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The effect of curing conditions and ageing on the thermo-mechanical properties of polyimide and polyimide–silica hybrids

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Abstract The effect of curing conditions and ageing on the thermo-mechanical properties of polyimide and its ceramers has been studied. Polyamic acid (PAA), a polyimide precursor, was prepared by the well known reaction of pyromellitic dianhydride and oxydianiline in dimethylacetamide as solvent. The silica network was developed in PAA solution by hydrolysis and condensation of tetraethoxysilane. The pure PAA films and those with 25 wt% silica content were imidized by six different curing protocols involving both step-wise and isothermal heatings. The dynamic mechanical thermal (DMTA) and thermal mechanical analyses (TMA) were performed on the pure and ceramer films cured under the different imidization conditions. The data for the mechanical properties were obtained for the same films left over for a year. The variations of storage and loss moduli and the glass transition temperature associated with α-relaxation and the linear thermal expansion coefficient have been explained in terms of degree of imidization and the effect of silica network densification under different conditions as a result of imidization and ageing.

Introduction

Polyimides (PIs) and their hybrid composites have been widely used [1, 2] for interlayer dielectrics in semiconductor devices, as wire coatings and as substrate for flexible printed circuits. The diverse nature of industrial applications of PIs stems not only from their outstanding thermal stability and chemical resistance to organic solvents, but also from their high modulus, high mechanical strength, low dielectric constants and good optical properties. The mechanical properties of PIs are further improved by incorporation of silica network in the matrix by sol–gel process [3–5].

PIs are generally obtained [1, 2, 6, 7] by the condensation reaction between dianhydrides and diamines in *N*,*N*-dimethylacetamide (DMAc) as aprotic solvent, forming poly(amic acid) (PAA), a soluble precursor of PI. Tetraethoxysilane (TEOS) is used to develop silica network through the sol–gel process in the PAA solution. Casting by solvent elution technique produces PAA films which can be cyclo-imidized to the final product using different curing methods. The solvents used in the PAA formation generally have high dipole moment and high boiling temperature. The interaction between the solvent and the PI pre-polymer tends to plasticize the film during imidization, which may help the curing process. Microwave energy has recently been used [8–10] to cure PI films. Nevertheless, thermal methods have proved to be more effective and still remain popular.

Although, thermal imidization of PAA has been studied extensively [8–13], there is no systematic comparison available on effect of different imidization conditions used to cyclize the PI precursor and ageing effect on the mechanical properties of the PI and its hybrid films. Understanding the details of the imidization reaction is important in optimizing curing process and ensuring optimum final properties of the PI film. Such a study is particularly important in a system involving the deposition of consecutive layers. The different values of coefficient of thermal expansion (CTE) can be the cause of the residual

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stress, which may result in mechanical failure by de-lamination, cracking and bending.

Various thermal curing conditions have been used to imidize the PAA films. Generally, step-wise heating methods are more popular though many workers have produced PIs using isothermal conditions. Kim et al. [12] and Morikawa et al. [13] have prepared PIs from pyromellitic dianhydride (PMDA) and oxydianiline (ODA) through step-wise heating at 100, 200 and 300 °C for 1 h each. Hisue et al. [14] prepared PIs using similar conditions but the films were heated for 2 h at 100 °C and 1 h each at 200 and 300 °C. Kita et al. [15] in their work imidized the PAA films for 20 h at 200 °C, whereas Kang et al. [16] heated the PAA films at 270 °C for 12 h. Heating for long period of time may also result in some degradation of polymeric material during the curing process. In the present work, using a limited time range (2–3 h) we have used certain isothermal and step-wise thermal curing pathways described in the literature [14–17]. The resulting PI and PI–silica hybrid films were tested for their thermo-mechanical properties before and after being kept under desiccator for 12 months. The glass transition temperature (T_g) measured form the temperature variation of loss modulus, the storage modulus and the thermal expansion coefficient are correlated with the PI structure and its degree of imidization and the ageing process. The effect of densification of silica network structure in the matrix has also been studied.

