Chemistry of curing and adhesion properties of phenolic resins

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The adhesive strength of joints bonded by phenolic resins is influenced by factors such as the concentration of hydroxymethyl groups and polyaromatic compounds in the resol and the acidity of the resol, which determines the curing mechanism. These aspects of adhesive chemistry have been investigated by determining the peel strength of specimens bonded with resols of differing composition, and the results are discussed. A low rate of precondensation of the resol and slight acidity is shown to lead the to best adhesion properties in the peel test.

Key words: adhesives; phenolic resins; resols; polycondensation; peel strength

Phenolic resins have been used for the joining of metals in the aircraft industry for more than 40 years. Their excellent durability after long service times is well proven, as the Fokker F27 civil aircraft and others show, but from the user's point of view phenolic resins have several disadvantages. The high curing temperature of the resins can impart a heat treatment to adherends such as aluminium alloys, and is one of the reasons why many manufacturers changed to epoxide adhesives. Another disadvantage is the high pressure required during curing to avoid a foamy structure in the glueline and low strength. In addition, especially at low service temperatures, the mechanical properties of phenolics are less good than those of epoxide adhesives. Yet another disadvantage is the health problems associated with the phenol and formaldehyde content of the adhesives.

However, the excellent in-service durability of phenolic adhesives has yet to be achieved by the modern epoxide adhesives used in the aircraft industry. Although epoxides have been in service for not much more than 15 years, some have given several problems in durability[1]. This was not due only to the adhesive but also to the surface treatment given to the aluminium alloys. While phenolic resins are mostly applied to anodized metal surfaces, epoxides were for many years applied to etched surfaces[2] which have not given such good long-term adhesion properties[3].

While epoxide adhesives have undergone a tremendous development up to the modern materials used today, there was almost no development of phenolic adhesives. Therefore, in this paper the basic chemistry of phenolic adhesives, first investigated some years ago[4], will be described and the priniciples of optimizing these adhesives will be discussed. This can be done without changing the curing mechanisms or adding other reactive materials to the resin and is a task for further research and development on the basis of known reaction mechanisms.

Chemistry of phenolic resins

Reaction between phenol and formaldehyde

The chemical reaction between phenol and formaldehyde is a nucleophilic addition, which can be catalysed by both acids and bases. The reaction product depends upon the catalyst used. For phenolic adhesives the base-catalysed reaction is used to produce a resol. Fig. 1 shows some typical components of a resol. The major reaction is the addition of the phenol to the formaldehyde, forming hydroxymethyl groups. The concentration of polyphenols, compounds in which aromatic rings are linked via methylene bridges, is relatively small.

The acid-catalysed reaction leads to the novolaks, which are used as additives for paints or, after reaction with epichlorhydrin, as epoxynovolaks in epoxy adhesives. Novolaks have a low concentration of hydroxymethyl groups and contain mostly polyphenols (see, for example, compound 5 in Fig. 1).

The base-catalysed reaction, which is the first step in poducing a resol, can be performed on a laboratory scale using barium hydroxide. On neutralizing this base with sulphuric acid, the inert barium sulphate is formed, which does not have to be separated from the resol. In the technical process the expensive barium hydroxide is replaced by ammonium or sodium hydroxide. In this case neutralization produces salts which are soluble in water. They will be present in the glueline after curing and may influence the durability of joints.

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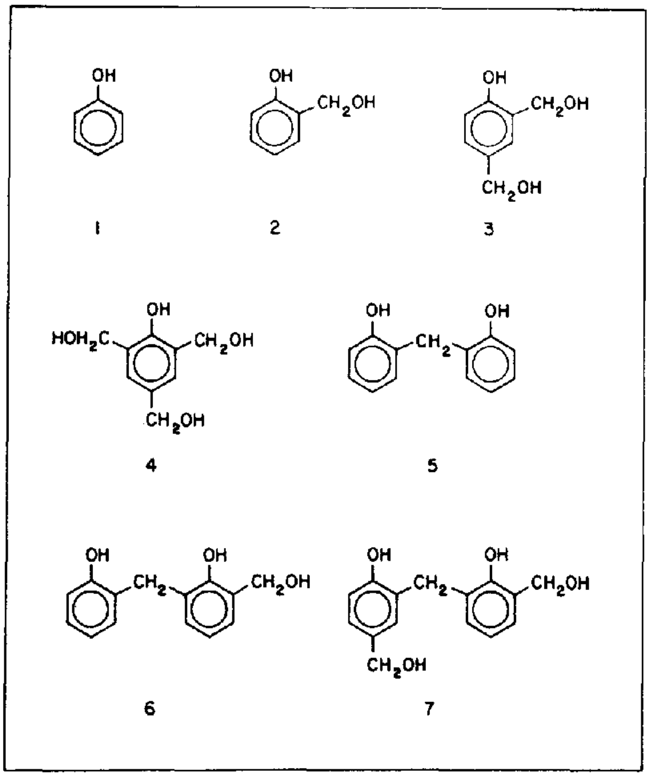

