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THERMAL ANALYSIS OF PHENYLETHYNYL END-CAPPED FLUORINATED IMIDE OLIGOMER AFR-PEPA-4

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Thermal analysis of phenylethynyl end-capped imide oligomer AFR-PEPA-4 was performed to characterize cure reaction, thermal stabilities and semicrystalline behavior of AFR-PEPA-4 oligomer and its cured polyimide. Cured AFR-PEPA-4 polyimide showed high T_gs up to 418°C. Both AFR-PEPA-4 oligomer and polyimide exhibit excellent thermal stabilities comparable to PETI-5 polyimides. AFR-PEPA-4 imide oligomer has a T_m of 330°C and exhibits spherulite crystalline morphology in the film. The crystallinity in AFR-PEPA-4 films could not be regenerated under any annealing conditions after the initial melt.

Keywords: *AFR-PEPA-4, phenylethynyl, polyimide, thermal analysis*

Introduction

Because of their high thermal stability and excellent mechanical, chemical and electrical properties, polyimides have been used in a wide range of applications from electronic industries to carbon fiber composites for aerospace structural applications [1]. Compared to norbornyl/amine or ethynyl terminated polyimides, phenylethynyl terminated polyimides exhibit many advantages [2–5] such as (1) no evolution of volatiles during the cure reaction, (2) larger processing window, (3) excellent mechanical properties, in particular outstanding fracture toughness values, and (4) higher hydrolytical stabilities.

NASA's PETI-5, for example, a phenylethynyl terminated imide oligomer that received enormous attention during the development of High Speed Civil Transportation program (HSCT) [6], is one of the most excellent thermosetting polyimides for use as a composite matrix and adhesive. The PETI-5 oligomers had good flow on the application of pressure (0.69~1.4 MPa) at temperatures greater than 250°C [5]. They are generally cross-linked in the 320–371°C temperature range and the cured polyimides exhibits extremely high toughness (strain to failure from 14 to 84% in the 23–177°C temperature range) [3]. However, the glass transition temperature (T_g) of cured PETI-5 is relatively low, which is 270°C [7–9]. Meanwhile, semicrystalline behavior was observed in the imide oligomers. Hou *et al*. [8] studied the composite properties of PETI-5/IM7 by using differential scanning calorimetry (DSC) and demonstrated that crystallinity is still present after PETI-5 was cured at or below 350°C. Fang *et al*. [10, 11] characterized the cure reactions and cure mechanisms of PETI-5 by using DSC, infrared spectroscopy (IR) and ^{13}C-NMR.

It was found that polyimides synthesized from 2,2'-*bis*(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA), with the structure of perfluoromethyl substituents, always have extremely high use temperatures and stabilities [1]. Recently, phenylethynyl terminated AFR-PEPA-N imide oligomers and their cured polyimides derived from 6FDA and 1,4-diaminobenzene (*p*-PDA) were prepared and investigated [12–15]. AFR-PEPA-N polyimides exhibited only a 3–5% decrease in dry T_g after hygrothermal exposure, which is similar to PETI-5. In addition, AFR-PEPA-N polyimides showed extremely high T_g's (435–455°C), excellent mechanical properties and the potential to be processed by resin transfer molding (RTM). In previous studies [15] we have worked to characterize the thermal cure kinetics and mechanisms of AFR-PEPA-4 imide oligomer. The activation energy of thermal cure reaction of AFR-PEPA-4 oligomer is 34.1 kcal mol^{-1} with the kinetic order of 1 when the reaction conversion is less than 80% [15].

In the present research, thermal analysis of phenylethynyl end-capped imide oligomer AFR-PEPA-4 was performed to characterize cure reaction, thermal stabilities and semicrystalline behavior of AFR-PEPA-4 oligomer and its cured polyimide.

Experimental

Materials

2,2'-*bis*(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6-FDA), 1,4-diaminobenzene (*p*-PDA),

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4-(phenylethynyl)phthalic anhydride (PEPA) were obtained from Performance Polymer Solutions Inc. *N*-methyl-2-pyrrolidinone (NMP), and methanol were obtained from Aldrich. All chemicals were used as received. AFR-PEPA-4 oligomer was synthesized by the method reported previously [15]. The oligomer had a theoretical molecular mass of 2634 g mol^{-1}. The chemical structure of AFR-PEPA-4 imide oligomer is shown in Fig. 1. AFR-PEPA-4 polyimide was prepared by curing the imide oligomer in small glass vials in a preheated furnace with desired temperature and time.

