

Preparation and Analysis of a Flexible Curing Agent for Epoxy Resin

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ABSTRACT: A kind of novel aromatic amine bis(4-nonyl-2,5-diamine-penoxyl)alkylate (RA_n) as curing agents for epoxy resins were prepared through three steps of reactions using nonyl phenol and dibromoalkylate as materials. Dynamic mechanical analysis (DMA) indicated that the secondary relaxation for the resins cured by RA_n were generated by the nonyls in RA_n molecules when temperature was below -50°C. Comparing with other reference resins, the enhancement for toughness of RA_n cured-resins were at least 15%, which were contributed by such secondary relaxation. Furthermore, stiffness of the networks and thermal properties of

the resins were not influenced by the flexible groups (nonyl) in RA_n after curing, since the groups were located only in the branched chains of the networks. The mechanical and thermal properties of the new material have been significantly enhanced. The relevant method and procedure developed through this research have been granted Chinese patent recently (Yang and Gong, Chin. Pat. CN1978483A, 2007). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2706–2710, 2009

Key words: curing agent; flexibilizer; epoxy resin; secondary relaxation

INTRODUCTION

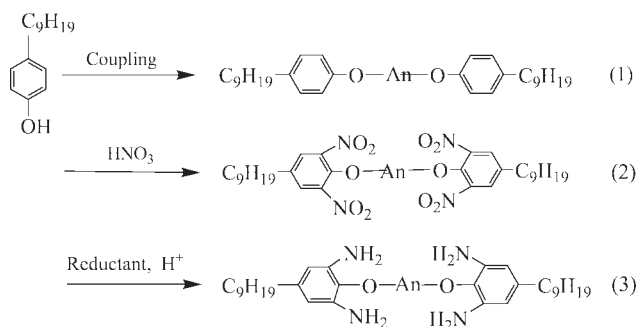
Widely used as raw materials in various industries and many engineering components, epoxy resins exhibit several advantageous material properties such as low shrinkage on curing, excellent chemistry and moisture resistance, good adherence on substrates, and high stiffness and strength.^{1–4} However, some disadvantages such as brittleness limit the usage of epoxy resins in several fields such as structure material adhesives, coating, and electronic encapsulation. To improve these deficiencies, epoxy resins are always modified via physical and chemical means.⁵

For common physical methods, the modifiers such as rubber are firstly mixed or resolved in fluid epoxy resins. After curing of resins, rubber particles which have distributed into the resin matrix are capable of absorbing the external energy and thus preventing crack propagation. The toughness can be obviously enhanced by this mean, but it is inefficient when the cross-linking density of matrix is much high.⁶ For chemical methods, on the other hand, flexibility of network are enhanced and toughness of resins are improved by the compounds with flexible molecular such as oligomers or low-molecular-weight agents

that react with the epoxy resins during the curing process. However, the cross-linking density is reduced when these modifiers limit the reaction between epoxy resins and curing agents.⁶ For this reason, the curing agents with flexible molecules have received intensive attention and are swiftly developed in recent years. For instance, Moon⁷ synthesized a novel aromatic amine which could cure epoxy resins at -10°C and obtain tough resins after curing. Xiu⁸ synthesized a novel curing agent with acid anhydride and flexible oligomers. The impact strength of epoxy resins cured by the agents is 23 KJ/m. It is noted that some penultimate-amido aromatic ether ketone⁹ have already been commercially used. However, the thermal properties of epoxy resins cured by such flexible compound are still very much unsatisfactory.

In this work, a novel agent bis(2,6-diamido-4-nonyl-phenoxy)alkylate (RA_n), which can be used as a toughener or hardener for epoxy resin is designed and synthesized. The flexible functional groups do not constitute the main chains of the networks but they are present in branched chains. As the contribution of this molecular structure, both stiffness and thermal properties of the cured-resins are considerably improved when comparing with the resins cured by normal aromatic amine hardeners. This processing has been granted a Chinese patent because of Yang and Gong.¹⁰

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Scheme 1 Synthesis of RA_n where A_n stand for the spacers of $-(CH_2)_n-$.

