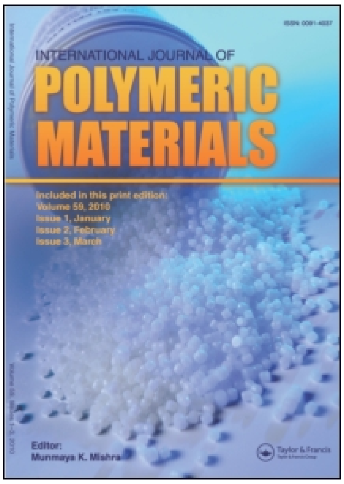

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Thermal and Mechanical Properties of Poly(Hydroxy-Imide)-Silica Nanocomposites

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Thermal and Mechanical Properties of Poly(Hydroxy-Imide)-Silica Nanocomposites

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Thermally stable nanocomposites from polyimide (PI) and silica have been prepared through the sol-gel process. PI matrix, prepared by the reaction of a mixture of phenylenediamine and oxydianiline with an equimolar amount of pyromellitic dianhydride, acted as a reference. The polymer matrix was modified by replacing phenylenediamine with 2,4-diaminophenol to include pendant hydroxyl groups on the chain. Composite films were prepared using different amounts of silica generated in-situ in both type of matrices. These were evaluated by a variety of techniques, including FTIR, SEM, tensile, dynamic mechanical, thermal, and thermogravimetric analyses. The presence of hydroxyl group on polymer chain caused an intimate dispersion of the two phases, which resulted in the formation of nano-sized co-continuous domains as compared to that of the corresponding PI system having no pendent hydroxyl groups. The mechanical and thermal properties of these composites have been compared and explained in term of increased matrix polarity.

Keywords: poly(hydroxy-imide), silica, nano-composites, interfacial interactions

INTRODUCTION

Polyimides (PIs) are of great interest for high-performance applications because they exhibit outstanding characteristics, such as high

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tensile strength and modulus, low coefficient of thermal expansion and dielectric constant, and good resistance to organic solvents. Specific examples of applications are their use as dielectric layers for the electronic and microelectronic industry, α-particle barriers, and insulating layers in multichip semiconductor packaging. The incorporation of silicate components into PI matrix in the form of organic-inorganic hybrids can improve the characteristics of the matrix.

The sol-gel process, where the inorganic network is generated insitu in the polymeric matrix is considered to be a convenient route for synthesis of such hybrids. The method allows one to combine the superior thermal stability, high refractive index, low thermal expansion coefficient, and wide range of permittivity of ceramics with the tremendous toughness, ductility, processability, and crack-deflection properties of polymers [1–2]. PI-silica hybrid composites possess a combination of properties and a diversity of applications unobtainable with polyimide or ceramic alone. The dispersion of silica particles, hence its size, depends on the type of interfacial interaction between the two phases. A number of studies have been conducted in the past by Ahmad et al. [3–4], Iyoku et al. [5–7], Mascia et al. [8–10], and others [11–18] on such hybrid PI composites using different organically substituted alkoxysilanes.

In 1990, McGrath and co-workers [11] reported the synthesis of functionalized PI oligomers, terminated by amine, capable of bonding themselves into sol-gel networks. Because only PI oligomers were used in this case, the mechanical properties of the resulting hybrid material were not of particular interest.

The first successful attempt to produce compatibilized PI-silica hybrid composites was carried out by Sen and co-workers [12–13]. They suggested that the metal alkoxide could be chemically bonded to the PI precursor, poly(amic acid) (PAA) through co-hydrolysis of carboxylic groups and thus be maintained in isolated packets. The coordination of the carbonyl group of polyimide to the metal centers on the surfaces of the particles may also play a role in preventing agglomeration of silica particles.

Kakimoto and co-workers [14–17] prepared PI hybrid films through introduction of functional groups in the PI backbone using alkoxylated diamines, and this provided bonding sites for the silica. The properties of the resultant hybrid films differed according to the type and concentration of pendant alkoxy side chains. Films containing silica were tough, and their transparencies increased with increasing ethoxysilyl group content in the PI matrix, which means that increasing the number of bonding sites leads to more interaction between the organic and inorganic phases. Thus, a reduction in the size of silica particles helps in homogenous distribution of such particles within the PI matrix.

Iyoku et al. [5–7] have studied PI hybrids in which the dispersed phase was a silica-siloxane material derived from methyl triethoxysilanes or phenyl triethoxysilanes, which acted as compatibilizers. The size of the dispersed silica was smaller, making the films more transparent than the hybrid containing similar contents of silica but derived from tetraethoxysilane (TEOS) alone.

Ahmad and co-workers [3–4] prepared bonded polyimide-silica hybrids using organically substituted alkoxysilanes, for example, (aminophenyl)trimethoxysilane (APTMOS), (aminoethylaminomethyl)phenethyl trimethoxysilane, or 1-trimethoxysilyl-2-(*m,p*-chloromethyl)phenylethane. The alkoxy ends of these silanes undergo hydrolysis and polycondesation along with TEOS to form silica or polymeric silicates, whereas the other end groups (such as amino or chloro) provide primary or secondary bonds with the PI chains. Some of these aromatic compounds were chosen for their high thermal stability, which is comparable to that of the PI itself. The transparency of the films was considerably improved upon addition of these trimethoxysilane bonding agents. SEM observation on the hybrid films containing the APTMOS showed that the silica particles were smaller and more homogenously distributed, and also with a rougher surface. Mascia and Kioul [8–10] and Menoyo et al. [18] reported the use of γ-glycidyloxypropyltrimethoxysilane (GPTMOS) and isocyanatopropyltrimethoxysilane (ICPTMOS) to bond PAA to the silicate network prior to the condensation reactions, leading to the formation of a ceramer. Better compatibility was achieved, leading to improvement in mechanical strength of the hybrids. The work on PI hybrids prepared through the sol-gel process and various techniques used to compatiblize the systems have recently been reviewed by the present author [19].

