

Synthesis of an Epoxy Resin Curing Agent Containing Maleimide Group

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Abstract. A novel N, N-(4-amino phenyl maleimide) diglycidyl amine (APMDGA) was synthesized from maleic anhydride, 4-nitroaniline, and epichlorohydrin by a few-step reactions via intermediate products N-(4-nitrophenyl)maleimide and N-(4-aminophenyl)maleimide. The chemical structure of APMDGA is confirmed by ¹H-NMR, FT-IR, and EA. The synthesis conditions have also been investigated. The final product APMDGA shows a yellow solid, and the yield is 48.6%.

Introduction

Epoxy resins have excellent dielectric properties, small product size shrinkage, good stability, strong adhesion to both metallic and non-metallic materials, high hardness, good flexibility, and excellent stability in many solvents and alkali solutions. They have been used as adhesives, coatings, and lamination materials in a wide range of industrial applications such as electronics, mechanics, construction, and aerospace. Epoxy curing agents are used to crosslink epoxy resins and form a three-dimensional network structure, providing the cured epoxy excellent performance. Therefore, the development of new curing agent for epoxy resin is of the same practical importance as the development of new epoxy resin.

To date, the leading epoxy curing agent is amine, followed by acid anhydride, "semi-inorganic polymer" curing agent containing B, Si, P, F, and Mg, modified phenol and mercaptan curing agent, and thiol functionalized block copolymer curing agent. For example, Wang et al. ^[1] prepared a curing agent BAOP using dichlorophenylphosphine and p-nitrophenol, which is ease of synthesis and has good storage stability, low toxicity, high electrical performance, and low cost. Due to its high phosphorus content, BAOP has excellent flame retardancy and thermal stability, and it can be used as environmentally friendly microelectronics packaging material. Yu et al. ^[2] synthesized 3,3',4,4'-diaminodiphenylmethane from 4,4'-Diaminodiphenyl methane. This curing agent has excellent adhesive strength and water resistance. Zhang et al. ^[3] synthesized 4, 4- glycidyl amino phenyl ether ketone benzene curing agent using 4-Aminophenol, DMF, and toluene, which has good moisture resistance and thermal performance.

In this paper, a novel epoxy curing agent, N, N- (4- amino phenyl maleimide) diglycidyl amine (APMDGA), is synthesized from maleic anhydride, 4-nitroaniline, and epichlorohydrin by a few-step reactions via intermediate products N-(4-nitrophenyl)maleimide and N-(4-aminophenyl)maleimide. The primary aim of this work is to enhance film-forming ability and performance of the epoxy resin by the introduction of the functional groups on the curing agent. Specifically, the double bond on the maleimide ring of the curing agent opens to crosslink the epoxy system when the film is formed, which brings about better stability to the film because other curing agents often lead to film with high reaction activity, i.e., the functional groups on the chain ends still remain active even after the curing reaction. As a result, the performance of the epoxy such as hardness and chemical stability will be improved. In addition, this new epoxy curing agent can also be used as a modifying agent for other polymers, i.e., the introduction of the N, N- (4- amino phenyl maleimide) functionality results in low porosity and high temperature resistance of the polymeric material.

Experimental Section

Materials: All reagents and solvents were in AR grade and were purchased from commercial sources. 4-nitroaniline was obtained from Shanghai Chemical Reagent Company, epichlorohydrin, cupric sulfate, maleic anhydride, magnesium sulfate anhydrous, and sodium carbonate anhydrous were obtained from Tianjin Bodi Chemical Co. Ltd. Toluene was obtained from Chongqing Beibei Chemical Reagent Factory. Hydroquinone, ethyl acetate, N, N- dimethylformamide (DMF), 4-toluenesulfonic acid, ethanol anhydrous, and sodium hydroxide were purchased from Chengdu Kelong Chemical Reagent Factory. Hydrochloric acid was from Guangdong Shantou Xilong Chemical Factory. Tin(II) chloride dihydrate was obtained from Tianjin Kermel Chemical Reagent Co. Ltd. Benzyl triethyl ammonium chloride was obtained from Chengdu Best Reagent Co. Ltd.