EXPERIMENTAL

Materials

The raw materials used in the experiment were, respectively, supplied by different companies in China. Diglycidyl ether of bisphenol-A epoxy resin (E51) was supplied by Wanhe Company, Beijing, China; nonyl phenol was offered by Chengdu Kelong Company, Chengdu, China; Dibromomethane and Tetraethyl ammonium bromide (TEAB) were obtained from Shanghai Agent Factory, Shanghai, China; hydrogen nitrate (63%), hydrochloric acid (36%), deoxidation ferrous, m-Phenylenediamine (m-PDA), and ethylether were all got from Beijing Chemical Factory, Beijing, China.

Synthesis of RA_n

The process of RA_n synthesizing was operated according to the route shown in Scheme 1 where A_n stands for the spacers of $-(CH_2)_n-$. The experiment procedure for RA_1 is described explicitly as follows.

In a first step, an amount of 44 g (0.2 mol) Nonyl phenol and 2.52 g (0.012 mol) TEAB were mixed into 500 mL three-necked flask. After adding 200 mL NaOH solution (15%), the mixture was stirred and heated to 70°C. Subsequently, 17.4 g (0.1 mol) of dibromomethane was added and the reaction mixture was completely stirred and refluxed for 5 h. Then, after cooling to room temperature, the resultant was extracted with ethylether. Subsequently, after drying with magnesium sulfate and distilling in a vacuum for the solution, the colorless viscous intermediate was obtained.

The next step involved resolving 4.87 g (0.01 mol) of intermediate in tetrahydrofuran (THF) and adding the mixture to a 250 mL three-necked flask and an amount of 10.2 g of hydrogen nitrate (37%) was added dropwise into the flask. The reaction mixture was stirred at 35°C for 10 h. Then, the resultant was washed by brine and dried with magnesium sulfate. After separating by column chromatographic, the yellow viscous intermediate was synthesized.

In a further step, 2.00 g (0.003 mol) of yellow intermediate was mixed with 0.2 g of deoxidation ferrous and 10 mL of hydrochloric acid (5%). The mixture was stirred and refluxed for 6 h and then filtered. The filtrate was extracted with ethylether and dried with magnesium sulfate. After the solvent was removed in a vacuum, the product as yellow crystals was eventually obtained (RA_1).

By following a similar procedure, other products (RA_n) were synthesized, and the details for the procedure could be referred to Yang and Gong.¹⁰

Curing of epoxy resins

In the curing process, the RA_n synthesized in the previous step was resolved in dichloroethane, and the solution was mixed with epoxy resins (E51) at 80°C. The mole ratio for RA_n /E51 was controlled in a very careful manner to ensure the unity mole ratio for amidoes hydrogen to epoxy groups. After mixing uniformly, the liquid was cured at 80°C for 10 h and then at 140°C for 4 h. Similar processing was performed when m-PDA was employed as curing agents.

Measurement

In measurement process, infrared spectroscopy (IR) spectrum was recorded by Nicolet NEXUS-470 spectrometer with KBr powder sample. ¹H nuclear magnetic resonance (¹H-NMR) spectrum was measured by using the spectrometer of AL-300(Japan) when resonance frequency was 300 MHz with CDCl₃ as solvent. Dynamic mechanical analysis (DMA) was performed by using instrument of Rheometric Scientific DMTA-V with frequency of 1 Hz at a heating rate of 5°C/min from -120°C to 200°C. Finally, the mechanical properties were tested according to GB/T2567-1995—GB/T2571-1995.⁹

RESULTS AND DISCUSSION

Structure of RA

Molecular structure for RA_1 , RA_2 , RA_4 , and RA_6 are shown in Figure 1.

