J MATER SCI 41 (2006) 2907–2914

New polyimide-silica nano-composites from the sol-gel process using organically-modified silica network structure

SH. AL-KANDARY, A. A. M. ALI, Z. AHMAD*
Department of Chemistry, Kuwait University, Faculty of Science, P.O. 5969, Safat 13060, State of Kuwait
E-mail: zahmad@kuc01.kuniv.edu.kw

The polyimide (PI) matrix prepared by the reaction of pyromellitic anhydride (PMDA) and oxydianiline (ODA) has been reinforced with organically-modified silica network structure using the sol-gel process. Aminophenyltrimethoxysilane (APTMOS) and PMDA were reacted in 2:1 molar ratio in dimethylacetamide (DMAc) as solvent to generate amic acid oligomeric species with alkoxy groups at the chain ends. Specific amounts of these along with tetraethoxysilane (TEOS) were mixed in the high molecular weight polyamic acid solution in DMAC to carry out the sol-gel process. Imidization was carried out by successively heating the hybid films up to 300°C. Morphology, thermal and mechanical properties of these hybrids using imide-modified silica network were studied as a function of silica content and compared with the one in which reinforcement of the PI matrix was achieved using pure silica network generated from TEOS only. SEM studies show a drastic decrease in the silica particle size when imide oliogmers were introduced in the silica network as spacer group. The diameter of the silica particles was in the range of 40 nm in the compatibilized system with no significant change observed on increasing silica content in the matrix. With the un-compatibilized system where silica network was generated directly from TEOS the particle diameter varied from 0.2 to 3 μm for 5 to 40% silica content respectively. Higher thermal stability and mechanical strength and improved transparency were observed in case of compatibilized hybrid system. The imide active silica therefore was found to be a better reinforcement for PIs than the pure silica obtained from TEOS.

---

1. Introduction

Polyimides (PIs) have been widely used in microelectronic industries because of their outstanding characteristics [1–3] such as high tensile strength and modulus, low thermal expansivity and dielectric constant, and good resistivity against organic solvents. Especially the aromatic PIs are used as dielectric layers, α-particle barriers, and insulating layers in multi-chip semiconductors. Thermal and mechanical properties of PIs can further be improved by inclusion of silica in the matrix [3, 4]. The sol-gel process [5, 6] has been used to develop silica particles *in-situ* in the polymer matrices. Introduction of inorganic material, however after a certain proportion in the organic component leads to phase separation. Various types of organosilanes have been employed as coupling agents in the preparation of PI-silica hybrids in the last decade where the organic part is supposed to interact with the polymer chain and alkoxy units on the other hand with the silica network. Some important coupling agents used in such systems by us [7, 8] and various other workers [9–14] are phenyltriethoxysilane (PTEOS), methyltriethoxysilane (MTEOS) aminophenyltrimethoxysilane (APTMOS) (aminoethylaminomethyl)-phenethyltrimethoxysilane, γ-glycidyloxypropyltrimethoxysilane (GOTMOS) 1-trimethoxysilyl-2-(m, p-chloromethyl)phenylethane, isocyanatopropyltrimethoxysilane and aminopropyltrimthoxysilane. The interaction between PI and silica through these coupling agents had pronounced effects on the morphology of the hybrid films and has in many

---

*Author to whom all correspondence should be addressed.

0022-2461
DOI: 10.1007/s10853-005-5123-5

cases improved the mechanical, thermal and dielectric properties.

Ahmad *et al.* [15] have reviewed the work on PI-silica hybrids carried out during the last two decades and discussed various techniques used to couple the organic and inorganic phases in these hybrids. Since then some more work has appeared in the literature. Hsiue *et al.* [16] carried out the preparation of PI-silica nano-composites using non-aqueous sol-gel process by polycondensation of PTEOS in the PI matrix. ^{29}Si NMR spectra [16] of the silicate structure in the nano-composites showed three major absorption peaks, dihydroxy-substituted silica, monohydroxy-substituted silica, and nonhydroxy-substituted silica. It was observed that the proportion of the nonhydroxy-substituted silica increases with increasing the silica content. This implies that increasing the silicon content of the PI-silica hybrid can favor the formation of silica glass structure, therefore providing a more complete PI-silica hybrid structure. Tsai *et al.* [17] have recently reported low dielectric PI silica hybrids prepared from polyamic acid (PAA) solution containing PTEOS at two chain ends and monoaryltrialkoxysilane using a self catalyzed sol-gel process. The dielectric constant and water absorption in the hybrid materials were found to reduce with the PTEOS contents because of increase in free volume and the hydrophobicity. Dynamic mechanical properties of PI-silica hybrids have also been studied [18] by the same authors.

