

Synthesis of Calcium-Containing Methacrylate Resin

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Received 6 September 2000; accepted 14 March 2001

ABSTRACT: The calcium salt of *p*-aminobenzoic acid [*p*-ABA(Ca)] was reacted with epichlorohydrin to yield the multifunctional epoxy resin. The epoxy resin was characterized by IR spectroscopy, epoxy equivalent, calcium estimation, high performance liquid chromatography (HPLC) and refractive index. The epoxy resin was further reacted with methacrylic acid to yield the calcium containing methacrylate resin, which was characterized by IR, hydroxyl value, iodine value, HPLC and refractive index. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2342–2346, 2001

Key words: *p*-aminobenzoic acid; calcium salt; epoxy resin; methacrylate resin

INTRODUCTION

In the last decade, a renewed interest in divalent metal salts was observed by some researchers.^{1,2} Divalent metal salts of *p*-aminobenzoic acid (*p*-ABA) were used for crosslinking of bisepoxide. It was reported that these metal-containing cured resins had good boiling water resistance and water resistance.^{3–5} Synthesis of polyureas from divalent metal salts of *p*-ABA was also carried out by Matsuda et al.^{1,2} They observed that the introduction of metals into polyurea lowered the thermal properties.

In the present study, synthesis of calcium-containing methacrylate was undertaken. The calcium salt of *p*-ABA was first reacted with epichlorohydrin to yield the multifunctional epoxy resin, which was further reacted with methacrylic acid to yield the corresponding methacrylate resin.

EXPERIMENTAL

Materials

The *p*-ABA(Ca) was prepared as reported by Matsuda et al.¹ Epichlorohydrin, hydroquinone, and 4-methoxy phenol were obtained from E-Merck, Mumbai, India. Calcium oxide, *p*-aminobenzoic acid, methacrylic acid, and benzyl triethyl ammonium chloride, were of analytical grade from local sources.

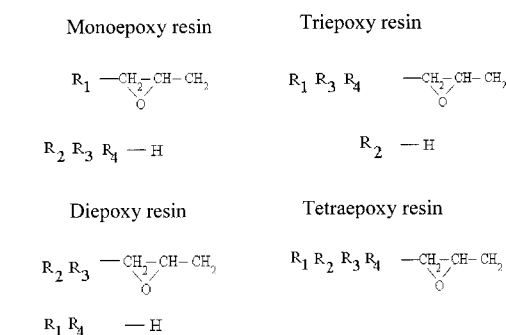
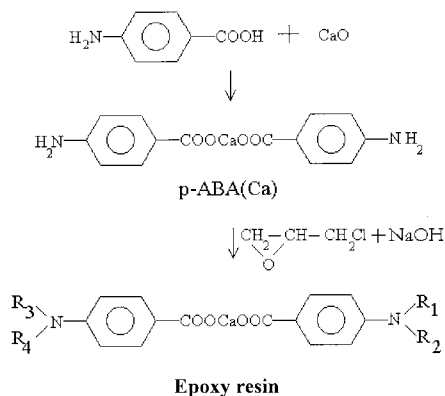
Synthesis of Epoxy Resin (Scheme 1)

The *p*-ABA(Ca) was prepared by neutralizing *p*-ABA with calcium oxide in aqueous medium. The product was precipitated by adding acetone and dried at 70°C for 5 h. It was then heated at 150°C for 5 h to remove the water of crystallization.¹

To the flask containing 15 g (0.048 mol) of *p*-ABA(Ca) was added 400 mL dimethyl formamide and 50 mL of water and stirred at room temperature until the mixture became homogeneous. Then, 176 g (1.92 mol) of epichlorohydrin were added and the mixture was stirred at 65°C for 80 h. The contents were then cooled to 55°C, and 30 g of sodium hydroxide as a 30% solution was added over a period of 1.5 h. The mixture was

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Journal of Applied Polymer Science, Vol. 82, 2342–2346 (2001)
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Scheme 1 Synthesis of epoxy resin.

further heated for 30 min. The excess epichlorohydrin was distilled off under vacuum. The epoxy resin was extracted with dichloromethane and washed several times with water to remove the impurities. The dichloromethane was then removed by flash evaporation.

Synthesis of Methacrylate Resin (Scheme 2)

Into a flat-bottomed flask equipped with a condenser and a stirrer, 7.5 g of epoxy resin and 5.4 mL of methacrylic acid were added. This procedure was followed by the addition of 0.0186 g of hydroquinone and 0.2076 g of benzyl triethyl ammonium chloride. The contents were stirred at 300 rpm for 18 h at 75°C. The methacrylate resin formed was diluted to three times its volume with dichloromethane. The diluted resin was washed several times with distilled water until it was free from impurities. To the pure resin in dichloromethane was added 100 ppm of 4-methoxy phenol from which the solvent was removed by flash evaporation.

