Ultra High Temperature Thermosetting Polyimides Composites

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INTRODUCTION

Considerable attention has been directed towards acetylene terminated oligomers over the last 20 years and recent work has focused on phenylethynyl terminated imide (PETI) oligomers [1,2]. There is a growing demand for polyimide resins that are processable, yet solvent resistant , and that will withstand temperature in excess of 371℃ for extended periods of time. NASA has developed some high temperature polyimides composites that suitable for 343 or 371 applications, such as PMR-II-50, V-CAP and AFR-700. However, the costs of 6FDA which was used for these matrix resins, are too high to be accepted [3].

In this paper, the polyimides/AS4 carbon fiber composites were fabricated with the modified polymerization of monomeric reactant (MPMR) method (dioxane or ethanol/water as solvent) [4,5]. Their thermal properties and mechanical properties were described.

RESULTS AND DISCUSSION

The 5% of weight loss of all the cured oligomers imides end-capped with 4- phenylethynylphthalic anhydride (PEPA) are over 510℃ whether in N_2 or in air (Seen in Table 1), they are obviously higher than that end-capped with NA having compared molecular weight.

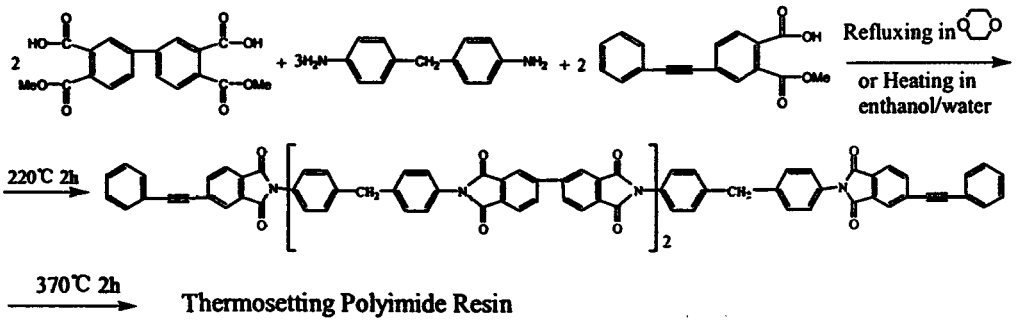
Table 1. Weight Loss of Cured Oligomers via the Amide-Acid Route*

Oligomers Structure and Ratio of Monomers	Temperature of Weight Loss			
	in N_2		in Air	
	5%	10%	5%	10%
BPDA/MDA/PEPA=2/3/2	539	572	540	560
BPDA/ODA/PEPA=2/3/2	539	572	545	571
BPDA/ODA/PEPA=3/4/2	551	575	539	573
BPDA/*m*-PDA/PEPA=2/3/2	542	582	537	576
BTDA/MDA/PEPA=2/3/2	520	554	515	548
BTDA/ODA/PEPA=2/3/2	520	561	528	560
BTDA/ODA/PEPA=3/4/2	530	560	534	559
HQDPA/ODA/PEPA=3/4/2	534	550	535	573
HQDPA/ODA/PEPA=9/10/2	531	560	532	563

* Samples Were Cured for 2h at 370 .

The method of polymerization of monomeric reactants (PMR) was developed in NASA and made a great progress in processing polyimides composites, especially for PMR-15 polyimide resin. Moreover, the conventional PMR technique is limited to diesters of pyromellitic acid (PMDE), 3,3',4,4'-

biphenyltertracarboxylic acid (BPDE), etc, for the reasons of solubility. In order to overcome this drawback, two modified PMR (MPMR) have been developed in our laboratory (seen in scheme 1), which use solvents other than alcohol, such as dioxane and ethanol/water (with a wide ratio). The precursor thus obtained not only keeps the attractive features of the original PMR procedure, such as high concentration and low viscosity but also much longer shelf life and greatly reduced toxicity [6].