Fig. 1 Typical compounds present in resols: 1—phenol; 2—a hydroxymethylphenol; 3—a bishydroxymethylphenol; 4—a trihydroxymethylphenol; 5—a dihydroxydiphenylmethane; 6—a hydroxymethyldihydroxydiphenylmethane; 7—a bishydroxymethyldihydroxydiphenylmethane

In both cases the resol is produced in the same way. The phenol and the base are added to an aqueous solution of formaldehyde and the mixture is heated slightly for several hours. The base is then neutralized and most of the water is distilled off. The resol obtained, a high viscosity liquid or a solid, is the non-plasticized material used as the adhesive. The plasticizer polyvinylformal can be added by the manufacturer to give a film adhesive. Alternatively some solvent may be added to the resol to give primers; when solid plasticizer is added to this by the user a liquid/powder system is obtained. In the commercial liquid products the water may not be distilled off and so the resol may also contain some formaldehyde.

Chemistry of curing

Applying the dissolved adhesive or melting the adhesive film immediately starts the adhesion reaction with the aluminium surface. Infrared spectroscopy has shown[5] that this mostly occurs via the acidic proton of the phenol and the hydroxymethyl group, giving a chelate complex with the surface. In addition, the methylene bridged diphenol seems to form a complex with the surface oxide layer. The resol bound to the surface is not available for further curing reactions and must therefore show a different reactivity than the free resol. This would suggest that a brittle boundary layer of adhesive is present on the surface, but it is not known how this influences the mechanical properties of the joint.

Further polycondensation of the resol occurs during curing. This is achieved by an electrophilic substitution reaction and leads to a methylene bridged, three-dimensional network of duroplastic polymer which gives the mechanical properties to the adhesive joint. The cross-linking of the resol is disturbed by the encapsulated particles of plasticizer. Since only the surfaces of the plasticizer particles can react with the resol, the size and distribution of the plasticizer particles strongly influence the mechanical properties of the joint[6]. The formation of a polymer product is also hindered by an excess of formaldehyde, which gives rise to extra hydroxymethyl groups. These groups are hydrophilic and increase the water uptake of the adhesive under service conditions, resulting in higher plasticization and lower strength. An increased concentration of water in the resol also increases the risk of destruction of adhesion.

Thus the formation of methylene bridges is the essential step for good adhesion. This reaction is catalysed by protons from the acid used for neutralization.

In this study, the effect of resol acidity on the mechanical properties of cured bonded joints is investigated. Seven synthesized and two commercial resols were used.

Experimental procedure

Synthesis of the resols

The resols were synthesized according to the method described in the literature[7].

In a 500 ml round bottom flask equipped with a stirrer and a thermometer, 1 mole (94 g) of phenol, 1.54 moles (125 g) of a 37% aqueous solution of formaldehyde and 0.015 moles (4.7 g) of barium hydroxide octahydrate were heated to 70°C for 2 hours. Sulphuric acid (10%) was added to give a mixture with a pH of between 6 and 7. Most of the water was removed in vacuo (2.5 kPa) at 40°C, so that the resols were free of formaldehyde.

A number of resols were prepared by various modifications of this procedure although the ratio of phenol to formaldehyde was always kept constant (2:3). The variations used in the preparation of the seven resols are given in Table 1.

In addition to the synthesized resols, various batches of commercial products were also investigated. They were Tegocoll DO 2 (from Goldschmidt AG) and Redux 775 (from Ciba Geigy Ltd); both were used as liquids. The batches of Tegocoll DO 2 had been stored at 8°C for 1, 5 or 7 years. Redux 775 was used fresh.

Analysis of the resols

The different compounds in the resols can be separated by thin layer chromatography with toluene/acetonitrile (3:1) as solvent on silica plates. Fourteen different fractions in the fresh Tegocoll DO2 could be separated but the amounts of the fractions obtained were too small for further analysis. Chromatography on columns was also unsuccessful because the resols polycondensed on the silica. Only phenol and 2-(hydroxymethyl) phenol could be identified.