Synthesis of N-(4-nitrophenyl)maleimide (NPMI)

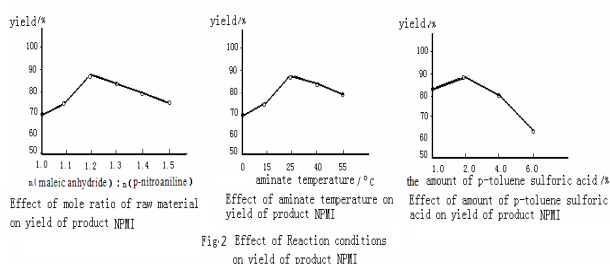
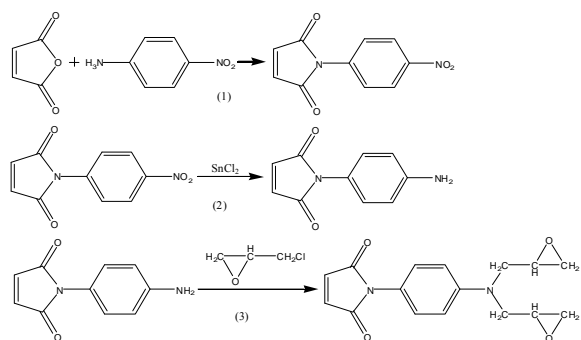
N-(4-nitrophenyl)maleimide (NPMI) was synthesized from p-nitroaniline and maleic anhydride by the following procedure as shown in Figure 1. A four-neck round bottom flask equipped with a mechanical stirrer, a condenser, and a Dean-Stark receiver, was charged with maleic anhydride (14.8 g), DMF (125 mL), and toluene (200 mL). The mixture was stirred for 10 min at room temperature to ensure complete dissolution of maleic anhydride. The flask was then cooled down to $< 10\text{ }^{\circ}\text{C}$ in an ice bath. To this mixture, 4-nitroaniline (17.35g) was added dropwise at a rate of 30 min/mL, and 0.05 g of hydroquinone was added as inhibitor. After the completion of the addition, the reaction was left for 12 h at room temperature under nitrogen while a yellow white slurry was formed.

The second stage of synthesis was accomplished via a cyclization reaction. 0.65 g of 4-toluenesulfonic acid and 0.065 g of cupric sulfate were added to the flask, heated up to 140 to 150 $^{\circ}\text{C}$ under nitrogen, and left to stir until no more water droplets appear in the distillate. The reactant turned into a brown-yellow transparent liquid. After cooling down the mixture to 60 $^{\circ}\text{C}$, a 6% aqueous NaHCO_3 solution was added to neutralize the mixture, and then the mixture was allowed to stand for 24 h to separate into two layers. The top layer was collected and dropped to 500 mL of cold deionized water with continuous stirring. Yellow solid precipitated out in water. The precipitate was filtered with a Büchner funnel, washed with deionized water, then vacuum-dried at 70 $^{\circ}\text{C}$ for 2 h. The final product, a light yellow solid, was obtained. The yield was 85%.

Synthesis of N-(4-aminophenyl)maleimide (APMI)

A three-neck round bottom flask, under nitrogen, equipped with a mechanical stirrer and a condenser, was charged with 10.0 g of NPMI, 51.9 g of Tin(II) chloride dehydrate, and 153 mL of hydrochloric acid (6 mol/L). The reactant was left under stirring for 12 h at 60 $^{\circ}\text{C}$, then cooled down to room temperature, and transferred to a 500 mL beaker. Na_2CO_3 was added to neutralize the mixture, followed by extracting with ethyl acetate (900 mL) three times. The extract solution was collected and dried with magnesium sulfate anhydrous, filtrated, and evaporated in vacuo on a rotary evaporator at 45 $^{\circ}\text{C}$ while a light yellow solid (5.20 g) was obtained. The yield of APMI was 50.2%.

Synthesis of N, N- (4- amino phenyl maleimide) diglycidyl amine (APMDGA)



APMI (6.0 g) and benzyl triethyl ammonium chloride (0.06 g) were dissolved in 200 mL of ethanol anhydrous. The solution was heated up to 65 $^{\circ}\text{C}$ under nitrogen, to which the mixture of epichlorohydrin (5.9 g) and ethanol anhydrous (100 mL) was added. The addition process was

completed within 1 h. The mixture was cooled down to 55 °C, and the reaction was left for 5 h. After completion, the mixture was cooled down to 50 °C and to which 15.5 g of 20% NaOH solution was added, and left to react for another 3 h at 50 °C.

