Synthesis and characterization of novel aramid-zirconium oxide micro-composites

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Abstract

New micro-composites containing different proportions of zirconium oxide in aromatic polyamide have been prepared via a sol–gel process. Poly(phenyleneterephthalamide) chains with carbonyl chloride end groups were synthesized by reacting a mixture of p- and m-phenylene diamines with terephthaloyl chloride. The chain ends were endcapped with aminophenyltrimethoxysilane. Appropriate amount of zirconium propoxide solution (82.3 wt.%) in propanol was mixed in the polymer solution and then a stoichiometric amount of water was added to the mixture to carry out the hydrolysis of methoxy and propoxy groups. Hybrid materials using different proportions of zirconium propoxide in the organic polymer were thus prepared. Thin films cast from this material were transparent, yellow in color and tough. A gradual increase in the tensile strength was observed with increase in the zirconia content (up to 10%). The tensile modulus of the hybrid mixture was in the range of 2.7 to 4.0 GPa at 25°C. The values of the tensile strength varied from 163 to 203 MPa at 25°C. The maximum strain at the break point initially increased but then decreased with further addition of zirconia. The glass transition temperature determined from the maxima of the tan δ data using dynamic mechanical thermal analysis increased with increase in the zirconia content. The thermal decomposition temperature of the hybrid material measured through thermogravimeteric analysis was around 450°C.

1. Introduction

The development of new materials containing both organic and inorganic structures is of great importance with respect to achievement of new combination of properties. The sol–gel process [1–6] has provided a process for making such materials under mild conditions. Properties of composites depend primarily upon the type of reinforcement, matrix and the interface interactions between the two. Ahmad and co-workers have prepared different types of aramid-silica composite [7–12] by combining a copolymer of meta- and para-(phenylene-terephthalamide) with different proportions of te-tramethoxysilane (TMOS) in dimethylacetamide (DMAC). In-situ hydrolysis and condensation of TMOS was carried out to produce a silica network in an aramid matrix. The covalent bonds between the polyaramid chains and silica network were developed [9] by endcapping the aramid chains with aminophenyltrimethoxysilane (APTMOS). The mechanical properties of chemically bonded aramid-silica hybrid materials with different percentages of

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silica were compared with a similar system having no bonding between the two phases [7]. The tensile strength was found to improve by chemically endlinking the aramid chains with the silica-network [9]. Chemically bonded titania-aramid composites have been prepared by the present authors [13]. Thin films of pure aramid film and that of composites containing up to 20% titania in aramid were transparent. The mechanical strength of the hybrid composite containing 10% titania was reported to be 193 MPa as compared to pure aramid (147 MPa). Maximum stress at rupture initial modulus and toughness improved up to 10% titania contents, however, the mechanical properties deteriorated with > 15% titania in aramid [13].

Morikawa and co-workers [14] have prepared polyimide-silica hybrid films by the sol–gel technique. The films containing the silica less than 8 wt.% were yellow and transparent, whereas the films with higher silica content were yellow and opaque. The modulus was found to increase with increasing silica content. Chemically bonded silica composites with linear and non-linear aromatic polyamides were prepared by Ahmad and co-workers [15] using sol–gel process. The films cast from material containing up to 25% silica were transparent and yellow in color. Thermal and mechanical properties of these films were studied. A gradual increase in tensile strength was observed with increase in silica contents which then decrease with higher silica contents of 15% or more. The overall values of the tensile strength were found to be less with the non-linear aramid chain as compared to the linear aramid. Wang and co-workers [16] have also reported polyimide-silica hybrid materials.

Zirconia reinforced composites using poly(tetramethylene oxide) matrices have also been reported by Wilkes et al. [17,18]. Preparation of organic–inorganic composites using epoxide as matrix and zirconia as reinforcing phase have been reported by Schmidt and co-workers [19,20]. Tanaka et al. [21] have studied the formation of uniform coating of TiO_2, and ZrO_2 layers on plastic sheets by dipping polycarbonate, polypropylene, PVC, polyacetal, or polyimide sheets in solutions containing their alkoxides.

Due to high thermal stability and good mechanical properties of aramids, we have synthesized some

new composites on the molecular level using zirconia as a reinforcement phase in aramid matrix. The m- and p-poly(phenylene-terephthalamide) chains were end-capped with carbonyl chloride groups. These aramid chains were then reacted with APTMOS and then the zirconia network was developed in-situ by mixing and hydrolyzing tetrapropyl zirconate (TPZ) in the aramid solution. Thin films of the hybrid material having different percentages of zirconia were cast and the optical, mechanical and thermal properties were measured.

