Poly(imide-siloxane)/Polybenzoxazine Composite

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1. Introduction

Polybenzoxazine has been studied as a novel class of phenol resins to overcome the shortcomings of the traditional phenol resins [1]. It has good dimensional stability because of the ring opening cure process and low viscosity. Also, it can be synthesized from inexpensive raw materials and cured without strong acid as a catalyst. However, it has a very brittle properties, as is usual for phenolic materials and this limits its applications. Polydimethylsiloxane (PDMS) elastomer has a unique properties such as good thermal and oxidative stability. However, due to its incompatibility with organic matrix, the modification of the PDMS is required to increase the dispersability in the polybenzoxazine matrix. An effective method to improve the compatibility and strength of PDMS is the copolymerization with high temperature polymers affording the PMDS-containing copolymers having good thermal and mechanical properties. In this study, we prepared soluble poly(imide-siloxane) copolymers with and without hydroxyl groups in polyimide segments to be used for improvement of the shortcomings of polybenzoxazine arising from its brittleness. The presence of PDMS will improve the toughness as well as the thermal properties. Furthermore, the presence of polyimide acts as a compatibilizer between polybenzoxazine and PDMS without sacrificing the thermal and mechanical properties. In this part of the study, we investigated the interaction between polyimide with and without hydroxyl groups in the backbone and polybenzoxazine.

2. Experimental

2.1 Preparation of poly(imide-siloxane).

Poly(imide-siloxane)s with and without hydroxyl fuctionalities, Fig 1, have been prepared modifying the reported method [2] by reacting a mixture of 6FDA, amine terminated polydimethylsiloxane and oxydianiline (ODA) or dihydroxy benzidene at room temperature for 10 h. The obtained yellow viscous solution was imidized by refluxing in *m*-cresol. The residue after removing the azeotropic solvent was precipitated in water and dried to give fibrous material. The content of PDMS in poly(imide-siloxane)s was 72 weight percent.

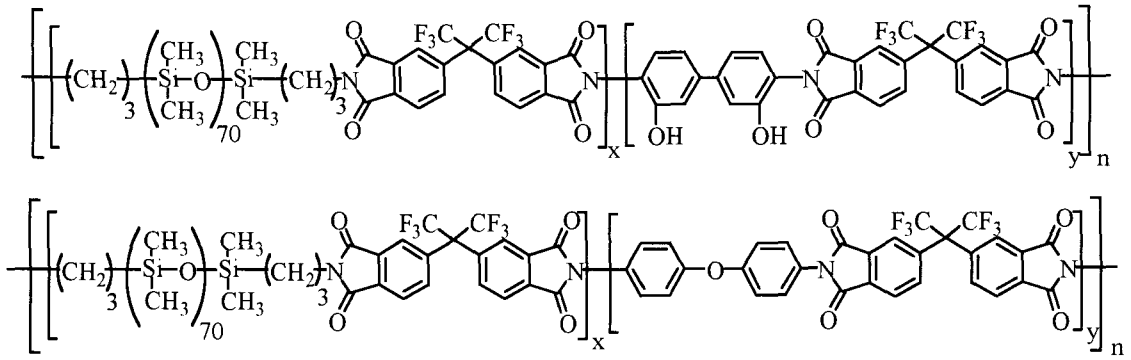

Fig. 1: Structure of poly(imide-siloxane)s with and without hydroxyl groups

2.2. Preparation of polybenzoxazine precursor

Polybenzoxazine precursor, Fig. 2, was prepared from bisphenol A with aniline and formaline according to the reported method [1]. The monomer was confirmed to be pure by NMR analysis.

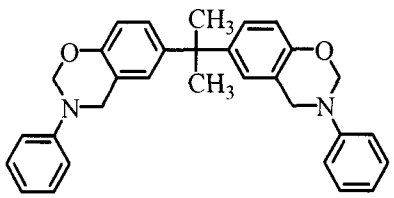

Fig 2. Structure of polybenzoxazine precursor

3. Results and Discussion

3.1. Preparation of poly(imide-siloxane)/polybenzoxazine composites

Poly(imide-siloxane)s with and without hydroxyl functionalities were mixed with polybenzoxazine precursor in different weight ratios using NMP. The clear solution was cast on glass plate, dried and cured at 150°C and 200°C for 1h each and 240°C for

