A HIGH T_g PMR POLYIMIDE COMPOSITES (DMBZ-15)

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ABSTRACT

A high Tg thermosetting PMR-type polyimide, designated as DMBZ-15, was developed by replacing methylene dianline (MDA) in PMR-15 with 2,2'-dimethylbenzidine. Polyimide/carbon fiber (T650-35) composites were fabricated from a formulation of 3,3', 4,4'-benzophenonetetracarboxylic acid dimethyl ester (BTDE) and 2,2'-dimethylbenzidine (DMBZ), along with nadic ester (NE) as the endcap. DMBZ-15 displays a higher glass transition temperature (T_g = 414 °C) than PMR-15 (T_g = 345 °C), and thus retains better mechanical properties for brief exposure above 400 °C. The physical properties and long-term thermo-oxidative stability of the DMBZ-15 polyimide/carbon fiber composites are also compared to that of PMR-15.

INTRODUCTON

Polyimides have been successfully used in the aerospace applications for 25 years, due to their high thermo-oxidative stability and outstanding mechanical properties. While the processing of condensation polyimides is often difficult, the use of oligomeric imides with reactive endcaps has greatly improved the processability of polyimide composites. PMR-15, an addition curing polyimide based on 3,3', 4,4'-benzophenonetetracarboxylic acid, dimethyl esters and methyline dianiline (MDA) with nadic ester as the endcap (Fig. 1), has been recognized as the state-of-the-art high temperature resin for composite application at 288°C (550°F). The PMR (*in situ* polymerization of monomer reactants) approach ensures easy processing of imide oligomers , using the ester-acid route[1]. As a result, PMR-15 is widely used in aircraft engine components. Over the years analogs of PMR-15, such as RP-46[2] and AMB-21[3,4] were developed by replacing the methylene dianiline (MDA) in PMR-15 with 3,4'-oxydianiline (3,4'-ODA) and 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP), respectively. The flexible ether and isopropylidene linkages in BAPP enabled AMB-21 to be processed successfully by the solvent-assisted resin transfer molding (SARTM) process[5]. Although the flexible ether linkages in BAPP and 3,4'-ODA tend to improve the processabililty of oligomers, they often resulted in polyimides with lower T_g and poor thermo-oxidative stability[6] than PMR-15. Traditionally, PMR-type polyimide[7] composites are designed for long-term use for thousands of hours at 288 –315 °C (550-600 °F)[8], as demonstrated by PMR-15 (Fig. 1) and PMR-II-50. However, new applications in Reusable Launch Vehicles (RLV) require light weight materials that can perform for brief exposures (tens of hours) up to 425 °C (800 °F). It is imperative to understand the mechanical response and failure mechanism of the composites during short excursions at elevated temperature near or exceeding their T_g's.

The objective of this research is to substitute methylene dianiline (MDA) in PMR-15 with 2,2'-dimethylbenzidine (DMBZ, i.e. m-tolidine) whose noncoplanar conformation is known to enhance the processability of addition polyimides.[9,10] DMBZ-15 and PMR-15 composites were prepared from 3,3',4,4'-benzophenone tetracarboxylic acid dimethyl esters (BTDE) and either DMBZ or MDA, respectively, along with the nadic ester (NE) as the endcap in a ratio of n : (n +1) : 2 (Fig. 2). The glass transition temperature (T_g), the thermo-oxidative stability (TOS) and the mechanical properties of DMBZ-15 polyimide/carbon fiber (T650-35) composites will be compared to that of PMR-15/T650-35 composites.

EXPERIMENTAL

Monomer solutions of DMBZ-15 and PMR-15 were prepared from a 50% methanol solution of BTDE, nadic ester (NE), and MDA or DMBZ, respectively. Prepreg was made by brush application of monomer solutions onto drum-wound T650-35 carbon fibers, and subsequently dried. The unidirectional composite panels used in the aging study were fabricated from 12 plies of unidirectional prepreg by a simulated autoclave process, using the standard PMR-15 curing cycle (Fig. 3). Similarly, composite panels in compression tests were fabricated from 8 plies of T650-35 fabrics (8 harness satin weave, with UC309 epoxy sizing) in zero direction. The T_g's of DMBZ-15 and PMR-15 were measured by thermal mechanical analysis (TMA, expansion probe, 5 g load) as well as dynamic mechanical analysis (DMA) on a Rheometrics RMS 800 at 1 Hz with 0.05% tension, using torsional rectangular geometry. The mechanical properties (flexural and shear) were measured on a Instron 450 with series 9 data collection software.