Characterization

Infrared Spectroscopy

Fourier transform infrared (FTIR) spectra of *p*-ABA, *p*-ABA(Ca), epoxy resin, and methacrylate resin were taken with a Nicolet Impact 410 Spectrophotometer. The FTIR spectra of solid samples were taken using KBr pellet method and that of the resin samples were taken by smearing them on sodium chloride window.

Refractive Index

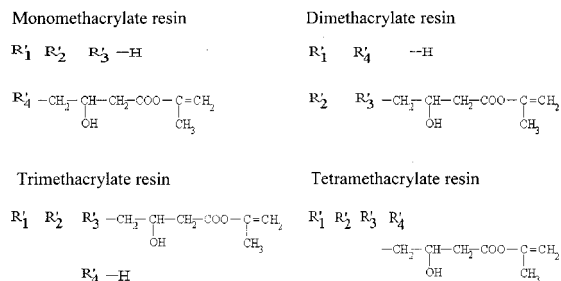
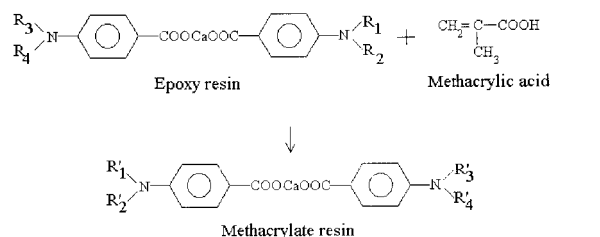
The refractive indices of the epoxy resin and methacrylate resin were measured with an ATAGO refractometer.

High-Performance Liquid Chromatography (HPLC)

The HPLC analysis was done with a Waters HPLC equipped with 486 ultraviolet (UV) detector at 254 nm. The solvent used was dichloromethane (HPLC grade) at a flow rate of 1 mL/min.

Epoxide Equivalent

The epoxide equivalent was determined by refluxing 2–4 mequiv of the epoxy resin with 50 mL of pyridine–pyridinium chloride (0.2M) for 30 min. The mixture was then titrated with alcoholic standard sodium hydroxide (0.5M) solution, using phenolphthalein as an indicator. A blank was also



Scheme 2 Synthesis of methacrylate resin.

Table I Physical Characterization of Resins

Resin Type	Color	State	Refractive Index
Epoxy resin	Light yellow	Viscous	1.5824
Methacrylate resin	Light brown	Viscous	1.5522

carried out. The epoxide equivalent was calculated from the titer value.⁶

Estimation of Calcium

The calcium contents of the calcium salt and the epoxy resin were determined by the complexometric method.⁷ A given amount of sample was incinerated at 800°C for 5 h, and the residue was digested with 1 : 1 HCl to give the sample solution for calcium determination.

Hydroxyl Value

A known weight of the methacrylate resin was heated with 10 mL of acetic anhydride pyridine (1 : 3) mixture for 30 min. Water was added to dilute the mixture, and the sample was titrated against the alcoholic standard sodium hydroxide (0.5M), using phenolphthalein as indicator. A blank was also conducted.⁸ The hydroxyl value was determined with eq. 1:

Hydroxyl value

$$= \frac{(V_2 - V_1) \times \text{Normality of NaOH} \times 56.1}{\text{Weight of sample}} \quad (1)$$

where V_2 is the volume of NaOH for blank and V_1 is the volume of NaOH for sample.

Iodine Value

A known weight of the methacrylate resin was dissolved in chloroform. Then, 25 mL of iodine monochloride in glacial acetic acid (wij's) was added and the solution was kept in the dark for 1 h. The excess iodine was determined by standard sodium thiosulfate, using starch as an indicator. A blank was also conducted.⁹ The iodine value was determined as follows:

Iodine value

$$= \frac{(V_2 - V_1) \times \text{Normality of thio} \times 12.69}{\text{Weight of sample}} \quad (2)$$

where V_2 is the volume of thiosulfate for blank and V_1 is the volume of thiosulfate for sample.

