

SYNTHESIS OF A NEW SILICONE-CONTAINING BISMALEIMIDE COPOLYMER RESIN

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ABSTRACT

A copolymer of bismaleimide-diallylbisphenol A-diphenylsilandiol was synthesized and the copolymerization was studied by using N-phenylmaleimide, bisphenol A and diphenylsilandiol as model compounds. The copolymer could be well cured around 200°C, and the cured resins had good thermal stability. In the range of 170–210°C, a higher curing temperature was favorable to obtain more thermal stable resin by reducing the content of diphenylsilandiol cyclo-homopolymer in resin which would spoil its thermal stability.

INTRODUCTION

Although bismaleimide (BMI) resin plays a very important role in the development of high-performance engineering plastics, it usually needs to be chemically modified to overcome its bulk brittleness when put into practical use. Traditionally aromatic diamines were introduced as toughener of BMI^[1]. Diallylbisphenol A (DABPA) was found to be one of the best modifiers of BMI since it was brought into this item by Chaudhari and other researchers^[1–3]. But there is still a default in this system that the cured resin has a fairly quick weight loss at high temperature in the process of heating according to our experiments^[4,5]. Owing to the slow heat-decomposition properties of aromatic silicones, diphenylsilandiol (DPSD) is expected to be a useful modifier to make up for this weakness. And at the point of the view of molecular design, DPSD which has two active hydroxyls may take addition reaction with the C=C of BMI. In contrast with the fact that the two phenyl groups of DPSD in the prepared polymer will compensate for the reducing of mechanical properties caused by Si—O bond, the Si—O bond can simultaneously counteract the increasing of dielectric constant and the reducing of adhesive properties caused

by phenyl groups in some extent. Therefore DPSD is expected to be a good modifier of BMI. In fact there are some explorations on this item and there also have some inspiring results^[6-8]. However the modifying mechanism and some technical problems need to be further studied.

We expect to gain a novel BMI copolymer resin by introducing DPSD as the third monomer and tertiary amine as catalyst into the BMI/DABPA system. This paper focuses on the synthesis of the copolymer, heat curing behavior of the oligomers and thermal stability of the cured resins.

EXPERIMENTAL

1. Reaction of *N*-phenylmaleimide (NPM) with DPSD

NPM and DPSD were added into a reactor in the mole ratio 1 : 1, 5% (mol) tributylamine and DMF were used as catalyst and solvent, respectively. The system was reacted at 100–140° C for 4 h, the products were extracted by acetone and alcohol, a brown powder was obtained and used for the structure analysis.

2. Reaction of DPSD with bisphenol A (BA)

DPSD and BA were added into a reactor in the mole ratio 1 : 1, 5% (mol) tributylamine and DMF were used as catalyst and solvent, respectively. The system was reacted at 140–200° C for 3 h, the products were extracted by alcohol, a white powder was obtained and used for the structure analysis.

3. Copolymerization of BMI-DABPA-DPSD

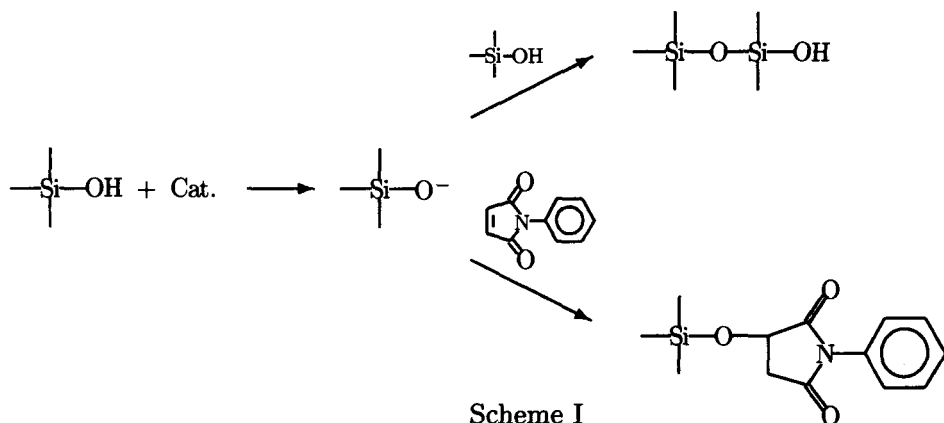
The three monomers were added into a reactor according to formulae, tributylamine (5% mol of BMI) and dioxane were used as catalyst and solvent, respectively. The system was reacted at 120° C for 4 h, a brown copolymer solution was obtained and then cured in a heater, the cured samples were used for the properties tests and structure analysis.

