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New Addition Curing Polyimides

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NEW ADDITION CURING POLYIMIDES

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Introduction

Polymers are gaining wide acceptance as matrix materials for composite structural applications. The best polymers to date for these applications, combining thermal-oxidative stability (TOS), processibility and good mechanical properties, are the PMR polyimides. The specific focus of our interest is on understanding and ultimately improving the TOS of the PMR-15 polyimide system. This resin, first developed at NASA LeRC,² is formed through a two step polymerization scheme. The first step involves the formation of a polyimide prepolymer via the condensation at 120-230 °C of three monomer reactants: 2-carbomethoxy-3-carboxy-5-norbornene (the monomethyl ester of nadic acid, NE), 4,4'-methylenedianiline (MDA) and 3,3'-dicarbomethoxy-4,4'-dicarboxybenzophenone (BTDE). The resulting low molecular weight polyimide oligomer undergoes cross-linking at 275-325 °C to produce a void free network structure. There is also a final post-cure which raises the glass transition temperature (T_g) of the resin.

The literature^{3,4} suggests that the most thermally labile bond in the polyimide system should be the $>N-C=O$ peptide bond, whose dissociation energy is a mere 50⁴ or 65⁵ kcal/mol. We reasoned (by analogy to sterically hindered dioxetanes)⁶ that steric blocking should help stabilize this linkage, forcing it to reclose rapidly and, thereby, improve its TOS. It was for this reason that we explored the properties of polyimides containing the new dianhydride 1,4-phenylene bis(phenylmaleic anhydride)⁷ [PPMA, see Figure 1].

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Results and Discussion

Two series of addition curing polyimides have been prepared using PPMA. The first (dubbed AAFI, see Figure 1) is a modification of PMR resins in which the PPMA replaces BTDA, used in PMR-15. This substitution resulted in improved prepolymer solubility (chloroform, methylene chloride, dioxane, 1,2-dichloroethane, DMF and NMP) and increased resin flow upon curing at 315 °C [600 °F]. Various formulations of polyimide prepolymers were prepared via chemical imidization (AcOAc in refluxing AcOH), theoretically ranging from $n=1.7$ to $n=20$. GPC studies (see Table 1) indicated, however, that there was a limiting average molecular weight (M_n) at around 3250, corresponding to $n=4.8$. As expected (Table 2), T_g values for the cured polymers were highest at low molecular weights, but ca. 10 °C lower than PMR-15. On the other hand, onset of decomposition and 10% decomposition were highest at the higher MW formulations but generally lower than PMR-15. The latter data predict a poorer TOS for the AAFI series, and this is, indeed, confirmed by long term weight-loss studies. As seen from Figure 2 and Table 2, weight loss after 600 hours at 315 °C for the various AAFI formulations was around 2.5 times that of PMR-15 under the same conditions. We speculate that the poor TOS results from the thermolysis and loss of the pendant phenyl groups.

Figure 1

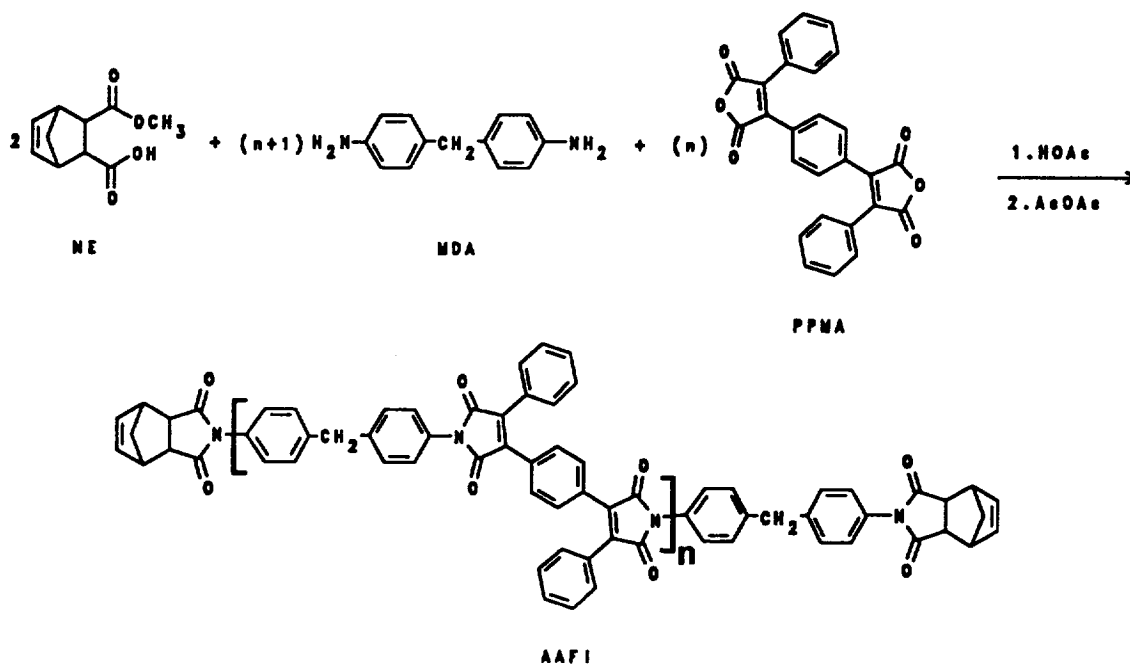


Table 1: Molecular Weight Data on AAFI Formulations

<u>N (# of Repeating Units)</u>		<u>Molecular Weight</u>	
<u>Formulated</u>	<u>Calculated^a</u>	<u>Formulated</u>	<u>Average (M_n)^b</u>
1.70	1.77	1500	1524
2.087	2.14	1711	1742
4.00	3.30	2829	2418
9.00	3.62	5752	2604
15.00	4.81	9260	3252
20.00	4.31	12183	3010

