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Inter-Phase Bonding in Poly(hydroxyamide)-silica Hybrids: Effect of Isocyanato-propyltriethoxysilane Addition on the Structure and Properties

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Novel aramid-silica ceramers with increased inter-phase bonding have been prepared via the sol-gel process. The aramid chains with pendant alkoxy groups were synthesized by reacting poly(hydroxyamide) chains with isocyanato-propyltriethoxysilane (ICTOS). The sol-gel process was carried out in this matrix after mixing an appropriate amount of tetraethoxysilane (TEOS) to produce a silica network structure chemically bonded to the matrix. The effect of ICTOS addition on morphology, thermal and mechanical properties of the composites has been studied. Properties of the composites were compared with the hybrid system where a similar matrix was used but the silica network was developed using a mixture of ICTOS and TEOS or TEOS alone. The hybrid materials in which ICTOS was added prior to TEOS in the matrix showed better mechanical and thermal properties as compared to the system in which ICTOS and TEOS were used together or where only TEOS was used in the pure aramid matrix. The glass transition temperature was found to increase and the coefficient of thermal expansion was considerably reduced in chemically bonded ceramers as compared to those having no interfacial bonding.

Keywords: poly(hydroxyamide); silica; ceramers; isocyanato-propyltriethoxysilane; visco-elastic properties

1 Introduction

Hybrid organic-inorganic materials are produced to combine the useful properties of the individual polymer and ceramic components (1). The sol-gel process is considered a very successful approach (2, 3), being a convenient and flexible route to achieve such hybrids under mild conditions where the composition and homogeneity of the materials can be controlled at a molecular level. The incorporation of organic polymers imparts flexibility to the inorganic glasses, while the introduction of the inorganic component can improve the properties of organic polymers. Such hybrids or ceramers are useful in many structural or coating applications (4–6). The inorganic component, especially silica, has been generated from the organic precursor; such as tetraethoxysilane (TEOS) in many polymer systems (7–9) due to its relatively slow and controllable rate of reaction. For multi-component hybrid materials different metal alkoxides, based on aluminum, titanium and zirconium, with relatively fast hydrolysis rates

have also been used (10–12). To optimize the performance of these materials, the dispersion of the inorganic phase into the organic matrix, at the micro- or nano-meter level, is very desirable.

For high performance applications, a natural combination with the ceramics are high temperature polymers, such as aromatic polyamides (13–17) and polyimides (PIs) (18–20). Aromatic polyamides, commonly known as ‘aramids’, play an important role in modern technology based on advanced materials, due to their high thermal stability, intermolecular bonding, specific strength and their high degree of stiffness. These thermally stable polymers are particularly useful in the aerospace industry, where their relatively low densities give them considerable advantage. However, these polymers (21) usually have a rigid chain structure and therefore, are very difficult to be treated in a sol-gel process because of their low solubility. Poly(phenyleneterephthalamide) resin used to prepare Kevlar® for example is not soluble in organic solvent. By introducing 15–20% meta linkages in such a polyamide it is possible to keep the copolymer in solution (13, 14). Using the sol-gel process, a silica network was produced *in situ* in such a matrix by the hydrolysis of tetramethoxysilane (TMOS). Mechanical properties of this hybrid material, however, did not show any

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distinguishable improvement (13). In another attempt, the aramid chains end-capped with aminophenyl-trimethoxysilane were used to synthesize hybrid material in which these were chemically end-linked to the silica network produced *in situ*. The transparency of the films and the tensile strength were improved (14) relative to a similar system without interfacial bonding (13). The increase in the mechanical strength was attributed to increased cohesion between the organic and inorganic phases due to end-linking of aramid chains with the inorganic network. Chemical bonding between the aramid chain and the inorganic network was, however, limited because of the limited number of chain ends available with a linear polymer chain. In other words, the higher the molecular weights of the polymer, the lesser the chain ends. The present authors (20) have prepared PI-silica hybrids by modifying the PI matrix to include pendant hydroxyl groups on the chain. The presence of a hydroxyl group on the PI chain resulted in the formation of nano-sized silica co-continuous domains in the matrix as compared to the corresponding PI system, where the silica particles were seen in the form of micron sized beads. Dubois et al. (22) used 3-isocyanato-propyltrithoxysilane (ICTOS) to prepare hybrids from polycaprolactone (PCL), using the sol-gel process after converting the hydroxyl groups on the chain into alkoxy groups using ICTOS. Since the hydroxyl groups of PCL are less reactive than the alkoxy groups, the TEM observation showed that the organic and inorganic phases became thoroughly mixed using ICTOS. The ICTOS has also been used recently as a coupling agent to increase the compatibility in epoxy-silica composites and these nano-composites showed better thermal properties than the pure resin (23).

In order to create a number of reactive sites on the aramid chain, hydroxyaramid chains were synthesized in the present work by the co-polymerization of a mixture of phenylene diamine and 2,4-diaminophenol with an equivalent amount of terephthaloyl chloride (TPC). ICTOS was then used to react with the hydroxyl groups to produce pendant alkoxy groups on the chain. The silica network in such a matrix was produced using an appropriate amount of TEOS in a sol-gel process. The properties of these hybrids, with different silica loadings, are compared with the hybrids in which TEOS and ICTOS were added together (24) in the sol-gel process or the matrix in which there were no reactive sites and silica was produced only from TEOS.

2 Experimental

2.1 Materials

Monomers used for the synthesis of the aramid, 1,4-phenylenediamine, 1,3-phenylene diamine, 2,4 diaminophenol dihydrochloride (96%) and terephthaloyl chloride (TPC) were analytical grade reagents obtained from Fluka. The 3-isocyanato-propyltriethoxysilane (ICTOS) (95%) was obtained from ABCR, Germany and used as received. The

