

Synthesis and Properties of Novel Imide Oligomers containing Pendent and Terminal Phenylethynyl Groups

Cholhyok Paek(白哲革), Guodong Dang(党国栋), Hongwei Zhou, Chunhai Chen(陈春海)*

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

E-mail: cch@jlu.edu.cn

Abstract

As an extension of study to develop phenylethynyl-terminated imide oligomers with good processability and high thermal stability for aerospace applications, novel imide oligomers containing pendent and terminal phenylethynyl groups (3200 g mol^{-1}) were prepared from 3,3',4,4'-biphenylenetetracarboxylic dianhydride (s-BPDA), 2,5-bis(4-aminophenoxy)-biphenyl (p-TPEQ), 4-phenylethynylphthalic anhydride (PEPA) with 3,5-diamino-4'-phenylethynyl benzophenone (DPEB) of 10, 20, 30, 40mol%. The oligomers exhibited favorable solubility and much lower melt viscosities at low temperatures, and thus provide wide processing windows. The curing behavior of the oligomers was investigated with DSC. The tensile and thermal properties of the cured films were evaluated. The film of imide oligomer with 20mol% DPEB exhibited the best combination of properties.

Keywords: Imide oligomers, Pendent phenylethynyl group, High temperature polymers

Introduction

Although polyimides have outstanding mechanical properties and high temperature capabilities, their poor processability (poor solubility in organic solvents, high melting viscosity, high melting temperature) have limited their widespread adoption as matrix resins for structural composites. In our laboratory, new kinds of all-aromatic phenylethynyl-terminated imide oligomers derived from 3,3',4,4'-biphenylenetetracarboxylic dianhydride (s-BPDA), 2,5-bis(4-aminophenoxy)-biphenyl (p-TPEQ), 4-phenylethynylphthalic anhydride (PEPA) with different molecular weights have been prepared and evaluated[1]. The incorporation of bulky substituent (pendant phenyl groups of p-TPEQ) improved the solubility and processability of the oligomers compared with PETI-5. The cured imide oligomers with M_n 3200 g mol^{-1} ($n=4$) had the best tensile properties, but the cured T_g (272°C) is relatively low. It is necessary to increase their T_g , because high-temperature performance is one of several important factors for aerospace applications, generally requiring a T_g greater than 300°C . To increase crosslink density by introducing pendent phenylethynyl groups along the main chain is an effective approach to increase T_g of the oligomer without sacrificing tensile properties [2]. In this paper, novel imide oligomers containing pendent and terminal phenylethynyl groups with different contents of 3, 5-diamino-4'-phenylethynyl benzophenone (DPEB) was synthesized and characterized.

Experimental

Synthesis of imide oligomers: Scheme1 represents the experimental procedure used to prepare the oligomers. For convenience, all oligomers are denominated as listed in Table 1. Imide oligomers containing pendent and terminal phenylethynyl groups were synthesized according to a published method [2] as illustrated by oligo-1.0. DPEB (0.625 g, 2 mmol) and DMAc (16 ml, 30 wt %) were placed into a flask equipped with a magnetic stirrer. After dissolution of DPEB, s-BPDA (2.3537 g, 8 mmol) was added into the flask at room temperature, and then stirred for 1 h. p-TPEQ (2.947 g, 8 mmol) was added and the mixture was stirred at room temperature for 3 h. 4-PEPA (0.993 g, 4 mmol)

was added and the mixture was stirred at room temperature for another 2 h. The solution of amide acid oligomer was put on Petri dishes and dried in an air oven at 80 °C and 150 °C for 1 h each, then the material was imidized at 200 °C for 1 h and 250 °C for 1.5 h in a vacuum oven, finally ground to obtain oligo-1.0 powder which has the polymerization degree of 4(calculated $M_n = 3200 \text{ g mol}^{-1}$).

Preparation of cured film: The obtained imide oligomers were molded by using $6 \times 6 \times 0.005 \text{ cm}^3$ polyimide film frame on a $15 \times 15 \text{ cm}^2$ stainless steel plate with UPILEX-S separator films under 1.4 MPa by heating initially to $T_g + 60 \text{ °C}$ for 20 min and subsequently to 370 °C for 1 h. The brown film-like specimens of $6 \times 6 \times 0.005 \text{ cm}^3$ were obtained.

Results and discussion

Imide oligomers: Five imide oligomers containing pendent and terminal phenylethynyl groups with different crosslink density were synthesized by changing content of DPEB. GPC analyses were performed on imide oligomers, their data were presented in Table 2. The measured M_n s were 3300-3800 g mol^{-1} , agreed well with the target M_n of 3200 g mol^{-1} . The oligomers exhibited narrow distributions with polydispersities of approximately 1.14.

