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Effects of a Noncoplanar Biphenyldiamine on the Processing and Properties of Addition Polyimides

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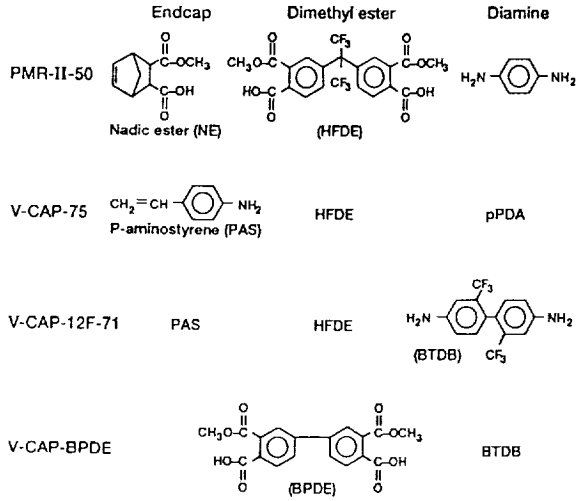
Introduction

PMR-15 is the most widely used polyimide resin for high temperature composite applications up to 288°C (550°F).[1] However, as the quest for higher temperature applications continue, thermally more stable monomer reactants or endcaps as well as higher molecular weight formulations (HMW) are required in order to achieve the desired thermo-oxidative stability (TOS). At present two matrix resins developed at NASA Lewis, namely PMR-II-50 and V-CAP-75, show promise for 371°C (700°F) application in advanced high temperature engines.[2,3] The use of HMW formulations, however, reduces the melt flow during processing. Recently, we reported that the substitution of 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (BTDB) for 1,4-phenylenediamine in either PMR-II or V-CAP formulation improved both the resin melt flow and thermo-oxidative stability of the cured resin.[4] The substitution of trifluoromethyl groups at 2 and 2′- positions of BTDB forces the two phenyl rings into adopting a noncoplanar conformation[5], which in turn disrupts the crystal packing of the oligomers. As a result, it lowers the melting temperature and melt viscosity of the prepolymers before final crosslinking. The noncoplanar conformation of 2,2′-substituted biphenyldiamine apparently provides more flexibility in the polyimide backbone whereas the biphenyl moiety imparts higher thermal stability. Our previous study also showed that resins formulated with p-aminostyrene (V-CAP) as an endcap were thermally more stable than the corresponding resins with nadic (NE) endcaps.[4] The objective of this research was to evaluate the thermo-oxidative stability of addition polyimides based on BTDB with various dianhydrides as well as the properties of the corresponding composites.

Monomers Used for Resin Synthesis



Experimental

The addition polyimides (n=9) were formulated from 50% methanolic solution of 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (BTDB), dimethyl esters of various dianhydrides and p-aminostyrene (V-CAP) in a ratio of n : n+1 : 2. The neat resin disks were prepared from imidized powders by holding the resin powders in a mold at 288°C under contact pressure for half an hour, followed by compression molding at 357°C for 2 h at 1500 psi. The prepreg tapes were made by brush application of methanolic monomer solution onto drum-wound G40-600 graphite fibers, which were subsequently dried. The laminates were then fabricated from 12 plies of unidirectional prepreg by vacuum bag lay-up, followed by the standard PMR-II curing cycle.[3]

Results and Discussion

A neat resin isothermal aging study based on BTDB with various dianhydrides (Table I) showed that VCAP-12F-71, prepared from HFDE/BTDB/PAS/n=9, exhibited the best overall thermo-oxidative stability. The V-CAP-75 and V-CAP-50 resins had slightly higher initial weight loss than VCAP-12F-71, but eventually these three resins fare similarly at the end of 1000 h under 1 atm. of air at 343°C (650°F). The thermo-oxidative stability of BTDB-based addition polyimides, formulated from dimethyl esters of 3,3′,4,4′-biphenyl dianhydride (BPDA), 3,3′,4,4′-benzophenone dianhydride (BTDA) and pyromellitic dianhydride (PMDA), was not as good as that of PMR-II-50 or V-CAP-75. The glass transition temperature (T_g) of VCAP-12F-71 neat resin (no post cure) ranged between 281°C and 295°C, depending on the test methods (Table II).