2. Experimental

A mixture of 1,4-and 1,3-phenylenediamine, 5.45 g (0.050 mol) in molar ratio 35:65 was placed in a 250 ml conical flask. To this mixture was added 150 g of DMAC as a solvent. It was stirred for 30 min in dark conditions until completely mixed. The solution was cooled to 0°C and to this was added 10.185 g (0.050 mol) terephthaloyl chloride (TPC) under anhydrous conditions. The reaction temperature of the mixture was allowed to rise to 25°C after 30 min of stirring. This temperature was necessary to avoid side reactions occurring during the polymerization reaction. Stirring continued for an additional 24 h and at this stage the polymerization reaction was assumed to be complete. In order to ensure the chains were end-capped with carbonyl chloride, 0.0005 mol TPC was then added to the reaction mixture. After 6 h stirring, stoichiometric amount of APTMOS was added to combine with the unreacted –COCl endgroups of the aramid chains and stirring continued for additional 6 h. The resulting solution served as stock solution to prepare aramid-zirconia hybrid composites. Different amounts of tetrapropyl zirconate in DMAC were added to the aramid solution and stirring was done for further 2 h. A stoichiometric amount of water in DMAC was then added to each sample to carry out hydrolysis of the methoxy and propoxy groups. HCl produced during the polymerization reaction acted as a catalyst. The reaction mixture was allowed 6 h stirring at 50°C to complete the hydrolysis and condensation of the inorganic network. Films of controlled and uniform thickness were cast in petri dishes by pouring the weighed amount of solutions and the solvent was baked out at
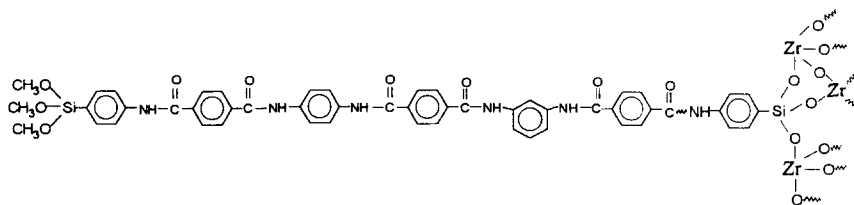
Fig. 1. Structure of chemically bonded ceramer.

70°C. Films thus formed, were soaked in water to leach out any HCl produced during polymerization. These films were then dried at 100°C under vacuum for 96 h. The structure of the aramid chain chemically bonded with zirconia network has been given in Fig. 1.

Mechanical properties of these films were studied using a tensile testing instrument (Instron Universal Testing Instrument Model TM-SM 1102 UK) at 25°C with a strain rate of 0.5 cm/min. Optical properties were recorded in visible range at three different wavelengths, 490, 530 and 600 nm with a UV-visible (Shimadzu) spectrophoto-meter. Dynamic mechanical thermal analysis was carried out (Rheometric Scientific DMTA III) in the temperature range 100 to 500°C using a frequency of 5 MHz. Thermogravimetric analysis was performed with a simultaneous thermal analyzer (Netzsch STA 429) in air at a heating rate of 5°C/min.

3. Results

The films of the hybrid materials containing up to 20% zirconia were yellow and transparent. The %

transmittance measured (± 2) at 490, 530 and 600 nm for a pure aramid film with 0.10 ± 0.02 mm thickness, was 76, 80 and 83 respectively which was reduced to 67, 71 and 76 respectively for a similar film containing 20% zirconia (Table 1). The films containing 25% zirconia were semi-transparent and those containing 35% or more zirconia were opaque and brittle and their mechanical properties were not measured.

Stress-strain behavior of pure aramid and composites containing different percentages of zirconia was studied. 5–7 samples in each case were analyzed and the values of the engineering stress are given in Table 2 and the Fig. 2. It is apparent from the figure that there is a considerable increase in the tensile strength as compared to that of pure aramid. The increase in the ultimate stress, however, decreases with zirconia contents > 10% (Fig. 3). The length at rupture also decreases with further increase in zirconia content (Fig. 4). Fig. 5 shows the variation of the tensile modulus calculated from the stress-strain data. Tensile modulus for the pure aramid was 2.86 ± 0.02 GPa which increases with addition of zirconia. The maximum value was 3.76 ± 0.02 GPa with 10% zirconia in aramid.

