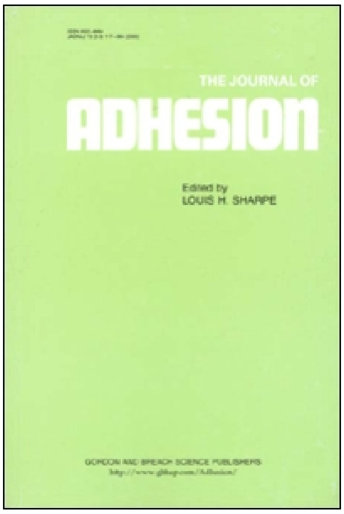

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Adhesives from Waste Paper by Means of Phenolation

Hirokuni Ono[a]; Tatsuhiko Yamada[b]; Yasunori Hatano[b]; Kenji Motohashi[c]
[a] Faculty of Agriculture, The university of Tokyo, Tokyo, Japan [b] Ministry of Agriculture Fisheries and Forestry, Forestry and Forest Products Research Institute, Tsukuba Ibaraki-ken, Japan [c] Ministry of Construction, Building Research Institute, Tsukuba Ibaraki-ken, Japan

To cite this Article Ono, Hirokuni , Yamada, Tatsuhiko , Hatano, Yasunori and Motohashi, Kenji(1996) 'Adhesives from Waste Paper by Means of Phenolation', The Journal of Adhesion, 59: 1, 135 — 145

To link to this Article: DOI: 10.1080/00218469608011083

URL: http://dx.doi.org/10.1080/00218469608011083

J. Adhesion, 1996, Vol. 59, pp. 135–145
Reprints available directly from the publisher
Photocopying permitted by license only

Adhesives from Waste Paper by Means of Phenolation*

HIROKUNI ONO**

Faculty of Agriculture, The university of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113, Japan

TATSUHIKO YAMADA, YASUNORI HATANO

Forestry and Forest Products Research Institute, Ministry of Agriculture, Fisheries and Forestry, Tsukuba, Ibaraki-ken, Japan

and

KENJI MOTOHASHI

Building Research Institute, Ministry of Construction, Tsukuba, Ibaraki-ken, Japan

(In final form January 16, 1996)

Recently the effective use of woody materials has been of interest from the viewpoint of forestry preservation. Newsprint is one of the most abundant of woody materials which are discarded into the environment after use. They would be, however, easily recovered from the market.

The application of phenolation to cellulosic materials is one possibility for the utilization of waste papers. Phenolation is a newly-established method by which lignocellulosic materials are completely converted to substances soluble in some polar organic solvents.

Waste newsprint is subjected to phenolation in the presence of an acidic catalyst. The phenolated product was then methylolated in order to prepare alkaline curable adheisve resins. The chemical characteristics of the phenolated products were studied and the properties of plywood adhesives from them were evaluated. The results indicated that cellulose decomposed and reacted with phenol, producing complicated compound having a phenolic moiety during phenolation and that the compound reacted with formaldehyde, leading to resinous substance which could be thermoset.

The adhesives from the resins of phenolated newsprint provided comparable properties to a commercial phenolic resin in cure behavior, resin viscosity and tensile bond strength. The products of cellulose phenolation, therefore, are expected to be a source of wood adhesives comparable with phenolic resins.

KEY WORDS: Cellulosic materials; phenolated waste newsprint; preparation of adhesive resins of plywood; adhesive formulation; gel permeation chromatography (GPC); NMR spectroscopy; torsional braid analysis.

INTRODUCTION

Substitution of inexpensive substances for phenolic resin is of interest, since phenolic resin is a rather expensive wood adhesive with excellent properties. Substances reacting with or dissolving in phenol would be suitable for phenolic wood adhesives

---

*Presented at the International Adhesion Symposium, *IAS'94 Japan*, at the 30th Anniversary Meeting of the Adhesion Society of Japan, Yokohama, Japan, November 6–10, 1994.

