SYNTHESIS AND CURING STUDY OF A NEW PHENOLPHTHALEIN–FORMALDEHYDE RESIN

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ABSTRACT

The preparation of a new methylolic resin derived from condensation of phenolphthalein and formaldehyde is described. The resin was characterised by spectroscopic, elemental analysis and moisture evolution analysis (MEA) techniques. The thermosetting (curing) characteristics of the resin were investigated by MEA and differential scanning calorimetry. Several thermosetting parameters were determined, i.e. rate of setting, degree of setting and the activation energy of the setting reactions, and the determined values for the latter parameter were found to be 58.2 and 18.29 kJ mol^{-1} which were related to the dehydration and dehydroformylation reactions respectively. The degree of setting varies linearly with temperature.

INTRODUCTION

The phenolic resins are established resins of outstanding commercial applications: they include mainly phenolformaldehyde resins (novolac and resol) either as thermosetting resins or as intermediates for other resins such as epoxy novolac resins [1], urethane resins [2] and unsaturated polyester resins [3]. In previous work we have synthesised and studied several new phenoplastic resins [4–10].

This paper is concerned with a new type of resinous intermediate based on phenolphthalein–formaldehyde resin which was synthesised and studied.

Phenolphthalein is an interesting monomer because of its various functional groups, i.e. phenolic, carboxylic and alcoholic. It is also well known as an indicator for analytical purposes. Several condensation polymers and copolymers based on this monomer have been prepared and their study has been reported in the literature, e.g. epoxy resins [11,12], polycarbonates [13,14], polyester and polyamide [13].

Owing to the above functionalities we transferred this interesting monomer to its resinous derivative using its condensation with formaldehyde, in the hope of obtaining a new cross-linkable resin with useful applications as a chelating polymer, polymeric indicator, laminating resin, etc.

EXPERIMENTAL

Synthesis of the phenolphthalein–formaldehyde resolic resin

A five-necked, flanged-top reaction vessel fitted with an efficient mechanical stirrer, condenser and thermometer was charged with phenolphthalein (0.1 M), formaldehyde (37% w/v, 0.6 M) and sodium hydroxide (0.2 M). The contents were stirred for 4 h at 70°C as determined through a prior series of experiments. At the end of the reaction time, the organic layer was separated off after neutralisation with phosphoric acid, purified and dried under vacuum (0.1 mmHg) for 24 h at 40°C.

Characterisation of the resin

The phenolphthalein–formaldehyde resolic resin (resin (I)) was characterised by IR spectroscopy (Fig. 1). The broad absorption band at 3300 cm^{-1} is a characteristic band of hydrogen-bonded methylol groups; it is absent from the spectrum of the ester derivative of the resin, see fig 1. The resin was also characterised by elemental analysis: % C, 63.27 (calculated, 63.15); % H, 5.81 (calculated, 5.26).
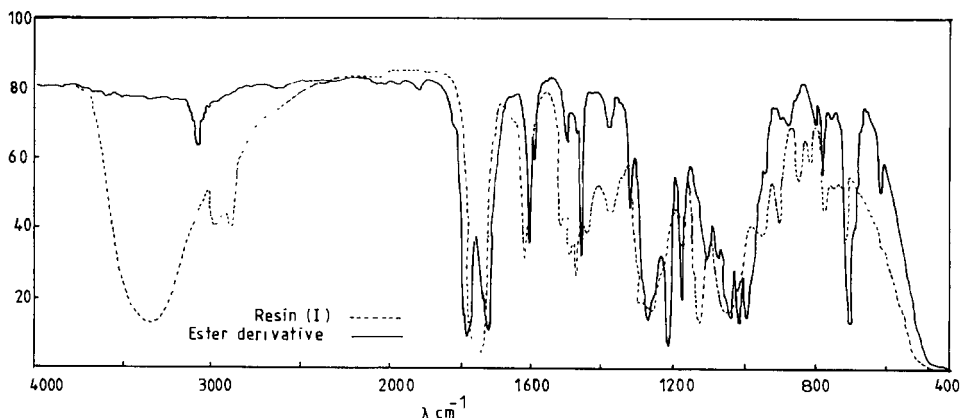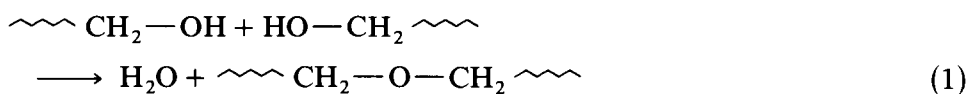

Fig. 1. Typical IR spectra of resin (I) and its ester derivative.

