# Viscoelastic Properties of the Phenolic Resin–Polyvinyl Butyral System

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## INTRODUCTION

For the past fifteen years, phenolic resin mixed with polyvinyl butyral and cured at high temperature has been in general use as a coating material for metal sheets and magnetic wires. It is known that polyvinyl butyral mixed with phenolic resin increases the flexibility and adhesiveness of phenolic resin. As the useful properties of this system appear only as a result of curing, it seems desirable to understand the state of dispersion and the structure resulting from curing. However, no elucidation of this question based on experimental results has yet appeared.

In the work reported here, the properties of phenolic resin mixed with polyvinyl butyral were studied by use of viscoelastic and dielectric methods. From among several kinds of phenolic resins[1,2] an ammoniac resol resin made from phenol and formaldehyde with or without o-cresol was chosen for study. The mechanical behavior of the phenolic resin–polyvinyl butyral system seems to indicate that the state of this system changes from homogeneous to heterogeneous under heat treatment at temperatures above 180°C., whereas when heated at below 170°C. the system remains homogeneous. These phenomena were studied primarily, and a model is suggested here for the explanation of this behavior.

Secondly, the chemical reaction between phenolic resin and polyvinyl butyral during the curing process was investigated with the use of model materials, since a chemical reaction was expected to occur in this system.[3]
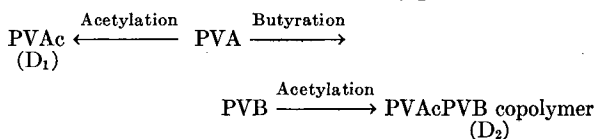
The properties of the cured mixture, as evidenced by the effect of temperature on the dynamic elastic storage modulus $E'$ and the mechanical loss, tan $\delta$, will be discussed. The results of dielectric measurements will be used for confirming the explanation based on dynamic measurements,[4,5] because the dielectric data corresponding to the viscoelastic dispersion in polymers is generally helpful in clarifying and confirming the mechanism under-

lying the mechanical dispersion, and because each of the components in the present specimens is a polar polymer and thus convenient for dielectric measurement.

## EXPERIMENTAL

### A. Specimens

The specimens were made with the use of powders of polyvinyl butyral and derivatives of it which were supplied by Sekisui Chemical Company, Ltd. In investigating the chemical reactions between the phenolic resin and the polyvinyl butyral, PVB, PVAc ($D_1$), and PVB-PVAc ($D_2$) were used as model materials having identical main chain structures but different side groups. These compounds have been prepared from polyvinyl alcohol (PVA of $\overline{DP}$ 285) in the following process:

$$\text{PVAc} \xleftarrow{\text{Acetylation}} \text{PVA} \xrightarrow{\text{Butyration}}$$
$$(D_1)$$

$$\text{PVB} \xrightarrow{\text{Acetylation}} \text{PVAcPVB copolymer}$$
$$(D_2)$$

PVA and PVB were acetylated by Kenyon's method,[6] which appears to be a general procedure for PVA. The analyses of these materials are given in Table I. A number of other types of polyvinyl butyral which are commercially supplied under different designations were also used in this work (see Table II).

The phenolic resins were synthesized from phenol, o-cresol, and formaldehyde under the influence of an aqueous $NH_4OH$ catalyst. One resin was a

TABLE I
Analytical Data for Polyvinyl Butyral and Derivatives

| | Composition, mole-% | | | |
|---|---|---|---|---|
| | Vinyl acetate | Vinyl butyral | Vinyl alcohol | $\overline{DP}$ |
| PVB | 2.1 | 61.3 | 36.6 | 285 |
| PVAc ($D_1$) | 100 | — | — | 360 |
| PVB–PVAc ($D_2$) | 38.7 | 61.3 | — | |

mixture of formaldehyde with phenol o-cresol 60:40 by weight (this is referred to as PR in this paper), and the other consisted simply of phenol and formaldehyde. In each case, the molar ratio of phenol (or phenol + o-cresol) to formaldehyde was 1:1.1. The resins obtained were washed with water and then treated at low pressure (20 mm. Hg) in order to remove the water and other volatile matter.

The test specimens were prepared as follows: The phenolic resins and polyvinyl butyral and its derivatives were separately dissolved in butanol and the resulting solutions were combined in various proportions by weight and mixed well. Films prepared from these solutions by the mercury amalgam technique were cured at a given temperature and for a given length of time. From these films which were 0.2 to 0.5 mm. thick, the test specimens were cut out. All samples except those of unmixed polyvinyl butyral were annealed at 160°C. and cooled gradually to room temperature before measurement. In order to remove residual water and solvent, all the samples were heated at 100°C. in vacuo to constant weight. Between runs, all specimens were kept in vacuo over $P_2O_5$ at room temperature.

## B. Methods

Dynamic mechanical measurements of the specimens over the temperature range of −70 to 200°C. were obtained by use of the vibrating reed method. The apparatus and calculating procedure were essentially those described by other authors.[7] Most of the measurements were made at the frequencies of 50 ± 5 cycles/sec.

The dielectric constant $\epsilon$ and the dielectric loss tan $\delta$ were measured on an inductive ratio arm bridge[8] at 60 cycles/sec.; each value given for dielectric loss in the high temperature region is the total loss less the loss component due to the steady d.c. conductance.