**Corresponding author.

from the viewpoint of adhesive properties. The utilization of phenolic wood components such as lignin and tannin incorporated with phenol resin as wood adhesives has already been studied[1,2,3]. Lignin and tannin have, however, some limitations in their obtainment as resin sources. Most lignin is burnt as a substitute fuel in paper mills and tannin is produced by extraction from barks only in some countries in the Southern hemisphere. It would be beneficial from an economic viewpoint, therefore, if inexpensive woody substances, instead of wood components, could be converted to wood adhesives without sacrificing adhesion properties.

In recent years the effective use of woody materials has been of interest from the viewpoint of environmental protection. Printing paper is one of the most abundant products among woody materials. Waste newsprint used to be collected and recycled in paper making systems. Since its recycling has been dependent on economic conditions, it has often been incinerated or discarded into the environment after use.

Phenolation has been developed in order to convert lignocellulosic materials into substances as polymer sources for adhesives and molding compounds[4,5]. The acidic degradation of woody components and the subsequent reaction of the degradation products with phenol have been considered to occur in phenolation[6].

Its application to waste paper would be one possibility to utilize woody materials effectively. The objectives of this research include preparation of adhesives from waste paper by phenolation and evaluation of their performance.

EXPERIMENTAL

Materials

Waste newspaper was shredded into strips *ca.* one mm wide and 30 mm in length and in this form was used for phenolation. It reportedly contained about 20% of lignin. Chemical reagents used for phenolation were the extra-grade in the Japanese industrial standard. A commercial phenolic resin (resin D-17 from Ohshika Shinko Ltd. Co.) was used for behavior and bond strength measurement for comparison with phenolated paper-based resins. A commercial catalyst (Hot-P from Ohshika Shinko Ltd. Co.) and a commercial wheat flour as extender (Akahana from Nissin Seihun Co. Ltd.) were used for adhesive formulation.

Phenolation of Newsprint

The phenolation of shredded waste newsprint was conducted by a method similar to that described in previous reports except for the addition procedure of the shredded newsprint[6]. Since it had been found difficult to obtain a homogeneous reaction mixture when all the newsprint was charged at once, it was added to phenol in portions during the early stages of the reaction procedure. The charge ratio of phenol to newsprint was 2 to 1 (wt./wt.) and sulfuric acid (0.8 mMol/g of the newsprint) was used as a catalyst.

After charging the fixed amount of the newsprint to the phenol stepwise, stirring of the contents at 100°C was continued until it became a homogeneous slurry, followed by reaction at 150°C until the contents dissolved completely in acetone. The product was stored after neutralization with sodium hydroxide aqueous solution.

Preparation of Adhesive Resins

The functionality of the phenolated newsprint (PN) was calculated to be 1.66 per 100 g[7]. Three methylolated resins from PN were prepared by varying the formaldehyde charge ratio in a manner similar to the preparation of resole-type phenolic resins[6]. The charge ratios for resin A, resin B and resin C were 1 mol, 1.33 mol and 1.66 mol per 100g of the PN, respectively. After adjusting the initial pH to around 10 with sodium hydroxide, the reactions of PN and the fixed mole ratios of formaldehyde as formalin were conducted at 55 ± 5 °C for six hours. The resulting resins were condensed with an evaporator and their solids contents were adjusted to around 40%. The resins were then stored in a refrigerator for further use.

Adhesive Formulation

Adhesives for bond strength testing consisted of 100 parts of the phenolated newsprint-based resin, 10 parts of the wheat flour and 4 parts of the commercial catalyst. This formulation is recommended for phenolic resins by Japanese adhesive manufacturers.

