Studies on the Thermal and Curing Behavior of Polyimide Blends

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SYNOPSIS

Blends of thermosetting (Thermid MC-600 and Thermid FA-700) and thermoplastic (ULTEM 1000) polyimide resins with different compositions were prepared. Curing and thermal behavior of the blends were investigated using differential scanning calorimetry and dynamic thermogravimetry in a nitrogen atmosphere. The peak exotherm temperature increased with increasing amount of thermoplastic resin, whereas the heat of polymerization decreased. The electrical characteristics of the blends were also investigated using a dielectric analyzer. Dynamic as well as isothermal scans were recorded. Ionic conductivity, permittivity, and the loss factor were measured as a function of temperature at various frequencies. These results showed the complete curing of the resins having 50% Ultem at 225°C in 1 h, whereas Thermid MC-600 required a postcuring step to observe fully cured resins. A marginal decrease in thermal stability was observed on blending. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In the past few years, many high-performance semi-interpenetrating networks (semi-IPNs) have been developed for use as composite matrices and adhesives for aerospace structural applications. The concept underlying the IPN approach is to combine easy-to-process but brittle thermosetting polyimides with a tough but difficult-to-process thermoplastic polyimides. This concept has been successfully applied to develop several semi-IPNs including acetylene-terminated polyimides,[1-5] bismaleimide,[6,7] polytriazine,[8] and epoxy-based materials.[9,10] An improvement in fracture toughness and synergy in processibility has also been reported.

Considerable attention has been directed on the toughening of acetylene-terminated imide resin (Thermid 600) using LARC-TPI[2,3]; however, no reports are available on the use of flexible thermoplastic poly(ether imide) [Ultem 1000]. A systematic investigation on the curing and thermal behavior of the thermosetting resin upon blending with varying amounts of thermoplastic resin has not been done. It was therefore considered of interest to evaluate systematically the effect of blending varying amounts of Ultem on the curing and thermal behavior of Thermid MC-600 and Thermid FA-700.

In this article, we present the results of our investigation of the effects of Ultem on the curing and thermal behavior of acetylene-terminated imide resins. A knowledge of the curing behavior is of great importance for interpreting the processing conditions for composite fabrication to obtain an optimum combination of properties. Curing of the blends was investigated using DSC, DEA, and FTIR.

EXPERIMENTAL

Materials

The chemical structure of the polyimide moieties are shown in Scheme 1:

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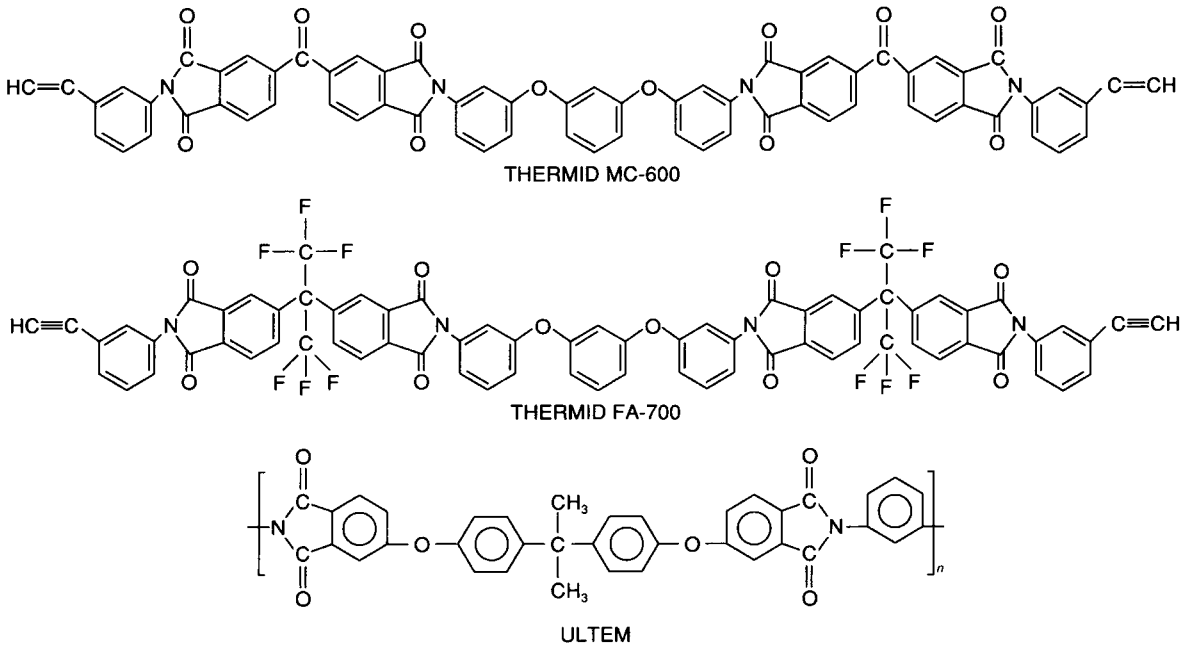

Scheme 1 Structure of Polyimide Resins

The flexible matrix used in the present study was poly(ether imide) [PEI], i.e., poly[2,2′-bis(3,4-dicarboxy phenoxy)phenyl propane-2-phenylene bisimide (ULTEM 1000, General Electric), which is an amorphous thermoplastic with a T_g of ~ 215°C. The $\bar{M}_n$ and $\bar{M}_w$ were 12,000 and 30,000, respectively. The thermosetting resins (Thermid MC-600 and Thermid FA-700) were procured from the National Starch Chemical Co., USA.

Preparation of Blends

Various blends were prepared by dissolving acetylene-terminated imide oligomers (Thermid MC-600 and FA-700) and poly(ether imide) (PEI) resins in NMP. The concentration of the polymer solution was 5–10 wt %. The solutions of various blend compositions were coagulated in water. The precipitates were washed thoroughly with water to remove the residual solvent. Finally, they were washed with methanol and then dried in a vacuum oven at 70°C until a constant weight was obtained. The precipitated powders were used for thermal studies.

The resin blends thus obtained have been designated on the basis of constituents and blend composition. Thus, e.g., blends of Thermid MC-600 containing 10, 20, 30, 40, and 50% (w/w) Ultem have been designated as MU-91, MU-82, MU-73, MU-64, and MU-55, respectively. The letters M and U stand for Thermid MC-600 and Ultem, respectively, and numerals represent their weight percent multiplied by 10. Similarly, the blends of Thermid FA-700 and Ultem have been designated as FU followed by numerals.

DSC experiments were carried out on a DuPont 9900 thermal analyzer having a 910 DSC module at a heating rate of 10°C/min under nitrogen (flow rate 50 mL/min). A sample of 6 ± 2 mg was used in each experiment.

The curing behavior of the blends was also evaluated using a Digilab Fourier transform infrared spectrophotometer (FTS 60). Spectra were recorded in KBr pellets at a resolution of 2 cm^{-1} and were the average of 64 scans. A high-temperature cell mounted in the spectrometer was employed to obtain spectra at elevated temperatures and each temperature was maintained for 3 min.

