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# Epoxy aniline formaldehyde resins modified with resin acids

**Summary** — The study is intended to develop new adhesives for pressure-sensitive tapes. Two types of resin acids-modified resins were prepared: (*i*) Aniline-formaldehyde novolac-type resins were prepared from aniline and formaldehyde under acid catalysis conditions; *N,N''*-dichlorohydrin aniline was made to react with paraformaldehyde and the product was dehydrochlorinated with NaOH; the aniline-formaldehyde resin was modified with glycidyl esters of resin acids. (*ii*) The epoxy aniline formaldehyde resin was modified with resin acids. IR (Fig. 1) and $^1$H NMR spectra (Fig. 2) were recorded and TG curves (Fig. 3, Table 1) were traced for the modified resins; the activation energies of the decomposition were evaluated (Table 1). When used in pressure-sensitive compositions of acrylic type, these polymers, found to carry hydrophenanthrene moieties in the chains, imparted good cohesion strength to pressure-sensitive tapes (Table 2).

**Key words**: epoxy aniline formaldehyde resins, modification with resin acids, pressure-sensitive adhesive.

Formaldehyde resins are most common polymers prepared by the reaction of formaldehyde (basic or acid catalysis) with phenols, substituted phenols, bisphenols, xylene, aniline, *etc.* [1]. Depending on the formulation, these resins can range from low-viscous free-flowing liquids to solid materials.

The OH and $NH_2$ groups present on the polymeric chains enable these resins to be modified by epoxidation and/or addition of other components [2—5]. The modified resins show improved mechanical, thermal, chemical and electrical properties and can be used for molding and metal-clad lamination, as materials of electronic parts, tackifiers for adhesives, *etc.* [6—11].

This paper sets out to report on the results of our studies on the synthesis and characterization of multifunctional epoxy aniline formaldehyde resins modified with resin acids. The effect of these modified resins on pressure-sensitive type adhesive compositions is also examined.

## EXPERIMENTAL

### Materials

Aniline, 2-ethylhexyl acrylate, acrylic acid, benzoyl peroxide, hydrochloric acid (HCl), sodium hydroxide (NaOH), and potassium hydroxide (KOH) were analytical grade reagents.

Epichlorohydrin, 1-methyl-2-pyrrolidone (NMP), 1,2-dichloroethane (DCE), and dimethyl sulfoxide (DMSO) were analytical grade organic solvents which were distilled before use.

Commercial-grade paraformaldehyde, 98% pure, was used as received.

Resin acids (acid number (a.n.) = 179 mg KOH $\cdot$ g$^{-1}$) were prepared from a commercial source as described in the literature [12].

A glicidyl ester of resin acids was obtained from resin acids [13] and had an epoxy equivalent EEW = 480 g $\cdot$ eq$^{-1}$.

A pressure-sensitive adhesive was prepared by methods reported elsewhere [14].

### Measurements

The acid number of resin acids was measured by direct titration with ethanolic 0.1 N KOH in the presence of phenolphthalein as indicator. The epoxy equivalent weight was determined by the Sander method and expressed in g $\cdot$ eq$^{-1}$ [15]. Average molecular weights were determined by cryoscopy using benzene and DMSO as solvents [16].

IR spectra were recorded on a Specord M80 (Carl Zeiss) spectophotometer by using KBr disks. $^1$H-NMR spectra were measured with the aid of a JEOL-JNMC 60 HL (Japan) instrument at 50°C, by using $CDCl_3$ and DMSO-$d_6$ as solvents and tetramethylsilane as internal standard. Thermal studies were carried out with a

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MOM Budapest derivatograph of the Paulik, Paulik-Erdey type, in air at 12°C/min.