Preparation of Plywood Panels and Test Specimens

A three-ply plywood specimen (30 x 30 cm) was prepared for each adhesive from 1.2 mm thick Red Meranti (Shorea Spp.) veneers whose moisture content had previously been adjusted to around six percent. The adhesives were spread on the veneer by a roller coater at the spreading rate of about 330 g/cm^2 for double glue lines. The assemblies of the veneers were first pressed at ambient temperature for one hour at 8 Kgf/cm^2, and then hotpressed at 135°C at 10 Kgf/cm^2 for 3min. These plywood preparation conditions were in accordance with the applicable Japanese Industrial Standard (JIS-K 6802).

Thirty test specimens were cut from the plywood. They were notched to the depth of the adhesive layer on either side 13 mm apart. Fourteen of them were randomly selected into two groups, and a tensile test was conducted for each group under different conditions. The site and shape of a specimen is illustrated in Figure 1.

Tensile Shear Strength Measurement

The tensile shear bond streangth was determined in accordance with the Japanese Agricultural Standard for constructive plywood (normal state and after 72-hour boilling) by using a Toyo Seiki Storograph W tensile tester. In the normal state test, the test specimens were conditioned for at least 48 hours at 25°C under a relative humidity of 65 percent and the tensile shear bond strengths of the conditioned specimens were measured. In the 72-hour boiling test, the specimens were subjected to immersion in boiling water for 72 hours, followed by immersion in running tap

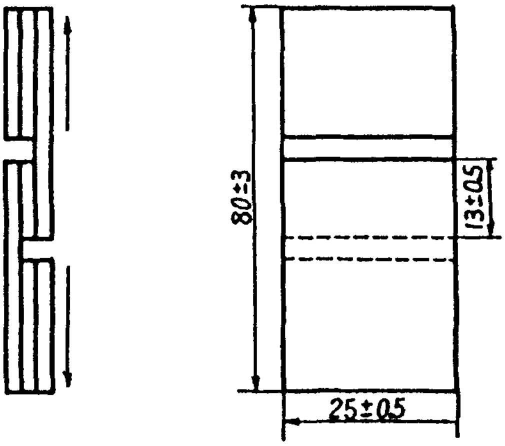

FIGURE 1 Size and shape of tensile test specimen (dimensions in mm).

water until cooled and the bond strengths were measured in the wet state. The bond strengths of 14 specimens in a group were averaged.

Gel Permeation Chromatography (GPC)

Molecular weight distribution of PN was determined at 40°C in tetrahydrofuran as the mobile phase by using a Toyo Soda HPLC-802 UR gel permeation chromatograph equipped with two 60 cm polystyrene gel columns in series (TSK-GEL H G2500 and G1000). The chromatograms were monitored by a refractometer.

NMR Spectroscopy

^{13}C-NMR measurements were carried out using either a JEOL JMN-GSX 400 spectrometer or a Bruker AC300 spectrometer. The analysis was conducted in DMSO-d_6 and D_2O mixture (10/1 vol/vol) for PN and in Pyridine-d_5 for methylolated PN resins at 27°C by using a complete decoupling technique.

Torsional Braid Analysis (TBA)

The mixtures of the phenolated newsprint-based resins and the phenolic resin with the catalyst were coated on a glass braid, and their cure behavior was examined by using a RHESCA RD-1100A torsional braid analyzer. The heating rate was 1°C/min.

RESULTS AND DISCUSSION

Phenolation of Waste Newsprint

Waste newsprint was selected as a source material for phenolation since pure cellulose had been easily phenolated in our previous work. It is considered to be a

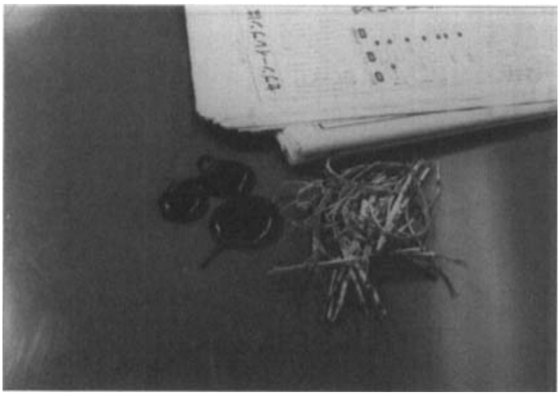

PHOTO 1 Appearance of phenolated newsprint. See Color Plate II.

technical advantage that no filtration process is needed for newsprint after phenolation since it contains no mineral substances.