## RESULTS

Figures 1–3 show the dynamic modulus, the mechanical loss, and the dielectric loss versus temperature for PR, PVB, and a mixture of them containing 30% PVB, respectively, cured at 170°C. or 200°C. for 30 min. In Figure 3 (lower graph), for the PR–PVB system cured at 200°C. for 30 min., the data indicate the presence of at least four dispersions, characterized by mechanical loss peaks at about −42°C., 100°C., 160°C., and above 200°C. In order to ascertain the mech-
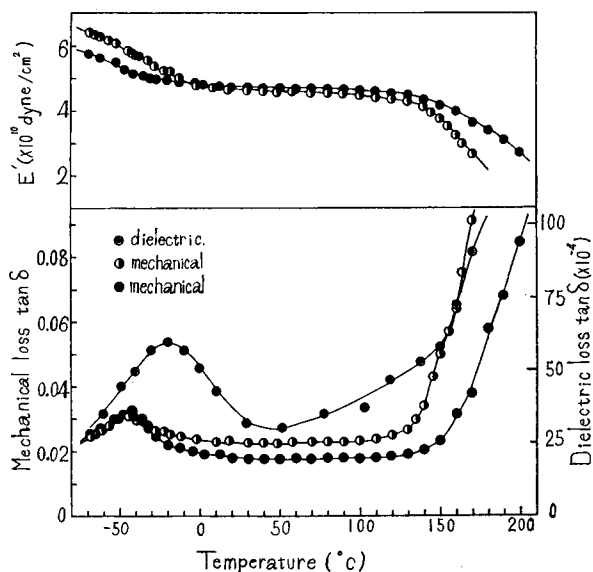


Fig. 1. Dynamic elastic storage modulus for PR: (⊙) dielectric, cure 30 min. at 200°C. (60 cycles/sec.); (◖) mechanical, cure 30 min. at 170°C.; (●) mechanical, cure 30 min. at 200°C.
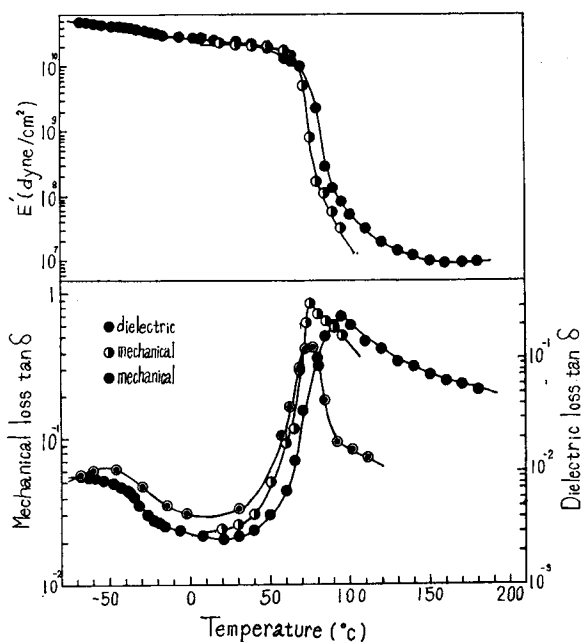


Fig. 2. Dynamic elastic storage modulus for PVB; symbols as in Figure 1.

anism responsible for these dispersions, the mechanical losses in PR, PVB, and the PR–PVB mixture are replotted in Figure 4, for ease of comparison.

The loss peak found at about 100°C. for the PR–PVB system seems to agree with the maximum dispersion of PVB alone, but the peak at about 160°C. is probably characteristic of the mixed
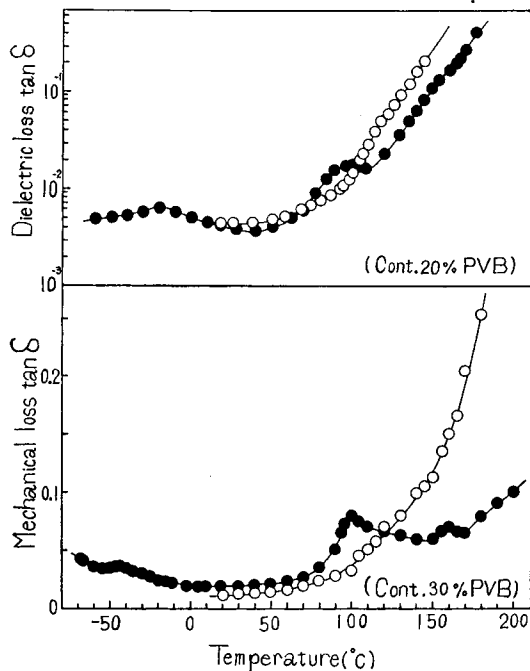
Fig. 3. Effects of curing conditions on dielectric and mechanical loss for PR-PVB system: (O) cure 30 min. at 170°C.; (●) 30 min. at 200°C.
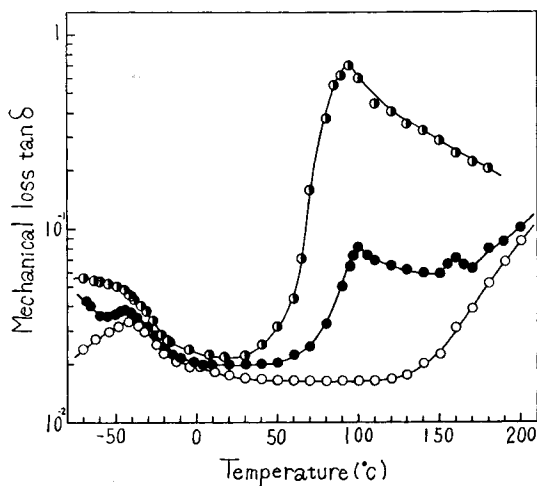


Fig. 4. Mechanical loss for PR, PVB, and PR-PVB system (cont., 30% PVB), cured at 200°C. for 30 min.: (O) PR; (●) PR-PVB; (◑) PVB.