The reactant was added dropwise to 1000 mL of deionized water, followed by adding hydrochloric acid to neutrality. The precipitate was filtered and extracted two times with 1000 mL of ethyl acetate, then dried with magnesium sulfate anhydrous, and evaporated in vacuo on a rotary evaporator at 45 °C. The final product, APMDGA solid (4.65 g) was obtained. The yield of APMDGA was 48.6 %.

Identification of Product: Proton nuclear magnetic resonance (¹H-NMR) spectra were performed by a Bruker Advance-400 MHz spectrometer, using DMSO-d₆ as a solvent and tetramethylsilane as the internal standard. Fourier transform infrared spectroscopy (FT-IR) were recorded with a Nicolet FTIR-560 spectrometer by the KBr salt slice method. Elementary analyses were performed using Italy Euro EA 3000 from Euro Vector S.P.A. Binocular stereo micromelting point apparatus were from Beijing Taike instrument company.

Characterization of NPMI monomers

Elemental analysis (molecular formula C₁₀H₆N₂O₄): C56.65 (55.74), H3.89 (4.20), N12.01 (13.45). The experimental results are in brackets, in accordance with the theoretical values. The melting temperature of NPMI is 175 °C.

FT-IR was performed in order to further confirm NPMI structure. The characteristic absorption at 3104 cm⁻¹ corresponds to the C=C stretching of the benzene ring. The stretching vibration peaks observed at 1523 and 1349 cm⁻¹ correspond to N=O. A characteristic absorption peak observed at 1719 cm⁻¹ corresponds to C=O stretching in the imide structure.

The shifts and splitting patterns of ¹H-NMR (DMSO-d₆) spectra of the NPMI monomer are as follows: δ7.68–7.71 (4H, Ph-H), δ7.26 (2H, –CH=CH–).

The ¹H-NMR, FT-IR, and EA results confirm the structure of the NPMI monomer.

Characterization of APMI monomers

Elemental analysis (molecular formula C₁₀H₈N₂O₂): C65.01 (64.10) , H5.46 (6.38) , N13.78 (14.66). The experimental results are in brackets, in agreement with the theoretical values. The melting temperature of APMI is 134 °C.

FT-IR (KBr, cm⁻¹): The characteristic absorption at 3007 cm⁻¹ corresponds to the C=C stretching of the benzene ring. The observed peak at 3374 cm⁻¹ corresponds to the stretching vibration peak of N-H. A characteristic absorption in the imide structure is at 1516 cm⁻¹ which corresponds to C=O stretching.

¹H-NMR (DMSO, d): δ4.171(2H, N-H), δ6.573-6.595 and 6.816-6.838(4H, Ph-H), δ6.344 (2H, –CH=CH–).

The ¹H-NMR, FT-IR, and EA results confirm the structure of the APMI monomer.

Characterization of APMDGA

FT-IR (KBr, cm⁻¹): The characteristic absorption peaks at 2953 cm⁻¹ and 2920 cm⁻¹ correspond to the C=C stretching of the benzene ring. The absorption peak observed at 2851 cm⁻¹ corresponds to =C-H stretching. A characteristic absorption peak at 1519 cm⁻¹ corresponds to the C=O stretching in the imide structure. The peaks at 1233 cm⁻¹ and 1188 cm⁻¹ are the asymmetric stretching of the C-O-C group. A characteristic absorption of epoxy structure is at 972cm⁻¹. A characteristic absorption peak at 1447 cm⁻¹ corresponds to the C=C stretching in the imide structure. The observed peak at 1383 cm⁻¹ stands for the C-N-C stretching modes.

¹H-NMR (DMSO, d): δ6.853-7.993(6H, Ph-H, -CH=CH-), δ3.079-3.611 (6H,). δ2.541-2.733 (4H, –CH₂–),

Elemental analysis (molecular formula C₁₆H₁₆N₂O₄): C 63.99 (63.05) , H5.37 (5.92) , N 9.33 (9.46), The experimental results are in brackets, in agreement with the theoretical values.