RESULTS AND DISCUSSION

Dynamic mechanical analysis (Fig. 4) and thermal mechanical analysis (TMA) data showed that DMBZ-15 exhibited a T_g greater than 400 °C (Table 1), about 50-70 °C higher than that of PMR-15 (T_g = 348°C, based on the onset decline of storage modulus G'). The reason that DMBZ-15 displays such a high T_g is due to the steric hinderance in the diamine (2,2'-dimethylbenzidine), produced by the two methyl groups on the biphenyl moiety. These sterically-hindered methyl substituents generate a high rotational barrier for polyimides during the glass transition phase[11]. Essentially, DMBZ-15 composites can be used directly after fabrication without postcure. Postcure has been used to boost the T_g of PMR polyimides, but it often initiates a certain degree of degradation. PMR-15 generally requires postcure at 315 °C for 16 hrs to achieve its optimal mechanical performance, but prolonged postcure at high temperature generally shorten the life time of composites.

Mechanical tests (Table 2) indicated that the initial flexural strength, flexural modulus and interlaminar shear strength of DMBZ-15 were very similar to that of the PMR-15 both at ambient temperature and 288 °C (550 °F). In addition PMR-15 and DMBZ-15 composites exhibited comparable compressive strength after 5 cycles of hot-wet open hole compressive test (Table 3). Due to its high T_g (> 400 °C), DMBZ-15 has better mechanical properties above 288 °C relative to PMR-15 (T_g = 345 °C) as shown in Table 2 and Figure 5. Therefore, DMBZ-15 is suitable for applications that required short excursion up to 400 °C. Testing at 400 °C for both PMR-15 and DMBZ-15 showed flexural samples failed in compression rather than tension, due to the softening of resins above T_g and delamination in shear specimens. Long-term isothermal aging at 288°C (550°F) in 1 atm of air revealed that DMBZ-15 composites had a higher weight loss than PMR-15 composites after 1000 hrs of aging at 288 °C (Fig.6). However, DMBZ-15 and PMR-15 neat resins showed almost identical percent of weight loss up to 2500 hour (Fig. 7). Although unidirectional DMBZ-15 composites still retained comparable flexural and interlaminar shear strength (fig. 8 and 9) after 2500 hours of aging at 288°C (550°F), the compressive strength of DMBZ-15 composites (T650-35 fabrics) decreased from 430 MPa to 268 Mpa after 1000 hour of aging at 550 °F, but PMR-15 still retained its strength at 670 MPa. It is rationalized that the higher T_g exhibited by DMBZ-15 composites created more stresses at resin-fiber interface, which in turn, resulted in the more microcrackings in DMBZ-15 than PMR-15 during long-term isothermal aging. Fig. 10 showed that the oxidative degradation of composites proceeded predominately from the edge and slower from the surface. Furthermore, there are more microcracks in the middle of DMBZ-15 composites than in PMR-15 after 1000 hour of aging, and once the cracks initiated, they eventually propagated throughout the entire DMBZ-15 composites.

SUMMMARY AND CONCLUSION

The replacement of methylene dianiline (MDA) in PMR-15 (T_g= 348 °C) with 2,2'-dimethylbenzidine (DMBZ) raises the glass transition temperature of the resulting polyimides (DMBZ-15) to T_g= 414 °C. Apparently, the two methyl substituents on the biphenyl moiety of DMBZ impart a higher rotational barrier on the polymer during the glass transition phase[12]. Therefore, DMBZ-15 exhibited better mechanical properties than PMR-15 beyond 300 – 400 °C for short excursion. Furthermore, DMBZ-15 polyimide/carbon fiber (T650-35) composites displayed comparable initial mechanical properties relative to PMR-15. After long-term aging at 288 °C (550 °F), DMBZ-15 composites retain comparable flexural and shear strength compared to PMR-15. However, the compressive strength of DMBZ-15 decreases dramatically after 1000 hrs of aging, due to the microcracking induced by thermal stress generated by high T_g. Since the DMBZ-15 neat resin appears to have similar thermo-oxidative stability as PMR-15, attempts are in progress to improve the toughness of DMBZ composites through formulations with different endcaps that would yield lighter crosslinking density than the nadic endcap.

