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Synthesis and Characterization of Dicyclopentadiene - cresol Epoxy Resin

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Summary

Starting from cresol, the synthesis of dicyclopentadiene (DCPD) - cresol epoxy resin was conducted. DCPD-containing phenol resin (DPR) was prepared via Friedel-Crafts alkylation, whereas DCPD-containing epoxy resin (DER) was prepared via epoxidation of DPR with epichlorohydrin. The chemical structure was characterized with FTIR and ^{1}HNMR. Cure behaviors and glass transition temperature (T_g) of the resulting polymers were studied by differential scanning calorimeter (DSC). The results clearly indicated that cured polymer with a mixture of DCPD-cresol epoxy resin and diglycidyl ether of bisphenol A (E51) had higher T_g comparing with E51.

Introduction

Epoxy resin has good thermal and dimensional stability, excellent chemical and corrosion resistance, high tensile strength and modulus, which ensures their wide applications to the electronic industries in the form of packaging materials [1, 2]. The properties of cured epoxy polymers largely depend on the nature of chemical structure of the starting resins. Hence, it is possible to tailor and synthesize various resins through incorporating types of moieties into the backbone of molecules to suit particular needs. Scientific efforts have been made to develop novel epoxy resins that can enhance the heat and moisture resistance [3-5]. For instance, by chemical bonding, the epoxy monomer containing groups of both aromatic unsaturation and cycloaliphatic ring are known to be one of the most common products for this purpose [6-12].

Cyclopentadiene (CPD) is a byproduct of C5 streams in oil refineries. The CPD monomer exists in the form of dicyclopentadiene (DCPD), a dimeric adduct through Diels-Alder reaction. The high purity DCPD (95%) can be widely applied as a comonomer in several polymer systems such as ethylene propylene diene monomer (EPDM), unsaturated polyester, olefin metathesis, and epoxy resin [13, 14].

In this paper, starting from cresol, a DCPD- cresol epoxy resin was synthesized. The characteristics of cure, thermal and mechanical properties of cured polymer were investigated by compareing with that of conventional diglycidyl ether of bisphenol A.

Experimental

Materials

Regent grade of cresol, boron trifluoride diethylether ($BF_3.Et_2O$), epichlorohydrin and methyl isobutyl ketone (MIBK) were commercially available and were used without processing. DCPD was washed with 5 wt% Na_2CO_3 aqueous solution and water, so that inhibitors can be removed; then it was dried over magnesium sulfate, followed with distillation before use. 4-methylhexahydrophthalic anhydride (MeHHPA) and polyamide 651 were used as the curing agents. Diglycidyl ether of bisphenol-A (DGEBA, E51, epoxy equivalent weight, EEW 196g/mol) was obtained from WuXi Resin Company.

Instruments

^{1}HNMR characterization was carried out by Bruker DRX 600 NMR spectrometer by using acetone-d1 as the solvent and tetramethylsilane (TMS) as internal standard. FTIR spectra were recorded on Bruker Vector22 infrared spectrometer. The EEWs of epoxy resin were determined by HClaq/acetone titration. Cure behaviors with different curing agents and the glass transition temperature (T_g) of the resulting polymers were measured with a Perkin–Elmer DSC-7 under nitrogen atmosphere with a heating rate of 10°C/min.