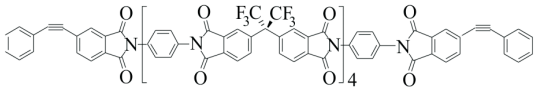

Fig. 1 Chemical structures of AFR-PEPA-4 imide oligomer

Methods

Dissolving tests of AFR-PEPA-4 imide oligomer were performed by using NMP as a solvent. The percentage by mass of NMP was varied. The solutions were stirred vigorously for approximately 10 min. The glass vials were heated from room temperature until 120°C on a Corning Hot Plate until the crystals appeared to dissolve. The solutions were also analyzed under cross-polarized light using an Olympus BX60 Optical Microscope to confirm that the crystals were completely dissolved.

AFR-PEPA-4 oligomer films were also prepared. Imide oligomer was dissolved in NMP and cast into ~0.2 mm thick films onto glass cover slides by evaporating NMP at 150°C. The films were then observed under cross-polarized light using an Olympus BX60 Optical microscope. The films were also annealed at an isotherm of 330°C for fifteen minutes. The morphology of the films before and after annealing was observed by the optical microscope.

Thermogravimetric analysis of oligomer and cured polyimide was performed on a TGA Q500 thermal analyzer. The heating atmospheres were air or nitrogen. 50 mg samples were heated to 800°C. Heating rates are from 2 to 20 K min^{-1}.

T_g and T_m of the uncured and cured samples were measured by a Perkin Elmer DSC Pyris 7 system. Temperature was scanned from 100 to 450°C at 20 K min^{-1}, with nitrogen as the carrier gas (20 cm^3 min^{-1}).

Results and discussion

DSC studies of AFR-PEPA-4 imide oligomer and cured polyimide

An illustration of the T_g before and after cure is shown in Fig. 2. AFR-PEPA-4 imide oligomer has an initial T_g

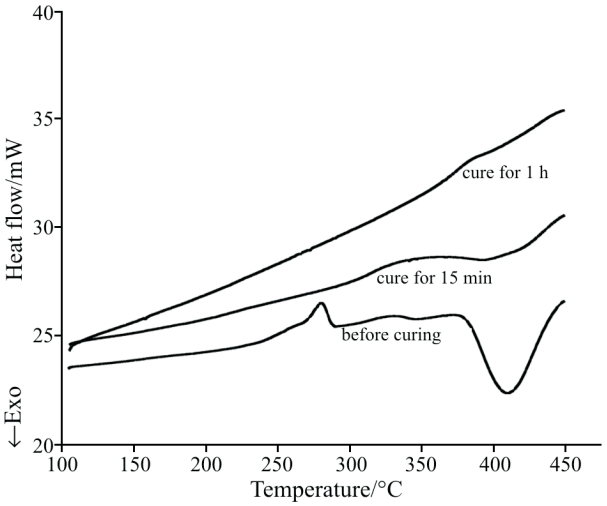

Fig. 2 DSC curves of AFR-PEPA-4 oligomer before and after cure at 350°C (scan rate: 20 K min^{-1})

of 238°C and a T_m of about 330°C. After 1 h cure at 350°C, the cured product did not exhibit a melt, indicating the disappearance of the crystallinity during the cross-linking reaction. Semicrystalline behavior has also been observed in phenylethynyl-terminated PETI-5 imide oligomers, which had T_ms of about 350°C [5, 8, 9]. However, Simone and Scola [9] did not observe the crystallinity of 4,4'-(2,2,2-trifluoro-1-phenylethylidene) diphthalic anhydride (3FDA) or 6FDA containing PETI-5 imide oligomers based on their DSC studies. They attributed the amorphous nature of these materials to a greater degree of molecular freedom and less intermolecular interaction.