For dielectric analysis, the ceramic single-surface sensor was utilized. The samples were ground in an agate mortar and pestle and 500 N of ram force was employed to press the fine powder onto the sensor. DEA scans were recorded using a DEA 2970 dielectric analyzer at frequencies ranging from 1 to 10,000 Hz in the temperature range of 25–400°C at a heating rate of 3°C/min. Isothermal scans were also recorded at 190, 210, and 225°C.

The thermal stability of the resins was evaluated

in nitrogen and air atmospheres using 1090 thermal analyzer having a 951 TG module. A heating rate of 10°C/min and a sample size of 10 ± 2 mg was used in each experiment.

RESULTS AND DISCUSSION

DSC traces of Thermid MC-600, FA-700, Ultem, and the various blend samples are shown in Figures

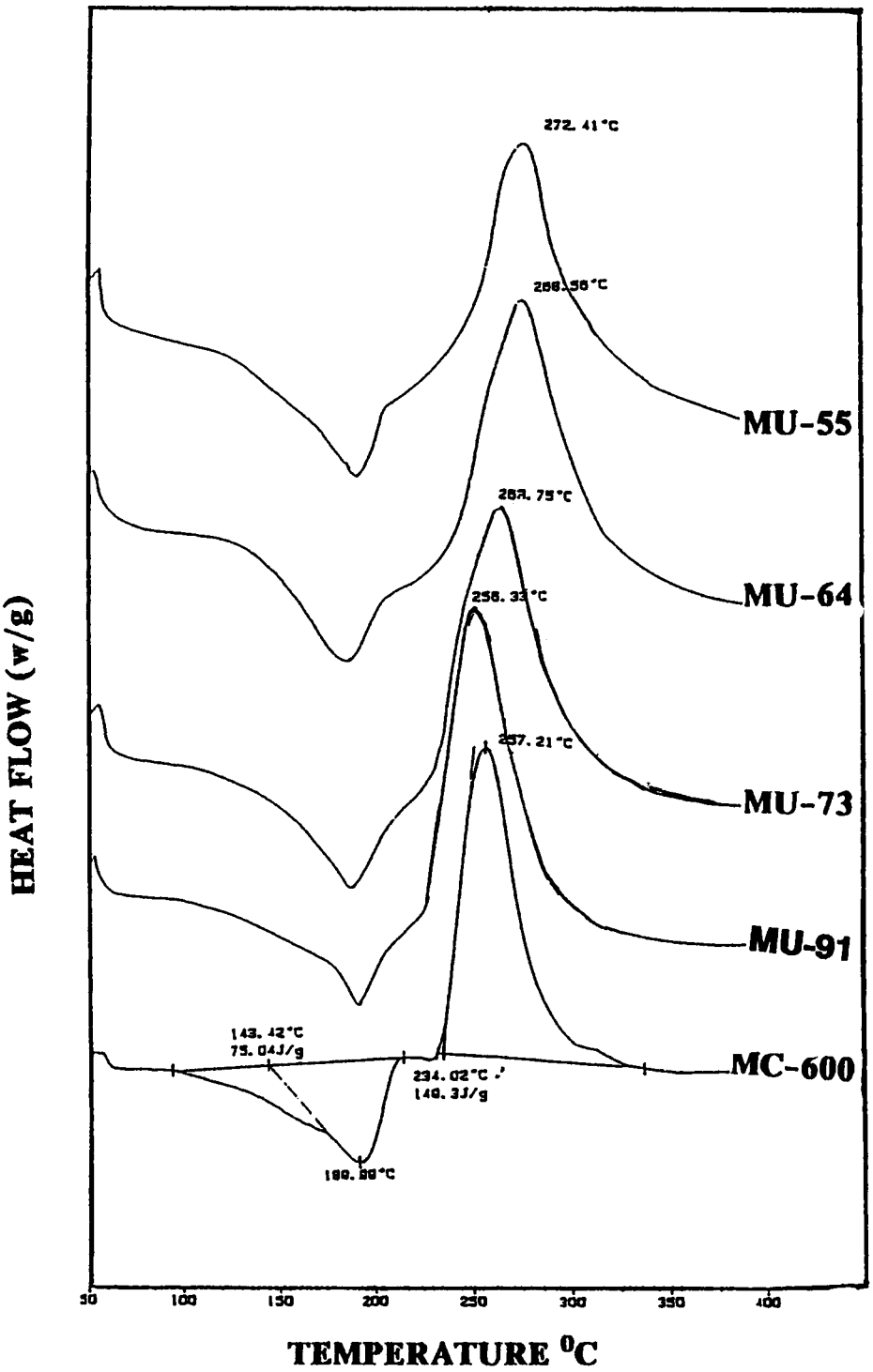

Figure 1 DSC traces of Thermid MC-600 and MU blends of varying compositions.