Gas chromatography (GC) was used as an alternative to liquid chromatography as derivatives of homonuclear hydroxymethyl phenols have already been determined by this technique[8]. Mass spectrometry (MS) was used in conjunction with GC to identify the

Table 1. Preparation parameters for the different resols

Material	Preparation
Resol 1	Prepared following given description (see experimental section)
Resol 14	Sulphuric acid was replaced by hydrochloric acid
Resol 23	Reaction mixture was not neutralized by an acid
Resol 242	Barium hydroxide was replaced by sodium hydroxide (1.2 g) and the sulphuric acid was replaced by hydrochloric acid
Resol 255	Barium hydroxide was replaced by sodium hydroxide (3.6 g). The reaction mixture was not neutralized by an acid
Resol 250	Reagents as in the preparation of resol 255, but with reaction time of 3.5 h. The base was not neutralized
Resol 251	Reagents as in the preparation of resol 255, reaction time 3.5 h. Reaction mixture neutralized with sulphuric acid to a pH value of 6-7

lower condensed products of the resols. The analysis was carried out with a Hewlett Packard HP5995 A instrument on an SE 54 capillary column. One to two microlitres of a 10% solution of the resol in acetone were injected.

^1H nuclear magnetic resonance (NMR) spectra were recorded in acetone-d_6 or chloroform-d solutions on a Bruker WP 80 instrument.

The characterization of the resols also included determining the acidity of the resol to distinguish the reaction mechanism during cure. This was done in a standardized procedure in which the pH of the resols was measured: to 0.5 g of the resol, which was free of solvent, 5 ml of distilled water were added. After shaking, the pH was determined with pH paper.

Mechanical testing

Because some of the batches tested had been stored for a long time, it had to be determined whether their mechanical properties had changed over this time. With the old batches, 180° peel tests had been carried out in the fresh condition[9]; therefore this test was also chosen in the present study.

For this test, 1.6 mm thick sheets of 2024 T3 clad aluminium alloy, 150 × 25 mm in size, and 0.2 mm thick foils of 99.5% pure aluminium were joined by the different resols using polyvinylformal as a plasticizer (liquid/powder system). All metal surfaces had been previously anodized in chromic acid[3]. The resols were cured at 180°C under 700 kPa pressure for 45 minutes. These specimens were peeled as shown in Fig. 2.

This test was originally developed for measuring adhesion because macroscopic adhesion failure is always observed. Microscopically, failure is observed very near to the metal surface. If water is applied to the crack tip during the peel test, the change of peel strength gives an indication of the durability of the bond. A strong decrease in strength in this wet peel test indicates poor durability under humid environmental conditions.

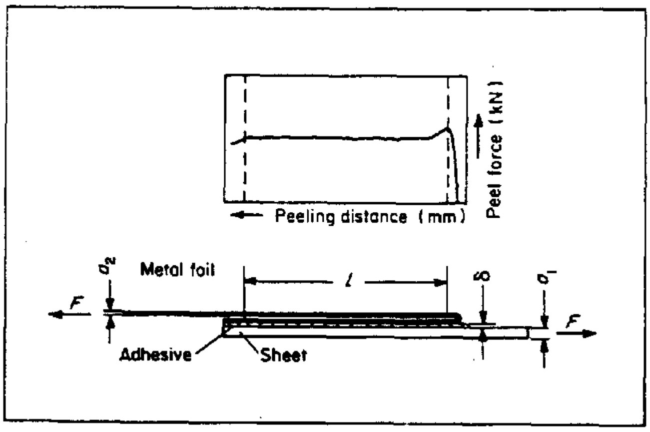

Fig. 2 Principle of the peel test

Results

Analysis of the resols

The gas chromatogram of resol 1 is shown in Fig. 3. The compounds corresponding to the four signals were identified as phenol (compound 1 in Fig. 1, retention time 3 min), hydroxymethylphenol (eg, compound 2 in Fig. 1, retention time 10 min), bishydroxymethylphenol (eg, compound 3 in Fig. 1, retention time 12-13 min) and trihydroxymethylphenol (compound 4 in Fig. 1, retention time 18 min).

The chromatogram of Tegocoll DO 2, run under a slightly different temperature programme, is shown in Fig. 4. The first four peaks correspond to those of resol 1. The compounds giving rise to the additional peaks with retention times of 16.5, 17.5 and 19.2 min have been identified as dihydroxydiphenylmethane (eg, compound 5 in Fig. 1), hydroxymethyldihydroxydiphenylmethane (eg, compound 6 in Fig. 1) and bishydroxymethyldihydroxydiphenylmethane (eg, compound 7 in Fig. 1) respectively.