Dynamic mechanical thermal analysis of pure aramid and composites containing various propor-

Table 1
Transmittance of aramid-zirconia composites containing different percentages of zirconia

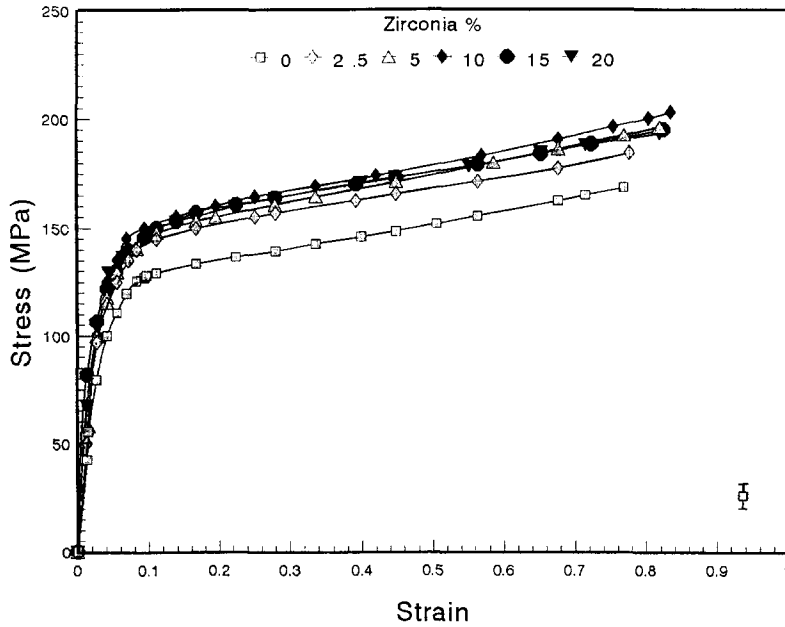| No.	ZrO$_2$ contents (%)	Film thickness (mm) ± 0.02	% Transmittance ± 2 at		
			490 nm	530 nm	600 nm
1	0.0	0.10	76	80	83
2	2.5	0.08	74	78	82
3	5.0	0.08	73	77	80
4	10.0	0.06	73	77	79
5	15.0	0.10	72	76	80
6	20.0	0.09	67	71	76

Fig. 2. Tensile strength of aramid-zirconia composites containing different percentages of zirconia at room temperature. Lines are drawn as guides for the eyes.

tions of zirconia was carried out in the temperature range 100 to 500°C. The temperature variation of the storage modulus (bending) is given in Fig. 6. The storage modulus initially increases with increase in temperature and but then at higher temperature it decreases. At constant temperature for composites containing increasing % of zirconia there is initially an increase in the value which then decreases. Fig. 7 shows the data for tan (as a function of temperature) for various zirconia contents. The peaks of pure aramid split giving a broad shoulder in data for the composites. The maxima in tan δ peaks shift towards higher temperature for composites containing larger zirconia contents and the peaks becomes broader and weaker.
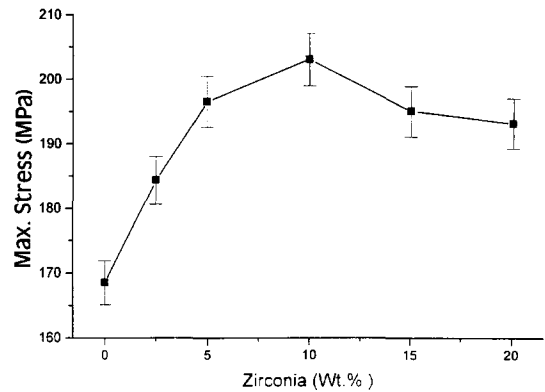

Fig. 3. Maximum stress versus percent zirconia in aramid-zirconia composites. The line is drawn as a guide for the eyes.

Table 2

Tensile strength, initial modulus and toughness of aramid-zirconia composites containing different percentages of zirconia

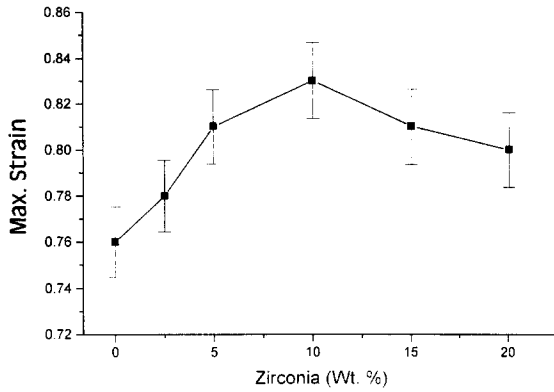| No.	ZrO$_2$ contents (%) in aramid	Tensile strength (MPa) $\pm$ 3	Initial modulus (GPa) $\pm$ 0.02	Toughness (MPa) $\pm$ 5
1	0.0	169	2.86	110
2	2.5	184	3.19	123
3	5.0	196	3.45	135
4	10.0	203	3.76	142
5	15.0	195	3.68	138
6	20.0	193	3.57	131

