High Performance Polyquinoline/Bismaleimide Miscible Blends

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Polyquinoline/bismaleimide blend thin films containing 5−60 wt % bismaleimide contents have been investigated as high-temperature resistant materials. Dynamic mechanical analysis and thermal gravimateric analysis were performed to evaluate the mechanical and thermal properties of blend thin films. From thermogravimetric analysis, 5% weight loss was observed between 450 and 535 °C for blend thin films containing 5−60 wt % bismaleimide loading. The glass transition temperatures were found to be between 275 and 360 °C for blend thin films containing 5−50 wt % bismaleimide contents. The prepolymer blend thin films showed thermosetting behavior on curing at elevated temperatures. These high performance miscible thermosetting polymers obtained by blending of bismaleimide exhibit interesting mechanical, thermal, and solvent-resistant properties without sacrificing the inherent physical properties of the polyquinoline backbone.

Introduction

High-temperature-resistant materials have attracted a great deal of interest in aerospace and microelectronics industries.[1−12] Polyimides are one of the most important classes of high-temperature-resistant materials that show interesting physical and electrical properties over an extremely wide temperature range. Polyimides are being used in electronics, aerospace, and various other industrial applications.[13−23] However thermal processing of polyimides from precursor polyamic acid solutions is accompanied with formation of byproducts that cause significant changes in the chemical structures and physical properties such as modulus, thermal expansion, orientation, and glass transition temperature

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(T_g) of cured polyimide films. The conventional poly-imides show a dielectric constant (ϵ) on the order of 3.0 and higher.[20] Polyimide backbones comprised of polar carbonyl (C=O) groups cause higher moisture absorption in these polymeric systems which consequentially increase the dielectric constant,[20] electric anisotropy,[17] and copper ion diffusion. However, fluorinated and nanofoamed polyimides offer comparatively lower dielectric constant ($\epsilon = 2.0$) and lower moisture absorption.[9,18] Likely other polymeric materials with low dielectric constant have been investigated for microelectronics packaging.[3,15,16] Polyquinolines discovered by Stille in 1976 are another important class of high-temperature-resistant polymeric materials that exhibit thermal stability over 500 °C.[24–30] Beever and Still[29] reported a low dielectric constant of 2.5 at 10^5 Hz for polyquinoline thin films. Hendricks and co-workers[31] evaluated polyquinoline (PQ-100) thin films for microelectronic applications and reported dielectric constants of 2.5–2.6 in the GHz frequency range and about 2.8 in the kHz range. PQ-100 also shows a low moisture absorption of about 0.3% on boiling in water for 24 h, whereas polyimides showed 6-fold increase under similar conditions.[32] Polyquinolines show excellent solubility in organic solvents and therefore can be easily processed into flexible thin films. Compared to the polyimides, polyquinolines offer a very low dielectric constant, exceptionally low moisture absorption, and better mechanical and thermal properties.[31–33] A general distinction between polyimides and polyquinolines is that the former involves the formation of byproducts during the imidization process that has a pronounced effect on the various physical properties while no such effects occur in polyquinolines. It is the quinoline units
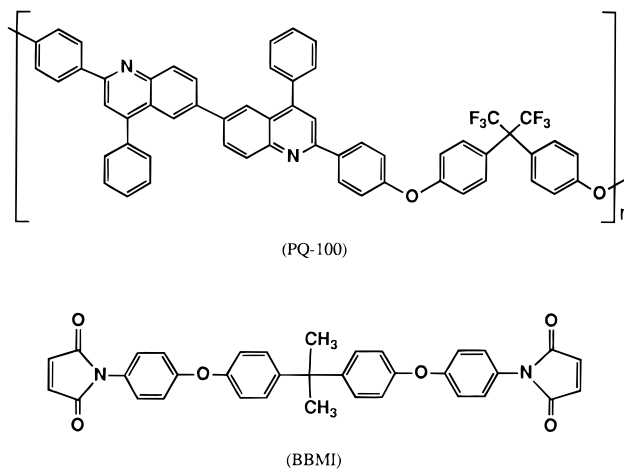

Figure 1. Chemical structures of polyquinoline designated PQ-100 and BBMI.

that imparts low dielectric constant and higher thermal as well as chemical stability to polyquinolines.

High-temperature-resistant polymer matrix–carbon fiber composites consisting of thermoplastic polyimides and thermosetting bismaleimide have been extensively studied for aerospace applications.[1,2] The curing reactions of bismaleimide composite matrixes have earlier been systematically studied by Fourier transform infrared spectroscopy, differential scanning calorimetry, and other spectroscopic techniques to understand the chemistry that occurs when the bismaleimide cures.[34,35] Like polyimides, polyquinolines are also inherently thermoplastic polymers. Therefore, to introduce thermosetting properties for applications in microelectronics packaging, we have blended them together with bismaleimides. Bismaleimides form a network of highly crosslinked polymers on heating at elevated temperatures that introduce thermosetting properties to parent thermoplastics, which is one of the simplest and most effective methods for preparing thermosetting polymer blends. We have obtained high-performance polyquinoline/bismaleimide blend thin films without sacrificing the inherent physical properties of the polyquinoline backbone. In this paper, processing, dynamic mechanical, and thermal stability properties of polyquinoline thermoplastic–bismaleimide thermoset blend thin films are reported. The effects of curing conditions on glass transition temperature, thermal degradation, and mechanical properties are discussed. The solvent resistance of polyquinoline/bismaleimide blend thin films was also investigated.