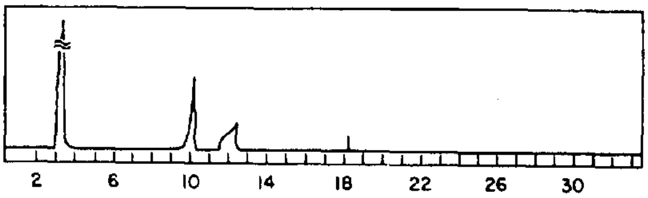

Fig. 3 Gas chromatrgram of resol 1

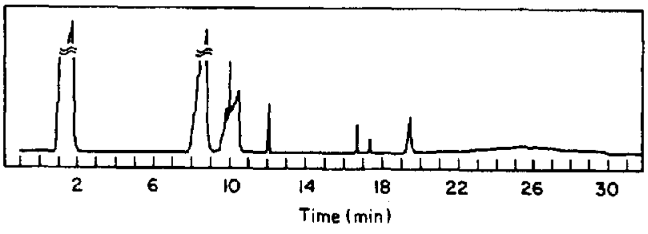

Fig. 4 Gas chromatogram of Tegocoll DO 2

Products with a higher degree of precondensation did not show up as distinct peaks in the chromatogram. Mass spectra recorded after 23 and 26 min indicated the presence of compounds with molecular masses of more than 400, corresponding to tri- and tetraphenols.

The chromatogram of Redux 775 was very similar to that of Tegocoll DO 2 (see Fig. 4).

The condensation products of the resols differ in the number of aromatic rings, which are bridged by methylene groups, and in the number of hydroxymethyl groups. As shown by Brockmann *et al.*, only methylene groups are formed during the condensation reaction of the phenols and no ether groups are found, as often reported[10, 11]. On the other hand, alcohols are the first products of the base-catalysed reaction between formaldehyde and phenol. Thus the ratio of CH_2-OH to ar-CH_2-ar protons indicates the rate of condensation in the resols, and this ratio can be measured by ^{1}H NMR spectroscopy. Figs 5-7 show the spectra of some different resols, in which the signals at 4.8 ppm are due to the hydroxymethyl groups and those at 3.7 ppm are due to the methylene bridges. The technical products have a higher content of polyphenols, while resol 1 contains compounds with only one aromatic ring. Redux 775 and Tegocoll DO 2 differ only in the ratio of higher condensed products. Table 2 shows the ratios of integrated NMR signals of the various resols.