DSC study shows that the exothermic cure reaction peak starts at 370°C and reaches its peak at 410°C. The dependences of T_g of cured oligomers on cure time at various cure temperatures in air are shown in Fig. 3. The T_g of the cured oligomer

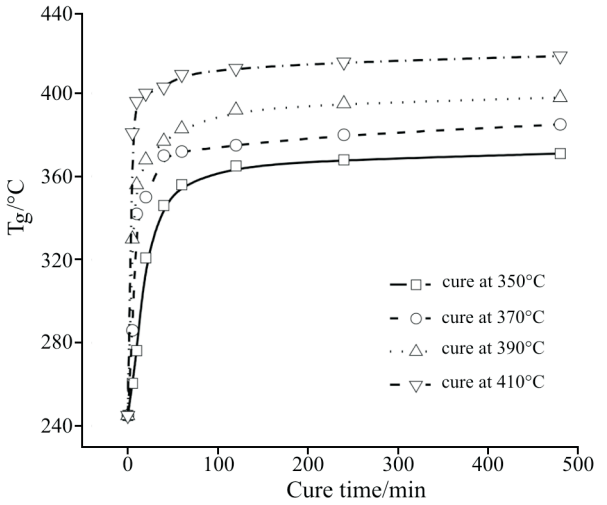

Fig. 3 T_g *vs*. cure time of AFR-PEPA-4 oligomer cured at various temperatures

increases with the increase of cure time and cure temperature. The cure temperature 410°C gave the highest cure reaction rate at the beginning of the curing, at which sample's T_g reached 381°C with only 5 min curing. The cure reaction rate tends to be stable after the curing reaches certain extent due to the diffusion control. The T_gs of cured oligomers after 8 h curing at 350, 370, 390 and 410 °C are 371, 385, 398 and 418°C, respectively.

Morphological investigation

The results of dissolving test of AFR-PEPA-4 imide oligomer in NMP were shown in Fig. 4. Only 20% by mass of AFR-PEPA-4 oligomer powders can be dissolved in NMP at 25°C. The undissolved oligomer crystals were observed from optical microscopy (Fig. 5). At 118°C the amount of dissolved oligomer powders increased 65% by mass. From this observation, it was realized that the crystals were inherent from the formation of the AFR-PEPA-4, which decrease the solubility of the oligomer.

Optical micrographs were also taken of the AFR-PEPA-4 films. The spherulite crystalline morphology was observed in AFR-PEPA-4 film (Fig. 6a), indicating that the high degree of rotation from 6FDA structure in AFR-PEPA-4 makes it folded chain site for spherulite formation. After annealing at 330°C for 15 min, the crystallinity of oligomer films was decreased significantly, though some small crystals with spherulite morphology still exist (Fig. 6b). A very small amount of crystals even exist after heating to 370°C. In fact, the crystallinity in AFR-PEPA-4 films could not be regenerated under any annealing conditions after the initial melt, which is similar to the observation on PETI-5 specimens by Hou *et al*. [8].

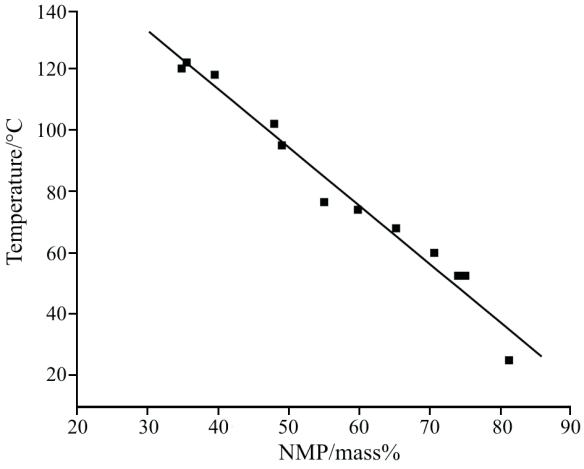

Fig. 4 AFR-PEPA-4/NMP solubility diagram

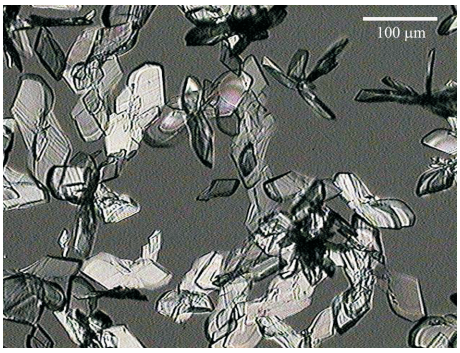

Fig. 5 Optical micrographs of undissolved AFR-PEPA-4 oligomer crystals in NMP at room temperature