Experimental Section

2,2-Bis(4-maleimide phenoxyphenyl)propane, abbreviated as BBMI, was purchased from Mitsui Chemical Inc. and was used as received. Figure 1 shows the chemical structures of polyquinoline, designated PQ-100, and BBMI used in this study. The generic chemical structure of PQ-100 discussed in this paper is entirely different than that reported by

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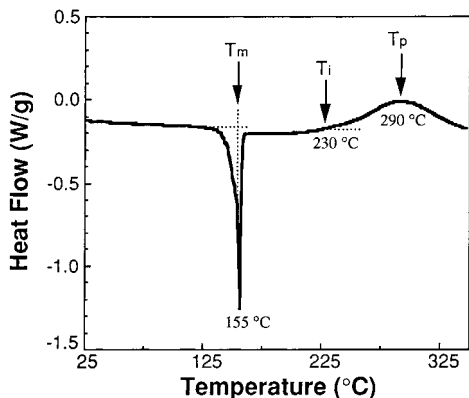(35) Pascal, T.; Sillion, B., Eds., *Advances in Interpenetrating Polymer Networks*; Technomic: Lancaster, PA, 1994.

Figure 2. DSC plot of BBMI powder sample recorded at a heating rate of 5 °C/min.

Figure 3. TGA plots of PQ-100 and BBMI samples.

Hendricks and co-workers.[31] If viewed carefully, the chemical structures of PQ-100 and BBMI have some common structural features which gives rise to a great comptability of these two systems to form miscible blends. The PQ-100 thin films show low dielectric constant at higher frequencies ($\epsilon = 2.5$ at 1 GHz), extremely low moisture absorption, good adhesion, high thermo-oxidative stability and glass transition temperature.[36,37] The moisture absorption of PQ-100 thin films was found to be 6−12% lower than that of polyimides films such as Kapton-H (Du Pont), PIQ-100 (Hitachi), and Upilex-R (ICI).

To prepare blends, 5−60 wt % of BBMI was dissolved in a cyclopentanone solution of PQ-100. Samples used in this study are assigned here on the basis of the BBMI contents and will be referred to as follows in the text: A-1 (PQ-100 only), B-1 (5 wt % BBMI), C-1 (10 wt % BBMI), D-1 (15 wt % BBMI), E−1 (20 wt % BBMI), F-1 (30 wt % BBMI), G-1 (40 wt % BBMI), H-1 (50 wt % BBMI), and I-1 (60 wt % BBMI). These blends were prepared at room temperature by mixing of the polyquinoline thermoplastic with a bismaleimide. The PQ-100/BBMI mixtures form homogeneous miscible blends and no phase separation was visible. The highly transparent yellow thin films were obtained after annealing. Figure 2 shows the differential scanning calorimetry (DSC) plot for a 10 mg BBMI powder sample recorded at a heating rate of 5 °C/min. BBMI shows a melting point (T_m) of around 155 °C, polymerization onset temperature (T_i) of the exothermic peak at 230 °C, and a polymerization peak temperature (T_p) of exothermic reaction around 290 °C. The thermal polymerization reaction of BBMI proceeds exothermically via double bonds. Therefore, viewing the cross-linking process of BBMI, we selected 280 and 300 °C as the curing temperatures for the PQ-100/BBMI blend thin films. The prepolymer (B-stage) films were prepared by removing solvent under 200 °C, which is lower than the exothermic temperature of BBMI. To examine the effect of curing, the prepolymer blend thin films were cured at 280 °C for 1 and 3 h and 300 °C for 1, 2, and 3 h.

Thermomechanical testing was performed with a dynamic mechanical analyzer (DVA-200) at a fixed frequency of 10 Hz, scanning the thin films over a temperature range of 20−400 °C in a nitrogen atmosphere. The heating rate of the sample thin films was kept 5 °C/min. DSC of the BBMI powder sample was recorded with a differential scanning calorimeter (model 910, Du Pont Instruments). Thermal degradation of powder and thin films of PQ-100 and BBMI were studied under a nitrogen atmosphere from room temperature to 1000 °C at a heating rate of 10 °C/min by using a thermogravimetric analyzer (model Hi-Res TGA 2950). Thermal characteristics of all blend thin films cured at 280 °C for 1 h were recorded under identical conditions. To examine the thermal stability of PQ-100/BMMI miscible blends, isothermal TGA of cured
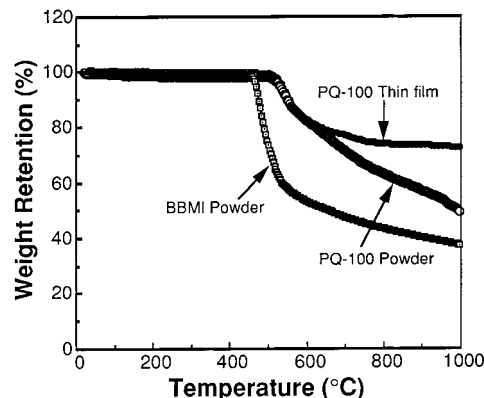
thin films was recorded for 3 h at 300 and 400 °C under a nitrogen atmosphere.

