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Phenol-urea-formaldehyde (PUF) co-condensed wood adhesives

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Abstract

The reaction of urea with methylolphenol under acidic conditions was investigated. The alternating copolymer of urea and phenol could be synthesized by the reaction of urea and 2,4,6-trimethylolphenol. The reactions of urea with polymethylolphenol mixtures also were investigated by changing the reaction conditions, such as the molar ratio and acidity. The co-condensates were analysed by carbon-13 nuclear magnetic resonance spectroscopy to determine the ratios of co-condensation.

Another synthetic method to obtain co-condensed resins was developed by reacting phenol with UF concentrate, which is a type of urea-formaldehyde resin prepared with a high molar ratio of formaldehyde to urea (F/U) such as greater than 2.5. Further, it was found that resol-type co-condensed resins can be synthesized by alkaline treatment of the co-condensed resins that were once prepared under acidic conditions. The curing process and thermal properties of resol-type co-condensed resins were investigated by torsional braid analysis. The co-condensed resins displayed almost the same curing behavior and heat resistance as a commercial resol. Their adhesive performance against plywood was evaluated by conducting a cyclic 4 h boil test and a 72 h boil test. The plywood test results passed the requirements for JAS special-grade structural plywood. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: urea; phenol; formaldehyde; co-condensation; resol; methylolphenols; structure; curing; thermal property; adhesive strength; plywood

1. Introduction

Polymers of phenol or urea with formaldehyde have dominated such areas as wood adhesives and molding plastics for many years. Phenolic resins (PF) have a proved performance in producing exterior-quality composites, while low-cost urea-formaldehyde resins (UF) have performed well in interior applications. Nevertheless, the potential scarcity and high cost of phenolic resins, together with concerns about rather low durability and formaldehyde emission from UF resins, have stimulated efforts to develop a new resin system.

Recently, so-called 'phenol-formaldehyde-urea co-condensed resins', which are generally made only by mechanical blending of UF resin and alkaline-type PF resins (resol), have been used as adhesives for the manufacture of wood products. However, since these resins are cured with ammonium chloride which will react with free formaldehyde in the resins to produce an acidic state gradually, curing of the UF resin is considered to precede that of the resol. Therefore, effective co-condensation cannot be expected between them. In order to develop

practical uses it is necessary to introduce co-condensation between phenol and urea at the time of resin preparation.

In previous work [1–3] we have determined the occurrence of co-condensation of phenol and urea/melamine by formaldehyde with carbon-13 nuclear magnetic resonance spectroscopy (¹³C-NMR) and established two synthetic methods for the co-condensed resins. One (resins I) is the reaction of methylolphenols with urea under acidic conditions [4]; the other is the reaction of UF concentrate with phenol under acidic conditions and conversion into resol-type resins (resin II) [5].

In this paper we shall introduce the synthetic methods for these two types of co-condensed resin, and report on their adhesive and thermal properties during and after curing [6,7].

2. Synthesis of alternating copolymer of phenol and urea

Sodium 2,4,6-trimethylolphenate was obtained according to the method of Freeman [8], and its water

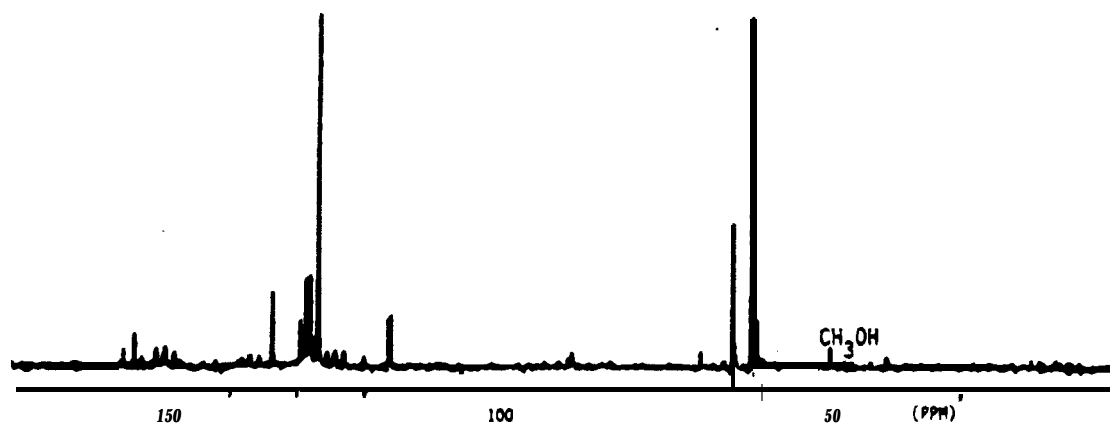


Fig. 1. ^{13}C -NMR spectrum of crude 2,4,6-trimethylolphenol after acidification.

solution was used as 2,4,6-trimethylolphenol after acidification. Fig. 1 shows the ^{13}C -NMR spectrum of the acidified solution, where the presence of self-condensates is almost negligible. Two large signals at 61.7 and 64.6 ppm were easily assigned to carbons of the *o*- and *p*-methylol groups of 2,4,6-trimethylolphenol, respectively [9,10]. The small signal at 61.5 ppm was assigned to the carbon of the *o*-methylol group in 2,4-dimethylolphenol [10]. The presence of 2,6-dimethylolphenol and monomethylolphenols in the sample was not detected in the NMR spectrum.

When the acidified solution (TMP) was reacted with urea (U) at the molar ratio of $\text{TMP/U} = 0.33$, oily products began to separate from the water layer after reacting under pH 2.0 at 85°C for 30 min. The gel permeation chromatogram (Fig 2) shows the formation of polymeric materials. In the ^{13}C -NMR spectrum (Fig. 3) three signals at 40.5, 44.3 and 49.2 ppm are observed, as well as the signal of unreacted *o*-methylol groups at 61.5 ppm [1,3,10]. Since the starting materials had quite a few free positions available for reaction with a methylol group, self-condensation of the methylene linkages was almost precluded, a fact also confirmed by the absence of the signal due to the *o,p*-linkage in the magnetic field around 36 ppm. Therefore the signal at 40.5 ppm was safely assigned to the co-condensed methylene carbons between the *o*-position and urea residues, and that at 44.3 ppm to those between the *p*-position and urea residues [3]. Further *N,N*-disubstituted methylene linkages were concluded to form mainly from *p*-methylol groups, because of the presence of the signal at 49.2 ppm. Therefore no self-condensation of phenols was recognized.