Experimental

Chemicals

The monomers employed for the preparation of polymer matrices, 4,4-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) were of AR grade and obtained from Fluka. These were used without further purification. Anhydrous dimethylacetamide (DMAc) with water content less than 0.005% was obtained from Aldrich. Tetraethoxysilane (TEOS) was obtained from Gelest Inc. and used as received.

Synthesis of PAAs

The PAA was prepared by the reaction of ODA with stoichiometric amount of PMDA in DMAc. In a typical synthesis, a 250 mL flask provided with magnetic stir bar was charged with 25 mmol (5.006 g) of ODA and 140 g DMAc under an inert atmosphere. The amine solution was stirred for 15 min. A stoichiometric amount of PMDA, 25 mmol (5.453 g), was added to the vigorously stirred amine solution, which resulted in highly viscous PAA solution. The solution was stirred for additional 24 h to complete the reaction. The chemical reactions leading to the formation of PAA is given in Fig. 1.

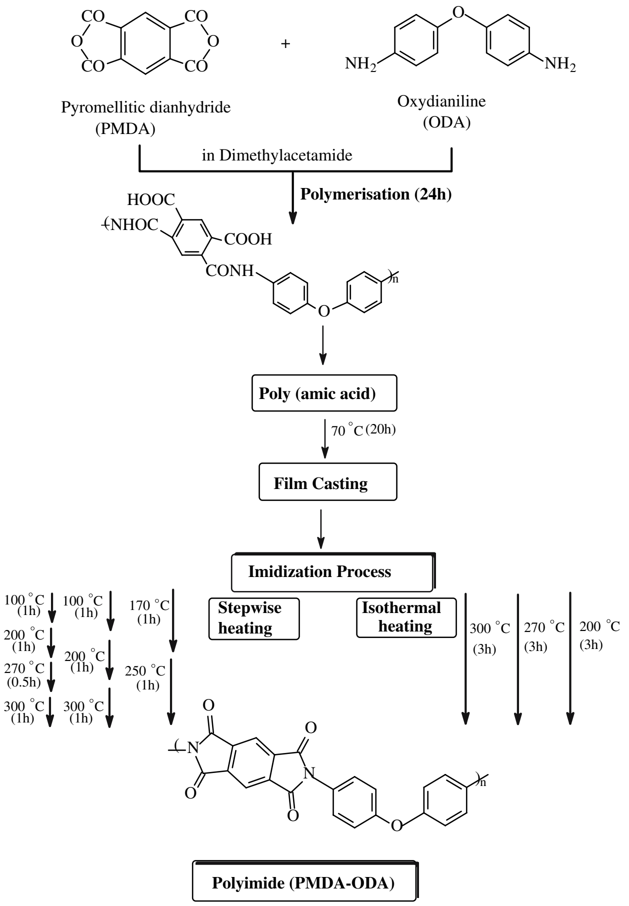


Fig. 1 Curing of PI films under different heating protocols

Preparation of hybrid films

Appropriate amount of TEOS was mixed in the PAA solutions to yield hybrids with 25 wt% of silica content in the matrix. In situ hydrolysis and condensation was carried out by adding the stoichiometric amount of water (as 20% w/w solution of 0.1 M HCl in DMAc) required. The HCl acted as catalyst for the sol–gel process. Resulting mixtures were stirred at 60 °C for 12 h. Thin films were cast on glass Petri dishes. Solvent elution was carried out at 70 °C for 20 h. The chemical reactions leading to the silica network formation has been described elsewhere [18, 19].

Imidization and ageing processes

Imidization process in polymer films depends on many factors, e.g. PAA film thickness, the nature and amount of residual solvent in the film and the curing temperature. The thicker films usually exhibit higher degree of imidization than the thinner ones. In order to study the effect of different curing temperatures only, the residual solvent in the imidization process in PAA films and the film thickness (approximately 20–25 m) were kept constant by casting the PAA films using the same amount of PAA solution in the Petri dish of uniform diameter. The solvent elution in all cases was carried out at 70 °C, for 20 h.