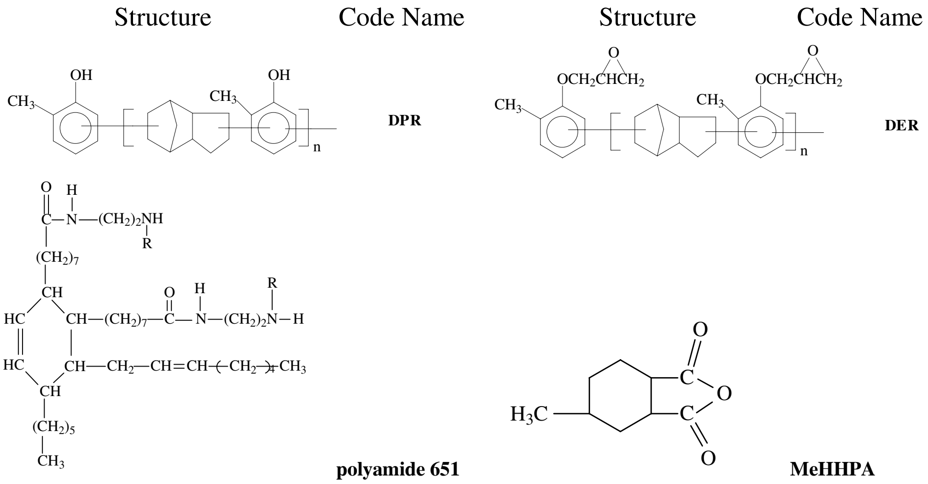
Synthesis of cresol and DCPD adducts

Cresol (8.0mol) and $BF_3.Et_2O$(0.5 wt %) in toluene were added into a 500ml four-necked flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and dropping funnel. While stirring, the mixture was heated to 70°C, and then DCPD (1.0mol) was added dropwise over 1h The temperature was then raised to 110-120°C for 3h more. After cooling down, the resultant mixture was neutralized with 5 wt% aqueous Na_2CO_3 solution, followed by washing with water. The organic phase was further concentrated to remove the toluene and excess phenol. A product with softening point around ambient temperature was obtained in 80-90% yield.

Epoxidation of adduts of cresol and DCPD

The adducts of cresol, DCPD and epichlorohydrin were put into a 500ml four-necked flask equipped with stirrer, a modified Dean-Stark trap with condenser and a vacuum controller. Then 48 wt% aqueous sodium hydroxide solution was added into the mixture via metering pump over a period of 4h while maintaining temperature at 65°C under a reduced pressure. The mixture was further stirred for an additional 2h. During the reaction, water was removed continuously from the system by azeotropic distillation, while the distilled epichlorohydrin was returned to the reactor. The mixture obtained was filtered to remove salt, and the organic phase was washed with water for three times. Finally, the excess epichlorohydrin was distilled to generate a light amber-colored semisolid product DER (epoxy equivalent weight, EEW 330g/mol).

The structure and code names of phenol adducts and epoxy resins are listed in Scheme 1.



Scheme 1 The structure and code names of curing agents, phenol adduct and epoxy resin

Preparation of cured polymers

The epoxy resins and curing agents in a molar stoichiometric ratio of 1:1 were dissolved in acetone. The solvent was evaporated under vacuum. The samples were kept in the refrigerator before performing the DSC experiment. The cured samples were prepared by mixing the reactants homogeneously at 80°C, which were then cured in vacuum.

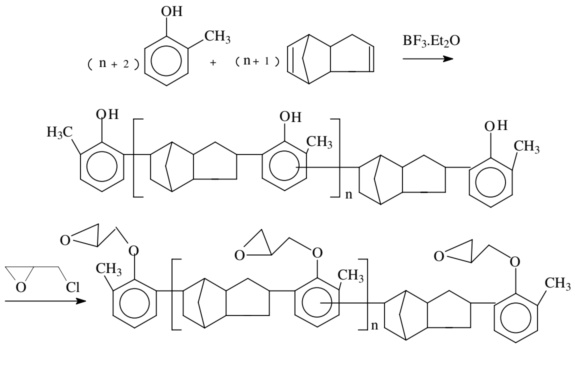
Results and discussion

Epoxy resins synthesis and characterization

DCPD-modified epoxy resin was prepared according to the chemical reactions outlined in Scheme 2. The overall synthesis involves two steps: (1) alkylation of cresol with DCPD in the presence of Freidel-Crafts catalyst to give phenolic resin, (2) epoxidation of phenolic resin with epichlorohydrin in the presence of sodium hydroxide to give epoxy resin. Boron trifluoride etherate and its acid complexes are the preferred catalysts in the first step. The function of catalyst lies in the formation of carbocation by reaction of carbon-carbon double bond with BF_3. These active carbocation acts as electrophile and attacks benzene ring at the ortho or para position of hydroxy.

The compound DER was characterized by FTIR and ^{1}H NMR. The ^{1}H NMR spectrum of DER was shown in Figure 1. The multiplet peaks at 1–2.3 ppm were attributed to the saturated protons of cycloaliphatic hydrocarbon. The chemical shifts of the aromatic protons ($–C_{10}H_6$) were observed at 6.8–7.8 ppm. The peaks at 2.3–4.2 ppm belong to the $—CH_2—$ near oxirane.

Figure 2 gave the FTIR spectra of DER and its precursor DPR. The strong absorption peak at 3448cm^{-1} corresponds to the vibration of –OH group in DPR. Loss of the hydroxyl group in DER revealed the occurrence of glycidyl etherification. The characteristic absorption peak for oxirane was observed at 910cm^{-1}.



