

Toughening cyanate ester resins with highly soluble thermoplastic polyimide

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Abstract: A series of modified cyanate ester (CE) resins were produced by dissolving thermoplastic polyimide in cyanate ester prepolymer, followed by curing at elevated temperature. The properties of cured resins were systematically investigated according to their glass transition temperatures, thermo-oxidative stability, and mechanical properties. The results indicated that polyimide-modified CE (TPI/CE) thermosets possessed higher impact strengths compared with pure CE thermoset. Tensile strength and flexural strength of TPI/CE thermosets spanned a range of 60-85 and 156-172 MPa, respectively. TPI/CE resins showed great potential in the application of matrix resins for high performance fiber-reinforced composites because of their combined properties of high toughness, high glass transition temperature, and excellent mechanical properties.

Key words: polyimide-modified cyanate ester, resins mechanical property, glass transition temperature

1. Introduction

Cyanate ester resins (CE) are a class of thermosetting polymers featuring excellent dielectric properties, radar transparency, low moisture uptake, high glass transition temperatures, and good long term thermal stability.^{1,2} Thus, CE resins have been widely used in electronic and aerospace industries. However, CE resins suffer from the drawback of brittleness stemmed from their high crosslinking density, which limits their application as the matrix resin for structural components in aerospace industry. Consequently, many research efforts have been aimed at toughening CE resins with thermoplastic or thermosetting polymers. A variety of polymers, such as epoxides, bismaleimides, reactive rubbers, and engineering plastics, have been used for the modification of CE resins. Modified CE resins with enhanced toughness were achieved by these approaches, however, the thermal, mechanical, or dielectric properties were usually compromised to some extent.^{3,4} In this work, thermal plastic polyimide was prepared using 2,3,3',4'-biphenyltetracarboxylic dianhydride (3,4_BPDA), 4,4'-oxydianiline (ODA), and 2,2'-bis(trifluoromethyl)4,4'-diamino biphenyl (TFMB) as the monomers. This polymer showed combined properties of high glass transition temperature (360 °C), good solubility in CE monomer and prepolymer, and low dielectric constant due to its rigid but non-coplanar architecture. This polyimide was then utilized as toughening agent for CE resin, and the thermal and mechanical properties of the resulting blends were fully characterized.

2. Results and discussion

Highly soluble thermoplastic polyimide was prepared via a conventional one-step method in *m*-cresol, using 3,4-BPDA, 4,4'-ODA (10%), and TFMB (90%) as the monomers. CE prepolymer was synthesized by heating 2,2'-bis(4-cyanatophenyl) propane at 170 °C for two hours, and the viscosity

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of the prepolymer, determined by rheological measurement, was around 250 mPa s (100 °C). The solubility of TPI in CE monomer and prepolymer was up to 15% because of its unique rigid but non-coplanar structure. Thus, TPI/CE prepolymers were formulated by simply dissolving TPI (3, 5, 10, 15 wt%) in CE prepolymers without the assist of any solvent, which is highly desired in the fabrication of void-free composites. The prepolymers were named by the percentages of TPI in the formulations, e.g. TPI/CE-5 is the prepolymer with 5% TPI and 95% CE. TPI/CE prepolymers were then cured at elevated temperature to afford TPI/CE thermosets.

The FTIR spectra of TPI, TPI/CE-5 prepolymer and TPI/CE-5 thermoset are shown in Figure 2. The absorption bands around 1779 (asymmetric C=O stretching), 1720 (symmetric C=O stretching), and 1370 (C-N stretching) cm^{-1} were assigned to the imide groups. The peaks at around 2275 and 2236 cm^{-1} corresponded to the triple bonds in cyanate groups. After cured, the peaks for cyanate groups completely disappeared. Meanwhile, the relative intensity of the peaks at about 1572 and 1364 cm^{-1} , which was attributed to the triazine ring, increased. The results confirmed the completion of the curing of cyanate groups.

The thermo-oxidative stability of TPI/CE thermosets were assessed by thermogravimetric analysis (TGA) in air, and the results are listed in Table 2. The $T_{5\%}$ values of TPI/CE thermosets spanned a range of 419-427 °C. Furthermore, no appreciable weight loss was observed below 400 °C. These results demonstrated that all the thermosets possessed excellent thermo-oxidative stability. In addition, the thermo-oxidative stability of TPI/CE thermosets increased slightly with the TPI contents.

Glass transition temperatures (T_g) of TPI/CE thermosets were characterized *via* DMTA, and the results are summarized in Table 2. The temperature dependence of storage modulus and $\tan \delta$ for TPI/CE thermosets are displayed in Figure 3. The T_g values of TPI/CE thermosets ranged from 306 to 313 °C. The T_g differences were minor for TPI/CE thermosets with different TPI contents. Table 2 summarizes the mechanical properties of TPI/CE thermosets. TPI/CE thermosets exhibited impact strength of 16-63 KJ m^{-2} , tensile strength of 60-85 MPa, tensile modulus of 2.2-3.1 GPa, elongation at break of 1.8-3.1%, flexural strength of 156-172 MPa, and flexural modulus of 3.1-3.8 GPa. The mechanical properties, especially impact strength, tensile strength, and flexural strength, were significantly enhanced by the introduction of high performance TPI.