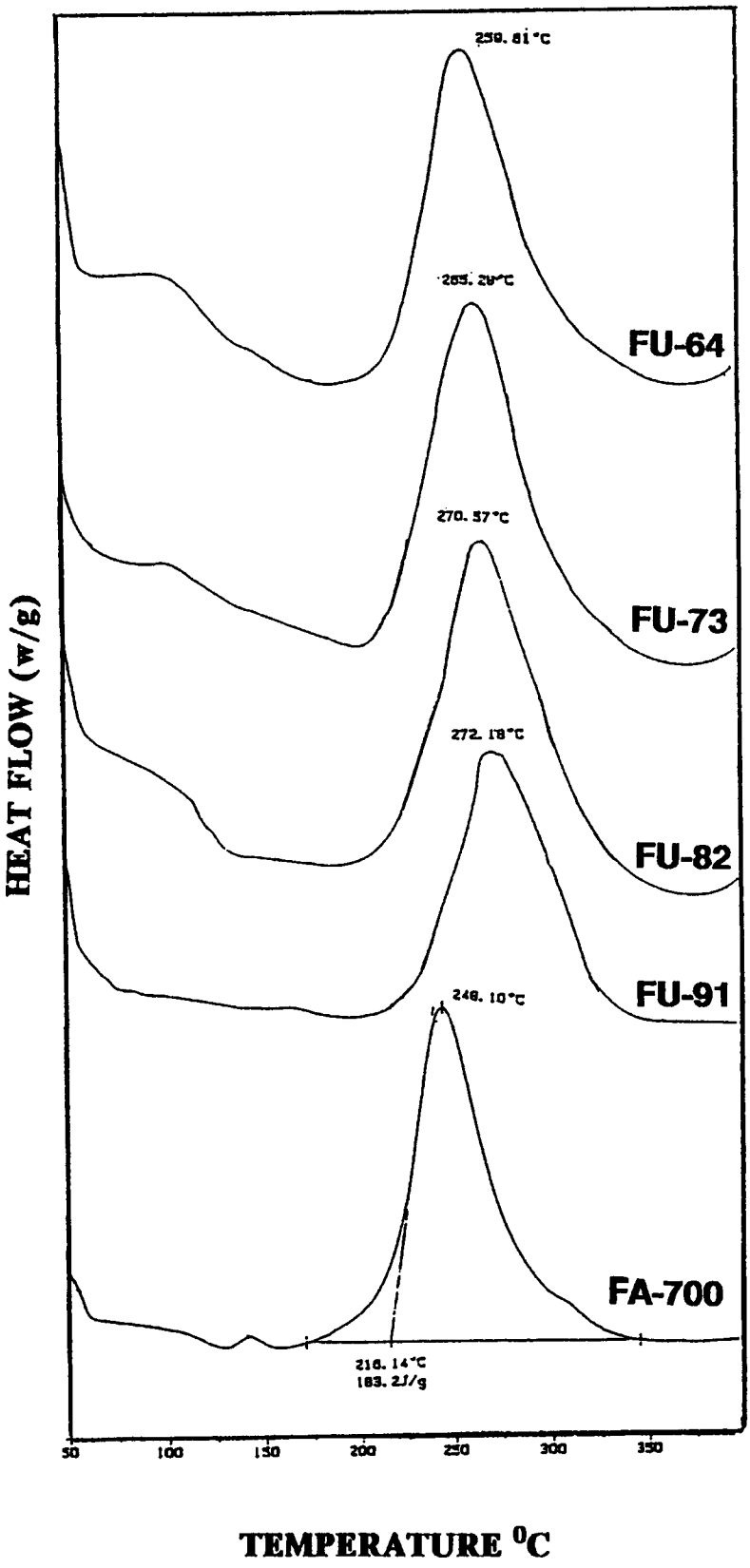

Figure 2 DSC traces of Thermid FA-700 and FU blends of varying compositions.

1–3. MC-600 showed a melting endotherm followed by an exotherm. FA-700 showed a broad exothermic transition in the temperature range of 171.7–346.7°C, with a peak exotherm temperature at 248.1°C. An endothermic transition at 215°C corresponding to the glass transition temperature was observed in the DSC scan of Ultem. All the blends (MU) showed a single broad exotherm in the temperature range of 216–350°C. The curing exotherms observed were characterized by

(i) T_i: the temperature at which the DSC trace departs from the base line;

(ii) T_{exo}: the peak exotherm temperature;

(iii) T_{onset}: the temperature obtained by drawing tangent to the low-temperature side of the exotherm;

(iv) T_f: the final temperture of curing; and

(v) ΔH_0: the heat of the polymerization reaction that was obtained from the area under the exotherm.

The DSC results for the various samples are summarized in Tables I and II. In MU blends, T_m increased from 190 to 195°C upon addition of 10% (w/w) of Ultem to Thermid MC-600. A further in-

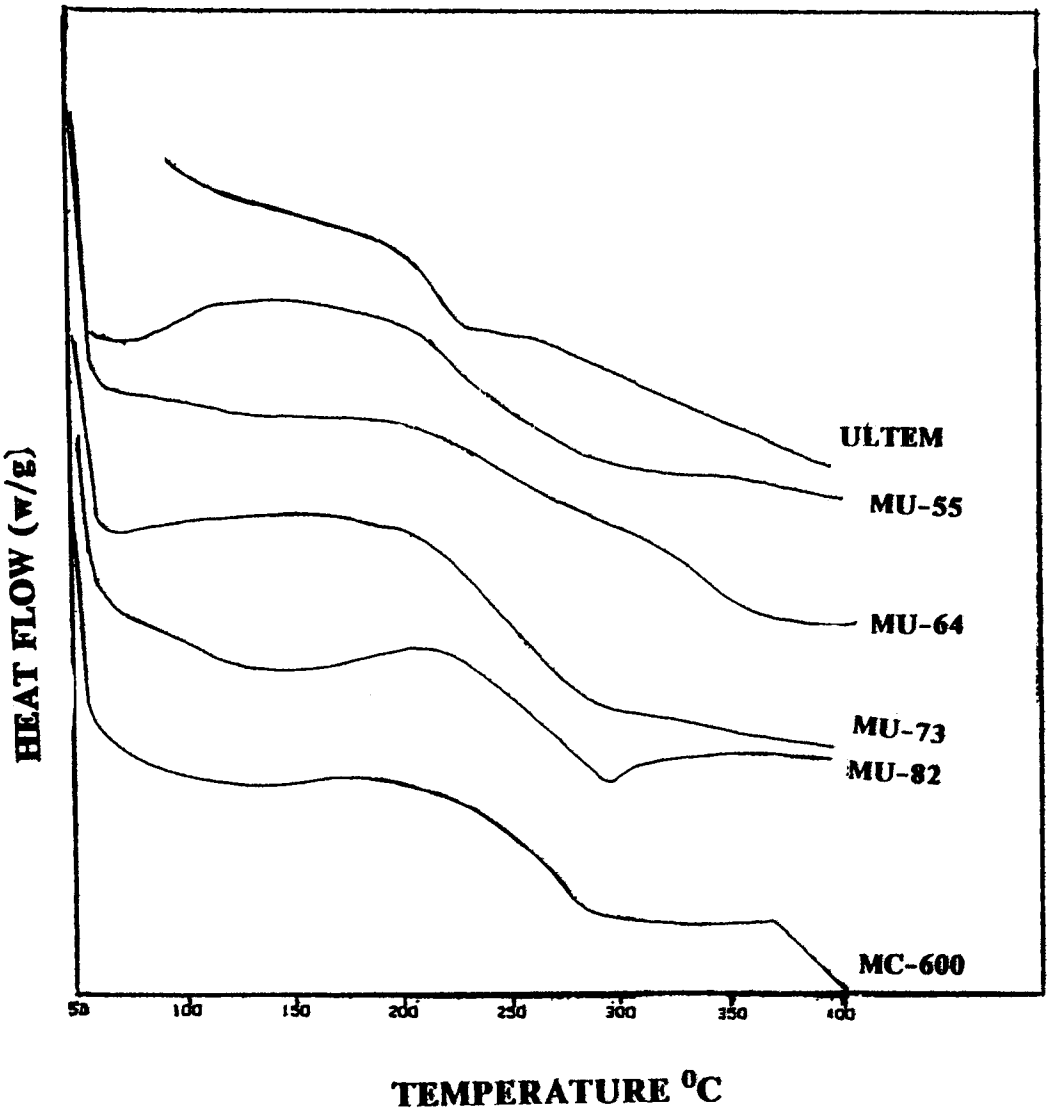

Figure 3 DSC traces of Thermid MC-600 and MU blends recorded after curing.