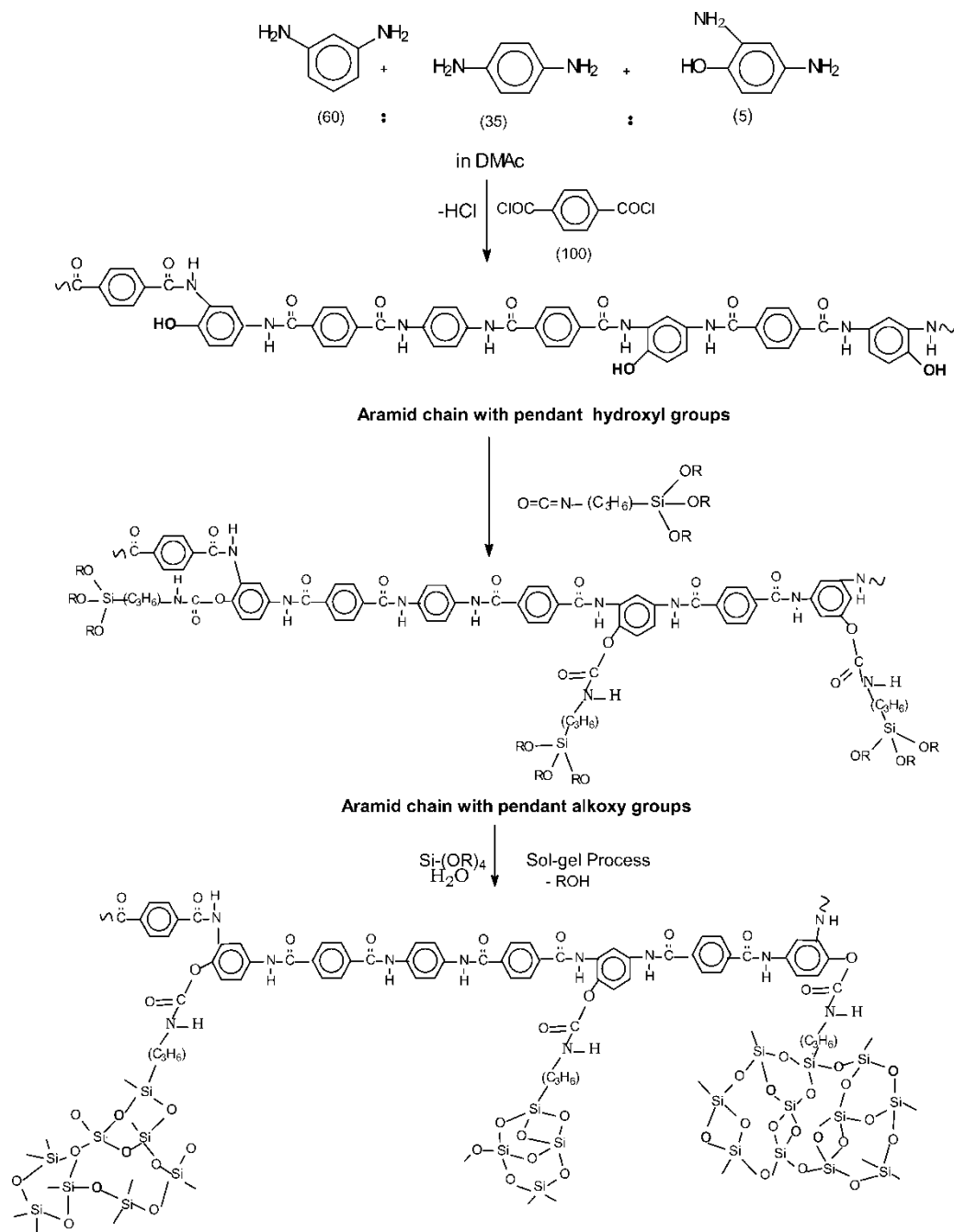
99% pure, anhydrous dimethylacetamide (DMAC), with water contents $\geq 0.005\%$, was obtained from Fluka.

2.2 Preparation of Hybrid Films

The PI matrix having pendant hydroxyl groups was synthesized by the copolymerization of a mixture of diamines (0.050 mol), 1,4- and 1,3-phenylene diamines and 2,4-diaminophenol dihydrochloride (using a 35 : 60 : 5 mole ratio, respectively) with an equivalent amount (0.050 mol) of TPC in DMAC. The hydroxyl groups remain unreacted in the above reaction leading to polyamide formation. A stoichiometric amount of ICTOS was added to react with the hydroxyl groups on the aramid chain. The aramid chain with pendant alkoxy groups (Scheme 1) was used to develop silica network in the matrix using the sol-gel process. Different amounts of TEOS in DMAC were added to the aramid solution and mixed by thorough stirring. A stoichiometric amount of water in DMAC was then added to each sample to carry out the sol-gel process. HCl produced during the polymerization reaction acted as a catalyst. The reaction mixture was allowed 12 h stirring at 60°C to complete the hydrolysis and co-condensation of the ICTOS alkoxy groups and TEOS to produce an inorganic network chemically bonded with the aramid matrix. Films of controlled and uniform thickness were cast in Petri dishes and the solvent was baked out at 70°C. These films were soaked in water and washed repeatedly to leach out any HCl produced during the polymerization reaction. Finally, the films were dried at 80°C and then at 120°C under vacuum for 48 h. The aramid hybrid films with various silica contents (2.5–20 wt%) were thus prepared. The procedural details are provided in Figure 1. A reference hybrid system, where no bonding existed between the phases, was also prepared. The matrix for this purpose was prepared by reacting a mixture of 1,4- and 1,3-phenylene diamines (0.050 mol, in molar ratio 35:65) with an equivalent amount of TPC under complete anhydrous conditions. The aramid hybrid films with various silica contents in this matrix were prepared using only TEOS as described above.

2.3 Characterization of the Hybrid Films

FTIR spectroscopic analysis was carried out on Perkin-Elmer FTIR-2000 spectrophotometer to monitor the reaction of hydroxyl groups of aramid chain with isocyanato groups of ICTOS and the silica network formation in the sol-gel process. Dynamical mechanical thermal analysis (DMTA) was carried out using DMA Q-800 (TA, USA). The measurements of storage modulus and $\tan \delta$ were made under tension mode in the temperature range 100–500°C at heating rate of 5 min/°C, using a frequency of 5 Hz under an inert atmosphere. Tensile measurements were carried out at 25°C under ASTM 882 at a uniform strain rate of 5 mm/min, using a Instron Electromechanical Tester 8562. The samples were vacuum dried at 100°C overnight before analysis.



Sch. 1. Structure of chemically bonded aramid-silica hybrids.

From the stress-strain analysis ultimate tensile strength, modulus and the strain at the break point were calculated. The average value obtained from the tensile measurements using 3–4 samples have been reported in each case. The linear coefficient of thermal expansion was measured on Shimadzu TMA-50 at a heating rate of 10°C/min with an applied load of 4.00 g under an inert atmosphere. Scanning electron microscopy (SEM) was conducted, using a JSM-630 J scanning electron microscope operated at 20 kV. The brittle-fractured films were sputter coated with gold by means of Balzer's SCD 050 sputter coater before analysis.

Thermogravimetry Analysis (TGA) was performed on 10 mg of the sample from ambient to 800°C at a heating rate of 10°C/min in a dynamic (30 ml/min) synthetic air atmosphere using TGA-50 Shimadzu automatic analyzer.

3 Results and Discussion

The pure aramid and aramid-silica composite films (thickness 0.08–0.1 mm) up to a maximum of 20 wt% silica content were light yellow in color. Transparency of the films was