Fig. 5. Effect of curing condition on mechanical loss PR-PVB system (cont., 30% PVB). Cure: (◐) 14 hr. at 170°C.; (◑) 0.5 hr. at 180°C.; (◒) 0.5 hr. at 190°C.; (●) first cure 0.5 hr. at 170°C., and second cure 0.5 hr. at 200°C.



Fig. 6. Effect of PVB content on the dynamic elastic storage modulus and mechanical loss for the PR-PVB system cured at 200°C. for 30 min.

system, because no peak is observed for either of the original substances in this temperature range. However, it is interesting to note in Figure 3 that the appearance of the mechanical loss peak at 100°C. for the mixed system is influenced by the curing of the specimen, and that the dielectric loss peak appears at the same temperature as the mechanical loss peak. Figure 5 indicates the effects of curing conditions on the multiple disper-
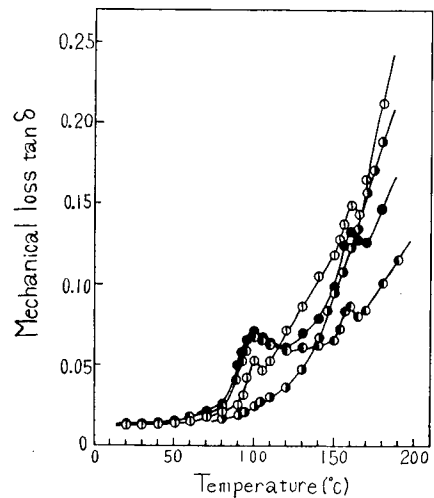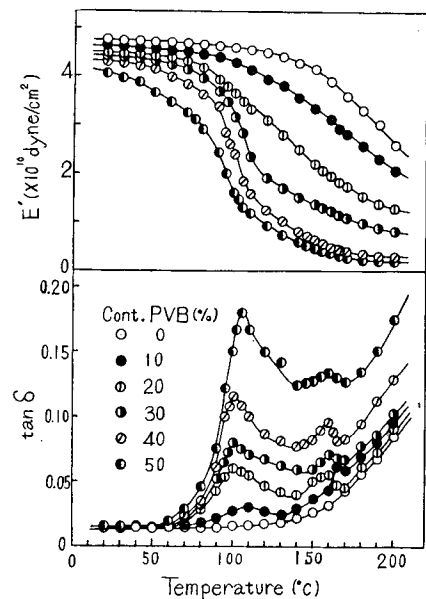
sion in the PR–PVB system: The loss peaks at 100 and 160°C. were not evident following cure at 170°C. in spite of the cure time of 14.5 hr., but the same sample cured over the range 180–200°C. developed these peaks, even though it was cured for only 30 min. It seems one can conclude that the curing temperature has more weight than the curing time in determining the occurrence of these dispersions.
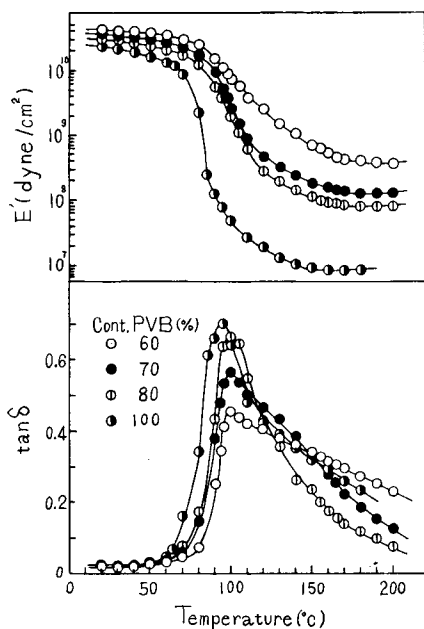
Fig. 7. Effect of PVB content on the dynamic elastic storage modulus and mechanical loss for the PR-PVB system cured at 200°C. for 30 min.
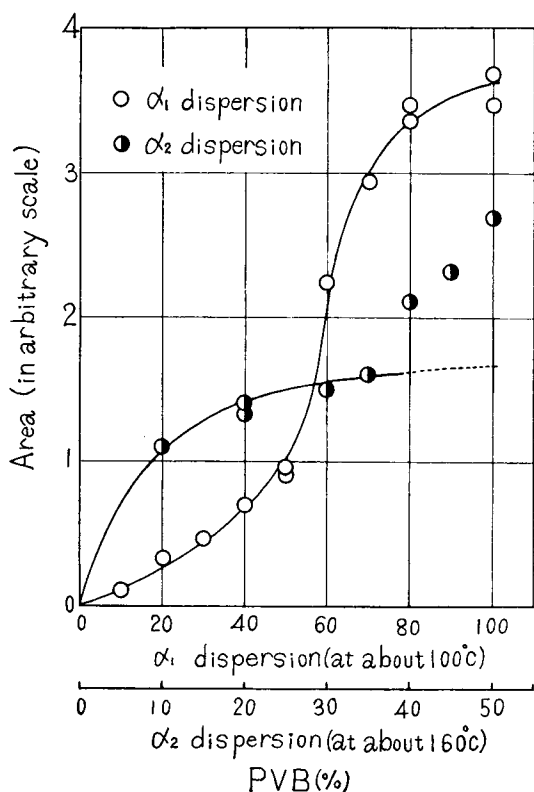