Six curing protocols reported in the literature were used to imidize the PAA and its hybrid films. In each case, the two films of PAA and its hybrid were imidized simultaneously. Using isothermal heating methods the films were heated for 3 h at 200, 270 or at 300 °C and these experimental systems are referred as 1S-200, 1S-270 and 1S-300, respectively. In the successive heating methods, the heating temperature was increased after certain interval of time. These protocols are denoted as 2S-250 (heating at 170 and 250 °C for 1 h each), 3S-300 (heating at 100, 200 and 300 °C for 1 h each), 4S-300 (heating at 100 °C for 1 h, 200 °C for 1 h, 270 °C for 0.5 h and 300 °C for 1 h). The PI and its hybrid films were kept in a vacuum oven at 100 °C for 24 h before analysis. The ageing effect on the degree of imidization and further cross-linking of silica-network in these films was measured after keeping the film at room temperature under dry condition for 12 months.

Characterization of the hybrid materials

Visco-elastic properties of virgin and the aged PI and its hybrid films were measured using Dynamic Mechanical Analyzer Q-800 (TA Instruments, USA) at a fixed frequency of 5 Hz. All the measurements were carried out in tensile mode in the temperature range 100–500 °C under nitrogen gas at a floating pressure of 60 Pa. A ramp value of 5 °C/min was used. The CTE values were determined using Shimadzu Thermal Mechanical Analyzer model TMA-60 in the temperature range 50–400 °C. The measurements were made on 15 mm long films under a tension load of 2 g. The heating rate of 10 °C/min was maintained and the experiments were performed under nitrogen gas at flow rate of 0.05 L/min.

Results and discussion

The PI and their hybrid films obtained using different curing conditions all were tough but it was not possible to obtain mechanically strong films under 1S-200 curing condition. The visco-elastic properties of such films, therefore, could not be studied.

The variation of loss modulus (tan δ) with temperature for pure PIs cured under different heating protocols is given in Fig. 2. The maxima of such curves gives a measure of T_g associated with the α-relaxations in the PI chain (Table 1). The T_g values using 3S-300 and 4S-300 protocols were relatively low (356–357 °C). The 2S-250 heating protocol gave a higher T_g (363 °C) whereas maximum values (366–368 °C) were obtained for 1S-270 and 1S-300 systems. The magnitude of the tan δ curves (Table 1) decreases in the same order as the PI films showing a less viscous response and more elastic behavior with imidization conditions involving higher temperatures. This can be attributed to the higher degree of cyclization, which makes the polymer chain more rigid and the T_g and the damping of tan δ curve is subsequently increased.

The β-relaxation below the T_g associated with local bond rotations and molecular segment motions along the polymer backbone is predominant in systems cured under 2S-250 and 1S-270 heating protocols (Fig. 2). The magnitude of this relaxation is proportional to the concentration of such segments, which seems to be greater in case of 2S-250. Such small-scale movements are possible because of loose molecular packing as such systems were not heated ultimately to a high (300 °C) temperature during the curing process.

The loss modulus (tan δ) variation with temperature for the PI–silica hybrids is shown in Fig. 3. The values of T_g are shifted to higher temperatures as compared to the PI cured under similar conditions (Table 1). The magnitude of tan δ decreased with the addition of silica content, which is a typical behavior of particle filled system. The increase in the T_g recorded for the hybrid systems cured under 1S-270 or 1S-300 was the maximum. The tan δ curve around T_g in case of 1S-270 and 1S-300 was also characterized by significant broadening as compared to the pure PI. The magnitude of tan δ peak at the T_g is a measure of energy damping characteristic of the material and its breadth is indicative of the cooperative nature of the relaxation process of the polymer chains. The silica network produced under 1S-300 and 1S-270 conditions is responsible for large non-cooperative movements in the hybrids as compared to pure PIs cured under the same conditions. This large damping in the tan δ curves and the increase in T_g can be attributed to relatively more rigid or highly condensed inorganic network, which reduces the mobility of the organic polymer chain thus resulting in a large increase in the T_g for such systems.