The ¹H-NMR, FT-IR, and EA results confirm the structure of APMDGA.

Results and Discussion

The synthesized path of APMDGA

The synthetic route of APMDGA is shown in Figure 1.

Synthesis of N-(4-nitrophenyl)maleimide (NPMI)

The common methods of synthesizing maleimide include one step, azeotropic distillation, acetic anhydride, phosgene, and esterify^[4-6]. The most common way is by the reaction of amine with maleic anhydride, via intermediate maleamic acid, then through cyclization, dehydration, and imidization. These methods can be divided into two categories, one using desiccant and the other using catalyst. The first desiccant method is to use excessive or equal amount of desiccant to conduct dehydrating imidization, which leads to high yield. However, this method requires large amount of desiccant, which increases production cost. Furthermore, the product is difficult to separate, which also makes it not suitable for industrial process scale-up. The second catalyst method does not require desiccant; however, if the catalyst has been chosen inappropriate, it will bring about side reactions that cause the yield to decrease^[7].

In this work, 4-nitrophenyl maleimide (NPMI) is synthesized with a two-step method from maleic anhydride and 4-nitroaniline in the presence of toluene and DMF, using 4-toluenesulfonic acid as main catalyst and cupric sulfate as second catalyst, with hydroquinol as polymerization inhibitor. The affecting factors for the synthesis were also studied, such as mole ratio of reactants, catalyst amount and reaction temperature. The experimental results are shown in Fig 2.

The optimal reaction conditions for the two-step method are as follows: the molar ratio of maleic anhydride and p-nitroaniline is 1.2:1; the amination temperature is 20 to 30 °C; the amount of p-toluene sulfonic acid is 1 to 2 percent of the reactant total mass; the amount of hydroquinone is 0.1 percent of reactant total mass; the amount of cupric sulfate is 0.1 to 0.5 percent of reactant total mass; the cyclization temperature is 145 to 150 °C; the volume ratio of toluene and DMF is 10:1, and the cyclization time is more than 6 h. The yield of product is better than 85%.

The synthesized of N-(4-aminophenyl) maleimide (APMI)

The common methods to deoxidize aromatic functionalized nitrogen-containing compounds into amino-compounds include catalytic hydrogenation, hydrazine hydrate deoxidization, metal deoxidization, electrochemistry deoxidization, etc.^[8-13] In this work, APMI is synthesized by a two-step method from NPMI, using Tin(II) chloride dihydrate and hydrochloric acid as catalysts. Using this method, the reaction conditions can be controlled easily, and the yield of the product is more than 50%. The effects of controlling factors such as reaction temperature, catalyst, acidity, and extraction times were investigated as well.

Based on the preliminary results, we investigate the key factors affecting the yield of APMI the reactions such as the amount of reducing agent (A), the amount of hydrochloric acid (B), reaction temperature (C), and the extraction times (D). The optimal conditions were confirmed by L₉(3⁴) orthogonal design as shown in Table 1.

Table 1 Factor and level of orthogonal experiment

Level	the amount of reducer (A) (mol)	the amount of hydrochloric acid (B) (mol)	the reaction temperature (C) (°C)	the extract times (D)
1	0.184	0.69	40	5
2	0.23	0.92	60	6
3	0.276	1.15	80	7

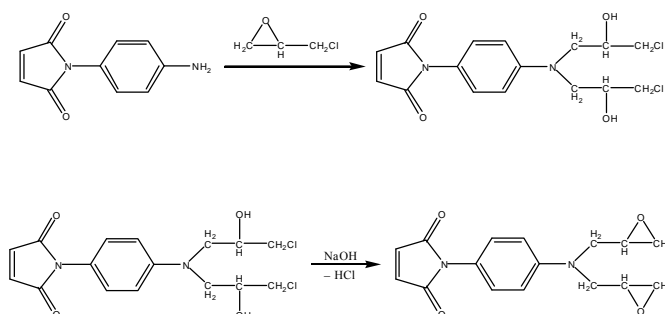


Fig3 The reaction of the amine and epichlorohydrin

The amount of NPMI is 10.0 g (0.046mol). The optimal conditions obtained from the orthogonal experiment results are as follows. The amount of Tin(II) chloride dihydrate reducing agent is 51.9 g (0.23 mol); the amount of hydrochloric acid is 153mL (0.92 mol); the reaction temperature is 60 °C, the extraction times are six. Three repeated experimental results show that the yield of APMI are 50.2%, 50.5%, 50.3%, indicating good reproducibility.

