Thermal and Mechanical Properties of Aramid-Based Titania Hybrid Composites

Z. AHMAD,[1] M. I. SARWAR,[1] J. E. MARK[2]

[1] Department of Chemistry, Quaid-i-Azam University, Islamabad-45320, Pakistan

[2] Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio 45221-0172 USA

ABSTRACT: The sol–gel process has been used to prepare various types of aramid–titania hybrid materials. Specifically, a mixture of *m*- and *p*-phenylenediamines was reacted with terephthaloyl chloride to produce linear polyamide chains in a dimethylacetamide solvent. Various proportions of tetrapropylorthotitanate (TPOT) were added, and its subsequent hydrolysis–condensation in the polymer solution produced a titania (TiO_2) network in the aramid matrix. Thin films prepared from these materials were tested for their tensile strength, which was found to decrease with increasing proportions of titania. To remedy this through chemical bonding between the matrix and the inorganic network, a slight excess of terephthaloyl chloride or 1,3,5-benzenetricarbonyl chloride was added near the end of the polymerization reaction. These aramid chains were thus end-capped with single or double carbonyl chloride groups. This allowed the chains to be further modified, with aminophenyltrimethoxysilane end caps. Chemically bonding the titania network to the aramid chains was then achieved by *in situ* hydrolysis–condensation of TPOT along with that of aminophenyltrimethoxysilane. In this way, thin transparent and tough films could be obtained with up to 30 wt % titania. The values of the tensile strength in the case of bonded hybrid materials increased with the addition of titania, and the polyamide system with nonlinear end groupings showed larger increases than did those with the linear chains ends. The systems with linear and nonlinear aramid chain ends were able to withstand maximum tensile stresses of the order of 193 and 246 MPa, respectively. This is presumably due to the extensive bonding between the polymeric chain ends and the inorganic phases as compared to the unbonded system. The thermal decomposition temperature of these composites was found to be in the range of 500–600°C and the overall weight loss was found to be minimized in an inert atmosphere. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 297–302, 1998

Key words: aramid polymers; composites; titania; sol–gel process; interphase bonding; mechanical and thermal properties

INTRODUCTION

Composites offer a combination of properties and a diversity of applications unobtainable with metals, polymers, and ceramics alone. Perhaps the most important property requirement for the use of composites in structural applications is toughness, which may be achieved using an appropriate method to combine a polymer with ceramics. The goals of a good component distribution and homogeneity may be achieved, for example, through the sol–gel process.[1–7] This method allows *in situ* development of inorganic ceramic networks within a polymeric matrix, thus producing

hybrid materials at the molecular level. Suitable polymers and ceramic materials can thereby be combined to produce strong, stiff, and tough materials capable of withstanding a wide range of temperatures.

The polyamides generally have high tensile and impact strengths, stability at high temperatures, good abrasion resistance, and self-lubricating properties as bearings, and this makes them an important class of engineering material. Two aromatic polyamides (aramids) established in the specialty fiber markets are Nomex® and Kevlar®. Nomex® has been successfully used in many industrial applications where unusual heat resistance is required. Kevlar® is more readily crystallized and oriented due to its *para* type of structure and is noted for its outstanding strength-to-weight ratio. Organometallic compounds (specifically alkoxides) have been used for the incorporation of inorganic metal oxides such as silica,[8–10] titania,[11] zirconia,[12] and alumina[13] into a variety of polymers.[14–19] The result is a reinforced inorganic polymer hybrid material having much improved dimensional and thermal stability.

The sol–gel process can be carried out, however, only if both the polymer and metal alkoxide have compatibility with a common solvent. Poly(1,4-phenylene-terephthalamide) cannot be employed for such purposes due to its insolubility in the organic solvents required for further processing. The problem of solubility[8] can be overcome, however, by using an optimal minimum amount of *meta* linkages, thus producing a few kinks in the linear amide chains. It was thus possible to prepare good mechanical strength aramid with high molecular weight and sufficient solubility in dimethylacetamide (DMAC) by using an appropriate mole ratio of *m*- and *p*-phenylenediamines reacted with a stoichiometric amount of terephthaloyl chloride (TPC) and keeping the weight ratio of the monomers about 8% to the total reaction mixture. Different hybrid materials based on these aramids were reported by Ahmad et al.[8–13]

In the present work, some additional types of aramid–titania hybrid materials have been produced with this sol–gel approach. In some preliminary experiments, the linear aramid chains were prepared and a titania network was introduced into the matrix without developing any interphase bonding. In subsequent experiments, chemical bonding between the matrix and the inorganic network was introduced by using a slight excess of TPC or 1,3,5-benzenetricarbonyl chloride (BTCC) near the end of the polymeriza-

tion reaction. This was done to end-cap the aramid chains with single or double carbonyl chloride groups, which allowed the chain ends to be further modified with aminophenyltrimethoxysilane (APTMOS). Titania networks chemically bonded to the aramid chains were then produced *in situ* by the hydrolysis–condensation of tetrapropylorthotitanate (TPOT) along with that of APTMOS. The mechanical and thermal properties of these modified systems were then studied and compared with those of the system having no interphase bonding.