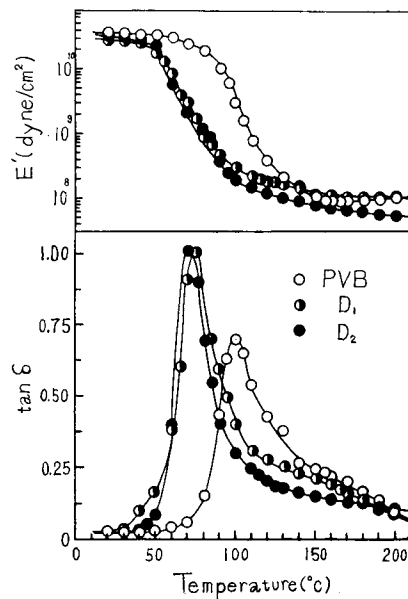
Fig. 9. Dynamic elastic storage modulus and mechanical loss for the PR-PVB or its derivative systems (ratio 20:80) cured at 200°C. for 30 min.



Fig. 8. Plot of the area under the $\alpha_1$ and $\alpha_2$-dispersion peaks against the PVB content in the PR-PVB system cured at 200°C. for 30 min.

The effects of PVB content on dynamic modulus and mechanical loss as functions of temperature over the range 20–200°C. are given in Figures 6 and 7 for PR–PVB systems cured at 200°C. for 30 min. with PVB contents ranging from 10 to 80%. The primary loss peak remains at about 100°C. but becomes progressively higher with increasing PVB content. The loss peak at about 160°C. is observed also to grow with increase in PVB content, up to 50%; however, above 60% PVB it cannot be distinguished. It may be that this loss peak is concealed in the right-hand slope of the large dispersion peak at about 100°C.

In Figure 8 the areas under the mechanical loss peaks at about 100 and 160°C. are plotted against PVB content in the PR–PVB system. For the loss peak at about 100°C. ($\alpha_1$ dispersion), the plots of area versus PVB content show not a linear but a sigmoidal form. The curve for the peak at about 160°C. ($\alpha_2$ dispersion) increases remarkably above 40% PVB, but it seems reasonable that this curve would be saturated to a finite value as shown by the dotted line, because the dispersions at about 100°C. and above 200°C. in Figure 6 may be superposed on the peak represented by this area.

In order to ascertain the mechanism of the characteristic mechanical loss peak of the mixed system at about 160°C., the samples $D_1$ (PVAc) and $D_2$ (PVB–PVAc), derivatives of PVB that differ from each other only in their side groups, were used with

TABLE II
Analysis and Dynamic Mechanical Behavior of Commercial Polyvinyl Butyral Resins

| Designation | $\overline{DP}$ | Composition, mole-% | | | Temperatures of mechanical loss peaks,[a] °C. | | Producer |
|---|---|---|---|---|---|---|---|
| | | Vinyl acetate | Vinyl butyral | Vinyl alcohol | $\alpha_1$ | $\alpha_2$ | |
| Slec BL-1 | 250–300 | 3.0 | 60.0 | 37.0 | 100 | 160 | Sekisui Chemical Co. |
| Slec BM-1 | 450–550 | 3.0 | 62.0 | 35.0 | 100 | 140 | Sekisui Chemical Co. |
| Slec BMS | 700–800 | 4.2 | 72.2 | 23.6 | 70 (110) | 150 | Sekisui Chemical Co. |
| XYHL | 570–670 | 1.1 | 66.6 | 32.3 | 100 | 145 | Bakelite Co. |
| Butvar B-73 | 900–1100 | 0.4 | 65.6 | 34.0 | 100 | 150 | Monsanto Chemical Co. |

[a] Measured on phenolic resin–polyvinyl butyral samples (20% PVB) curved at 200°C. for 30 min.

PR in place of PVB. The dynamic moduli and mechanical losses for the PR–$D_1$ and PR–$D_2$ systems are given as functions of temperature in Figures 9–11. In Figure 9, the maximum losses at about 100, 73, and 70°C. correspond to PVB, $D_1$, and $D_2$ at levels of 80% in the mixed systems. These losses may be related to the second-order transition of the main component in the mixed system. In addition, the films of the mixtures containing $D_1$ and $D_2$ looked hazy under visible light, even though the mechanical loss values indicated monodispersion in the temperature range of 20 to 200°C.

The loss peak attributed to 80% $D_1$ in the mixture is not observed for the specimen containing 20% $D_1$ (Fig. 10), but for the 40% $D_1$ specimen

a shoulder in the region of 70 to 80°C. is apparent. This indistinct loss peak may be due to hydrogen bonding or polar attraction between the acetyl groups of $D_1$ and the phenolic resin molecules. In the temperature range investigated no peak was found for the PR–$D_1$ system corresponding to the characteristic peak of the PR–PVB system at 160°C. This fact seems to suggest that the acetyl group of the PVB molecule is not involved in the occurrence of the characteristic peak of the PR–PVB mixture.

