

Preparation and properties of hybrid organic–inorganic composites prepared from poly(phenylene terephthalamide) and titania

Z. Ahmad and M. I. Sarwar

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

and S. Wang* and J. E. Mark†

Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH 45221-0172, USA

(Received 6 June 1996; revised 13 November 1996)

The sol–gel process was used to prepare a class of composites in which a high-temperature polymer, poly(phenylene terephthalamide), was reinforced with varying amounts of *in-situ* generated titania. The polymer was synthesized by reacting a mixture of *p*- and *m*-phenylene diamines with terephthaloyl chloride in dimethylacetamide, using stoichiometry yielding chains with carbonyl chloride end groups. These chain ends were then replaced with methoxy groups using aminophenyltrimethoxysilane, and a titania network generated which should be chemically bonded to the polymer matrix through the hydrolysis of appropriate proportions of tetrapropylorthotitanate and water. The resulting composite films had amounts of titania ranging from 2.5 to 40 wt%, and were characterized with regard to their mechanical and thermal properties. The films containing relatively small amounts of titania were transparent and tough, and had tensile strengths the order of 193 MPa (relative to the 147 MPa of the pure copolymer). Thermal decomposition temperatures were in the range 350–450°C, and the weights of the samples remaining after heating to 800°C were found to be roughly proportional to the titania contents. Water absorption of the films consisting of pure Aramid was rather high (12.8 wt%), but decreased with increased amounts of titania. Dynamic mechanical thermal analysis showed a systematic increase in the glass transition temperature with increase in titania content. Increased amounts of titania also caused the $\tan \delta$ peaks to shift to higher temperatures and to become broader and weaker, indicating the extent to which the mobility of the polymer chains was diminished by the titania phase. © 1997 Elsevier Science Ltd.

(Keywords: polymeric composite materials; sol–gel process; Aramids)

INTRODUCTION

Advances in technology demand either altogether new materials or the improvement of already-existing, more traditional materials. An example of an approach leading to totally new materials is the synthesis of inorganic–organic hybrid materials through the synergistic combination of polymers and ceramics¹. This provides a way of exploiting the strengths and advantages of these rather disparate materials. For example, ceramics are useful due to their high thermal stabilities, strengths, and high moduli, but are usually very brittle. Polymers, on the other hand, are much easier to process and are very tough, but are less thermally stable.

Linear polyamides (often referred to as ‘nylons’) have frequently been chosen for commercial applications because of their excellent physical and chemical properties, and the relatively low cost and the ready

availability of the required starting materials. The aromatic types of polyamides, commonly referred as ‘Aramids’, have been particularly useful as high-performance materials because of their very high thermal stabilities and specific strengths, their high degrees of stiffness, and their low densities². For example, poly(*m*-phenylene isophthalamide) and poly(*p*-phenylene terephthalamide) (marketed under the trade names Nomex[®] and Kevlar[®], respectively) are important commercial fibres. They offer outstanding tensile strength coupled with excellent high-temperature properties; because of their low densities, they are more than competitive with steel and glass fibres in many applications. Kevlar[®] and graphite composites are also being widely used in the aerospace industry.

The properties of this class of polymers can possibly be improved by incorporating a ceramic phase such as silica or titania. In this regard, there is now available a ‘sol-gel’ process which allows the *in-situ* development of ceramic phases within a polymer matrix at low temperatures. In this way, one can readily produce novel inorganic–organic hybrid composites, frequently called ‘ceramers’.

* Present address: Du Pont Dow Elastomers, 5 Tralee Industrial Park, Newark, DE 19711-5444, USA

† To whom correspondence should be addressed. Jemark@ucbehsan.uc.edu

This idea of *in-situ* generation of hybrid inorganic–organic composite materials involves the use of preparative techniques heavily based on chemical reactions, for example the generation of ceramic-type phases by the hydrolysis of an organometallic compound such as an organosilicate or organotitanate^{3–7}. In the case of composite materials, the goal is to carry out reactions of this type in the presence of organic molecules which are typically polymeric and contain functional groups to improve their bonding to the ceramic phase. Some of this research on the sol–gel approach to hybrid composites is described in sections of some of the books and review articles cited above for the sol–gel process in general. In addition, there have been two books devoted entirely to the topic^{1,8}, and a number of additional recent review articles^{7,9–16}.