RESULTS AND DISCUSSION

In the trinary system of BMI/DABPA/DPSD there are many active functional groups, so that the reactions in this system are very complicated. Apart from some known reactions such as the Michael addition reactions of C=C of BMI with the allyl group and the OH group of DABPA^[5], and self-polymerizations of BMI and DPSD, there probably exist the reactions between DPSD and BMI, DPSD and DABPA. This paper investigates these reactions by model compounds at first.

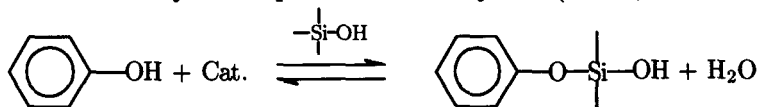
NPM and DPSD (triphenylsilanol can not be used as model compound for the reactivity of its OH is quite different from that of DPSD) were used as model compounds to study the reaction between OH and C=C of DPSD and BMI, respectively.

Products of this system was analyzed by elemental analysis, $^1\text{H-NMR}$, and FTIR. In the FTIR spectrum of the products, a strong absorption at 1012 cm^{-1} presents the formation of Si-O-C structure, and the existence of silanol peak at 3520 cm^{-1} implies that not all the OH of silanols take part in the reaction and thus the mixtures are produced. This is also identified by elemental analysis, from which C% is 63.91—69.96, N% is 2.69—1.99 and H% is 4.90—4.97. The results varied with different reaction conditions, and they are corresponding to the different ratios of DPSD/NPM (molecule number) products in the range of 1.66—2.57. A suggested reaction mechanism of this system can be expressed as Scheme I.



Through further investigation, the obtained mixtures were found to contain different number of Si-O segments, which showed that there was a competition between cross-reaction and homopolymerizations of two compounds. In the experiments, lower temperature and shorter reaction time benefit the reaction between BMI and DPSD, while higher temperature ($> 130^\circ\text{C}$) and longer time were favorable to the homopolymerizations of each, and when the homopolymer of DPSD contained more than 5 Si-O segments, its OH could not adduct to NPM any longer.

In order to investigate the reaction between DPSD and DABPA (i.e. reaction between OH of the two monomers), bisphenol A (BPA) was taken as a model compound instead of DABPA. The reaction between the two monomers was found to be a reversible reaction in DMF and in the presence of tertiary amine as catalyst, as shown in Scheme II. The yield of product was very low ($< 9\%$, $140\text{--}200^\circ\text{C}$, 3 h).



This reaction could get on only when the produced water were removed immedi-

ately. But in molten reaction at 200°C, we got a polymer which had nearly the same elemental ratio in its structure as its burden, and in FTIR there was a strong Si—O—Ar absorption at 1240 cm⁻¹ which identified that the product was a true copolymer of DPSD and BPA.

Then in this copolymerization system, there were such reactions as “ene” addition between C=C of DABPA and BMI, Michael addition between OH of DABPA or DPSD and C=C of BMI, and condensation between OH of DABPA and DPSD at higher temperature, as well as the homopolymerizations of BMI and DPSD.

Based on the studies of above model reactions, we synthesized a copolymer of BMI-DABPA-DPSD in the presence of tributylamine in dioxane solvent. A dark brown copolymer solution was obtained at the condition of 126°C and 4 h, and the copolymer was found to be used only as thermosetting polymer. Then the curing properties of the copolymer and thermal stability of the cured resin were studied.

Table 1 Relationship between curing temperature T_c and curing degree C of resins

Formulae, mole ratio (BMI:DABPA:DPSD)	T_c (°C)				
	170	180	190 $C\%$	200	210
1 : 1 : 2	51.8	64.5	89.7	97.4	98.3
1 : 1 : 1	59.7	75.8	92.4	98.5	98.9
2 : 1 : 1	74.1	89.5	96.8	98.4	98.8
3 : 1 : 1	83.2	94.7	98.5	98.8	98.7
2 : 2 : 1	89.5	94.3	98.9	99.2	99.1
3 : 2 : 1	92.3	97.4	98.8	99.1	99.3

Table 1 presented the influence of curing temperature on the curing degree of the copolymer resins (cured for 3 h and the products were extracted by acetone for 36 h). It can be seen obviously that the best curing temperature is around 200°C in the consideration of a higher curing degree and a better processing condition. The apparent activation energy of the curing reaction is $E_a = 90.35$ kJ/mol calculated with Kissinger's equation by DSC.