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Table 1 T_g's of PMR-15 and DMBZ-15 Polyimide-T650-35 Cabon Fiber Composites[a]

Property	**DMA[b]** **G' (onset)[d], °C**		**DMA** **Tan δ, ° C**		**TMA[c]** **°C**	
Resin	**NPC[e]**	**APC[f]**	**NPC**	**APC**	**NPC**	**APC**
DMBZ-15	409	414	425	430	403	420
PMR-15	345	348	375	376	320	346

[a] Composites were fabricated from 12 plies of unidirectional T650-35 unsized carbon fibers

[b] DMA = Dynamical mechanical analysis at a heating rate of 5 °C/min by a Rheometric RMS 800, using a torsional rectangular geometry at 1 Hz and 0.05% tension.

[c] TMA = Thermal mechanical analysis by expansion probe, with 5 g load and a heating rate of 10 °C/min.

[d] G' = onset decline of storage modulus.

[e] NPC = No postcure

[f] APC = Air postcure at 315 °C (600 °F)

Table 2 Mechanical Properties of DMBZ-15 and PMR-15 T650-35 Fabric Composites[a]

Resin Physical Properties	DMBZ-15	PMR-15
Flexural Strength (MPa)		
23 °C (74 °F)-NPC[b]	(1030 ± 15[d])	----
23 °C (74 °F)-PC[c]	1027 ± 15	1082 ± 89
288 °C (550 °F)-NPC	(578 ± 50)	----
288 °C (550 °F)-PC	577± 48	747 ± 66
371 °C (700 °F)-NPC	(350 ± 45)	----
371 °C (700 °F)-PC	466 ± 32	244 ± 29
427 °C (800 °F)-NPC	(218 ± 7)	----
427 °C (800 °F)-PC	193 ± 19	146 ± 5
Flexural Modulus (GPa)		
23 °C (74 °F)-NPC[b]	(58 ± 1)	----
23 °C (74 °F)-PC[c]	58 ± 1	58 ± 2
288 °C (550 °F)-NPC	(48 ± 3)	----
288 °C (550 °F)-PC	52 ± 1	57 ± 2
371 °C (700 °F)-NPC	(45 ± 2)	----
371 °C (700 °F)-PC	52 ± 2	31 ± 2
427 °C (800 °F)-NPC	(22 ± 4)	----
427 °C (800 °F)-PC	24 ± 1	16 ± 3
ILL Shear Strength (Mpa)		
23 °C (74 °F)-NPC[b]	61 ± 4	----
23 °C (74 °F)-PC[c]	58 ± 4	61 ± 2
288 °C (550 °F)-NPC	(40 ± 1)	----
288 °C (550 °F)-PC	45 ± 1	43 ± 2
371 °C (700 °F)-NPC	(28 ± 2)	----
371 °C (700 °F)-PC	36 ± 1	25 ± 1
427 °C (800 °F)-NPC	(12 ± 1)	----
427 °C (800 °F)-PC	17 ± 3	6 ± 1

[a] Polyimide composites were fabricated from 8 plies of T650-35, 8 harness satin weave, with UC309 epoxy sizing.

[b] NPC = No postcure.

[c] PC = Postcured in air at 315 °C (600 °F) for 16 hrs.

[d] The error bar equals to one standard deviation.

Table 3 Compressive Properties of DMBZ-15 and PMR-15 T650-35 Fabric composites

Resin Compressive Properties	DMBZ-15 Postcured[c]	PMR-15[d] Postcured
Compressive Strength (MPa)		
23 °C (74 °F)[a]	603 ± 18	758
232 °C (450 °F)[a]	449 ± 5	388
288 °C (550 °F)[a]	436 ± 29	489
After 5 hot/wet cycles (550°F)[a,b]	431 ± 22	406
Compressive Modulus (GPa)		
23 °C (74 °F)	59 ± 2	66
232 °C (450 °F)	55 ± 2	66
288 °C (500 °F)	55 ± 1	65
After 5 hot/wet cycles (550 °F)	58 ± 8	65

[a] Dry at 121 °C for 16 hrs before testing.