Table I DSC Results of Thermid MC-600/Ultem Blends in Nitrogen (Flow Rate = 50 mL/Min)

Sample Designation	T_m (°C)	T_i (°C)	T_{onset} (°C)	T_{exo} (°C)	T_f (°C)	ΔH_0 (J/g)
MC-600	189.9	230.0	234.0	257.2	335.0	149.3
MU-91	195.4	220.0	231.1	256.3	340.4	146.2
MU-37	190.4	221.6	232.4	263.7	346.5	128.9
MU-46	186.0	220.0	235.3	268.6	346.6	131.3
MU-55	192.1	216.7	231.8	272.4	341.7	109.3

Table II DSC Results of Thermid FA-700/Ultem Blends in Nitrogen (Flow Rate = 50 mL/Min)

Sample Designation	T_i (°C)	T_{onset} (°C)	T_{exo} (°C)	T_f (°C)	ΔH_0 (J/g)
FA-700	171.7	216.1	248.1	346.7	183.2
FU-91	211.7	230.2	272.2	350.0	147.4
FU-82	196.7	223.6	270.6	356.0	150.8
FU-73	201.7	223.9	265.3	345.0	120.2
FU-46	198.3	221.6	259.6	345.0	114.6

crease of Ultem weight percent resulted in a decrease in T_m, but all the blends had a higher T_m than that of MC-600. The heat of polymerization decreased, whereas T_{exo} and T_f increased with an increasing amount of Ultem in the blends. T_{onset} was marginally affected. All the blends have a Tonset of 233.3 ± 2°C. A significant decrease in T_i was observed upon blending with 10 wt % of Ultem. Further increase in the Ultem weight percent had a marginal effect on T_i.

In FU blends, a single exotherm was observed. An addition of 10% (w/w) of Ultem (sample Fu-91) resulted an increase in T_{onset}, T_i, and T_{exo}. Further addition of Ultem resulted in a decrease in T_i and T_{exo} temperatures, but all these temperatures are still higher than those of the FA-700 resin. T_{onset}, on the other hand, did not change as the concentration was increased from 20 to 30 wt % and decreased marginally on increasing the concentration up to 40 wt % (Table II).

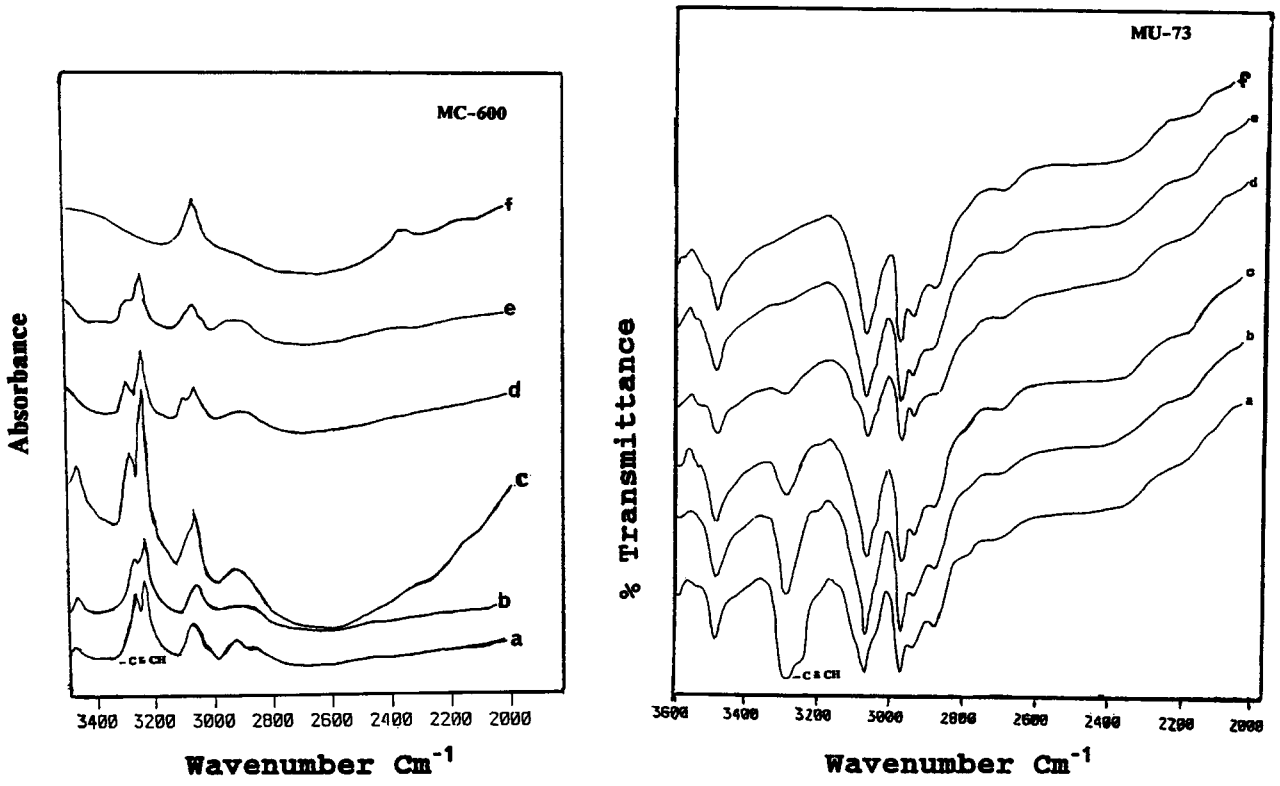

Figure 4 FTIR spectra of MC-600 (a) RT; (b) 180°C; (c) 240°C; (d) isothermal at 240°C for 20 min; (e) 250°C; (f) isothermal at 250°C for 20 min and MU-73 (a) RT; (b) 200°C; (c) 220°C; (d) 230°C; (e) isothermal at 230°C for 5 min; (f) 240°C.

Figure 4 shows the IR spectra of MC-600 and UM-37 samples recorded at room temperature and after heating at various temperatures. A gradual disappearance of the HC=C vibration at ~ 3300 cm^{-1} with increasing temperature was observed. A complete disappearance of this vibration band occurred at 240°C in MU-73, whereas it took a longer time in MC-600, thus showing that blending with a thermoplastic resin helps in the curing reaction.

The samples were cured in oven at 220°C for different intervals of time and DSC scans were recorded. The absence of an exotherm indicates the completion of curing. A shift in the base line was observed in all the samples corresponding to the glass transition temperature. A broad transition was observed in all the samples; however, a midpoint in the MC-600 resin was observed at a lower temperature than that of all the blends (Fig. 5).

Figures 6–8 shows DEA scans for samples Thermid MC-600 and MU-55. The data are plotted as permittivity (e'), ionic conductivity, and loss factor vs. temperature. Ionic conductivity ($e'' \times 2\pi f$) is quite useful for representing the events associated with the curing cycle.

There are approximately five events in the curing of Thermid MC-600. The first event initiates around 120°C (1 Hz, e' curve) in MC-600, which was absent in MU-55. The second and the strongest transition occurs around 175°C. This is probably due to the glass transition of MC-600 as this is apparent in both the samples, but much weaker in MU-55.