The dynamic moduli and mechanical losses for the PR–$D_2$ specimens containing 20 and 40% $D_2$ are plotted against temperature in Figure 11. The loss peak attributed to $D_2$ increases in height with
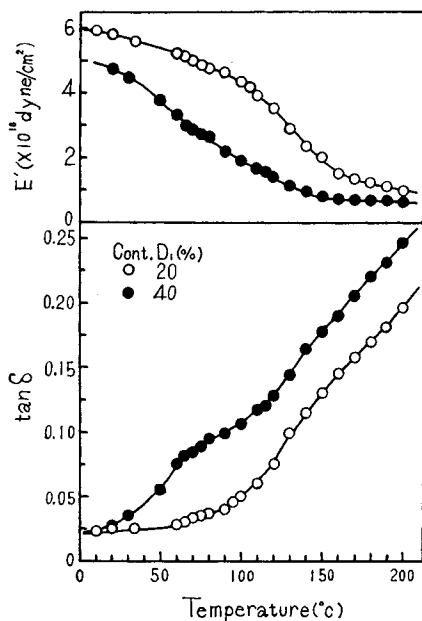
Fig. 10. Dynamic elastic storage modulus and mechanical loss for the PR-$D_1$ system cured at 200°C. for 30 min.
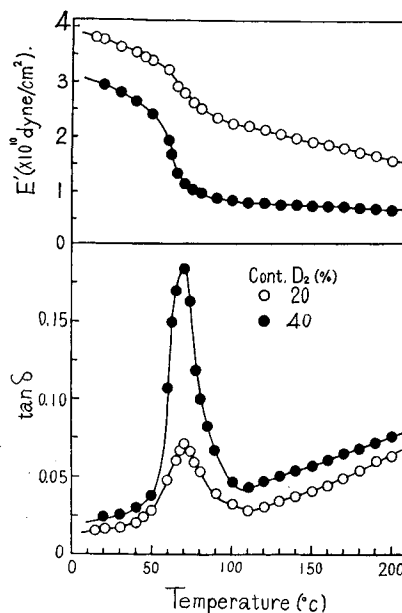
Fig. 11. Dynamic elastic storage modulus and mechanical loss for the PR-$D_2$ system cured at 200°C. for 30 min.
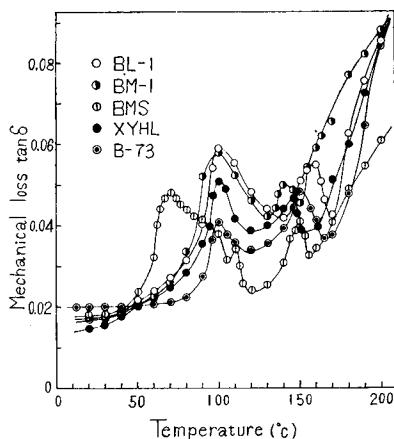
Fig. 12. Mechanical loss for PR and polyvinyl-butyral resins system (cont. each of the polyvinyl butyral resins, 20%) cured at 200°C. for 30 min.
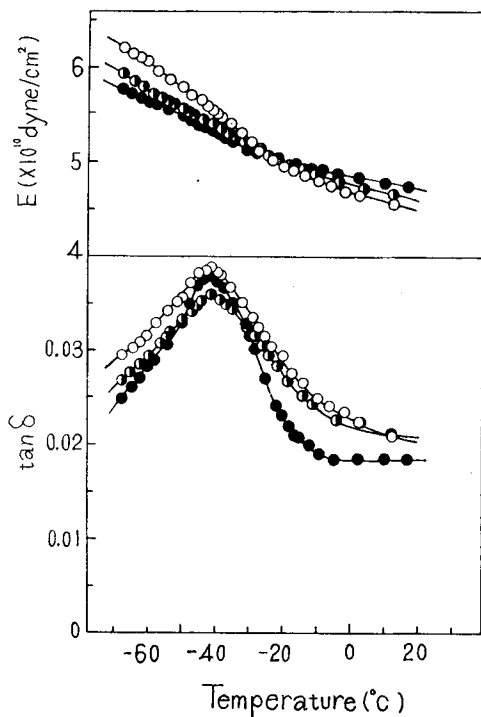


Fig. 13. Effect of curing condition on the dynamic elastic storage modulus and mechanical loss for phenol formaldehyde resin: (O) cure 30 min. at 150°C.; (◐) cure 30 min. at 170°C.; (●) cure 30 min. at 200°C.

increase in the content of $D_2$ from 20 to 40% while the temperature of the maximum loss stays constant at about 70°C. Moreover, it is seen that the butyral group, and the acetyl group, as before, are unrelated to the occurrence of the characteristic loss peak.
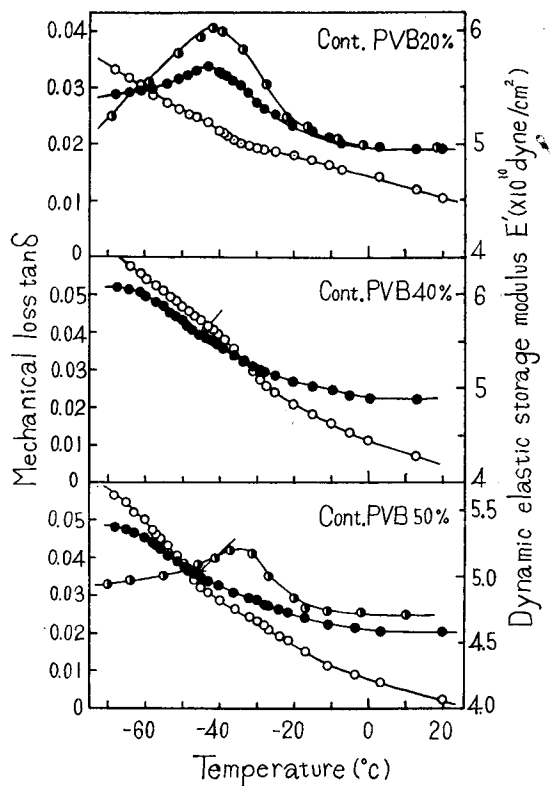
In Figure 12 are given the losses in systems



Fig. 14. Effect of residual solvent and water on the dynamic elastic storage modulus and mechanical loss for the PR-PVB system cured at 200°C. for 30 min: (O) E'; (●) mechanical loss tan δ (these specimens treated in vacuum under heating before measurement); (◐) mechanical loss tan δ (specimen not so treated before measurement).

containing 20% commercial polyvinyl butyral resins (Table II) which were cured at 200°C. for 30 min. In this case, the loss peaks of all the mixed systems are found in the regions of 70 to 100°C. and 140 to 160°C. The shifts in position of these peaks are due more probably to variations in the molar ratio of hydroxyl to butyral groups in the PVB molecule than to variations in degree of polymerization.