PI-silica nano-composites were recently prepared by Raun *et al.* [19] by hot pressing a mixture of PI and highly porous silica powder. The silica powder was produced using the sol-gel process. The effect of loading, cure and post cure temperature on fracture toughness were investigated. The addition of silica was found to improve fracture toughness of the material. Huang *et al.* [20] have prepared PI materials with a low value of coefficient of thermal expansion (CTE) while still retaining high strength and toughness. The silica was incorporated through sol-gel process in homo- and co-polyimides with highly rigid chain structures. The hybrid films possessed low in plane CTE ranging from 14.9 to 31.1 ppm. The co-polyimide were strengthened and toughened with the introduction of appropriate amount of silica.

Liu Jing and coworkers [21] prepared PI-silica nanocomposites where benzophenone tetracarboxylic acid dianhydride was reacted with 4,4′-oxyphenyl diamine to produce PI and TEOS was hydrolyzed in the matrix by the water released from the imidization process. Clear and flexible hybrid films with pale yellow color were obtained though the films containing 19 wt% silica were half transparent. The SEM showed the silica particles appearing as white beads with a diameter of 30–50 nm which were dispersed homogeneously.

A series of hybrid PI-silica composites has been prepared from a functionalized fluorinated PIs, tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMOS) and phenyltrimthoxysilane (PTMOS) via the sol-gel process by Cornelius *et al.* [22]. PIs were solution imidized employing the 4, 4′-hexa-fluroisopropylidenediphthalic anhydride, and various amount of the 4,4′-hexa-fluroisopropylidene dianiline and 3,5-diaminobenzoic acid. The degree of cross-linking between the silica structures and the PI matrix, as well as the morphology of the hybrid materials were found highly dependent on the type and the content of the alkoxide employed. The high functionality and reactivity of the TMOS gave rise to highly cross-linked, homogenous hybrid films, while the MTMOS and PTMOS based hybrid films were phase separated and the silica structures largely uncondensed. Although the thermal stability of the hybrid films changed a little, the incorporation of the silica structure in the PI matrix increased the rigidity and the mechanical strength of the resulting hybrid materials, particularly at higher temperatures.

In the present work the interfacial interaction between the inorganic phase and the polyimide matrix has been developed not through using an alkoxysilane having any type of organic group [7–14] but by modifying the silica network itself using imide linkage. The physical interaction due to the organically modified silica network may constrain the phase separation phenomenon between the PI and inorganic clusters as seen in the previous studies to a smaller scale thus providing transparent materials with improved properties. These aromatic imide groups present on silica network are thermally stable and their inclusion can improve the thermal and mechanical performance of PI. The amic acid (AA) dimers were prepared by reacting APTMOS with PMDA in the molar ratio 2:1 in DMAC as solvent. The APTMOS present at the end-groups is used to link the AA dimer with TEOS which on further hydrolysis and condensation reaction produce silica network in the high molecular weight PAA solution. The resulting material is imidized by heating the hybrid films up to 300 °C. The mechanical and thermal properties of such hybrids have been compared with the system where pure silica network was used in the PI matrix.

2. Experimental

2.1. Chemical used

Pyromellitic dianhydride (PMDA) purity 97%, and tetraethoxysilane (TEOS), purity 98% were purchased from Aldrich and were used as received. The monomer 4,4′-oxydianiline (ODA), purity $\geq$ 98%, and anhydrous *N*,*N*-dimethylacetamide (DMAc), purity 99.99%, (water content $<$ 0.01%) used as solvent in the polymerization reaction were obtained from Fluka. Aminophenyltrimethoxy silane (APTMOS), purity 95% (Huls America) was used as received.

All the experiments were carried out under complete anhydrous conditions under nitrogen gas as the solvent, DMAc as well as monomer, PMDA are very sensitive to the moisture.