EXPERIMENTAL

Reagents

The monomers 1,4-phenylenediamine and 1,3-phenylenediamine, TPC, BTCC, and the solvent DMAC were all obtained from Aldrich as AR-grade reagents. Both APTMOS (97%) and TPOT (98%) were obtained from Hüls America Inc. They all were used as received.

Linear Aramid–Titania Ceramers Without Interphase Bonding

The polymerization reaction was performed under completely anhydrous conditions in an Erlenmeyer flask provided with a stirrer. A mixture of 1,3- and 1,4-phenylenediamines consisting of a total of 0.050 mol in a 35 : 65 ratio was placed into the flask, followed by the addition of DMAC (150 mL) as a solvent under an inert atmosphere. After complete mixing, the contents of the flask were cooled to 0°C and TPC (0.050 mol) was added under anhydrous conditions. The reaction mixture was then allowed to come to ambient temperature, and stirring was continued for 24 h. The desired amount of TPOT was then mixed with an appropriate amount of the polymer solution. After complete mixing, a measured amount of water in DMAC was mixed for the hydrolysis and condensation of TPOT for forming the titania network. Further stirring was carried out for about 6 h at 60°C. Films of a controlled thickness were obtained from the samples containing various proportions of titania by a solvent-extraction technique. The films were then soaked in distilled water to leach out any HCl formed during the polymerization and were finally dried at 80°C under a vacuum for at least 72 h to a constant weight.

Table I   Mechanical Properties of Unbonded Aramid–Titania Composites

Sample No.	Titania Contents (%)	Maximum Stress (MPa)	Maximum Strain	Initial Modulus (GPa)	Toughness (MPa)
1	0.0	147.5	1.0	2.0	127.6
2	5.0	138.1	0.9	4.0	117.8
3	10.0	133.1	0.9	3.5	104.3
4	15.0	132.5	0.9	3.1	102.8
5	20.0	120.0	0.7	2.9	78.1

Chemically Bonded Linear Aramid–Titania Ceramers

The polymerization reaction was carried as described above; however, after 24 h, the monomer TPC in 1% excess was added to end-cap the chains with carbonyl chloride groups. These chain ends were then modified further using measured amounts of the bonding agent (APTMOS). The reaction mixture was stirred for an additional 6 h at 40°C, under completely anhydrous conditions. The material thus prepared was used as a stock solution, into which various proportions of TPOT in DMAC were added under an inert atmosphere. A stoichiometric amount of water in DMAC was mixed with constant stirring at 60°C for 6 h to carry out the hydrolysis and condensation of TPOT and APTMOS to produce *in situ* chemically bonded titania networks. Thin films of the hybrid material containing various proportions of titania were thus obtained.

Chemically Bonded Linear–Nonlinear Aramid–Titania Ceramers

Aramid chains that were linear except for the branched groups at their ends were also pre-

pared. The purpose was to have more reactive sites than the previous system, which was limited in the number of chain ends for chemical bonding with the inorganic network. Specifically, BTCC (1%) was used instead of TPC near the end of the reaction to produce aramid chains with double carbonyl chloride end groups. The resulting chains were further end-capped with APTMOS using the stoichiometric amount, again under completely anhydrous conditions. Hybrid films having varying proportions of titania in the aramid matrix were then produced by the sol–gel process described above.

Characterization

Mechanical properties of these films were measured with an Instron universal testing instrument Model TM-SM 1102 UK, by the method described under ASTM 882. Thermal analyses were performed on these samples at a heating rate of 10°C/min in nitrogen and in air atmospheres using a Seiko Instrument TG/DTA 220, 320 thermogravimetric analyzer.