The appearance of PN obtained after phenolation of waste newsprint is shown in Photo 1. The shredded newsprint was converted into PN as a black, viscous, tar-like substance. It was soluble in polar organic solvents such as acetone, dioxane, pyridine and dimethylsulfoxide, as well as in alkaline aqueous solution, which was very advantageous for alkaline-catalyzed methylolation with formaldehyde.

The molecular weight distribution of PN is shown in Figure 2. The GPC profile shows that PN has two main fractions, a high molecular weight one (broad peak

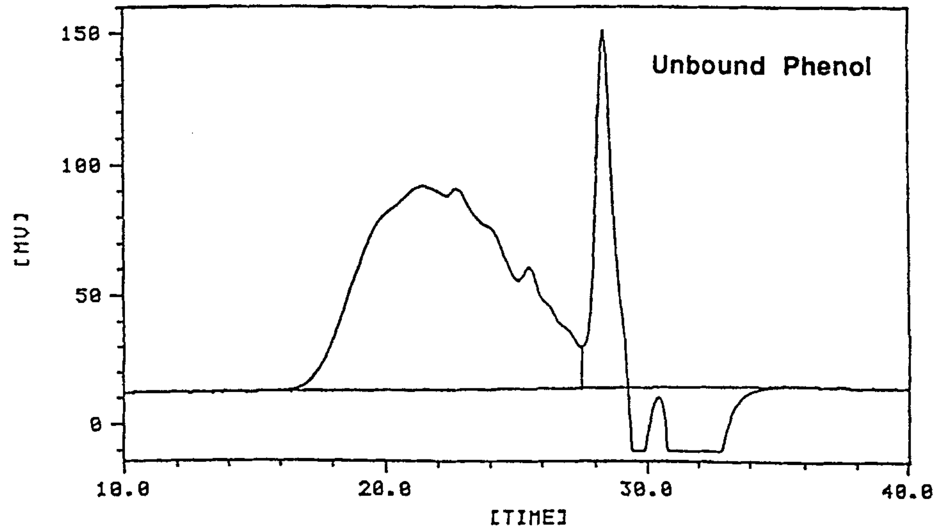

FIGURE 2 GPC profile of phenolated newsprint.

