

# Glycidyl Amine Adducts as Accelerators for the Curing of Unsaturated Polyester Resin

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**ABSTRACT:** The behavior of the adducts of aromatic amines with epoxide compounds as accelerators in curing of an unsaturated polyester resin was studied. To determine their usefulness, the gelation times, peak exotherm temperatures, and chromatographic and gravimetric analyses of the products extracted from the cured resin samples were investigated. The effectiveness of the adducts was compared with that for *N,N*-dimethylaniline. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1525–1531, 1997

## INTRODUCTION

Unsaturated polyester resins involve a broad group of macromolecular compounds widely used for the fabrication of glass-reinforced plastics and composite materials. It is well known that unsaturated polyester resins can, in practice, be hardened either at an elevated temperature or at a room temperature in combination with a suitable initiating system. The hardening reaction at room temperature is usually started with a system containing an organic peroxide initiator and a cobalt salt accelerator. Another initiation system, occupying the second position with respect to the frequency of use for the hardening of unsaturated resins at room temperature, comprises dibenzoyl peroxide in combination with *N,N*-dimethylaniline or a derivative thereof.<sup>1–3</sup> The fact that aniline and its derivatives are classified as toxic substances makes their use more difficult and a concern to the health of the workers when improperly handled. According to the data published by the U.S. Environmental Protection Agency, aromatic amines are suspected to have mutagenic properties even at very low concentrations.<sup>4,5</sup> Addition-

ally, these compounds are characterized by high volatility. *N,N*-dimethylaniline and its derivatives are especially harmful for the operators preparing the hardening formulations for unsaturated polyester resins without adequate protective measures. These compounds may also be released from the cured resins as it is not proven that they are chemically bonded to the polymer network. To overcome these problems, other systems were proposed. Recently Kalenda<sup>6</sup> has used ferrocene and some of its derivatives as accelerators of curing reactions in unsaturated polyester resins.

This paper presents the possibility of using the adducts of aniline and *p*-toluidine with epoxide compounds as the accelerators for the hardening reactions. The adducts synthesized according to Boutevin and colleagues<sup>7</sup> possess a tertiary amine bonded to the aromatic ring. Thus they may accelerate the curing reaction of unsaturated polyester resins. On the other hand, these compounds are not volatile, are easy to obtain, and are convenient in handling. All of the obtained adducts were used for curing commercially available unsaturated polyester resin POLIMAL 109 in combination with dibenzoyl peroxide.

To study their usefulness, the gelation times, peak exotherm temperatures, and chromato-

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**Table I** Quantitative Compositions of the Synthesized Amine Adducts

No.	Amine Adduct	Amine	Epoxide Compound
1.	Aniline + phenyl glycidyl ether	Aniline 1 m (93 g)	Phenyl glycidyl ether 2 m (300 g)
2.	Aniline + <i>m</i> -cresyl glycidyl ether	Aniline 1 m (93 g)	<i>m</i> -Cresyl glycidyl ether 2 m (330 g)
3.	<i>p</i> -Toluidine + phenyl glycidyl ether	<i>p</i> -Toluidine 1 m (107 g)	Phenyl glycidyl ether 2 m (300 g)
4.	<i>p</i> -Toluidine + <i>m</i> -cresyl glycidyl ether	<i>p</i> -Toluidine 1 m (107 g)	<i>m</i> -Cresyl glycidyl ether 2 m (330 g)
5.	Aniline + Epidian 5	Aniline 3 m (73 g)	Epidian 5 4R (400 g)
6.	Aniline + Epidian F	Aniline 3 m (73 g)	Epidian F 4R (364 g)
7.	<i>p</i> -Toluidine + Epidian 5	<i>p</i> -Toluidine 3 m (93 g)	Epidian 5 4R (400 g)
8.	<i>p</i> -Toluidine + Epidian F	<i>p</i> -Toluidine 3 m (93 g)	Epidian F 4R (364 g)

graphic and gravimetric analyses of the products extracted from the cured resin samples with dichloromethane were determined.

## EXPERIMENTAL

### Materials

The unsaturated polyester resin POLIMAL 109 and dibenzoyl peroxide (50% paste) were obtained from the Organika-Sarzyna Chemical Plant (New Sarzyna, Poland). *N,N*-dimethylaniline, aniline, *p*-toluidine, and phenyl glycidyl ether were obtained from POCh (Gliwice, Poland). Other epoxide compounds used for the adducts preparation—*m*-cresyl glycidyl ether, Epidian 5 (the resin based on Bisphenol A), and Epidian F (the resin based on *p,p'*-dihydroxydiphenylmethane)—came from Organika-Sarzyna. Dichloromethane (HPLC grade) was from Merck (Darmstadt, Germany).