The number of methylolic groups in the resin was determined by MEA. Four groups per unit were found depending on the reaction

$$\sim\sim CH_2-OH + HO-CH_2 \sim\sim$$
$$\longrightarrow H_2O + \sim\sim CH_2-O-CH_2 \sim\sim \tag{1}$$

The percentage of H_2O found for the thermally set resin was 7.92%; the calculated value is 7.89%. The resin was transferred to its ester derivative as benzoate by treating the resin with the suitable acid chloride, followed by refluxing for 3 h. The ester derivative was purified and characterised by IR (Fig. 1) and back-titrated in order to determine the number of methylol groups per unit.

Thermosetting characteristics

Thermosetting study by MEA
A Du Pont MEA model 903 H was used after being calibrated with standard materials.

Samples (10–15 mg) were heated at different temperatures (110–150 °C). The amount of moisture liberated from the cross-linking reaction was measured by the conductivity cell as a function of time; typical results are shown in Fig. 2. The total amount of H_2O evolved from completely set resin was also determined.
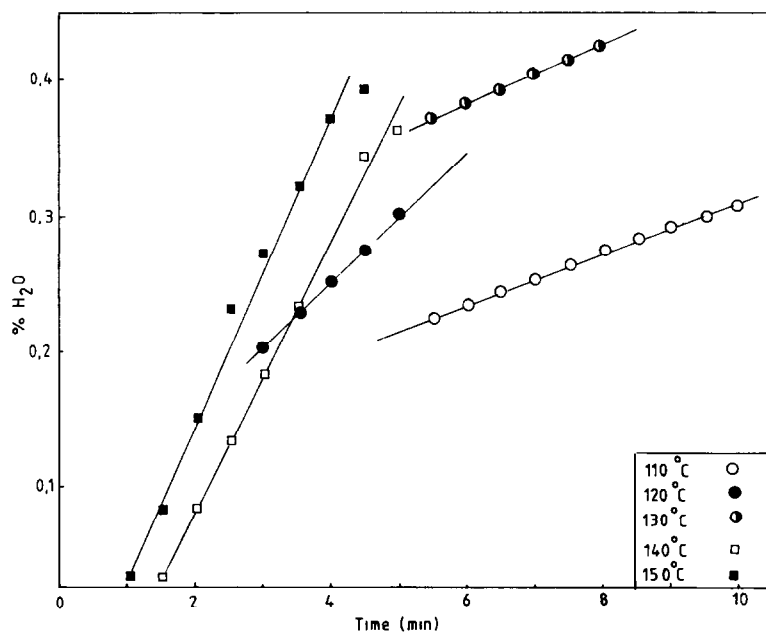

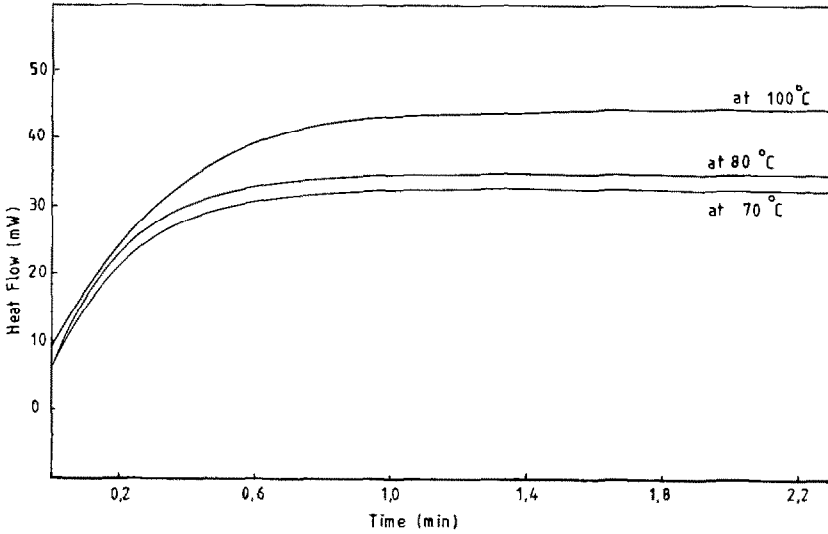Fig. 2. The effect of temperature on the rate of setting of resin (I).