The next series of transitions are likely to be curing followed by vitrification and then devitrification. The curing appears as a downturn in the conductivity curve. There are two downturns in MC-600 at ~ 200 and 235°C, respectively. There is also a sharp decrease in the e' curves around 235°C, which would indicate vitrification. In MU-55, the two steps

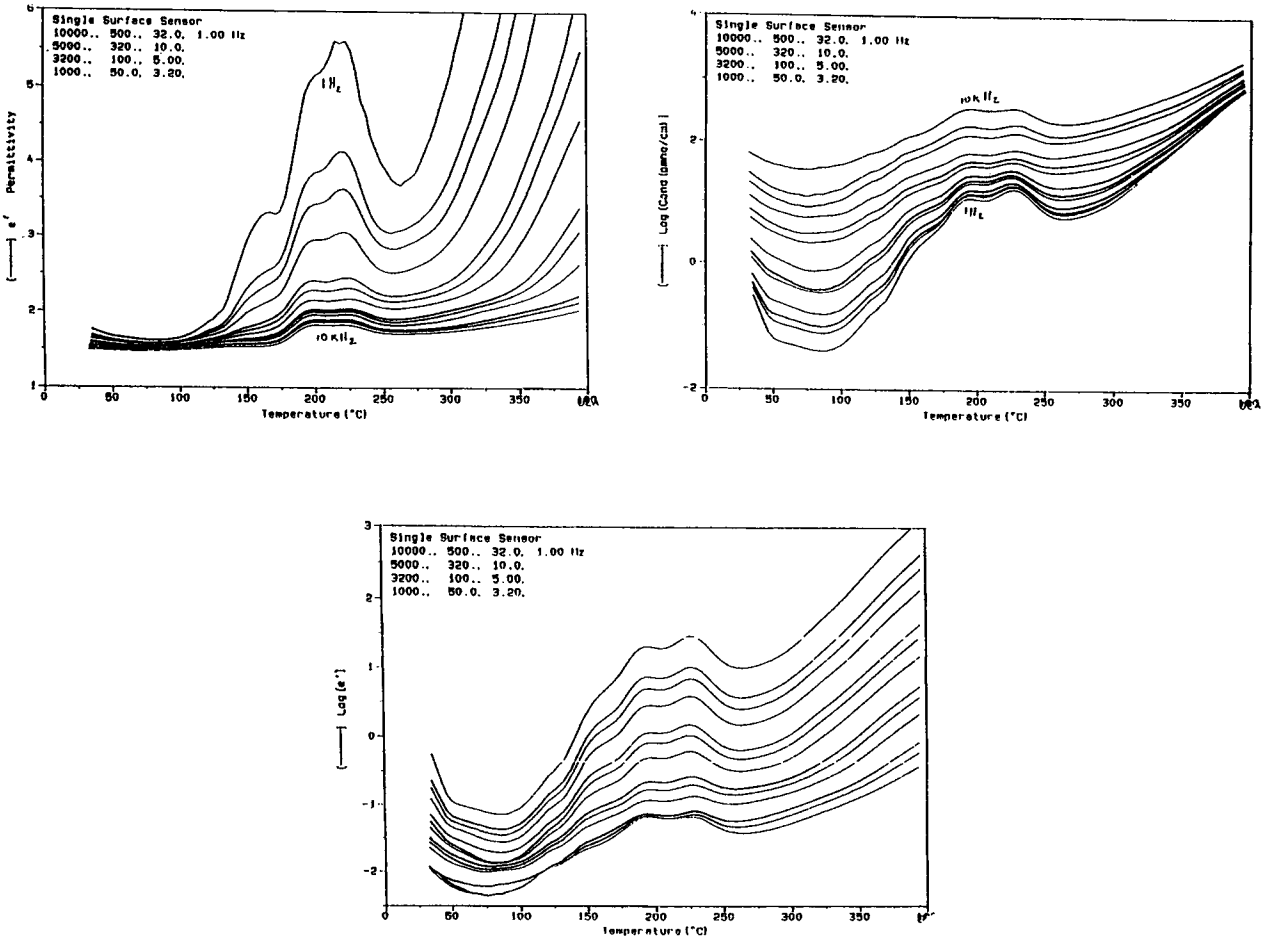

Figure 5 DEA scans of Thermid MC-600.