High-temperature polymers such as the Aramids² are very difficult to treat in the usual sol–gel technique, but some studies have been carried out on a few aromatic polyamides^{14,17–21}, a number of polyimides^{22–27}, and several benzoxazole and benzobisthiazole polymers^{28–32}. The unreactivity that many such polymers must have to qualify as high-temperature, high-performance materials is the main disadvantage in this application, since it generally causes poor interfacial bonding between the polymers and the ceramic phases. Because of this resistance to bonding, one of the challenges in this area of high-performance polymers is to obtain significant improvements, particularly since many of these polymers already have superb thermal and mechanical properties. The interfacial problem can be solved, at least in part, either by functionalizing the polymer, by adding a bonding agent, or by doing both.

In view of the importance of the Aramid polymers, the present work focuses on some new composites prepared by introducing titania phases into Aramid matrices at low temperatures using the sol–gel technique. The chains of poly(phenylene terephthalamide) employed were prepared so as to have carbonyl chloride end-groups. These chains were then end-capped with aminophenyl trimethoxysilane and a titania network which could bond with the polymer chains was then developed *in-situ*. The amount of titania was varied from 2.5 to 40 wt%, with the amounts calculated assuming complete conversion of titanium propoxide to TiO₂. The composites thus obtained were characterized with regard to their tensile strength, water absorption, optical properties, and thermal behaviour (specifically, using dynamic mechanical thermal analysis, d.m.t.a., and thermal gravimetric analysis, t.g.a.).

EXPERIMENTAL

Chemicals

The monomers 1,4-phenylenediamine, 1,3-phenylenediamine, and terephthaloyl chloride (TPC), and the solvent dimethyl acetamide (DMAC) were all obtained from Aldrich as AR-grade materials, and used as received. Tetrapropylorthotitanate (TPOT) (98% pure) was obtained from Aldrich, and the bonding agent aminophenyltrimethoxysilane (APT MOS) (97% pure) was obtained from Huls America, Inc. Both were used as received.

Preparation of the hybrid materials

A mixture of 1,4- and 1,3-phenylenediamines, 5.4460 g

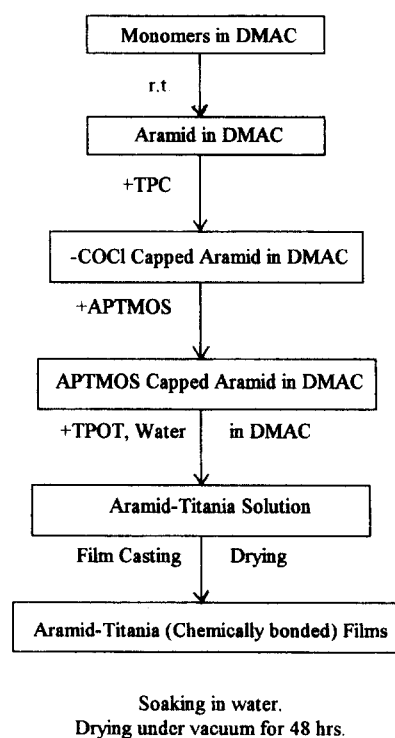


Figure 1 Preparative scheme for the Aramid–titania composite films

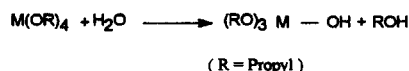
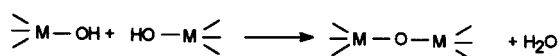
(0.05 mol) in a mole ratio of 35/65 was placed into a 250 ml conical flask under completely anhydrous conditions. DMAC (146.0 ml) was added to the flask and the solution stirred for 0.5 h. The contents of the flask were then cooled to 0°C and 10.151 g (0.05 mol) of TPC added, still under anhydrous conditions. After about 0.5 h of reaction time, the mixture was allowed to come to room temperature, and the stirring was continued for 24 h. A slight excess of the acid chloride was then added in order to produce carbonyl chain ends. The polymer thus prepared had an inherent viscosity of 1.40 dl g⁻¹, as estimated from a solution of 0.500 g polymer in 100 ml of DMAC at 30°C. A stoichiometric amount of APTMOS was added to a solution of the polymer, to react with the acid chloride groups, with stirring being continued for about 12 h at room temperature.