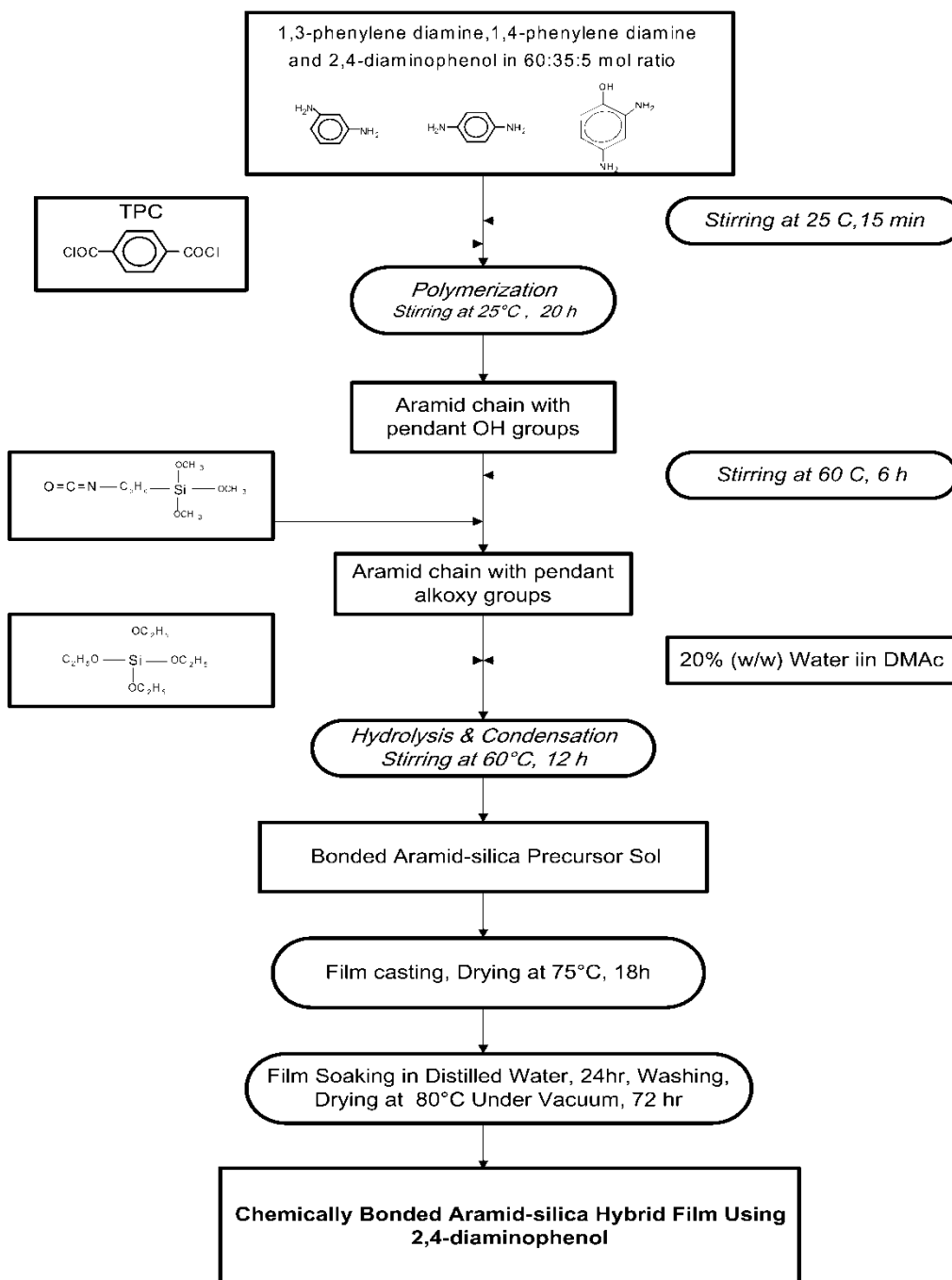


Fig. 1. Flow sheet diagram for the synthesis of chemically bonded aramid-silica hybrids.

better in the bonded hybrids case. The films beyond 20 wt% silica content were slightly opaque and brittle and these were not characterized for their mechanical behavior.

3.1 FTIR Analysis

FTIR spectroscopy was carried out to monitor the reaction of the hydroxyl groups on the aramid chain with the ICTOS isocyanato groups and the silica network formation from alkoxy groups in the sol-gel process. The FTIR spectrum of pure

aramid film dried under vacuum at 120°C for 48 h is shown in Figure 2. A broad band around 1640–1680 cm^{-1} , called amide I mode, involves contributions from C=O and C-N stretching (25). The bands at 1524–1565 cm^{-1} , known as amide II mode, is a mixed contribution of N-H in plane bending, the C-N and C-C stretching. The relatively lower intensity of the amide II mode along with shift towards lower frequency clearly shows that strong hydrogen bonding exists (26). The broad band appearing at 1273 cm^{-1} is due (27) to secondary amide groups (amide III mode). The FTIR spectrum of

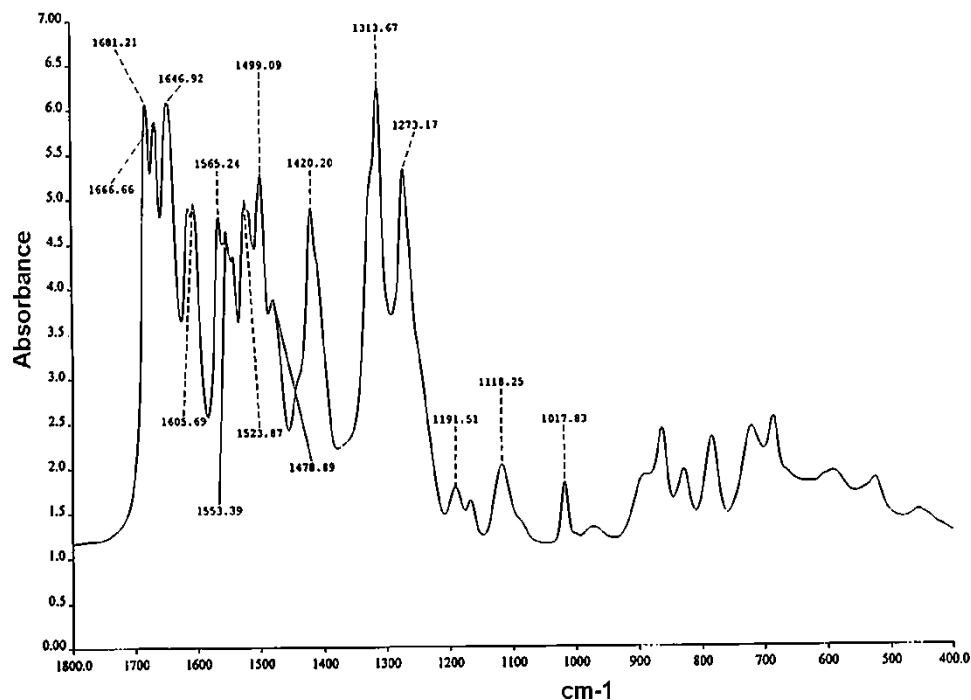


Fig. 2. FTIR spectra for pure amide film.

the dried hybrid film, in which silica network is bonded through ICTOS, is shown in Figure 3. The reaction of phenol groups present on the amide chain with ICTOS results in the formation of the aryl urethane linkage. The aryl urethane linkage absorbs in the 1553 cm^{-1} range. This bond is very clear in Figure 3, showing that the binding agent ICTOS has reacted with the amide chain. The presence of ICTOS within the matrix is

also visible due to absorbance in the 1103 cm^{-1} region, indicating the presence of Si-C bond and 1321 cm^{-1} due to the $\text{CH}_2\text{-N}$ bond. FTIR can also be used to detect the silica network formation (28) in the hybrid films. The band at $415\text{--}420\text{ cm}^{-1}$ is assigned to the Si-O-Si bending vibration. The absorption domain in the region $1000\text{--}1250\text{ cm}^{-1}$ show higher absorbance as compared to pure amide film