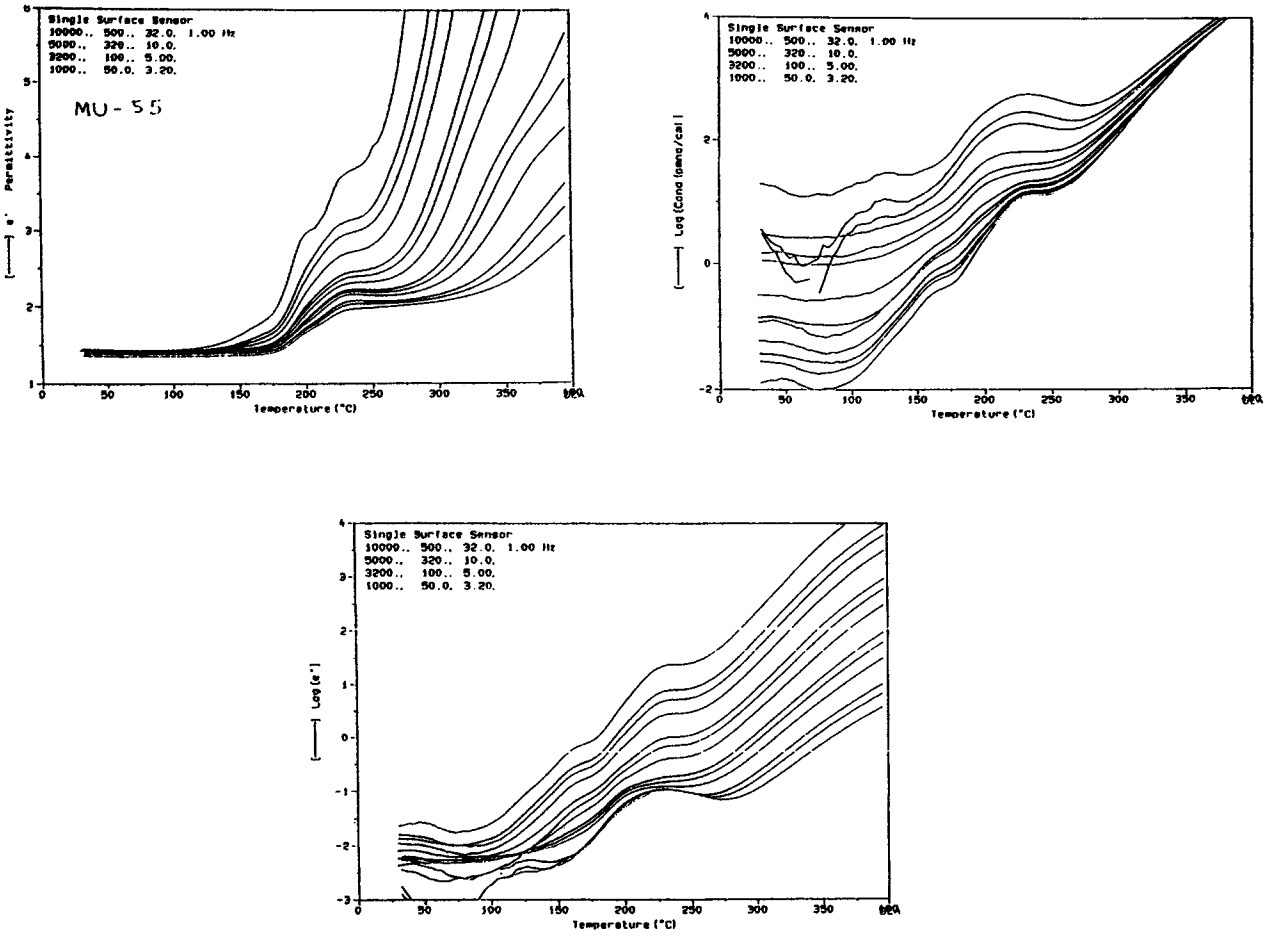

Figure 6 DEA scans of MU-55.

are not resolved, nor is the decrease in conductivity as great. In this material, there is a competition between the thermoplastic glass transition and curing/vitrification. The glass transition would increase conductivity and permittivity, whereas curing would lower both the properties.

The devitrification appears as the upturn in the conductivity curves. The conductivity of MU-55 is higher than that of MC-600. This could be due to the thermoplastic nature of Ultem, which allows the flow of ions above the glass transition temperature. These results thus indicate that events that occur during curing are qualitatively similar except for the competition between the thermoplastic glass transition and the final stages of curing.

Isothermal experiments were conducted at 190, 210, and 225°C (Fig. 8). Both MU-55 and MC-600 cured at 225°C in ~ 60 min. After the isothermal experiment at 225°C, the samples were furnace-cooled and heated at 3°C/min to view subsequent curing. In case of MC-600, a dramatic decrease in conductivity was observed around 240°C, which may be associated with postcuring. This was also observed physically, as the samples were powdery, indicating that the material was not highly cured. On the other hand, heating of sample MU-55 after the cure indicates that the material was nearly fully cured. Isothermal experiments thus indicate that such a blending can lead to the elimination of the postcuring step, which is advantageous from the processing point of view. These results further support that blending with thermoplastic resin facilitates the curing of the thermosetting resin. Enhancement in the rate of imidization of polyamic acid in blends has already been observed by Makhija et al.[12]

Thermal stability of the blends before and after curing was evaluated using dynamic thermogravimetry in a nitrogen and oxygen atmosphere. The thermal stability was compared by comparing initial decomposition temperature (IDT), temperature of maximum rate of weight loss (T_{max}), and % residual

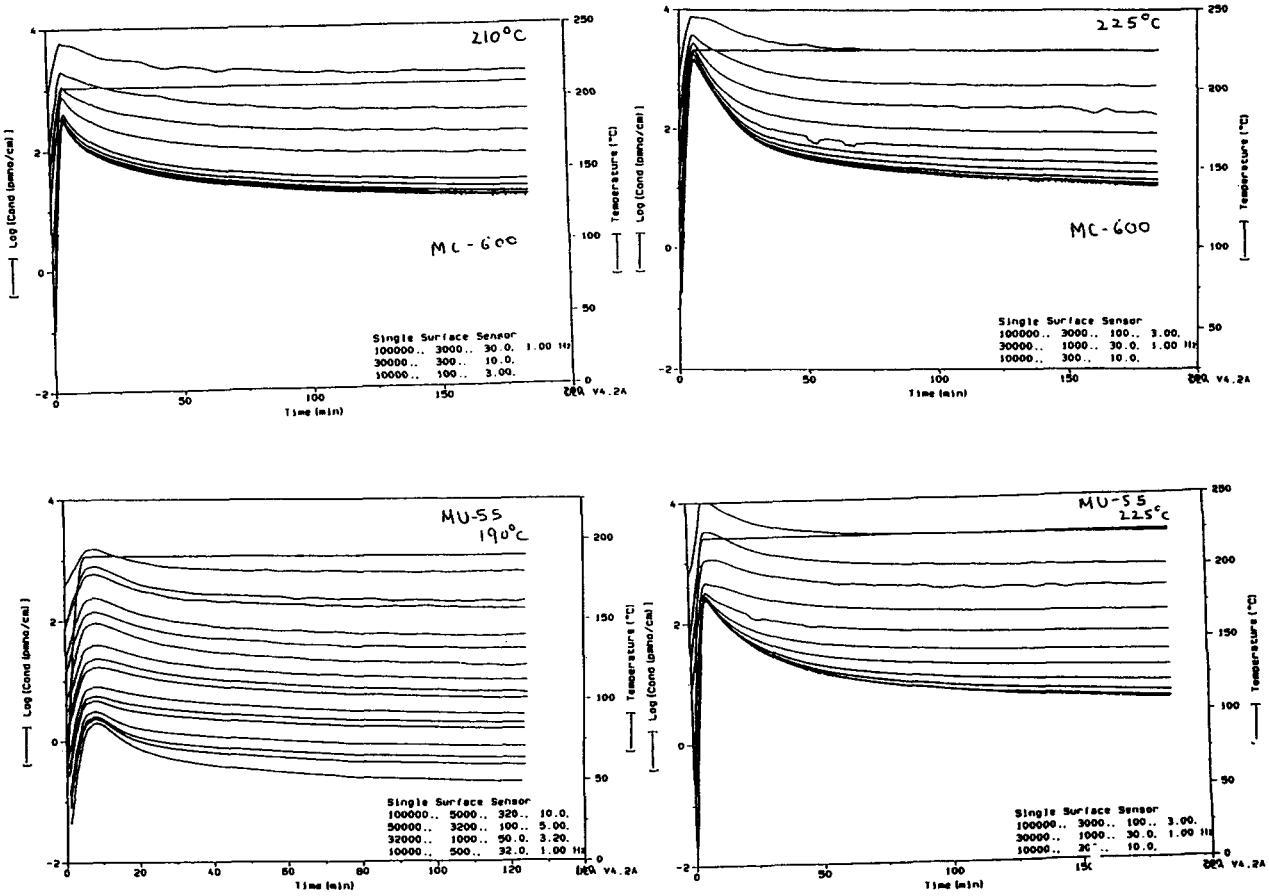

Figure 7 DEA scans of samples recorded isothermally at (a) 210°C (MC-600), (b) 225°C (MC-600), (c) 190°C (MU-55), and (d) 225°C (MU-55).

weight at 750°C. The integral procedural decomposition temperature (IPDT), which sums up the shape of the thermogravimetric trace, was also calculated according to the method of Doyle[13] and the results are summarized in Tables III and IV.

A weight loss of 4 ± 2 mg % was observed below 200°C in MU blends. This weight loss could be due to the moisture or solvent that was difficult to remove. The weight loss was maximum in Thermid MC-600 and decreased with an increasing amount of Ultem in the blends. A single-step degradation was observed in MC-600 and Ultem resins. All the blends showed a two-step decomposition.