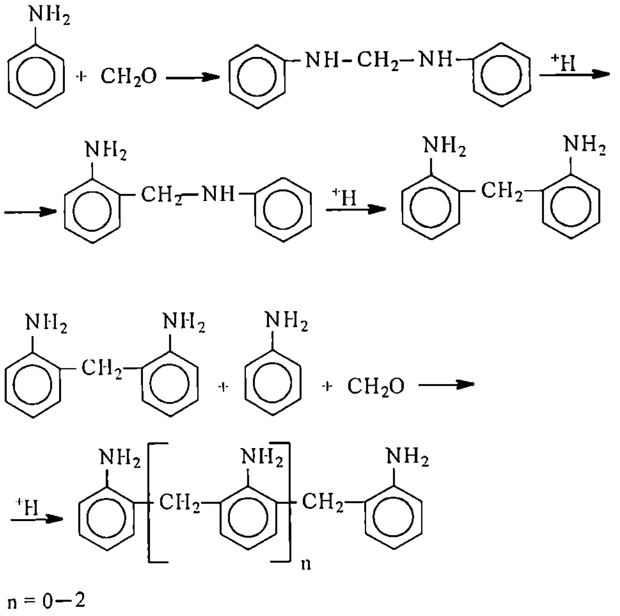
The tack of pressure-sensitive adhesives was measured by the ASTM D-1000 standard method. The cohesive and adhesive strengths were measured by using the 0°C angle hold test [17].

## Synthesis of the resins

The modified epoxy aniline formaldehyde resins were prepared by the following two procedures:

### (a) Synthesis of aniline formaldehyde resin

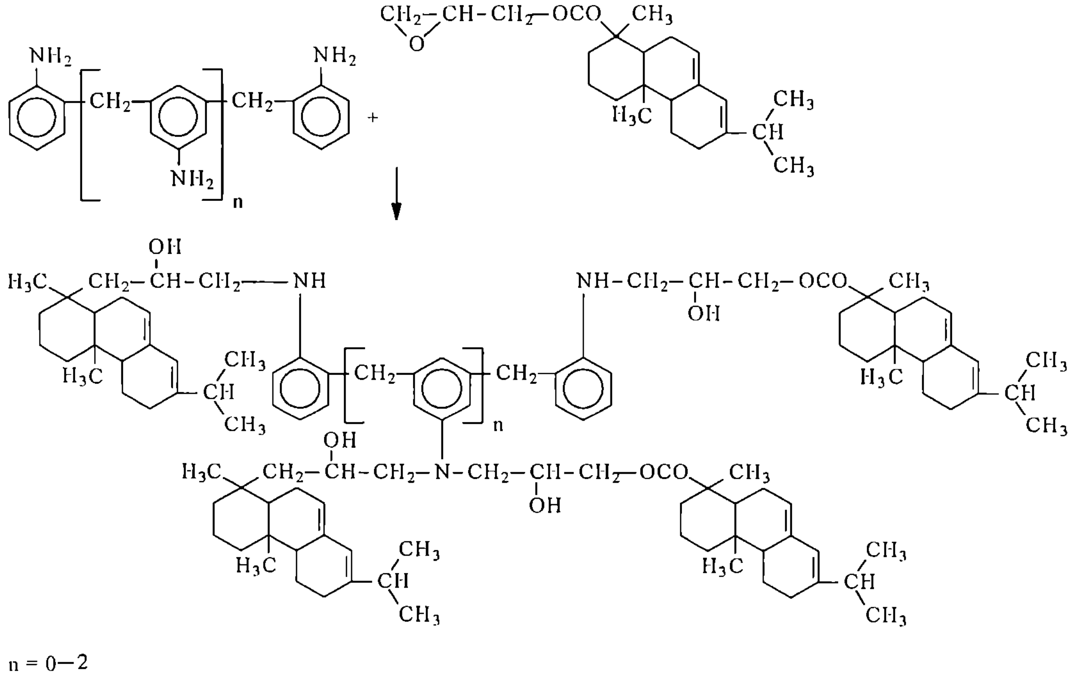
In a 0.5-L reaction flask fitted with a mechanical stirrer, thermometer, water cooler and a heating mantle, 93.15 g (1 mol) aniline and 22.5 g paraformaldehyde were mixed together at room temperature (25°C) with stirring. The reaction mixture was heated to about 65°C and 1.3 mL HCl (32%) was added. An exothermic effect was observed (Δt = 10°C). The temperature was raised up to 85—90°C and stirring was continued at this temperature for 90 min to insert methylol (-$CH_2OH$) groups. Then, 30 mL (2:1) NMP—DCE was added and a Dean-Stark separator was fixed at the top of the cooler. The mixture was refluxed and the forming water was removed by azeotropic distillation with DCE. The reaction mixture was washed twice with 40 mL of aqueous 10% NaOH and with distilled water to a neutral point. The aqueous phase was decanted and the organic layer was distilled under reduced pressure at 130°C to collect a pale yellow resin, 84.86 g (yield 83.2%); average molecular weight, 410 (Scheme 1).