RESULTS AND DISCUSSION

The films obtained from the pure aramid and the aramid–titania unbonded hybrids were light yellow and transparent to titania concentrations up to 20 wt %. Films containing 25 wt % titania became semitransparent. The unbonded films containing 20 wt % or more titania were found to be brittle, to the extent that their mechanical properties could not be measured at all. The composite films in which the titania network was chemically end-linked to the polymer matrix had much better transparencies than those of the unbonded system. It seems that as the titania inorganic network structure became extensive there was an increasing tendency toward particle-size growth. These particles then agglomerate and
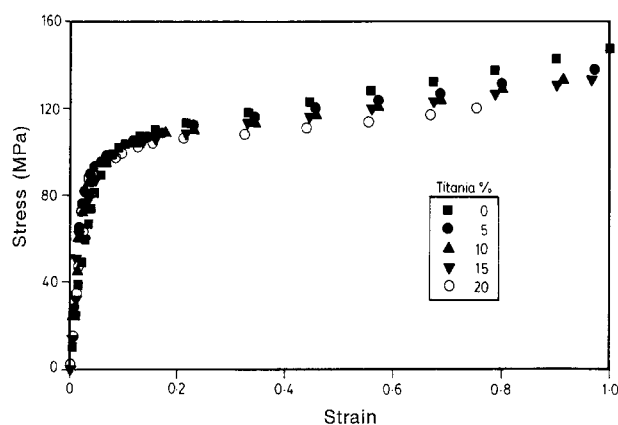
Figure 1   Stress–strain data; aramid–titania composites not having interphase bonding.

Table II   Mechanical Properties of Aramid–Titania Composites Having Interphase Bonding Through Linear Chain Ends

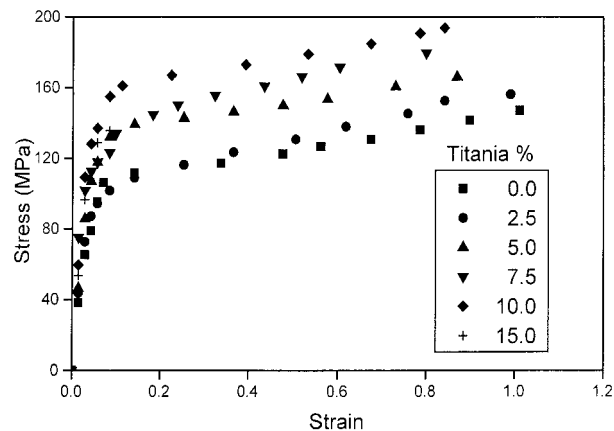| Sample No.	Titania Contents (%)	Maximum Stress (MPa)	Maximum Strain	Initial Modulus (GPa)	Toughness (MPa)
1	0.0	147.0	1.0	2.3	120.4
2	2.5	156.1	0.9	2.5	124.6
3	5.0	165.8	0.8	3.0	126.0
4	7.5	179.5	0.8	3.6	123.2
5	10.0	193.7	0.8	3.8	142.8
6	15.0	135.7	0.0	3.4	8.3

their distribution became irregular. This tendency decreased the transparency and was much stronger in the unbonded system. In the bonded systems, the interaction between the organic and inorganic phases helped to keep the spatial distribution of inorganic particles in the matrix uniform, thus maintaining the transparency of the films.

The stress–strain data for the hybrid films having no interphase bonding are described in Table I and Figure 1. The results indicate a decrease in the tensile strength of the hybrid materials relative to the pure polymer. The percent elongation at rupture and the toughness of these materials showed similar results (Table I). However, the initial modulus first increased and then decreased with higher proportions of titania. The inorganic particle size increased, possibly by forming clusters. This may make the distribution of the inorganic phase in the matrix less uniform, thus increasing the numbers of defects or flaws in the hybrid material which can cause brittleness.

The stress–strain data of the linear aramid chains chemically end-linked to the inorganic network through the binding agent APTMOS are given in Table II and Figure 2. Significant increases in the ultimate strength were observed above that for the pure aramid, with a maximum value of 193 MPa being obtained for 10 wt % titania. The strength then, however, decreased sharply. The moduli behaved similarly, with increases for increased titania contents up to 10 wt %, followed by another marked decrease. The elongation at break decreases with increase in titania content. The toughness of these hybrid materials undergoes first an increase up to 10 wt % titania, then a rapid decrease, as can be seen from Table II. These results demonstrated significant improvements from chemically bonding the polymer chains to the titania.

The number of chain ends available for such bonding obviously becomes smaller as the molecular weight of the polymer chain is increased. It was anticipated in our previous work that greater bonding could be achieved if a random nonlinear (branched) polyamide with a larger number of chain ends is used as it may provide more endlinking sites to the inorganic structure. Unfortunately, the results obtained showed only minor improvements, possibly because of the branching interfering with interchain attractions.[9,10]

In the present work, increased bonding between two phases was achieved again using branching to give more functional groups, but restricting this nonlinearity to the *ends* of the polyamide chains. This was done in the end-capping with BTCC, followed by APTMOS. These results are shown in Table III and Figure 3. The tensile strength of the pure aramid increased relative to the pure linear polymer, and also the ultimate strength of the hybrid material in-

Figure 2   Stress–strain data; aramid–titania composites having limited amount of interphase bonding.