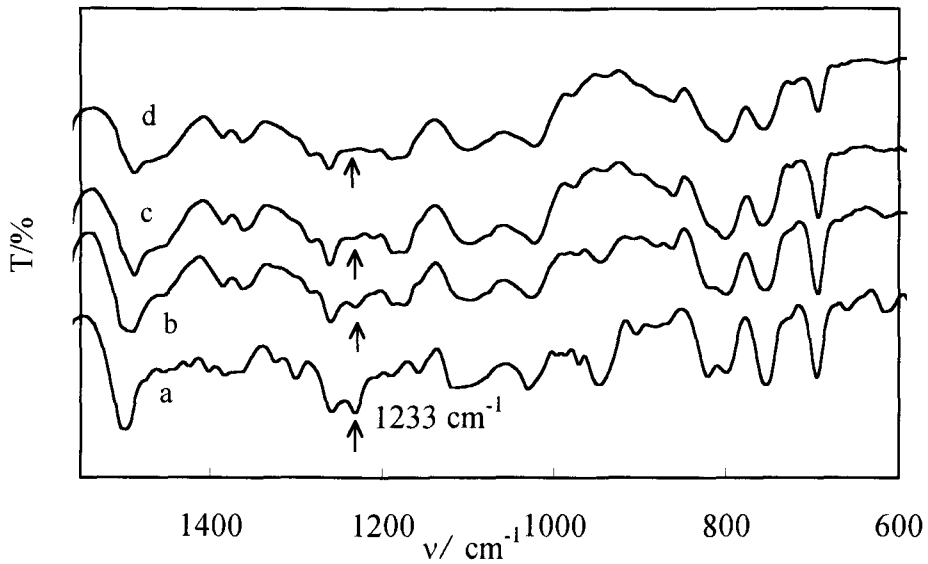

Fig. 3: IR spectra of poly(imide-siloxane)/polybenzoxazine composite (5/95) after thermal treatment at various temperatures. a; 60°C /10h, b;150°C/1, c; 200°C/1h and d; 240°C/1h.

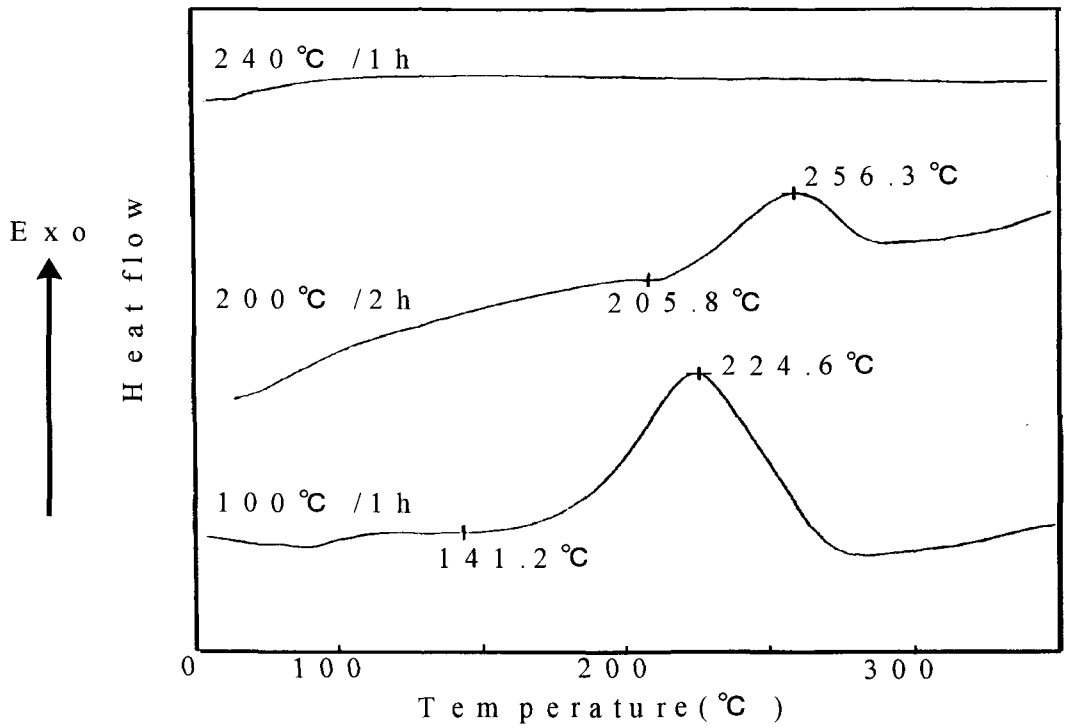

Fig. 4: DSC of poly(imide-siloxane)/polybenzoxazine composite (5/95) after thermal treatment at different temperatures