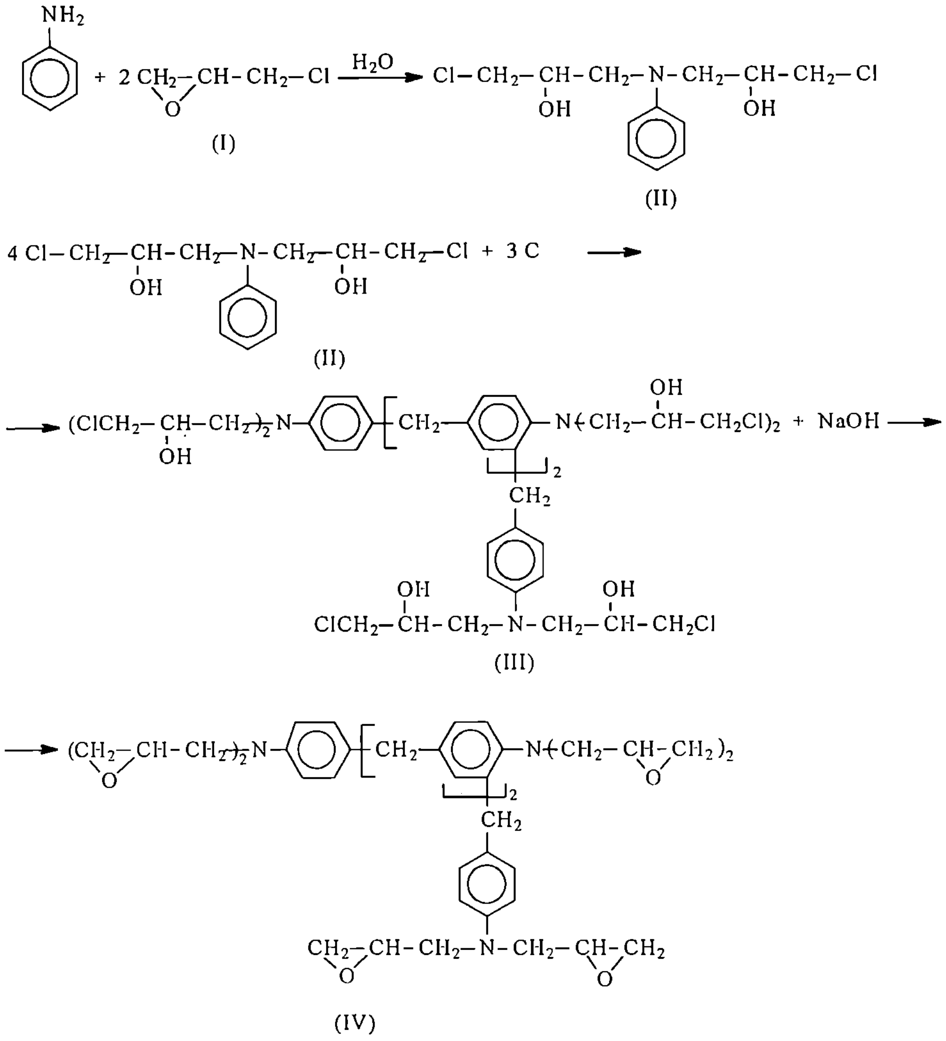
Scheme 1

### Synthesis of modified resin with glycidyl ester of resin acids

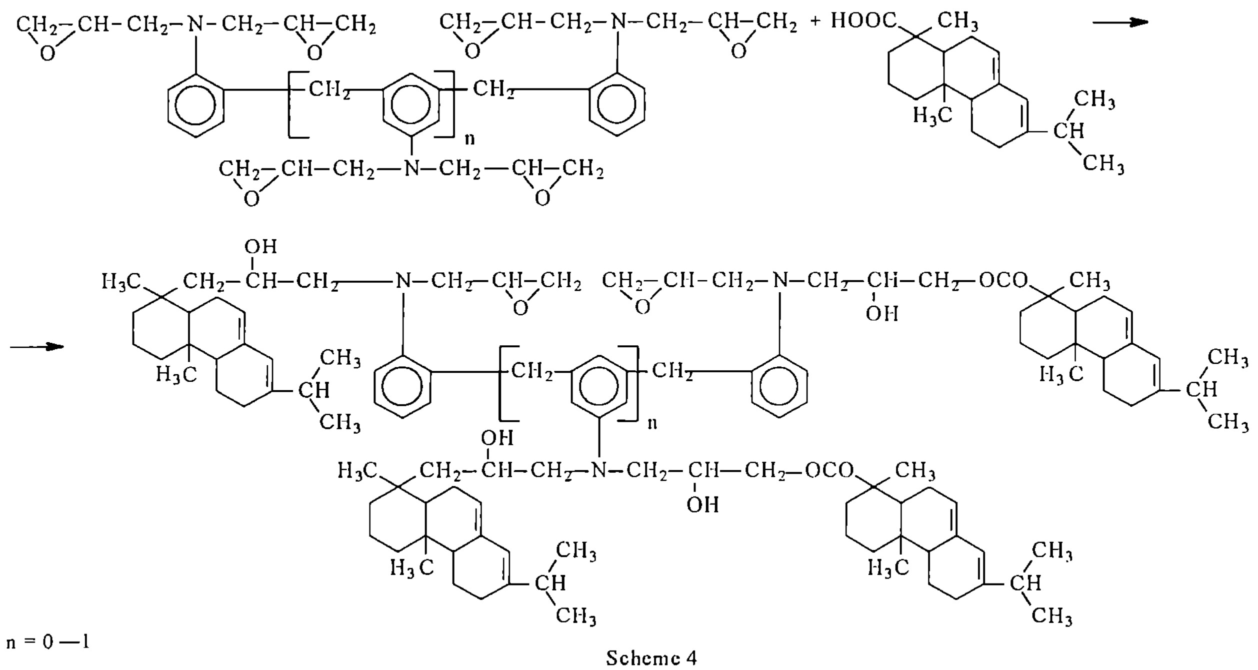
Aniline formaldehyde resin, 10 g, and 80 g glycidyl ester of resin acids (EEW, 480 g · $eq^{-1}$) were mixed together and heated at 100°C and 0.5 g tributylbenzylammonium chloride was added. The reaction mixture was stirred at 120°C for 1 h and at 150°C for 2 h. Finally, the modified resin was separated as fine particles suspended in a large excess of hot methanol (60°C) (1:10 w/w), stirred for 2 h, decanted, and dried at 60°C under vacuum to collect 52.5 g (yield 75%) of the product ($M_{av}$ = 2210) (Scheme 2).



Scheme 2



Scheme 3



Scheme 4

### (b) Synthesis of epoxy aniline formaldehyde resin from aniline dichlorohydrin

The epoxy aniline formaldehyde resin was synthesized by a modified Podzimek method in three steps [18].

In a similar experimental setup, 46.57 g (0.5 mol) aniline, 187 g (2 mols) epichlorohydrin, and 18 mL water were mixed together and heated at 80°C for 5 h. Then, 30 mL (2:1) NMP—DCE, 11.25 g paraformaldehyde and 1.3 mL of conc. (32%) HCl were added. The reaction mixture was refluxed for 5 h with stirring and the resulting water was removed azeotropically. The reaction mixture was cooled to 55°C and 40 g of aqueous 30 wt % NaOH was added with vigorous stirring over 5 h. Finally, the reaction products were washed with distilled water to a neutral point. Water, DCE and epichlorohydrin were removed at 130°C under reduced pressure to collect a brown resin, 121.1 g (yield 90.1%); EEW, 140 g · $eq^{-1}$ (Scheme 3).