These results proved that this polymer was the alternating copolymer of urea and phenol joined through methylene linkages like the structure represented in Fig 4. It is particularly significant that the alternating copolymer can be synthesized by a simple method under acidic conditions.

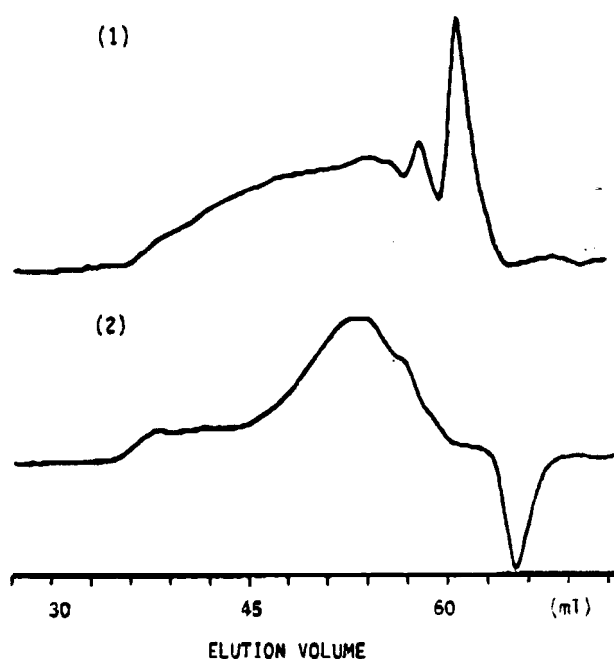


Fig. 2. Gel permeation chromatograms of (1) the whole reactant from urea and 2,4,6-trimethylolphenol and (2) oily precipitates. Reaction conditions: $\text{TMP/U} = 0.33$, pH 2.0. WC. 30 min.

3. Synthesis of co-condensed resins (resin I)

In the previous section, crude 2,4,6-trimethylolphenolate, purified as a precipitate according to Freeman's method, was used as a starting material to synthesize the copolymer. The precipitates were dissolved in water and acidified with sulfuric acid before reaction with urea. In the present experiments, the solutions of sodium methylolphenacet, which were prepared only by mixing phenol with sodium hydroxide and formalin, were applied directly to react with urea after acidification. It was confirmed from the absence of signals due to free formaldehyde in the ^{13}C -NMR spectra (Fig. 5) of the mixtures of

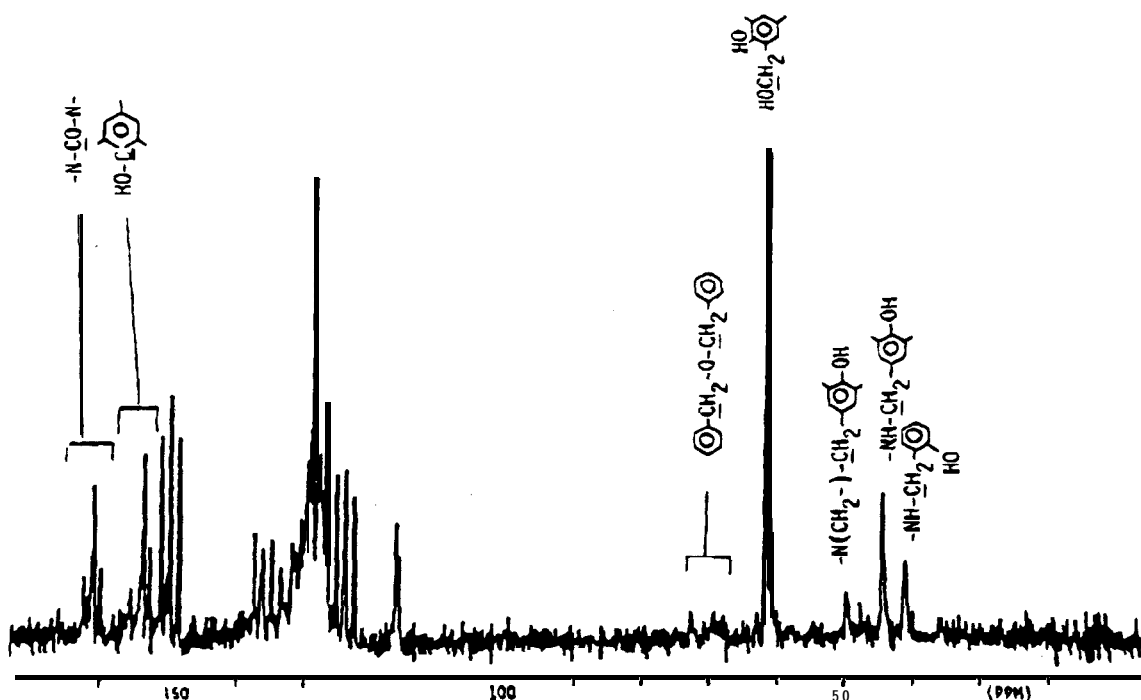


Fig. 3. ^{13}C -NMR spectrum of the co-condensed resin from urea and 2,4,6-trimethylolphenol. Synthesis conditions are the same as those in Fig. 2.

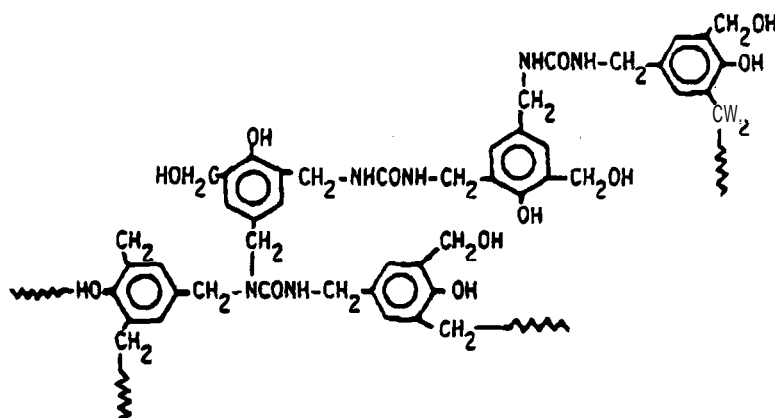


Fig. 4. Proposed structure of the alternating copolymer from urea and 2,4,6-trimethylolphenol.

sodium methylolphenates that the methylolations were almost complete after allowing the reaction mixtures to stand at room temperature for three or four days. Furthermore, the formation of self-condensations between phenols was absent at this stage because signals attributed to methylene linkages [3,9] and benzylether groups [10], the chemical shift assignments of which are shown in Table I, were not observed in the ^{13}C -NMR spectra as shown in Fig. 5 [1-3,11]. Several types of solution of sodium methylolphenate were employed to co-condense with urea as shown in Table 2, which summarizes the effects of the F/P/U molar ratio on the structures of the co-condensed resins.

