

On poly(ester imide)s modified bismaleimide resins, 1

Synthesis and properties of organo-soluble poly(ester imide)s

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Abstract A series of aromatic poly(ester imide)s containing benzidine and its derivatives in main chain were prepared by polycondensation of 2,2-bis(p-trimellitoxylphenyl)propane dianhydride (BTPDA) and *t*-butyl-*p*-phenylenebis(trimellitate) dianhydride (BPBDA) with benzidine and its derivatives. The poly(ester imide)s obtained show that the incorporation of noncoplanar structure, led by introducing methyl groups on benzidine, can improve the solubility of poly(ester imide)s in organic solvents.

Key words soluble poly(ester imide)s, noncoplanar structure, solubility

Introduction

In recent years bismaleimide (BMI) resins as a high performance thermosetting resins have been widely used as matrices for advanced composites. However, the BMI resins are extremely brittle due to its highly crosslinked structure. Various attempts have been made to improve the impact and fracture toughness of bismaleimide resins. An excellent modification is the use of an diallyl compound to copolymerize with bismaleimides. For the past two decades, a good toughening approach has been to utilize thermoplastic resin to serve as toughener for the thermosetting networks. In our previous work, a series of polyetherimide with novel structure was used to modify thermosetting resin, the modified resin display excellent toughening effect without sacrificing other important properties^[1-3].

In order to further improve the thermal stability and flexural modulus of modified BMI resins, some attempts have been made to use organo-soluble poly(ester imide)s as toughener to modify BMI resin. Much research has been done in synthesizing poly(ester imide)s^[4-8]. As the first step, the relationship between solubility and chemical structure of this material must be clarified so that these new poly(ester imide)s could be as a potential tougheners in thermosetting resin for getting the better toughening effect. It is reported that it can improve the solubility of aromatic polyimides by introducing out-of-plane biphenyl groups

into the main chain of polyimides without reducing other properties^[9]. In this work, a series of poly(ester imide)s, (PEsI), were synthesized for toughening thermoset resins. The chemical structure of PEsI is shown in Fig.1.

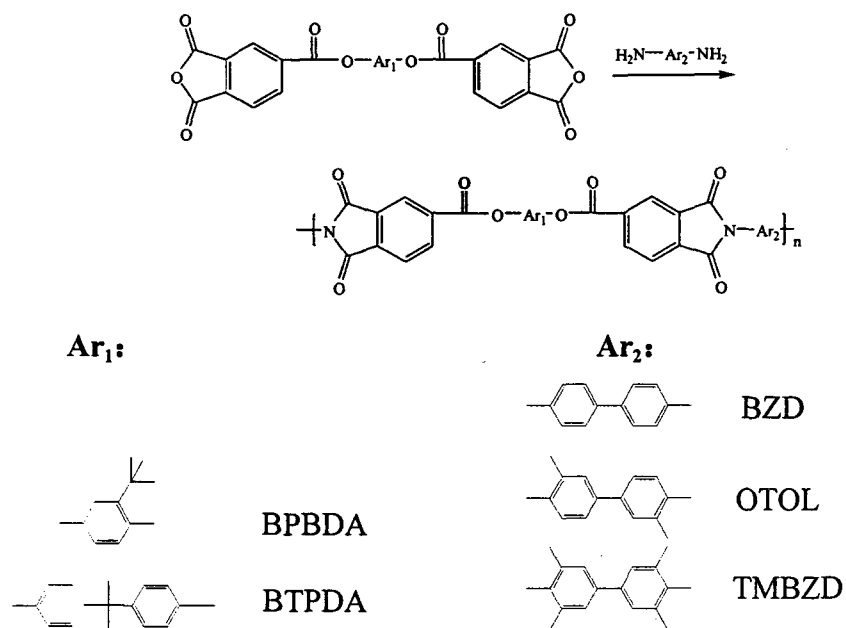


Fig.1 Chemical Structure of Poly(ester imide)s

Experimental

2,2-bis(p-trimellitoyloxyphenyl)propane dianhydride (BTPDA) and *t*-butyl-*p*-phenylene-bis(trimellitate) dianhydride (BPBDA) were synthesized as the same procedure^[4].