In the present work, the PI matrix was prepared by the reaction of a mixture of 1,3-phenylenediamine and oxydianiline (ODA) in dimethylacetamide (DMAc) with equimolar amount of pyromellitic dianhydride (PMDA), which acted as a reference system. On the other hand, modified PI matrix was synthesized by replacing 1,3-diaminobenzene with 2,4-diaminophenol to include pendant hydroxyl groups on the chain. In both cases, silica network was produced from TEOS using the sol-gel process. The effect of introduction of the hydroxyl group into polymer chain was investigated from the viewpoint of the mechanical and thermal properties of PI-SiO_2 hybrid materials and related to the morphology and dispersion of silica particles in the PI matrix.

EXPERIMENTAL

Chemicals

The monomers used to synthesize the polyimide were pyromellitic dianhydride (PMDA), 4,4′-oxydianiline (ODA), and 1,3-diaminobenzene (1,3-DAB). These monomers and tetraethoxysilane (TEOS), triethylamine (TEA), and the solvent anhydrous DMAc were obtained from Aldrich. All chemicals and reagents were of AR grade and used without further purification. 2,4-diaminophenol dihydrochloride (2,4-DAP·2HCl) was obtained from Fluka and HCl was extracted from the salt using TEA.

Preparation of Polyamic Acid Solution

A mixture of ODA and 1,3-DAB (0.025 mol) in molar ratio 95:5, respectively, was placed into a 250 quickfit flask and dissolved in DMAc solvent with stirring. PMDA (0.025 mol) was added into it under complete anhydrous conditions. The reaction (Figure 1) was allowed to proceed at room temperature for 24 h to ensure completion. The inherent viscosity of the PI solutions measured at 25°C was in the range 2.1–2.33 dL/g.

Preparation of the Poly(hydroxy amic acid) Solution

In order to prepare PI precursor with pendent hydroxyl groups, 1,3-DAB was replaced with 2,4-DAP in the PAA synthesis. As only the salt of this compound was available it was purified as follows: In a 100 ml glass bottle, 0.254 g of 2,4-DAP·2HCl (1.25 milli mol) was taken. Stoichiometric amount of TEA was added to neutralize HCl completely. About 10 g DMAc was then added to the mixture. The mixture was stirred for a few minutes and finally filtered under vacuum to remove the precipitate of triethyl ammonium hydrochloride. To this solution of 2,4-DAP, 4.853 g of ODA (23.75 millimol) and 170 g of solvent were added and stirred thoroughly for complete dissolution. An equimolar amount of PMDA (5.622 g, 0.025 mol) was added to react with the diamines. The reaction mixture was stirred for additional 24 h to ensure complete reaction (Figure 2).

Preparation of Hybrid Films via the Sol-Gel Process

Silica network was produced in the aforementioned polymer solutions by carrying out the sol-gel process. A measured amount of TEOS was added to the polymer precursor solution with continued stirring until the solution became homogenous. A stoichiometric amount of water as 10 wt% 0.1 N HCl solution in DMAc was then added. The stirring

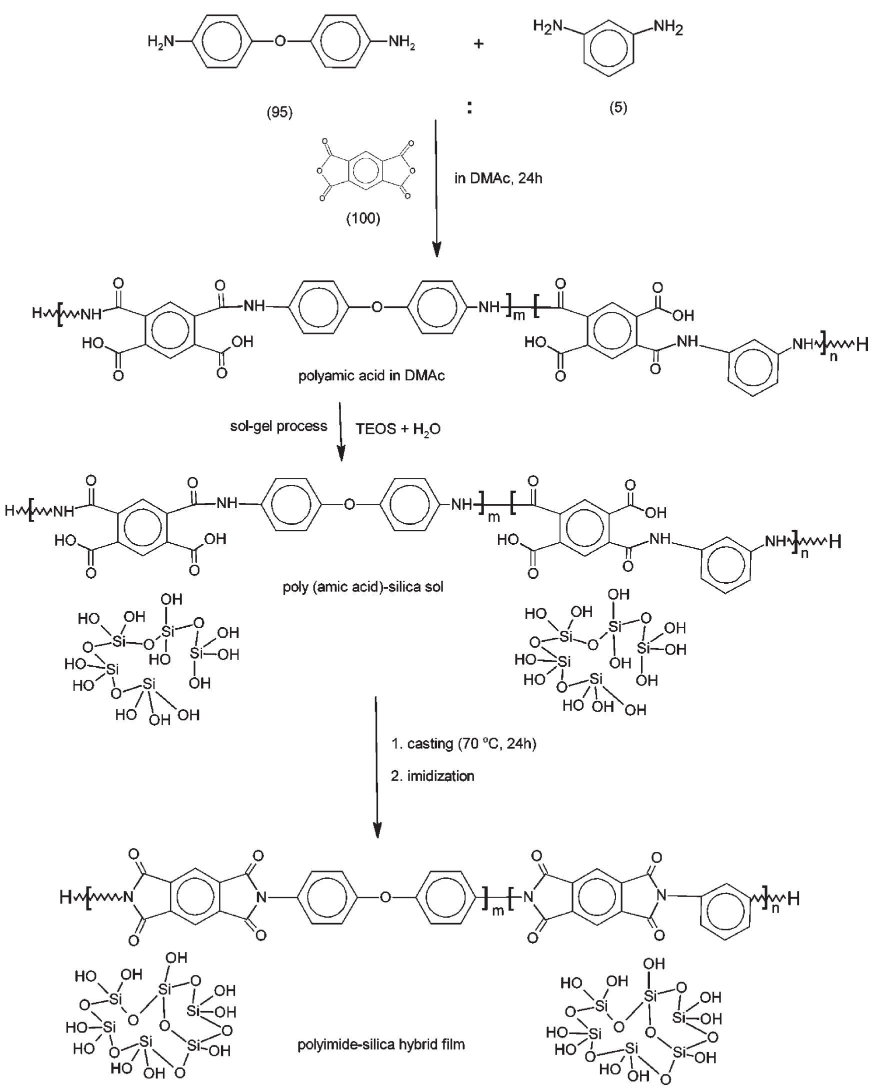


FIGURE 1 Synthesis of PIHs.

continued for 4 h at 60°C. Hybrids with various silica contents ranging from 5–40 wt% were prepared and the films were cast by solvent elution at 70°C. These hybrid films were heated for 1 h at 100°C, 1 h at 200°C, 0.5 h at 270°C, and 1 h at 300°C in sequence to carry out the imidization process. The silica network formation simultaneously took place with the imidization process (Figures 2 and 3). The hybrids from