4. Structural analysis of co-condensed resins (resin I)

The results of structural assignments and quantitative data from ^{13}C -NMR spectra are summarized in Tables 1 and 2, respectively. Although the co-condensation between polymethylolphenol and urea was predominant, the copolymer was indicated to contain self-condensed linkages between phenols to a small extent. This involved the formation of both methylene and benzylether linkages. Three kinds of chemical shift due to the carbon of methylene linkages, *o,o*-, *o,p*- and *p,p*-methylene linkages, were determined [1,9]. As to the chemical shifts of the carbons in the benzylether linkage, only the *o*-linkage has

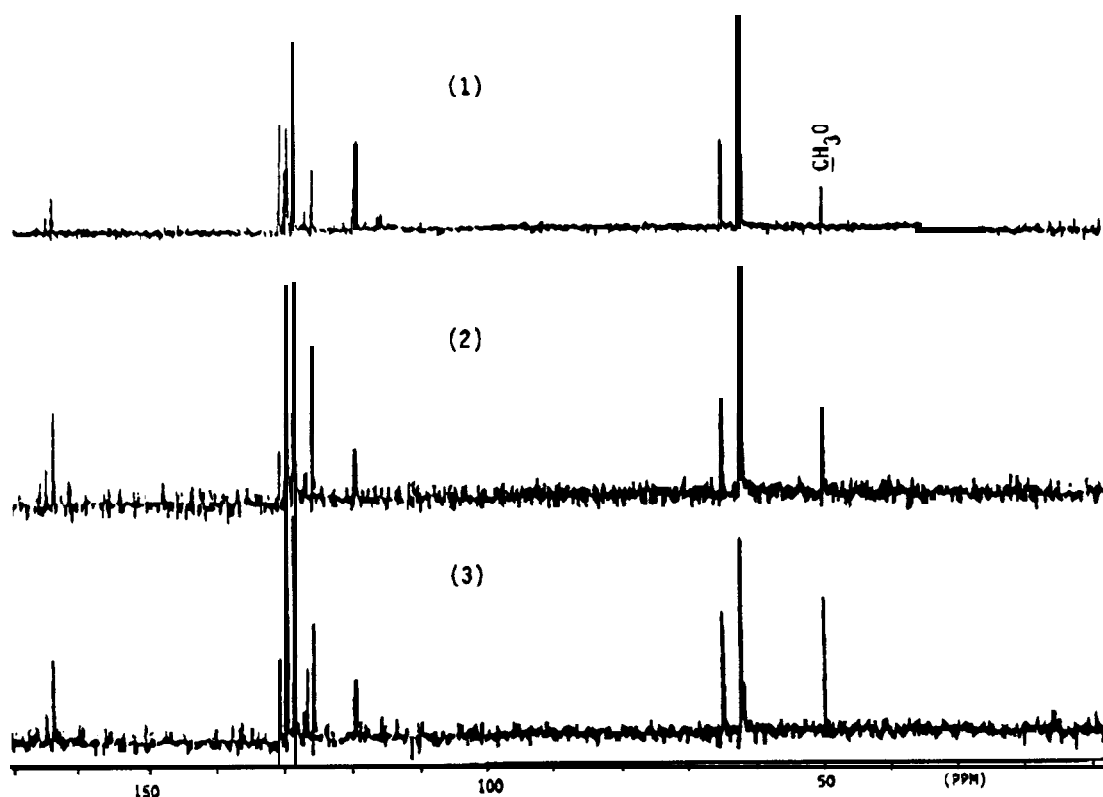


Fig. 5. ^{13}C -NMR spectra of sodium methylolphenates differing in the synthetic molar ratio of F/P/NaOH: (1) F/P/NaOH = 2.2/1/1, (2) F/P/NaOH = 2.5/1/1, (3) F/P/NaOH = 3.0/1/1. All spectra were taken after allowing the mixture to stand at room temperature for 4 days after mixing.

Table 1
 ^{13}C -NMR assignments for urea-formaldehyde-phenol copolymer

| Structure | Chemical shift (ppm) ^a |
|---|-----------------------------------|
| Phenolic methylol group | |
| <i>o</i> -Ph- CH_2OH | 61.1 |
| <i>p</i> -Ph- CH_2OH | 64.7 |
| Methylene group between phenols | |
| <i>o,o</i> -Ph- $\text{CH}_2\text{-Ph}$ | 29.6 |
| <i>o,p</i> -Ph- $\text{CH}_2\text{-Ph}$ | 35.8 |
| <i>p,p</i> -Ph- $\text{CH}_2\text{-Ph}$ | 40.6 |
| Benzylether group between phenols | |
| <i>o</i> -Ph- $\text{CH}_2\text{-O-CH}_2\text{-Ph}$ | 69.1 |
| <i>p</i> -Ph- $\text{CH}_2\text{-O-CH}_2\text{-Ph}$ | 72-73 |
| Co-condensed methylene group | |
| <i>o</i> -Ph- $\text{CH}_2\text{-NHCO-}$ | 40.6 |
| <i>o</i> -Ph- $\text{CH}_2\text{-N(CH}_2\text{-)CO-}$ | 46.4 |
| <i>p</i> -Ph- $\text{CH}_2\text{-NHCO-}$ | 44.2 |
| <i>p</i> -Ph- $\text{CH}_2\text{-N(CH}_2\text{-)CO-}$ | 49.2 |
| Methylene group between ureas | |
| -NH- $\text{CH}_2\text{-NH-}$ | 47.7 |
| -NH- $\text{CH}_2\text{-N(CH}_2\text{-)}$ | 53.5 |
| -N(CH ₂ -)- $\text{CH}_2\text{-N(CH}_2\text{-)}$ | 60.0 |
| Phenolic carbon | |
| HO-C | 15-162 |
| Urea residue | |
| -CO- | 162-158 |

The chemical shifts are based on internal pyridine-*d*₅ at 123.6 ppm

been assigned at 69.7 ppm [10]. However, the present copolymers showed signals at 72-73 ppm. This downfield shift by 2-3 ppm from the *o*-benzylether was identical with that observed between the *o*- and *p*-methylol groups (61.1 and 64.7 ppm, respectively). Therefore it was concluded that the signals observed at 72-73 ppm could be attributed to *p*-benzylether.