Fig. 4. Maximum strain versus percent zirconia in aramid-zirconia composites. The line is drawn as a guide for the eye.
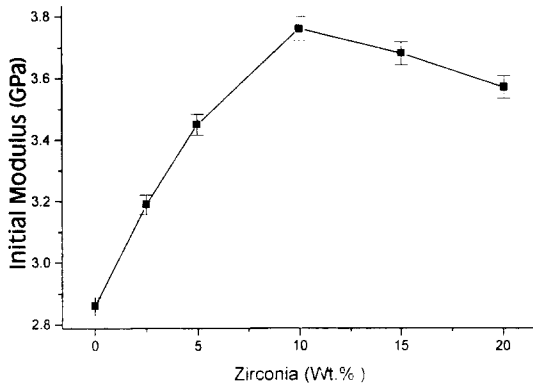

Fig. 7. Variation of the loss tangent (tan δ) with temperature for aramid–zirconia composites at 5 Hz, zirconia % in aramid: 0 (————), 2.5 ($\cdots$), 5 (— —), 10 (— · —), 15 (— · · —), 20 (— · · · —).

Fig. 5. Initial modulus versus percent zirconia in aramid-zirconia composites. The line is drawn as a guide for the eye.
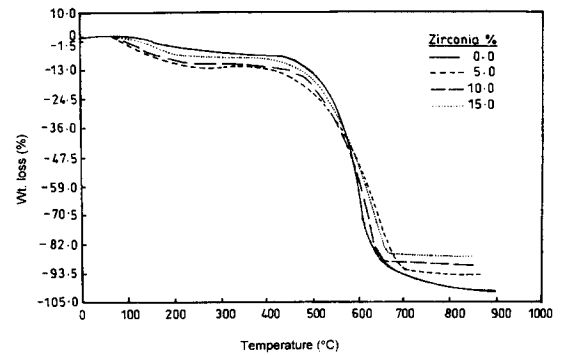
Fig. 8. TGA curves for aramid-zirconia composites containing different percentages of zirconia.

Thermogravimetric analysis (TGA) was carried out in air at 5°C/min for a temperature range 100 to 800°C and the data are shown in Fig. 8. The thermal decomposition temperature of aramid and composites was in the range of 430 to 480°C and the weight retained at higher temperature was approximately proportional to the zirconia contents in the composites.

4. Discussion

The films containing up to 20% of zirconia were transparent but the transparency decreased with increase in zirconia contents. The transparency of such composites depend on the size, size distribution and spatial distribution of zirconia particles in the polymeric matrix. It seems that with increasing zirconia
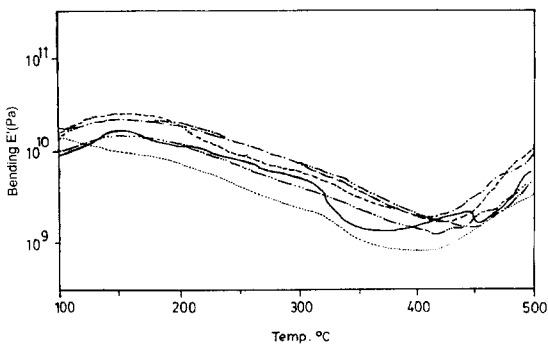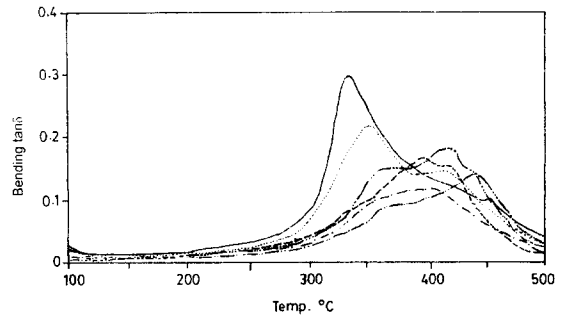

Fig. 6. Temperature dependence of storage modulus for aramid–zirconia composites at 5 Hz, zirconia % in aramid: 0 (————), 2.5 ($\cdots$), 5 (— — —), 10 (— · —), 15 (— · · —), 20 (— — · · · — —).

content, the inorganic network becomes extensive, there is a tendency for inorganic particle size to increase and when it becomes greater than the wavelength of light, these films become opaque.

