Synthesis and Characterization of Phenoxy Resins Prepared from Diglycidyl Ether of Bisphenol A and Various Aromatic Dihydroxyl Monomers

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ABSTRACT: This work describes the synthesis of various phenoxy resins by in situ fusion reaction of aromatic dihydroxyl and low molecular weight liquid diglycidyl ether of bisphenol A (DGEBA) with an aryl phosphonium salt catalyst. FTIR and ¹H-NMR spectra and GPC analyses were performed to characterize the resins. Analyses results indicated that resins have an adequate high molecular weight and physical properties when the reaction occurred after 5–10 min at 225–230°C. In addition, DSC and TGA analyses were performed to investigate the thermal properties of these phenoxy resins. According to these results, the lack of steric hindrance of the molecular structure in these phenoxy resins depressed the changes of T_g and weight loss. A series of phenoxy modified epoxy networks containing narrower polydisperity and higher M_n will exhibit the most significant effect on impact toughness. Moreover, the FTIR spectrum of the phenoxy resin as a function of temperature correlates well with the glass transition temperature. Furthermore, results presented herein demonstrate effective miscibility with thermoplastic polyurethane elastomer (TPU). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2369–2376, 1999

Key words: phenoxy resins; diglycidyl ether of bisphenol A; aromatic dihydroxyl monomers; toughening agent

INTRODUCTION

Previous literature generally regards a copolymer based on the reaction between bisphenol A and epichlorohydrin as a phenoxy resin¹:



Phenoxy resins are tough and ductile thermoplastics with high cohesive strength and excellent impact resistance. Their ether linkages and pendant hydroxyl groups promote wetting and bonding to polar substrates and fillers.

Previous investigators¹⁻⁴ have repeatedly verified the ability of phenoxy resins to form miscible blends with a variety of other polymers, such as polyesters, polysulfones, or polycarbonates. The hydroxyl groups that take part in an extremely repetitive unit appear to be the origin of such miscibility capacity, via the formation of specific interactions with other functional groups. Compatible with many polymers, they are efficient flexibilizers for crosslinked phenolic and epoxy resins. Related investigations have also shown the feasibility of promoting blends of incompatible resins, acting as compatibilizers.

In practice, phenoxy resins are prepared by reacting high-purity bisphenol A with epichlorohydrin in a 1:1 mol ratio or from high-purity

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diglycidyl ethers of bisphenol A (DGEBA) and bisphenol A in a 1 : 1 mol ratio. The solution polymerization can be performed to achieve the high molecular weight and processibility deemed necessary. In addition, the polymerization reaction between a dihydric phenol and a diglycidyl ether of a dihydric phenol, to produce the desired thermoplastic polyether resin, requires base-catalyzed condensation. The catalyst may be added as either a concentrated aqueous solution of sodium or potassium hydroxide or a quaternary ammonium hydroxide, or it may be even be used as anhydrous ammonia or amine.

Quaternary phosphonium salts⁵ have received extensive interest in past decades as effective latent accelerators and catalysts for phenolic resin and preparation of phenoxy resin systems. However, their applications are generally made at a lower reaction temperature using solution polymerization. In general, there has been broad interest in high-temperature and *in situ* polymerization with a quaternary phosphonium salts from diphenols and diepoxides. In this work, we synthesize and characterize these high molecular weight thermoplastic polyhydroxyethers.

EXPERIMENTAL

Materials

Table I lists the materials used in this work. The epoxy resin used herein, DER 332, was purchased from Dow Chemical Corporation, USA. DER 332 is a low molecular weight liquid diglycidyl ether of Bisphenol A (DGEBA) with an epoxide equivalent weight of 174. Phenolic monomers were reagent grade and used without further purification. The thermoplastic polyurethane elastomer (DE-1085) was purchased from Dahin Chemical Corporation, Taiwan. Quaternary phosphonium salt was used as a catalyst for the condensation of liquid epoxy resins with phenolic materials.