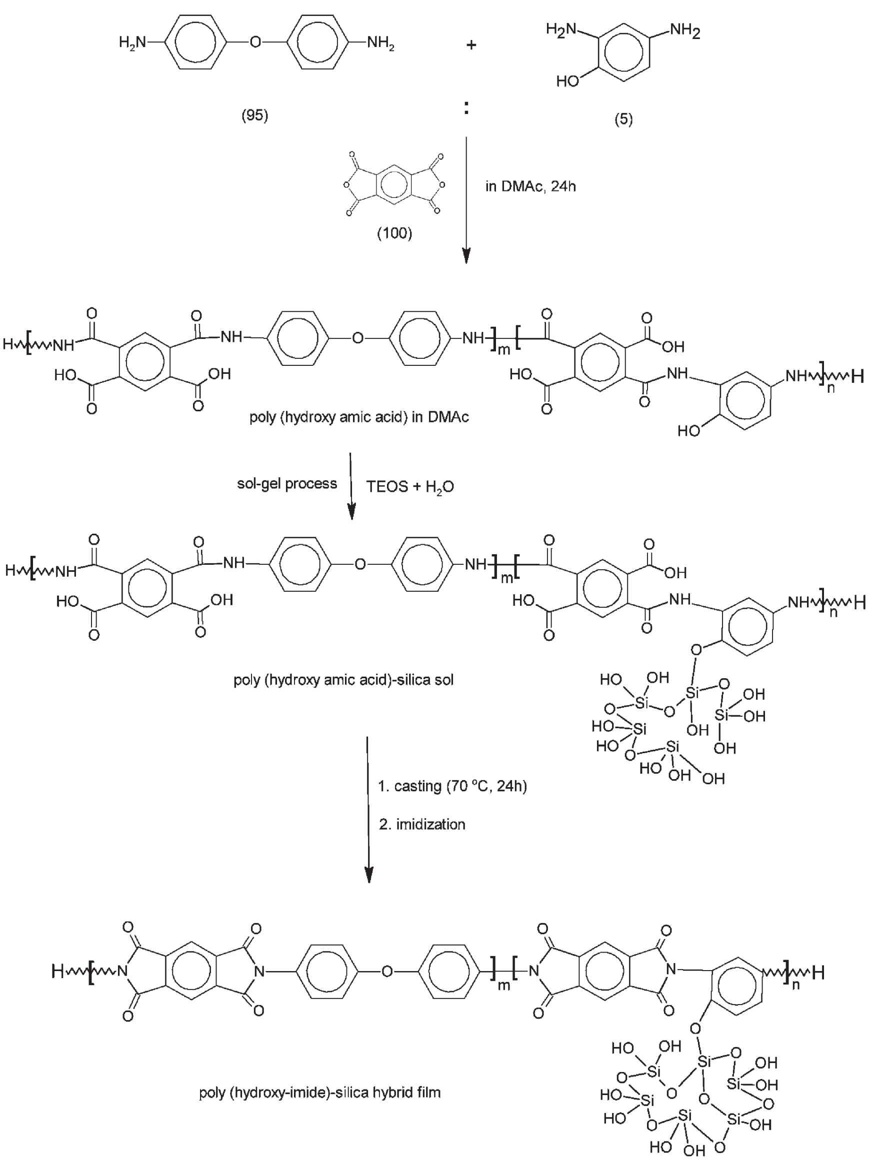


FIGURE 2 Synthesis of PHIHs.

the PI matrix without hydroxyl groups are referred to as PIHs and those with hydroxyl groups as PHIHs. The flow sheet diagram used for the synthesis of the hybrid materials is given in Figure 3.

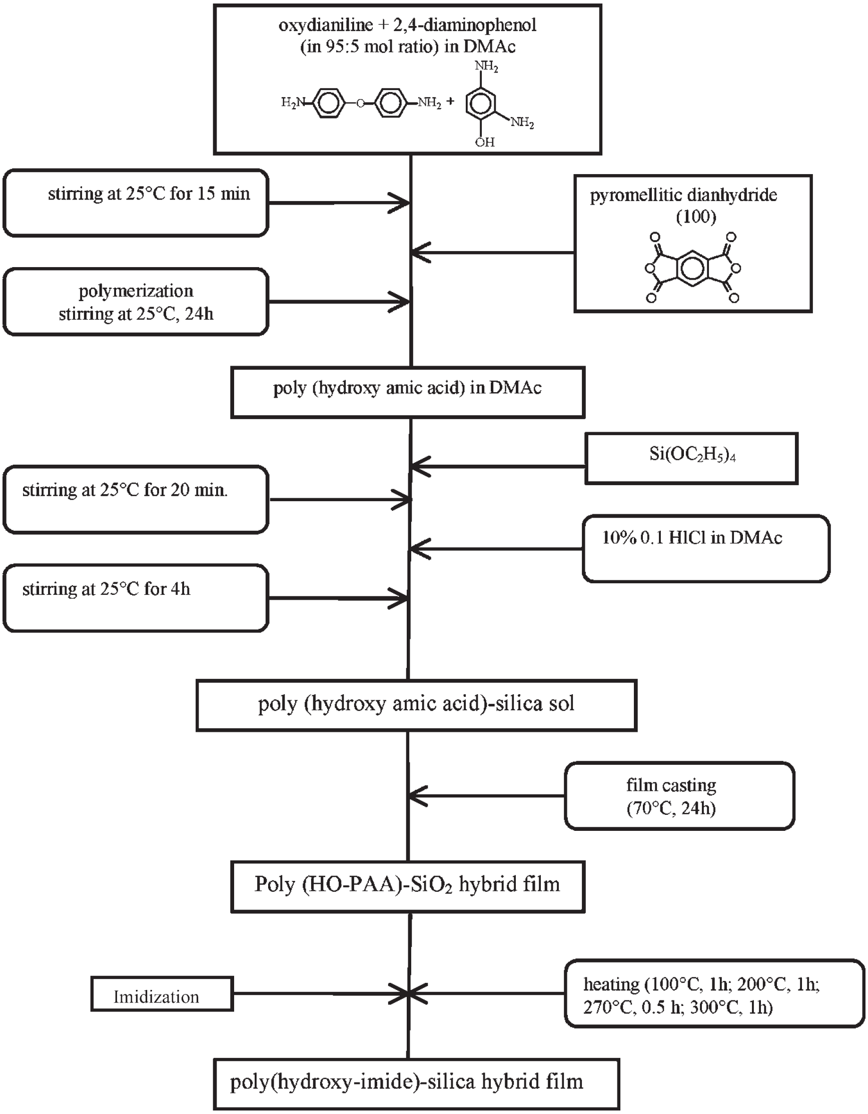


FIGURE 3 Flow sheet diagram for the preparation of the PHIHs film.

