Thermal and mechanical properties of chemically bonded aramid–silica nano-composites

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Abstract

Thermally stable aramid–silica nano-composites have been prepared via the sol–gel process. Two types of aramid matrices were used. Polyamide chains having no pendant hydroxyl groups were prepared by reacting a mixture of 1,3- and 1,4-phenylenediamine in 65:35 mole ratio with equivalent amount of terephthaloyl chloride (TPC) in dimethylacetamide (DMAc) as solvent. The silica network was developed in the matrix by hydrolysis and condensation of various proportions of tetraethoxysilane (TEOS) and this system was used as reference. The matrix having pendant hydroxyl groups was synthesized by the co-polymerization of a mixture of phenylenediamines and 2,4-diaminophenol with equivalent amount of TPC in DMAc. The hydroxyl groups on the chain were reacted with isocyanatopropyltriethoxysilane (ICTOS), which together with TEOS produced silica network structure bonded with the polymer chain. The morphology, thermal and mechanical properties of both types of composites, with and without chemical bonding with silica network have been studied. The glass transition temperature as determined from the maxima of tan δ data using dynamic mechanical thermal analysis showed a large increase in case of bonded system in comparison to the unbonded system. The value of the storage modulus was also found to be considerably higher in case of bonded system. The values of thermal expansion coefficient decreased with inclusion of silica in the matrix. The thermal decomposition temperature of these hybrids in air was in the range of 480–500 °C.

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1. Introduction

Polymeric materials being organic in nature have their limitations for the high performance applications because they are mechanically weak and also thermally unstable. Incorporating inorganic materials can provide enhancement in mechanical and thermal properties. Many of the natural materials, which provide structural strength and toughness in living organisms, e.g. bone and wood are the composite materials [1,2] in which inorganic components have been distributed at very fine level in the organic matrix. By mixing polymers and ceramics at micro-level, it is possible to create similar hybrid materials. A successful synthetic approach for preparation of such materials is the in situ polymerization of metal alkoxides via the sol–gel process [3,4]. The inorganic metal oxide precursor is mixed in the polymer solution and hydrolysis and condensation is slowly carried at moderate temperature to incorporate inorganic network structure. Ahmad and Mark have reviewed the work on organic–inorganic hybrid materials [25,6] and have identified some key aspects of biomaterials design in natural fibers and composites [2] which can be useful in synthetic procedure for hybrids and nano-composites. These hybrid materials commonly known as ceramers [7] can exhibit useful properties of both: heat resistance, retention of mechanical properties at high temperature and low thermal expansion from ceramics and toughness, ductility, and ease in processability from the high polymers. Silica is considered as the most common inorganic component though many other metal oxides such as titania, boehmite, and zirconia have also been used to reinforce the organic polymers. Some of the important polymers used in preparation of hybrid materials in the recent past have been poly(dimethylsiloxane) [8–11], epoxies [12–14], poly(organophosphazenes) [15,16], polyacrylates [17–19], polyimides [20–27] and polyaramids [28–31] and polybenzoxazoles [33–36].

For the high performance applications of these ceramers the polymer component used must be very stable in nature. Polyimide, polybenzoxazole and polyaramid types of polymers, which have high thermal decomposition temperatures,
Triethoxysilane (ICTOS) along with TEOS in DMAc was used to produce silica network. The polymer chain was bonded with the silica network through the reaction of hydroxyl groups on the chain with ICTOS during the sol–gel process. Thermodynamic properties of both types of hybrids have been studied. Temperature dependence of tan δ gave a measure of the glass transition temperature (Tg) of the hybrid material. The change in the Tg is related to the extent of bonding between the organic and inorganic phases. The effect of increased bonding between the phases on the morphology of the resulting hybrids and their thermal mechanical properties has been described.

2. Experimental

2.1. Materials

Monomers 1,4-phenylenediamine and 1,3-phenylenediamine, tetraethoxysilane (TEOS) and the solvent DMAC were AR-grade products of Aldrich Chemicals. Terephthaloyl chloride (99%), 2,4-diaminophenol dihydrochloride (96%) were obtained from Fluka and 3-isocyanatopropyltriethoxysilane (ICTOS) (95%) from ABCR. All chemicals and reagents were of AR grades and used as received.