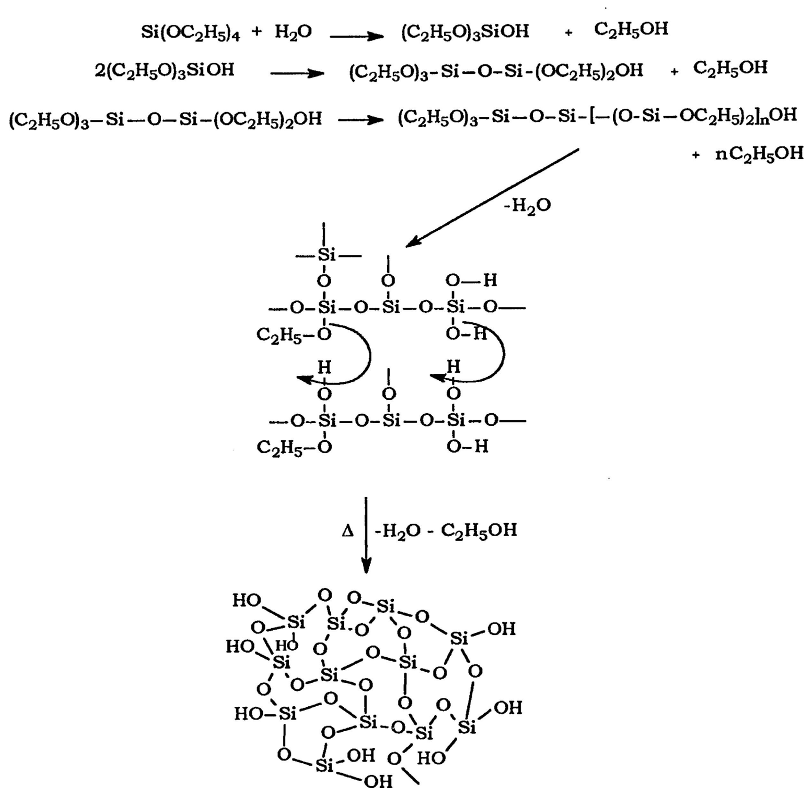

Figure 1 Sol-gel process leading to silica network formation.

2.2. Preparation of polyamic acid

In a 250 ml conical flask, 5.1086 g (0.025 mol) of ODA and 140 g of DMAc were taken and the contents were stirred at room temperature until a clear solution of diamine was obtained. Then 5.6126 g (0.025 mol) of PMDA was added to the amine solution with continued stirring. The viscosity of the reaction was found to increase with further addition of 1% of PMDA. In all experiments 1% extra amount of PMDA were therefore used. The reaction mixture was stirred for 24 hour to obtain a highly viscous solution of PAA.

2.3. Silica network formation

The sol-gel process leading to the formation of silica network through the hydrolysis and condensation of TEOS is represented in Fig. 1. For the preparation of PI modified silica network, PMDA (0.830 mmol) in 15.0 g of DMAc was taken and stirred with magnetic stirrer. Then 1.66 mmol of APTMOS was added drop-wise at room temperature with continued stirring for 4 h to produce AA dimers. To this reaction mixture, 0.0323 mol of TEOS was added with continually stirring. The amount of TEOS was adjusted so as to generate 95% silica from TEOS and 5% from the AA alkoxysilane. Fig. 2 illustrates the reaction scheme for the preparation of AA modified silica network precursor.

2.4. Preparation of hybrid films

TEOS or TEOS and AA dimer solutions in DMAc were added in a required amount in the PAA solution and the sol-gel process was carried out at 60 °C to generate two types of hybrid materials one in which pure silica network and other in which polymer modified silica network was generated in the matrix. The hybrid films were prepared by the solvent elution technique. These films were heated successively at 100 °C, 200 °C, 270 °C, 300 °C for 1 h, 1 h, 30 min, 1 h, respectively, to carry out the imidization process (Fig. 3). The imidization process was monitored by FTIR analysis; decrease in amide carbonyl absorption at 1650 cm^{-1} and increase in imide carbonyl absorption at 1720 and 1780 cm^{-1} and imide (C-N) band at 1371 cm^{-1}. The morphology, mechanical and thermal properties of such hybrids with various proportions of silica have been studied.

2.5. Characterization of hybrid films

Stress-strain analysis was carried out under ASTM 882 Standard Test Method that covers the measurements of tensile properties of plastics in the form of thin films. All the samples were vacuum dried at 100°C over-night before analysis. The tensile measurements were made on Instron Electromechanical Tester 8562, at uniform strain rate of 5 mm/min at 25°C. 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 was reported in each case. The morphology of the hybrid films has been studied using scattering electron microscopy (SEM). The films were fractured using the microtone at liquid nitrogen temperature, coated with gold and examined at 2020 KV