[b] 1 Hot/wet cycle: 93 °C (200 °F) water soak to > 1% gain, Dry out: 233 °C (500 °F) to <1% loss.

[c] Postcured at 315 °C (600 °F) in air for 16 hrs. before undergoing standard compressive testing at Cincinnati Testing Lab.

[d] Data obtained from ref. 6.

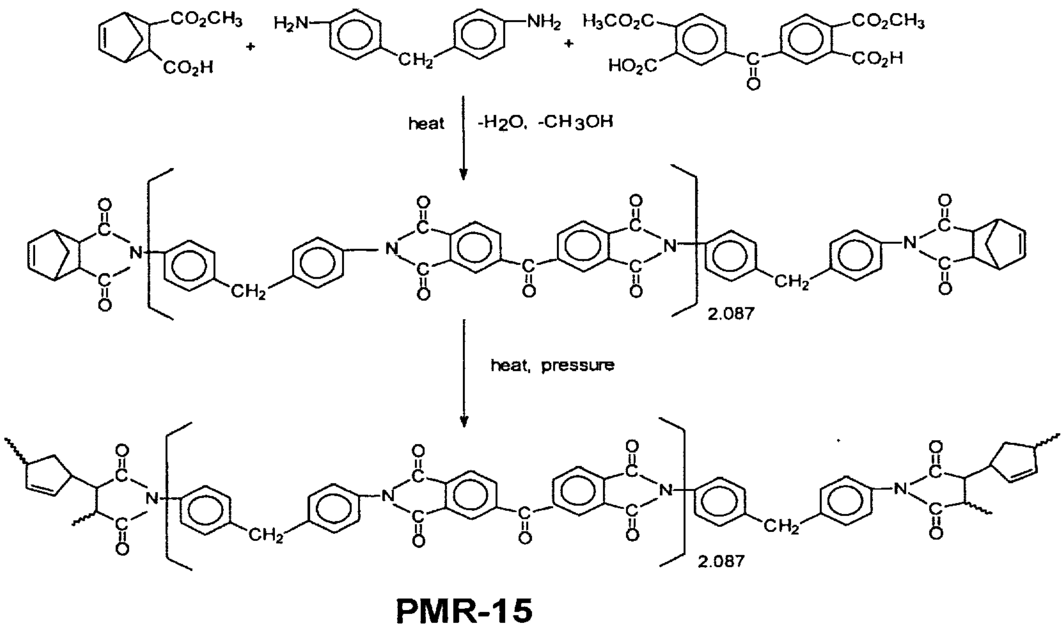


Figure 1 Processing of PMR-15 Polyimide

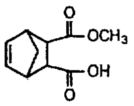
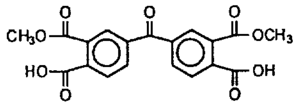
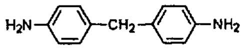
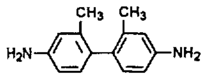
	Endcap	**Dimethyl Esters**	**Diamine**	**Repeating Unit(n)**
Molar Ratio	2	n	n+1	
PMR-15	 NE	 BTDE	 MDA	2.087
DMBZ-15	NE	BTDE	 DMBZ	2