The polymer solution thus prepared served as a stock solution to which various amounts of tetrapropylorthotitanate in DMAC were added. Each solution thus obtained was then stirred for 6 h at 40°C. In each case, a measured amount of water in DMAC was then added for the hydrolysis and condensation used to produce the titania phase. Films of uniform thickness containing various amounts of titania were prepared by baking out the solvent from a known amount of titania–Aramid composite solution at 75–80°C. They were further dried under vacuum, at 80°C for 48 h. The scheme for the preparation of these composite films is summarized in Figure 1. The reactions involving hydrolysis and condensation of the titania network leading to the development of the chemically-bonded ceramers is given in Figure 2.

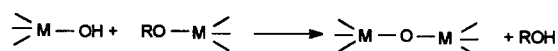
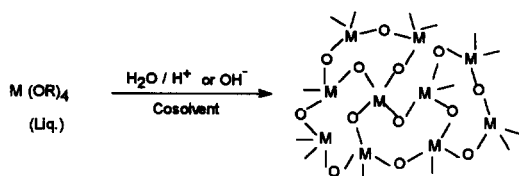
The films were characterized with regard to their mechanical properties using an Instron Universal Testing Instrument (Model TM-SM 1102 UK) at room temperature. Water absorption of these composites as a function of time was measured at 25°C (using ASTM

procedure D570-81). Optical properties were recorded in the visible range at three wavelengths, specifically at 490, 530 and 600 nm, using an ultraviolet-visible (u.v.-vis) Shimadzu Spectrophotometer. D.m.t.a. was carried out with a Rheometrics d.m.t.a. (III), and t.g.a. was performed with a NETZSCH Simultaneous Thermal Analyzer (STA 429).

a

Hydrolysis:**Condensation:**

and / or

**Net Reaction:**

b

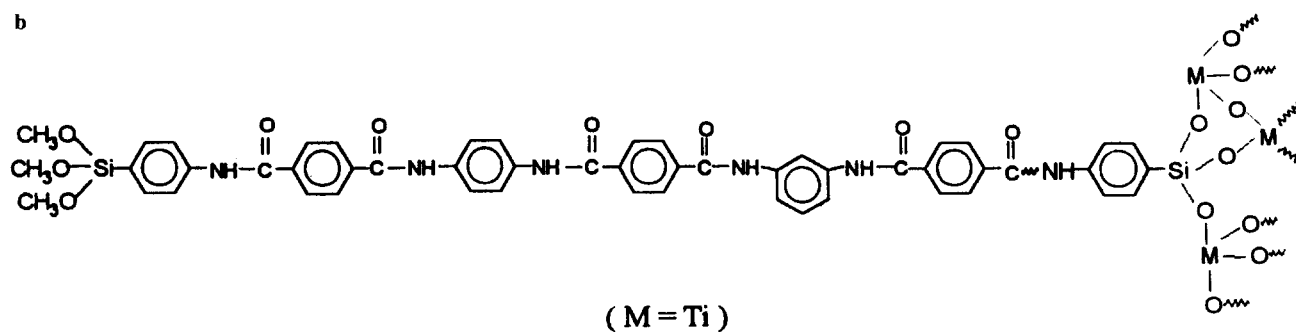


Figure 2 Hydrolysis and condensation of a metal alkoxide to form a metal oxide network (a), and the structure of the chemically-bonded composites (b)

Table 1 Transmittances of the titania-Aramid hybrid materials

Samples	TiO ₂ contents (%)	Film thicknesses (mm)	% Transmittances		
			490 nm	530 nm	600 nm
1	0.0	0.19	69.5	71.8	77.6
2	2.5	0.10	70.1	72.3	79.1
3	5.0	0.10	68.4	71.2	80.4
4	7.5	0.12	65.2	71.8	79.9
5	10.5	0.10	59.3	65.2	76.0
6	15.0	0.07	64.2	70.7	76.6

DISCUSSION

The pure Aramid film and Aramid-titania composite films were light yellow, and transparent at concentrations of titania up to 20 wt%. More quantitative measurements, of transmittances at 490, 530, and 600 nm, are reported in *Table 1*. The colour of the films became darker with increase of an amount of titania, and the films containing 25% or more were only semi-transparent (and were also brittle). The transparency of such composites depends on the size, size distribution, and spatial distribution of the titania particles in the polymeric matrix. Films containing up to 20% titania were transparent, presumably because the average particle size was less than the wavelength of light, and the distribution of titania was relatively homogeneous. However, at titania contents beyond 20%, increase of particle size and decrease of homogeneity cause opaqueness and brittleness. In fact, the films in this range could not be meaningfully analysed for mechanical strength.