The variation of storage modulus, E' versus temperature for PIs is shown in Fig. 4. The storage modulus drops by almost an order of magnitude in the rubbery region in case PIs cured by step-wise methods. In the isothermal heating, however, there is significant difference in these curves above the T_g. The modulus values are retained in the rubbery plateau region for the systems where the samples were heated at higher temperature for longer time. Some polymer degradation also occurred in isothermal heating at 300 °C, which is evident from the slightly less value of storage modulus for 1S-300 system as compared to IS-270.

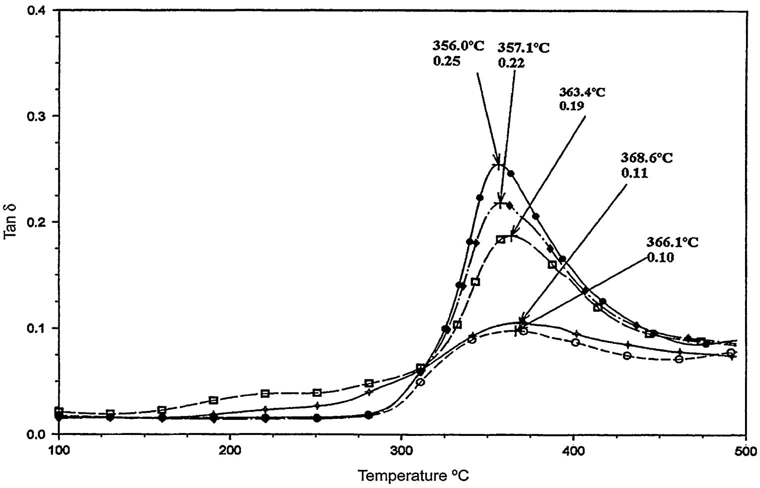


Fig. 2 Temperature variation of tan δ for PIs cured under different conditions: 3S-300(●), 4S-300(♦), 2S-250(□), 1S-270(□),1S-300 (○)

Table 1 The visco-elastic properties of PIs and PI–silica hybrids cured under different conditions

Imidization protocol	T_g (°C)		Storage modulus (GPa)		Loss modulus(tan δ)	
	Pure PI	PI/SiO$_2$	Pure PI	PI/SiO$_2$	Pure PI	PI/SiO$_2$
3S-300	356(370)	367(377)	2.16(2.65)	3.01(2.80)	0.255(0.238)	0.215(0.216)
4S-300	357(369)	366(377)	1.9(2.06)	2.90(3.06)	0.218(0.214)	0.201(0.196)
2S-250	363(375)	371(377)	2.16(2.47)	3.24(3.30)	0.187(0.179)	0.158(0.161)
1S-270	369(380)	383(389)	2.30(1.94)	3.38(2.99)	0.106(0.120)	0.083(0.093)
1S-300	366(383)	390(397)	2.24(2.37)	2.62(3.23)	0.098(0.106)	0.077(0.068)

The values given in brackets are for the aged samples

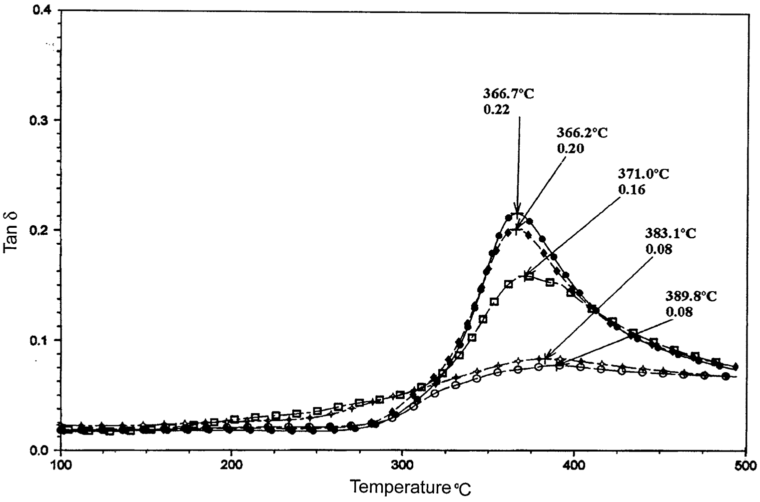


Fig. 3 Temperature variation of tan δ for PI–silica hybrids cured under different conditions: 3S-300(●), 4S-300(♦), 2S-250(□), 1S-270(□),1S-300 (○)

