

The preparation of a new kind of phenylethynyl-terminated polyimide oligomers based on PMDA

Zhuomin Jin(金卓敏), Guodong Dang(党国栋), Hongwei Zhou, Xianhua Rao, Chunhai Chen(陈春海)*

Alan G. MacDiarmid Institute, Jilin University, Changchun 130012, P. R. China;

E-mail: cch@jlu.edu.cn

1. Introduction

More and more attention has been focused on the study of phenylethynyl-terminated imide oligomers for high temperature aerospace and aircraft applications [1]. PETI-5 was the best evaluated one with a unique combination of excellent mechanical properties and good processability. Although PETI-5 exhibits excellent heat resistance for HSCT, the operation temperature is restricted below 200°C. In order to improve heat resistance of cured polyimide, recent efforts have focused on increasing the use temperature by modifying the chemistry to effect as high a T_g as possible without causing an increase in melt viscosity. An approach has been developed that focuses on using a combination of aromatic diamines to impart flexibility (for low melt viscosity) and rigidity (for high T_g), dianhydride and endcapping with PEPA. Therefore, we selected PMDA and p-TPEQ as dianhydride and diamine, respectively in this paper. Herein, a series of oligomers with different molecular weight (n=2,4,6) were prepared and characterized.

2. Experimental

The chemical structure of imide oligomer is shown in Figure 1. The amide acid oligomers were made by reaction of calculated stoichiometric ratios of anhydride (PMDA) and diamine (p-TPEQ) with PEPA in DMAc and subsequently cyclodehydrated by thermal imidization to obtain a series of phenylethynyl terminated imide oligomers with different molecular weight. The cured imide oligomers were obtained from compressive molding at 370°C for 1h. [2,3]

3. Result and Discussion

The thermal and rheometer properties of all uncured oligomer powder with different molecular weights were measured by DSC and dynamic rheometer instrument. Table.1 shows thermal and rheological behavior of all oligomers. The glass transition temperature of all cured imide oligomer is related to crosslink density. The uncured oligomers with lower molecular weight exhibit lower melt temperature and lower melt viscosity, and their corresponding cured oligomers have higher T_g. All oligomers can be compressed into

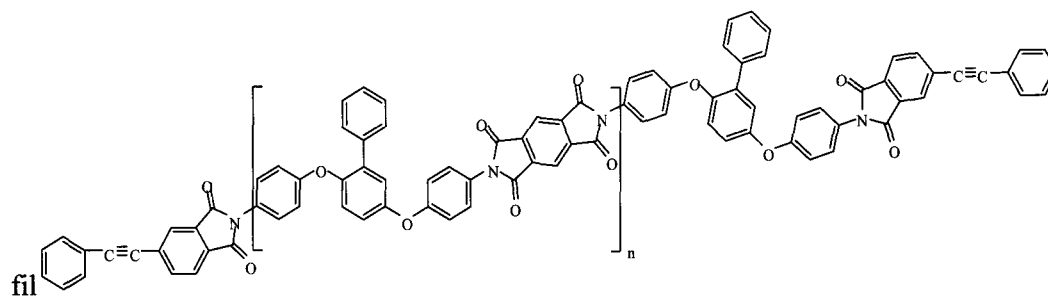


Figure1. The chemical structure of imide oligomer

ms and tensile properties of the films are listed in table.2. All oligomers can be compressed into films and the films exhibited excellent thermal stability and mechanical properties expect for oligo-1 with high cross link density. Consequently, this new kind of phenylethynyl end-capped imide oligomers prepared by PMDA and p-TPEQ with PEPA demonstrate a promising potential for future aerospace applications.

Table1. Properties of the oligomers

Oligomer	Molecular weight(g mol ⁻¹)	Melt flow viscosity (Pa s)	DSC run			
			Uncured Tg(Tm)(°C)	Cured Tg(°C)	Texo (°C)	ΔH(J/g)
Oligo-2	2036	9 (313°C)	158(273)	310	422	93
Oligo-6	4380	212(322°C)	210(273)	293	434	34
Oligo-9	6138	2209(330°C)	217(314)	284	416	33

1. Uncured Tg: glass transition temperature of the oligomers determined on powdered sample by DSC at a heating rate of 20°C/min in the first run
2. Cured Tg: glass transition temperature determined on samples by DSC at a heating rate 20°C/min in the second heating run.
3. Texo: the temperature of exothermic peaks on DSC curves

Table2. Properties of the cured films from the oligomers

Oligomer	DMA Tg(°C)	TGA(N ₂)		Tensile properties		
		Td ₅ (°C)	Retain (%)	Strength (MPa)	Modulus(GPa)	Elongation (%)
Oligo-2	322	527	65.5	113	2.2	7.4
Oligo-6	291	523	59.8	110	2.4	8.9
Oligo-9	287	532	61.2	103	2.4	10.7

References

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