### Synthesis of modified resin with resin acids

The epoxy aniline formaldehyde resin, 20.1 g; EEW 140 g · $eq^{-1}$; prepared as above, was mixed with 44.9 g resin acids (a.n. = 179 mg KOH $g^{-1}$). The mixture was heated at 100°C and 1 g tributylbenzylammonium chloride was added. The reaction mixture was heated at 120°C for 1 h and at 150°C for 2 h. The modified resin was purified as above to yield 60.23 g product (yield 94.1%) ($M_{av}$ = 2530) (Scheme 4).

### Synthesis of pressure-sensitive compositions

Pressure-sensitive adhesives were prepared by mixing (for weight ratio see Table 1) the acrylic adhesive prepared as described elsewhere [14] with the modified resins prepared as described above.

**Table 1. Thermal parameters of aniline formaldehyde resins modified with resin acids**

| Sample | Weight loss at temperature, °C | | Weight loss at 500°C, % | Decomposition activation energy kJ/mol |
|---|---|---|---|---|
| | 10% | 50% | | |
| Aniline formaldehyde resin | 350 | 510 | 50 | 53.48 |
| Aniline formaldehyde resin modified with glycidyl ester of resin acids | 308 | 400 | 26 | 64.64 |
| Epoxy aniline formaldehyde resin modified with resin acids | 328 | 416 | 28 | 69.90 |

### Pressure-sensitive tapes

The pressure-sensitive composition (Table 1) was applied on a release paper in a conventional manner and dried for 15 min in a hot air stream. Then, a polyester type nonwoven fabric (50 g · $m^{-2}$) was pressed on the adhesive surface and the release paper was removed. In the dried nonwoven tapes the adhesive coating was 25 g · $m^{-2}$ in weight. The coated nonwoven was cut into 25-mm strips which were tested for peel adhesion and for cohesion strength on a steel plate. The main properties of the tapes are presented in Table 1.

## RESULTS AND DISCUSSION

The chemical reactions involved in the synthesis are summarized in Schemes 1—4. In the presence of formaldehyde and acid catalyst, aniline is known to form $-NH-CH_2-$ groups which, as the temperature is increased, rearrange to yield a polymer with methylene bridges in the aromatic rings [19, 20] (Scheme 1). The $NH_2$ groups situated on the aromatic ring were made to react with epichlorohydrin to yield *N,N'*-dichlorohydrin aniline. A large excess of epichlorohydrin was used to prepare a low-crosslinked resin. *N,N'*-Dichlorohydrin aniline was made to react with paraformaldehyde to form formaldehyde resins. These resins were dehydrochlorinated in the presence of NaOH to prepare epoxy aniline formaldehyde resins (Scheme 2). Aniline formaldehyde resins were modified with glycidyl ester of resin

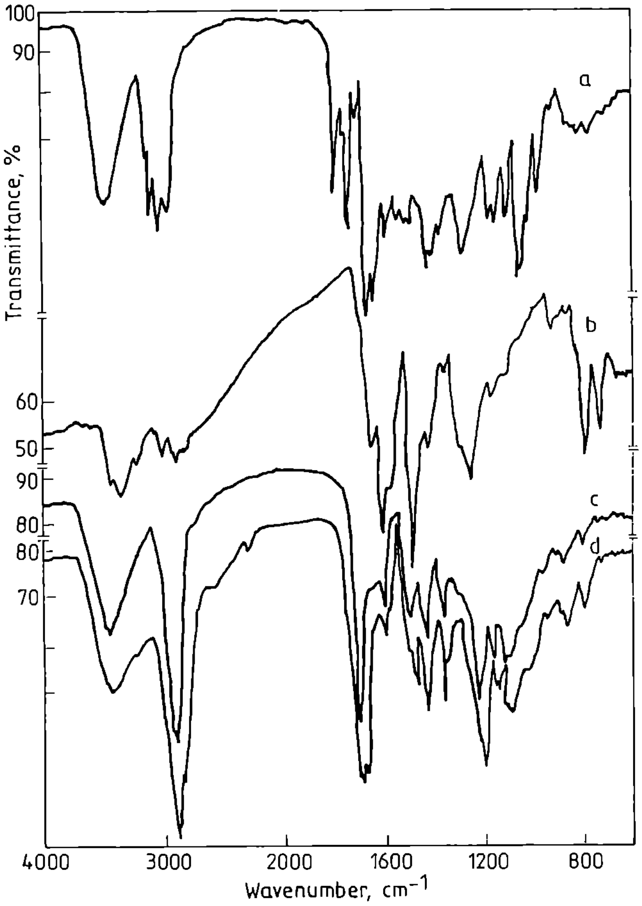


*Fig. 1. IR spectra: (a) epoxyaniline formaldehyde resin; (b) aniline formaldehyde resin; (c) epoxyaniline formaldehyde resins modified with resin acids; (d) modified aniline formaldehyde resin with glycidyl ester of resin acids*

