A tri-branched Phenylethynyl-terminated aryl ether ketone oligomer used as reactive diluent for PETI-5

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Introduction

In the past 30 years, phenylethynyl-containing aromatic polyimides/oligoimides have received considerable attention in aircraft for structural and electrical applications as a potential material for coating, adhesives, films and composite matrix resins. The phenylethynyl systems displayed very attractive processing and mechanical behaviour characteristics. [1-4]

Among these studies, one NASA developed system, PETI-5 (Figure 1) imide oligomer, has been investigated as a resin matrix in carbon composites for High-Speed Civil Transport (HSCT) applications. It has excellent mechanical properties and thermo-oxidative stability but it has relatively lower T_g of cured sample at 270 ℃. The uncured resin with optimum molecular weight of 5000 g mol^{-1} has good autoclave processibility, while, Its' melt viscosity was too high (1000~6000 Pa.S at 370 ℃) to fabricate composites by the more versatile and low cost manufacturing processes such as: resin infusion (RI) and resin transfer molding (RTM). These methods required a resin with low (preferably <3 Pa.S) and Stable (>2hr at the injection or infiltration temperature) melt viscosity during part fabrication. [5-6] Considerable work on PETI-5 was continued on the decreasing of its melt viscosity. [7-8]

We have successfully designed a new tri-branched, phenylethynyl-terminated aryl ether oligomer (Tri-PE-PAEK) which posses low melt low melt temperature (252 ℃) and low melt viscosity as low as 0.1 poise at 280 ℃ and high solubility before cure, while the cured polymer demonstrated excellent thermal stability, high glass transition temperature (T_g) and high modulus. The objective of this work has been to take the low molecular weight Tri-PE-PAEK oligomer as a reactive diluent to modify PETI-5. The approach is to blend Tri-PE-PAEK oligomer with PETI-5. It was expected to lower the viscosity (i.e improve processibility) improve solvent resistance, hydrolytic stability, mechanical properties without sacrificing the thermal properties of PETI-5.

Experimental Section

Materials

PETI-5 （5000g.mol^{-1}） was kindly supplied by professor Yokota (Japan Aerospace exploration Agency) ， the chemical structure was shown in Figure 1. Tri-PE-PAEK oligomer was synthesized in-house. The chemical structure was shown in Figure 2. In our investigation, the uncured Tri-PE-PAEK oligomer powder was physically blended with PETI-5 imide powder at loading levels of 10, 20, 25, 30 wt%. The obtained imide oligomer mixtures were molded into plates and films to evaluate the properties.

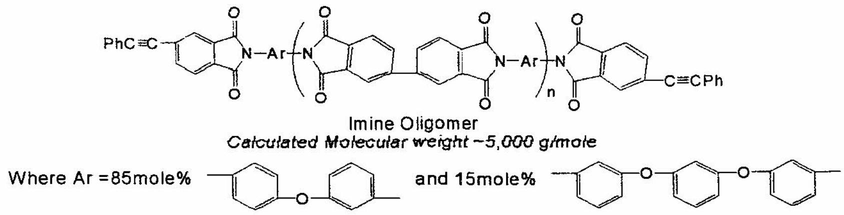

Figure 1 Structure of PETI-5.

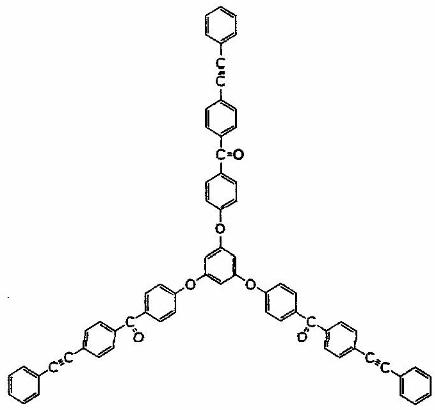

Figure 2 Structure of Tri-PE-PAEK.

Results and Disscussion

The cured aryl ether oligomer (tri-PE-PAEK) film was obtained from compressive molding at 370 ℃ for 1 h. The cured oligomer exhibits a higher T_g at 370℃. The cured sample displayed a high storage modulus and has a good retention even above the glass transition temperature (about 400 ℃), which may be due to the high crosslinking density and existence of the polar carbonyl group and rigid structures in the compound backbone. The 5 % weight loss values fo the cured oligomer in air and nitrogen occurred at 517 ℃ and 523 ℃, respectively. The TGA data indicated that the cured oligomer film had excellent thermal stability.