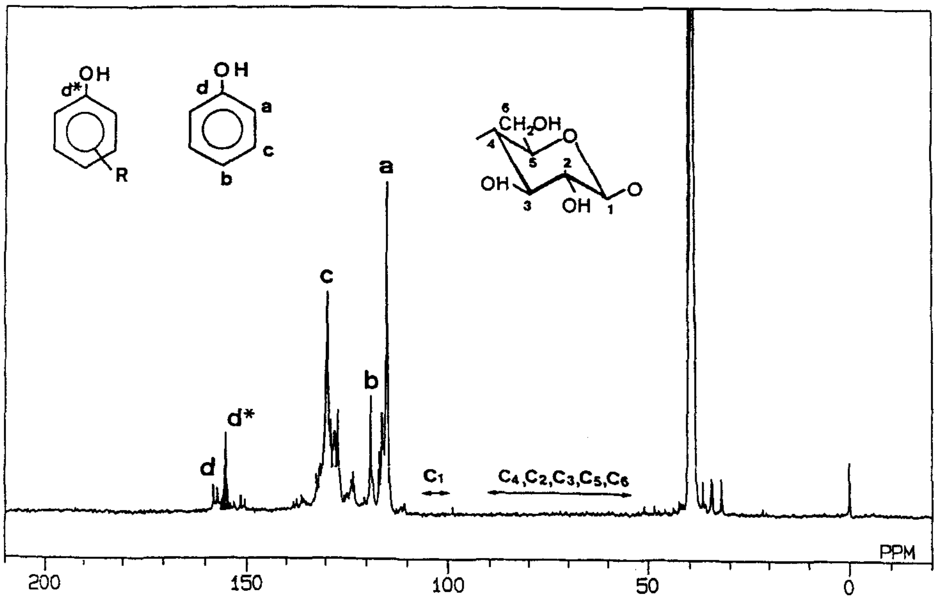

FIGURE 3 Carbon-13 NMR spectrum of phenolated newsprint in DMSO-d_6 and D_2O mixture.

group from 17 to 28 min. elution) and a low molecular weight one (sharp peak at 28.8 min. elution). The low molecular fraction was assigned to phenol which had not reacted with the newsprint (unbound phenol). The high molecular weight fraction is the resultant of phenolation. PN was found to contain 19% unbound phenol by weight based on the calculations of the GPC analysis[7].

The ^{13}C-NMR spectrum of the high molecular weight substance after removal of unbound phenol from the PN is shown in Figure 3. The removal of unbound phenol was conducted by steam-distillation and was assured by the absence of the phenol peak in the GPC profile. The spectrum provides strong signals due to aromatic ring carbons over the range from 110 to 160 ppm. The complicated signal pattern of the high molecular fraction in PN suggests that phenol reacts with the newsprint. Phenol has a signal at 157.3 ppm due to the carbon with a hydroxy group. This signal shifts upfield when phenol is substituted. The signal at 155.4 ppm is assigned to the carbon having the hydroxy group in bound phenol. The spectrum clearly indicates that the main chemical species in PN possess phenolic moieties.

Note that no signal exists in the range of 50 to 100 ppm where the signals due to the pyranose unit of cellulose are normally observed[8], which demonstrates that the cellulose component could be completely degraded and converted into a different substance.

Since it is reported that cellulose is converted to 5-hydroxy methyl furfural in acidic conditions[9], we temporarily postulate the molecular structures of the main substance of PN as illustrated in Figure 4.

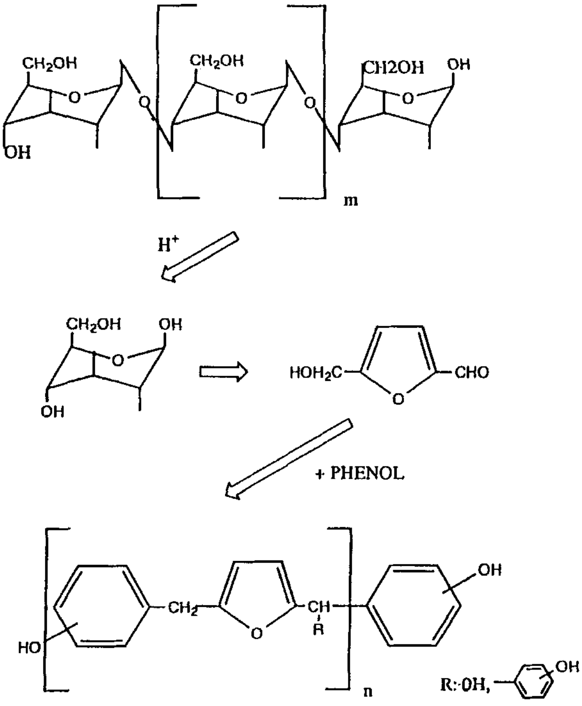

FIGURE 4 Proposed phenolation reaction of cellulose.