The solubilities of the imide oligomers in NMP were investigated, and the results were presented in Table 3. The oligomers exhibited favorable solubility and it showed that introducing of pendent phenylethynyl group didn't give obvious influence on their solubility.

The thermal properties of all uncured oligomer powder were measured by DSC. Fig.2 shows the DSC curves of oligo-1.0 powder in the first and second scan. All other oligomers had similar thermal behavior. Glass transition temperature of the oligomers (T_g^1) and glass transition temperature of the cured polymers (T_g^2), the onset curing temperatures (T_{onset}), exothermic peaks (T_{exo}) and normalized heat enthalpy (ΔH) are all listed in Table 3. The T_g^1 s of oligomers varied from 193 °C to 200 °C with increasing content of phenylethynyl and were near equivalent. The exothermic peak due to the crosslinking reaction appeared at 372-383 °C in the first heating run of DSC. Exothermic enthalpy (ΔH) increased as the content of phenylethynyl increased. T_g^2 of oligo-1.5 and oligo-2.0 were not presented. T_g^2 of oligo-0.0, oligo-0.5 and oligo-1.0 were presented at 265 °C, 291 °C and 322 °C respectively, and it showed that introducing of pendent phenylethynyl led to increase T_g of cured oligomer.

Minimum melt viscosities of Oligo-0.0, oligo-0.5, oligo-1.0, oligo-1.5, oligo-2.0 were lower than 60000 Pa s (371 °C) of PETI-5 [3].

Film properties: The cured imide oligomer films were prepared by molding the oligomer powder at 370 °C for 1 h under pressure. Glass transition temperature of films were measured by DMA, data were listed in Table 4. T_g of film increased as content of pendent increased.

The thermal stability of films was evaluated by TGA in N_2 and air atmospheres at a heating rate of 5°C min^{-1} . The data are listed in Table 4. The temperatures of 5% weight loss were all above 540 °C, 520 °C in N_2 and air respectively, and the char yields reported at 700 °C in N_2 is above 67%. It showed that all films exhibited excellent thermal stability.

The room temperature tensile properties of cured films are presented in Table 4. The films of oligo-1.5 and oligo-2.0 exhibited lower tensile properties than others due to higher crosslink density. The films of oligo-0.0, oligo-0.5 and oligo-1.0 showed excellent tensile properties. Comparing their thermal properties and tensile properties, it was considered that oligo-1.0 offered the best combination of properties, with a T_g of 310 °C, strength of 110 MPa, a modulus of 2.8 GPa, and 6% elongation.

Conclusion

Novel imide oligomers containing pendent and terminal phenylethynyl groups ($M_n = 3200 \text{ g mol}^{-1}$) were prepared and characterized. Results showed that introducing phenylethynyl groups led to increase T_g of cured films while maintaining wide processing windows (favorable solubility and low melt viscosities at low temperatures) and mechanical properties.

References

- [1] Rao XH, Zhou HW, Dang GD, Chen CH, Wu ZW. *Polymer* 2006;47:6091.
[2] Sasaki T, Yokota R. *High Perform Polym* 2006;18:199.
2000;C40(2&3):207-30.

(continue from p106)

- 8 J.G. Smith Jr., J.W. Connell and P.M. Hergenrother, *J. Comp. Mater.*, **34** (7), pp 614-628 (2000)
9 R. Yokota, S. Yamamoto, S. Yano, T. Sawaguchi, M. Hasegawa, H. Ozawa and R. Sato, *High Perform. Polym.*, **13**, pp S61-S72 (2001)
8 R. Yokota, S. Yamamoto, S. Yano, T. Sawaguchi, M. Hasegawa, H. Ozawa and R. Sato, *Polyimides and Other High Temp. Polym.*, **1** (1), pp 101-111 (2001)
9 T. Ogasawara, T. Ishikawa, R. Yokota, H. Ozawa, M. Taguchi, R. Sato, Y. Shigenari and K. Miyagawa, *Adv. Composites Mater.*, **11** (3), pp 277-286 (2003)
10 Y. Ishida, T. Ogasawara and R. Yokota, *High Perform. Polym.*, **18** (5), pp 727-737 (2006)
11 Y. Ishida, T. Ogasawara and R. Yokota, *Proceedings of the 37th SAMPE Fall Technical Conference (37th ISTC)*, Seattle, CD-ROM (2005)