Figure 2 Resin formulation of DMBZ-15 and PMR-15

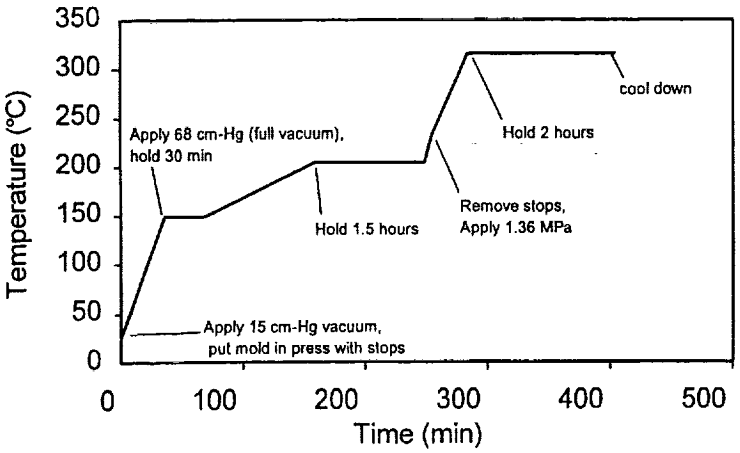


Figure 3 Curing cycle for DMBZ-15 and PMR-15

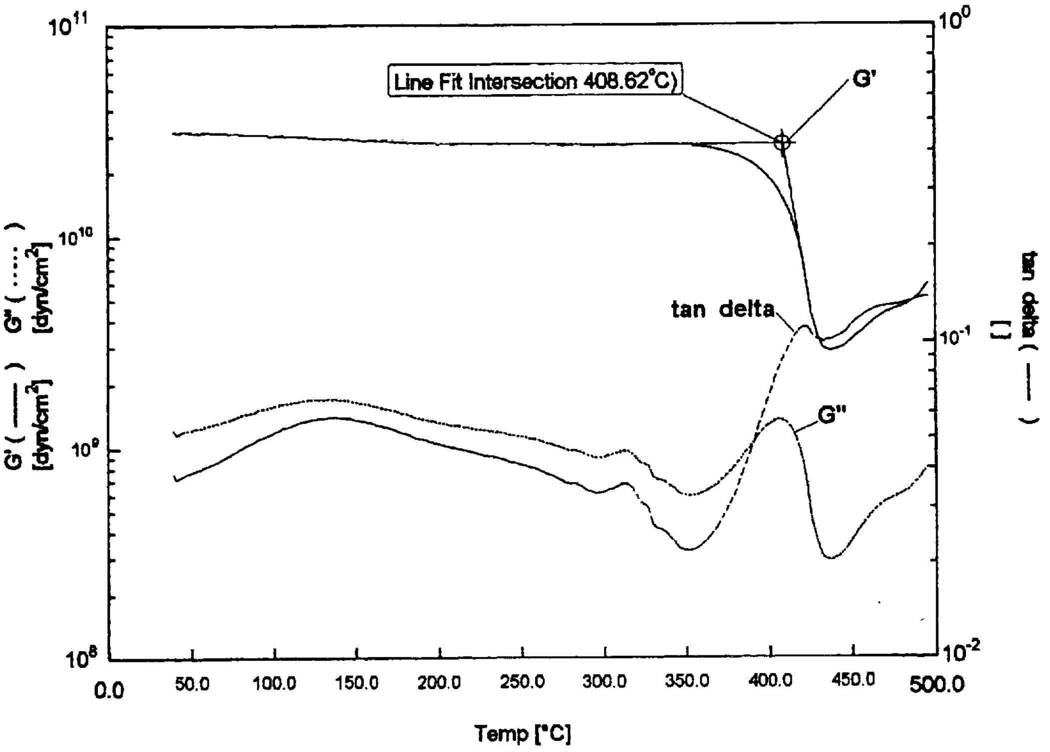


Figure 4 Dynamical mechanical analysis of nonpostcure DMBZ-15 composites