Fig. 3. Typical isothermal DSC setting curves of resin (I) at different temperatures.

Thermosetting study by DSC

The thermosetting characteristics of the resin were also investigated by DSC using a Du Pont thermoanalyser model 1090. Two types of measurements were carried out: (a) by heating the samples at a constant heating rate, $20°C$ min^{-1}, the complete DSC setting thermograms were recorded
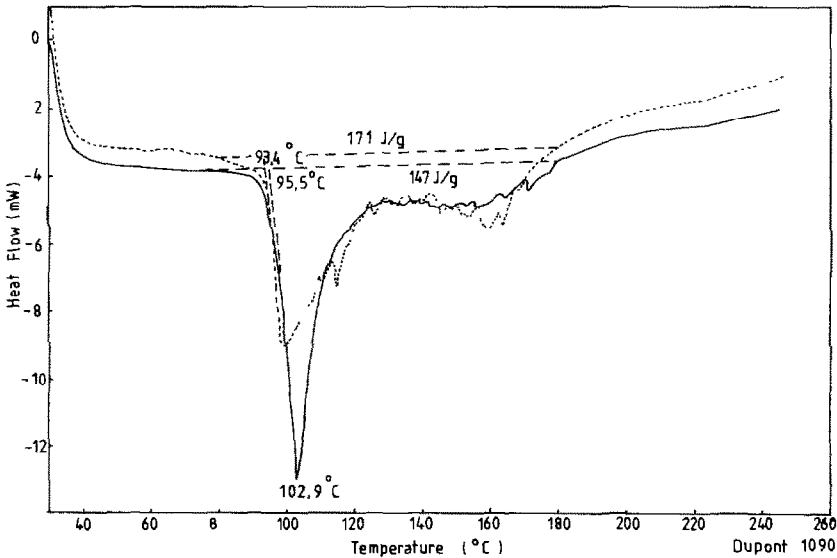

Fig. 4. Typical DSC curves showing the energy of setting of resin (I): ——, set at $80°C$ for 15 min; - - - - - -, set at $90°C$ for 15 min. Heating rate (DSC), $20°C$ min^{-1}.
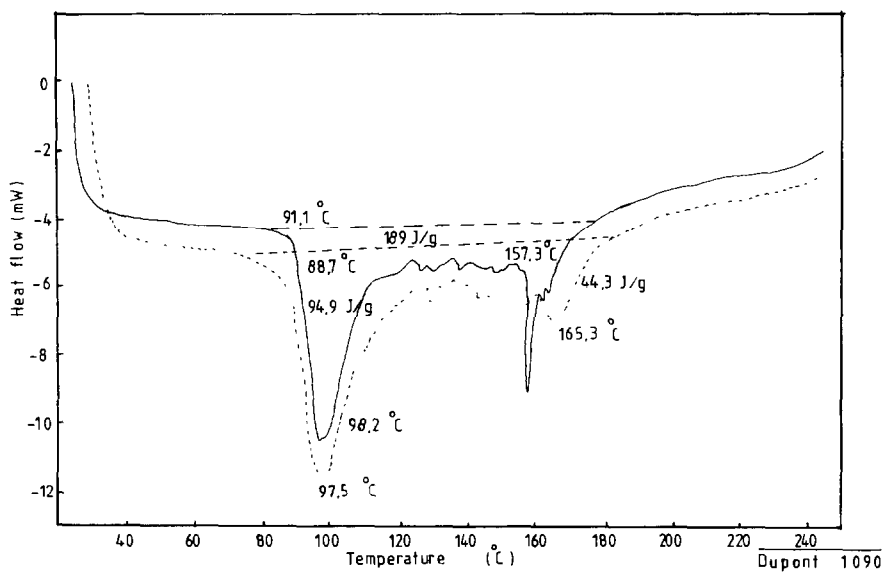
Fig. 5. Typical DSC curves showing the energy of setting of resin (I): - - - - - -, set at 70 °C for 15 min; ———, untreated resin. Heating rate (DSC), 20 °C min^{-1}.