The stress-strain curves of the pure Aramid and the Aramid-titania composite materials with 2.5–15 wt% titania are shown in *Figure 3*. The results show a large increase in tensile strength of the titania composite materials, relative to that of the pure Aramid copolymer. The development of a titania network within the polymer matrix reinforces the polymer, giving the observed increases in this important mechanical property. This represents an interesting 'delegation of responsibilities', since the organic phase, which generally has a large free volume and low glass transition temperature (T_g), cannot withstand high stresses, but can exhibit very large strains. In the present case, this is presumably due to the *meta-para* copolymeric nature of these chains, as opposed to the considerably stiffer chains of Kevlar[®] itself. On the other hand, the inorganic ceramic phase,

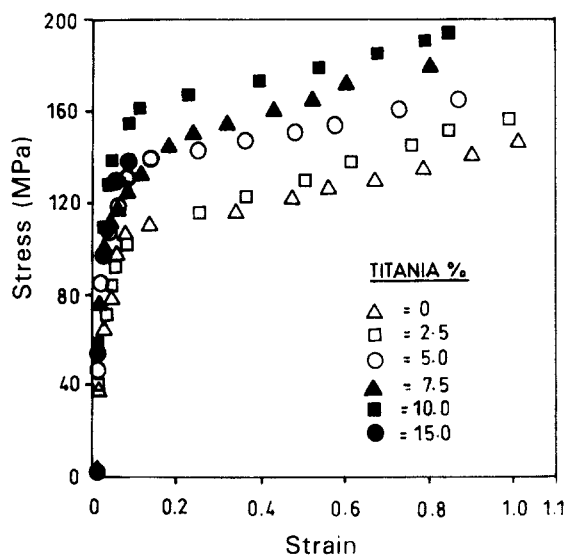


Figure 3 Stress-strain isotherms in elongation at room temperature for the Aramid-titania composites. The amount of the titania phase present is indicated in the inset

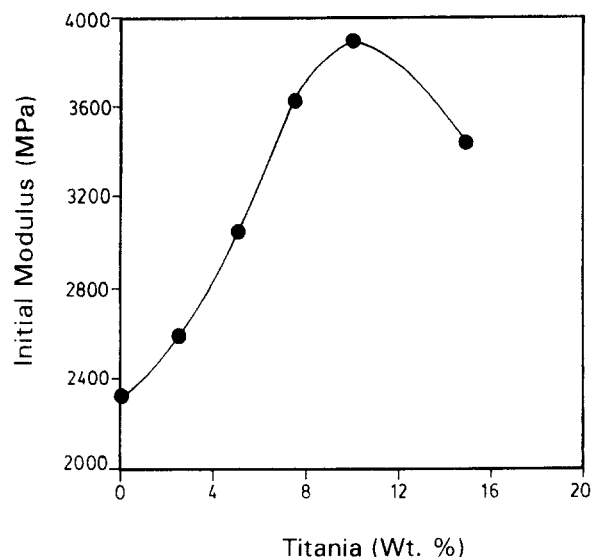


Figure 5 Dependence of the initial modulus on the amount of titania

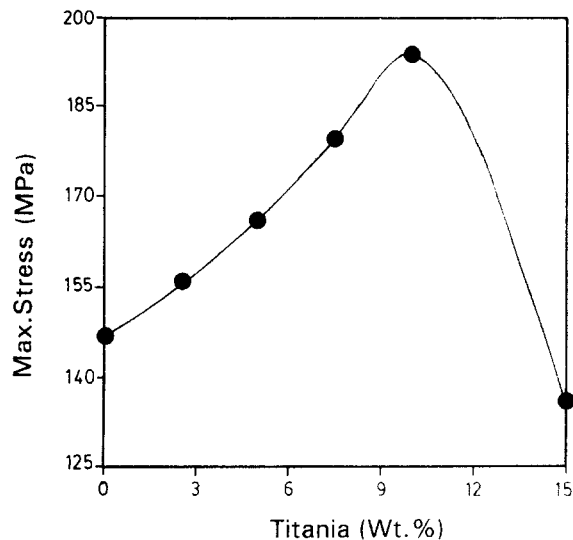


Figure 4 Dependence of the ultimate strength (maximum stress, at rupture) on the amount of titania introduced