Table III   Mechanical Properties of Aramid–Titania Composites Having Interphase Bonding Through Nonlinear Chain Ends

Sample No.	Titania Contents (%)	Maximum Stress (MPa)	Maximum Strain	Initial Modulus (GPa)	Toughness (MPa)
1	0.0	208.7	1.1	2.9	180.8
2	2.5	238.5	1.0	3.1	203.5
3	5.0	246.3	0.9	3.6	194.4
4	7.5	219.8	0.9	4.5	175.9
5	10.0	216.0	0.8	3.6	146.9
6	15.0	207.4	0.7	3.5	127.6

creased up to 5 wt % titania (246 MPa), before decreasing again with further incorporation of titania. Similarly, the tensile modulus increased up to 5 wt % titania, but also decreased with further addition of titania (Table III). The extension at rupture decreased relative to that of the pure aramid. The toughness of these materials first showed increases up to 5 wt % titania, but was followed again by a decrease (Table III). Comparing these results with the previously bonded system[11] indicates that an amount as small as 5 wt % titania was sufficient to increase the strength, and the value of the maximum strength obtained in this system was 246 MPa. This value is significantly higher than that of the system with linear chain ends.

The addition of titania beyond 5 wt % diminished the mechanical properties of the hybrid materials. This may be because with increase in the titania only a part of the network becomes chemically linked with the polymeric matrix. As the inorganic network became extensive, the ten-

dency for particle-size growth increased, and their agglomeration made their distribution in the matrix irregular. These particles would then form clusters, thus making the inorganic structure porous[20] and brittle, which would cause a decrease in the tensile strength and other associated mechanical properties of the hybrid material.

TGA curves carried out under a nitrogen atmosphere for the system with nonlinear aramid chain ends combined with titania networks are shown in Figure 4. Figure 5 shows the decomposition results in air for a similar system. The initial change of weight in both figures seems to be due to loss of water from some of the unhydrolyzed titania network. The thermal decomposition temperatures of the materials were generally in the range 500–600°C. The net weight loss in nitrogen was much less than that in air. The weights of residue left after the
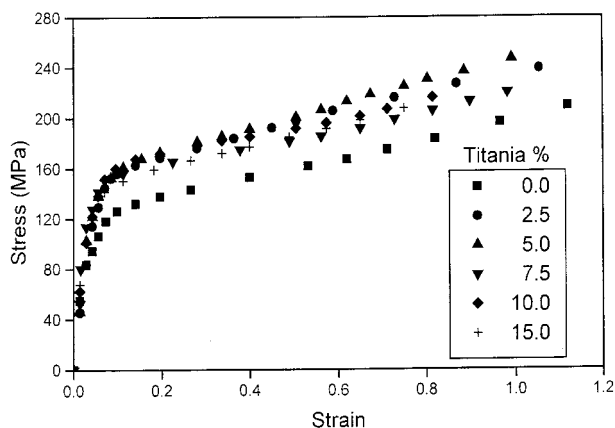
Figure 3   Stress–strain data; aramid–titania composites having increased interphase bonding, through the use of nonlinear chain ends.
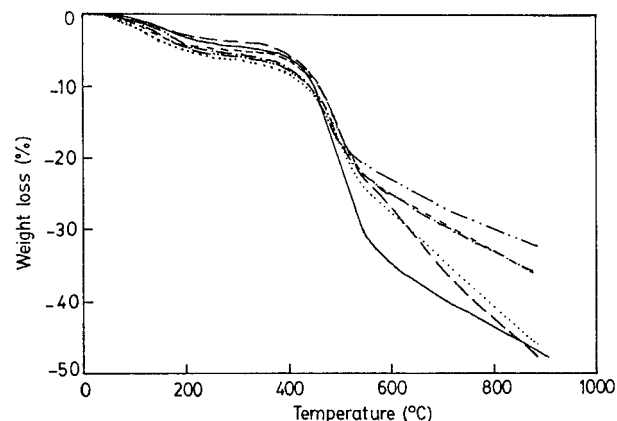
Figure 4   TGA curves for aramid–titania composites having interphase bonding through nonlinear chain ends at a heating rate of 10°C/min in nitrogen; titania wt % in aramid: (—) 0; (. . . . .) 5; (– – –) 7.5; (— —) 10; (— · —) 15; (— · · —) 20.
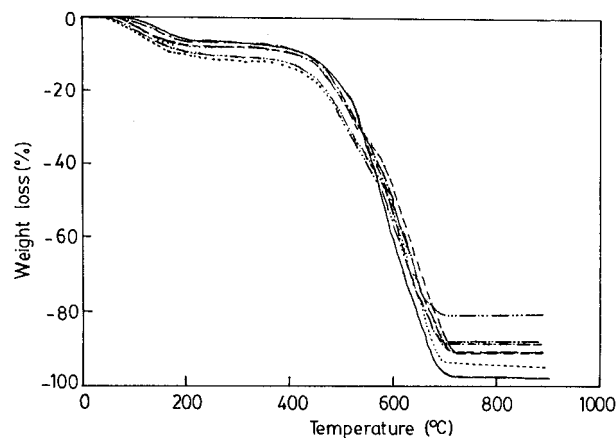
Figure 5 TGA curves for aramid–titania composites having interphase bonding through nonlinear chain ends at a heating rate of 10°C/min in air; titania wt % in aramid: (—) 0; (. . . . .) 2.5; (– – –) 5; (— —) 7.5; (— · —) 10; (— · · —) 15; (— · · · —) 20.