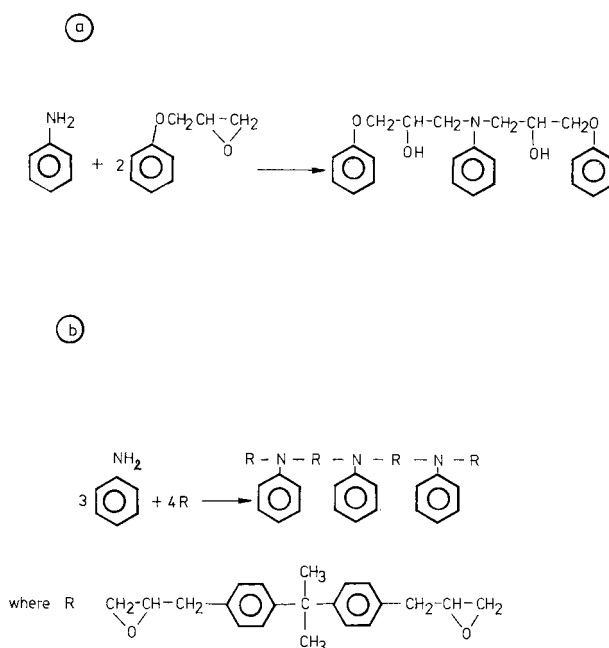
### Preparation of the Adducts

Eight different adducts were prepared. The detailed recipes used in this study are given in Table I. All reactions were performed in a 750-mL glass reactor equipped with a stirrer and thermometer. The typical procedure was as follows: 300 g of phenyl glycidyl ether (2 mol) and 1 drop of water as a catalyst were heated in the reactor to about 90°C. Then 93 g (1 mol) of aniline was added in portions while heating. At the temperature of 110–120°C the exothermic reaction started. The temperature of the reactor should be maintained in this range. After the addition of the last portion of aniline the reactor content was kept at the tem-

perature of 110–120°C for 1 h. The hot product was then poured into an aluminum mold to solidify.

As an example, the reaction between aniline and phenyl glycidyl ether is presented in Figure 1(a). In the case of the adducts with epoxide resins, the amounts of the reagents were chosen in such a way that 3 mol of aniline or *p*-toluidine were reacted with 4 equivalents (4R) of epoxide compound [Fig. 1(b)].

For the adducts with epoxide resins, exother-



**Figure 1** Chemical structure of the adduct: (a) aniline + phenyl glycidyl ether; (b) aniline + Epidian 5.

**Table II** Properties of the Amine Adducts

No.	Elemental Analysis						Initial Decomposition Temperature in Air (°C)
	Theoretical			Measured			
	C	H	N	C	H	N	
1.	73.3	6.9	3.6	73.0	6.9	3.5	260
2.	74.1	7.4	3.4	74.2	7.4	3.5	250
3.	73.7	7.1	3.4	73.2	7.1	3.5	245
4.	74.5	7.6	3.2	74.3	7.6	3.2	265
5.	81.0	12.1	2.8	76.4	9.0	2.6	330
6.	80.6	11.9	3.0	75.9	8.5	3.0	320
7.	81.1	12.2	2.7	75.9	8.6	2.5	335
8.	80.7	12.0	2.9	75.9	8.7	2.6	340

mic effects started at 130–140°C so the reaction was carried out at that temperature.

### Studies of the Adducts' Properties

#### Elemental Analysis

Elemental analyses were made using a Perkin–Elmer Model 2400 CHN analyser (Perkin–Elmer Norwalk, CT). The results for all the studied amine adducts are presented in Table II.

#### Thermogravimetric (TG) Measurements

The measurements were carried out on a derivatograph (MOM, Budapest, Hungary) at a heating rate of 5°C/min in the range from 20 to 1,000°C in the air. The initial decomposition temperatures were determined from the TG curves. The obtained data are summarized in Table II.

### Use of the Adducts for the Curing of Unsaturated Polyester Resin

The obtained amine adducts were tested as accelerators for POLIMAL 109 curing. The amounts of the compounds corresponded to the amounts of nitrogen in 1, 2, and 3% of *N,N*-dimethylaniline. For example 1 g of *N,N*-dimethylaniline contains 0.11 g of nitrogen. The same amount of nitrogen is in 3.08 g of the adduct: aniline + phenyl glycidyl ether.