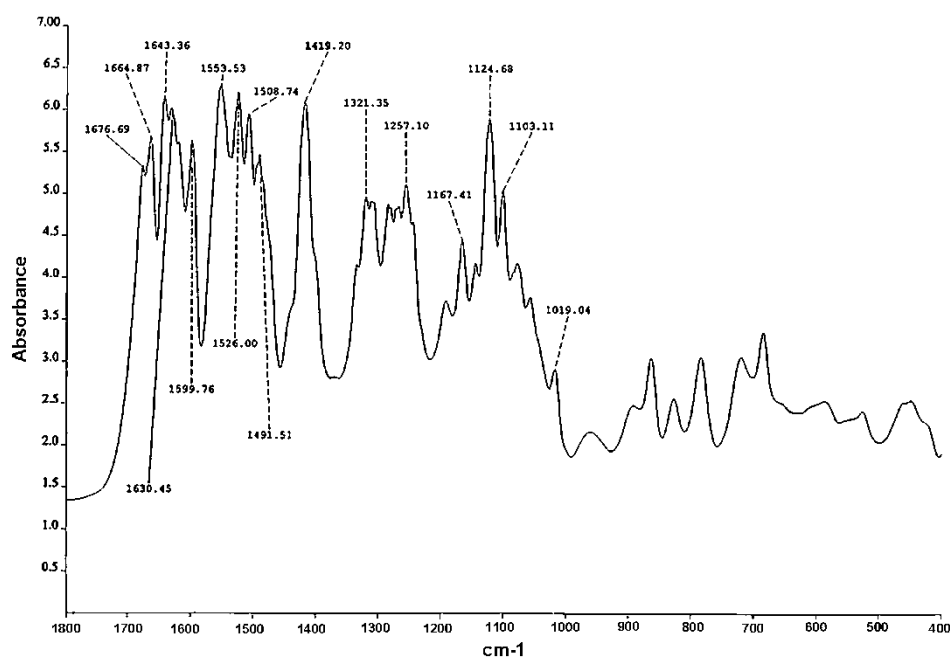


Fig. 3. FTIR spectra for the bonded amide silica hybrid film: 10 wt% silica in the matrix.

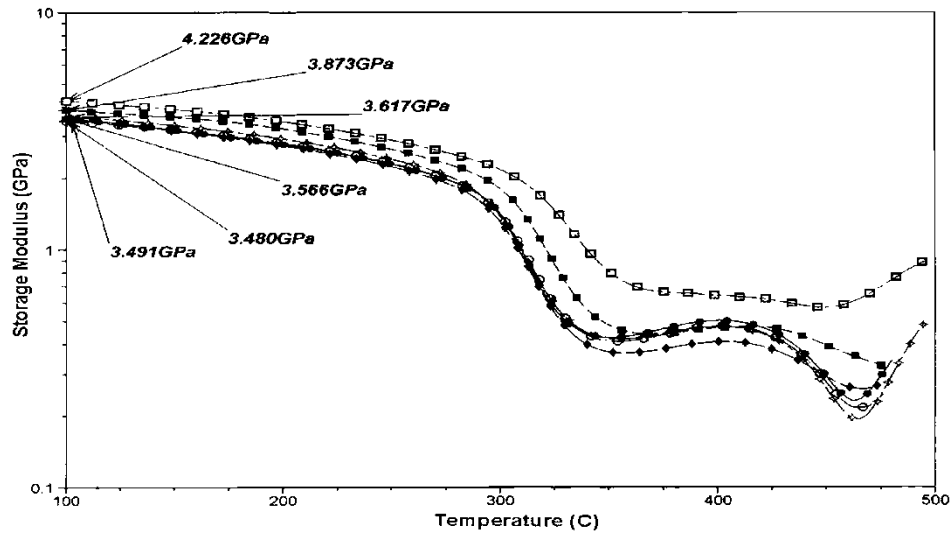


Fig. 4. Temperature variation of storage modulus for the unbonded aramid silica hybrids: silica wt% in the matrix; 0 (●), 2.5 (○), 5 (◆), 10 (◇), 15 (■), 20 (□).

(Figure 2), mainly due to the presence of Si-O-Si linear and cyclic rings formation resulting from the hydrolysis and condensation of TEOS along with ICTOS.

3.2 Dynamical Mechanical Thermal Analysis

The temperature variation of the storage modulus for the reference or unbonded hybrid system is shown in Figure 4. The modulus of pure aramid film was 3.48 GPa at 100°C. It increases with an increase in the silica content, with the maximum value recorded as 4.23 GPa for 20 wt% silica (Table 1). As the temperature is increased, the storage modulus drops in the rubbery region. This decrease is less for the hybrids with increased silica content. However, in the temperature range of 350–400°C, there is again a slight increase above the T_g in the case of pure polymer, which may be due to the cyclic stress during DMTA measurements that could possibly induce alignment of the polymer chains. As the polymer softens above 425°C a sharp drop in the E' value is observed, except in the case where the matrix has

15 wt% silica or more. The presence of silica increases the softening point and therefore the hybrids having large wt% of silica tends to retain modulus above the T_g , due to the formation of a highly condensed silica network (29). It has been observed (30) that the proportion of the nonhydroxy-substituted silica increases with increase in the silicon content in the sol-gel process, particularly at high temperatures. In the region above 460°C, the storage modulus for pure polymer and the hybrids was found to rise again. The softening and the thermal decomposition temperature of the polyaramids lie very close to each other. The free radicals produced due to degradation phenomenon may cause cross-linking of the chains and as the network structure is formed the modulus shows steep rise above 460°C.

A systematic variation in the storage modulus with an increasing amount of silica content was observed in the case of the bonded hybrid system (Figure 5) The value of E' increased constantly with an increasing amount of silica and the maximum value recorded for 20 wt% silica was 5.26 GPa at 100°C. The E' values at 100°C are higher in

Table 1. Viscoelastic properties of aramid-silica hybrids at different silica contents

SiO ₂ (wt.%)	Storage modulus (GPa) at 100°C		Storage modulus (GPa) at 360°C		T _g (°C)		Tan δ	
	Un-bonded hybrids	Bonded hybrids	Un-bonded hybrids	Bonded hybrids	Un-bonded hybrids	Bonded hybrids	Un-bonded hybrids	Bonded hybrids
0	3.50	3.31	0.43	0.38	322.97	318.92	0.3062	0.2869
2.5	3.48	4.04	0.41	0.38	323.93	320.42	0.2987	0.2915
5	3.57	4.37	0.37	0.43	324.02	327.03	0.2986	0.2380
10	3.61	4.51	0.42	0.61	327.00	332.36	0.2675	0.2317
15	3.88	4.90	0.44	1.05	331.28	337.44	0.2047	0.1897
20	4.23	5.26	0.71	1.72	335.11	342.24	0.1941	0.1618