The synthesized of N, N- (4-amino phenyl maleimide) diglycidyl amine (APMDGA)

To date, there are two main methods of synthesizing glycidyl amine, i.e., one-step and two-step method^[14-18]. For the one-step method, the reaction of ring opening addition and dehydrochlorination occur at the same time under the presence of concentrated alkali, using trimethylamine and epichlorohydrin as raw materials. The production process requires long reaction time, is easy to form a polymer, and the yield is low. Therefore, it is difficult to scale up. The two-step method also utilizes amine and epichlorohydrin as raw materials. According to the phase transfer catalysis technology from Makosza, Starks, and Bradstrom in late 1960s, the first step reaction is formation of intermediate product amino chloro propanol, then form glycidyl amine in the presence of concentrated alkali. As compared to the one-step method, the two-step method has the advantages such as mild reaction conditions, ease of operation, high selectivity, and high yield. However, the feed ratio n (Epichlorohydrin) to n (amine) is large, which requires more epichlorohydrin amount; furthermore, the cost of glycidyl amine is high, so production is not easy to scale up.

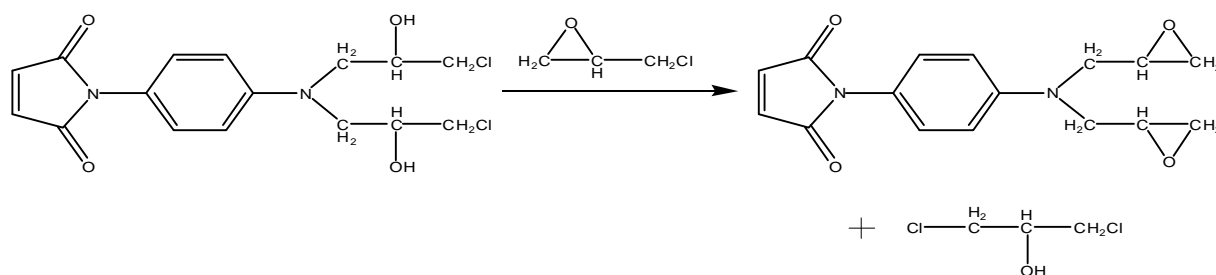


Fig4 The exchange reaction

In this work, we employ the two-step method to synthesize glycidyl amine, using benzyl triethyl ammonium chloride as the phase transfer catalyst. Benzyl triethyl ammonium chloride has good dissolution ability in both aqueous phase and organic phase, i.e., cations and anions of quaternary ammonium salt form ion pairs in the aqueous phase, anions could transfer from the aqueous phase to the organic phase. In the organic phase, anions could not provide solvation. Additionally, due to the large size of quaternary ammonium cation, the distance between cations and anions is large, resulting in weak interactions, which accelerates the reaction rate.

The first step is to form the intermediates amino chloro propanol from amine and epichlorohydrin, then to produce glycidyl amine in the presence of sodium hydroxide, as shown in Figure 3. The addition reaction rate of amine and epichlorohydrin is often very slow; however, in the presence of a small amount of phase transfer catalyst and second catalyst, the reaction rate accelerates while the intermediate product amino chloro propanol is produced. Then amino chloro propanol form glycidyl amine by exchange with excess epichlorohydrin in the system, as shown in Figure 4. The conversion of this reaction depends on the structure of amine.

Conclusion

A novel N, N- (4- amino phenyl maleimide) diglycidyl amine (APMDGA) was synthesized from maleic anhydride, p-nitroaniline, epichlorohydrin by a few-step reactions via intermediate products N-(4-nitrophenyl)maleimide and N-(4-aminophenyl)maleimide. The chemical structure of APMDGA was confirmed by 1H-NMR, FT-IR, and EA. The synthesis conditions have also been investigated. The final product APMDGA shows a yellow solid, and the yield is 48.6%. The application of APMDGA is under investigation.

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