The melting point of BTPDA was 191°C and the yield was 73%.

The melting point of BPBDA was 216°C and the yield was 81%.

Benzidine (BZD), o-tolidine (OTOL), 3,3,5,5-tetramethyl benzidine (TMBZD), 4,4'-[1,4-phenylenebis(1-methylethylidene)]bisaniiline (BISP) and *m*-phenylenediamine (MDA) were dried in vacuum oven before polymerization without further purification.

PEsI was synthesized as follows: diamine was dissolved in N-methyl-2-pyrrolidone. Then bis(ester)anhydride was added at the stoichiometric ratio of diamine and Poly(amic acid) (PAA) was obtained. PAA was converted to the corresponding poly(ester imide)s at ambient temperature by treatment of acetic anhydride and triethyl amine (3:1 at volume ratio). The mixture was stirred at room temperature for 3 hours. Then it was precipitated in methanol, and the polymer was dried in vacuum oven. The yield of PEsI was about 97%.

The glass transition temperatures (T_g) of Poly(ester imide)s were determined by SETARAM differential scanning calorimetry (DSC) instrument from room temperature to 350°C at a heating rate of 10°C min.

Result and discussion

T_g of poly(ester imide)s (PEsI) and poly(ether imide)s (PEI) synthesized from BISP and MDA are listed in table 1. The results show that T_g of poly(ester imide)s are higher than those of poly(ether imide)s which have the similar structure.

Table 2 shows that the solubility of poly(ester imide)s in organic solvents was related to the number of introducing methyl groups on biphenyl backbone. The PEsIs based on TMBZD have the best solubility owing to the noncoplanar structure of imide unit, while the one based on BZD is insoluble in familiar organic solvents. We have calculated the bond rotation angle between imide ring and phenylene ring through molecular mechanics method. It is shown that the dihedral angle between these two rings is less than 10 degree in PEsIs based on BZD, the dihedral angle increases with the number of methyl substitute in BZD. The chemical structure and bond rotation angle of BZD, OTOL and TMBZD are shown in Fig. 2.

The primary experiments show that most of the poly(ester imide)s can be dissolved in BMI and epoxy resins, meanwhile, the morphology of cocontinuous and phase inversion were observed by controlling the process of phase separation. The detailed work is underway.

Table 1. T_g of PEI and PEsI synthesized from bisphenol A dianhydride and different diamines

	PEI/°C	PEsI/°C
BISP	221	239
MDA	212	246

Table 2. T_g and solubility of PEsI in organic solvents

Solvent	Chloroform	THF	NMP	m-Cresol	[η]* (0.5g/dL)	T _g (°C)
BPBDA-BZD	i s	i s	i s	i s	-	274
BPBDA-OTOL	p s	i s	i s	i s	-	265
BPBDA-TMBZD	s	p s	s	p s	0.49	249
BTPDA-BZD	i s	i s	i s	i s	-	299
BTPDA-OTOL	s	p s	s	p s	0.99	279
BTPDA-TMBZD	s	p s	s	S	0.46	289

*Inherent viscosity [η] of PEsI was determined in N-methyl-2-pyrrolidone at 30°C.

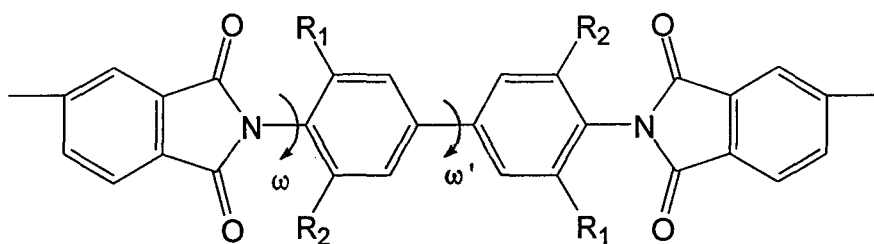


Fig. 2 Chemical structure and bond rotation

Diamine		ω	ω'
BZD	($R_1=R_2=H$)	9°	37°
OTOL	($R_1=CH_3$ $R_2=H$)	38°	36°
TMBZD	($R_1=R_2=CH_3$)	53°	33°

数据来源：文献不明。

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