3. Conclusion

In this work, a series of TPI/CE prepolymers and thermosets were developed. The toughness of TPI/CE thermosets was much higher than pure CE thermoset. Furthermore, TPI/CE thermosets maintained most of the advantages of CE thermosets, including high T_g , excellent thermo-oxidative stability, and good mechanical properties. TPI/CE prepolymers showed great potential as matrix resins for high performance thermosets because of their excellent overall properties. This work provided some insights on how to improve the toughness of CE resins while maintaining their thermal and mechanical properties.

Table 1. Properties of thermoplastic polyimide

M_n (kg mol^{-1}) ^a	M_w (kg mol^{-1}) ^a	PDI ^a	T_g ($^{\circ}\text{C}$) ^b	$T_{5\%}$ ($^{\circ}\text{C}$) ^c
42	76	1.82	360	569

^a Measured by GPC.

^b Glass transition temperature, measured by DMTA.

^c 5% Weight loss temperature, measured by TGA in air.

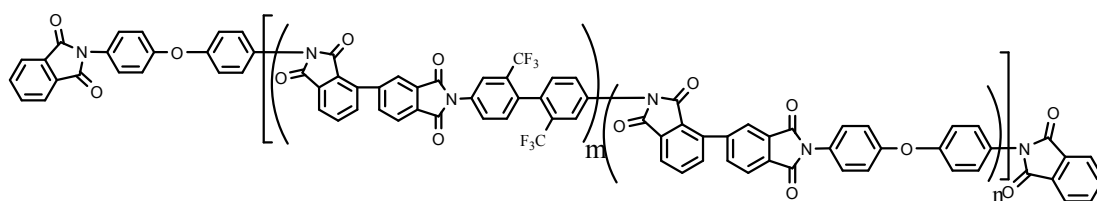


Figure 1. Structure of thermoplastic polyimide

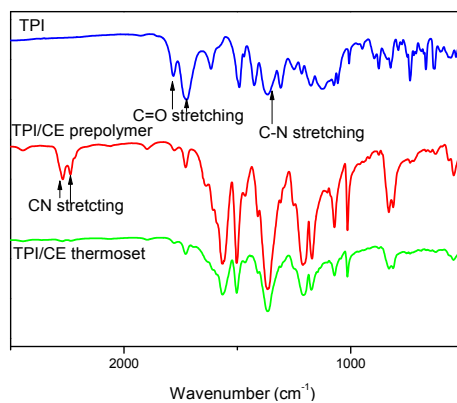


Figure 2. FTIR spectra of TPI, TPI/CE prepolymer, and TPI/CE thermoset

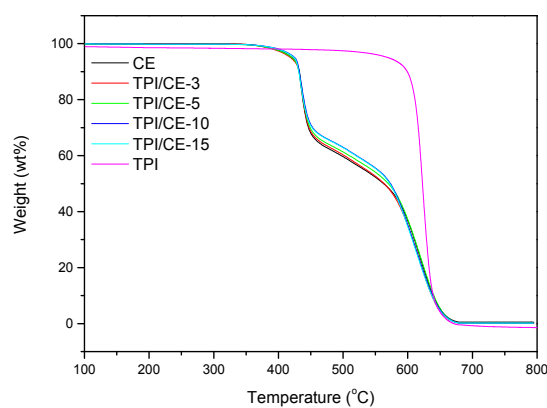


Figure 3. TGA curves of TPI and TPI/CE thermosets

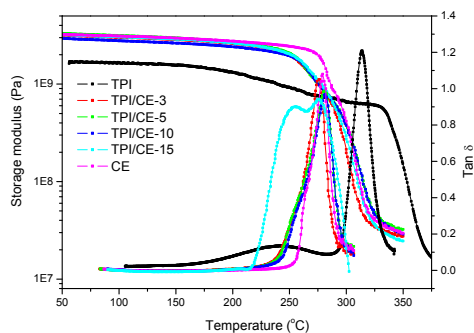


Figure 4. DMTA curves of TPI and TPI/CE thermosets

Table 2. Thermal and mechanical properties of TPI/CE thermosets

Thermosets	CE	TPI/CE-3	TPI/CE-5	TPI/CE-10	TPI/CE-15
Tensile strength (MPa)	53	60	82	84	85
Elongation at break (%)	1.8	2.2	3.1	3.1	3.1
Tensile modulus (GPa)	3.1	3.2	3.0	3.2	3.3
Flexural strength (MPa)	149	156	170	171	172
Flexural modulus (GPa)	3.2	3.3	3.4	3.8	3.1
Compression strength (MPa)	150	150	153	155	156
Impact strength (KJ m ⁻²)	16	22	26	32	63
$T_{5\%}$ (°C)	422	419	421	425	427
T_g (°C)	310	306	312	313	306

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