from which the total energy of setting was determined; and (b) other samples were heated isothermally in the DSC calorimeter as a function of time in the temperature range 60–100°C; typical DSC isothermal thermograms are shown in Fig. 3. The partially set samples were examined in the calorimeter and the energy required for partial setting was also determined; typical DSC curves are shown in Figs. 4 and 5.

RESULTS AND DISCUSSION

The synthesis of the phenolphthalein–formaldehyde resolic resin depends on several factors: pH, temperature, reaction time and reactant ratio. Failure to satisfy the necessary conditions leads to formation of the cross-linked product in the reaction vessel. The optimum conditions for its synthesis have been determined, see ref. 15.

Several thermosetting characteristics of the resin were studied by MEA and DSC. Thus, the rate of setting of the resin was calculated from the per cent H_2O loss as a function of time at each temperature; the results obtained are shown in Fig. 2 and the slopes of the curves represent the rate of setting at each particular temperature.

In the DSC measurements the rate of setting was also estimated from the slopes of the initial stages of the isothermal DSC thermograms in the temperature range 60–100°C, shown in Fig. 3. The rate of setting determined by DSC and MEA were plotted against temperature (K), see
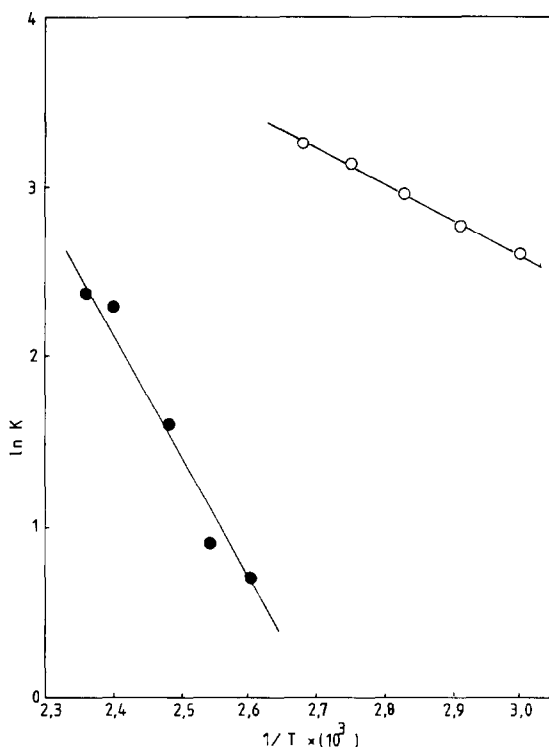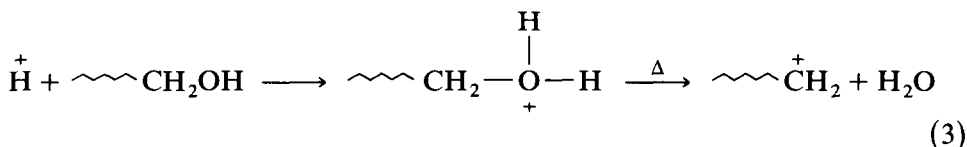
Fig. 6. Arrhenius plot showing the effect of temperature on the rate of setting of resin (I) by MEA (●) and DSC (○) techniques.