Scheme 1. Preperation of Polyimide Oligomers Resin

Both of the polyimides resins and composites of compression molded show very high thermo-oxidative stability (table 2). The weight loss of the resin BPDE/PDA/PEPE was only 1.8% after 200h aging in flowing air at 371℃. The weight loss of the composites BPDE/MDA/PEPE with ethanol/water as solvent was 2.8% after 100h aging at 371℃. The ratio of ethanol/water could be 8:1 to 1:4. The induction of H_2O slightly decreased the thermoxidative stability of the materials.

Table 2. Thermo-Oxidative Stability of Resins and Composites at 371℃ in Flowing Air

Structure	Solvent	Type	Weight Loss (%)							
			25h	50h	75h	100h	125h	150h	175h	200h
BPDE/MDA/PEPE	1,4-Dioxane	Resin	0.2	0.5	0.8	1.0	1.4	1.7	1.9	2.0
		Composite	0.4	0.9	1.4	1.8	2.0	2.2	2.5	2.9
BPDE/MDA/PEPE	Ethanol/Water=4:1	Resin	0.3	0.7	0.9	1.1	1.9	2.1	2.4	2.9
		Composite	0.5	1.3	2.5	2.8	—	—	—	—
BPDE/(*p*-,*m*-)PDA/PEPE	Ethanol/Water=4:1	Resin	0.4	0.5	0.6	0.8	1.1	1.3	1.7	1.8
		Composite	0.6	1.6	1.9	2.5	—	—	—	—

The mechanical properties of polyimides composites are shown in table 3. The flexural strength of the composites determined at 371℃ maintain more than 50% of that at RT. The modulus of the composites at 371℃decrease slightly compared with that at RT. The flexural strength at 371℃ can still keep 50% after aging in air for 100h at 371℃. The DMA curve of polyimide composite is shown in figure 2. The dynamic modulus of composite (E') did not decrease before 410℃. From the data of the curve tan δ , we can see the glass transition temperature is as high as 449℃.

Table 3. The Mechanical Properties of the Polyimides Composites

Structure	Percent of CF (%)	Test Temperature (℃)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Interlaminar Shear Strength (MPa)
BPDE/MDA/PEPE with dioxane as solvent	60	RT	1224	99	55
		371℃	675	106	25.5
		371 *	1017	119	32.9
BPDE/MDA/PEPE with ethanol/water as solvent	56	RT	1453	122	54.7
		371℃	670	106	27
		RT*	—	—	74.6
		371 *	825	115	36
BPDE/(*p*-,*m*-)PDA/PEPE with ethanol/water as solvent	64	RT	1139	141.8	24
		371℃	691	151	18
		RT*	—	—	65
		371 *	—	—	12

* Aging in Air for 100h at 371

CONCLUSION

The polyimides end-capped with PEPA were synthesized. The resins and composites obtained from dioxane or ethanol/water system possess high thermal stability. The flexural and interlaminar Shear strength of the composites determined at 371℃ maintained more than 50% of that at RT. The glass transition temperature(DMA) of BPDE/MDA/PEPE composite is up to 449℃.

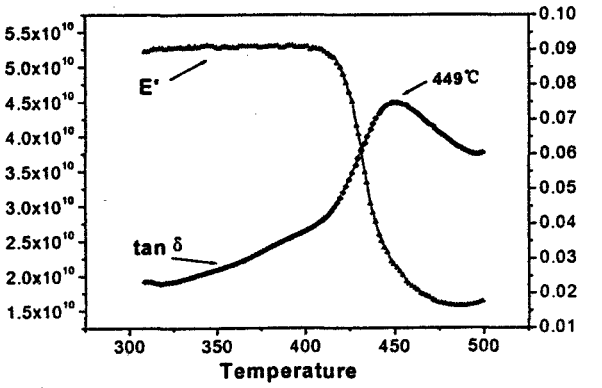


Figure 1. DMA Curve of BPDE/MDA/PEPA Polyimide Composite with Dioxane as Solvent

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