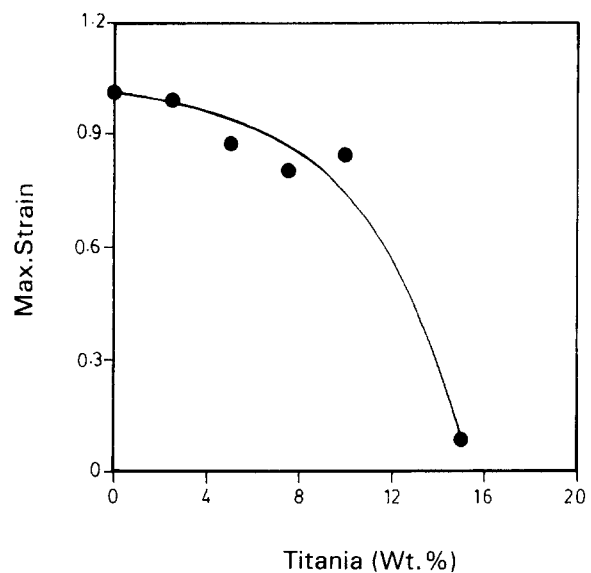


Figure 6 Dependence of the maximum extensibility (strain at rupture) on the amount of titania

which generally has a small free volume and high T_g , has the capability of tolerating large stresses but only small strains. The intimate blending of the two phases, presumably with the covalent bonding between them, provides a combination of some of the best properties of the two components.

The variation in maximum stress at break (ultimate strength) with titania content can be seen from *Figure 4*. The maximum stress was found to increase initially with increase in titania content, and at 10% titania showed a maximum value of 193 MPa (relative to the 147 MPa of the pure copolymer), which represents an excellent improvement in tensile strength. Further addition of titania decreases the strength because of increasing brittleness, as already mentioned. Values of the modulus calculated from the initial slopes of the stress-strain curves are presented in *Figure 5*. As was the case for the maximum stress at break, the values of the initial modulus showed a maximum with increase of titania

content at 10 wt%. The length at rupture (maximum extensibility) was found to decrease monotonically with increase of titania, as shown in *Figure 6*. The toughness of these materials, determined by calculating the area under the stress-strain curves, is described in *Figure 7*. The results indicate that toughness initially shows an increase, up to 10% titania, followed by a sharp decrease.

As can be seen from the above results on mechanical properties, there is considerable reinforcement, presumably from bonding between the polyamide chains and the titania. However, the higher the molecular weight of the polymer, the fewer the end groups available for bonding to the ceramic phase. Perhaps titania particles in excess of those linkable to Aramid chains contribute particularly markedly to the eventual brittleness that is observed.

The thermograms obtained for these materials under a nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ are

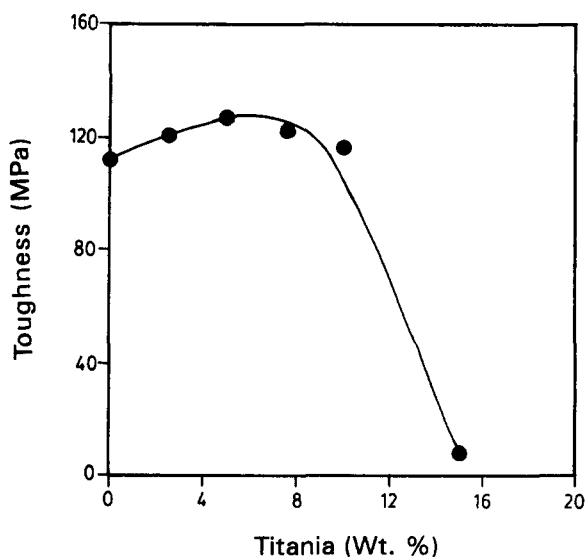


Figure 7 Dependence of the toughness (energy to rupture) on the amount of titania