As solutions of polymethylolphenol mixtures of the starting material were confirmed not to contain free formaldehyde, it was shown from ^{13}C -NMR spectra that all of the copolymers did not contain self-condensed units between urea residues even if the reactions were performed under strongly acidic conditions [11].

The aromatic-ring carbons attached to phenolic OH groups appeared in the magnetic field between 152 and 158 ppm in a pyridine-*d*₅ solution, whereas the carbonyl carbons of urea residues gave signals at 158-162 ppm according to the substitution pattern. Each quantity of combined formaldehyde was normalized and represented as the molar ratio (F/P) against phenolic nuclei by using their integral values in Table 2. The ratio of urea incorporated into the copolymer also was normalized as the molar ratio of U/P.

The analytical results of several co-condensed resins are compared in Table 2. As reported in our papers

Table 2
 "C-NMR analysis of urea-formaldehyde-phenol copolymers"

| | Resin | | | | | | |
|---|---------|---------|---------|---------|---------|---------|---------|
| | I | II | III | IV | V | VI | VII |
| Synthetic molar ratio (F/P/U) | 2.2/1/1 | 2.2/1/2 | 2.5/1/1 | 2.5/1/2 | 2.5/1/3 | 3.0/1/1 | 3.0/1/3 |
| Reaction pH | 2.25 | 2.30 | 2.0 | 2.3 | 2.0 | 2.2 | 3.0 |
| Reaction time (min) at 90°C | 60 | 60 | 30 | 30 | 30 | 60 | 180 |
| [1] Phenolic methylol group | 0.71 | 0.71 | 0.81 | 0.73 | 0.67 | 1.10 | 1.12 |
| <i>o</i> -Ph-CH ₂ OH | 0.71 | 0.71 | 0.81 | 0.73 | 0.61 | 1.10 | 1.22 |
| <i>p</i> -Ph-CH ₂ OH | — | — | — | — | — | — | — |
| [2] Methylene group between phenols | 0.19 | 0.27 | 0.30 | 0.17 | 0.30 | 0.21 | 0.17 |
| <i>o,o</i> -Ph-CH ₂ -Ph | — | — | 0.08 | — | — | — | — |
| <i>o,p</i> -Ph-CH ₂ -Ph | 0.19 | 0.27 | 0.22 | 0.17 | 0.30 | 0.21 | 0.17 |
| <i>p,p</i> -Ph-CH ₂ -Ph | — | — | — | — | — | — | — |
| [3] Benzylether group between phenols | 0.29 | 0.14 | 0.25 | 0.20 | 0.11 | 0.30 | 0.14 |
| <i>o</i> -Ph-CH ₂ -O-CH ₂ -Ph | 0.29 | 0.14 | 0.19 | 0.20 | 0.11 | 0.20 | 0.11 |
| <i>p</i> -Ph-CH ₂ -O-CH ₂ -Ph | — | — | 0.06 | — | — | 0.10 | 0.05 |
| [4] Co-condensed methylene group | 1.05 | 1.15 | 1.00 | 1.32 | 1.42 | 1.20 | 1.41 |
| <i>o</i> -Ph-CH ₂ -NHCO- | 0.29 | 0.32 | 0.30 | 0.40 | 0.49 | 0.34 | 0.58 |
| <i>o</i> -Ph-CH ₂ -N(CH ₂ -)CO- | 0.10 | 0.08 | 0.12 | 0.16 | 0.09 | 0.19 | 0.24 |
| <i>p</i> -Ph-CH ₂ -NHCO- | 0.38 | 0.52 | 0.39 | 0.59 | 0.65 | 0.38 | 0.51 |
| <i>p</i> -Ph-CH ₂ -N(CH ₂ -)CO- | 0.28 | 0.23 | 0.19 | 0.17 | 0.19 | 0.29 | 0.14 |
| [5] Methylene group between ureas | — | — | — | — | — | — | — |
| -NH-CH ₂ -NH- | — | — | — | — | — | — | — |
| -NH-CH ₂ -N(CH ₂ -) | — | — | — | — | — | — | — |
| -N(CH ₂ -)-CH ₂ -N(CH ₂ -) | — | — | — | — | — | — | — |
| [6] Total formaldehyde ^a | 2.24 | 2.27 | 2.36 | 2.42 | 2.50 | 2.81 | 2.9 |
| [7] Phenol (Ph) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| [8] Urea (C=O) (U/P) | 0.46 | 0.69 | 0.65 | 0.90 | 1.0 | 0.65 | 1.0 |
| Rate of condensation, R ^c | 0.94 | 0.88 | 0.86 | 0.84 | 0.89 | 0.94 | 0.86 |
| Degree of polymerization, P _n ^d | 16.7 | 8.3 | 7.1 | 6.3 | 9.1 | 20 | 7.1 |
| Rate of co-condensation, R _{co} ^e | 76X | 77% | 70% | 83% | 80% | 11% | 86% |
| Degree of substitution ^f | | | | | | | |
| Phenol | 2.4 | 2.5 | 2.7 | 2.6 | 2.8 | 3.0 | 3.1 |
| Urea | 2.3 | 1.7 | 1.5 | 1.5 | 1.4 | 1.8 | 1.5 |

^aThe quantities combined formaldehyde and urea are represented by the molar ratio of phenol (F/P) and (U/P)

^b[6] = [1] + [2] + C31 + [4] + [5]

^cR = ([2] + 1/2[3] + [4] + [5])/([7] + [8])

^dP_n = 1/(1 - R)

^eR_{co} (%) = 100[4]/([2] + 1/2[3] + [4] + [5])

^fDegree of substitution: ([II] + 2[3] + [3] + [4])/[7] for phenol; ([4] + 2[5])/[8] for urea.