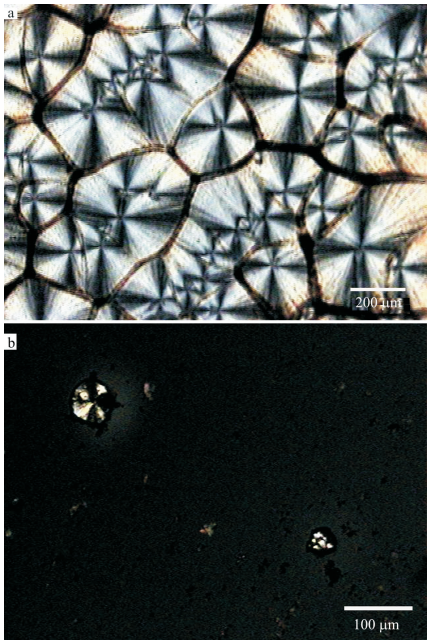

Fig. 6 Optical micrographs of AFR-PEPA-4 oligomer crystals. a – cast at 150°C without annealing; b – cast at 150°C and then annealed at 330°C for 15 min

Thermal stabilities of AFR-PEPA-4 imide oligomer and cured polyimide

TG/DTG curves characterizing the thermal degradation of the AFR-PEPA-4 imide oligomers on heating in air or N_2 in the range 20–800°C are presented in Fig. 7. The oligomer has less than 2% mass loss in both air and N_2 when the temperature is lower than 480°C. Based on the thermal analysis results, the temperature window for thermal curing of AFR-PEPA-4 oligomer can be chosen from 340 to 430°C to ensure the occurrence of cross-linking reaction without serious thermal degradation.

From Fig. 7, there is no residue when AFR-PEPA-4 was heated to 800°C under air due to oxygen combustion. However, AFR-PEPA-4 oligomer shows higher decomposition temperature and higher temperature for maximum mass loss rate in air. The rea-

Table 1 TG characterization data of phenylethynyl-terminated imide oligomers and their cured products

Sample	Decomp. onset/°C	$T_d^{5\%}$/°C	$T_d^{10\%}$/°C	Char yield at 800°C/%
AFR-PEPA-4 in air	548	524	544	0
AFR-PEPA-4 in N_2	525	527	549	57.9
PETI-5 in N_2*	510	532	548	62.9
Cured AFR-PEPA-4 in air	552	524	544	0
Cured AFR-PEPA-4 in N_2	522	529	553	57.4

*data reported by Simone and Scola [9].

son probably is that the network structure of AFR-PEPA-4 polyimide formed during the heating in air is different from that formed in nitrogen atmosphere. There is less than 0.5% mass loss from 220–290°C (Fig. 7b), which is due to evolution of NMP and monomer residues in the sample. The temperatures at which a mass loss of 5% ($T_d^{5\%}$) and 10% ($T_d^{10\%}$), along with the char yield at 800°C, are compared to those data of PETI-5 and listed in Table 1. It is shown that both phenylethynyl terminated oligomer imide AFR-PEPA-4 and PETI-5 have similar thermal stabilities.

Thermal stabilities of cured AFR-PEPA-4 samples (390°C for 1 h) were also characterized. Samples were heated at rates of 10 K min^{-1} under air and N_2 to 800°C in TG (Fig. 8). In curves shown in Fig. 8, the mass loss around 100°C is due to the evaporation of the moisture in the sample. There is no mass loss between 220–290°C for cured AFR-PEPA-4 polyimides, indicating that NMP and monomer residues existing in oligomers were released during the curing process at higher temperature (390°C). The temperatures at which a mass loss of 5% ($T_d^{5\%}$) and 10% ($T_d^{10\%}$), along with the char yield at 800°C were also listed in Table 1.

It is noticed that both TG properties and DTG characteristics of the AFR-PEPA-4 oligomer did not change much after curing. It may suggest that both