RESULTS AND DISCUSSION

The synthesis of the epoxy resin was carried out in two steps. The first step involves the ring opening of the epichlorohydrin during the process of being attached to the *p*-ABA(Ca). The second step involves the dehydrohalogenation with sodium hydroxide. In the synthesis of methacrylate resin, the hydroquinone acts as the inhibitor for the self-polymerization of methacrylic acid, whereas the benzyl triethyl ammonium chloride acts as the catalyst for acid-epoxide reaction. It has been found that the tertiary amines are used to catalyze the acid-epoxide reaction, which not only affects the rate of the reaction but also largely suppresses the undesirable side reaction.¹⁰

The physical properties of the two resins are listed in Table I. The resins obtained were colored, viscous liquids. The solubility studies revealed that both the resins were soluble in polar solvents like methanol, dichloromethane, chloroform, etc. The refractive indices of the epoxy resin

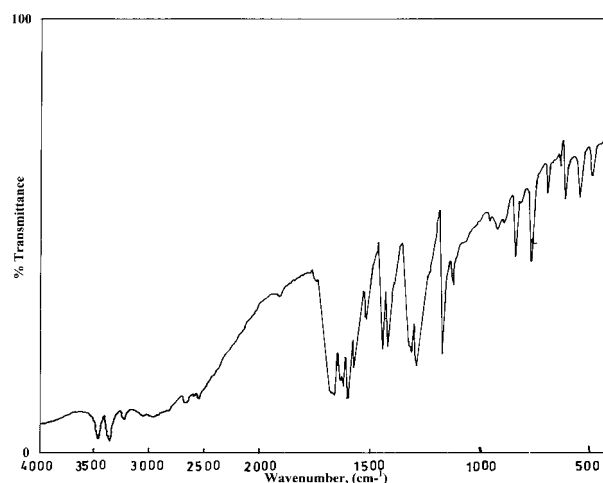


Figure 1 FTIR spectra of *p*-ABA.

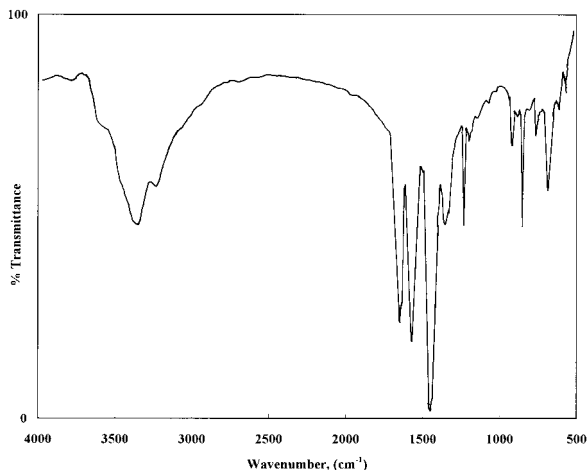


Figure 2 FTIR spectra of *p*-ABA(Ca).

and the methacrylate resin at 25°C were 1.5824 and 1.5522, respectively.

The FTIR spectra of *p*-ABA, *p*-ABA(Ca), epoxy resin, and methacrylate resin are given in Figures 1, 2, 3, and 4, respectively. In Figure 1 it can be seen that the two peaks at 1667 and 1600 cm^{-1} in the case of *p*-ABA have merged into a single peak at 1660 cm^{-1} in the case of *p*-ABA(Ca) (Figure 2). This peak along with the peak at 1386 cm^{-1} confirm the formation of a static ionic bond between Ca(II) and the carboxyl group attached to a phenyl ring.¹ The two peaks at 3347 and 3221 cm^{-1} in the spectra of *p*-ABA(Ca) confirm the presence of free amino groups. The formation of the epoxy resin was confirmed by the peaks at 907 and 1275 cm^{-1} in Figure 3, which are due to the terminal epoxy absorption. It is interesting to note that the spectrum of the epoxy resin showed

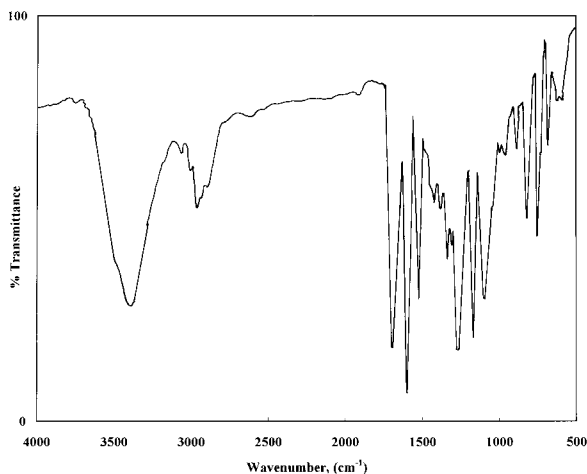


Figure 3 FTIR spectra of epoxy resin.