[12-14], *o*-methylol groups of methylolphenols were shown to be less reactive with urea than *p*-methylol groups. Therefore *o*-methylol groups remained unreacted in fairly large amounts, whereas *p*-methylol groups were found to be consumed completely. These unreacted *o*-methylol groups, however, are considered to have potential reactivity either with functional crosslinking agents or during cure at high temperatures. As the ratio of co-condensation (R_{co}) reached 70-86% in each resin, it was concluded that the sequence was composed mainly

of the co-condensation. This fact also was supported by the ratios of urea incorporated into these resins.

5. Synthesis of co-condensed resins (resin II)

UF concentrate is a kind of urea-formaldehyde resin prepared under acidic conditions with a high molar ratio of formaldehyde to urea (F/U) such as greater than 2.5. Several UF concentrates were synthesized by changing

the F/U molar ratio and the reaction pH. UF concentrate was adjusted at the target pH level between 2.0 and 4.5, and then phenol was added. The amounts of phenol added were determined by the molar ratio of F/U/P. For example, when the UF concentrate prepared with F/U = 3.0 (973 g of 37% formalin and 240 g of urea) was used, 418 g of 90% phenol (4 mol) was added at room temperature with stirring. The mixture was adjusted again to the target pH, and maintained at 90°C for a certain time. Several samples were prepared by changing the pH and reaction time. The resins thus obtained were called 'resin II'. When the reaction was performed under a strongly acidic condition for a long reaction time, oily precipitates were produced.

The resin II was generally soluble in alkaline conditions. It was adjusted to pH 9.0-10.5 with sodium hydroxide at room temperature, and heated at 90°C for 30 min with constant stirring. Several samples were prepared by changing the alkaline condition. After these treatments, the resol-type co-condensed resin was obtained.

Fig. 6 shows the ^{13}C -NMR spectrum of a whole product (resin II) from the reaction of UF concentrate and phenol under strongly acidic conditions, in which the signals due to co-condensed methylene carbons are clearly observed at around 44 ppm as well as those due to free formaldehyde and unreacted phenol [1,3]. A longer reaction time resulted in the formation of oily precipitates which had larger amounts of co-condensed methylene linkages than self-condensations between urea residues or phenolic rings, as shown in Table 3, where chemical shift assignments and quantitative determination are referred to our reports [3]. Since it was also shown in Fig. 3 that resin II had a large amount of unreacted phenol as well as free formaldehyde consisting of many kinds of methylene glycol species, synthesis of the resol-type co-condensed resins was attempted by treatment under alkaline conditions. The resol-type co-condensed resin thus obtained was shown to contain large amounts of phenolic methylol group and methylene linkages in condensation as shown in Table 3, although it had self-condensed units between urea residues or

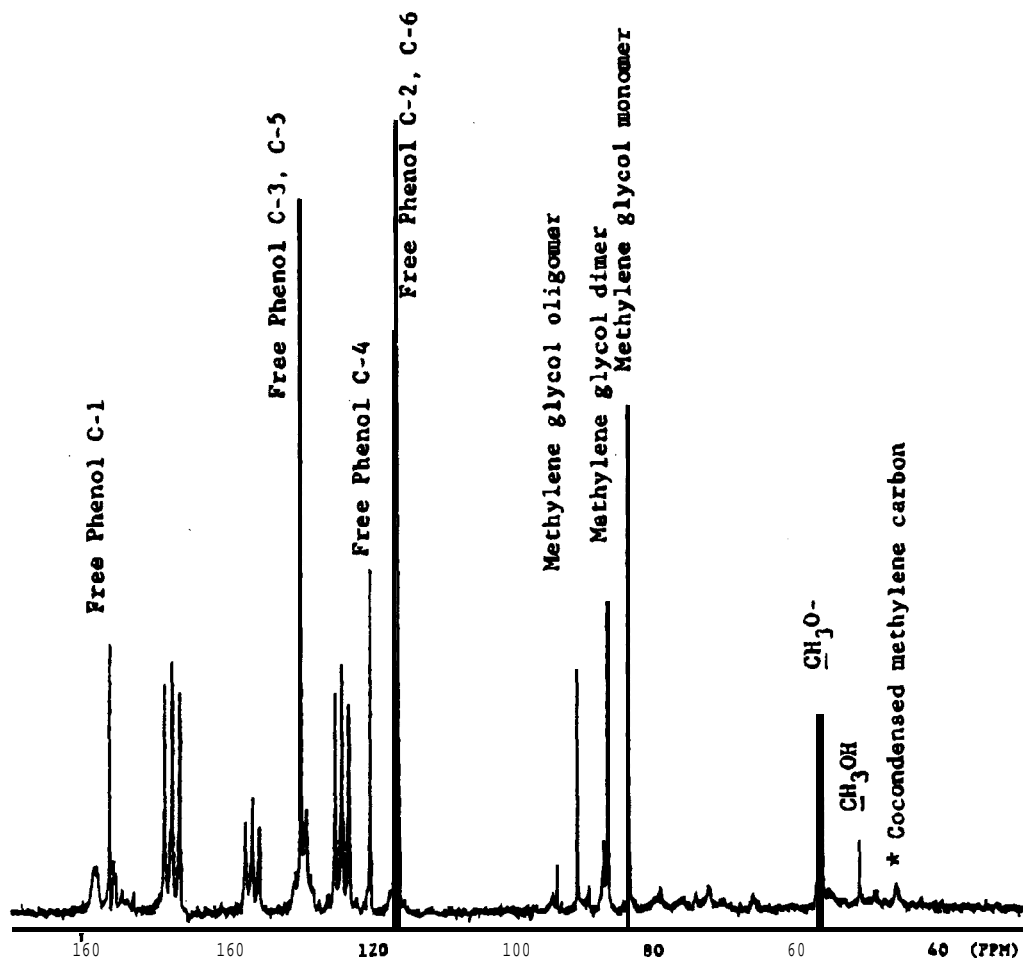


Fig. 6. ^{13}C -NMR spectrum of phenol-urea-formaldehyde co-condensed resin (resin II) with the molar ratio of F/U/P = 4.0/1/1 in pyridine- d_5 solution.