Synthesis of the Phenoxy Resins

DER 332 and the phenolic monomers were poured into a three-necked 500-mL glass vessel equipped with a stirrer of anchor shape metal and a thermometer. The reaction occurred under dry nitrogen atmosphere. Next, the mixture of DER 332 (0.2 mol) and phenols (0.2 mol) was heated to 160°C with agitation, and a clear liquid was formed. The solid triphenyl butyl phosphonium bromide (TBPB) (0.03 g) was added to a batch; the temperature was gradually raised to 225–230°C. The reaction mixture became a viscous liquid. The torque of the reactor was also increased for several minutes at 225°C. Thereafter, the reaction was completed by maintaining the system at 225–230°C for 30 min. The reaction product obtained was a transparent solid.

Infrared spectra were obtained on a Perkin-Elmer 842 Infrared Spectrometer with a resolution of 2.4 cm⁻¹ in the transmission mode. IR spectra at elevated temperatures were measured using a heating cell directly located in the sample. All films used in this work were sufficiently thin to be within an absorbance range where the Beer-Lambert law is obeyed. Moreover, in the compartment of the spectrometer, the sample was placed between two KBr plates.

The thermogravimetric analysis was conducted with a DuPont TGA at room temperature to 800°C, and at a heating rate of 5°C/min under a nitrogen gas atmosphere. Differential scanning calorimetric analysis was performed on a DuPont 2100 Instrument at a heating rate of 10°C/min from room temperature to 250°C with nitrogen gas flow; sample weight was about 5 mg. T_g was measured on the DSC curve as the intersection point of the extrapolated base line at the low temperature end and the tangent to the curve at the inflection point.

A Shimadzu SPD-10A liquid chromatograph provided with a set of 500, 10^4 , 10^5 , and 10^6 A Ultrastyragel columns was used in GPC measurements. The mobile phase (tetrahydrofuran, THF) flow rate was 1 mL/min. The gel permeation chromatography was performed using a refractive index (RI), and the column was calibrated by means of polystyrene standards.

Blending Procedure

Phenoxy resins were used to modify the epoxy/ dicyandiamide (dicy) system (Table I). Epoxy resin systems containing 0–10 phr of the various phenoxys were prepared by the following procedure. The phenoxy powders were mixed with epoxy without curing agent at room temperature, and the mixture was heated at 160°C for 2 h with stirring. The hardener and accelerator were dispersed in the pure epoxy and the various phenoxy-toughened epoxy resins, then poured into an open chrome steel mold that had been preheated in an oven to 80°C. The mixture was degassed under vacuum for 1 h at 80–85°C and cured for 1 h 150°C. Postcuring was carried out at 160°C for 2 h.

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Name	Structure	Supplier
DGEBA (DER 332)	$CH_2 - CH - CH_2O - O - O - O - O - O - O - O - O - O -$	Dow Chemical Co.
4,4'-Dihydroxydiphenylmethane (BPF)	HO-O-OH H	Honshu Chemical Industry Co.
4,4'-Cyclohexylidenebisphenol (BPZ)	но-О-он	Honshu Chemical Industry Co.
2,2-Bis(4-hydroxyphenyl)propane (BPA)	HO- \bigcirc CH ₃ CH ₃ CH ₃ CH ₃	Tokyo Kasei, Kogyo Co.
α, α' -Bis(4-hydroxyphenyl)-1, 4-diisopropylbenzene (BPT)	HO- \bigcirc $ \bigcirc$ $ \bigcirc$ $ \bigcirc$ $ \bigcirc$ $ \bigcirc$ $ \bigcirc$ $ -$	Tokyo Kasei, Kogyo Co.
Phenoxy resin (PKHH)	$- \left[- 0 - \left(\bigcirc \right) - \left[- \left(\bigcirc \right) - \left(\bigcirc - \left(\bigcirc \right) - \left(\odot \right) - \left(\cap \right) - \left(\cap \right) - \left(\odot \right) - \left(\cap \right) - \left(\cap \right) - \left(\cap \right) - \left$	Union Carbide Corp.
Triphenyl Butylphosphonium-Bromide (TBPB)	$[\mathrm{CH}_3(\mathrm{CH}_2)_3\mathrm{P}(\mathrm{C}_6\mathrm{H}_5)_3]\mathrm{Br}$	Tokyo Kasei, Kogyo Co.

Table I Epoxy Resin and Phenols Used in This Study



Figure 1 Adhesion test specimens for lap shear strength.