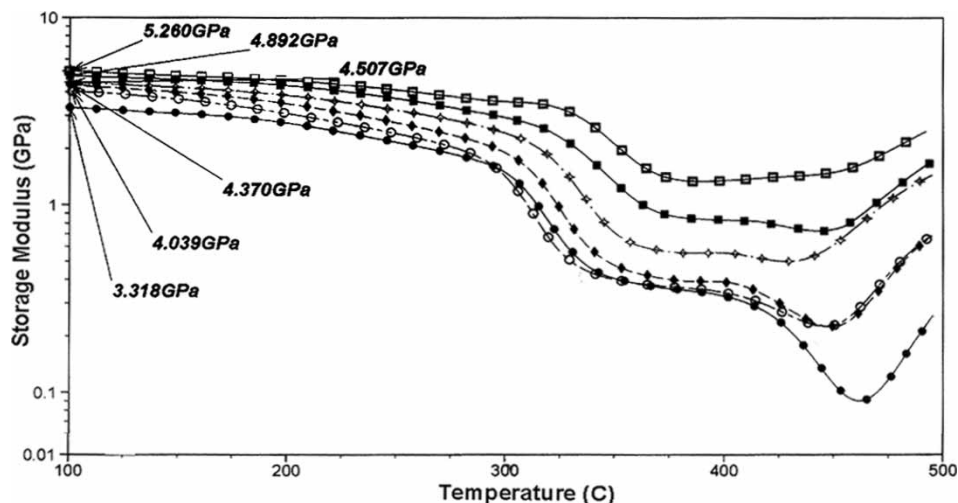


Fig. 5. Temperature variation of storage modulus for the bonded aramid silica hybrids: silica wt.% in the matrix: 0 (●), 2.5 (○), 5 (◆), 10 (◇), 15 (■), 20 (□).

the case of bonded ceramers (Table 1). The modulus decreases linearly with an increase in temperature up to 300°C and at the T_g , a rapid decrease is witnessed. The chemically bonded hybrid materials, however, tend to retain much higher values of E' as compared to the unbonded hybrids in the rubbery regime above 360°C. The interfacial bonding between the phases seems responsible for retaining high modulus even above T_g . At a temperature above 460°C there is an abrupt increase in the modulus, which may be due to further crosslinking of the polymer chain, as well that of the silica network structure (29).

Figures 6 and 7 show the temperature variation of $\tan \delta$ for the unbonded and bonded ceramers, respectively. The position of the maxima of the curve very accurately shows the T_g values associated with α -relaxations. These values have been shifted to a higher temperature region with an increase in the silica contents in both cases, with the shift much more in the case of bonded ceramers. The T_g for the pure polymer is around 321–323°C, which is increased to 335°C for the unbonded ceramers with 20 wt% silica. This value becomes 342°C for chemically bonded ceramers with a similar concentration. A higher increase in the case of bonded ceramers suggests that the mobility of the polymer

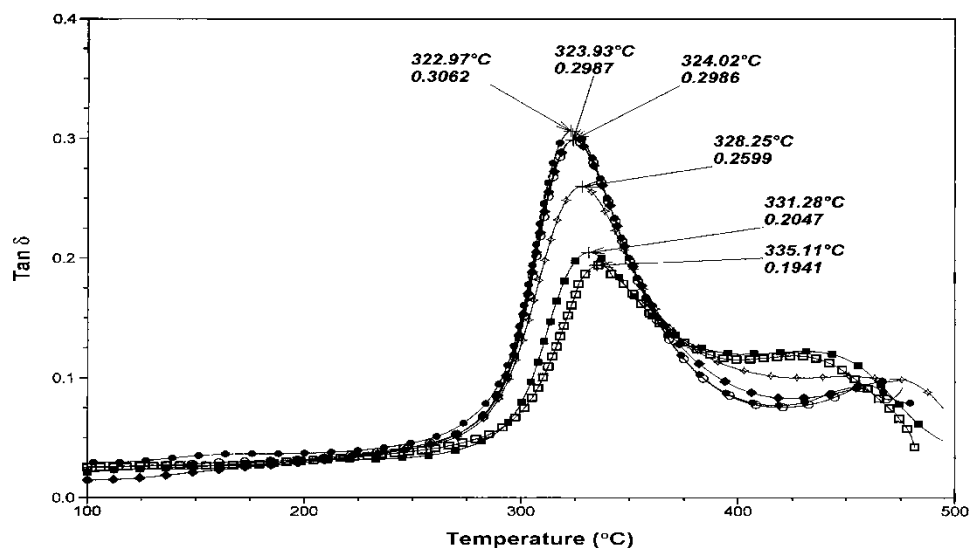


Fig. 6. Temperature variation of $\tan \delta$ for the unbonded aramid silica hybrids: silica wt.% in the matrix; 0 (●), 2.5 (○), 5 (◆), 10 (◇), 15 (■), 20 (□).

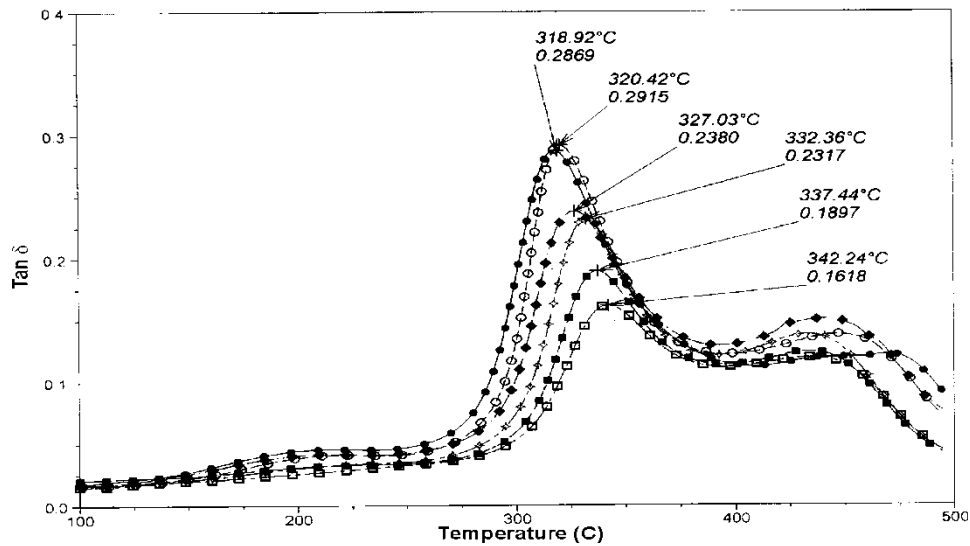


Fig. 7. Temperature variation of $\tan \delta$ for the bonded aramid silica hybrids: silica wt% in the matrix; 0 (●), 2.5 (○), 5 (◆), 10 (◇), 15 (■), 20 (□).

chain is further restricted due to bonding of polymer chains on the silica surface. This is further evident from the height of $\tan \delta$ curves, which show a much more damping effect on increasing the silica content in the matrix as compared to the system in which the two phases were not bonded. The large damping in the $\tan \delta$ curves and increase in T_g for the bonded hybrids is attributed to improved adhesion due to the reaction between alkoxy groups present on the aramid chain and that of TEOS which help the polymer chains to bind on the surface of silica particles during the sol-gel process.

The major disadvantage with the polymeric materials in structural applications is their tendency to flow because of their visco-elastic behavior. However, with inclusion of a rigid silica network and its binding with the matrix, the viscous behavior is changed to elastic as is evidenced by large dampening in the $\tan \delta$ curves. These thermally stable polymers with higher modulus value, less viscous behavior and higher glass transition temperature produced by chemically bonding the silica network can, therefore, perform as high performance materials under harsh environmental conditions such as high temperature.