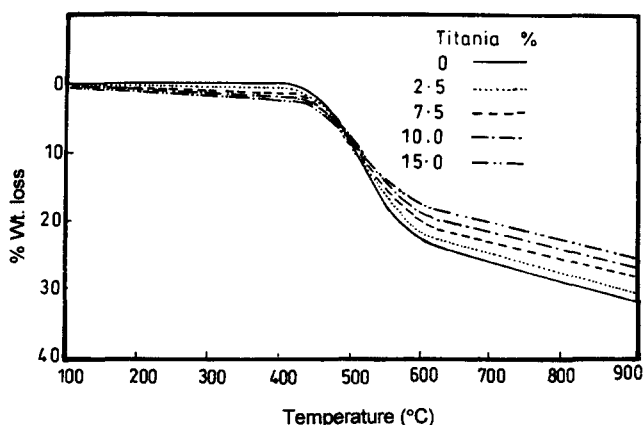


Figure 8 Thermogravimetric analysis results on the Aramid-titania composites

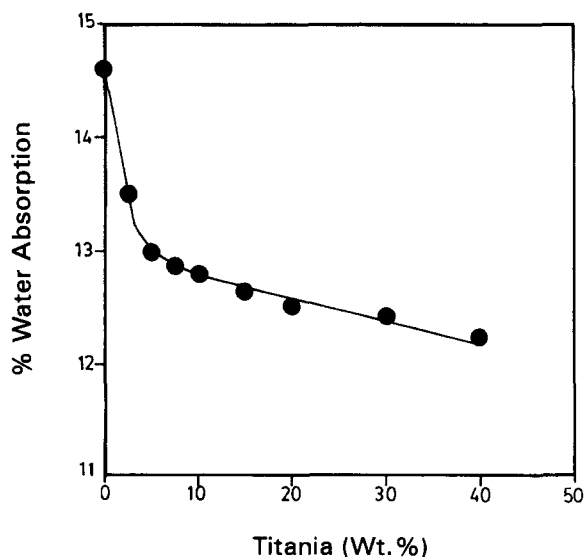


Figure 9 Dependence of the extent of water absorption on the amount of titania

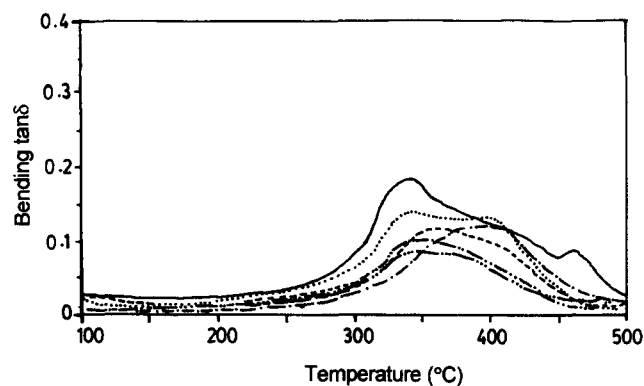


Figure 10 Variation of the loss tangent ($\tan \delta$) with temperature for the following wt percentages of titania: 0.0, —; 2.5,; 5.0, - - - -; 7.5, · · · · ·; 10, - · - · - ·; 15, - · - · - ·

Table 2 Storage moduli and glass transition temperatures of the titania-Aramid hybrid materials

Samples	TiO ₂ contents (%)	Storage moduli (GPa)	Glass transition temperatures (°C)
1	0.0	7.62	335.2
2	2.5	10.71	372.0
3	5.0	13.23	370.1
4	7.5	13.09	400.0
5	10.0	12.38	366.4
6	15.0	14.76	364.5

shown in Figure 8. The results indicate that the thermal decomposition temperatures of all the samples lie in the range 350–450°C. The weight retained by these samples at 800°C is roughly proportional to the amount of titania in the composite, as expected.

The amounts of water absorption of these composites under saturation conditions for 168 h are shown in Figure 9. The Aramids contain polar $-\text{CO}-\text{NH}$ groups which have a tendency to absorb water through hydrogen bonding; this is obviously important since it can adversely affect mechanical and dielectric properties. The results show a maximum water absorption for the pure Aramid at 12.8 wt%, with a monotonic but asymptotic decrease thereafter. Similar results have been reported for other polyamides^{14,20}, and for functionalized polybenzoxazoles and polybenzobisthiazoles^{31,32}. The titania particles obviously limit access of the water to the hydrogen-bonding sites on the polymer chains.

Figure 10 and Table 2 show the d.m.t.a. results used to determine the T_g s and the storage moduli E' in the range 100–500°C. They involve the loss $\tan \delta$ in bending as a function of temperature for the titania contents investigated. With increase of temperature, a stage is reached where segmental motion starts, as marked by a pronounced increase in $\tan \delta$. Furthermore, each peak splits up into two parts, consisting of a primary maximum around 350°C and generally a shoulder at higher temperatures. Also, the peaks decrease in intensity and becomes broader with increased amounts of titania. On a molecular level, the inorganic network