Results and Discussion

PQ-100 shows good solubility in cyclopentanone and can be easily processed into free-standing, tough thin films. Thermal, mechanical, and dielectric properties of PQ-100/BBMI blend thin films are significantly affected with increasing BBMI contents, as we have recently reported.[37] The PQ-100 thin films show a dielectric constant of 2.90, 2.80, and 2.50 at kHz, MHz, and GHz frequencies, respectively. The PQ-100 thin films have a dielectric constant of 2.90 at the kHz range, whereas on loading BBMI, the dielectric constant increased to 3.10 for the blend thin films containing 50 wt % BBMI contents. Likely, the tan δ increases from 0.004 to 0.007 as the BBMI contents increased from 0 to 50%. PQ-100 thin films show about 9% elongation that decreases to 6% for the blend containing 50 wt % BBMI, this also indicates that there is a continuous thermoplastic phase. However, no significant change in tensile strength of PQ-100/BBMI blend thin films was observed with increasing BBMI contents. These interesting properties of PQ-100 are related to its high glass transition temperature and the restricted motion of phenylene groups in the polyquinoline backbone. We have introduced thermosetting properties in PQ-100 by blending it with BBMI without sacrificing the inherent physical properties of the polyquinoline backbone.

Figure 3 shows the thermal stability of PQ-100 and BBMI samples. PQ-100 thin films cured at 280 °C for 1 h showed 2, 5, and 10% weight losses at 530, 538, and 558 °C, respectively. TGA characteristics of PQ-100 thin films and powder samples were found to be similar. Both PQ-100 thin films and powder exhibited excellent thermal stability and no weight loss was observed up to 500 °C. BBMI showed a 2% weight loss at 455 °C and a 5% weight loss at 471 °C. As evident from the TGA curves, PQ-100 shows much higher thermal stability compared to BBMI powder. Figure 4 compares the TGA curves of PQ-100/BBMI blend thin films containing 5 wt % (B-1) and 50 wt % (H-1) BBMI contents. The 5% weight loss was observed at 530 and 450 °C for blend thin films containing 5 and 50 wt % BBMI loading, respectively. This indicates a decrease of 80 °C in thermal stability with a 10-fold increase in BBMI loading. Over entire temperature region, the B-1 sample shows lower thermal degradation than that of the H-1

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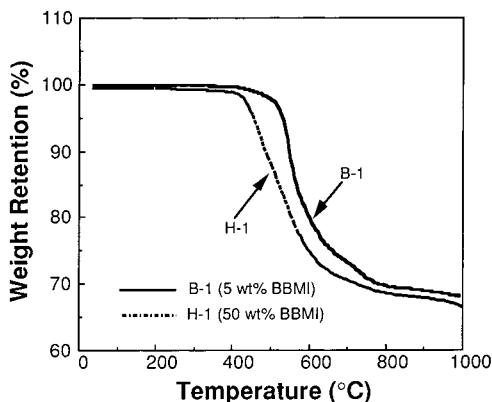(37) Nalwa, H. S.; Suzuki, M.; Takahashi, A.; Kageyama, A. *Appl. Phys. Lett.* **1998**, *72*, 1311.

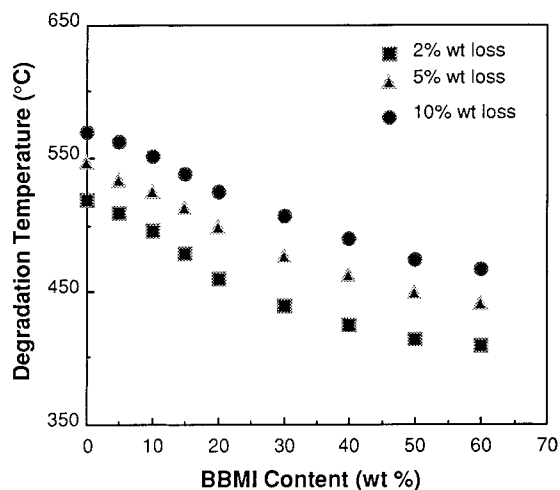**Figure 4.** A comparison of the thermal stability of PQ-100/BBMI blend thin films containing 5 and 50 wt % BBMI contents.

Figure 5. Degradation temperature of A-1 to I-1 thin films recorded from TGA data.