Fig. 6. Linear relationships were obtained. From the slopes of these curves the activation energy of the setting reactions was determined; the values obtained by MEA and DSC were 58.20 and 18.24 kJ mol^{-1} respectively.

The MEA value represents the heat of the dehydration setting reaction

$$\sim\sim\sim CH_2OH + HO-CH_2 \sim\sim\sim$$
$$\longrightarrow \sim\sim\sim CH_2-O-CH_2 \sim\sim\sim + H_2O \qquad (2)$$
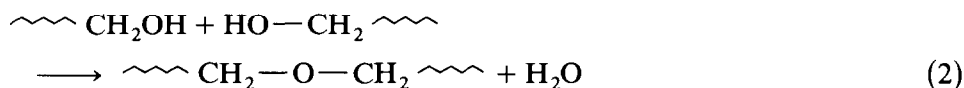
The activation energy of the dehydration reaction for this resin (58.2 kJ mol^{-1}) is relatively low compared with those obtained for other methylolic resins previously studied derived from other phenols, e.g. phenol, bisphenol A and bisphenol S, respectively 87.9, 75.5 and 74.3 kJ mol^{-1} [16]. This can be attributed to the catalytic dehydration effect of the carboxylic groups present in the resin as the methylolic resins undergo catalytic setting even at room temperature
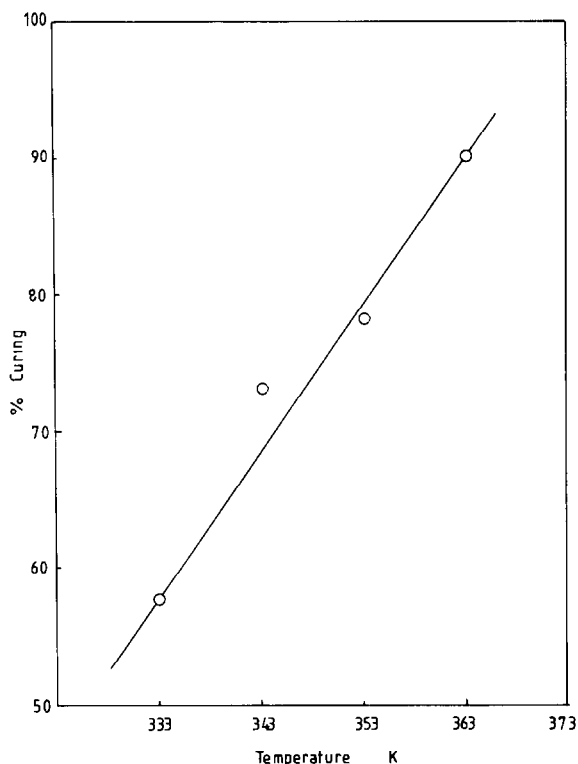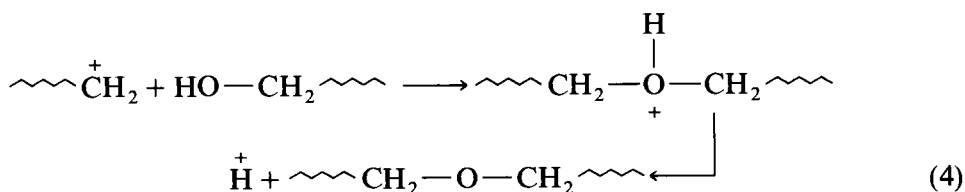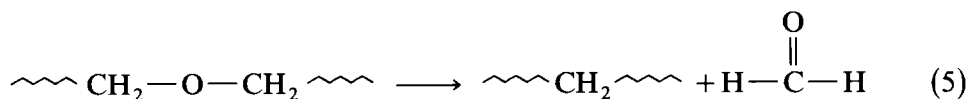
$$\overset{+}{H} + \sim\sim\sim CH_2OH \longrightarrow \sim\sim\sim CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{+}{O}}-H \overset{\Delta}{\longrightarrow} \sim\sim\sim \overset{+}{C}H_2 + H_2O$$

$$(3)$$

Fig. 7. The relationship between % curing of resin (I) and temperature (K) as measured by DSC.