IDT decreased, $T_{max\text{-}1}$ increased slightly, and $T_{max\text{-}2}$ remained unchanged upon blending. Percent derivative decreased in the first step and increased in the second step with increasing amount of Ultem in the blends. This clearly shows that the degradation in the first step is due mainly to Thermid MC-600 and in the second step due to Ultem. Percent char decreased with increasing amount of Ultem. Percent char was also calculated theoretically using the additive method. Both calculated and theoretical values were comparable before curing.

Thermal scans were also recorded after curing at 220°C for 2 and 4 h. All the samples were stable up to 500°C and started losing weight above this. IDT, T_{max}, and % char increased upon curing. Percent derivative per minute increased with an increasing amount of Ultem in the blends, whereas in the second step, it varied from 3 to 3.5%. Percent char determined experimentally was found to be higher than the values calculated from the additive method. These results thus indicate that the two components do not behave independently after curing. The higher char yield observed than sum of the two constituents could be due to the interpenetration upon curing. An increase in thermal stability has also been reported by various authors in PU/PMMA or PU/PS IPNs[13] due to the formation of an interpenetrating network.

The effect of curing time on thermal stability was

Table III Thermogravimetric Results of Polyimide Resins in a Nitrogen Atmosphere (Heating Rate = 10°C/Min) Before and After Curing Isothermally at 220°C

Sample Designation	IDT (°C)	T_{max-1} (°C)	T_{max-2} (°C)	% Char at 750°C	IPDT (°C)
MC-600	528.0	—	590.9	61.0	661.9
MC-600[a]	536.4	—	601.1	59.6	691.8
MC-600[b]	524.0	—	581.2	67.7	693.3
MU-91	517.8	—	589.5		
MU-91[a]	524.0	535.0	601.6	64.3	699.5
MU-91[b]	513.0	—	583.4	67.1	693.5
MU-82	505.0	530.0	600.0	60.0	665.7
MU-82[a]	510.4	536.7	609.8	59.2	683.8
MU-73	490.0	525.0	600.0	59.5	670.2
MU-73[a]	500.0	—	605.0	59.6	683.3
MU-73[b]	502.0	541.7	—	63.3	688.6
MU-64	485.0	525.0	590.0	59.5	666.7
MU-64[a]	501.5	535.2	605.0	59.5	673.0
MU-64[b]	499.0	536.0	—	62.0	681.4
MU-55	507.5	530.0	595.0	58.5	681.3
MU-55[a]	512.4	539.8	605.0	57.3	682.7
MU-55[b]	499.0	533.8	—	64.7	689.4
ULTEM	530.0	547.0		54.0	

[a] Data for the samples cured isothermally at 220°C for 2 h.
[b] Data for the samples cured isothermally at 220°C for 4 h.

also evaluated. Percent char yield increased with increasing cure time. The extent of curing was also followed from the solubility measurements. After curing for a specified time, the samples were boiled with NMP for 30 min, followed by filtration. The residue was washed repeatedly with NMP followed

Table IV Results of Thermogravimetric Analysis of Polyimide Resins in Nitrogen Atmosphere (Heating Rate = 10°C/Min)

Sample Designation	IDT (°C)	T_{max-1} (°C)	T_{max-2} (°C)	% Char at 750°C	IPDT (°C)
FA-700	510.0	560.0	—	61.7	
FU-91	535.0	563.0	650.0	62.5	689.6
FU-91[a]	519.1	559.6	630.0	61.5	—
FU-82	511.9	546.8	625.0	61.7	668.0
FU-82[a]	515.4	548.9	630.0	61.5	—
FU-73	513.8	547.8	640.0	61.6	689.3
FU-73[a]	514.2	548.8	—	61.6	—
FU-64	513.1	542.8	625.0	58.6	680.5
FU-64[a]	511.0	542.9	630.0	58.4	—
FU-55	515.5	542.6	620.0	59.4	
FU-55[a]	517.2	546.1		57.6	

[a] Data for the samples cured at 220°C for 4 h.