Characterization of the Hybrid Films

The process of imidization was measured by FTIR analysis using a Perkin Elmer FTIR 2000 spectrophotometer. The conversion of PAA to PI resulted in a decrease in the amide carbonyl peak at 1660 cm^{-1} and by the appearance of imide carbonyl peaks at 1730 and 1780 cm^{-1}. In addition, the appearance of absorption peaks at 1100 and 830 cm^{-1} confirmed the formation of silicon-oxygen bonds, that is, the silica network.

The scanning electron microscopy (SEM) using JSM-630 Joel scanning electron microscope was carried out on the ruptured samples coated with thin gold layer. Tensile properties of the hybrid materials were studied under ASTM 882 by Instron mechanical testing machine model 4206. The measurements were taken at 25°C with strain rate of 5 mm/min. Dynamic mechanical analysis was performed using TA's DMA model Q-800. The measurements were taken under tension mode in temperature range 100–500°C, at a heating rate of 5°C/min using a frequency of 5 Hz under nitrogen gas at floating pressure of 60 Pa. Thermogravimetric analysis (TGA) was performed on a Shimadzu thermogravimetric analyzer Model TGA-50 in air (50 mL/min) at a heating rate of 10°C/min from ambient to 900°C.

RESULTS AND DISCUSSION

The solutions of the precursor polyamic acid-silica mixtures prior to casting were homogeneous in all cases. In the case of PIHs, the films having up to 5 wt% silica were transparent, and those with more than this concentration were opaque. In the case of PHIHs, the transparent-opaque changing point of the film was 10 wt%. Thus some improvement in the optical transparency was achieved by the introduction of the hydroxyl groups in the matrix polyimide.

SEM Studies

The scanning electron micrographs showing the effect of matrix modification and silica loading on the morphology of the resulting hybrids are given in Figure 4. In case of PIHs there is a gross phase separation of silica particles as seen in Figure 4 (a_1, b_1, c_1) with average diameter of the particles increasing from 0.8 to 10 μm as the silica contents are increased from 10 to 40 wt%. The particle size in case of PHIHs hybrid as seen in Figure 4 (a_2, b_2, c_2) is considerably reduced. The size reduction in case of PHIHs with 10 wt% silica is nearly 90% as compared to PIHs. With 40 wt% silica the particle diameter for PHIHs was in the range of 3.8 to 4.0 μm, that is, with size reduction of around 60%. This system displayed a more adhesive interface between the silica particles and the matrix PI thus leading to homogenous distribution of silica particles and retarding their phase separation from the matrix. Very small amount of monomer with hydroxyl groups (i.e., 5 mol%) in the PI matrix thus retarded the tendency of silica

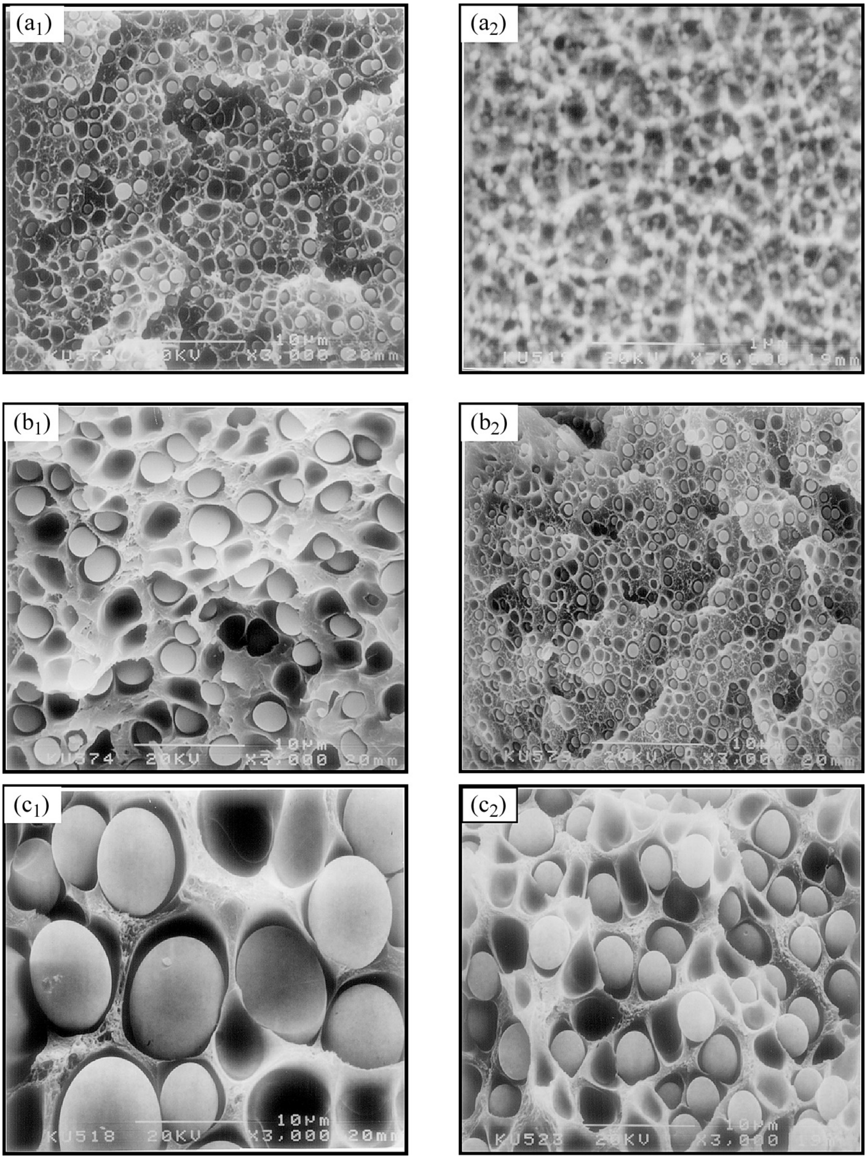


FIGURE 4 SEM micrographs for PIHs with silica wt% (a_1) 10, (b_1) 20, and (c_1) 40, and for PHIHs (a_2) 10, (b_2) 20, and (c_2) 40.

network to agglomerate into large particles in the matrix and made the distribution of the inorganic network more homogenous.