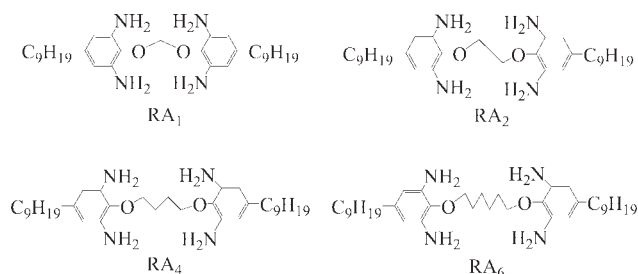


Figure 1 Molecular formulas of RA_n .

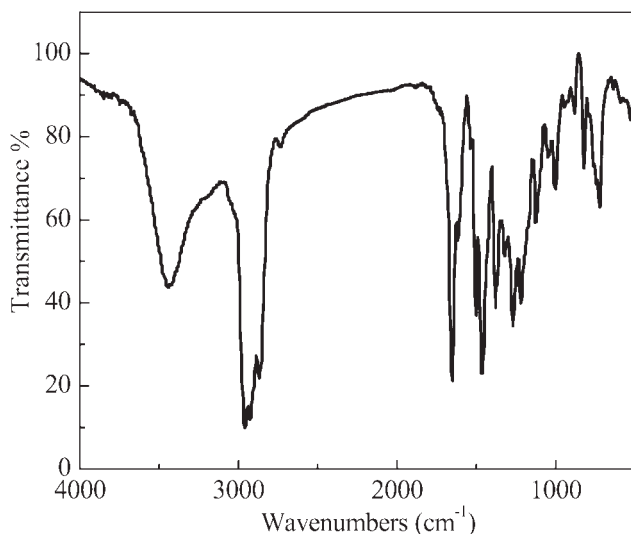


Figure 2 IR spectrum for RA₁.

The result of IR and ¹H-NMR for structure details of Bis(2,6-diamido-4-nonyl- phenoxy)methane(RA₁) are shown in Figures 2 and 3.

As shown in Figure 2 of IR spectrum for RA₁, the absorption peak at 3471.1 cm⁻¹ is contributed by N—H; peaks at 2957.7 cm⁻¹ and 2871.6 cm⁻¹ indicate the C—H bonds in nonyls; peaks at 1226 cm⁻¹ and 1045.2 cm⁻¹ are produced by C—O bond; peaks at 861.2 cm⁻¹ and 1614.9 cm⁻¹ are character peaks for the bond of Ar—H; and the peak at 1364.4 cm⁻¹ is contributed by Ar—N bond.

The details of ¹H-NMR spectrum of RA₁ are shown in Figure 3 that the chemical shifts of 34 hydroxy protons on nonyl are 0.557–2.112 ppm; the eight amine protons are found when chemical shifts

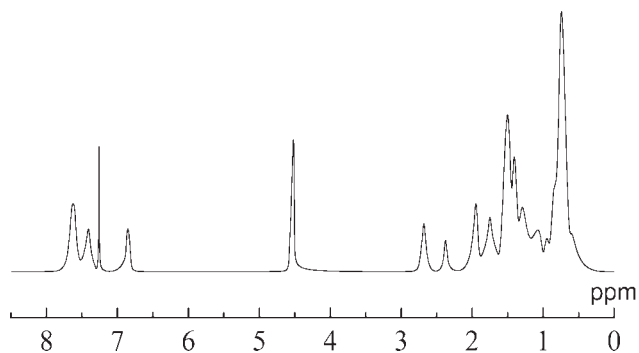


Figure 3 ¹H-NMR spectrum for RA₁.

are 7.675 ppm; the peak at 4.523 ppm confirm the two alkoxy protons; and the peak between 6.800 and 7.205 ppm produced by the four protons on benzene ring.

From results of IR and ¹H-NMR, the structure of RA₁ has been confirmed. Further details and analysis about other structures of RA_n could be referred to the Ref. 10.