Scheme 2 Synthesis of DCPD-modified epoxy resin starting from cresol and DCPD

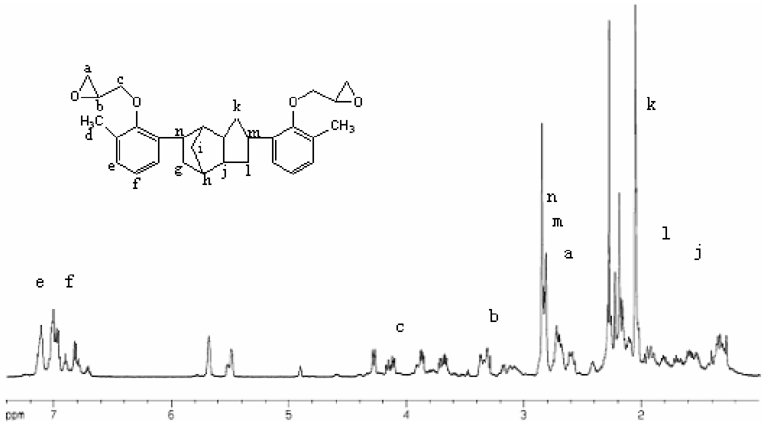


Figure 1 ^{1}HNMR spectrum of DER

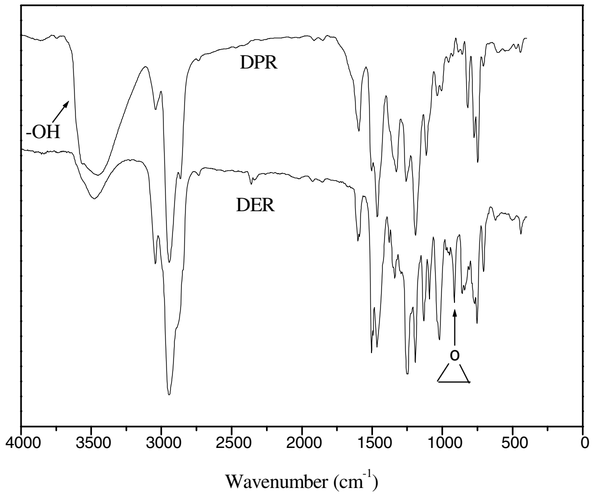


Figure 2 FT-IR spectra of the DPR and DER

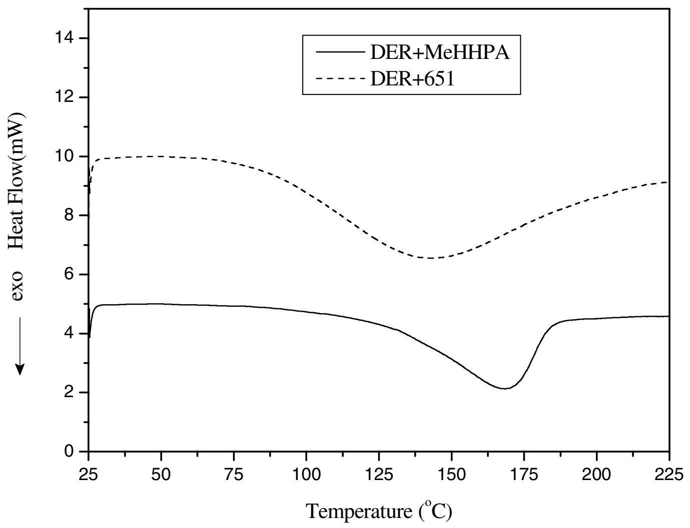


Figure 3 The DSC traces of DER/ MeHHPA and DER/ polyamide 651

Thermal cure

The thermal cure behavior of DER was determined by DSC. MeHHPA and polyamide 651 were used as counterpart curing agents. The DSC traces of DER/ MeHHPA and DER/ polyamide 651 were presented in Figure 3. Table 1 summarized the cure reaction parameters of two epoxy systems. Both DSC scans of ER/ MeHHPA and DER/ polyamide 651 showed an exothermic peak, which implied the occurrence of cure reactions. In the case of DER/ MeHHPA, the exothermic peak T_p centered at 168.4°C, which corresponded to the cure reaction of DER and the functional group of MeHHPA. As for the mixture of DER and polyamide 651, Tp was observed at 141.4°C. The total heat of cure reaction ΔH was 39.7 and 90.1 kJ/eq for DER/ MeHHPA and DER/ polyamide 651 respectively.