1h. The curing behavior of polybenzoxazine precursor in the presence of poly(imide-siloxane) was monitored by IR spectra, Fig. 3, which showed the disappearance of the absorption at 1233cm^{-1} due to the ring opening of benzoxazine precursor. Also, the DSC showed the complete disappearance of the exotherm due to curing of polybenzoxazine precursor by the end of 240°C cure stage as shown in Fig. 4.

3.2. Dynamic Mechanical properties

The dynamic mechanical properties of poly(imide-siloxane)/polybenzoxazine composite were examined as a function of temperature. When polybenzoxazine was modified with poly(imide-siloxane) without hydroxyl functionalities, a phase separation occurred between polyimide and polybenzoxazine as confirmed from the presence of two maxima of E" at 150°C for polybenzoxazine and ca. 250°C for polyimide as shown in Fig. 5. In case of hydroxyl functionalized polyimide, no phase separation occurred as confirmed by the presence of one broad maximum for the E" at ca. 280°C as shown in Fig. 6. We think that the polybenzoxazine precursor copolymerized with hydroxyl functionalized polyimide. On the other hand, in case of polyimide without hydroxy

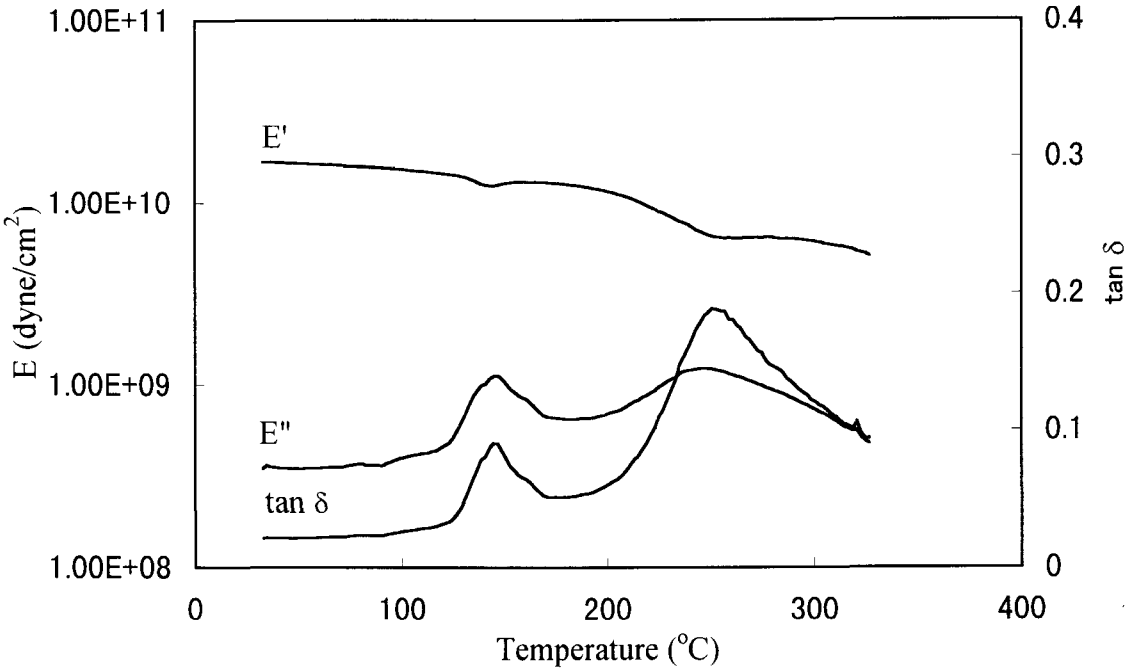

Fig. 5. Viscoelastic analysis of poly(imide-siloxane)/polybenzoxazine composite without hydroxyl groups in the polyimide segment