Dynamic mechanical analysis and mechanics property

The results of DMA for cured-resins are presented in Figure 4(a–e). In these cases, all resins cured by RA_n and m-PDA were investigated. According to Figure 4, the peaks of loss module (E'') and tangent of the loss angle ($\tan \delta$) contributed by the secondary relaxation at low temperature (less than -50°C) are obviously indicated in RA-cured networks. The same peaks cannot be discovered in Figure 4 when

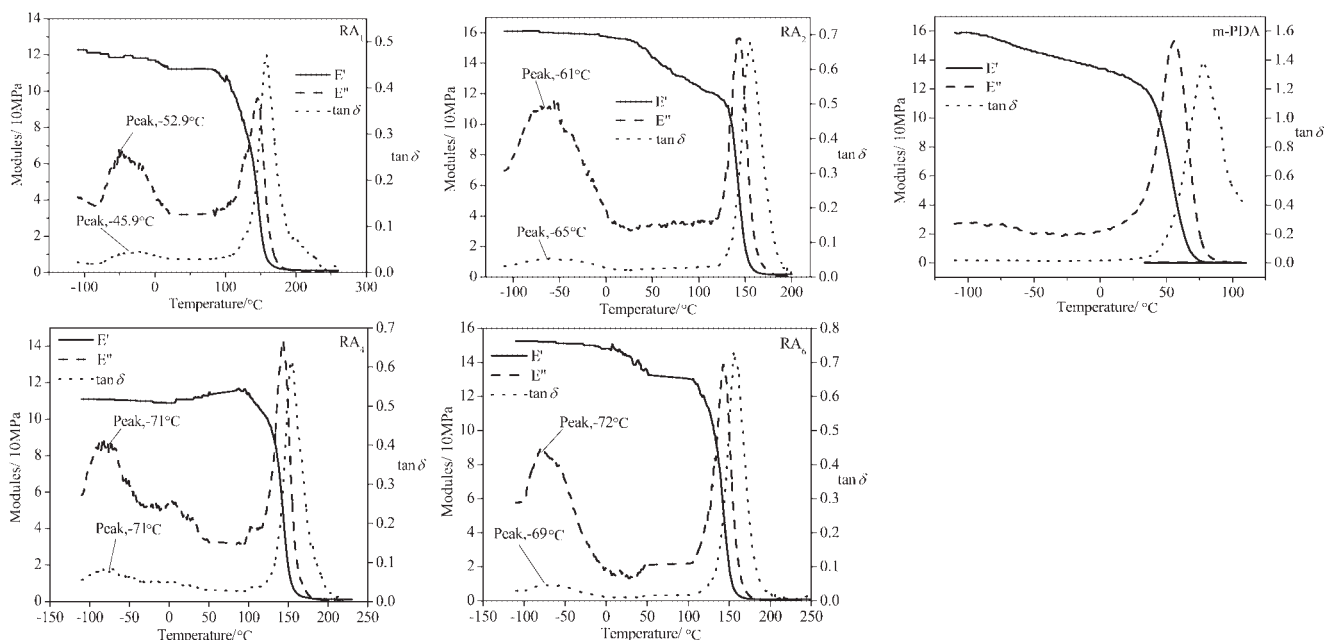


Figure 4 Dynamic mechanical analysis.