acids to prepare epoxy aniline formaldehyde resins which were modified with resin acids (Schemes 3, 4). The modified resins were brittle red-brown solids, soluble in most aromatic solvents and insoluble in petroleum ether and methanol. The hydrophenanthrene moieties in the polymeric chain suggest these resins to be useful as tackifiers in adhesive compositions or in paint formulations. The structures of the resins were confirmed by IR and $^1$H-NMR spectra (Fig. 1, 2).

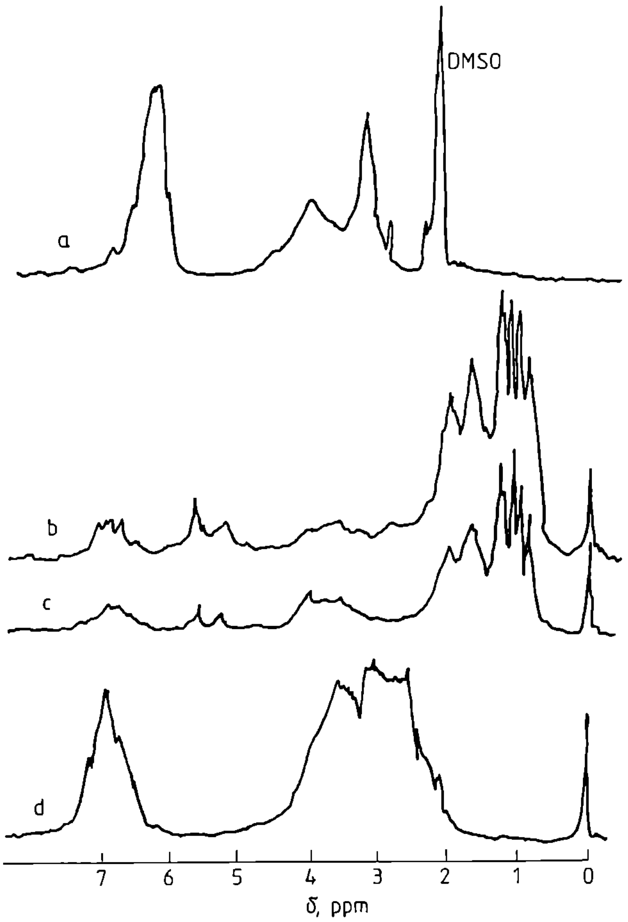


*Fig. 2. $^1$H-NMR spectra: (a) aniline formaldehyde resin; (b) modified aniline formaldehyde resin with glycidyl ester of resin acids; (c) epoxyaniline formaldehyde resins modified with resin acids; (d) epoxyaniline formaldehyde resin*

The IR spectra of aniline formaldehyde resins show a strong absorption in the 3450—3350 cm$^{-1}$ region, which is specific to NH$_2$ groups. At 1280 cm$^{-1}$, aromatic substitution of NH$_2$ is seen to have occurred.

In the $^1$H-NMR spectra, the aromatic protons are situated at 6.65—7.4 ppm chemical shifts. The peak located at the 3.72 ppm chemical shift is specific to the methylene bridges situated in the aromatic rings.

At 915 cm$^{-1}$ and 840 cm$^{-1}$, the IR spectra of epoxy aniline formaldehyde resins exhibit the peaks specific to the epoxy ring. In the $^1$H-NMR spectra the signals assignable to the glycidyl group are located at 2.5—2.8, 3.15, and 3.7—4.2 ppm chemical shifts. The aromatic protons situated in the phenyl ring are located at 6.65—7.25 ppm chemical shifts. The IR and $^1$H-NMR spectra of the modified resins prepared by the two procedures (**a** and **b**), are similar and confirm the presence of the hydrophenanthrene moiety (Fig. 1, 2). The peak assigned to the glycidyl group is seen to disappear and to reappear as the OH group at 3450 cm$^{-1}$ and as an ester group at 1740 cm$^{-1}$ and within a range of 1150—1250 cm$^{-1}$. In the $^1$H-NMR spectra, the protons attributed to the hydrophenanthrene ring are located at the 0.8—2.8 ppm chemical shift and confirm the reaction pathway.