3.3 Tensile Properties

Stress-strain analysis for both types of hybrid systems was carried out according to ASTM-882, which covers tensile properties measurements of plastics in the form of thin films. From the stress-strain analysis, ultimate tensile strength, modulus and the strain at the break point were calculated (Table 2). In both cases, the modulus was found to increase initially with the silica fraction (Figure 8). The chemically bonded system had a higher modulus than the unbonded hybrids. This system also tends to retain the modulus value with an increase in the silica content as compared to the unbonded system. In the bonded hybrids the polymer chains interact chemically with the silica network, being absorbed on its surface. Thus, for a given silica content, it makes the polymer chains stiff, which explains why the bonded hybrids have higher Young's modulus than that of unbonded hybrids for similar silica loading.

The tensile strength was found (Figure 9) to increase initially on increasing the silica contents to ca. 5%. But, it decreased slightly with 20% silica loading for the bonded

Table 2. Tensile properties of aramid-silica hybrids at different silica contents

SiO ₂ wt%	Tensile modulus (GPa)		Elongation at break		Tensile strength (MPa)	
	Un-bonded hybrids	Bonded hybrids	Un-bonded hybrids	Bonded hybrids	Un-bonded hybrids	Bonded hybrids
0	3.24	3.55	0.95	0.92	126.5	129.4
2.5	4.05	4.20	1.05	0.97	153.5	158.3
5	3.78	4.55	0.77	0.62	133.9	184.2
10	3.50	4.22	0.55	0.47	110.2	163.3
15	3.36	4.18	0.41	0.25	95.8	154.9
20	3.10	4.15	0.35	0.14	82.6	140.3

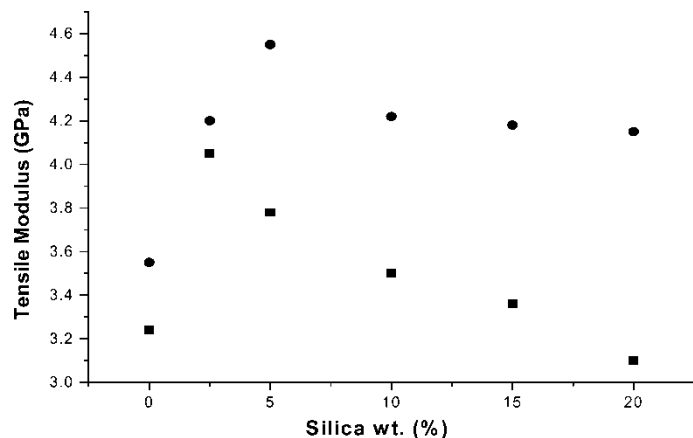


Fig. 8. Variation of tensile modulus with silica content in aramid-silica unbonded (■), bonded (●) hybrids.

system. In contrast, there was a drastic decrease in the case of unbonded hybrids. The strength of a particulate system depends upon many factors e.g., elastic modulus, fracture energy and the crack size, and are influenced by the particulate phase. As the external stresses in plastic composites are transferred from matrix to the filler, the ultimate properties of the hybrid materials are dependent on the extent of bonding between the two phases and the surface area of the filler, and the arrangements between the filler particles. Chemically bonded hybrid transparent films therefore show better tensile strength as compared to an unbonded system for the similar silica loading. The strain values at the break point for these hybrids are shown in Figure 10. It is naturally expected that as the modulus of the material increases the elongation at the break point of the film will decrease. There was however little plasticization effect in case of hybrids with 2.5% silica. The bonded ceramics however, show better performance in toughness as compared to the unbonded hybrids.

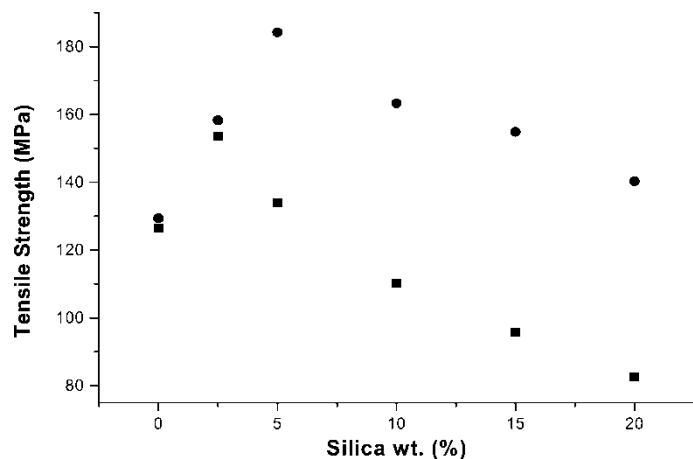


Fig. 9. Variation of tensile strength with silica content in aramid-silica un-bonded (■), bonded (●) hybrids.

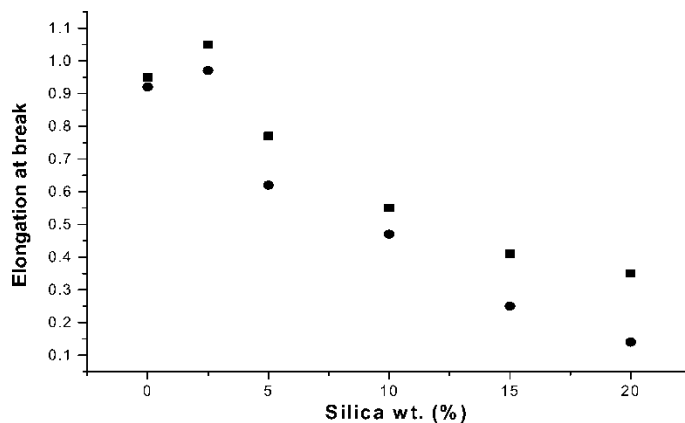


Fig. 10. Variation of Elongation at break with silica content in aramid-silica unbonded (■), bonded (●) hybrids.

3.4 Thermal Mechanical Analysis

Thermal mechanical analysis results for aramids and their hybrid films, with 20% silica bonded within the polymer chain is shown in Figure 11. The linear coefficient of