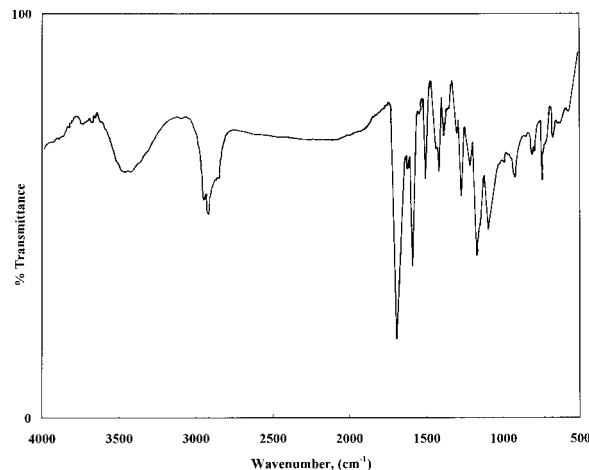


Figure 4 FTIR spectra of methacrylate resin.

a NH stretching frequency at 3384 cm^{-1} due to some free NH groups in the epoxy resin. The formation of the methacrylate resin was confirmed by the disappearance of 907 cm^{-1} peak as evident in Figure 4. The formation of methacrylate resin was further confirmed by a new peak at

1642 cm^{-1} due to the $\text{C}=\text{CH}_2$ stretching mode.

In addition to these peaks, a broad absorption peak at 3467 cm^{-1} , which is due to the presence of the —OH group, confirms the formation of the methacrylate resin. It is to be noted that the spectra of both the resins showed peaks at 1604 cm^{-1} (phenyl ring and carboxylate) and 1386–1402 cm^{-1} (carboxylate group).

The values of calcium content, epoxide equivalent, hydroxyl value, and iodine value are given in Table II. The calcium content of *p*-ABA(Ca) and the epoxy resin were 11.7 and 8.1%, respectively, with only slight deviation from theoretical values of 12.9% (for *p*-ABA(Ca)) and 8.3% (for triepoxy resin). The average epoxy equivalent of the epoxy resin was 171 g/equiv, which is close to the theoretical value for a triepoxy resin (160 g/equiv). However the resin obtained was a mixture of tetra-, tri-, and di-functionalities, with minor quantities of mono-functionalities as evidenced by HPLC. The IR spectra in Figure 3, which indicates the presence of unreacted NH groups, also supports this observation. The hydroxyl value of the methacrylate resin was 210 mgKOH/g of resin, which showed only a marginal deviation from the theoretical value for a trimethacrylate resin (i.e., 228 mg KOH/g of resin). The slightly lower hydroxyl content may be very well ac-

Table II Analysis Report of *p*-ABA(Ca) and Resins

Material	Calcium Content (%)		Epoxy Content (g/equiv)		Hydroxyl Value (mg KOH/g of resin)	
	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical
<i>p</i> -ABA(Ca)	11.7	12.9	—	—	—	—
Epoxy resin	8.1	8.3	171	160	—	—
		triepoxy		triepoxy		
Methacrylate resin	—	—	nil	nil	210	228
						trimethacrylate

counted for by the fact that the epoxy resin obtained does not correspond to a true triepoxy resin but a mixture of different functionalities. Also, the epoxy equivalent of the methacrylate resin was determined and found to be nil. The *w*_i's iodine value of the methacrylate resin was 87, with only slight deviation from the theoretical value for a trimethacrylate resin, which is 103. This result along with the hydroxyl value confirm the formation of methacrylate resin.

Even though the hydroxyl value and iodine value were close to that of trimethacrylate resin, the HPLC of the methacrylate resin showed that the resin contains a mixture of tetra-, tri-, and di-functionalities, with minor amounts of mono-functional methacrylate resin.

CONCLUSIONS

A multifunctional epoxy resin was synthesized from calcium salt of *p*-ABA by reaction with epichlorohydrin. The epoxy resin was obtained as a clear yellow viscous liquid. The epoxy resin obtained was a mixture of tetra-, tri-, and di-functionalities, with minor quantities of mono-functionalities, with an average epoxy value close to that of a true triepoxy resin. The methacrylate resin was obtained from the epoxy resin by reac-

tion with methacrylic acid. Further studies of this novel resin are in progress.

The authors thank Dr. K. Sreenivasan and Mr. P. R. Hari of Laboratory for Polymer Analysis for running the HPLC of the resins.

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