Table 3
 ^{13}C -NMR analysis of co-condensed resin synthesized from UF concentrate and phenol

| Structure | Ratio to total F (%) | |
|--|----------------------|------------|
| | Resin II-1 | Resin II-2 |
| Methylene linkage | | |
| co-condensation $\text{Ph}-\text{CH}_2-\text{N}=\text{O}$ | 66 | 25 |
| self-condensation $\text{Ph}-\text{CH}_2-\text{Ph}$ | 4 | 9 |
| self-condensation $\text{N}-\text{CH}_2-\text{N}=\text{O}$ | 3 | 12 |
| Dimethylene ether linkage | | |
| self-condensation $\text{N}-\text{CH}_2\text{OCH}_2-\text{N}=\text{O}$ | 25 | 6 |
| co-condensation $\text{Ph}-\text{CH}_2\text{OCH}_2-\text{N}=\text{O}$ | 3 | 3 |
| Methylol group | | |
| urea residue $\text{N}-\text{CH}_2\text{OH}$ | 2 | 3 |
| phenol ring $\text{Ph}-\text{CH}_2\text{OH}$ | 0 | 42 |

Note: Both resins were synthesized with the molar ratio of F/P/U = 3/1/1. Resin II-1 was the oily precipitate and resin II-2 was the resol-type resin obtained from resin I.

phenolic nuclei to some extent as well as dimethylene ether linkages. It should be noted that this resin can be cured like resol, and that its synthetic method is quite simple for practical applications.

6. Analysis of curing processes and thermal properties of resol-type co-condensed resins

The successful synthesis of co-condensed resins by reacting a mixture of methylolphenols and urea has been introduced, and these resins were named 'resin I'. Further, another method to synthesize phenol-urea-formaldehyde co-condensed resins (resin II) was introduced in the previous section. Moreover, it was found that this co-condensed resin can be converted into a resol-type resin by a simple alkaline treatment. Since these co-condensed resins seem to cure like resols, an investigation of their curing behavior and thermal properties were attempted by means of torsional braid analysis (TBA).

The curing process of the co-condensed resin (resin II) synthesized from methylolphenols and urea was compared with that of a commercial resol, a commercial UF resin and a blended resin of resol and UF resin by the TBA method. This method is well known for discriminating the dynamic mechanical variation of curing processes for thermosetting resins as a function of time or temperature. The changes of relative rigidity, G_t/G_0 , of four resins are compared in Fig. 7. The curing process of the commercial resol is well demonstrated by a remarkable increase of relative rigidity. Both gelation and the curing process involving the removal of water were complete when the relative rigidity began to drop slightly. This drop was considered to be due to shrinkage of the cured resin.

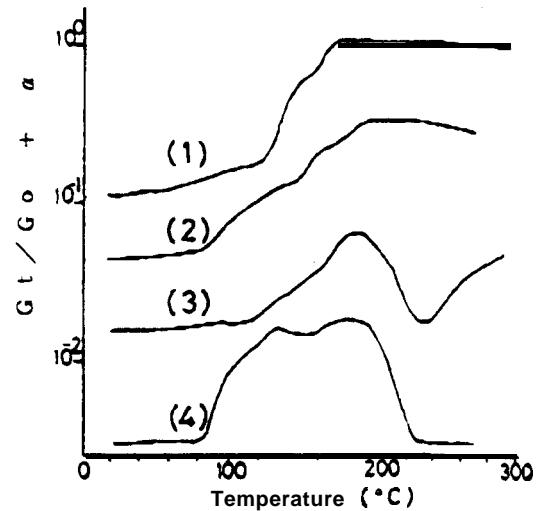


Fig. 7. Torsional braid analysis on the curing reaction of various resins: (1) a commercial resol, (2) co-condensed resin (resin I) with pH 3.0, (3) mechanical blend of UF resin and resol with ammonium chloride, (4) commercial UF resin with ammonium chloride.

In the curing process of UF resin catalysed with ammonium chloride, the curing reaction began at 80°C and had almost finished at 135°C (Fig. 7). After completion of curing, the resin began to decompose at about 200°C as indicated by the remarkable drop in the relative rigidity. The blended resin of resol and UF with ammonium chloride showed quite a different curing process from that of resol itself or UF resin itself (Fig. 7). On the other hand, the chemically co-condensed resin (resin I) followed almost the same curing process as resol except for the cure beginning at the lower temperature of 80°C. Also, the relative rigidity of the co-condensed resin did not decrease obviously after completing the curing reaction. Therefore, it is concluded that co-condensed resin has as high a heat resistance as the resol.

The resol-type co-condensed resin also exhibited a curing process and heat resistance quite similar to those of the resol, as shown in Fig. 8. It should be noted that a great difference could be observed between the thermal properties of the two types of co-condensed resin (resin I and resin II) and the blended resin (comprising resol and UF resin with ammonium chloride).

Fig. 9 shows the results of dynamic mechanical measurements of the resol-type co-condensed resins synthesized with different molar ratios (F/U/P) after curing at the alkaline condition of pH 10.0. The resin prepared with F/U/P = 3/1/2 showed a remarkable drop of relative rigidity at about 160°C, caused by a lower crosslinking density owing to a shortage of formaldehyde at preparation. A similar drop in relative rigidity at about 200°C was observed for the resin with F/U/P = 3/1/0.5. This phenomenon would result from a low heat resistance owing to the self-condensed networks of UF resin, because the amount of phenol incorporated into the co-condensed resin was low.

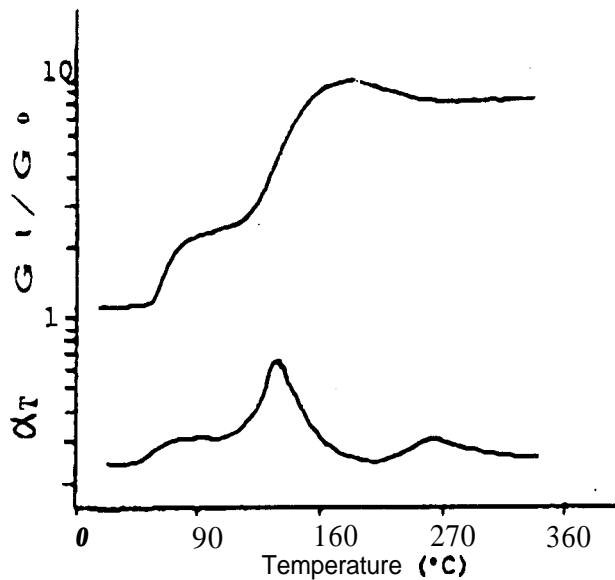


Fig. 8. Torsional braid analysis on the curing reaction of the resol-type co-condensed resin at pH 9.5 (resin II).