Figure 6. A 3 h isothermal TGA of PQ-100/BBMI blend thin films recorded at 300 °C (A) and 400 °C (B) under a nitrogen atmosphere.

thin films, which is virtually associated with loaded BBMI contents. Figure 5 shows the degradation temperatures of all A-1 to I-1 thin film samples cured at 280 °C for 1 h, where 2, 5, and 10% weight losses were recorded. For thin films of A-1 to C-1 samples, 5% weight loss was recorded above 535 °C, whereas for D-1 and E-1 samples the loss occurs around 500 °C. For F-1 to I-1 thin films, 5% weight loss was observed above 450 °C. This substantiates that the thermal stability of PQ-100/BBMI blends decreases with increasing BBMI contents. A similar pattern of 2% and 10% weight losses were also observed. BBMI shows 2, 5, and 10% weight losses at 455, 471, and 537 °C, respectively, which are noticeably lower than that of the PQ-100 samples. The 5% weight loss was observed between 450 and 535 °C for thin films containing 5−60 wt % bismaleimide loading. This indicates the high thermal stability of these blends compared with other thermosetting polymers. It seems that the initial thermal stability in blend thin films is imparted both from the PQ-100 backbone as well as from the cross-linked BBMI polymer network.

To evaluate the thermal stability parameters of the PQ-100/BBMI blend thin films in microelectronics fabrication process, thin films cured at 300 °C for 3 h were subjected to isothermal TGA studies, which provide distinctive information on thermal stability as opposed to a scanning TGA. Figure 6 shows a 3 h isothermal TGA of PQ-100 and blend thin films recorded at 300
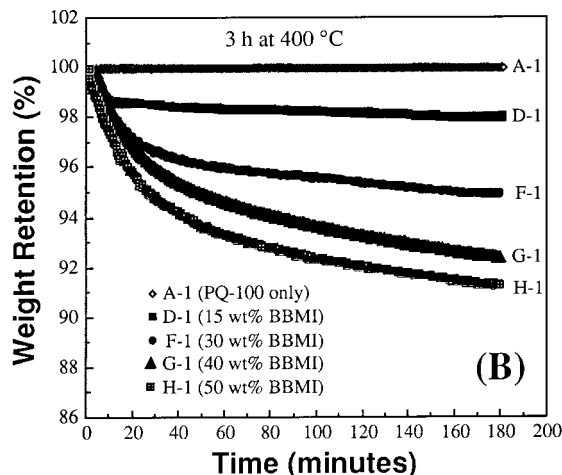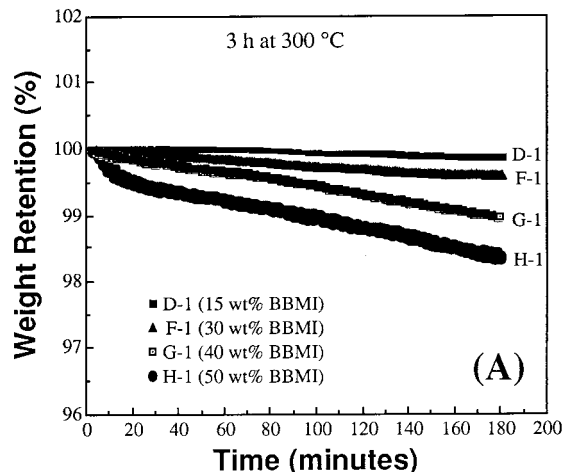
and 400 °C under a nitrogen atmosphere. The first 10 min of isothermal heating showed some adjustment of temperature and a slight outgassing from thin films. The A-1 (PQ-100) thin films showed no weight loss both at 300 and 400 °C, indicating significantly higher thermal stability of the polyquinoline backbone. However, some weight loss was observed for BBMI-containing thin films which varied as a function of BBMI loading. A weight loss of 0.15, 0.40, 1.0, and 1.60% was observed after 3 h at 300 °C for D-1, F-1, G-1, and H-1 thin films, respectively. An increase in weight loss was observed from the isothermal TGA recorded at higher temperatures. For example, thin films of D-1, F-1, G-1, and H-1 samples showed a weight loss of 2.0, 5.0, 7.5, and 9.0% after 3 h at 400 °C, respectively. An isothermal decomposition rate of about 0.13, 0.33, and 0.50 wt %/h was observed for F-1, G-1, and H-1 thin films at 300 °C, respectively. The PQ-100/BBMI blend thin films containing 5−15 wt % BBMI contents showed excellent thermally stability at 300 and 400 °C for a period of 3 h as their weight retention was in the range 99.85−100% at 300 °C and 98−99% at 400 °C. It is apparent that a gradual increase in weight loss at higher temperatures is associated with a higher degree of BBMI loading because no such behavior was observed from A-1 thin films.
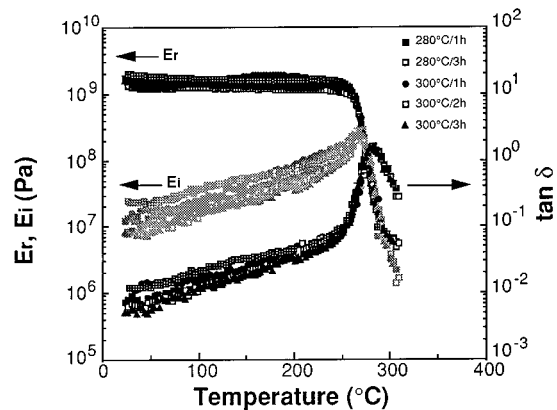
Figure 7. DMA of A-1 (PQ-100) thin films cured under different conditions.