Several BTDB-based addition polyimides composites were fabricated on G40-600 graphite fibers, and their mechanical properties and TOS were evaluated. The G40-600 graphite fiber was chosen because previous study has shown that G40-600 graphite fiber reinforced PMR-II-50 and V-CAP-75 composites yielded the best overall combination of mechanical properties and oxidative resistance.[6] The T_g's of these composites were measured by dynamic mechanical method, and characterized either as the onset decline of storage modulus G′ or tan δ (Table III). The flexural strength and interlaminar shear strength of these composites are listed in Table IV. These data indicated that BTDB-based resins formulated with HFDE displayed better mechanical properties at elevated temperature than those prepared from BPDE. An attempt to reduce the cost by mixing p-PDA and BTDB (1:1) in HFDE-containing formulations afforded a composite with slightly poorer mechanical performance and lower thermal stability, although it still performed better than the BPDE-containing composites.

The isothermal aging study at 371°C (Figure 3) again confirmed that VCAP-12F-71 had highest TOS among all the BTDB-based composites. Furthermore, the thermo-oxidative stability of VCAP-12F-71 composites at 371°C (700°F) is superior to either PMR-II-50 or V-CAP-75 (Figure 4).

Summary and Conclusion

Addition curing polyimide composites prepared from HFDE/BTDB/PAS/n=9 with G40-600 graphite fibers, designated as VCAP-12F-71, exhibited superior thermo-oxidative stability at 371°C (700°F) to either PMR-II-50 or V-CAP-75 composites. The incorporation of noncoplanar 2,2′-bis(trifluoromethyl)-4,4′-biphenyldiamine (BTDB) in the polyimide backbone not only improved the processability of PMR type oligomers, but also enhanced the thermal stability of the cured polyimides.

References

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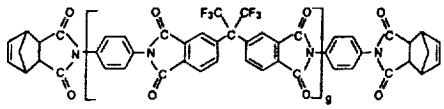
PMR-II-50



V-CAP

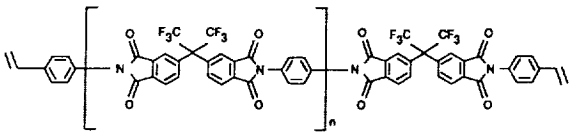


Figure 1.—PMR-II-50 and V-CAP oligomers.

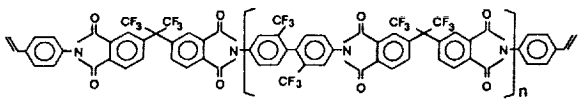


Figure 2.—Formulation of V-CAP-12F.

TABLE I.—650 °F ISOTHERMAL AGING OF BTDB-BASED ADDITION POLYMIDES (NEAT RESINS)

Dianhydride	Amine	Endcap	n-value	Percent weight loss after-	
				500 hr	1000 hr
HFDE	BTDB	PAS	9	8.1	20.2
HFDE	BTDB	NE	9	17.4	35.4
HFDE	pPDA	PAS	14	11.6	22.6
HFDE	pPDA	PAS	9	10.4	20.0
HFDE	pPDA	NE	9	18.4	33.7
BPDE	BTDB	PAS	4	19.3	42.8
BTDE	BTDB	PAS	9	20.4	47.1
PMDE	BTDB	PAS	9	20.1	50.7

Table II.--T_g's OF VCAP-12F NEAT RESIN (NO POST CURE)

Dynamic Mechanical Analysis (DMA)[a]	281 °C
Thermal Mechanical Analysis (TMA)[b]	294 °C
Three Point Bending on TMA	295 °C

[a]Taken as the onset decline of storage modulus G'.
[b]Measured by expansion probe.