Reaction of PN with Formaldehhyde

It is expected that PN would react with formaldehyde since it consists of unbound phenol and a high molecular weight substance which posseses phenolic moieties. The ^{13}C NMR spectrum of the high molecular weight substance treated with formalin in the presence of alkaline catalystis shown in Figure 5 (b). The spectrum exhibits strong signals over the range from 50 to 100 ppm where no signal has been observed in the spectrum of PN. Besides the signal of methyl alcohol and methyleneglycol attributed to reaction products of formalin, the very strong signals due to p-substituted and o-substituted methylol groups are found[10]. It is important that PN reacts with formaldehyde, leading to a methylolated product that would react further with other methylolated products and/or methylolated unbound phenol. We anticipate, therefore, that PN would not work as a filler but would react with formaldehyde and then contribute to the network formation of a thermosetting polymer, when used as an adhesive.

Three PN-based resins with varied formaldehyde charge ratio were prepared. Some properties of these adhesive resins are shown in Table I in comparison with those of a commercial phenolic resin. It was thought that the PN-based resins would have higher viscosity than the phenolic resin. Little difference in resin properties, however, is found among the PN-based resins and the phenolic resin. The viscosity of the PN-based resins are unexpectedly low and meet the Japanese Industrial

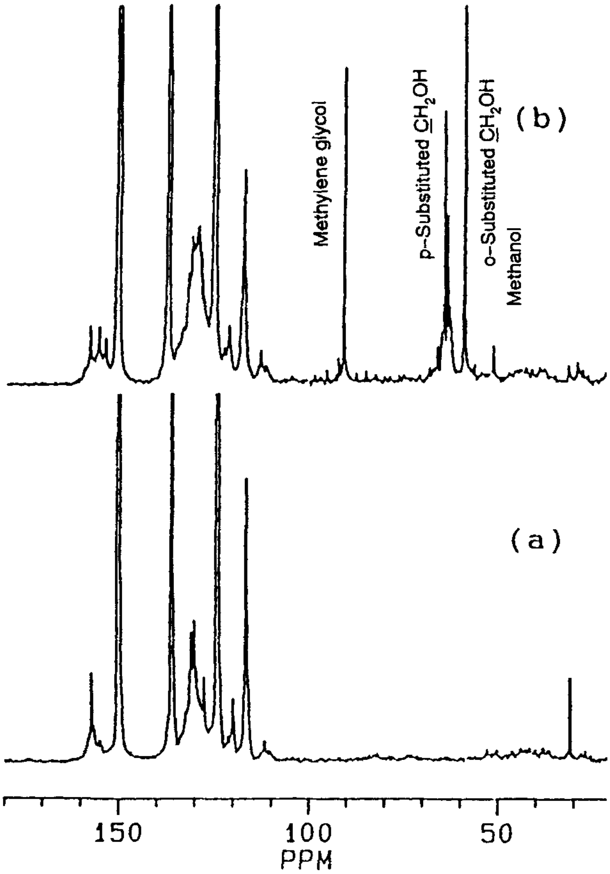

FIGURE 5 Carbon-13 NMR spectra of (a) phenolated newsprint and (b) its methylolated resin in pyridine-d_5.

TABLE I
Properties of PN-Based Adhesive Resins

Resin Name	Solid Content(%)	pH	Viscosity (Poise)
Resin A	41.5	10.0	1.20
Resin B	41.2	10.0	0.91
Resin C	40.5	10.1	0.90
Phenolic Resin	43.2	10.1	0.62
JIS Requirement	38 <	7-12	0.1-1.0

JIS: Japanese Industrial Standard.