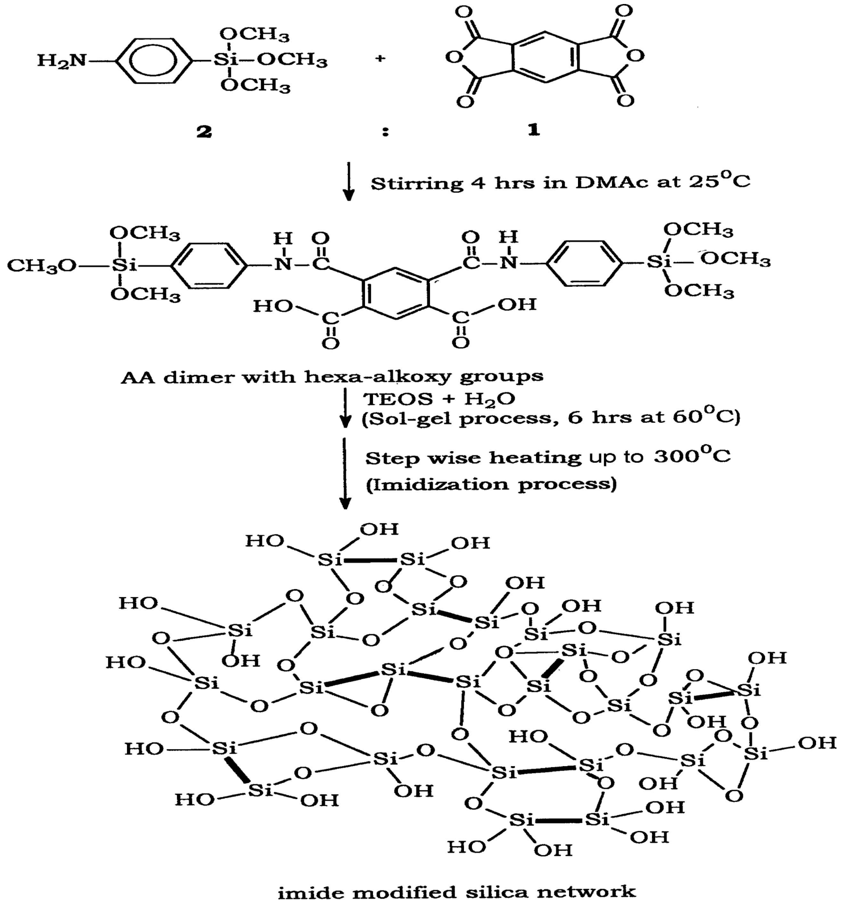

Figure 2 Formation of imide modified silica network where(–) is imide linkage.

using Japan's Jeols SEM instrument model JSM-6300. The Thermogravimetric analysis (TGA) on the samples was performed using Schimadzu TG analyzer by heating the sample (~15 mg) from ambient to 900°C at a heating rate of 10°C min^{-1} with air flow rate of 50 $\text{cm}^3\ \text{min}^{-1}$.

3. Results and discussion

The non-compatibilized PI-silica hybrid films having the silica content up to 40 wt.% were obtained in self-standing form, but the films with 30 and 40 wt.% silica were brittle and therefore not tested for the mechanical properties. In the compatibilized system, all the films obtained were in self-standing form but those with 40 wt.% silica content were brittle. The color of the films for both systems gradually change from yellow, yellow brown, brown to dark brown with increase in silica content. In case of non-compatibilized system the films obtained up to 5 wt.% silica were transparent where as in case of compatibilized one the films were transparent up to 10 wt.% silica. Semi-transparent films were obtained for higher concentrations than these, however, opaque films were obtained with 20 wt.% silica in case of non-compatibilized system, but in case of compatibilized one, even with 30 wt.% silica were semi-transparent. It seems that with increased silica content the inorganic network becomes extensive, the tendency for the particle size to grow increase and the agglomeration of the silica particles then results in the form of clusters and when they become greater than the wavelength of the light, it cannot pass through the film, as a result the films become opaque. In general for the same silica content the transparency of the compatibilized films was found better than that of non-compatibilized ones.

The stress-strain data for the non-compatibilized PI-silica hybrid films using pure silica are given in Fig. 4. Similar data for compatibilized system using PI modified silica are given in Fig. 5. In case of non-compatibilized system, the value of the tensile strength for pure polymer was 119 MPa which increased to 122 MPa for 2.5 wt.% silica and then this value constantly decreased with further addition of silica (Table I). In case of compatibilized system, the value of the tensile strength of pure polyimide was 124 MPa. This value is slightly different from the value for pure PI obtained from the Fig. 4 as it was a different experimental system. Any change in the mechanical property on addition of silica may therefore be considered on relative basis i.e., in relation to the pure polyimide used in that system. The value of the tensile strength in case of compatibilized system increases constantly until the silica content in the matrix is 10% and then it decreases. The maximum value of tensile strength in case of compatibilized system