Dibenzoyl peroxide, in the amounts of 1, 2, and 3%, was used as an initiator. As a comparable

curing system *N,N*-dimethylaniline in combination with dibenzoyl peroxide was also used.

The gelation times and peak exotherm temperatures of the investigated compositions were determined in a temperature-controlled bath (20°C) according to Polish Standard PN-75/C-89082. The results are given in Table III.

### Extraction of the Cured Polyester Resin

Extraction was carried out for the resin samples cured in the presence of 3% amine adduct and 2% dibenzoyl peroxide. Before extraction, all samples were ground to particles of about 2 mm diameter. Two grams of the ground polymer was extracted with 50 mL of dichloromethane in a Soxhlet apparatus for 4 h. The extract was concentrated in a vacuum evaporator to the volume of 5–8 mL and then diluted to 10 mL in a measuring flask with dichloromethane.

### Chromatographic Analysis of the Extracts

The chromatographic measurements were carried out on a GC-505M gas chromatograph (Inco, Wroclaw, Poland) equipped with a FID detector and stainless steel column (100 cm × 3 mm I.D.) packed with 10% Penwalt 223 + 4% KOH on 80/100 Gas Chrom R (Applied Sciences, Deerfield, MA). The temperature of the column was 160°C. Nitrogen at a flow rate of 40 mL/min was used as a carrier gas. The flow rates of hydrogen and air were 40 and 200 mL/min, respectively. A total of

**Table III Influence of the Concentrations of Amine Adduct and Dibenzoyl Peroxide on the Gelation Time and Peak Exotherm Temperature for POLIMAL 109 Unsaturated Polyester Resin**

Amine Adduct wt % (g)	Dibenzoyl Peroxide wt % (g)	Gelation Time (min)	Peak Exotherm Temperature (°C)
<b>Aniline + phenyl glycidyl ether</b>			
1 (3.08)	1 (2.0)	13.3	108.8
2 (6.17)		10.5	80.7
3 (9.26)		9.6	61.6
1 (3.08)	2 (4.0)	9.5	109.2
2 (6.17)		8.1	100.7
3 (9.26)		7.2	90.0
1 (3.08)	3 (6.0)	9.1	121.3
2 (6.17)		8.5	100.7
3 (9.26)		7.1	92.3
<b>Aniline + <i>m</i>-cresyl glycidyl ether</b>			
1 (3.30)	1 (2.0)	20.5	112.6
2 (6.61)		16.3	70.7
3 (9.92)		14.3	52.5
1 (3.30)	2 (4.0)	9.2	113.9
2 (6.61)		6.2	94.1
3 (9.92)		4.2	73.5
1 (3.30)	3 (6.0)	8.5	110.4
2 (6.61)		7.2	98.6
3 (9.92)		6.4	92.3
<b><i>p</i>-Toluidine + phenyl glycidyl ether</b>			
1 (3.19)	1 (2.0)	6.0	97.8
2 (6.39)		3.6	86.6
3 (9.59)		3.2	67.0
1 (3.19)	2 (4.0)	4.2	111.9
2 (6.39)		2.5	104.8
3 (9.59)		2.3	87.7
1 (3.19)	3 (6.0)	2.4	117.4
2 (6.39)		2.3	109.8
3 (9.59)		2.2	101.4
<b><i>p</i>-Toluidine + <i>m</i>-cresyl glycidyl ether</b>			
1 (3.41)	1 (2.0)	4.9	100.0
2 (6.83)		4.1	77.1
3 (10.25)		3.1	58.8
1 (3.41)	2 (4.0)	3.1	116.6
2 (6.83)		2.3	95.6
3 (10.25)		2.1	80.1
1 (3.41)	3 (6.0)	2.5	112.3
2 (6.83)		1.6	94.1
3 (10.25)		1.3	90.4

5  $\mu$ l of the extracts were injected by means of a 10- $\mu$ l syringe (SGE, North Melbourne, Australia). The same volumes of standard dichloromethane solutions of aniline and *p*-toluidine, at con-

centrations of 0.2, 2.0, and 20.0 mg/10 mL, were also injected to calibrate the detector. Concentrations of these solutions were equivalent to 0.01, 0.1, and 1% content, respectively, of the studied