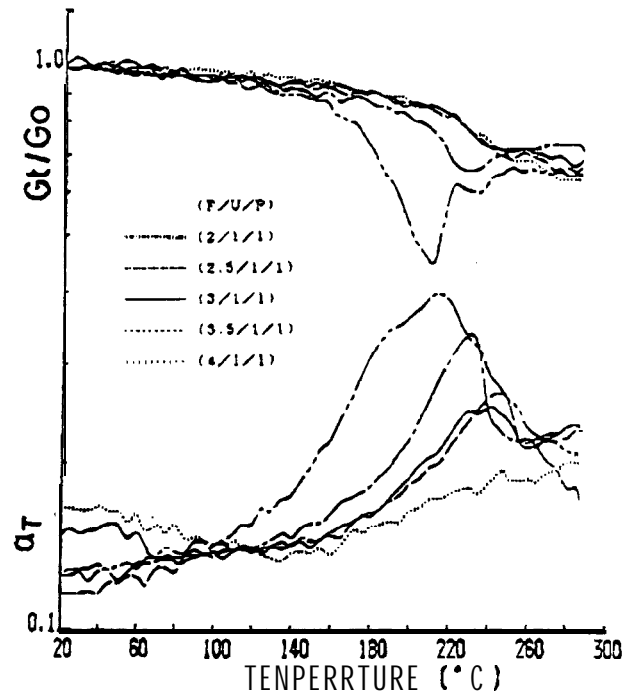


Fig. 10. Effects of the synthetic molar ratio (F/U/P) on dynamic mechanical properties for resol-type co-condensed resin cured under pH 10.0 at 150°C for 30 min.

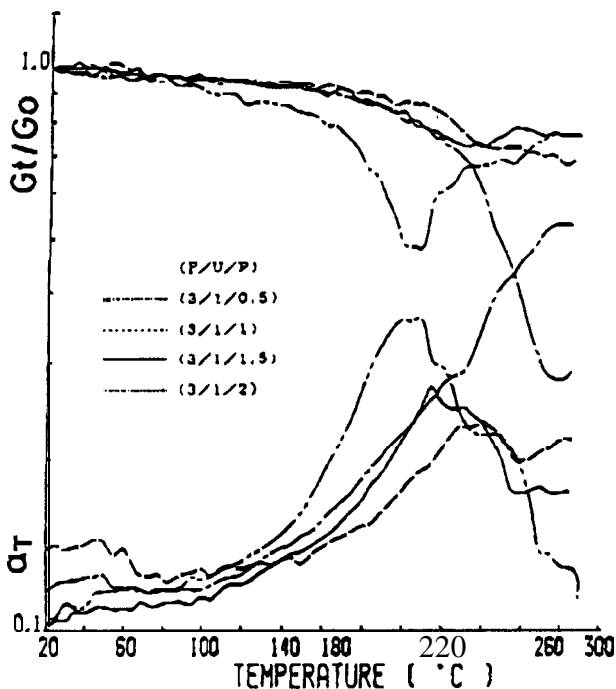


Fig. 9. Effects of the synthetic molar ratio (F/U/P) on dynamic mechanical properties for resol-type co-condensed resins cured under pH 10.0 at 150°C for 30 min.

Fig. 10 shows the effects of formaldehyde content on the thermal properties of cured resins, where the molar ratio of urea to phenol was kept constant at $U/P = 1/1$. It was observed that two resins having $F/U/P = 2/1/1$ and $2.5/1/1$ displayed a low heat resistance. On the other hand, the three resins of $F/U/P = 3/1/1$, $3.5/1/1$ and $4/1/1$

showed a high heat resistance like resol. Therefore, these molar ratios were considered to be desirable to obtain the effects of co-condensation.

7. Apparent activation energy of gelation

Arrhenius plots of gelation time were compared at various pHs for co-condensed resins with the molar ratio of $F/U/P = 3.5/1/1$, and with those for UF resin and resol at pH 11.1. Apparent activation energies calculated for three kinds of resin are summarized in Table 4. A great difference between the UF resin and resol, due to the difference in reactivity, was recognized. On the other hand, the resol-type co-condensed resin had similar values of apparent activation energy to the resol, and its pH dependence was quite low. Therefore, it can be concluded that the gelation or curing of the resol-type co-condensed resin was dominated by the self-condensations between phenolic nuclei via the formation of methylene linkages.

8. Adhesive performance of resol-type co-condensed resin

The resol-type co-condensed resins seem to have practical application for wood adhesives since they can be cured like industrial resols. Their adhesive qualities were evaluated according to a JAS plywood test. The

Table 4
Comparison of apparent activation energies of gelation among resol-type co-condensed resin, UF resin and PF resins

| Type of resin | Reaction pH | Apparent activation energy, E_a (kcal mol ⁻¹) |
|--------------------|-------------|---|
| UF resin | 11.1 | 32.9 |
| PF resin | 11.1 | 24.5 |
| Co-condensed resin | 9.6 | 24.1 |
| | 10.0 | 23.9 |
| | 11.1 | 22.8 |

preliminary results of plywood tests are summarized and compared with those from a commercial resol as shown in Table 5, where the effects of the synthetic molar ratio and hot-press temperature were investigated as variables. The resins synthesized with the lower molar ratio of F/U/P = 3/1/1 generally had a poor water resistance in both a 4 h cyclic boil test and a 72 h boil test, but had good adhesive strengths in a normal dry shear test. This result is probably caused by a low crosslinking density. On the other hand, the resin synthesized with F/U/P = 4/1/1 displayed a high water resistance after soaking in boiling water for 72 h and passed the JAS requirement (7 kgf cm⁻²) for the special grade of structural plywood. However, the effect of hot-press temperature was obvious, and a low temperature of 130°C did not give a high water resistance after soaking in boiling water. This result may be due to a low resin pH (below 10.0), compared with the resol pH of 10.6. For resol, it is

well known that a weak alkaline condition requires a longer curing time to attain a satisfactory adhesive strength. Therefore, further investigation by changing the synthetic molar ratio and alkaline conditions may improve the adhesion properties,

The adhesive strength of a normal dry shear test and a 72 h boil test were investigated by changing the molar ratio and curing temperature while curing pH was maintained at 10.0. The results are shown in Table 6, where the effects of changes in the molar ratio on adhesive strengths were not obvious in a normal test. On the other hand, it was clearly observed that adhesive strengths in a 72 h boil test were dependent on the molar ratio, and that a molar ratio of between 3.5/1/1 and 4.5/1/1 was desirable to pass the JAS minimum shear strength value. Simultaneously, a plywood curing temperature higher than 150°C was required to pass the standard value. These results are identical to those obtained in the preliminary test as shown in Table 6.