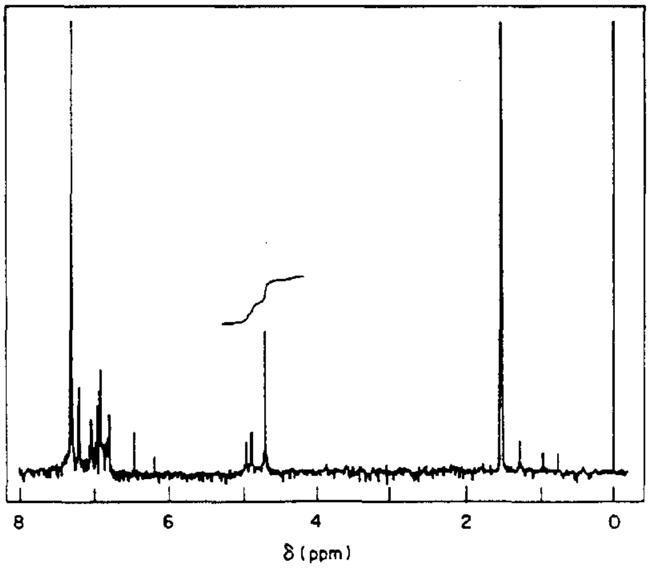

Fig. 5 ^{1}H NMR spectrum of resol 1

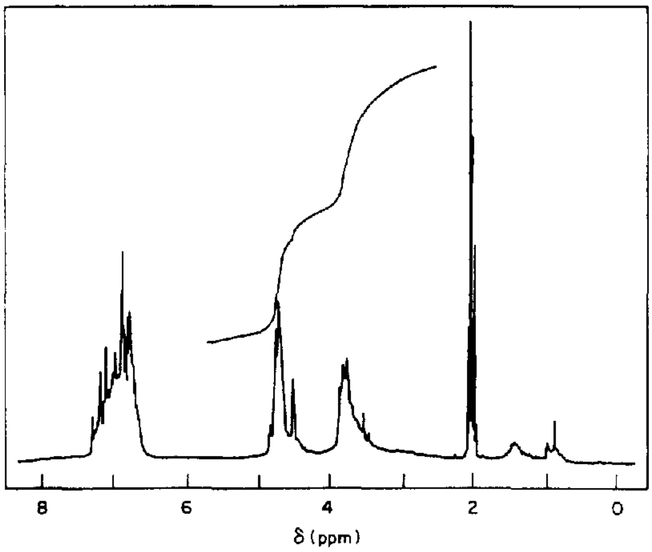

Fig. 6 ^{1}H NMR spectrum of Tegocoll DO 2

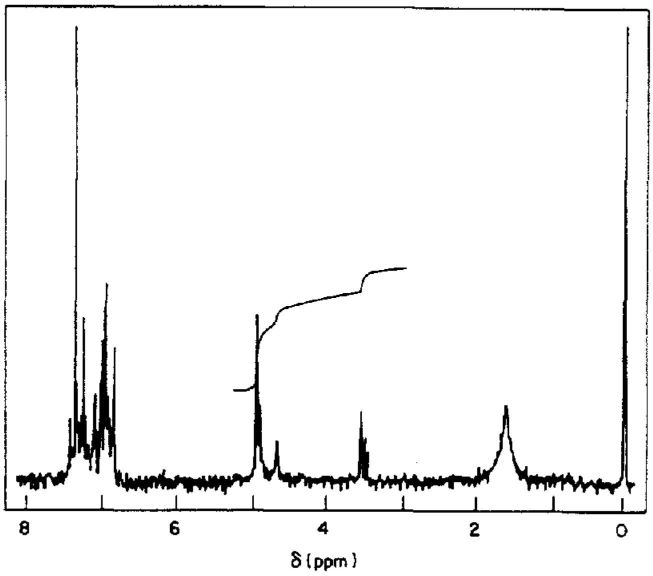

Fig. 7 ^{1}H NMR spectrum of resol 250

The pHs of the various resols are given in Table 3. There are remarkable differences between the pH values, even for the commercial products. For the Tegocoll DO 2 there is no indication that these differences arise from the extremely long storage times.

Peel strengths

The measured peel strengths are summarized in Table 4. The long time of storage prior to use did not

Table 2. Ratio of integrated ^{1}H NMR signals of hydroxymethyl and bridging methylene groups

Resol	$-CH_2OH$	$-CH_2-$
Resol 1	1	0*
Resol 250	1	0.25
Tegocoll DO 2	1	1.3
Redux 775	1	0.6

*Not detectable

Table 3. pH values of the resols

Resol	pH
Tegocoll DO 2-7*	6
Tegocoll DO 2-5*	6
Tegocoll DO 2-1*	8.5
Tegocoll DO 2-0*	8.5
Redux 775	7
Resol 1	6.5
Resol 14	6.5
Resol 23	9
Resol 242	7.5
Resol 250	9
Resol 255	9
Resol 251	6.5

*The figure following the dash (-) is the age of the resol in years

Table 4. Peel strengths of bonded joints made with the resols

Resol	Peel strength (N mm^{-1})
Tegocoll DO 2-7*	4.0
Tegocoll DO 2-5*	4.3
Tegocoll DO 2-1*	4.0
Tegocoll DO 2-0*	4.7
Redux 775	4.2
Resol 1	4.0
Resol 14	5.0
Resol 23	3.5
Resol 242	3.9
Resol 250	2.8
Resol 255	2.5
Resol 251	3.7

*The figure following the dash (-) is the age of the resol in years

have strong effect on the peel strength: the peel strength was decreased only about 0.2 Nmm^{-1} by the storing.

Discussion

The GC/MS and NMR spectroscopy both led to the same conclusion, that the commercial products are more highly condensed than the experimental resols and that the concentration of hydroxymethyl groups is lower.

While in the first step of precondensation, which is base catalysed, mostly hydroxymethyl groups are formed, all further steps build up more polyphenols. If in this first step not enough hydroxymethyl groups are produced, the extent of cross-linking in the later steps will be reduced and the adhesion will be poor. The hydroxymethyl groups are also needed for the adhesion reaction with the aluminium surface.

Highly precondensed products are of lower reactivity in the curing reactions because they contain a low concentration of hydroxymethyl groups, and have a higher viscosity. Besides the degree of precondensation, the pH values are important for the curing behaviour of the resols in the curing process itself. From the chemical point of view, slightly acid resols have the greatest potential for further polycondensation.

The condensation reactions did not depend on the type of acid or base used. However, the strength of the cured resin did depend on the reaction time for preparing the resol, because larger molecules form at longer times.

The mechanical behaviour of an adhesive-bonded joint made with phenolic resin depends on the degree of precondensation, the concentration of hydroxymethyl groups and strongly on the alkalinity or acidity of the resol. Optimum peel strengths were obtained from resols with a pH of approximately 6. All resols with a high pH showed a remarkably low strength.

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