2.2. Preparation of the hybrid films

A mixture of 1,4- and 1,3-phenylenediamine, 5.450 g (0.050 mol) in molar ratio 35:65 was placed in a 250 ml conical flask. To this mixture, 150 g of solvent DMAC was added. It was stirred for 15 min until completely mixed. To this solution was added 0.185 g (0.050 mol) of TPC under complete anhydrous conditions. Stirring continued for an additional 24 h and at this stage the polymerization reaction (Scheme 1) was assumed to be complete. Different amounts of TEOS in DMAC were added to the aramid solution and stirring was done for further 4 h. 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 condensation of the inorganic network. The sol–gel process leading to the formation of silica network from TEOS has been described elsewhere [3,4]. Films of controlled and uniform thickness were cast in petri dishes and the solvent was baked out at 70 °C. Films thus formed, were soaked in water and washed repeatedly to leach out any HCl produced during polymerization. Finally, the films were dried at 80 °C and then at 120 °C under vacuum for 48 h for each temperature. The aramid hybrid films with various silica contents (2.5–20 wt%) were prepared and this aramid–silica unbonded hybrids system (ArSiU) acts as reference in comparing the characteristics of hybrid material.

The matrix having pendant hydroxyl groups was synthesized by the co-polymerization of a mixture 1,3- and 1,4-phenylenediamine and 2,4-diaminophenol dihydrochloride taken in 60:35:5 mole ratio, respectively, with equivalent amount of TPC in DMAC. The hydroxyl groups remain unreacted in the above reaction leading to polyamide...
A suitable amount of ICTOS along with TEOS (5% of the silica is derived from ICTOS) in DMAc was then mixed with the polymer solution. The isocyanato groups on ICTOS reacted with the hydroxyl groups present on the polymer chain. The hydrolysis and condensation of ICTOS together with TEOS through sol–gel process yielded silica network structure bonded with the polymer chain (Scheme 2). The properties of these chemically bonded aramid–silica hybrids (ArSiB) were compared with the reference system where no hydroxy groups were available on the polymer chain. The properties of these chemically bonded aramid–silica hybrids have been compared with the reference system where no hydroxy groups were available on the polymer chain for chemically binding the silica network.

2.3. Characterization of the hybrid films

Visco-elastic properties were studied as a function of temperature using Dynamic Mechanical Analyzer Q-800 (TA, USA). Temperature variation of tan δ gave a measure of the $T_g$. The measurements were taken under tension mode in the temperature range 100–500 °C, at a heating rate of 5 °C/min using, frequency, 5 Hz under nitrogen gas at the floating pressure of 60 Pa.

The 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, prior to admission into the microscope. Thermal mechanical measurements to measure the linear coefficient of thermal expansion were performed on Schimadzu TMA-50 at a heating rate of 10 °C/min with an applied load of 4.00g under nitrogen gas. Thermogravimetry (TG) was performed on approximately 10 mg of the sample from ambient to 800 °C at a heating rate of 10 °C/min in a dynamic synthetic air atmosphere (30 ml/min), using TGA-50 Shimadzu automatic analyzer.

3. Results and discussion

The hybrid films both from the non-bonded and bonded ceramers up to 20 wt% silica were transparent and light yellow in color. The non-bonded ceramers with more than 25 wt% silica were opaque, whereas bonded ceramers were semi-transparent. The thermo-elastic properties of these films were studied using DMTA. The temperature variation of the storage modulus for the ArSiB hybrids is shown in Fig. 1. The storage modulus of pure aramid film was 3.48 GPa at 100 °C, as one would expect for a high molecular weight amorphous polymer below $T_g$. It increases with the increase in the silica content and the maximum value recorded was 4.23 GPa for 20 wt% silica. As the temperature is increased the storage modulus drops to about an order of magnitude in the rubbery region for pure polymer. However, in the temperature range of 350–400 °C there is again a slight increase, as the polymer is above the $T_g$, the cyclic stress may induce alignment of the polymer chain thus increasing the modulus value to increase. But then as the polymer softens above 425 °C there is a sharp drop in the $E'$ value except with the matrix having 15 wt% silica or more. The presence of silica increases the softening point. In the temperature range 350–400 °C the syneresis process [38] involving the condensation of silanols and/or alkoxides to form siloxane bonds results in the ripening of the polysilicate phase. Therefore, hybrids having large wt% of silica tends to retain the modulus above the $T_g$ due to the formation of highly condensed silica network. [29] NMR studies [27], carried out on the silicate structure in polyimide-composites have shown three major absorption peaks: dihydroxy-substituted silica, monohydroxy-substituted silica, and non-hydroxy-substituted silica. It is observed that the proportion of the non-hydroxy-substituted silica increases as the network increases in the silicon content. Thus with higher wt% of silica, i.e. 15 or 20% silica contents the cross-link density of the network increases in the matrix and higher modulus values are, therefore, retained in such systems. 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-radical produced due to degradation phenomenon causes cross-linking of the chains and as the network structure is formed the modulus show steep rise above 460 °C.