The peak found at about −42°C. for the PR–PVB system in Figure 3 seems to be clearly attributable to the PR itself (see Fig. 1). In Figure 13 the effects of curing temperature on the dynamic modulus and mechanical loss in the phenol–formaldehyde resin alone are given as functions of temperature. The higher the curing temperature, the narrower is the dispersion and the smaller the area under the loss peak, whereas the temperature of the maximum is not affected by changes in cure temperature. Figure 14 indicates that the loss peak appears clearly at about −42°C. for the 20% PVB specimen, whereas for the 40% and 50% PVB specimens the dispersion either appears as

the shoulder on the lower temperature peak due to the PVB near −70°C. or merges with this peak. At the same time, the dispersion region broadens as the PVB content is increased from 20 to 50%. In addition, it is readily apparent from Figure 14 that the presence of residual solvent and the water in the specimen significantly alters the mechanical loss, so that the peak for "wet" specimens found in the range of −35 to −42°C. is higher and also distinct from the lower temperature (ca. −70°C.) dispersion.

## DISCUSSION

Dispersions such as those shown in Figure 3b are generally labeled $\alpha$, $\beta$, $\gamma$, etc., in order of descending temperature. In this paper, the four principal dispersions of the PR–PVB system cured at 200°C. for 30 min. are designated $\alpha$, $\alpha_2$, $\alpha_1$, and $\beta$ for dispersion locations of greater than 200, 160, 100, and −42°C., respectively.

The $\alpha$ dispersion, appearing above 200°C., may be due to the movement of large sections such as macromolecules of crosslinked phenolic resin.

The $\alpha_1$ dispersion, at about 100°C., nearly coincides with the maximum loss peak of PVB itself (see Fig. 4). A phenomenological interpretation of this, based on heterogeneity in the mixture of two polymers, was proposed by Nielsen and Buchdall.[9] The fact that the mixture exhibits the dispersions characteristic of each constituent means that the different polymers do not interact sufficiently for their own second-order transitions to be hindered. Nohara[10] proposed a theoretical equation for the viscoelastic behavior of a heterogeneous system of two polymers, which indicates that the magnitude of the loss peak increases linearly with the content of one of the polymers, while the temperature of the loss peak remains constant. In accordance with the above opinions, it seems possible to consider the PR–PVB system as a heterogeneous system of two polymers. However, the PR–PVB system shows one property not mentioned by Nielsen and Nohara, namely, the dependence of the $\alpha_1$ dispersion on curing temperature (see Fig. 5). This phenomenon requires clarification through further study.

The $\alpha_2$ peak, at about 160°C., is the characteristic one for the mixture, because neither of the constituents alone exhibits this loss peak, as shown in Figure 4.

The following possible reasons for the occurrence of the $\alpha_2$ peak will be considered:

(1) Residual stress stored in the specimens.
(2) Mutual solubility of the PR and PVB.
(3) Copolymerization of the PR and PVB.

Since all the specimens were dried almost completely before use (except where specified otherwise), the effect of the residual solvent or water in the specimen is considered negligible.

When the plasticizer PVB is mixed into the phenolic resin, the residual stress in the specimen might decrease, owing to the decrease in the shrinkage of the phenolic resin, due to crosslinking. This would bring about a decrease in the $\alpha_2$ peak with increase in PVB. However, the height of the $\alpha_2$ peak in Figure 6 increased with increase of the PVB content. Furthermore, in order to ascertain the effect of residual stress, which had been annealed for 2 hr. at 190–200°C., losses in the 50-60% PVB samples were measured first at temperatures increasing to 200°C. and again during cooling, and the $\alpha_2$ peak at 160°C. was produced both times. This seems to be evidence that item (1) has no effect on the $\alpha_2$ peak.

If the $\alpha_2$ peak is to be attributed to the solubility of one polymer in the other, the ratio of dissolved portions of the two components has to vary with the original mixing ratio, for equilibrium to be attained. Consequently, at different compositions of the dissolved part the second-order transition temperature may shift to lower or higher values depending on the ratio of the two components.[11] Figure 6 indicates that the temperature of the $\alpha_2$ peak was constant at about 160°C. and independent of the PVB content, although the height of area of the $\alpha_2$ peak increases with increase in the PVB content (see Figs. 6 and 8). This reasoning permits one to neglect item (2).