$$\sim\!\!\sim\!\!\overset{+}{C}H_2 + HO-CH_2\sim\!\!\sim \longrightarrow \sim\!\!\sim CH_2-\overset{\displaystyle\overset{H}{|}}{O}-CH_2\sim\!\!\sim$$

$$\overset{+}{H} + \sim\!\!\sim CH_2-O-CH_2\sim\!\!\sim \longleftarrow\!\!\!\!\rule{0pt}{0pt}\qquad\qquad(4)$$

The DSC value could be related to the dehydroformylation reaction

$$\sim\!\!\sim CH_2-O-CH_2\sim\!\!\sim \longrightarrow \sim\!\!\sim CH_2\sim\!\!\sim + H-\overset{\displaystyle\overset{O}{\|}}{C}-H \qquad(5)$$
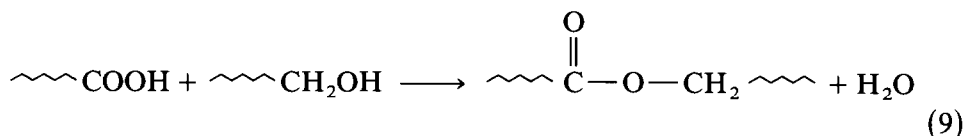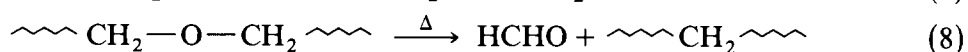
The value obtained is in good agreement with the values obtained for other methylolic resins in the some temperature range.

However, the degree of setting was found to be temperature and time dependent (Fig. 7). Thus, the degree of setting of the partially set resins due to isothermal treatment was determined by dividing the energy required for partial setting by the energy of the complete setting, 189 J g^{-1}; typical DSC setting curves are shown in Figs. 4 and 5. The setting energy of this resin is also lower than the setting energy of the methylolic resins derived from

bisphenol A and bisphenol S (254 and 209.9 J g^{-1} respectively); this can also be attributed to the catalytic effect of the carboxylic acid group in the new resin which leads to the catalytic dehydroformylation, the acid catalytic dehydroformylation being a familiar phenomenon in the thermal degradation of polyformaldehyde [17].

The DSC setting curves indicate the presence of two major types of endothermic setting reactions at 100 and 160°C (Figs. 4 and 5) which can be related to the dehydration and dehydroformylation reactions respectively. Other minor side reactions are also expected to take place due to the thermal treatment, i.e.

$$2 \text{~~~} CH_2OH \xrightarrow{\Delta} H_2O + \text{~~~} CH_2-O-CH_2 \text{~~~} \tag{6}$$

$$2 \text{~~~} CH_2OH \xrightarrow{\Delta} \text{~~~} CH_2 \text{~~~} + H_2O + H-\overset{\overset{\displaystyle O}{\|}}{C}-H \tag{7}$$

$$\text{~~~} CH_2-O-CH_2 \text{~~~} \xrightarrow{\Delta} HCHO + \text{~~~} CH_2 \text{~~~} \tag{8}$$

$$\text{~~~} COOH + \text{~~~} CH_2OH \longrightarrow \text{~~~} \overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2 \text{~~~} + H_2O \tag{9}$$
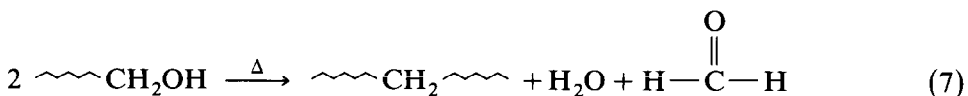
Thus, the small endothermic DSC peak at 115°C (Figs. 4 and 5) can be related to the latter reaction.

Thermoset phenolphthalein–formaldehyde resin formed as moulded sheets shows interesting applicational characteristics, for instance as indicators for acid-based titrations [15], moreover, the set resin shows outstanding efficiency as a chelating resin for several metal ions and the esters of the resin behave as good plasticising agents for PVC [15].

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