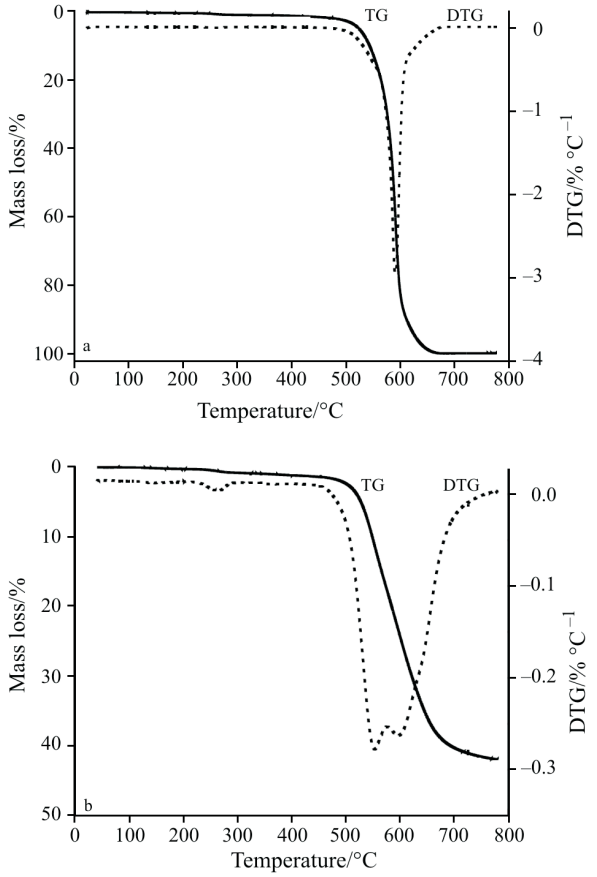

Fig. 7 Results of thermogravimetry: TG and DTG curves measured during heating of AFR-PEPA-4 imide oligomers in a – air and b – nitrogen. Heating rate: 10 K min^{-1}

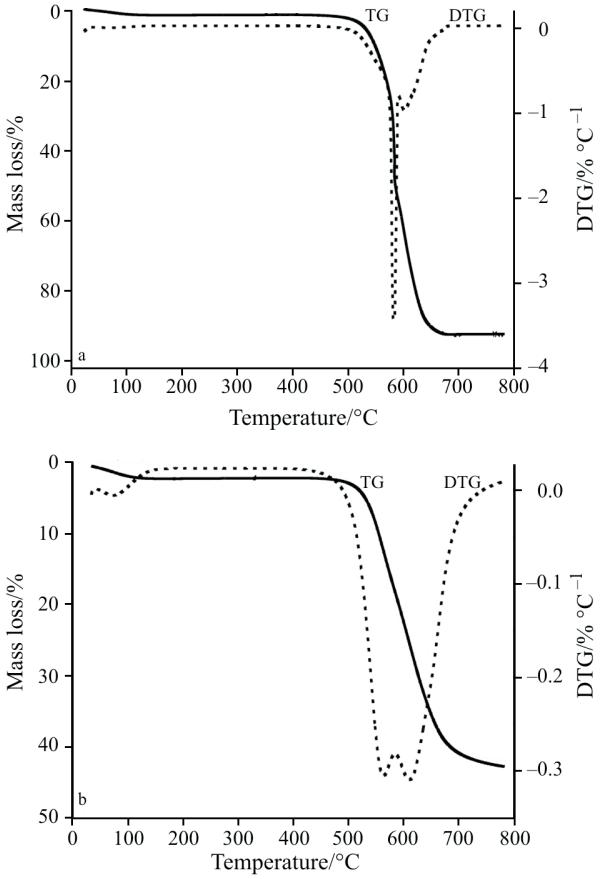

Fig. 8 Results of thermogravimetry: TG and DTG curves measured during heating of cured AFR-PEPA-4 polyimides in a – air and b – nitrogen. Heating rate: 10 K min^{-1}

oligomer and its cured product have the similar mode and mechanism of thermal decomposition. In other words, the degradation should first take place on the weakest linkages in imide backbonds (C–N bond or fluorinated groups), but not the chemical bonds formed from phenylethynyl end groups during the cross-linking. Scheiman *et al*. [16] studied thermal stabilities of several 6FDA containing polyimides and proposed two different pathways of degradation. One is the cleavage of C–N bond and another is loss of CF3 and F species from 6F linkages. Therefore, AFR-PEPA-4 oligomer and its cured polyimide may also follow such decomposition mechanisms.

Conclusions

DSC and TG were used to characterize cure reaction and thermal stabilities of AFR-PEPA-4 oligomer and polyimide. Both AFR-PEPA-4 oligomer and polyimide exhibit excellent thermal stabilities comparable to PETI-5 polyimides. The temperature window for thermal curing of AFR-PEPA-4 oligomer can be chosen from 350 from 430°C to ensure the occurrence of cross-linking reaction without serious thermal degradation. AFR-PEPA-4 imide oligomer has a T_m of 330°C and exhibit spherulite crystalline morphology in the film. The crystallinity in AFR-PEPA-4 films could not be regenerated under any annealing conditions after the initial melt.

Acknowledgements

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