decomposition in air at 800°C were found to be nearly proportional to the titania contents in the original composites.

CONCLUSIONS

New thermally stable aramid–titania hybrid materials were prepared via the sol–gel process. Aramid chains with more reactive chain ends were used to provide extensive chemical bonding between the organic and inorganic phases. This results in excellent improvements in mechanical strength relative to the system in which there was little or no bonding between the two phases.

REFERENCES

1. L. C. Klein, Ed., *Sol–Gel Technology for Thin Films, Preforms, Electronics and Specialty Shapes,* Noyes, Park Ridge, NJ, 1988.
2. J. E. Mark, *CHEMTECH,* **19,** 230 (1989).
3. C. J. Brinker and G. W. Scherer, *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing,* Academic Press, Boston, 1990.
4. J. E. Mark, *J. Appl. Polym. Sci. Appl. Polym. Symp.,* **50,** 273 (1992).
5. J. E. Mark, *J. Inorg. Orgmet. Polym.,* **1,** 431 (1993).
6. H. Schmidt, *J. Sol–Gel Sci. Tech.,* **1,** 217 (1994).
7. J. E. Mark, S. Wang, and Z. Ahmad, *Macromol. Chem. Macromol. Symp.,* **98,** 731 (1995).
8. Z. Ahmad, S. Wang, and J. E. Mark, *ACS Div. Polym. Chem. Polym. Prepr.,* **34,** 745 (1993).
9. Z. Ahmad, S. Wang, and J. E. Mark, in *Better Ceramics Through Chemistry,* Vol. 6, K. Cheetham, C. J. Brinker, M. L. Mecartney, and C. Sanchez, Eds., Material Research Society, Pittsburgh, 1994.
10. Z. Ahmad, M. I. Sarwar, and J. E. Mark, *J. Mater. Chem.,* **7,** 259 (1997).
11. Z. Ahmad, M. I. Sarwar, S. Wang, and J. E. Mark, *Polymer,* **38,** 4523 (1997).
12. H. U. Rehman, M. I. Sarwar, Z. Ahmad, H. Krug, and H. Schmidt, *J. Non-Cryst. Solids,* **211,** 105 (1997).
13. Z. Ahmad, M. I. Sarwar, H. Krug, and H. Schmidt, *Angew. Makromol. Chem.,* **248,** 139 (1997).
14. Z. Ahmad, M. I. Sarwar, and J. E. Mark, *J. Appl. Polym. Sci.,* **63,** 1345 (1997).
15. Z. Ahmad, S. Wang, and J. E. Mark, *Polym. Bull.,* **31,** 323 (1993).
16. S. Wang, Z. Ahmad, and J. E. Mark, *Polym. Mater. Sci. Eng.,* **70,** 425 (1994).
17. B. Wang and G. L. Wilkes, *J. Polym. Sci. Polym. Ed.,* **29,** 905 (1991).
18. R. H. Glaser and G. L. Wilkes, *Polym. Bull.,* **22,** 527 (1989).
19. Z. Ahmad, S. Wang, and J. E. Mark, in *Hybrid Organic–Inorganic Composites,* J. E. Mark, C. Y.-C. Lee, and P. A. Bianconi, Eds., American Chemical Society, Washington, DC, 1995.
20. A. B. Brennan and G. L. Wilkes, *Polymer,* **32,** 733 (1991).