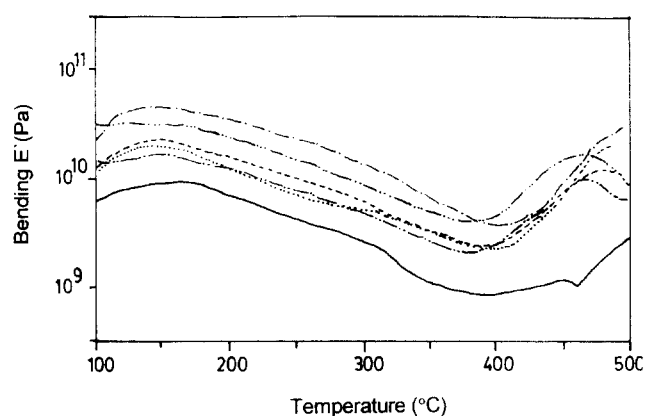


Figure 11 Variation of the storage modulus with temperature for the following wt percentages of titania: 0.0, —; 2.5, ·····; 5.0, - - - -; 7.5, ······; 10, - - - - -; 15, ······.

reduces the segmental motion of the polymer chains^{33,34}, resulting in the increases in T_g listed in *Table 2*.

The temperature variations of the storage moduli are shown in *Figure 11*. The storage modulus at 100°C initially increases with increase of titania content, but then decreases. The initial increase may be due to completion of condensation processes leading to more nearly complete network formation. The sharp decreases in modulus with onset of thermal motions are seen to occur at higher temperatures. The value of the modulus beyond 400–450°C is seen to increase again with temperature, possibly due to increases in crosslinking. The t.g.a. results presented in *Figure 8* show that the aramid chains begin to decompose around 400°C, and this may produce free radicals which could result in increased crosslinking. At constant temperature, increasing the amounts of the titania generally increases the storage modulus, because of titania's hardness and small free volume. This simple dependence can be complicated, however, by the fact that beyond a relatively low concentration of titania, there are no longer any reactive polymer ends left for the desired interfacial bonding.

CONCLUSIONS

The present work shows that the sol-gel process can successfully be used to prepare novel Aramid-titania composites at low temperatures, and that reactions capable of creating bonding between the inorganic and organic phases can provide considerable reinforcement in these materials. Because of the limited number of polymer chain ends available for interfacial bonding, however, there is an optimal titania content of approximately 10 wt% for maximizing the tensile strengths of these materials.

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the financial support provided by the Air Force Office of Scientific Research (Directorate of Chemistry and Materials Science) through Grant F49620-96-1-0052.