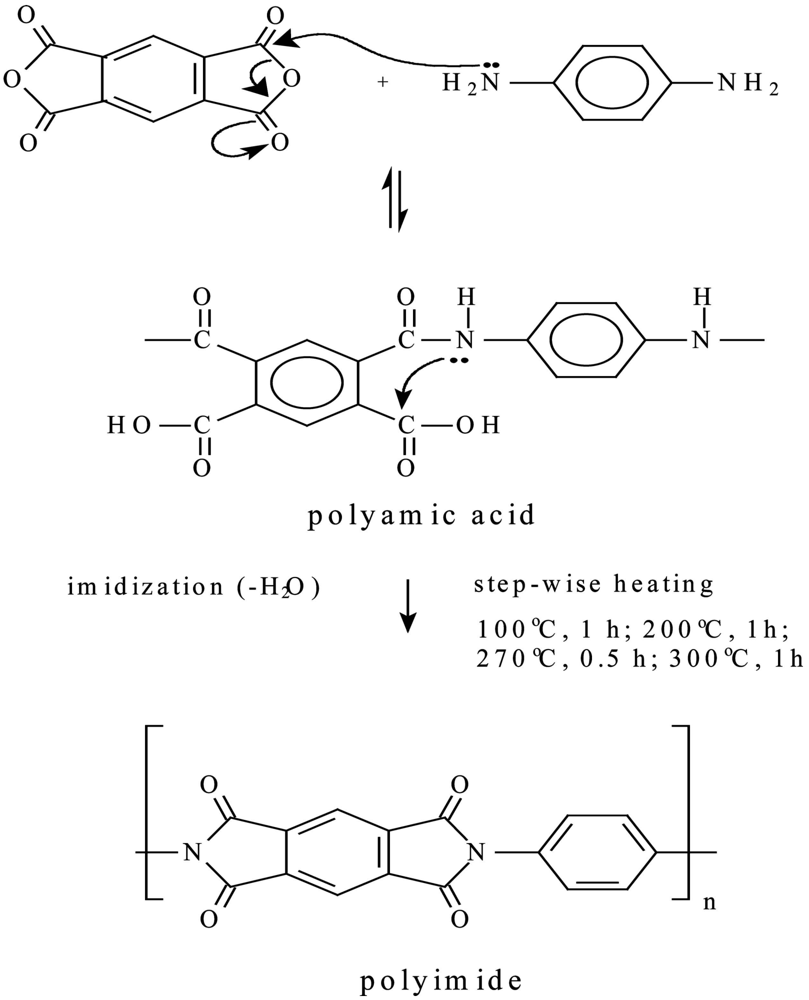

Figure 3 Synthesis of polyimide.

is 165 MPa. The modulus value for compatibilized system constantly increase with increase in silica contents with the maximum value of 3.40 GPa obtained in case of 20 wt.% silica, whereas for non-compatibilized system it increases up to 2.54 GPa for 15 wt.% silica but then decreases at higher silica contents. The elongation at rupture slightly increases initially but then decreases with higher amount of silica in both types of systems. In the present work, in comparison to the pure polyimide, the ultimate strength and the initial modulus increases especially at lower silica contents, but the ultimate elongation decreases with increase in the silica contents. It is generally believed that external stress on a plastic composite is transferred from continuous phase (polymer matrix) to discontinuous phase (silica network). Thus the ultimate properties of the hybrids depend on the extent of the bonding between the two phases. The polyimide modified silica network has more interaction with the PI matrix due to the development of secondary bond forces between the two phases. The compatibilized system therefore shows better mechanical properties than the non-compatibilized one. Better interfacial interaction between the phases was further confirmed from the studies using SEM analysis.

The average diameter of the silica particles ranges from 0.2 to 0.3 μm (5 wt.% silica in the matrix) to the order $\sim$2.5 μm (with 40 wt.% silica). The SEM micrograph for the non-compatibilized hybrids with 10 wt.% silica in the matrix is shown in the Fig. 6. The silica particles appear as small beads in the matrix. The size distribution becomes broader as the silica% in the matrix increases. The particles in such system have sharp and clear boundaries. Under the condition of stress it can lead to stress transfer problem at the phase boundaries resulting in the material with relative low tensile strength. The average diameter of silica particles where the silica was modified during the sol-gel process by introducing PI oligomers in the network is much smaller i.e., in the range of 10 nm (5 wt.%) to 40 nm (40 wt.%) silica in the matrix. The SEM micrograph for the compatibilized systems with 10 wt.% silica contents in the matrix is shown in the Fig. 7. There is a narrow size distribution of the silica particles in case of the compatibilized hybrids. The organic polyimide groups present in the silica network acts as a spacer group and do not allow the agglomeration of silica particles. The surface structure of silica in case of compatibilized system shows a rougher surface. This is because of the presence