The DSC traces of DER+E51 / MeHHPA were shown in Figure 4. The cure reaction parameters were also summarized in Table 1. Compared with the cure reaction of DER/ MeHHPA, the blend displayed relatively lower T_o, whereas T_p was almost the same. The total heat for the blend of DER+E51 is lower than that of DER.

The total heat value for the blend towards DER and polyamide 651 fell in the range of DGEBA + amine system (90-100kJ/mol) [12]. The heat value for the blends towards

Table 1 Dynamic cure parameters of various epoxy systems

Sample	To (°C)	Tp (°C)	ΔH (kJ/eq)
DER/ MeHHPA	133.8	168.4	39.7
DER/ polyamide 651	88.5	141.4	90.1
DER+E51(3:1)/ MeHHPA	126.8	180.9	16.1
DER+E51(2:1)/ MeHHPA	113.3	181.5	21.7
DER+E51(1:2)/ MeHHPA	106.9	180.1	27.2

* The relation DER: E51 is in mass. The EEW of E51 is 196g.mol^{-1}. The EEW of DER is 330g.mol^{-1}.

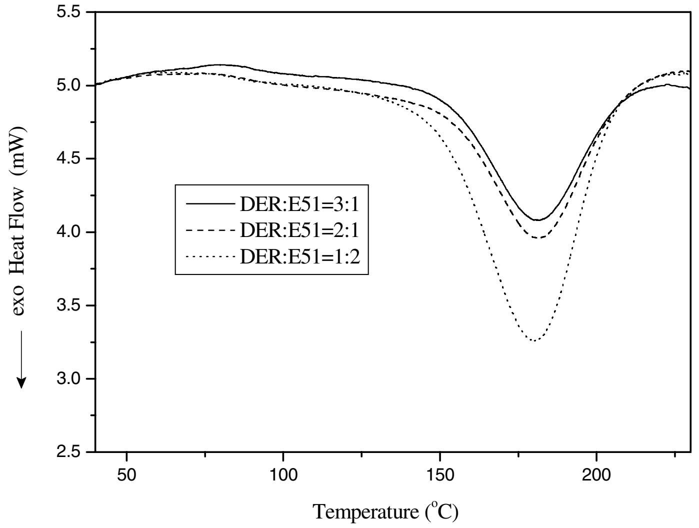


Figure 4 The DSC traces of DER+E51/ MeHHPA

DER+MeHHPA and (DER+E51) + MeHHPA were lower than DGEBA+MeHHPA (64-75kJ/mol) [15].

The thermal properties of cured mixture of DER and E51

The thermal properties evaluations of the polymerization of the mixture of DER + E51/ MeHHPA were performed by DSC (Figure 5). It was shown that, T_g of the cured mixture of DER + E51 was about 20°C higher than that of the cured E51. In general, the T_g of the cured polymer strongly depends on its chemical structure. Therefore, this result may confirm that the T_g value of epoxy system can be elevated by introducing

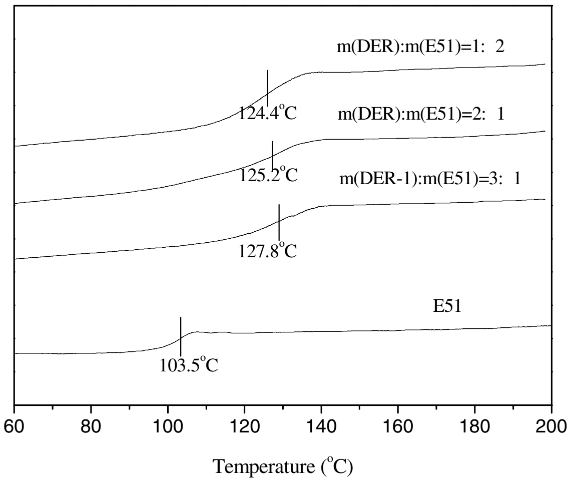


Figure 5 DSC traces of the polymer of DER + E51/ MeHHPA

some rigid group into the backbone of epoxy monomer. Most likely, it arises from the higher rigidity of cycloaliphatic skeleton in the molecular backbone.

Conclusions

By introducing cycloaliphatic moiety into the backbone, DER epoxy resin was prepared by simple synthetic methods. DSC traces of DER/ MeHHPA and DER/ polyamide 651 showed that the cure reactions occurred. T_g of the resulting polymers from the mixture of DER + E51 was about 20°C higher than that from the E51.

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