Effect of Curing on Thermal and Mechanical Properties

Figure 7 shows the temperature dependence of the storage modulus (E_r), loss modulus (E_i), and mechanical tan δ of A-1 thin films cured under different conditions. The dynamic mechanical scan shows an E_i peak around 265 °C, where a large drop in modulus (E_r) was observed. On the other hand, the tan δ peak is large, centered at 282 °C for all samples. There is no effect of curing conditions on the magnitude of either E_r, E_i, or tan δ, because PQ-100 is a pure thermoplastic. All A-1 samples show similar characteristic patterns, indicating that PQ-100 thin films have no effect of curing conditions on mechanical properties whatsoever, because it has no BBMI. The T_g of PQ-100 thin films determined from tan δ is about 30 °C higher than those recorded from TMA studies. The restricted rotation of the phenylene groups in the polyquinoline backbone could be the main attributing factor to a higher T_g for PQ-100.

Figure 8 shows the trends of variation of the storage modulus, loss modulus, and tan δ with temperature for different blend thin films (5–60 wt % BBMI) cured at 280 °C for 1 h. Storage and loss modulus values show a slight difference in their magnitude with variation of BBMI contents, though there is a shift in the trend of their temperature variability. The loss modulus peak shifts to lower temperature up to 20 wt % BBMI loading and then starts shifting to higher tempratures from 30 to 60 wt % BBMI. The storage modulus follows a similar trend. Likely, the tan δ peak shifts in a similar manner with BBMI loading. The T_g deduced from the tan δ peak value decreases with up to 20 wt % BBMI loading (E-1) and then starts increasing thereafter, which is quite visible from these plots. There is a continuous increase in T_g from 20 to 60 wt % BBMI loading, where a 10 °C increase in tan δ peak temperature was observed for every 10 wt % increase in BBMI contents. We consider 280 °C as a critical temperature for curing, being in a close proximity to the T_g of PQ-100 and the exothermic reaction temperature peak of BBMI. The T_g of blend thin films is also associated with BBMI loading, and when the BBMI contents are lower, the molecular motion is somewhat restricted. For more than 20 wt % BBMI contents, the flowing viscosity of the blend decreases with increasing BBMI contents due to increased BBMI cross-linked network. PQ-100 dis-
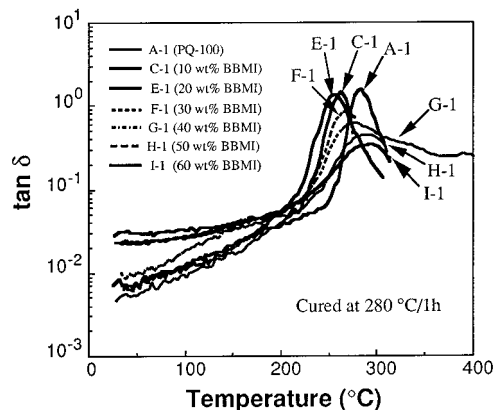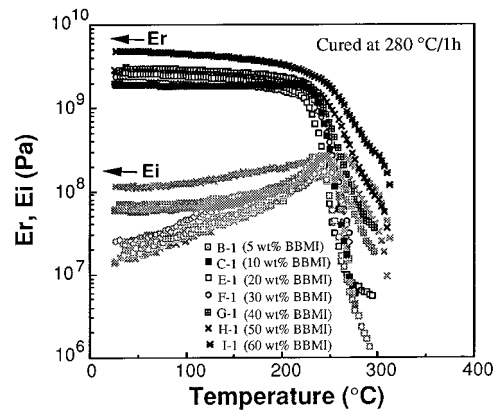

Figure 8. DMA of blend thin films containing 5–60 wt % BBMI contents. Here T_g was determined from the tan δ peak temparture of thin films cured at 280 °C for 1 h.

solved in BBMI is already molted; therefore, it is easy to cure due to increased molecular movement.

Figure 9 shows the effect of BBMI contents on E_r, E_i, and tan δ peak for B-1, C-1, E-1, F-1, and H-1 thin films cured at 280 °C for 3 h. Both B-1 and C-1 thin films show a tan δ peak around 275 °C; however, the tan δ peak shifts to higher temperatures as the BBMI content is increased further. Contrary to Figure 8, T_g of thin films cured for 3 h does not decrease with 5–20 wt % BBMI blend films but instead it starts increasing after 15 wt % BBMI loading. This characteristic pattern is quite apparent from plots of E-1, F-1, and H-1. There is a continuous increase in T_g from 10 to 50 wt % BBMI loading. The T_gs of 280, 285, 295, and 310 °C were recorded from tan δ peaks of the E-1, F-1, G-1, and H-1 samples, respectively. The blend thin films cured at 280 °C for 3 h show T_gs at 10–25 °C higher temperatures than those cured for 1 h at the same temperature, demonstrating that longer curing times increase the cross-linking network of BBMI.