Mechanical Properties

The variation of tensile modulus of PIHs and PHIHs with silica concentration is shown in Figure 5. The stress-strain behavior varies considerably for both hybrids (Table 1). The relative low strength and higher strain for PIHs is typical inert filler behavior whereas higher strength and relatively small strain for PHIHs represents a bonded system. The modulus was found to increase slightly and then decreased with higher silica contents in case of PIHs. The PHIHs showed a higher modulus for similar silica contents. Because PHIHs consist of smaller silica particles as compared to that of PIHs, these particles have high surface to volume ratio. More surface area available to bond/adsorb the polymer chains for given silica content makes the polymer chains stiffer. This explains why the PHIHs had higher Young's modulus than that of the PIHs for the same silica loading.

The variation of tensile strength with the silica content for both types of hybrids is shown in Table 1. For PIHs the strength decreased monotonously with increasing amount of silica. In contrast, the PHIHs showed slightly higher tensile strength than that of pure matrix for

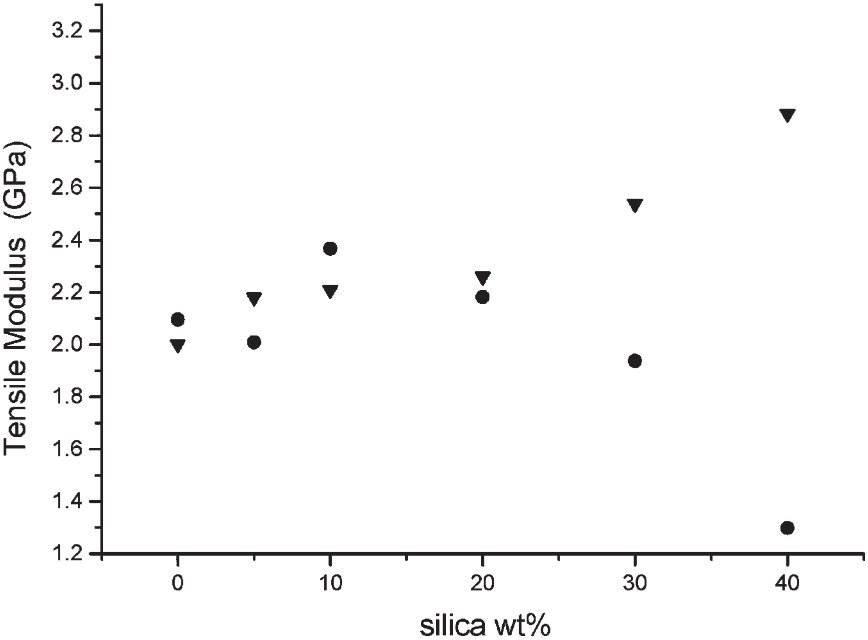


FIGURE 5 Variation of tensile modulus with silica wt% for hybrid films: (a) PIHs (●), and (b) PHIHs (▼).

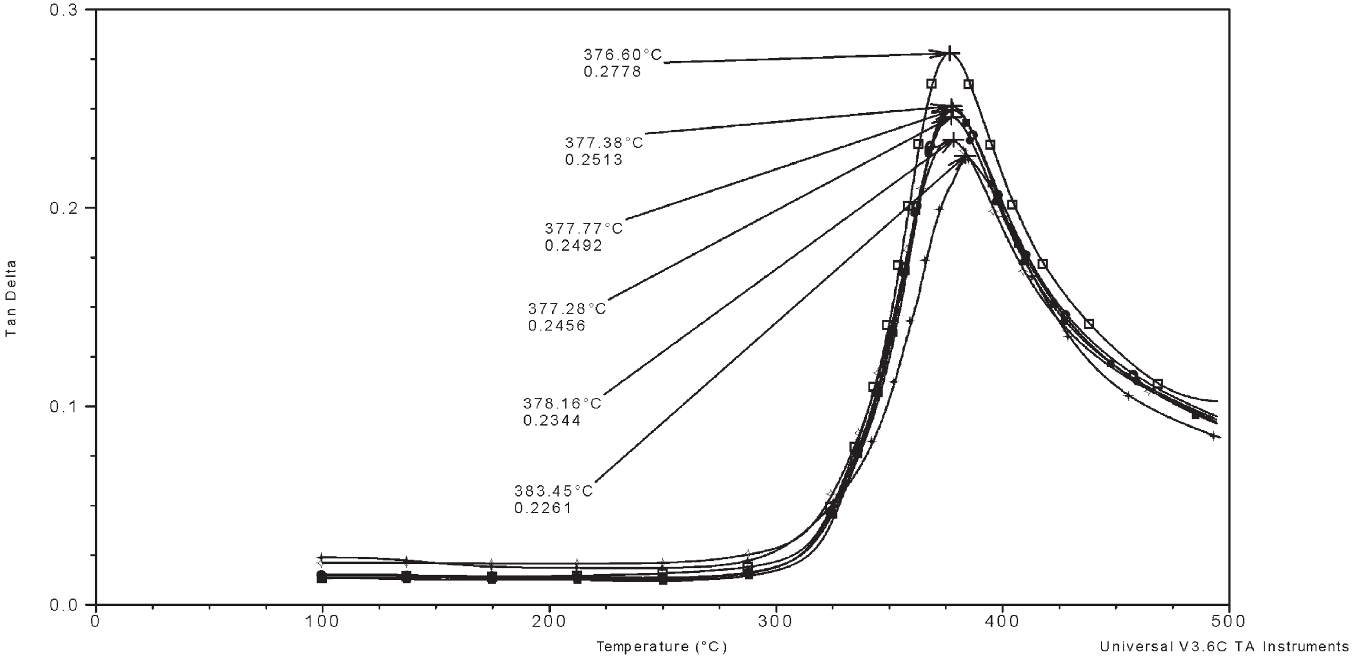
TABLE 1 Tensile Properties of Polyimide-Silica Hybrids at Different Silica Contents