REFERENCES

1. Mark, J. E., Lee, C. Y.-C. and Bianconi, P. A. (ed.), *Hybrid Organic-Inorganic Composites*. American Chemical Society, Washington, 1995, Vol. 585.
2. Wolfe, J. F., in *Encyclopedia of Polymer Science and Engineering*, ed. H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges. Wiley-Interscience, New York, 1987, p. 635.
3. Brinker, C. J. and Scherer, G. W., *Sol-Gel Science*. Academic Press, New York, 1990.
4. Hench, L. L. and West, J. K. (ed.), *Chemical Processing of Advanced Materials*. Wiley, New York, 1992.
5. Mark, J. E., in *Physical Properties of Polymers*, 2nd edn, ed. J. E. Mark, A. Eisenberg, W. W. Graessley, L. Mandelkern, E. T. Samulski, J. L. Koenig and G. D. Wignall. American Chemical Society, Washington, DC, 1993, p. 3.
6. Cheetham, A. K., Brinker, C. J., Mecartney, M. L. and Sanchez, C. (ed.), *Better Ceramics Through Chemistry VI*. Materials Research Society, Pittsburgh, 1994, Vol. 346.
7. Mark, J. E., *Hetero. Chem. Rev.*, 1996, **3**, 307.
8. Sanchez, C. and Ribot, F. (ed.), *Proceedings of the First European Workshop on Hybrid Organic-Inorganic Materials*. Chimie de la Matière Condensée, Chateau de Bierville, France, 1993.
9. Novak, B. M., *Adv. Mater.*, 1993, **5**, 422.
10. Schmidt, H. and Krug, H., in *Inorganic and Organometallic Polymers II*, Vol. 572, ed. P. Wisian-Neilson, H. R. Allcock and K. J. Wynne. American Chemical Society, Washington, 1994, p. 183.
11. Mark, J. E. and Calvert, P. D., *J. Mater. Sci., Part C*, 1994, **1**, 159.
12. Mark, J. E., in *Diversity into the Next Century*, Vol. 27, ed. R. J. Martinez, H. Arris, J. A. Emerson and G. Pike. SAMPE, Covina, CA, 1995.
13. Mark, J. E., *Macromol. Symp.*, 1995, **93**, 89.
14. Mark, J. E., Wang, S. and Ahmad, Z., *Macromol. Symp.*, 1995, **98**, 731.
15. Wen, J. and Wilkes, G. L., in *Polymeric Materials Encyclopedia: Synthesis, Properties, and Applications*, ed. J. C. Salamone. CRC Press, Boca Raton, 1996.
16. Mark, J. E., *Polym. Eng. Sci.*, 1996, **36**, 2905.
17. Landry, C. J. T., Coltrain, B. K., Wesson, J. A., Zumbulyadis, N. and Lippert, J. L., *Polymer*, 1992, **33**, 1496.
18. Wang, S., Ahmad, Z. and Mark, J. E., *Polym. Bulletin*, 1993, **31**, 323.
19. Ahmad, Z., Wang, S. and Mark, J. E., in *Better Ceramics Through Chemistry VI*, Vol. 346, ed. A. K. Cheetham, C. J. Brinker, M. L. Mecartney and C. Sanchez. Materials Research Society, Pittsburgh, 1994, p. 127.
20. Ahmad, Z., Wang, S. and Mark, J. E., in *Hybrid Organic-Inorganic Composites*, Vol. 585, ed. J. E. Mark, C. Y.-C. Lee and P. A. Bianconi. American Chemical Society, Washington, 1995, p. 291.
21. Ahmad, Z., Sarwar, M. I. and Mark, J. E., *J. Mater. Chem.*, 1997, in press.
22. Yano, K., Usuki, A., Okada, A., Kurauchi, T. and Kamigaito, O., *J. Polym. Sci., Polym. Chem. Ed.*, 1993, **32**, 625.
23. Mascia, L. and Kioul, A., *J. Mater. Sci. Letters*, 1994, **13**, 641.
24. Chen, X., Gonsalves, K. E., Chow, G.-M. and Xiao, T. D., *Adv. Mater.*, 1994, **6**, 481.
25. Wang, S., Ahmad, Z. and Mark, J. E., *J. Macromol. Sci., Macromol. Reports*, 1994, **31**, 411.
26. Wang, S., Ahmad, Z. and Mark, J. E., *Chem. Mater.*, 1994, **6**, 943.
27. Mascia, L. and Kioul, A., *Polymer*, 1995, **36**, 3649.
28. Jenekhe, S. A. and Osaheni, J. A., *Chem. Mater.*, 1994, **6**, 1906.
29. Chen, J. P., Ahmad, Z., Wang, S., Mark, J. E. and Arnold, F. E., in *Hybrid Organic-Inorganic Composites*, Vol. 585, ed. J. E. Mark, C. Y.-C. Lee and P. A. Bianconi. American Chemical Society, Washington, 1995, p. 297.
30. Dang, T. D., Chen, J. P. and Arnold, F. E., in *Hybrid Organic-Inorganic Composites*, Vol. 585, ed. J. E. Mark, C. Y.-C. Lee and P. A. Bianconi. American Chemical Society, Washington, 1995, p. 280.
31. Premachandra, J., Kumudinie, C., Zhao, W., Mark, J. E., Dang, T. D., Chen, J. P. and Arnold, F. E., *J. Sol-Gel Sci. Technol.*, 1996, **7**, 163.
32. Mark, J. E., Premachandra, J., Kumudinie, C., Zhao, W.,

- Dang, T. D., Chen, J. P. and Arnold, F. E., in *Better Ceramics Through Chemistry VII. Organic/Inorganic Hybrid Materials*, ed. B. K. Coltrain, C. Sanchez, D. W. Schaefer and G. L. Wilkes. Materials Research Society, Pittsburgh, 1996.
33. Wilkes, G. L., Huang, H.-H. and Glaser, R. H., in *Silicon-Based Polymer Science*, Vol. 224, ed. J. M. Zeigler and F. W. G. Fearon. American Chemical Society, Washington, DC, 1990, p. 207.
34. Brennan, A. B., Rodrigues, D. E., Wang, B. and Wilkes, G. L., in *Chemical Processing of Advanced Materials*, ed. L. L. Hench and J. K. West. Wiley, New York, 1992, p. 807.