**Table III** (Continued from the previous page)

Amine Adduct wt % (g)	Dibenzoyl Peroxide wt % (g)	Gelation Time (min)	Peak Exotherm Temperature (°C)
<b>Aniline + Epidian 5</b>			
1 (3.96)	1 (2.0)	15.5	112.3
2 (7.92)		12.4	66.2
3 (11.88)		11.4	50.9
1 (3.96)	2 (4.0)	11.4	109.5
2 (7.92)		10.0	88.5
3 (11.88)		9.3	72.7
1 (3.96)	3 (6.0)	9.1	120.0
2 (7.92)		8.3	99.4
3 (11.88)		7.3	95.6
<b>Aniline + Epidian F</b>			
1 (3.66)	1 (2.0)	21.2	107.4
2 (7.32)		19.0	91.4
3 (10.99)		15.3	78.9
1 (3.66)	2 (4.0)	17.2	118.7
2 (7.32)		11.4	97.1
3 (10.99)		7.4	88.5
1 (3.66)	3 (6.0)	12.2	118.5
2 (7.32)		7.1	102.7
3 (10.99)		6.3	95.6
<b>p-Toluidine + Epidian 5</b>			
1 (4.06)	1 (2.0)	5.2	122.6
2 (8.13)		4.4	96.3
3 (12.20)		3.0	88.5
1 (4.06)	2 (4.0)	3.0	126.4
2 (8.13)		2.2	100.7
3 (12.20)		1.3	95.6
1 (4.06)	3 (6.0)	2.4	107.4
2 (8.13)		2.0	101.7
3 (12.20)		1.2	91.7
<b>p-Toluidine + Epidian F</b>			
1 (3.77)	1 (2.0)	5.5	103.0
2 (7.54)		4.3	100.0
3 (11.32)		4.1	74.6
1 (3.77)	2 (4.0)	3.5	107.4
2 (7.54)		2.3	102.2
3 (11.32)		2.1	81.0
1 (3.77)	3 (6.0)	3.1	118.7
2 (7.54)		1.7	104.2
3 (11.32)		1.4	92.8
<b>N,N-Dimethylaniline</b>			
1 (1.00)	1 (2.0)	6.9	72.2
2 (2.00)		5.2	64.3
3 (3.00)		4.7	54.0
1 (1.00)	2 (4.0)	4.1	92.0
2 (2.00)		3.2	84.1
3 (3.00)		2.4	81.1
1 (1.00)	3 (6.0)	3.1	100.9
2 (2.00)		2.4	89.0
3 (3.00)		1.9	83.2



higher decomposition temperatures. For these adducts, the values exceed 320°C.

The data in Table III show that all the obtained adducts accelerate the cure of unsaturated polyester resins. Among the studied adducts, those of *p*-toluidine are more effective. The shortest gelation times are obtained for the adduct of *p*-toluidine + Epidian 5 and *p*-toluidine + Epidian F. The longest gelation times are for the adducts of aniline + *m*-cresyl glycidyl ether and aniline + Epidian F. In all cases the increase of accelerator concentration shortens the gelation time. Simultaneously, the exothermic peaks become smaller. On the other hand, the increase of initiator concentration causes an insignificant increase of peak exotherm temperature. For the system *N,N*-dimethylaniline and dibenzoyl peroxide a similar phenomenon is observed but exothermic effects are significantly lower. A typical dependence of the exotherm peak temperature on the concentration of the adduct aniline + Epidian 5 is presented in Figure 2.

Chemical structure of the obtained adducts suggest that they can be built in the chains of polyester, so the extracts were carefully examined. The results of the chromatographic and gravimetric analyses are summarized in Table IV. Of the nine peaks observed on the chromatograms, none correspond to the peaks of aniline (retention time = 3.16 min), *p*-toluidine (retention time = 5.13 min), or aniline and *p*-toluidine

adducts with glycidyl ethers (retention times longer than 20 min). This means that in the volatile extract compounds, neither aniline nor *p*-toluidine derivatives are present. On the other hand, the gravimetric analysis indicates that noticeable amounts of the products of high viscosities are extracted from the cured POLIMAL 109 samples. Elemental analyses for nitrogen content confirm an absence of aniline and *p*-toluidine derivatives in these extracts. Probably, polyester chains characterized by a low degree of cross-linkage are extracted.

The results presented here indicate that the amine adducts remain in the polyester resin as permanently bonded fragments.

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