Figure 10 shows the effect of curing conditions on T_g of PQ-100/BBMI blends extracted from DMA data. The T_g determined from tan δ peak temperature showed continuous increase as a function of curing temperature and time. T_g increased over 20 °C for all D-1 to H-1 samples as the time of curing was raised from 1 to 3 h at 280 °C. Moreover, the T_g of these blend thin films also increases with increasing BBMI contents. For example, D-1 (15 wt % BBMI) and H-1 (50 wt % BBMI) blend thin films cured at 280 °C for 3 h, show T_gs at 275 and 310 °C, respectively. There is a difference of 35 °C in T_g with increasing BBMI loading. Interest-
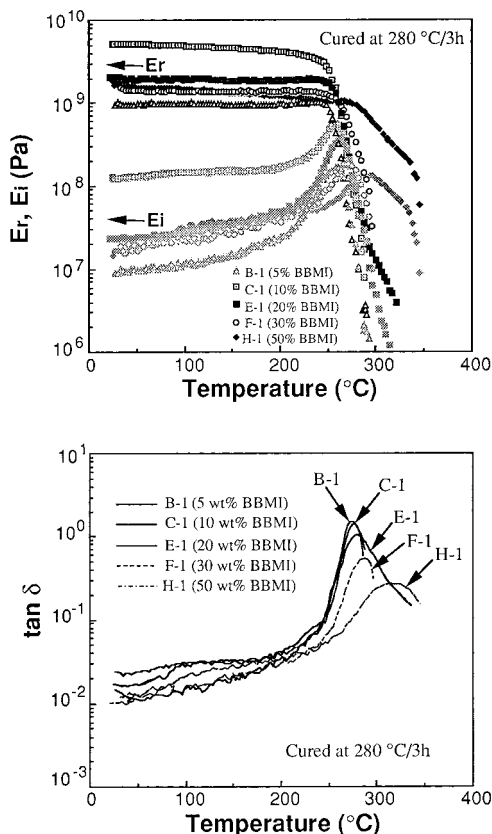
Figure 9. DMA of blend thin films containing 5−60 wt % BBMI contents cured at 280 °C for 3 h.
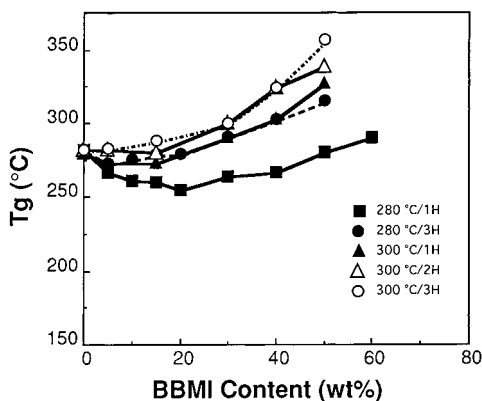

Figure 10. Effect of curing conditions on T_g of PQ-100/BBMI blend thin films. T_g was determined from the tan δ peak temperature of DMA data.

ingly, T_g reached as high as 360 °C for H-1 thin films cured at 300 °C for 3 h, whereas the T_g of H-1 thin films cured at 280 °C for 1 h was 286 °C. Therefore, the T_g increased by 80 °C with varying curing conditions. One of the interesting features is that the dynamic mechanical properties and T_g of blend thin films cured at 280 °C for 3 h and 300 °C for 1 h were found to be exactly the same. It seems that BBMI cure reactions are incomplete at 280 °C due to a glassy state and further curing occurs at 300 °C for 1, 2, and 3 h, resulting in an increase in T_g and associated mechanical properties. However, no effect of curing temperature as well as time was observed for A-1 thin films that have no BBMI. This suggests that mechanical properties are significantly affected by loaded BBMI contents and curing conditions. The cross-linking of BBMI increases as the temperature
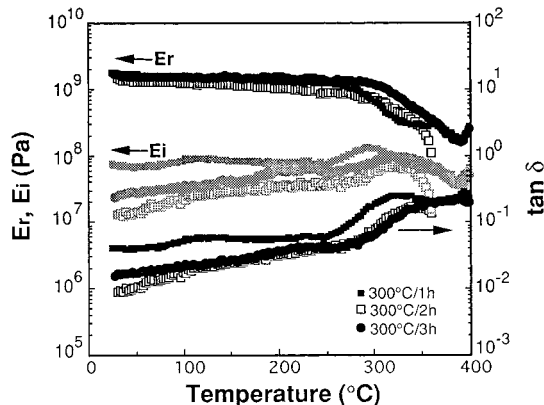

Figure 11. Effect of curing conditions on the mechanical properties for H-1 thin films (blend containing 50 wt % BBMI contents).

and the time of curing are raised, this increased cross-linked polymer network leads to an increase in T_gs.