The effects of curing pH on both adhesive strengths were determined at three levels of curing temperature while keeping a constant molar ratio of F/U/P = 3.5/1/1. The normal dry shear tests displayed the pH dependence on adhesive strength at every curing temperature as shown in Table 7. Furthermore, it was found that the pH dependence became obvious as the curing temperature was lowered. The 72 h boil tests also displayed the same pH dependence in Table 7. It can be concluded that the curing temperature is the most important among these three factors to obtain a high adhesive strength in a 72 h boil test

Table 5
Results of adhesive tests of mol-type phenol-urea-formaldehyde co-condensed resins for plywood

| Resin | Molar ratio (F/U/P) | Resin content (%) | Viscosity (P) | Hot press temp. (°C) | Adhesive strength (kgf cm ⁻²) (w.f. %) ^a | | |
|-------|---------------------|-------------------|---------------|----------------------|---|--------------|-----------|
| | | | | | Normal | 4 h/4 h boil | 72 h boil |
| Resol | — | 46.0 | 44.3 | 130 | 16.9 (35) | 12.7 (50) | 12.2 (55) |
| | | | | 150 | 18.2 (85) | 12.4 (80) | 14.3 (70) |
| 3-1 | 3/1/1 | 53.1 | 3.6 | 130 | 6.6 (5) | 0 | 0 |
| | | | | 150 | 13.0 (25) | 1.6 (0) | 0 |
| 3-1* | | | | 150 | 13.2 (25) | 6.6 (0) | 0 |
| 3-2 | 3/1/1 | 53.0 | 9.4 | 130 | 8.7 (0) | 0 | 0 |
| | | | | 150 | 12.9 (10) | 5.3 (0) | 0 |
| 4-1 | 4/1/1 | 49.2 | 24 | 130 | 5.3 (0) | 0 | 0 |
| | | | | 150 | 12.8 (20) | 4.9 (5) | 0 |
| 4-1* | | | | 150 | 15.5 (25) | 9.6 (0) | 8.6 (5) |
| 4-L | 4/1/1 | 55.0 | 110.3 | 130 | 11.4 (15) | 0 | 0 |
| | | | | 150 | 13.1 (85) | 10.8 (35) | 10.6 (10) |

Note: All resins had 10 pbr of coconut shell powder added except for resins 3-1* and 4-1*, which had 20 pbr
^aw.f. is wood failure.

Table 6

Effects of the synthetic molar ratio of **resol-type co-condensed resin** on adhesive strength for curing at **pH 10.0** at various hot-press temperatures

| Molar ratio (F/U/P) | Hot-press temp. (°C) | Adhesive strength (kgf cm ⁻²) (w.f., %) | |
|---------------------|----------------------|---|------------------|
| | | Normal test | 72 h boil |
| 3/1/1 | 130 | 10.2 (0) | 0 (0) |
| | 140 | 14.2 (5) | 0 (0) |
| | 150 | 16.4 (0) | 4.6 (0) |
| | 160 | 15.7 (70) | 10.0 (45) |
| 3.5/1/1 | 130 | 8.8 (0) | 0 (0) |
| | 140 | 13.9 (35) | 0 (0) |
| | 150 | 16.9 (20) | 7.5 (0) |
| | 160 | 18.2 (85) | 11.4 (35) |
| 4/1/1 | 130 | 122 (5) | 0 (0) |
| | 140 | 15.7 (60) | 5.0 (0) |
| | 150 | 15.4 (20) | 7.7 (10) |
| | 160 | 15.7 (40) | 9.7 (20) |
| 4.5/1/1 | 130 | 11.3 (0) | 0 (0) |
| | 140 | 13.0 (0) | 0 (0) |
| | 150 | 17.9 (30) | 7.1 (0) |
| | 160 | 19.0 (65) | 10.4 (40) |

Table 7

Effects of curing **pH** on adhesive strength for **resol-type co-condensed resin** of F/U/P = 3.5/1/1 for various hot-press temperatures

| Curing pH | Hot-press temp. (°C) | Adhesive strength (kgf cm ⁻²) (w.f., %) | |
|-----------|----------------------|---|----------------|
| | | Normal test | 72 h boil |
| 10.2 | 130 | 10.5 (0) | 0 (0) |
| | 140 | 13.7 (0) | 0 (0) |
| | 150 | 15.8 (0) | 4.2 (0) |
| 10.5 | 130 | 12.6 (0) | 0 (0) |
| | 140 | 14.2 (0) | 0 (0) |
| | 150 | 16.7 (0) | 7.1 (0) |
| 11.2 | 130 | 14.6 (5) | 1.6 (0) |
| | 140 | 15.7 (10) | 6.1 (0) |
| | 150 | 17.6 (15) | 7.6 (0) |
| 11.5 | 130 | 14.9 (15) | 5.1 (0) |
| | 140 | 15.6 (30) | 6.3 (0) |
| | 150 | 17.4 (25) | 7.5 (0) |
| 11.9 | 130 | 16.8 (50) | 6.8 (0) |
| | 140 | 17.4 (45) | 7.1 (0) |
| | 150 | 19.6 (75) | 8.7 (0) |

9. Conclusion

It is of importance that the alternating copolymer was obtained from the reaction of urea with **trimethylol-phenol** and that practical co-condensed resins, which contained certain amounts of self-condensed linkages between phenols, could be obtained easily by the

reaction of a crude polymethylolphenol mixture and urea. Further, it should be noted that the **resol-type** co-condensed resins were prepared by simple methods from the **UF** concentrates and phenol. Since these **resol-type** resins can be considered for practical applications such as **resol** wood adhesives, further development is encouraged.

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