The stress-strain behavior shows the mechanical strength of the hybrid composites increases initially with increase in zirconia contents. The value of the engineering stress at rupture was 168 ± 3 MPa for pure polymer which increased to 203 ± 3 MPa for the composites containing 10% zirconia. The development of zirconia network and its chemical bonding with the matrix does provide reinforcement to the matrix. We have observed similar behavior with silica and titania network when they were chemically bonded in such matrices [13,9]. The strength, however, decreased with further increase beyond 10% zirconia in the matrix. The increased brittleness seems due to the tendency in the inorganic structure to agglomerate [22] in to particles which may then have a porous structure. The tensile modulus also show similar behavior. The toughness of the aramid-zirconia hybrid systems was calculated from the area under the stress-strain curves and Fig. 9 shows the toughness against zirconia contents in the hybrid composites. It is clear that the toughness of these chemically bonded systems increases relative to pure aramid and that beyond 10% of zirconia it decreases. The endlinking of the aramid chain with zirconia network through aminophenyltrimethoxysilane has given considerable reinforcement to the hybrid material, however, as the binding is provided by the chain ends of aramid, the number of which is limited, increase in zirconia contents beyond 10% then re-
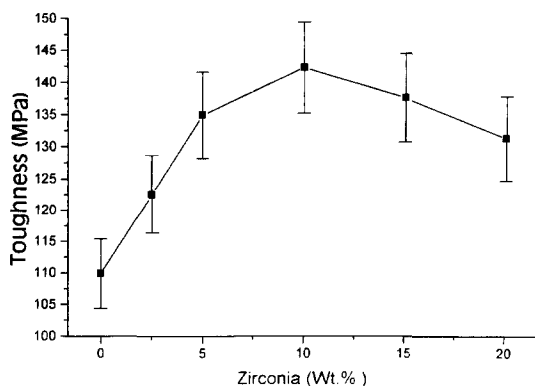
Table 3
Storage modulus and glass transition temperature of aramid-zirconia composites containing different percentages of zirconia

No.	ZrO_2 contents (%)	Storage modulus (GPa) ± 0.02	Glass transition temperature (°C) ± 3
1	0.0	9.76	333
2	2.5	10.52	346
3	5.0	11.00	400
4	10.0	10.82	403
5	15.0	10.40	418
6	20.0	10.00	417

sults in poor bonding between the phases. Zirconium particle size increases also and the structure of the inorganic domain becomes irregular and porous. The mechanical properties of the composites, therefore, are degraded.

The storage modulus (bending) showed a small increase initially around 100°C which may be due to completion of the condensation process leading to zirconia network formation. A decrease in modulus occurs at higher temperature for composites containing > 10% zirconia. The increase in modulus at temperature higher then 400°C is, in fact, due to thermal degradation of the material which may produce free radicals thus causing cross-linking of the amide chains.

The tan δ peak for pure polymer is obtained around 332 ± 3°C. The T_g of Kevlar is around 400°C but inclusion of meta units in the chain reduces its value. This peak then splits into two for composites containing small % of zirconia. The peak corresponds to the unbounded aramid and the shoulder which appears at higher temperature corresponds to the aramid chains linked with inorganic network. We suggest that with increased amount of zirconia, part of the aramid chains become linked with the inorganic phase which restricts their motion resulting in relatively high T_g. The T_g for the pure aramid chain is 332 ± 3°C and it gradually shifts towards 417 ± 3°C for 20% zirconia content. Table 3 shows variation of T_g with increased proportions of zirconia network. As tan δ peaks shift toward higher temperature the amplitudes become less and their width increases. Tan δ peak for the composite containing 10% zirconia suggests a greater cohesion between the organic and inorganic phases than for the other compositions thus imparting maximum tensile

Fig. 9. Toughness versus percent zirconia in aramid-zirconia composites. The line is drawn as a guide for the eye.

strength in the systems in comparison to different compositions studied.

TGA results show that the pure aramid has a thermal decomposition temperature around 450°C. The hybrid composites show a small decrease in the weight around 150°C which may be due to the completion of the condensation process leading to the formation of volatile by-products and completion of zirconia network formation. The weight retained beyond 700°C is roughly proportional to the inorganic content in the hybrid composites.

5. Conclusions

Chemically bonded aramid-zirconium oxide micro-composites have successfully been prepared using sol–gel process. These composites are yellow in color and transparent. Tensile strength of these composites was considerably improved over pure aramid and lies in the range of 163 to 203 MPa at 25°C.

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