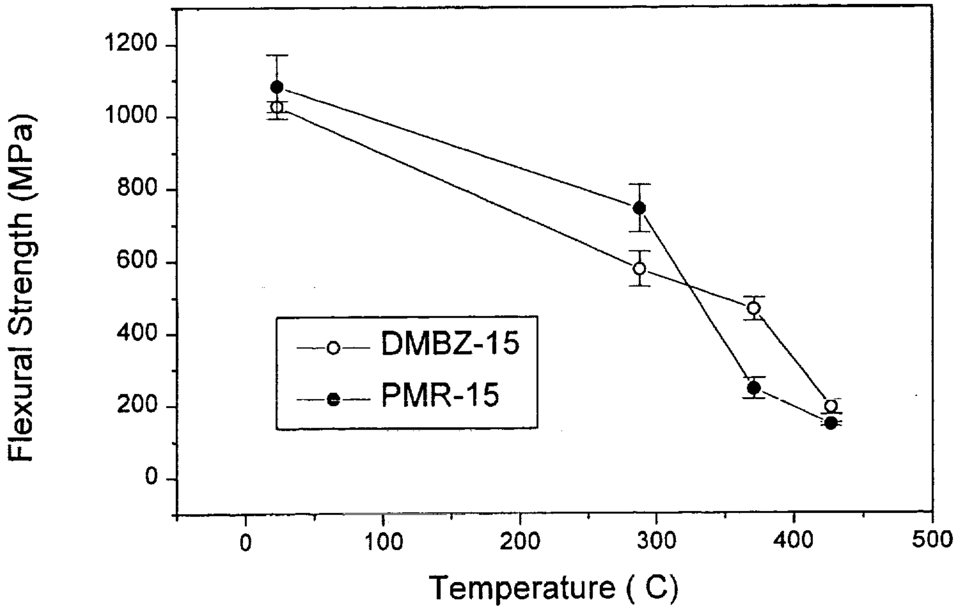


Figure 5 Flexural strength of DMBZ-15 and PMR-15 versus temperature

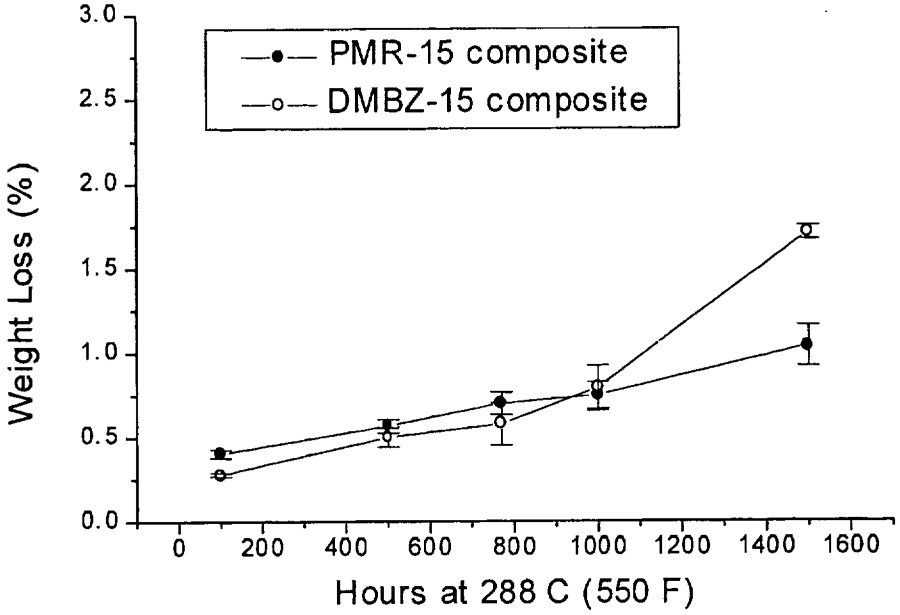


Figure 6 Weight Loss during isothermal aging of unidirectional T650-35 Polyimide composites at 288 °C (550 °F) in 1 atm of circulating air