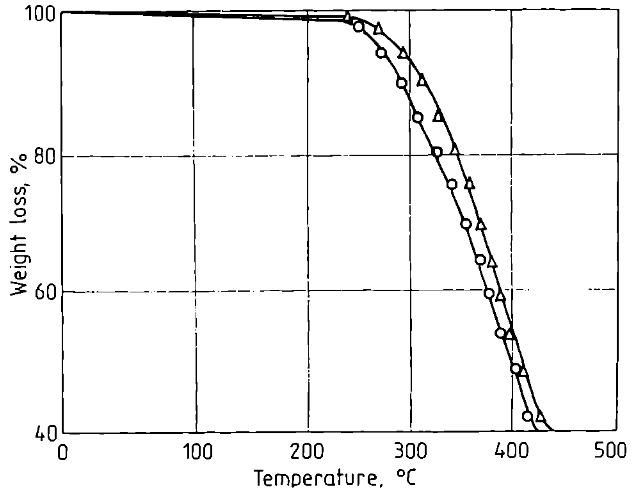


*Fig. 3. TG curves of epoxyaniline formaldehyde resins modified with resin acid (o) and aniline formaldehyde resin modified with glycidyl ester of resin acids (Δ)*

TG curves (Fig. 3) show the modified resins to be reasonably thermostable with an initial weight loss of 5% at 320°C. The rate of decomposition indicates to a single-stage process which is very fast within a range of 320—420°C. The main thermal haracteristics of the resins is presented in Table 1.

The relative thermal stability of the resins was estimated by comparing the decomposition energies calculated by the Coats and Redfern method for a first-order reaction ($n = 1$) [20]. The slopes of the straight-line plots, $-\log[-\log(1 - \alpha) \cdot T^{-2}]$ versus $T^{-1}$, allowed to evaluate the activation energies of decomposition (Table 1). The activation energies of decomposition of the modified resins prepared from resin acids and epoxy aniline formaldehyde resins are lower than those of the resins prepared from an aniline formaldehyde resin and a glycidyl ester of resin acids. One possible explanation of this lower value is the existence of unconverted NH$_2$ groups in the polymeric chains.

The pressure-sensitive tapes prepared from the pressure-sensitive composition containing the modified re-

**Table 2. The composition of adhesives used for the production of adhesive tapes and their characteristics**

| Sample | Adhesive formula | | Adhesive tape characteristics | |
|---|---|---|---|---|
| | Composition | Weight ratio (w/w) | 0° Hold test (min) | 180° Peel test (g · cm$^{-1}$) |
| A | Acrylic copolymer | 100 | 3.00 | 510 |
| B | Acrylic copolymer/Aniline formaldehyde resin modified with glycidyl ester of resin acids | 90/10 | 4.33 | 570 |
| | | 80/20 | 5.50 | 500 |
| | | 70/30 | 6.40 | 500 |
| C | Acrylic copolymer/Epoxy aniline formaldehyde resin modified with resin acids | 90/10 | 5.33 | 610 |
| | | 80/20 | 5.41 | 600 |
| | | 70/30 | 6.55 | 680 |

sin (Table 2) show an improved tack and a better cohesion strength as compared with the pressure-sensitive tape obtained from acrylic adhesive only.

## CONCLUSIONS

Epoxy aniline formaldehyde resins were modified with resin acids in two ways. In the first case, the aniline formaldehyde resin was made to react with a glycidyl ester of resin acids and, in the second case, the epoxy aniline formaldehyde resin was made to react with resin acids in the presence of tributylbenzylammonium chloride. These resins were used as tackifiers in pressure-sensitive formulations. At resin ratios lower than 20%, these resins impart a better cohesion with the adhesion strength remaining unaffected.

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