Properties of Tri-PE-PAEK/PETT-5 blends

In the present investigation we wish to report on our work to improve the properties of PETI-5, by the addition of a tribranched aryl ether oligomer as reactive diluent.

After thermal treatment, the phenylethynyl groups underwent a complex reaction involving chain extension, branching and crosslinking between PETI-5 and the Tri-PE-PAEK to afford a pseudo three-dimensional network. Thus we can believe that with the increasing of Tri-PE-PAEK content in the mixture, the crosslink density was increased, the T_gs of the blends were expected to increase. Table 1 shows the properties of the pure oligomer and the blends thereform. *With the addition of Tri-PE-PAEK, the T_g values of cured blends were increased* from 264 to 280 ℃, this values were not linearity with the content of the mixture, cured blend (PETI-5/ Tri-PE-PAEK= 80/20) showed the highest Tg values of 280 ℃.

Dynamic rheological properties were measured on powder moulded discs of PETI-5 and one blend (PETI-5/Tri-PE-PAEK=70/30) only, as reported in Table 1 and in Figure 3, at 30 wt%

loading level of Tri-PE-PAEK, the minimum viscosity reduced to 40% that of PETI-5 and the temperature of minimum viscosity decrease from 354 ℃ to 335 ℃, this suggests a lower temperature and lower pressure are need to process over the pure PETI-5 resin. Surely, higher level of Tri-PE-PAEK will lead to further improvement in process.

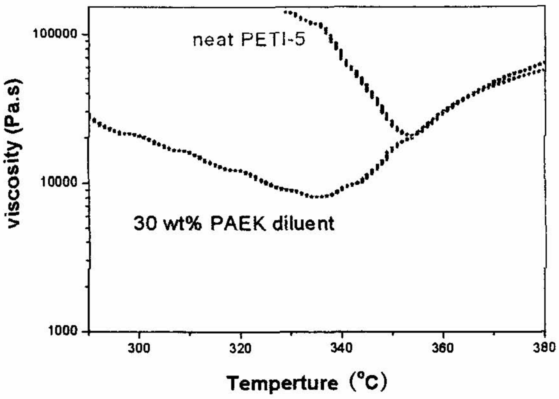

Figure 3. Complex viscosity curve of PETI-5 and one blend (PETI-5/Tri-PE-PAEK=70/30).

Table 1. Properties of pure PETI-5 oligomer and physically mixed with Tri-PE-PAEK.

compositions		Thermal transition temperature by DSC(before cure) (℃)		Thermal transition temperature by DSC (after cure) (℃)	Minimum complex melt viscosity (Pa s)	Temperature of minimum viscosity (℃)
PETI-5(wt%)	Tri-PE-PAEK(wt%)	T_g (T_{m1})	T_{m2}	T_g		
100	0	232	356	264	20500 (60000)[1]	354 (370)[1]
90	10	232(250)	348	272	--	--
80	20	232(250)	348	280	--	--
75	25	232(250)	347	276	--	--
70	30	232(250)	346	276	8140	335

To our most surprising was that, at the loading of 10 wt % Tri-PE-PAEK diluent in the PETI-5 system, the cured film shows 90% elongation of the original, aberrancy with the other, this is a typical thermoplastic materilal behavior. Further increase of the diluent led to higher modulus and higher strength of the films due to the higher crosslink density and the crosslinking between PETI-5 and Tri-PE-PAEK to afford a pseudo three-dimensional network. The reason why the 10 wt % loading Tri-PE-PAEK oligomer in the PETI-5 system demonstrated the highest toughness is under investigation. Tensile properties were related to the molding temperature.

Conclusions.

A phenylethynyl-terminated branched aryl ether (Tri-PE-PAEK) oligomer has been synthesized. This low molecular weight oligomer exhibited good processibility. It is a good candidate material to processing techniques such as resin infusion (RIM) and/or resin transifer molding (RTM) which are attractive methodologies for the economical manufacture of polymer matrix/carbon fiber composites.

In addition, the phenylethynyl-terminated branched aryl ether oligomer as a reactive diluent for PETI-5 can not only reduced the viscosity of PETI-5 and the temperature of minimum viscosity, but also it can increase the tensile properties of the cured polymer without compromise the other properties. Especially, the toughness of PETI-5 themoset polymer was very greatly increased by the addition of just 10% Tri-PE-PAEK oligomer into PETI-5.

References and Notes

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