	Tensile strength (MPa)		Elongation at break		Tensile modulus (GPa)	
SiO_2 (wt%)	PIHs	PHIHs	PIHs	PHIHs	PIHs	PHIHs
0	99.63	101.0	0.3895	0.1560	2.096	2.001
5	83.06	102.3	0.3495	0.1500	2.009	2.180
10	75.59	95.31	0.2735	0.1595	2.368	2.209
20	67.42	72.58	0.2565	0.1300	2.182	2.260
30	44.94	56.32	0.1855	0.076	1.937	2.538
40	32.79	48.56	0.0885	0.0605	1.298	2.883

5 wt% silica but then it decreased; however, these values lie well above the values obtained in case of PIHs. Lower strength is expected if there is weak bonding between the organic polymer phase and the inorganic ceramic phase, and in this case the silica acts as non-reactive, non-reinforcing filler. As the external stresses on a plastic composite are transferred from polymer matrix to the filler, the ultimate properties of the hybrid materials are dependent on the extent of bonding between the two phases, the surface area of the filler, and the arrangements between the filler particles. PHIHs system therefore shows better tensile strength as compared to PIHs for the similar silica loading.

Dynamical Mechanical Thermal Analysis

The variation of loss modulus (tan δ) with temperature for PIHs and PHIHs is presented in Figures 6a and b. Comparison of the peak height of the pure PI with that of PIH matrix shows that PIH has lower value of tan δ than that of PI. This is due to greater interaction between the chains due to the presence of polar hydroxyl groups. The magnitude of the tan δ curves decreases with increasing amount of silica (Table 2). This suggests that the mobility of the polymer chains is restricted due to presence of silica in the matrix. The T_g associated with α-relaxation measured from the maxima of the curve for PIHs with 40 wt% silica shows an increase of 5°C from pure PI. On the other hand, for PHIHs an increase of about 12°C in Tg was observed with increasing silica content from zero to 40 wt %. The large reduction in the tan δ curves and increase in T_g for PHIHs can be attributed to the enhanced miscibility/chemical bonding between the organic and inorganic phases because of the hydroxyl groups present along the polymer chains (Figure 2).



(a)

FIGURE 6 (a) Temperature variation of tan δ for the PIHs: silica wt% 0 (□), 5 (■), 10 (**O**), 20 (●), 30 (✧), 40 (✦).

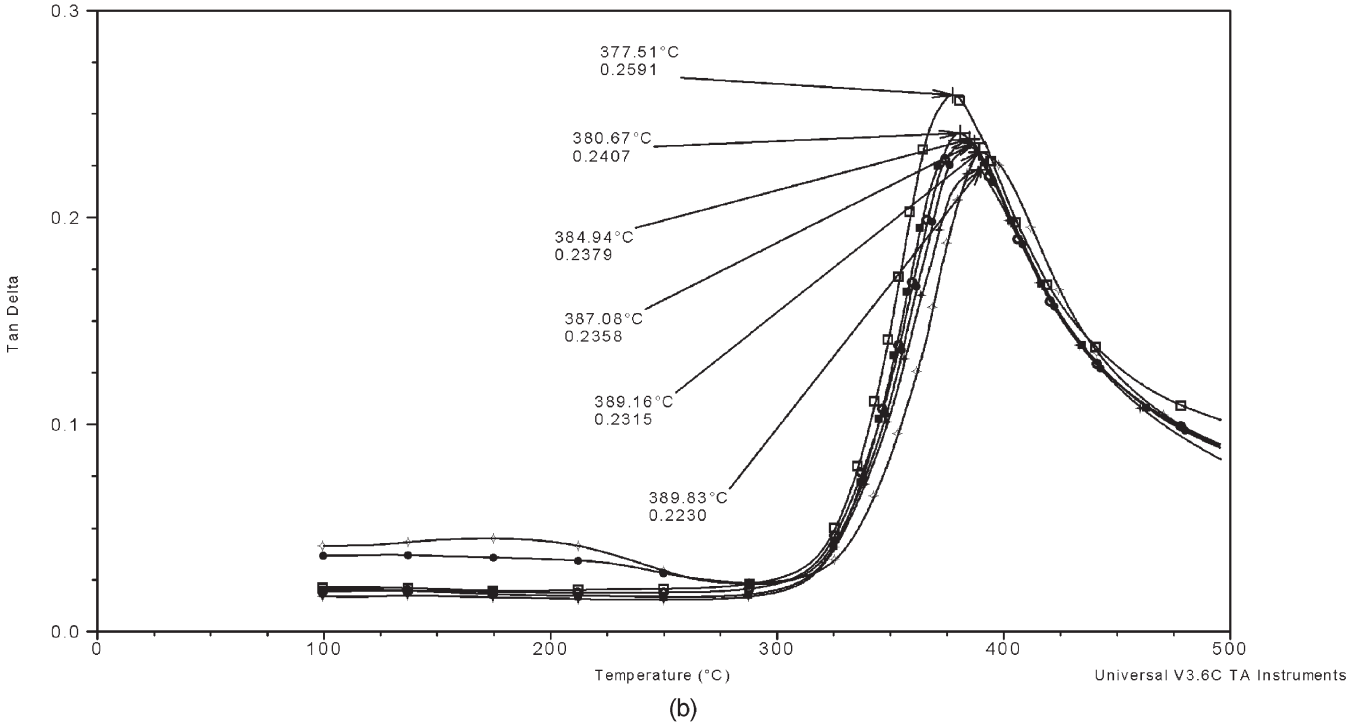


FIGURE 6 (b) Temperature variation of tan δ for the PHIHs: silica wt% 0 (□), 5 (■), 10 (**O**), 20 (●), 30 (✧), 40 (✦).