Finally, item (3) seems the most reasonable of any. In PVB the acetyl, hydroxyl, and butyral groups are attached as side chains to the carbon chain skeleton. The chemical reactions between the phenolic resin molecule and the three types of side groups on PVB were investigated, with the use of the PVB derivatives $D_1$ and $D_2$, and the results obtained by the viscoelastic method (Figs. 9–11) seem to indicate that the occurrence of the $\alpha_2$ peak of the PR–PVB system is related to presence of the hydroxyl group, rather than of the acetyl or butyral groups, on the PVB molecule. This conclusion is supported by the experimental results obtained with different commercial types of polyvinyl butyral (see Fig. 12). The effect of hydroxyl groups on the polyvinyl butyral molecule mixed with the phenolic resin may be explained as follows:
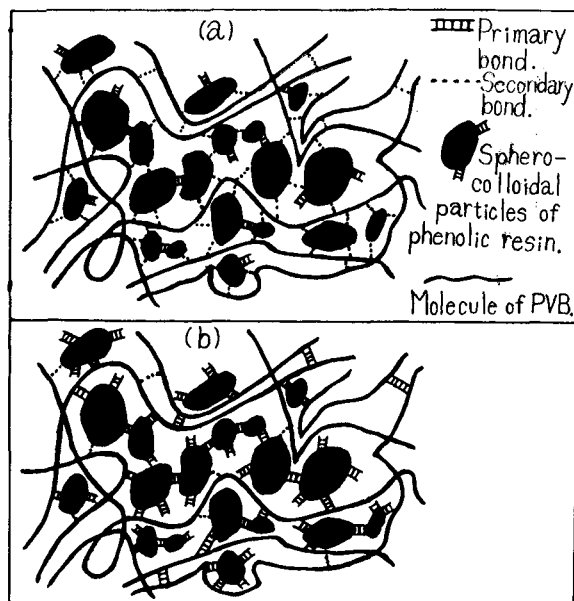
Fig. 15. A model to explain the dispersed state of the phenolic resin–PVB mixture: (a) initial stage of curing reaction; molecules of both resins interact on each other by secondary bonds; (b) the near-final stage of curing reaction; most of the polar functional groups on the spherocolloidal particles are consumed in the formation of the network structure of phenolic resin, so that the secondary bonds between both resins decrease.

During the initial condensation of phenol, o-cresol, and formaldehyde under the influence of aqueous $NH_4OH$ (designated State A), many phenolic intermediates containing methylol or amino groups are produced.[1,12] When the mixture of phenolic resin (from Stage A) and polyvinyl butyral is heated to high temperature, then, during the course of the curing reaction, some grafted or crosslinked structure would be produced by the condensation between the hydroxyl groups of the polyvinyl butyral and the methylol or amino groups of the phenolic resin. This hypothesis is supported by the fact that, except at very high degrees of crosslinking, the dynamic modulus for PVB crosslinked by the phenolic resin becomes larger again above 180°C. (Fig. 7) as described in the previous paper,[13] behavior which is in agreement with the theory of rubberlike elasticity.

In Figure 15 is shown a model for explanation of the appearance of the $\alpha_1$ and $\alpha_2$ peaks of the PR–PVB system, based on the experimentally found mechanical and dielectric properties of the specimens. It should be kept in mind that phenoplast condensation, by its very nature, leads to highly branched macromolecules probably more or less spherical in form.[2] During cure of the PR–PVB

mixture at below 170°C., a considerable number of polar, functional methylol and amino groups may remain attached to the spherocolloidal particles of the phenolic resin, although the phenolic nuclei are growing by incorporating the less functional portions of the mixture. Hydrogen bonding or polar attraction may thus occur between the spherocolloidal particles and the adjacent polar groups on the PVB molecules (see Fig. 15a). Therefore, the segments of the PVB molecule may move in cooperation with the nearest spherocolloidal particles when an alternating mechanical or electrical force is applied to the mixed system. This may be the reason why no $\alpha_1$ peak was observed in the system cured at 170°C., as shown in Figures 3 and 5. When the system is cured at above 180°C., the crosslinking reaction among the spherocolloidal particles predominates. Since most of the polar functional groups on the spherocolloidal particles are consumed in the formation of the network structure of the phenolic resin, the PVB molecules may be released from secondary valence bonding with the spherocolloidal particles (see Fig. 15b) so that the $\alpha_1$ peak can readily be detected, as is also shown in Figures 3 and 5. The fact that the effects of curing temperature on the dielectric loss peak for the mixed system are similar to those for the mechanical loss peak in the same temperature range (Figs. 3 and 5) also lends support to the hypothesis that the polar functional groups of the system play the decisive role in the occurrence of the $\alpha_1$ peak. During the curing reaction, some of the secondary valence bonds between the PR and PVB molecules may change to primary bonds, so that grafting or copolymerization unites the two materials. Therefore, the $\alpha_2$ peak characteristic of the PR–PVB system may be attributed to molecular heterogeneity in the form of grafted or crosslinked structure. However, explanation of the effects of curing temperature on the $\alpha_1$ dispersion for the mixture, which differ for temperatures above 180°C. and below 170°C., remains for future research.

The $\beta$ peak found at about $-42$°C. for the PR–PVB system is clearly attributable to the PR itself (see Fig. 4). In order to ascertain whether the occurrence of the $\beta$ peak is due to the o-cresol in the PR, an ammoniac-resol type of unsubstituted phenol–formaldehyde resin was studied; however, this sample was found to exhibit a peak also at about $-42$°C. (see Fig. 13). In addition, as was recently found in our laboratory, the unsubstituted phenolic resin specimen extracted with acetone in a Soxhlet apparatus for about 300 hr. showed a

narrower dispersion in the same temperature range with, however, no decrease in peak height.

The dielectric loss peak at about $-20°C$. for the PR may occur through the same relaxation mechanism as that causing the mechanical loss peak at about $-42°C$., even though the former peak occurs at a higher temperature (see Fig. 1). These dielectric data, which correspond to the viscoelastic dispersion of the polymers, may be used to provide general support for our interpretation of the mechanical dispersions. The apparent dielectric activation energy $\Delta H^*$ for the PR samples were recently reported in detail:[14] $\Delta H^*$ for the dispersion observed at about $-20°C$. was 17 kcal./mole and almost independent of curing temperature.