The BPZ-phenoxys (see Table I) containing 50% by weight of the thermoplastic urethane elastomer were prepared on a two roll mill using a time of 10 min and a milling temperature of 160–180°C. The blends were then compression molded into test plaques at 180–200°C.

Properties Measurement

The Charpy impact strength was measured according to ASTM D-256. Five samples were tested for impact strength with each formulation, with the average value being recorded as Charpy impact strength. The adhesion properties of phenoxy resin-blended Epon-828 with a stoichiometric amount of hardener were measured by ASTM D-1002. Lap shear strength measures the degree of adhesion to a substrate and the rigidity of the bond. The strength deemed necessary to pull the specimen apart in the direction was shown in Figure 1 was measured as well.

RESULTS AND DISCUSSION

Preparation of Phenoxy Resins

Table II presents the general reaction scheme and the structures of the various phenoxy resins.







Figure 2 Gel permeation chromatography curves of various phenoxy resins.

The phenoxy resins were synthesized by reacting various aromatic dihydroxyl monomers and DER332 with an arylphosphonium salt catalyst. The fusion reaction was performed at temperatures ranging between 225-230°C for about 30 min with a nitrogen blanket to minimize the oxidative degradative reactions. At the beginning of the reaction of phenolic groups with epoxide the concentration of aliphatic hydroxyl groups is zero. As the reaction progresses, the concentration of secondary alcoholic groups increases and the possibility of side-chain branching increases.^{5–8} The GPC curves were used to determine the molecular weight distribution and the hydroxyl value (g OH/ 100 g resin) directly.⁹ Figure 2 displays a GPC curve of phenoxy resins, indicating that the reaction occurred after 30 min at 225-230°C. According to the GPC results, the average molecular weights and the the polydispersities (M_w/M_n) of BPA-phenoxy, BPF-phenoxy, BPZ-phenoxy, and BPT-phenoxy are summarized in Table III.

For the reactions conducted for 5–10 min at 225–230°C, i.e., the formation of high molecular weight, GPC was used herein to measure the molecular weight of the phenoxy resin. Experimental results indicated that quaternary phosphonium salts are effective and faster catalysts for the advancement of liquid epoxy resins with

Table IIIThe Average Molecular Weight andPolydispersities of the Various Phenoxy Resins

Sample	M_n , g/mol	M_w , g/mol	M_w/M_n
BPA–phenoxy BPF–phenoxy	$11,400 \\ 10,040$	37,000 248,100	$3.243 \\ 24.711$
BPZ–phenoxy BPT–phenoxy	$12,800 \\ 9980$	$51,900 \\ 80,700$	$4.052 \\ 8.354$



Figure 3 Glass transition temperature curves of various phenoxy resins.

phenolic material at 225–230°C. As is generally known, hydroxyl equivalent is the weight of the phenoxy containing one equivalent weight of a hydroxyl group. Hydroxyl equivalents can be determined with acetyl chloride. Titration results indicated that the hydroxyl value (equivalents/ 100 g) of the BPA-phenoxy, BPF-phenoxy, BPZphenoxy, and BPT-phenoxy were 0.288, 0.275, 0.280, and 0.264, respectively.

FTIR and ¹H-NMR spectral measurements were taken to identify the synthesized phenoxy resins. According to the FTIR spectra, all resins exhibit characteristic OH and aromatic group absorption frequencies. For instance, BPZ-phenoxy contains a sharp band at 3650 cm⁻¹ for free OH. In addition, a broad band appears at 3550–3350 cm⁻¹ for polymeric intermolecular hydrogen bonding and sharp bands at 1605, 1500, and 1480 cm⁻¹ for the aromatic ring.

According to the ¹H-NMR spectra,^{10,11} the benzylic ring absorption appears at around 6.6-7.3 ppm, and benzylic methyl absorption at around 1.4-1.8 ppm. In addition, the opening of the epoxide ring to form phenoxy results in the concurrent disappearance of peaks in the range of 2.6-3.7 ppm and corresponding increase in the glycerol resonance at 3.9-4.6 ppm. This observation indicates that the epoxy-phenol reaction occurs rather than the secondary alcohol-epoxy reaction. The area ranging between 4.1 and 4.3 ppm consists of contributions from the ether methylene and the carbinol methene.