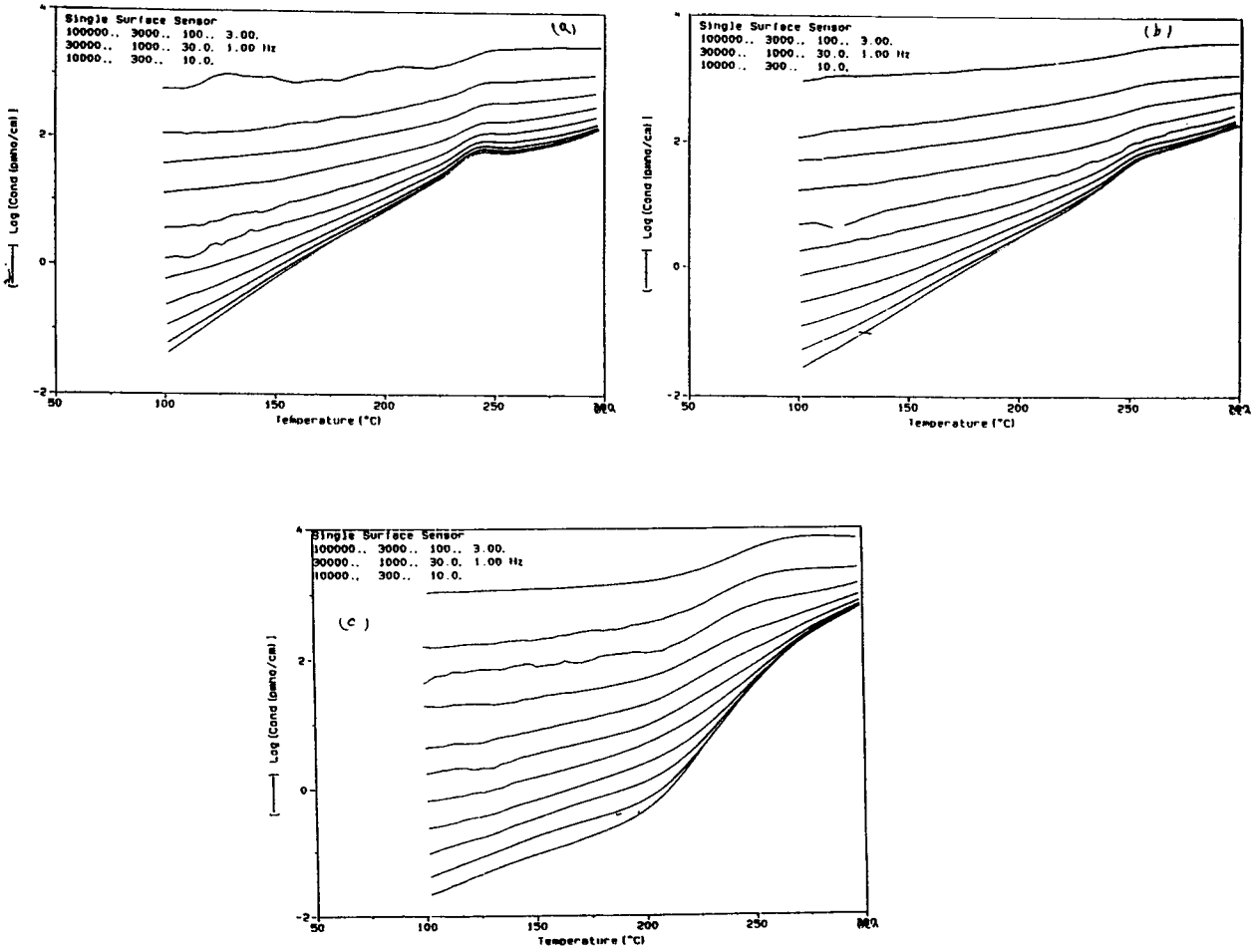

Figure 8 DEA scans of samples recorded after curing isothermally for 3 h at (a) 210°C (MC-600), (b) 225°C (MC-600), and (c) 225°C (MU-55).

by acetone. The samples were then dried in the vacuum oven to constant weight. The percent solubility was calculated using $[wa - wb/wa) \times 100]$, where *wa* is the original weight and *wb* is the weight after extraction. The percent solubility increased with increasing amount of Ultem in the blends, e.g., after curing for 2 h, the percent solubility was found to be 2.6 (MC-600), 4.3 (MU-91), 6.6 (MU-82), 11.6 (MU-73), 14.5 (MU-64), and 23.0 (MU-55). The percent solubility decreased with increasing cure time; however, % solubility was less as compared to the amount of Ultem added in the blend. The lower % solubility could be due to the presence of Ultem within the network.

In FU blends, all the samples were stable up to 500°C and started losing weight above this temperature. First, a 10% addition of Ultem (FU-91) resulted in an increase in IDT, T_{max}, and percent char. An increase in Ultem content in blends ~ 40% (w/w) resulted in a decrease in these temperatures. A further increase of Ultem content (FU-55) resulted in an increase in IDT and T_{max}.

The thermooxidative stability of the cured resins

Table V Thermogravimetric Results of Polyimide Resins in Air Atmosphere (Heating Rate = 10°C/Min; Air Flow = 20 mL/Min)

Sample Designation	IDT (°C)	T_{max} (°C)	FDT (°C)	IPDT (°C)
MC-600	565.7	615.0	640.6	604.2
MU-91	575.1	623.6	645.3	601.0
MU-73	570.2	615.0	637.0	—
MU-55	574.1	617.0	634.0	597.0
FA-700	549.0	583.5	613.5	590.0
FU-91	551.0	589.8	625.3	597.5
FU-73	525.9	563.6	589.3	603.2
Ultem	525.0	545.0 640.0	678.8	618.7

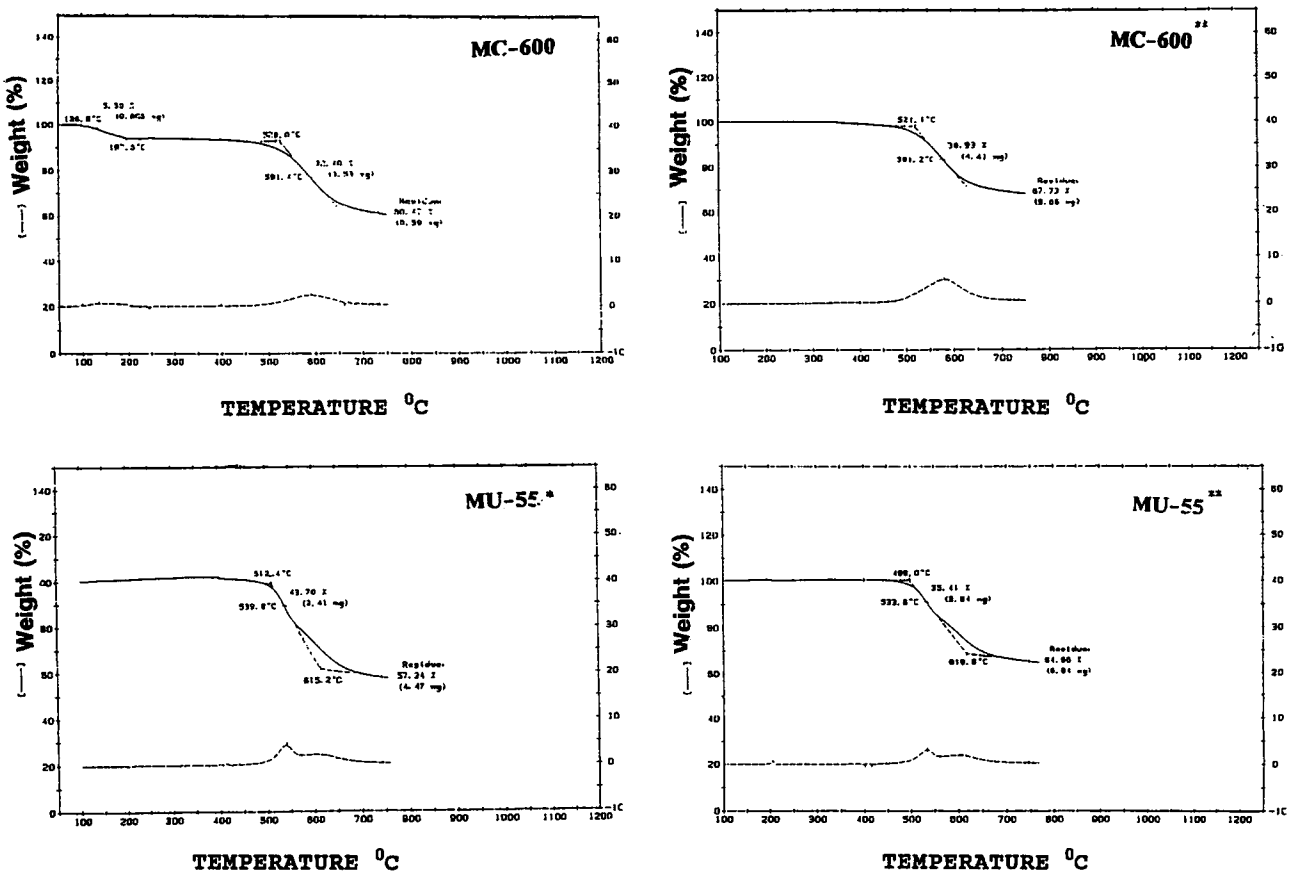

Figure 9 TG and DTG taces of MC-600 and MU-55 resins.

as a function of blend composition was also investigated and the results are summarized in Table V. A single-step degradation was observed in all the samples except in Ultem, which showed a two-step degradation. All the samples were stable up to 525 + 25°C and started degrading above this. All the blend samples had higher IDT than either of its constituents except for FU-73, which had IDT lower than FA-700.

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