In general, higher modulus values retained at temperatures above the T_g are due to increased cross-linking reactions. The PI–silica hybrids all have higher E' (Fig. 5) values at 100 °C (Table 1) as compared to the pure PI indicating good adhesion between the organic and inorganic phases. The modulus decreases linearly with temperature up to about 300 °C and at the T_g a rapid decrease in E' is witnessed. The rate of decrease of E', however, was considerably low with 1S-270 and 1S-300 systems in the rubbery region above the T_g. The higher values of E' above the T_g with silica loading in such systems is due to increased degree of syneresis process involving silica network.

The effect of ageing on thermal–mechanical properties of PIs and PI–silica hybrids cured under different heating

Fig. 4 Temperature variation of storage modulus for PIs cured under different conditions: 3S-300(●), 4S-300(♦), 2S-250(□),1S-270(□),1S-300 (○)

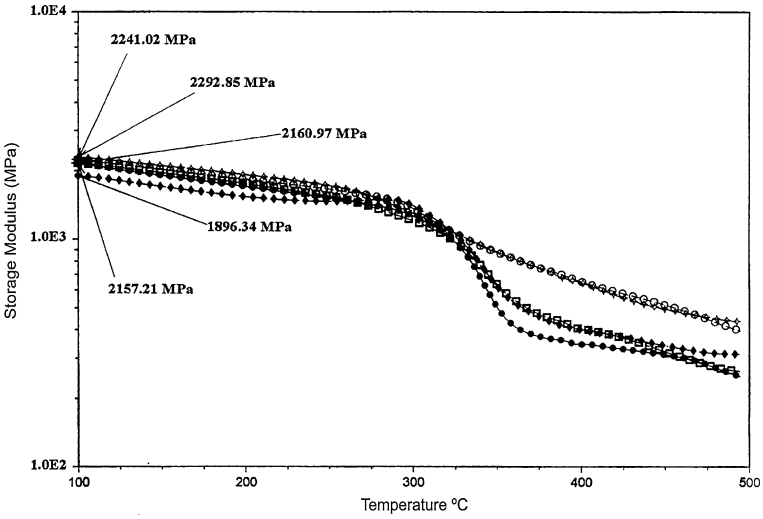
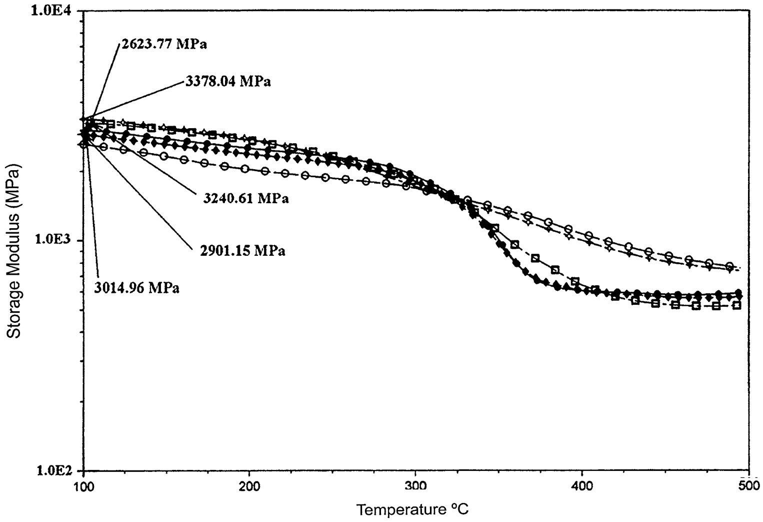