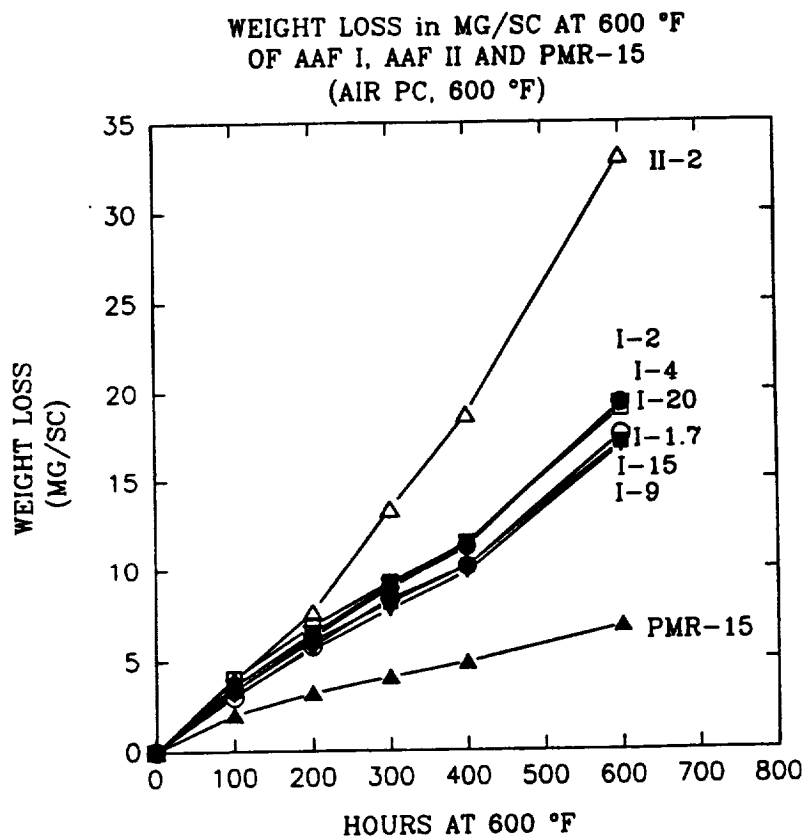
a. Calculated by interpolation from M_n values.

b. Based on gel permeation chromatography data.

**Table 2: Thermal Data on Various Polymers
(Cure and Aging Temperature: 315 °C [600 °F])**

<u>Polymer</u> <u>N (Form.)</u>	<u>T_g(TMA)</u>		<u>TGA</u>		<u>Wt. Loss (600h)</u>		<u>Density</u> <u>(g/cc)</u>
	<u>NPC</u>	<u>PC</u>	<u>Onset</u>	<u>10%</u>	<u>mg/cm²</u>	<u>Percent</u>	
AAFI							
1.7	289	333	464	486	17.5± 1.0	36.2± 1.8	
2.087	272	323	467	488	19.3± 1.2	30.7± 2.0	1.26
4	265	306	474	497	19.3± 0.9	32.8± 1.4	
9	237	297	479	503	16.9± 0.6	28.3± 1.0	1.27
15	242	296	480	506	17.1± 0.4	32.0± 2.0	
20	244	295	484	509	19.0± 0.7	39.5± 1.8	1.26
AAFII							
2.087	390	408	463	484	33.1± 2.7	51.1± 0.6	1.30
PMR-15							
2.087	319	340	480	533	6.8± 0.2	9.64± 0.2	1.30

Figure 2



A second series of nadic endcapped prepolymers (named AAFII) was prepared from PPMA and p-phenylenediamine (PPDA) with a theoretical formulation of $n=2.087$ (MW 1432). The prepolymer had only a very limited solubility. Compression molded neat resin samples had a T_g of 408 °C after air post-cure, close to 70 °C higher than PMR-15. Much to our chagrin, however, here too the onset and 10% decomposition values were significantly lower and weight loss significantly higher than PMR-15 and even the AAFI series (see Table 2).

Nitrogen post-curing (399 °C [750 °F] for 24 h)⁸ of AAFI and AAFII substantially raised the T_g , as well as the onset and 10% decomposition values. Nevertheless, it had a seriously detrimental effect on the TOS as determined by long-term aging studies. Thus, after 600 hr at 315 °C the observed weight loss for AAFI and AAFII was 33 mg/cm² (ca 62%) and 50 mg/cm² (ca 80%), respectively.

Model compounds of AAFI and AAFII ($n=1$) were prepared by chemical imidization of PPMA with mononadic MDA or PPDA.

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References and Footnotes

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13. ABSTRACT (Maximum 200 words) In an attempt to improve the thermal-oxidative stability (TOS) of PMR-type polymers, the use of 1,4-phenylenebis (phenylmaleic anhydride), PPMA, has been evaluated. Two series of nadic end-capped addition curing polyimides have been prepared by imidizing PPMA with either 4,4'-methylenedianiline or p-phenylenediamine. The first resulted in improved solubility and increased resin flow while the latter yielded a compression molded neat resin sample with a T _g of 408 °C, close to 70 °C higher than PMR-15. The performance of these materials in long term weight loss studies was below that of PMR-15, independent of post-cure conditions. These results can be rationalized in terms of the thermal lability of the pendant phenyl groups and the incomplete imidization of the sterically congested PPMA. The preparation of model compounds as well as future research directions are discussed.			
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