TABLE I Variation of tensile strength, modulus, strain at the break point in the non-compatibilized and the compatibilized PI-SiO_2 hybrid materials

	Tensile strength (MPa)		Modulus (GPa)		Strain at the break point	
Silica wt.%	Noncomp.	Comp.	Noncomp.	Comp.	Noncomp.	Comp.
0	119	124	1.38	1.65	0.15	0.20
2.5	122	129	1.50	1.99	0.33	0.43
5	99	128	1.80	2.40	0.13	0.17
10	81	165	2.34	2.77	0.16	0.15
15	79	125	2.54	3.00	0.15	0.13
20	75	100	2.12	3.40	0.08	0.05

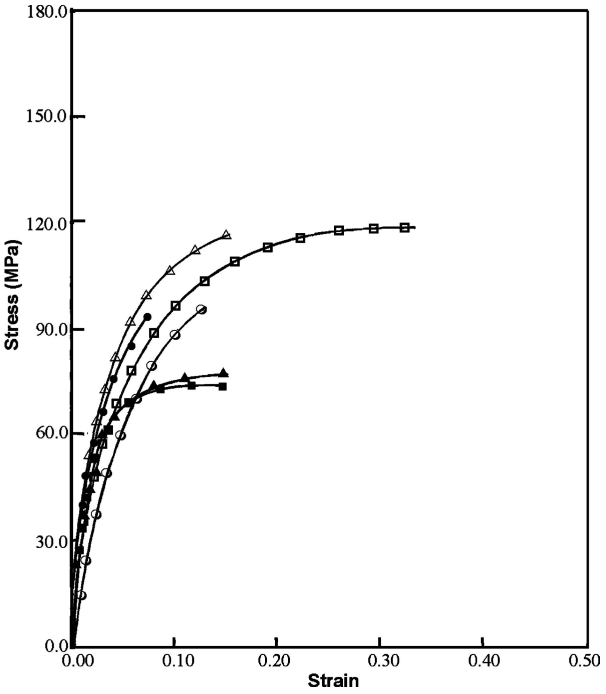

Figure 4 Stress-strain isotherms in elongation mode at 30°C for PI-SiO_2 non-compatibilized system. Silica wt.% in the matrix; 0(△), 2.5 (□), 5 (○), 10 (▲), 15 (■), 20 (●).

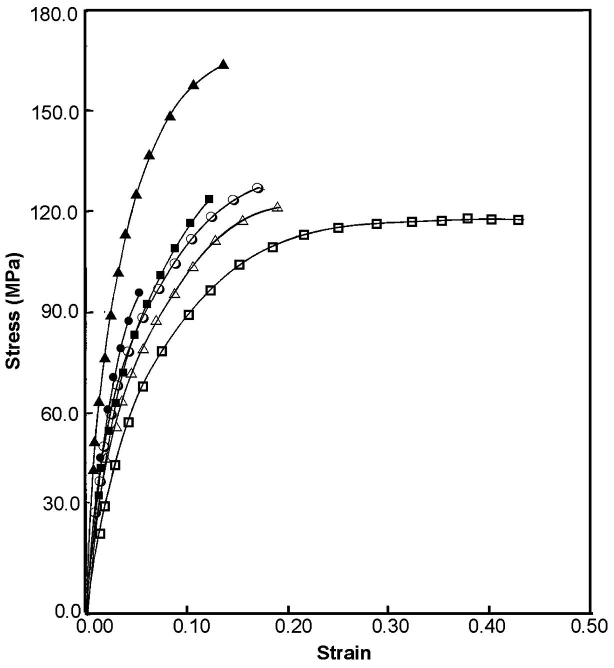

Figure 5 Stress-strain isotherms in elongation mode at 30°C for PI-SiO_2 compatibilized system. Silica wt.% in the matrix; 0(△), 2.5 (□), 5 (○), 10 (▲), 15 (■), 20 (●).

of imide linkages in the silica network, which disturbs the symmetrical growth of the silica. The boundaries between the phases are more diffused in case of the compatibilized system because of the more interaction between the polyimide matrix. As there is more homogeneity, which remains even with higher silica amounts, the tensile strength as compared to unbonded system was observed higher in this case.