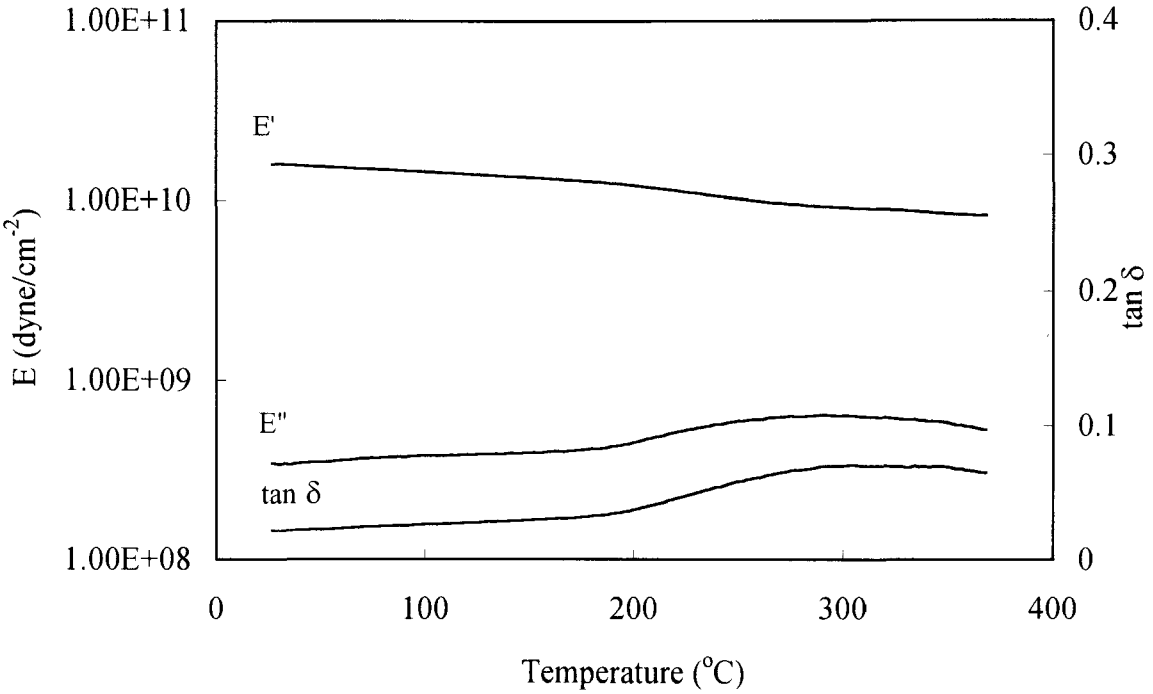

Fig. 6. Viscoelastic analysis of poly(imide-siloxane)/polybenzoxazine composite with hydroxyl groups in the polyimide segment

functionalities, polybenzoxazine could not copolymerize with the polyimide, and thus homopolymerized.

3.3. Thermal stability of poly(imide-siloxane)/polybenzoxazine composites

Thermal stability of the poly(imide-siloxane)/polybenzoxazine composites were investigated by TGA. Table 1 shows the temperature of 5% and 10% weight loss of poly(imide-siloxane)/ polybenzoxazine composites with and without hydroxy groups in the polyimide segments. As shown in the table, the thermal stability of polybenzoxazine was improved to some extent by the incorporation of poly(imide-siloxane). The presence or absence of hydroxyl functionalities on the polyimide segments gave little difference on the thermal stabilities.

Table 1. Thermogravimetric analysis of poly(imide-siloxane)/polybenzoxazine composites with and without hydroxyl groups in the imide segments

Poly(imide-siloxane) content wt (%)	Decomposition temperature (°C) without OH groups		Decomposition temperature (°C) with OH groups	
	5%	10%	5%	10%
0	328	351	328	351
5	338	362	338	367
10	346	375	342	377
15	365	394	362	389
20	373	413	371	401
100	448	469	412	442

4. References

1. Ning, X. and Ishida, H., *J. Polym. Sci., Part A: Polym. Chem.*, 1994, **32**, 1121.
2. Bott, R. H., Summers, J. D., Arnold, C. A., Taylor, L. T., Ward, T. C., and McGrath, J. E., *J Adhesion*, 1987, **23**, 67.