Thermal and Physical Properties

Thermal properties of phenoxy resins were studied by DSC and TGA analysis. The DSC samples were prepared with the structure of various phenoxy resins in Table II. Figure 3 presents the



Figure 4 The Charpy impact strength of pure epoxy and various phenoxy-toughened epoxy resins.

glass transition temperature (T_g) curves of various phenoxy resins. The BPF–phenoxy and BPA–phenoxy have relatively lower amounts of aromatic groups, which exhibit lower glass transition temperatures, while the BPZ–phenoxy and BPT–phenoxy have higher glass transition temperatures. These results can be due to the BPZ–phenoxy and BPT–phenoxy and BPT–phenoxy hindering large chain motion.

The thermogravimetric analysis of the phenoxy resins was performed using TGA from room temperature to 800°C at a heating rate of 5°C/min under a nitrogen gas atmosphere. This result indicates that the weight loss parallels the T_g change from the DSC analysis. The weight loss curves at the inflection point of BPA-phenoxy, BPF-phenoxy, BPZ-phenoxy, and BPT-phenoxy were 400°C (61.14%), 406°C (72%), 432°C (54.86%), and 428.82°C (54.31%), respectively. According to the DSC and TGA analyses results, BPT-phenoxy and BPZ-phenoxy should possess higher thermal properties than BPF-phenoxy and BPA-phenoxy from the perspective of the molecular structure. It is considered likely that the amount of restricted rotation of the aromatic rings and the saturated rings are responsible for the observed variations.

Herein, thermoplastics were used to toughen and improve the epoxy resin. Previous investigators¹² indicated that 10 phr phenoxy-toughened epoxy resin provides the best toughness and thermal stabilization. In this study, phenoxy resins were used to modify the epoxy/dicyandiamide (dicy) system. The materials of Epon-828 (100 phr)/dicy (7 phr)/3-phenyl-1, 1-dimethylurea (3 phr)/phenoxy resin (10 phr) in stoichiometric quantity were used as the matrix/curing agent/ accelerating agent/toughening agent. Figure 4 illustrates the Charpy impact of pure epoxy and epoxy resin toughened with 10 phr of various phenoxys, respectively. This figure reveals higher toughness than pure resin for Charpy impact strength. Comparing phenoxy/epoxy systems, BPA-phenoxy and BPZ-phenoxy reveal higher toughness than BPF-phenoxy and BPT-phenoxy. This finding suggests that narrower polydispersity and higher M_n have the most significant effect on impact toughness.

Figure 5 exhibits the lap adhesive strength of pure epoxy and various phenoxy-toughened epoxy resins. The model adhesive resins analyzed herein were prepared from the formulation of phenoxy-toughened epoxy resin. In addition, Fe-Fe/Al-Al were the substrates used to study the adhesive properties. The adhesive strength has a minimum value for pure resin combinations, indicating a maximum value of 233.58 kgf/cm² (Fe-Fe)/105.03 kgf/cm² (Al-Al) for the composition in which BPF-phenoxy was used. The above results indicate that the phenoxy formulation affected the bonding ability of the adhesive to the metal. Therefore, the adhesive capability is a complex function of wetting and secondary bonding interactions. The bond strengths of the compositions reveal that, when phenoxys are used in the mixture the hydroxyl group concentration correspondingly increases, giving rise to an increased interaction with the epoxy to provide more wetting and bonding in the structure. Hence, the strength was improved gradually, and a higher value was obtained for the composition containing the phenoxy with the most hydroxyl equivalents (BPT-phenoxy).



Figure 5 Lap adhesive strength of pure epoxy and various phenoxy-toughened epoxy resins.



Figure 6 FTIR spectra of BPZ-phenoxy from $4000-2000 \text{ cm}^{-1}$ recorded at 25, 50, 100, 150, 200°C.

Infrared Spectra of Various Phenoxy Resins

Although previous investigations^{1–3} have used infrared spectra for a number of different phenoxy resins, to our knowledge, very few detailed vibration analyses have been performed for any of these polymers. As expected, the spectra are characterized by relatively narrow bands attributed to localized normal vibrations. These vibrations are mainly associated with rigid phenyl and methyl groups and relatively broad bands, which are predominantly attributed to the remaining chemical groups that are in highly coupled conformationalsensitive modes.