Fig. 5 Temperature variation of storage modulus for PI–silica hybrids cured under different conditions: 3S-300(●), 4S-300(♦), 2S-250(□), 1S-270(□), 1S-300 (○)



protocols was also studied by keeping these samples for a period of 12 months at room temperature under anhydrous conditions. The visco-elastic data obtained on these samples have been given in Table 1. Figures 6 and 7 show a comparison of the temperature variation of storage and loss moduli for the virgin and aged samples of PI and its hybrids cured under two heating protocols i.e., 1S-300 and 2S-250, respectively. In general, the storage modulus increases with the ageing process. There is a significant increase in the value of T_g and in general slight damping of the tancurves taking place with the aged samples. It seems that the cross-link density of the silica network and the degree of imidization of the polymer chain slightly increases as the samples are kept for long time. The dangling or uncondensed parts of the network and the polymer chain due to thermal motions are able to slowly orient themselves thus leading to cyclization/imidization reaction which enhances the rigidness of the film thus increasing the storage modulus and the T_g.

The TMA analysis on PI and PI–silica hybrids with 3S-300 and 1S-300 protocols was performed before and after ageing for 12 months. The results for the virgin samples for these two protocols are shown in Figs. 8 and 9, respectively. The CTE value for PI matrix was 48 ppm/°C for 3S-300 and 51 ppm/°C for the 1S-300 conditions. This is found to be in agreement with the value of 48.5 ppm/°C reported recently by Southward et al. [20]. The CTE values for the PI hybrids containing 25 wt% silica was reduced considerably, i.e., 35 ppm/°C and 40 ppm/°C for the two films, respectively. The values obtained for the same films after ageing were in the same range. In both virgin and aged films almost a constant value of CTE in the temperature 50–300 °C range is very significant for PI–silica hybrids cured under 1S-300 conditions (Fig. 7). This is attributed to higher % of imidization, adsorption of PI chain on the silica network which reduces its mobility, and increased cross-link density of silica as the system was cured for relatively longer time at higher temperature. As

Fig. 6 Temperature variation of storage modulus and tan delta for the films cured under the 1S-300 imidization protocol; PI-pure (○), Pl pure-aged (●), Pl–silica hybrids(□), Pl–silica hybrids-aged (■)

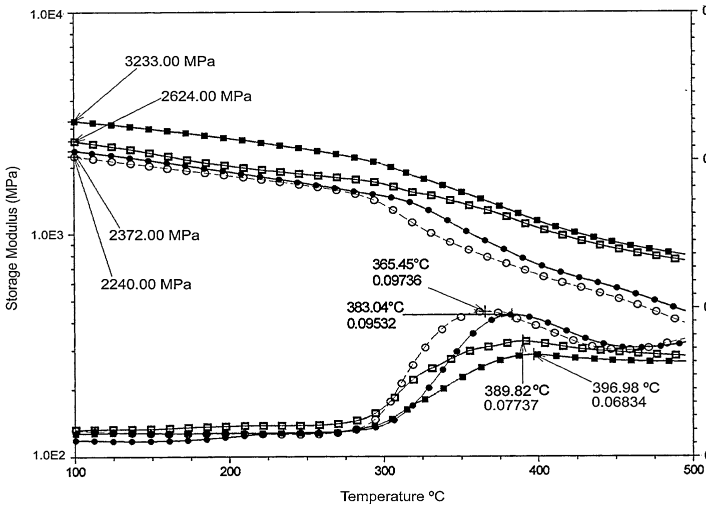
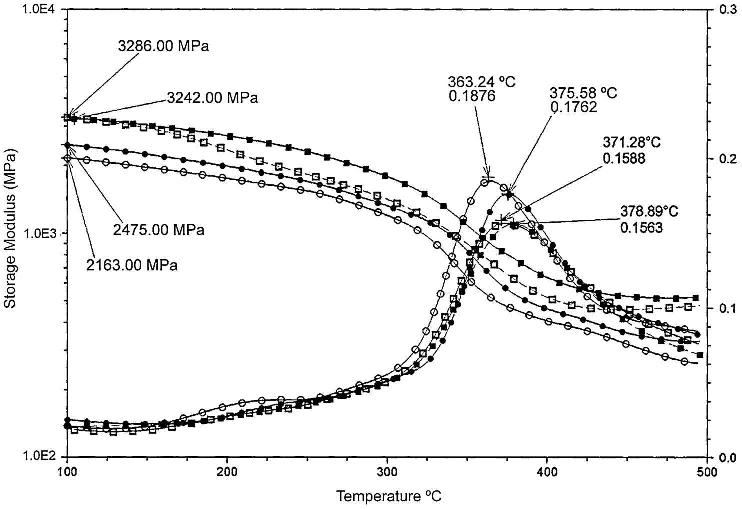