A more systematic variation in the storage modulus with increasing amount of silica content was observed in case of ArSiB system (Fig. 2). The value of $E'$ increased constantly with increasing amount of silica and the maximum value recorded for 20 wt% silica was 4.86 GPa at 100 °C. Fig. 3 shows a comparison of the variation of the modulus vs. 

![Scheme 1. Structure of the aramid chain.](image-url)
silica contents with ArSiU system at 100 °C. The $E'$ values are higher in case of bonded ceramers. The modulus decreases linearly with increase in temperature up to 300 °C and at the $T_g$ a rapid decrease is witnessed. The chemically bonded hybrid materials tend to retain much higher values of $E'$ as compared to the ArSiU system (Figs. 1 and 2) in the rubbery regime above 360 °C. The interfacial bonding between the phases seems responsible for retaining high modulus even above $T_g$. At temperature above 460 °C there is an abrupt increase in the modulus, which may be due to cross-linking of the polymer chain as well that of the silica network structure.

Scheme 2. Structure of chemically bonded aramid–silica ceramer.
Figs. 4 and 5 show the temperature variation of tan δ for the unbonded and bonded ceramers, respectively. The position of the maxima of the curve shows very accurately the $T_g$ values associated with $\alpha$-relaxations. These values have been shifted to higher temperature region in both cases but this shift is much more in case of bonded ceramers. The variation of the $T_g$ with silica content for both systems is shown in Fig. 6. The $T_g$ for the pure polymer is around 321–323 °C, which is increased to 335 °C for the ArSiU ceramers with 20 wt% silica but this value is 342 °C for the ArSiB type ceramers with similar concentration. The increase in case of non-bonded system seems due to secondary bond interactions between the polymer chain and the silica network. Higher increase in case of bonded ceramers suggests that the mobility of the polymer chain is further restricted due to bonding of the polymer chain on the silica surface. This is further evident from the tan δ curves which show 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 δ curves and increase in $T_g$ for the bonded hybrids can be attributed to improved adhesion due to the reaction between hydroxyl groups present on the aramid chain and isocyanato groups of ICTOS which help the polymer chains to absorb on the surface of silica particles.

Thermal mechanical analysis results for the pure aramid, hydroxyaramid and hybrid film with 20% silica bonded with the polymer chain is shown in Fig. 7. The average value of
Linear thermal expansion coefficient (CET) measured in the temperature range 50–280 °C for pure aramid film is 36.11 ppm/°C. The polymer gets softened above 300 °C. However, introduction of hydroxyl groups increases the softening point and the average value of CET measured in the same temperature range is 34.11 ppm/°C. Inclusion of silica in case of bonded system decreases the CET value to 18.20 ppm/°C. Slight fluctuation observed above 300 °C in case of hybrids film may be due to weak propyl linkage of ICTOS which was used as binding agent. The large decrease in CET in the hybrid film, however, shows increased interaction between the organic and the inorganic phase as the polymer chain seems to get absorbed on the silica network.

Figs. 8 and 9 show the SEM micrographs for the unbonded and bonded ceramers with 20 wt% silica. The silica network produced in the matrix from TEOS only show almost round or oblong shaped silica particles with large variation in size, i.e. diameter varying from 50 to 200 nm. The silica particles produced from using ICTOS and TEOS together in hydroxy amide, however show different morphology with highly blurred surface. Due to the presence of isocyanato groups in the silane and their interaction with the hydroxyl groups on the polymer chain, the surface of silica particles is rather diffused. It seems that the polymer chains are adsorbed on the surface of the particles. Also, the growth of the silica network may not be uniform in all directions as in case of silica particle produced from TEOS only. The particle diameter is also relatively smaller than those found in unbonded ceramers.

Fig. 10 shows the weight loss versus temperature for the pure polymer and the hybrid material with 20% silica. The thermal decomposition temperature of these hybrid materials is around 480–500 °C. At higher temperature the hybrid material, show more stable behavior than the pure polymer. It seems the presence of silica protect the polymer chains to some extent 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 alkoxysilanes were completely hydrolyzed and condensed to silica network and there was no loss during the sol–gel process.

4. Conclusions

Novel thermally stable aramid ceramers with a very low CET values have been produced by the sol–gel process. Suitable modification of aramid chain with pendant hydroxyl groups provided extensive bonding between the silica network and the polymer chain. The $T_g$ as determined from the DMTA data showed a large increase and the modulus values are retained at higher value of temperature in case of bonded ceramers. The SEM analysis shows blurred silica particle surface, which is considerably different from the system where the chain has no sites available for bonding with the silica network. Absorption of polymer chains on the silica network results in considerable low values of CET of the hybrid material. The thermal decomposition temperature of these ceramers in air is in the range of 480–500 °C.

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