Previous investigations^{13–15} have examined the FTIR spectrum of the phenoxy polymer as a function of temperature. In this study, the hydroxyl stretching region of the spectrum between $3700-3000 \text{ cm}^{-1}$ was examined. Figure 6 depicts the BPZ-phenoxy IR spectra in the 4000-2000cm⁻¹ region recorded at different temperatures. The pure BPZ-phenoxy polymer was cast from compression molding at 260°C, and exhibits an extremely broad band centered at 3420 cm⁻¹, indicative of extensively hydrogen bonded hydroxyl groups. In addition, there is a small spectral contribution observed at 3650 cm⁻¹ associated with the free hydroxyl group (Fig. 6 at 25°C).

Heating of the BPZ–phenoxy film results in an increase in the relative contribution of the 3650 cm⁻¹ absorption at the expense of the broad absorption attributed to hydrogen-bonded hydroxyl groups. At an elevated temperature (above the T_g of the polymer) a sufficient amount of energy is available to disrupt a significant number of the intermolecular hydrogen bonds, yielding a higher concentration of free hydroxyl groups. In other words, the shift of the hydrogen-bonded hydroxyl

stretching mode to a higher frequency indicates a weaker hydrogen bonded system (Fig. 6 at $50-200^{\circ}$ C).

Figure 7 displays the FTIR spectra of BPZphenoxy/TPU blends from 4000-1000 cm⁻¹ recorded at 25, 50, 100, 150, and 200°C. As the phenoxy was blended with the thermoplastic polyurethane elastomer, it was associated with the glass transition temperature, which shifted to a lower temperature. For the blends containing 50 wt % of the TPU, the glass transition peak occurred at about 40°C by DSC measurement. The curve of phenoxy/TPU reveals that a broad band centered at 3420 cm^{-1} is attributed to the intermolecular hydrogen-bonded hydroxyl groups in which phenoxy is a highly associated polymer. However, the minor contribution at 3650 cm^{-1} to free hydroxyl groups cannot be observed. When the temperature was elevated to 50°C (above the T_g of the blends), a broad band at 3800-3000 cm^{-1} shifted to the two frequencies. The shift of the hydrogen-bonded hydroxyl band of phenoxy provides evidence for a hydrogen bond between the hydroxyl groups of phenoxy and the amide groups of TPU. The most striking feature of these spectra is the appearance and increasing intensity of two shoulders centered at approximately 3520 cm^{-1} and 3310 cm^{-1} with an increase in temperature of the blends. In sum, the broad phenoxy hydrogen bonded hydroxyl band is attributed to free hydroxyl groups at different temperatures. In contrast, the intermolecular interaction among phenoxy/TPU blends is stronger than that for a pure phenoxy polymer.



Figure 7 FTIR spectra of BPZ-phenoxy/TPU (50/50 wt %) from $3800-1200 \text{ cm}^{-1}$ recorded at 25, 50, 100, 150, 200°C.

CONCLUSIONS

This study investigated the synthesis and the physical properties of various phenoxy resins. Based on the results presented herein, we can conclude the following:

- 1. The BPT/BPZ/BPF/BPA-phenoxy resins can be synthesized by reaction of various aromatic dihydroxyl monomers and DER 332 with an arylphosphonium salt catalyst. The *in situ* fusion reaction is performed at a temperature ranging between 225-230°C for 30 min.
- 2. According to DSC and TGA analyses results, BPT-phenoxy and BPZ-phenoxy should possess higher thermal properties than BPF-phenoxy and BPA-phenoxy from the perspectives of the steric hindrance of the molecular structure.
- 3. Comparing the phenoxy/epoxy systems, BPA-phenoxy and BPZ-phenoxy show higher toughness than BPF-phenoxy and BPT-phenoxy. The bond strength of the compositions shows that the BPF-phenoxy and BPT-phenoxy possess a higher lap adhesive strength than BPA-phenoxy and BPZ-phenoxy.
- 4. The FTIR spectrum of the BPZ-phenoxy/ TPU, as a function of temperature, reveals that hydrogen bonding interaction of blends occurs between the hydroxyl groups of phenoxy and the amide groups of TPU at

room temperature. When the temperature surpasses the T_g of the blends, the hydrogen-bonding interactions become too weak to induce miscibility of the phenoxy/TPU blends.

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