Figure 11 shows the effect of curing conditions on storage modulus, mechanical loss modulus, and tan δ for H-1 sample (50 wt % BBMI contents). This is a typical example here having 50 wt % each of PQ-100 and BBMI. The loss modulus (E_i) peak appeared at 257 and 290 °C, whereas the tan δ peak was located as 286 and 310 °C for thin films cured at 280 °C for 1 and 3 h, respectively. The E_i peak shifted by 34 °C, while the tan δ peak shifted by 24 °C as the curing time was raised from 1 to 3 h at 280 °C. H-1 thin films cured at 280 °C for 3 h and at 300 °C for 1 h exhibited the similar characteristic features, as both samples showed E_i and tan δ peaks in the same temperature regions. The E_i peak appeared at 312 and 320 °C, whereas the tan δ peak was at 340 and 360 °C for thin films cured at 300 °C for 2 and 3 h, respectively. Both peaks are shifted by 8−20 °C as curing time was increased from 2 to 3 h at 300 °C. This shift in tan δ peaks at 300 °C is caused by the increased BBMI cross-linking due to prolonged curing time. One of the interesting features here is an increase of 70 °C in T_g between thin films cured at 280 °C for 1 h to those cured at 300 °C for 3 h. A similar temperature difference was noticed for E_i peak positions. It is quite encouraging that mechanical properties of all samples were improved with varying curing conditions.

The thermosetting behavior of PQ-100/BBMI blends is demonstrated by comparing the mechanical properties of B-stage thin films and then curing those films at 280 °C for 1 h. Figure 12 shows storage modulus and loss modulus of blend thin films of the A-1, C-1, F-1, G-1, H-1, and I−I samples. The B-stage and cured thin films of A-1 (PQ-100) show similar characteristics, supporting their thermoplastic properties and absence of thermosetting features. On the other hand, all other blend thin films show the significant effect of both curing conditions and BBMI contents on mechanical properties. For C-1 to I-1 thin films, the mechanical properties of blends are governed by the loaded BBMI. Interestingly, the temperature range of storage modulus and loss modulus broadens with increasing BBMI contents in thin films. The temperature range shifts at least by 100 °C or even more for G-1, H-1, and I-1 thin films when their B-stage films were cured at 280 °C for 1 h. Comparatively, the shift in temperature range of C-1 sample is very narrow because the BBMI
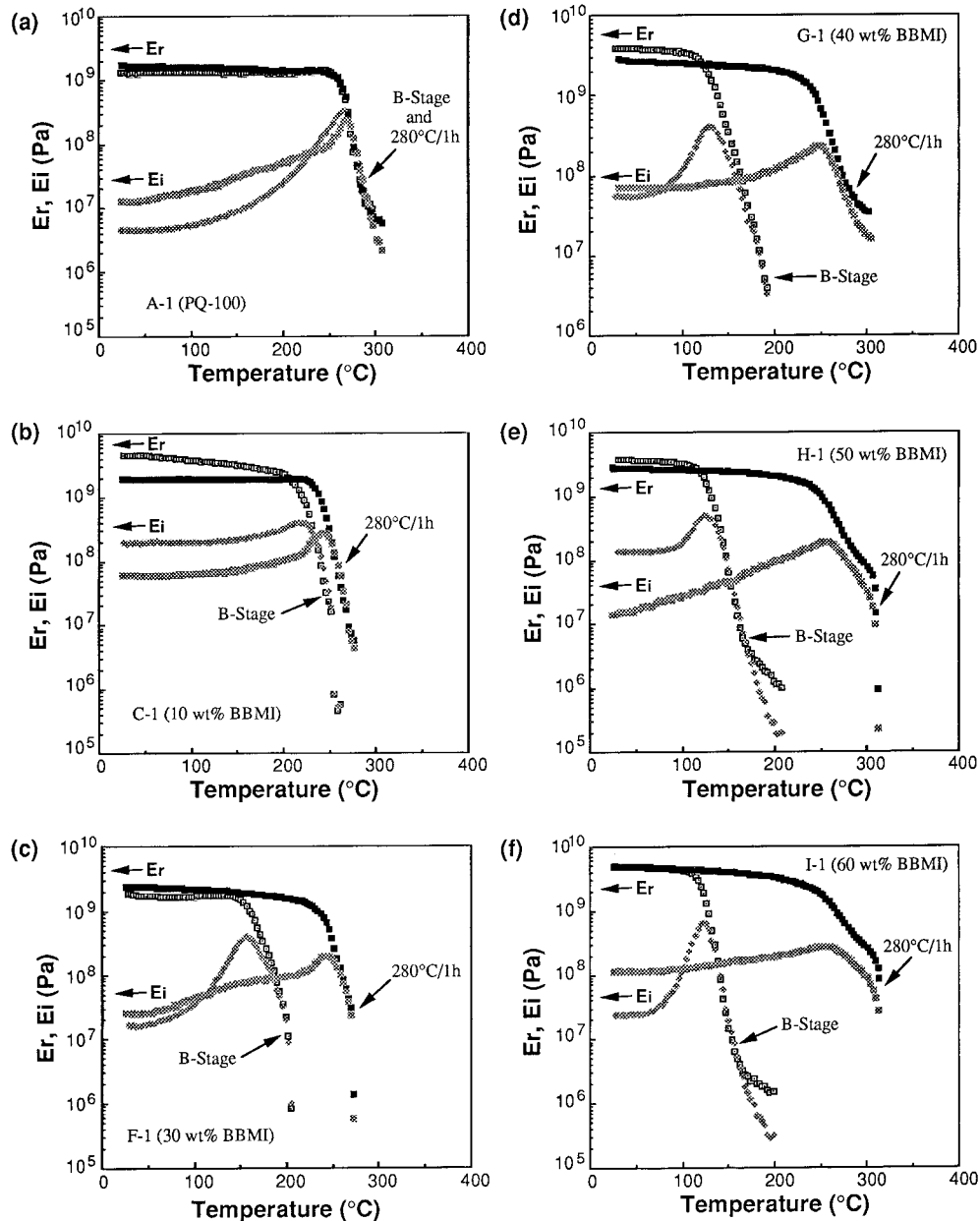
Figure 12. A comparison of the mechanical properties of (a) A-1 (PQ-100), (b) C-1 (10 wt % BBMI), (c) F-1 (30 wt % BBMI), (d) G-1 (40 wt % BBMI), (e) H-1 (50 wt % BBMI), and (f) I−I (60 wt % BBMI) thin films thermally treated at B-stage and then cured at 280 °C for 1 h. This demonstrates the thermosetting behavior of the blend thin films.