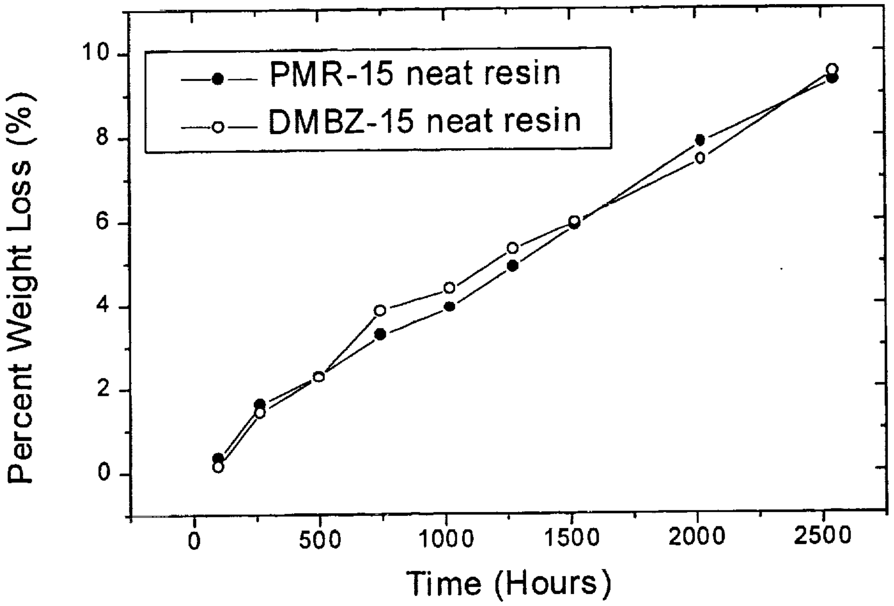


Figure 7 Weight loss during isothermal aging of DMBZ-15 and PMR-15 neat resin at 288 °C (550 °F) in 1 atm of circulating air

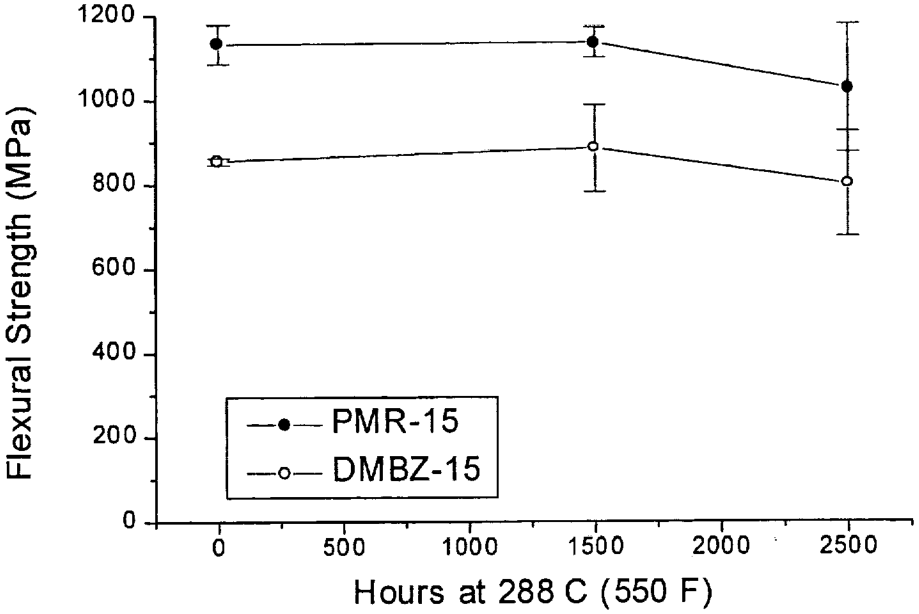


Figure 8 Flexural strength of unidirectional T650-35 polyimide composites as a function of isothermal aging at 288 °C (550 °F)