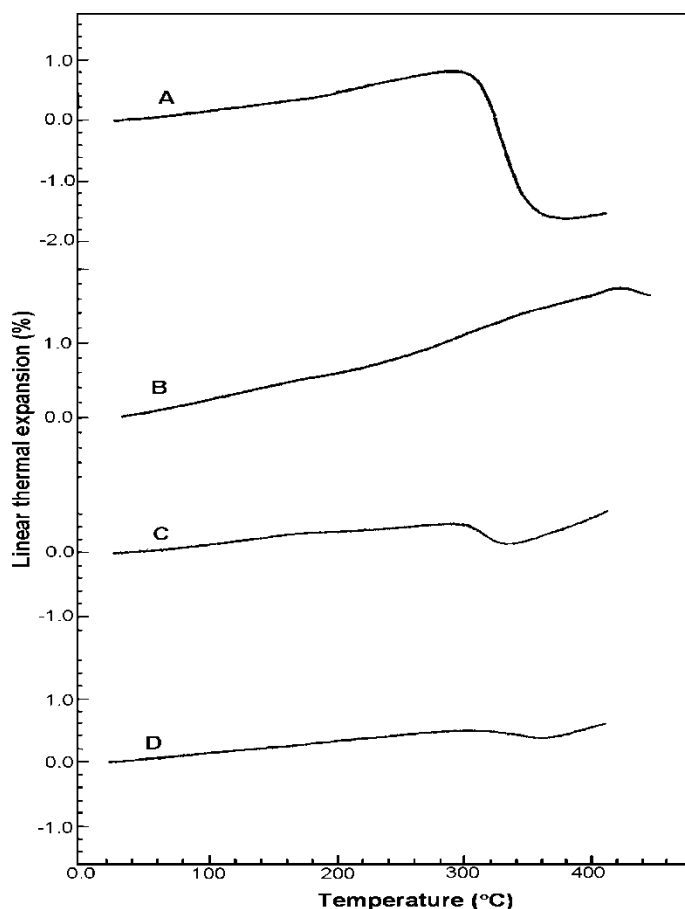


Fig. 11. Thermal mechanical analysis: A) Pure aramid, B) Aramid with hydroxy groups, C) Aramid with alkoxy groups, D) Aramid-silica bonded hybrids with 20 wt% silica.

Table 3. Coefficient of thermal expansion (ppm/°C) for aramids And aramid-silica hybrids

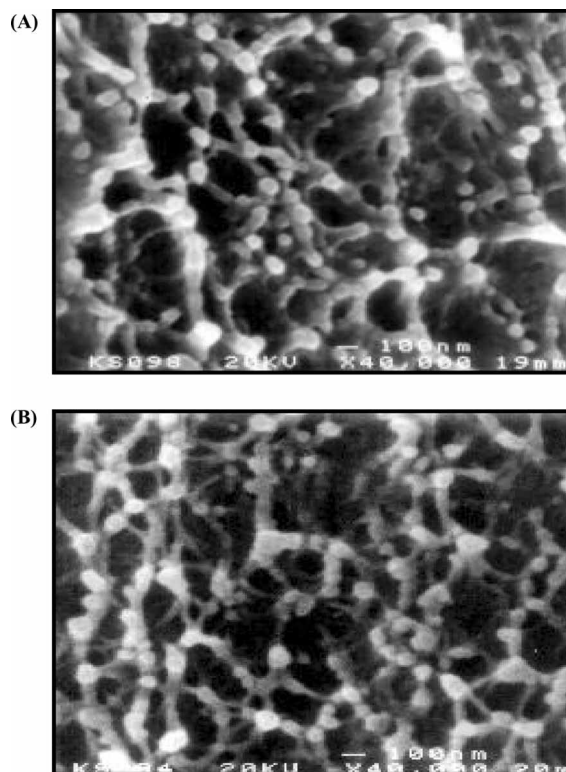
Temperature range (°C)	Aramid with			Bonded
	Aramid	hydroxy groups	alkoxy groups	Aramid-silica hybrids with 20% silica
50–280	36.11	34.31	21.31	16.95

thermal expansion (CTE) values are given in Table 3. The average value of CTE measured in the temperature range 50–280°C for pure aramid film (A) is 36.11 ppm/°C. The polymer softens above 300°C. However, introduction of hydroxyl groups (B) increases the softening point and the average value of CTE measured in the same temperature range is 34.11–31.29 ppm/°C. The slight decrease, as compared to pure aramid chain, may be due to increased secondary bond interactions. When this chain is further reacted with ICTOS and during the film formation as the alkoxy groups combine inter-molecularly the CTE value is considerably reduced to 21.31 ppm/°C (C). The fluctuation observed above 300°C in the case of such a film may be due to weak propyl linkage of ICTOS, which is very flexible at high temperature. The inclusion of silica through TEOS decreases further the CTE value to 16.95 ppm/°C (D). The large decrease in CTE in the hybrid film shows increased interaction between the organic and the inorganic phase as the polymer chain seems to get absorbed on the silica network. The value of CTE plays an important role in the multi-layered structural composites, in particular, when these materials are used at high temperature, i.e., low values of CTE prevent deformation making them useful over a wider range of temperature.

3.5 Electron Microscopic Analysis

Scanning electron micrographs for the unbonded hybrids are shown in the Figure 12. The particle appears as a condensed phase in the matrix. The shape of many of the particles is round with a large variation in size. The diameter varies from 50–200 nm. The surface of many particles is rather blurred where as the smaller one have sharp boundaries.

Figure 13 shows the SEM micrographs for the bonded ceramics where ICTOS was first added in the matrix with hydroxyl-aramid and TEOS was added later in the reaction mixture. The silica particles, which are usually seen as round particles, lost their shape completely and the silica network itself became aligned with the polymer chains. The two phases became intermingled with each other due to increased chemical interactions. This is very important in the polymeric composites as the mechanical properties of such materials depend on how the exerted stress on the material is transferred from one phase to the other. If sharp boundaries exist between the phases the stress transfer problem results in lower strength of the material. So, where

**Fig. 12.** SEM Micrographs for the unbonded aramid-silica hybrids, wt% of silica in the matrix: (A) 10, (B) 20.

as the condensed phase helps the rare (polymeric) phase with large free volume to resist high stress values (higher tensile modulus and strength) the interconnectivity is also an important factor which we successfully achieved in the present work.

The SEM micrographs of the aramid-silica hybrid system where hydroxy-aramids were used as the matrix and the coupling agent ICTOS with TEOS was added together during the sol-gel process (23), showed different morphology (Figure 14). The alkoxy groups on the chains interacted with the hydrolyzed TEOS and might have slightly reacted with ICTOS. The polymer chains get adsorbed on the surface of the particle, but the interaction between the phases was far less than achieved in the present study. It seems when we add ICTOS and TEOS together, the secondary bond interaction between silanol groups and the pendant hydroxyl groups, present on the aramid chain, blocks these groups which were supposed to react with the isocyanato groups of ICTOS. The latter results in less chemical bonding between the phases.

3.6 Thermal Stability

Figure 15 shows the weight loss vs. temperature for the pure polymer chain with that of hydroxy-amide (pure matrices). As can be seen, the thermal stability of the polymer chain with phenolic hydroxyl groups is more than that of the pure aramid chain. It seems that the hydroxyl groups act as a

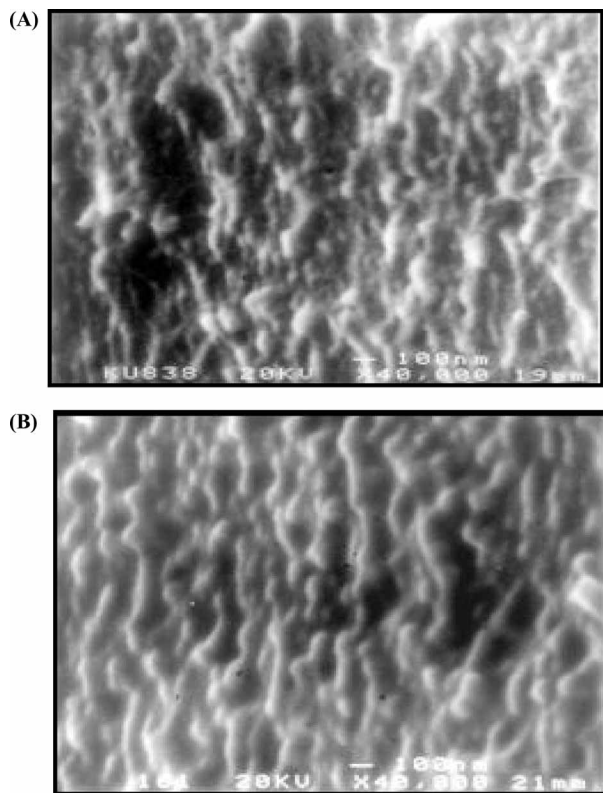


Fig. 13. SEM Micrographs for the bonded aramid-silica hybrids, wt% of silica in the matrix: (A) 10, (B) 20.