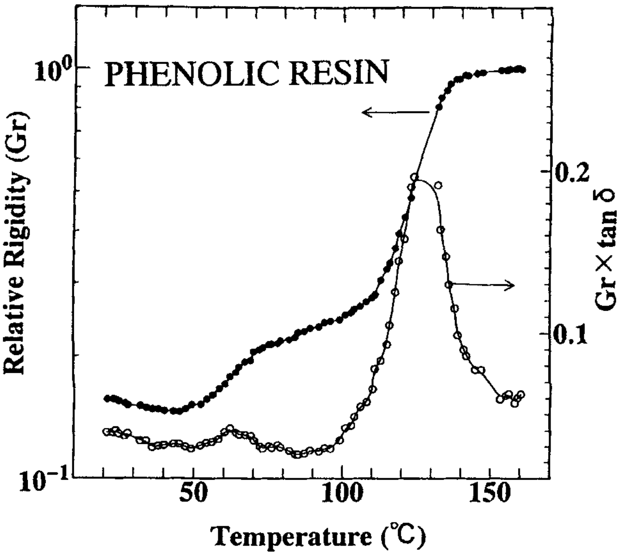

FIGURE 6 Cure behavior of commercial phenolic resin.

Standard (JIS K 6802). This is probably caused by application of lower temperature in the preparation of the resins as compared with that for the phenolic resin. The low viscosity of the resins is an advantage in the usage of conventional spreading machines when applying PN-based resin in a mixture with partly or fully substituted a commercial phenolic resin.

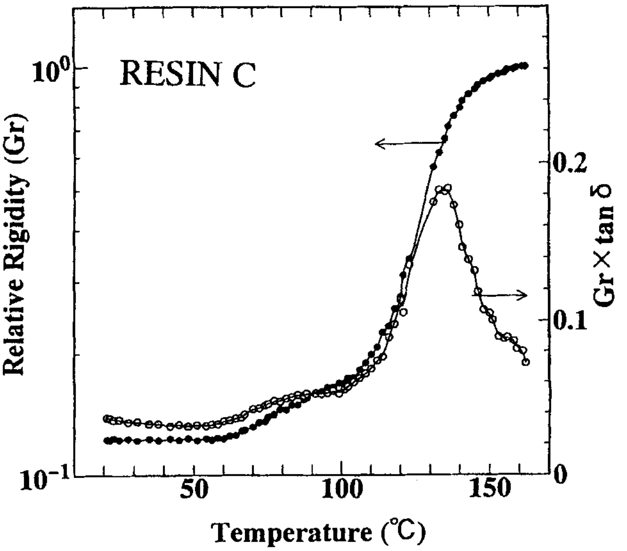

FIGURE 7 Cure behavior of resin C.

TABLE II
Cure Temperature of PN-Based Adhesive Resins

Resin Name	Temperature at Max. kE'' (°C)
Resin A	140
Resin B	136
Resin C	135
Phenolic Resin	132

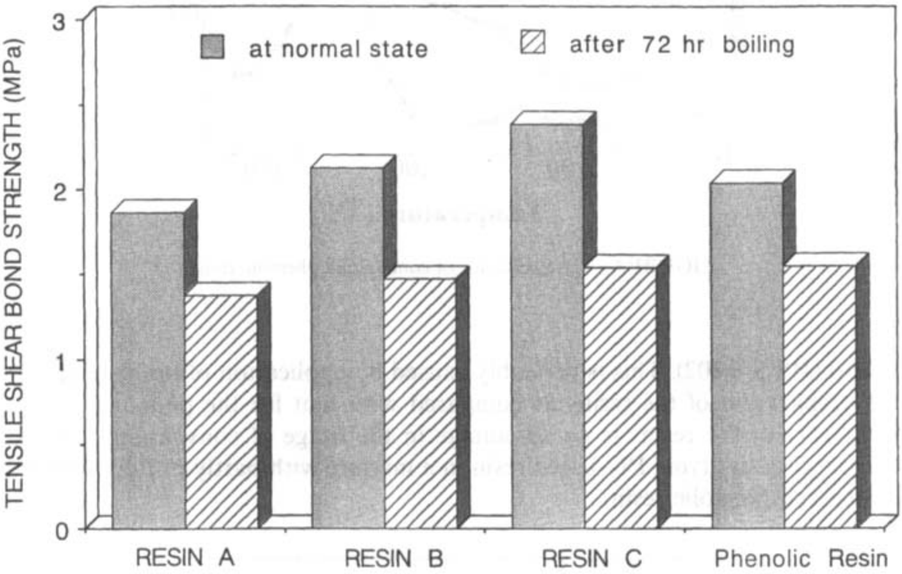

FIGURE 8 Tensile shear strength of phenolated newsprint-based resins and phenolic resin. Formaldehyde charge ratio to the calculated functionality of the phenolated newsprint in Resin A, Resin B and Resin C are 0.6, 0.8 and 1.0, respectively.