TABLE I
Mechanical Properties of Cured-Resins

Curing agent	Impact strength (KJ/m ²)	Tension strength (MPa)	Compress strength (MPa)	Flexural strength (MPa)
RA1	2.3	65	70	118
RA2	2.5	69	68	119
RA4	2.5	68	70	116
RA6	2.6	72	69	116
m-PDA ⁹	1.6	56	74	109
DDM ⁹	2.0	57	74	123
DDS ⁹	2.0	60	76	126

the resins were cured by m-PDA. Such phenomenon was caused by the contribution of free volume according to Halary and coworkers.^{11–13} The free volume in the networks cured by RA_n is more extensive than other networks because of the influence produced by nonyls in RA_n molecules. Thus, the secondary relaxation of the networks was reinforced when sufficient free volume was provided to the sectional motion of the networks in glass morphology. Another case is the various of storage module (E') at low temperature is weaker than the correspond value of E . Similar results have been obtained when the curing agents with similar structure were employed.¹⁴

The segment motion of the network is also influenced by the spacer chain. Comparing with short spacer chain, the longer one with higher flexibility due to lower potential for the barrier segment motion, and the secondary relaxation is generated at lower temperature. Figure 4 further illustrate such variation that the secondary relaxation temperatures (T_{β}) for E'' and $\tan \delta$ reduces from -52.9°C to -72°C when the structure of the spacers varies from methane (RA₁) to hexyl (RA₆).

Table I indicates the mechanical properties of resins cured by RA_n and other usual aromatic amine curing agents including m-PDA, DDM(4,4'-Diaminodiphenyl methane) and DDS(3,3'-diaminodiphenyl sulphone) with respect to identical curing conditions. All agents have similar structure stiffness except flexible chains in RA_n. As shown in Table I, the impact strength of RA_n cured-resins is above 2.3 KJ/m², which is nearly 15% higher than DDM and DDS cured-resins (2.0 KJ/m²) and nearly 50% higher than m-PDA cured-resins (1.6KJ/m²). Furthermore, the tension strength of RA_ncured-resins is nearly 70 MPa, almost 15 MPa higher than the resins cured by the other three agents. An explanation could be offered as follows. The secondary relaxation at low temperature for RA_n cured-resins improves the ability of the networks to absorb external energy from instantaneous impact at room temperature. This case results in the enhancement of resins' toughness. The compression strength and flexural strength of RA

cured-resins are lower than the resins cured by the other three agents. Such effect is contributed by the flexibility of RA_n molecular. However, the main flexible groups of RA_n only based on the branched chains in the networks and the rigidity of the main chains are not affected.^{15,16} Comparing with the enhancement of toughness, the reduction in these two mechanical properties are lower than 5%. Such low level of reduction demonstrates that the influence from RA_n to the stiffness and intensity of cured-resins are limited.¹⁶

It can be seen from Table I that the impact strength of cured-resins enhances from 2.3 to 2.6 KJ/m² and the tension strength increases from 65 to 72 MPa when structure of RA_n change from RA₁ to RA₆. Such improvement is contributed by the enhancement of the flexibility for spacers. However, the influence is not obvious.

Thermal property

Since the stiff molecule structure which is similar with usual aromatic amines, such as DDM, DDS, and m-PDA, the molecular networks of RA_n cured-resins are rigid that lead to high-glass transition temperature (T_g).⁹ As is shown in Figure 4, T_g of the resins cured by RA_n are all above 140°C. Comparing to other molecule flexible curing agents such as aliphatic amine, polyamide, and acid anhydride, this value is nearly 30°C higher.⁹ In conclusion, comparing with some common aromatic amine curing agents (DDM, DDS, and m-PDA), RA_n are efficient elasticizers for epoxy resins with excellent thermal properties.

CONCLUSIONS

An invention for synthesizing a new kind of material with superior mechanical and thermal properties is reported in this article. A novel type of amine epoxy curing agents RA_n, which could be used as tougheners for epoxy resins, were prepared with nonyl phenol and dibromoalkylate. The secondary relaxation, contributed by nonyls in the side chains of networks cured by RA_n, was confirmed from DMA results. The test of mechanical properties showed that the toughness of these cured-resins were enhanced more than 15% comparing with common aromatic curing agents. Furthermore, due to the molecule stiffness of RA_n, the thermal properties of cured-resins were shown better than the resins cured by usual curing agents with flexible molecules.

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