TGA curves for non-compatibilized and compatibilized hybrids with various silica contents are shown in Figs 8 and 9 respectively. Very small continuous weight loss was observed before decomposition of the matrix polyimide. This implies that the sol-gel process was nearly complete. The decomposition rate and the slope of the curve showing weight loss are steeper in case of hybrids containing less silica. The presence of silica network seems to protect the polymer from oxidation at higher temperature. In general the decomposition of PI occurs in the range of 560–630°C. Thermal decomposition temperature of the hybrids slightly increased with inclusion of silica in case

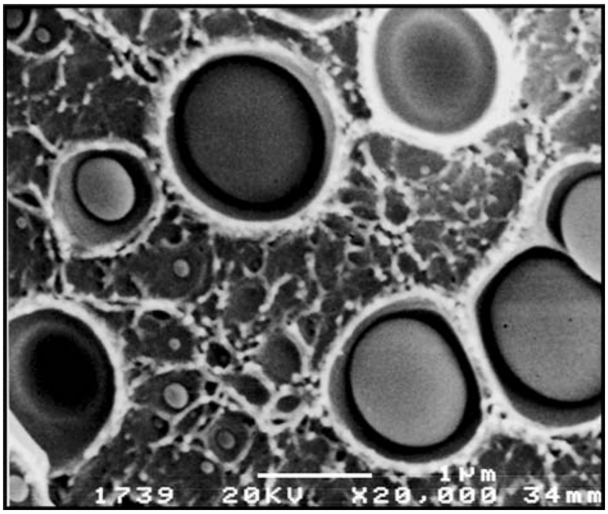

Figure 6 Scanning electron micrograph for non-compatibilized PI-SiO_2 hybrids (silica content 10 wt.%).

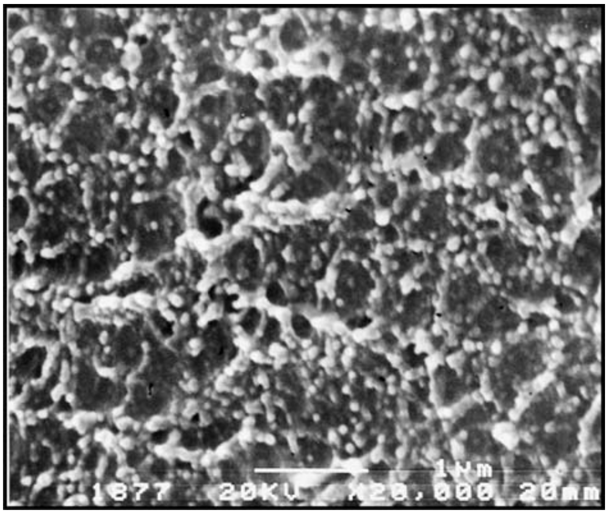

Figure 7 Scanning electron micrograph for compatibilized PI-SiO_2 hybrids (silica content 10 wt.%).

of the non-compatibilized system whereas the increase is relatively more in case of compatibilized system. It seems that presence of silica bonded with polymer chain protect it more from oxidation due to greater cohesion and the degradation process is hindered more as compared to the non-compatibilized system. The thermal decomposition temperature therefore increases slightly with silica content in the matrix. In comparison to the previous work, the hybrids prepared in the present work did not show much continuous loss in weight at low temperature and the thermal decomposition temperature was higher (560–630°C). Shaws *et al.* [14] reported 20% weight loss at 400°C, which increased with the higher loading of coupling agents in PI hybrids. This may be attributed to the higher proportions of aliphatic groups present in MTEOS or GOTMS used by them. In the present work the imide spacer group introduced in the silica network were aromatic in nature which were stable at higher temperature. The weight residue obtained after 800°C in the hybrids is mainly due to presence of SiO_2 in the matrix. The residue retained was almost proportional to the SiO_2 content, which means the sol-gel process was almost complete.

4. Conclusions

The present studies in the polyimide-silica hybrids show that inclusion of polyimide linkage in the silica network produce hybrids with better optical, mechanical and thermal properties. The morphology of these hybrids shows much finer distribution of silica particles with diffused boundaries and the agglomeration of silica particle is prevented by the presence of spacer imide groups in the silica network. This results in better tensile and thermal properties of the hybrid material as compared to the one in which pure silica is used in the matrix.