Fig. 7 Temperature variation of storage modulus and tan δ for the films cured under the 2S-250 imidization protocol; PI-pure (○), Pl pure-aged (●), Pl–silica hybrids (□), Pl–silica hybrids aged (■)



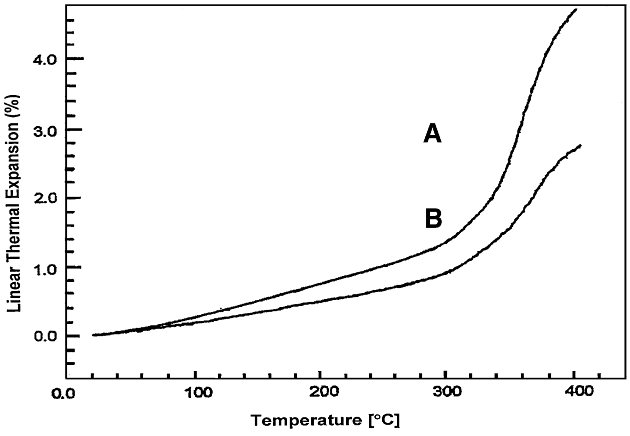


Fig. 8 Thermal mechanical analysis results for (**A**) pure Pl (**A**) and Pl–silica hybrid with 25% silica (**B**) cured under 3S-300 heating protocol. The CTE values were calculated from the slope between 50 °C and 300 °C

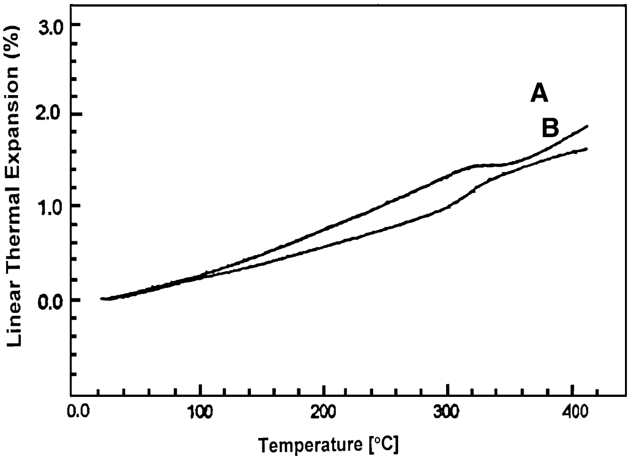


Fig. 9 Thermal mechanical analysis results for pure Pl (**A**) and Pl–silica hybrid with 25% silica (**B**) cured under 1S-300 heating protocol. The CTE values were calculated from the slope between 50 °C and 300 °C

the PI films are used in printed circuit boards and as interlayer dielectrics, the thermal expansion coefficient of the material plays an important role. The PI–silica system cured under 1S-300 can, therefore, be a useful option for such applications.

Conclusions

PI and PI–silica hybrid films imidized under different heating protocols were studied for their thermo-mechanical properties. The hybrid films imidized under isothermal heating at 300 °C for 3 h gave a high value of T_g, retained high value of modulus even at elevated temperatures and exhibited low and uniform values of CTE in the temperature range 50–400 °C. The aged samples of PI and its hybrids kept at room temperature for 12 months show a slight improvement in their mechanical properties in comparison to the virgin samples.

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