Table 2 Thermal weight-loss data of the cured resins

Formulae, mole ratio BMI:DABPA:DPSD	T_i (°C)	T_5 (°C)	T_{30} (°C)	T_{max} (°C)	T_h (°C)
1 : 1 : 2	287	337	507	379	215
2 : 2 : 1	325	377	524	451	228
3 : 2 : 1	368	405	487	540	223
3 : 1 : 1	323	389	540	452	235
2 : 1 : 1	308	337	533	452	223

* where T_i : initial thermal weight-loss temperature; T_5 : temperature at 5% weight-loss; T_{30} : temperature at 30% weight-loss; T_{max} : temperature at the maximum weight-loss rate; T_h : heat-resistant index, $T_h = 0.49[T_5 + 0.6(T_{30} - T_5)]$

Table 2 showed the dependence of thermal stability of cured resins (heat-treated at 250° C for 6 h) on their formulae. The adding of DPSD slowed the heat-decomposition procedure comparing with that of no-DPSD system^[5] yet it caused a reducing of the initial thermal weight-loss temperature of resins. Through further investigation, we found that the cyclo-homopolymer of DPSD in the cured resins was the problem to lead a lower initial thermal weight-loss temperature. In order to reduce the content of the cyclo-homopolymer of DPSD in the cured resins, a higher curing temperature was taken, and it showed good results. Since the OH group of DPSD and DABPA could condense with each other at high temperature (e.g. 200° C), thus the formation of cyclo-homopolymer of DPSD was reduced and the initial thermal weight-loss temperature of resins was improved (see Fig.1).

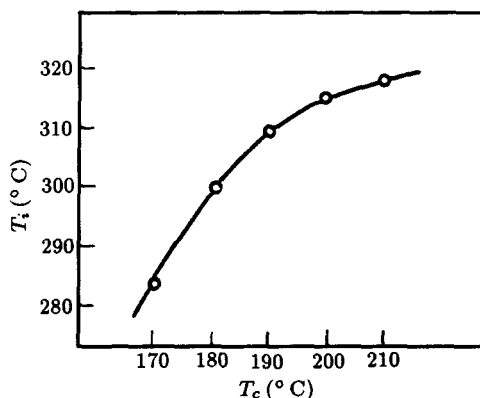


Fig. 1 Influence of T_c on the T_i of the resin (mol ratio 2 : 1 : 1)

Keywords:

Bismaleimide; Diallylbisphenol A; Diphenylsilandiol; Copolymer

REFERENCES

- [1] Kuang, W.F.; Jiang, L.X. and Cai, X.X., *China Synthetic Resin and Plastics* (in Chinese), **1995**, 12(2): 55.
- [2] Chaudhari, M.; Galvin, T. and King, J., *SAMPLE J*, **1986**, (7)/(8): 79.
- [3] Huang, F.R.; Zhong, X.J.; Liu, Y.J., Wang, J.L. and Zhang, X. *Journal of Material Research* (in Chinese), **1994**, 8(4): 356.
- [4] Kuang, W.F.; Jiang L.X. and Cai, X.X., *China Synthetic Resin and Plastics* (in Chinese), **1995**, 12(4): 32.
- [5] Kuang, W.F.; Jiang, L.X. and Cai, X.X., *Chinese Journal of Synthetic Chemistry* (in Chinese), **1996**, (1): 25.
- [6] Xiang, M.; Xie, M.L. and Cai, X.X., *J. of Chengdu University of Science and Technology* (in Chinese), **1989**, (6): 29.
- [7] Ralouta, M. and Balme, M., *Polymer J*, **1987**, 19(1): 173.
- [8] Kuang, W.F., Jiang, L.X. and Cai, X.X., *Materials Review* (in Chinese), **1996**, (4): 52.