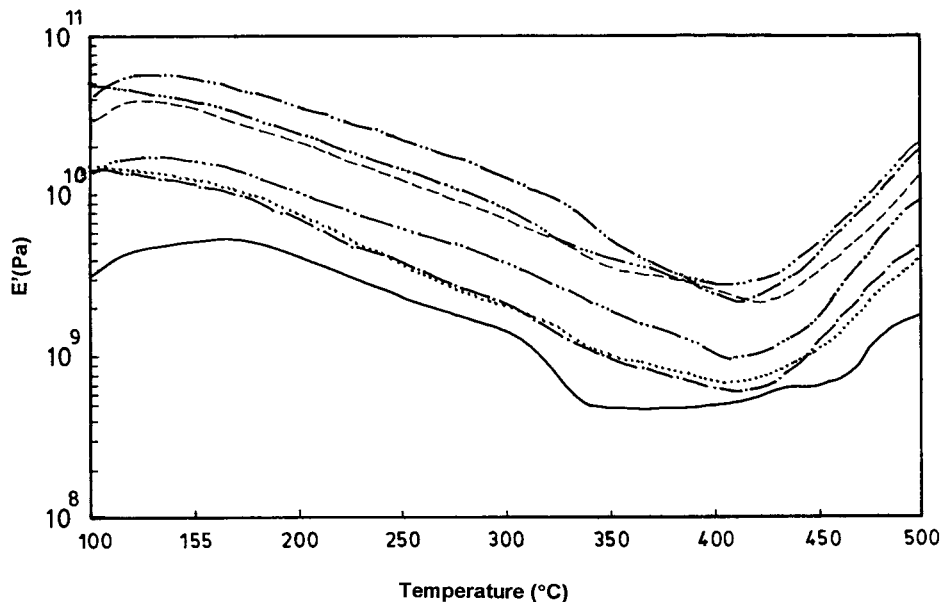


Figure 6 Temperature dependence of the storage modulus for chemically bonded linear-nonlinear aramid-silica composites. % Silica in the composite: 0 (—), 2.5 (·····), 5 (---), 7.5 (-·-·-), 10 (- - - -), 15 (- · · · · -), and 20 (- · · · · ·).

ear-nonlinear aramid-silica hybrid materials, are shown in Figure 5. As can be seen from these results, and from those given in Table III, the T_g s of the aramid polymer are shifted to higher temperatures than in the case of the totally linear aramid chains. The hybrid materials containing various amounts of silica show a small peak around 340°C, followed by a sharp peak above 400°C. This suggests that there are indeed more chain ends available for bonding, and that this bonding of the nonlinear aramid chains with the silica is the origin of the considerable shifts in the T_g values. On this basis, the maximum interfacial interactions occur at approximately 10% silica. The temperature variation of the storage modulus is shown in Figure 6. The storage modulus at 100°C initially increases with an increase in silica content. The sharp decrease in modulus with onset of the thermal motion starts at yet higher temperatures. In addition, the values of the storage modulus itself in this system were found to be maximized due to nonlinear structure of the aramid chain, with the associated increased bonding with the silica.

Morphological Model

A possible morphological model for these hybrid systems is shown schematically in Figure 7. For the unbonded aramid-silica system, it appears

that the distribution of the silica is irregular, as shown in part (i) of the figure. There is a tendency towards particle agglomeration, which is consistent with previous observations that transparency is greatly reduced at large amounts of silica.^{9,11} Figure 7(ii) represents the chemically endlinked linear aramid-silica composites where the inorganic network is bonded with the linear aramid chains. In this case, there is presumably a more regular distribution of the silica structure in the matrix; this would explain the observation that composites of this type having higher silica contents were more transparent than the corresponding non-bonded systems.¹¹ Finally, part (iii) of the figure depicts the chemically endlinked linear-nonlinear composites showing maximum bonding between the two phases from the increased number of chain ends available for interfacial bonding.

CONCLUSIONS

Composites in which a linear aramid polymer is not chemically bonded to a silica phase showed only small increases in glass transition temperature T_g above that of the pure polymer, which is consistent with relatively poor bonding between the organic and inorganic phases. However, when the aramid chains were chemically endlinked into

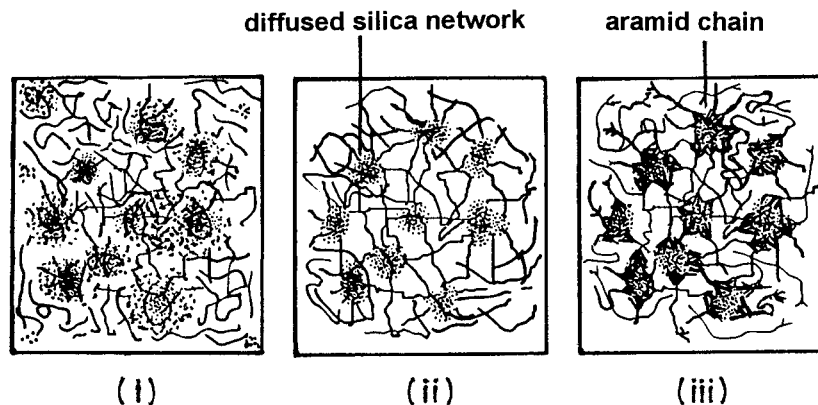


Figure 7 Morphological model suggested for the aramid-silica hybrids: (i) non-bonded aramid-silica composite, (ii) chemically bonded linear-aramid composite, and (iii) chemically bonded linear-nonlinear aramid composite.

the inorganic network, the shifts in T_g were much larger. For example, with the bonding polymer, the increase in T_g with 5 wt % silica is nearly the same as that obtained with 20% silica in the non-bonding case. This increase in T_g could be useful in a variety of high-temperature applications. Chemical bonding between the phases thus results in better cohesion between the phases and more marked decreases in segmental mobility of the polymer. The highest value of the T_g was observed for 10% silica (407°C), which gave an attractive tensile strength of 150 MPa,¹¹ suggesting maximal interactions between the phases.

If the linear aramid chains are modified so as to have nonlinear groupings of functional groups at the chain ends, then even stronger bonding with the silica occurs. This is indicated, for example, by the overall moduli of the linear-nonlinear aramid composites being higher than those containing bonding but totally linear polymer. It should be possible to optimize the properties of this class of composites by varying the lengths of the linear sequences of the polymer and the types of branched structures placed at the ends of the polymer chains.

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