Table III. DYNAMIC MECHANICAL PROPERTIES OF G40-600 FIBER REINFORCED POLYIMIDE COMPOSITES

Resin	G'(onset)[a]		tan δ	
	NPC[b]	PC[c]	NPC[b]	PC[c]
VCAP-12F-71	300 °C	342 °C	330 °C	386 °C
V-CAP-50	310 °C	327 °C	340 °C	402 °C
PMR-II-50	344 °C	385 °C	340 °C	370 °C

[a]Onset of decline in storage modulus G'.
[b]NPC = no post-cure.
[c]PC = 16 h of air post-cure at 700°F.

TABLE IV.—MECHANICAL PROPERTIES OF BTDB-BASED POLYIMIDE COMPOSITES

Dianhydride	Diamine	Endcap	n Value	Flexural (ksi)		Shear (ksi)[a]	
				RT	700 °F	RT	700 °F
HFDE	BTDB	PAS	9	187	71.7	8.4	4.2
HFDE	BTDB/pPDA	PAS	9	220	60.2	7.8	3.5
BPDE	BTDB	PAS	9	---	32.0	---	2.2
BPDE	BTDB	NE	4	---	36.5	---	2.4

[a]Interlaminar shear strength.

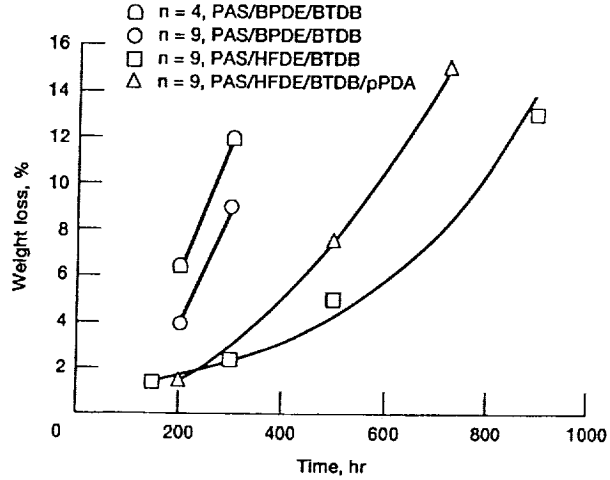


Figure 3.—Effect of BTDB-based resin composition on the thermo-oxidative stability of G40-600 graphite polyimide composites exposed to 1 atm of air at 700 °F.

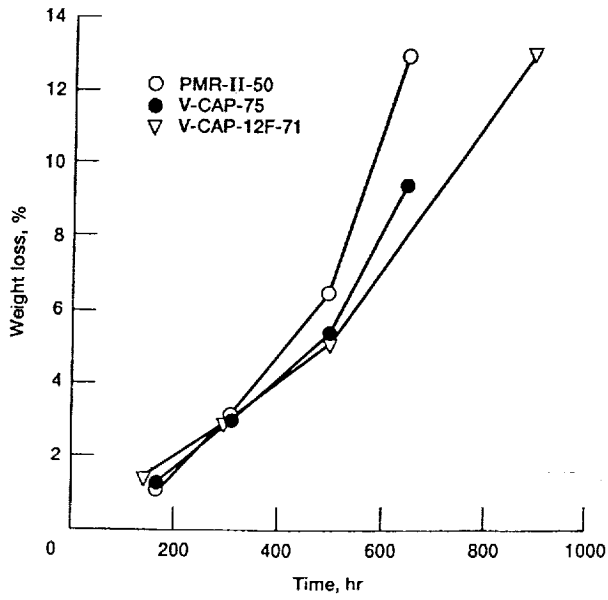


Figure 4.—Comparative thermo-oxidative stability of G40-600 graphite fiber reinforced polyimide composites exposed to 1 atm of air at 700 °F.

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Addition curing polyimides, prepared from noncoplanar 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (BTDB) with various dianhydrides, were evaluated as high temperature polymer matrix materials. T_g of these polyimides were measured by mechanical method along with thermal mechanical analysis. Physical and mechanical properties as well as the thermo-oxidative stability of neat resins and the corresponding G40-600 graphite fiber reinforced composites were compared to that of PMR-II-50 and V-CAP-75.

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