content is significantly lower and it may be the PQ-100 that mainly governs the mechanical properties in this case. As BBMI contents in PQ-100 increases, the temperature range of storage modulus and loss modulus broadens, which is quite apparent by the comparison of C-1, F-1, G-1, and H-1 with I-1 samples. The mechanical performance of these blend thin films increases on curing at high temperatures, as expected with the formation of thermoset resins. The PQ-100/BBMI system forms homogeneous miscible blends, and no phase separation was observed from DMA data of cured thin films.

In the fabrication of multilayer interconnects, organic dielectrics are subjected to solvent treatment. One of the major drawbacks of organic low dielectric constant materials is their lack of solvent resistance. To ensure solvent resistance in polyquinoline systems, the effect
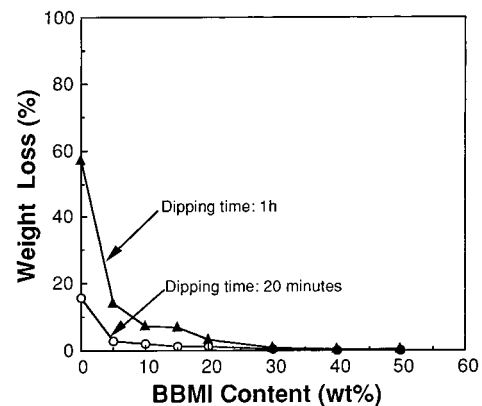

Figure 13. BBMI content dependence of weight loss of cured (280 °C for 1 h) PQ-100/BBMI blend thin films emmersed in cyclopentanone for 20 and 60 min.

of bismaleimide addition on blend thin films was studied to evaluate the applications of PQ-100/BBMI thermosets in microelectronics packaging. Figure 13 shows the BBMI-content-dependent weight loss of cured (280 °C for 1 h) PQ-100/BBMI blend thin films, emmersed in cyclopentanone for 20 and 60 min. As apparent that weight loss was minimized with increasing BBMI contents in blend thin films. Interestingly no weight loss was observed for blend thin films containing 30–50 wt % BBMI contents, indicating that solvent resistance was improved significantly by blending PQ-100 with BBMI. PQ-100/BBMI blends containing 5–20 wt % BBMI contents (samples B-1 through E-1) have been investigated as the thin film materials for spin-coating. On the other hand, we are investigating blends containing 40–60 wt % BBMI contents (samples G-1 and H-1) as the adhesive films for laminated thin film multilayer substrate applications, as these blends show excellent fluidity on heating.

Conclusions

In conclusion, PQ-100/BBMI blends having bismaleimide contents between 5 and 60 wt % showed good compitability, high thermal stablility, high mechanical strength, and excellent resistance to solvent, demonstrating their potential for applications as high-temperature-resistant materials. Curing conditions of PQ-100/BBMI blend thin films showed significant effects on their mechanical and thermal properties. PQ-100/BBMI blend thin films were found to be homogeneous, as no phase separation was observed after curing. The blending of bismaleimide with polyquinoline provides high-performance thermoset blends without sacrificing the generic physical properties of the polyquinoline backbone.