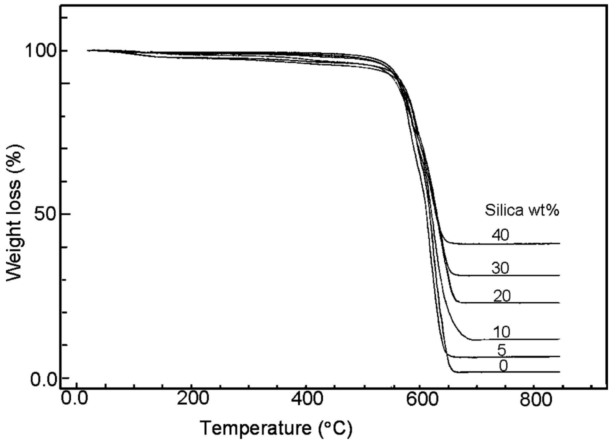

Figure 8 TGA curves for non-compatibilized PI-SiO_2 hybrids with various silica contents.

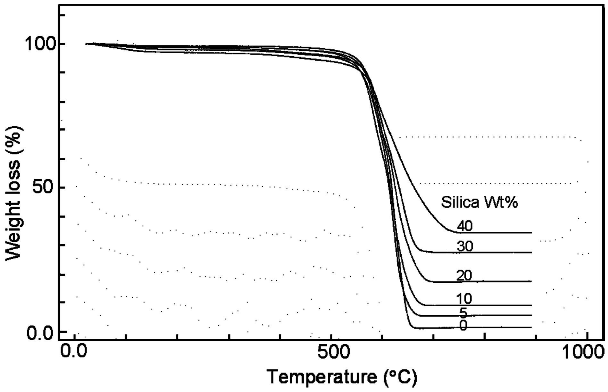

Figure 9 TGA curves for compatibilized PI-SiO_2 hybrids with various silica contents.

Acknowledgments

We wish to acknowledge the research facilities provided by the research administration of KU (Project 07/01), the ANALAB (Project 01/01), the Electron Microscopy units of SAF and the Material Science Laboratory of Kuwait University.

References

1. M. K. GOSH and K. L. MITTEL (Eds.), Polyimides: Fundamental and Applications (Marcel Dekker, New York, 1996).
2. K. L. MITTEL (Ed.), *Polyimides and Other High Temperature Polymers* (VSP publishers, 2003) Vol. **2**.
3. Z. AHMAD, "The Encyclopedia of Materials; Science and Technology" (Elsiever Science, 2001) Section 5, Chapter 10.
4. Z. AHMAD and J. E. MARK, *Mater. Sci. Eng.* **C-6** (1998) 183.
5. C. J. BRINKER, "Better Ceramics Through Chemistry" (Material Research Society, Pittsburgh, PA. 1988).
6. C. J. BRINKER and G. W. SCHERER, "Sol-Gel Science" (Academic Press, New York, 1990).
7. S. WANG, Z. AHMAD and J. E. MARK, *Macromol. Reports* **A31** (Suppls. 3, 4) (1994) 411.
8. *Idem.*, *Chem. Mater.* **6** (1994) 943.
9. A. KIOUL and L. MASCIA, *J. Non-Cryst. Solids* **175** (1994) 169.

10. Y. IYOKU, M. KAKIMOTO and Y. IMAI, *High Perform. Polym*, **6** (1994) 43.
11. *Idem.*, *Trans. Mater. Res. Soc. Jpn.* **16B** (1994) 755.
12. A. KIOUL and L. J. MASCIA, N*on-Cryst. Solids,* **175** (1994) 169.
13. J. C. SCHROTTER, M. SMAIHI and C. GUIZARD, *J. Appl. Polym. Sci.* **61** (1996) 2137.
14. C. XENOPOULOS, L. MASCIA, and S. SHAW, *J. Mater. Sci. and Eng.* **6** (1998) 99.
15. Z. AHMAD and J.E. MARK, *Chem. Mater.* **13** (2001) 3320.
16. G. HISUE, J. CHEN and Y. LIU, *J. Appl. Polym., Sci.* **76** (2000) 1609.
17. M. TASI and W. WHANG, *Polymer* **42** (2001) 4197.
18. *Idem.*, *J. Appl. Polym. Sci.* **81** (2001) 2500.
19. S. RUAN, J. LANNUTTI, S. PRYBYLA and R. R. SEGHI, *J. Mater. Res.* **16(7)** (2001) 1975.
20. J. C. HUANG, Z. ZHU, D.J. ZHANG and X. QIAN, *J. Appl. Polym. Sci.* **79(5)** (2001) 794.
21. J. LIU, G. YAN, W. FUUDONG, L. DECAL and X. JIE, *J. Mater. Sci.* **37** (2002) 3085.
22. C. J. CORNELIUS and E. MARAND, *Polymer* **43**(8) (2002) 2385.

Received 26 April 2004
and accepted 13 July 2005