TABLE 2 Viscoelastic Properties of Polyimide-Silica Hybrids at Different Silica Contents

	Storage modulus (GPa) at 100°C		T_g (°C)		tan δ	
SiO_2 (wt%)	PIHs	PHIHs	PIHs	PHIHs	PIHs	PHIHs
0	1.340	1.690	376.60	377.51	0.2778	0.2591
5	1.719	1.749	377.38	380.67	0.2513	0.2407
10	1.807	1.947	377.77	384.94	0.2492	0.2379
20	2.252	2.316	377.28	387.08	0.2456	0.2358
30	2.317	2.585	378.16	389.16	0.2344	0.2315
40	2.476	2.891	383.45	389.83	0.2261	0.2230

The variation of storage modulus, E′, versus temperature for PIHs and PHIHs systems is shown in Figures 7a and b. As expected, the storage modulus drops by about an order of magnitude in the rubbery region in case of pure PI. The PIHs samples with different silica contents all have higher E′ values in the rubbery region compared to the pure PI (Table 2). In case of PHIHs the storage modulus linearly increases with increasing amount of silica at 100°C. The modulus decreases linearly with temperature up to about 340°C and at T_g a rapid decrease in E′ is witnessed. The rate of decrease of E′, however, was considerably less with large silica contents. Comparatively lower E′ values of PIHs in the rubbery region are due to less interaction between the phases as already confirmed by SEM analysis.

Thermal Stability

The thermal decomposition of PHIHs in air is shown in Figure 8. The decomposition temperature of the pure PI was around 630°C. Slight decrease in the weight at lower temperature for the hybrids could be due the loss of by-products (H_2O, EtOH) from the condensation reaction of the silica network. The degradation behavior of the PHIHs at higher temperature, however, is different as these showed a gradual weight loss with increasing temperature up to 770°C. The effect is more pronounced in case where large percent of silica was used in the matrix. This behavior can be explained as due to increased interaction between the polymer chain and the silica. The polymer chains absorbed or trapped in the network are protected from thermo-oxidative process and this hinders the process of degradation. The weight retained above 770°C in all the hybrids was, however, found to be proportional to the silica contents used in the matrix,

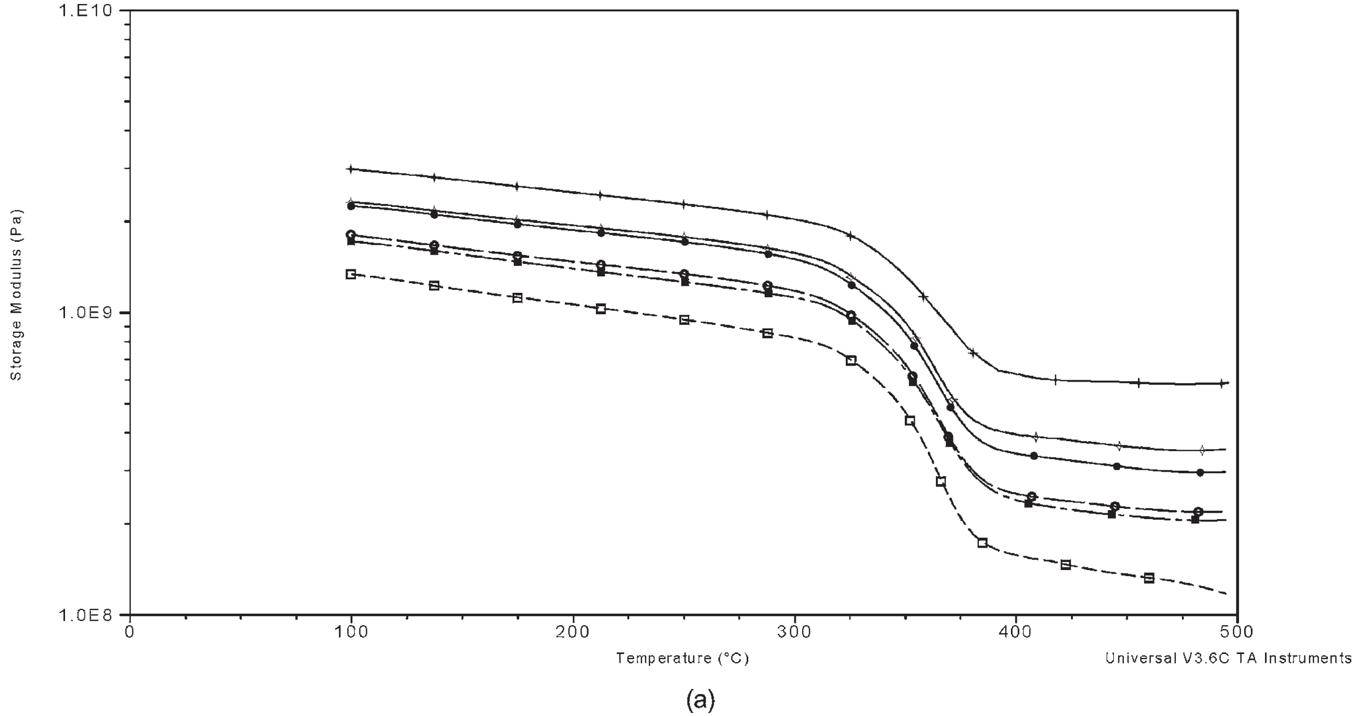


FIGURE 7 (a) Temperature variation of storage modulus for the PIHs: silica wt% 0 (□), 5 (■), 10 (O), 20 (●), 30 (✧), 40 (✦).