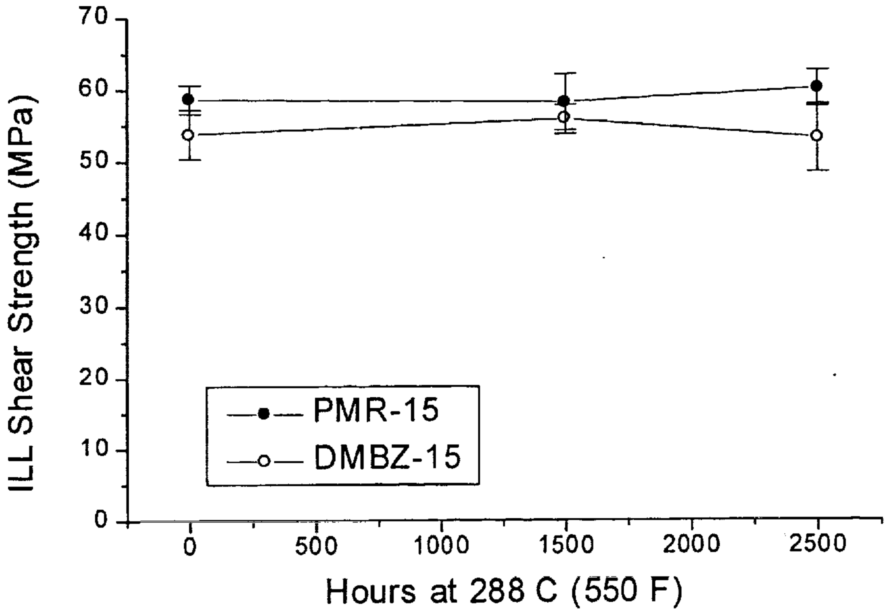


Figure 9 Interlaminar shear strength of unidirectional polyimide composites as a function of isothermal aging at 288 °C (550 °F)

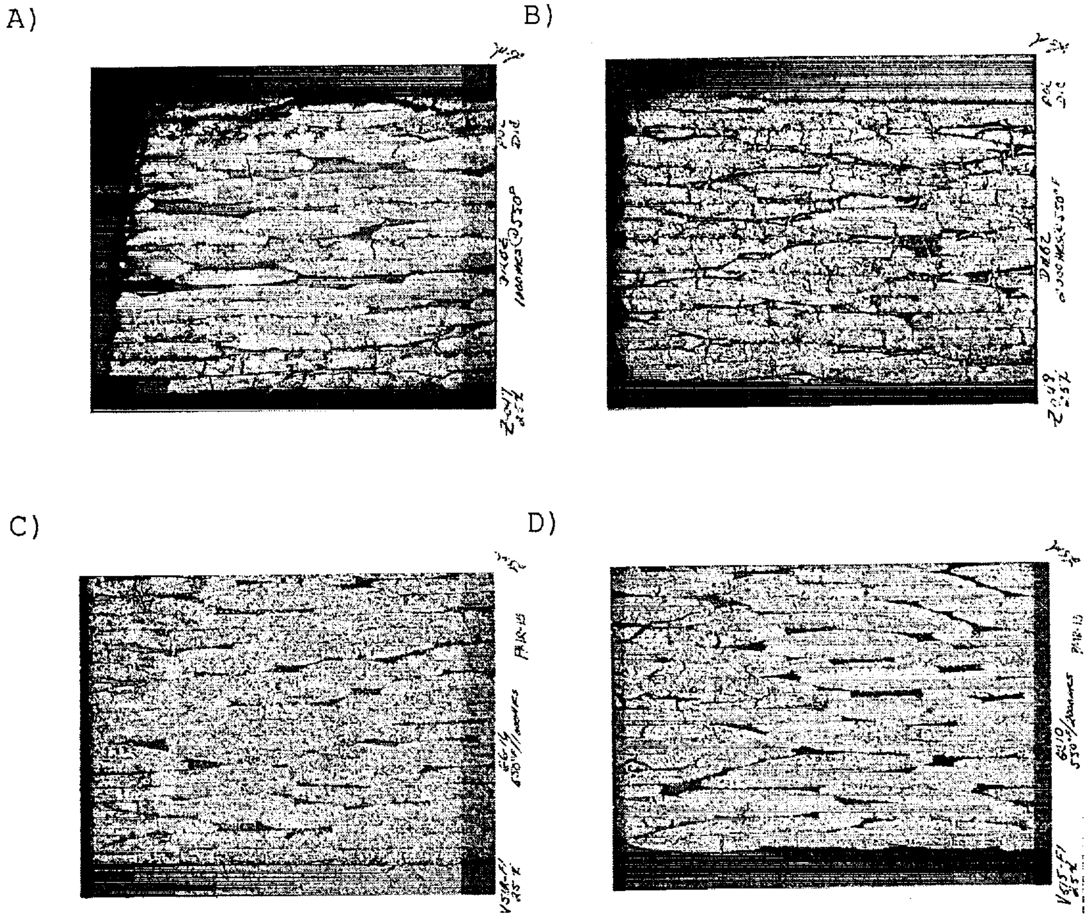


Figure 10 Photomicrographs (25X) of polyimide composites after isothermal aging at 288 °C (550 °F):
A) DMBZ-15 after 1000 h B) DMBZ-15 after 2000 h
C) PMR-15 after 1000 h D) PMR-15 after 2000h