Curing Behavior of PN-Based Adhesive Resins

The curing behavior of the phenolic resin and resin C as a typical example of the PN-based resins is shown in Figures 6 and 7, respectively. The apparent cure rate is estimated by the slope of Gr vs. temperature curve. The product (kE'') of loss tangent (tan d) and relative rigidity (Gr) is a physical value related to loss modulus. The temperature of the maximum kE'' is positioned at the beginning of the Gr saturation among the resins. The temperature at the maximum of the product curve, therefore, is considered to be an index of cure temperature of each resin. The cure temperatures of the PN-based resins are shown in Table II. These resins show cure temperatures similar to the phenolic resin. Therefore, the same cure temperature as used for phenolic resin could be applied to these PN-based resins.

Tensile Shear Strength of Adhesives from PN-Based Resin

Tensile shear strength, in a normal state and after 72-hour boiling of the test specimens glued with the PN-based adhesive resins, is shown in Figure 8 in comparison with that of phenolic resin. As the formaldehyde charge ratio nears the stoichiometric ratio, the bond strengths of the PN-based adhesives tend to increase. Resin B provides an almost similar bond strength in the normal state and after 72-hour boiling as compared with the phenolic resin. Resin C provides better bond strength in the normal state and a similar bond strength after 72-hour boiling. Resin A, however, provides poorer results. These findings suggest that a PN-based resin with appropriate formaldehyde charge ratio would provide excellent adhesive properties comparable with phenolic resins.

CONCLUSIONS

Phenol reacts with newsprint, introducing a phenolic functional group into the product. Phenolated newsprint reacts with formaldehyde as phenol does. Phenolated newsprint product therefore, would be converted into a thermosetting resin, in which phenolated newsprint-based adhesive resin would contribute to the network formation of the cured resin.

The phenolated newsprint products would be a potential and economically viable, resin source of adhesives, especially for wood, providing suitable viscosity and excellent adhesion properties comparable with commercial phenolic resins, since newsprint is commonly an inexpensive source for phenolated product.

Acknowledgements

This research was funded by the Japanese Ministry of Agriculture, Fisheries and Forestry under Contract No. BPR-III-1.

References

1. R. Kreibich and R. W. Hemingway, in *Adhesives from Renewable Resources*, R. W. Hemingway and A. H. Conner, Eds. (ACS, Washington, D.C., 1989), Chap. 15.
2. J.-F. Matte and J. Doucet, *Cellulose Chem. Technol.* **22**, 71 (1988).
3. A. Pizzi, *J. Macromol. Rev. Macromol. Chem.*, **C18**(2), 247 (1980).
4. N. Shiraishi, N. Tsujimoto and S. Fu, Japanese Pat. 86/261358 (1986).
5. H. Ono, and K. Sudo, Japanese Pat. 89/217070 (1989).
6. H. Ono, *Mokuzai Kogyo*, **18**(12), 590 (1993).
7. H. Ono, *ibid.* **19**(1), 8 (1994).
8. R. H. Atalla, J. C. Gast and D. W. Sindorf, *J. Am. Chem. Soc.* **102**, 3249 (1980).
9. A. H. Conners, B. R. River and L. F. Lorenz, *Wood Chem. Technol.* **6**(4), 591 (1986).
10. D. D. Werstler, *Polymer* **27**, 757 (1986).