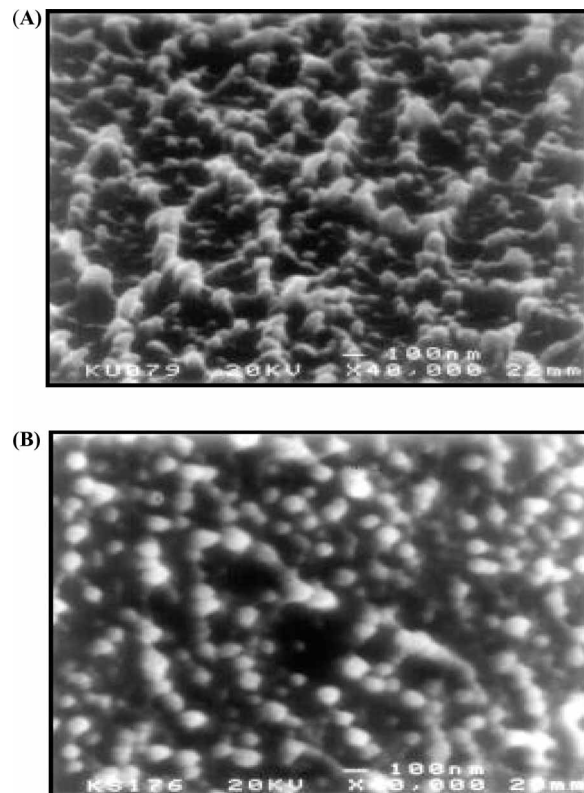


Fig. 14. SEM Micrographs for the bonded aramid-silica hybrids using ICTOS and TEOS together, wt% of silica in the matrix: (A) 10, (B) 20, (Reference 24).

free radical quencher as the polymer begins to degrade. The free radicals produced are absorbed by the reaction with the OH groups on the chain. This is familiar to the action hindered phenols commonly used as stabilizers in polymeric materials.

The TGA curves for the unbonded ceramers are shown in Figure 16, whereas the bonded ceramers are shown in Figure 17. The thermal decomposition temperature of these hybrid materials is around 480–500°C. At higher

temperature, the hybrid materials with higher silica contents, show more stable behavior than the pure polymer. It seems the presence of silica protect the polymer chains absorbed on it, from the oxidative degradation process. The weight loss above 750°C is due to the complete decomposition of the organic matrix. The weight retained after this temperature was found to be almost proportional to the amount of silica in the matrix. This confirms that

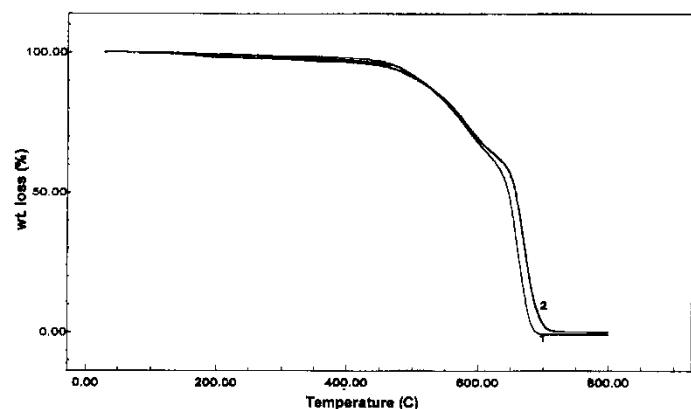


Fig. 15. Comparative Thermograms: 1) pure aramid, 2) hydroxy aramid.

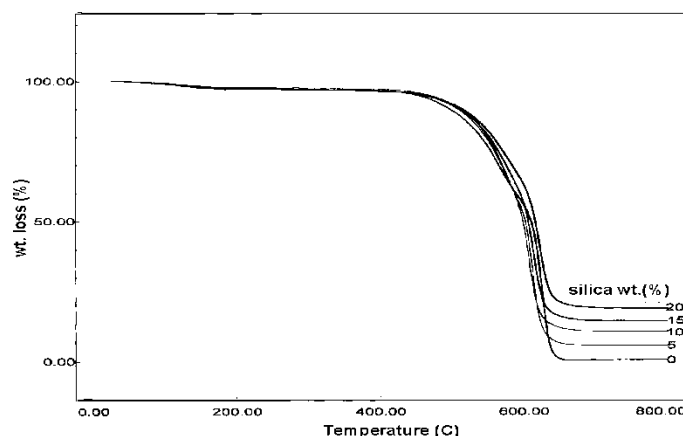


Fig. 16. Thermograms for unbonded aramid-silica hybrids with various silica contents.

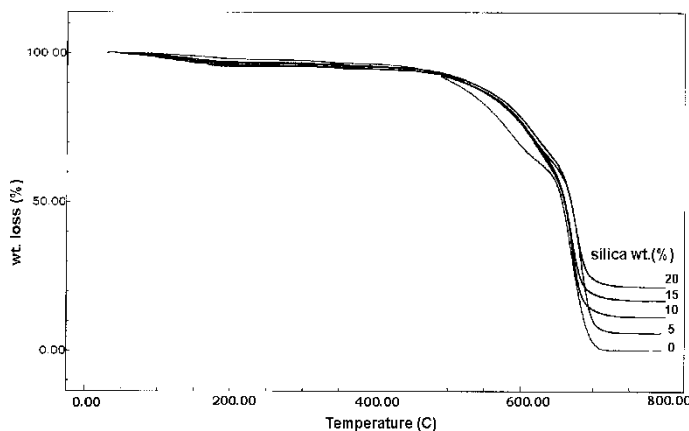


Fig. 17. Thermograms for bonded aramid-silica hybrids with various silica contents.

alkoxysilanes were completely hydrolyzed and condensed to silica network and there was no loss during the sol-gel process.

4 Conclusions

Novel thermally stable ceramers with very low CTE values have been produced by the sol-gel process. Suitable modification of the polymer chain with pendant alkoxy groups provided extensive bonding between the silica network and the polymer matrix. The T_g , as determined from the DMTA data, showed a large increase and the modulus values are retained at a higher value of temperature in the case of bonded ceramers. The SEM analysis shows very blurred silica particles, with the morphology considerably different from the system where ICTOS and TEOS were added together. A smooth transition from one phase to the other solves stress-transfer problems in the hybrid materials, resulting in better thermal mechanical properties.

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