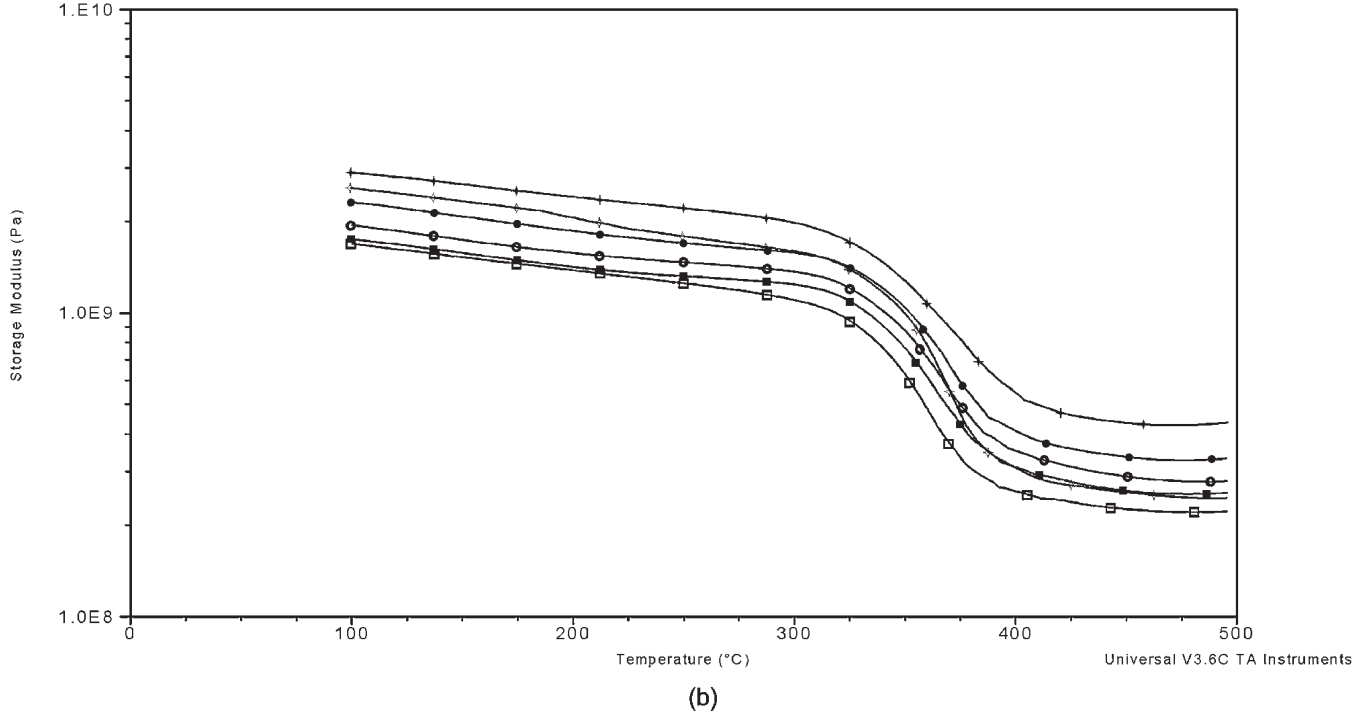


FIGURE 7 (b) Temperature variation of storage modulus for the PHIHs: silica wt% 0 (□), 5 (■), 10 (○), 20 (●), 30 (✧), 40 (✦).

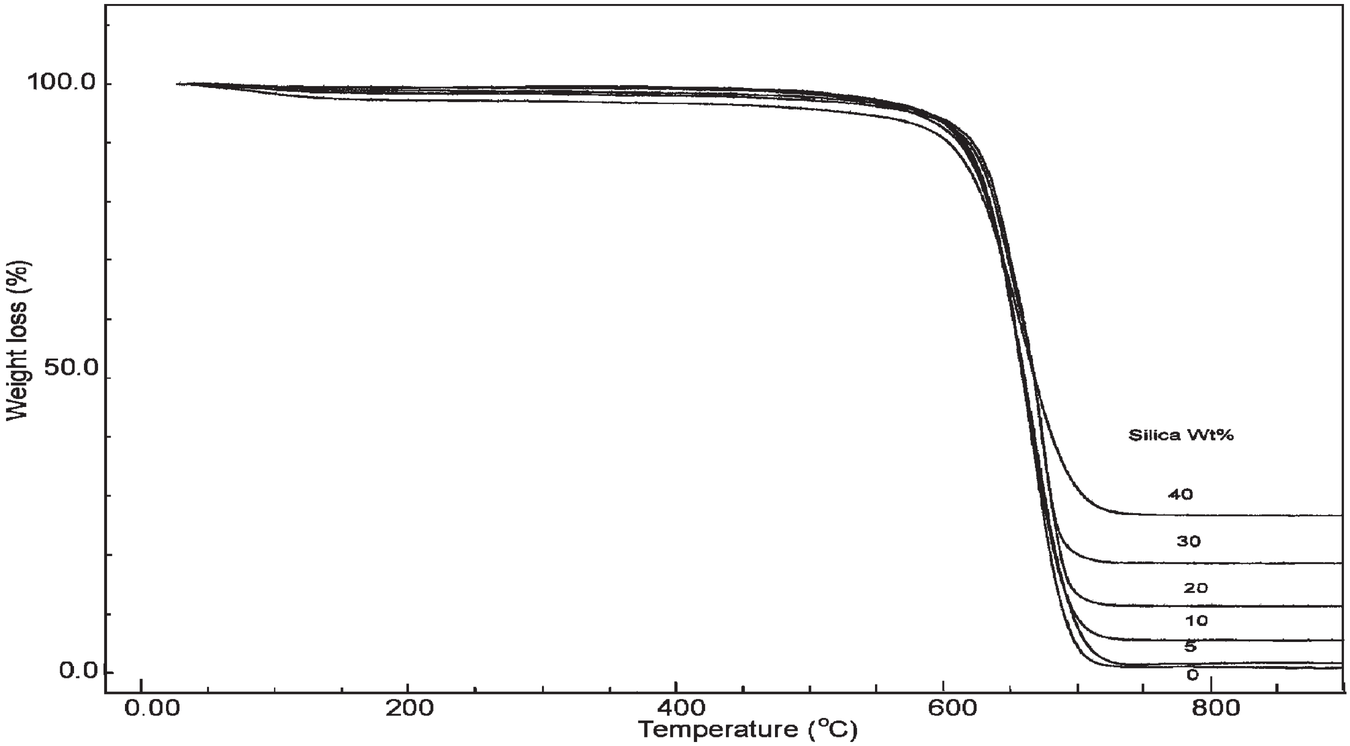


FIGURE 8 TGA thermograms for the PHIHs.

meaning thereby that the sol-gel process was carried out almost completely in the present studies.

CONCLUSIONS

The present studies on PI-Silica hybrids show that few pendant hydroxyl groups on the polymer chain prevent the agglomeration of silica particles thus reducing the particle size and making their distribution more homogenous in the matrix. The improved interfacial interaction between the phases results in better mechanical and thermal properties of the hybrid materials.

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