The viscoelastic and dielectric behavior of the phenolic resin above room temperature is now relatively well known,[15,16] but that below room temperature has not yet been reported. Accordingly, it is of interest to consider the molecular mechanism responsible for the dispersion occurring at lower temperature. Thus, in the mixture the portion of lower $\overline{DP}$ and less crosslinking, consisting of a few phenolic nuclei, must be assumed to be trapped between the spherocolloidal, phenolic resin particles (see Fig. 15). This portion is a viscous but more mobile material which is often referred to as *Harzbrei*. However, the mechanical loss peak at $-42°C$. for the PR can scarcely be attributed to the movement of this lower $\overline{DP}$ portion, which consists of stiff molecules such as phenolic nuclei, because at $-42°C$. this movement cannot take place. On the other hand, the observed value of the apparent dielectric activation energy is of the same order as that reported for the orientation of local parts such as side groups on the main chains of cellulose,[17] polymethyl methacrylate,[18] polyamides,[19,20] etc. Therefore, it appears that this dispersion is caused by the local motions of side chains, especially the unreacted methylol and amino groups on the molecules of lower $\overline{DP}$ and on the spherocolloidal particles of phenolic resin, which may be almost unaffected by the configuration of the phenolic nuclei, although there is no additional support for this expectation. When curing of the phenolic resin proceeds at higher temperatures, the polar, functional methylol and amino groups may be largely consumed in the formation of the phenolic resin network structure. Thus the area under the loss peak may decrease with increase in the curing temperature, as shown in Figure 13. Because of some particular features of the structure, however, not all sites that may be chemically active will be able to react.

In the case of residual water and solvent in the PR–PVB specimens (see Fig. 14), these small molecules may move with the unreacted methylol and amino groups on the phenolic resin molecules and thus contribute to the upswing of the mechanical loss peak. Analogous phenomena have been reported recently by Woodward and co-workers[21] for a polyamide containing water or methanol.

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## Synopsis

The viscoelastic properties of the phenolic resin–polyvinyl butyral system were studied over a wide range of temperature by means of the vibrating reed method, at about 50 cycles/sec., and dielectrically, at 60 cycles/sec. Two mechanical loss peaks due to polyvinyl butyral in the mixed system, occurring at about 100 and 160°C., were readily observed. These peaks are influenced by the curing temperatures, being readily detected in specimens cured in the range 180–200°C. but not in those cured below 170°C. The effect of cure temperature on the appearance of a dielectric loss peak at about 100°C. for the system agrees in trend with the effect of cure temperature on the mechanical loss peak in the same temperature range. This result may lend some support to the hypothesis that the polar functional groups of the system play some important role in the appearance of a loss peak. The loss peak at about 100°C. coincides approximately with the maximum loss peak for polyvinyl butyral in the mixed system, and hence this peak may be due to the second-order transition of the polyvinyl butyral which seems to be in a heterogeneous state in the specimen. Another peak, found at about 160°C., may be attributed to grafting or crosslinking between the phenolic resin and the polyvinyl butyral, resulting from chemical reaction between the two materials during the curing process, as was shown by results for the mixtures of the phenolic resin with PVB and with two PVB derivatives. A model of the state of dispersion of the two constituents in the system is proposed on the basis of these results. Finally, the loss peak occurring at about −42°C. for the system is clearly attributable to the phenolic resin alone. The molecular mechanism for this dispersion, on the basis of results of viscoelastic and dielectric measurements, may be the local movement of side chains, especially unreacted methylol and amino groups on the phenolic resin molecules, although there is no additional clear support for this conclusion.

## Résumé

Les propriétés viscoélastiques du système résine phénolique–butyral polyvinylique, ont été étudiées sur une grande gamme de température, à l'aide d'une méthode à plume vibrante aux environs de 50 cycles/sec et également à l'aide de la méthode diélectrique à 60 cycles/sec. On a aisément pu observer deux maxima de perte mécanique dûs au butyral polyvinylique dans le mélange et situés aux environs de 100 et de 160°C; ces maxima sont cependant influencés par la température de vulcanisation des échantillons. Ces maxima s'observent aisément dans les systèmes vulcanisés aux environs de 180–200°C mais ne peuvent être mis en évidence lors de vulcanisations à des températures inférieures à 170°C. L'influence de la température de recuite sur l'apparition du pic de perte diélectrique aux environs de 100°C pour le système considéré, concorde bien avec l'influence sur le pic de perte mécanique dans le même domaine de températures. Ce résultat pourra dès lors donner un certain poids à l'hypothèse que les groupes fonctionnels polaires d'un système jouent un rôle important dans l'apparition des maxima de perte. Un des maxima, trouvé aux environs de 100°C, concorde assez bien avec le pic de perte maximum du butyral polyvinylique dans le mélange et on peut supposer qu'il est dû à une transition de second ordre du butyral polyvinylique, qui dans l'échantillon, apparaît comme phase hétérogène. Un autre pic, trouvé aux environs de 160°C, peut être du à la formation de greffons ou d'une structure pontée de la résine phénolique-butyral polyvinylique qui est formé par réaction chimique entre les deux résines lors de la vulcanisation, comme le montrent les résultats concernant les mélanges butyral polyvinylique—et ses dérivés—résines phénoliques. A partir de ces résultats on propose une explication de l'état de dispersion des 2 constituants du système. Enfin le pic de perte, situé aux environs de −42°C pour le système envisagé, est sans aucun doute attribuable à la résine phénoliquelle-même et son mécanisme moléculaire est discuté. Au dépens des résultats des mesures viscoélastiques et diélectriques, on peut prévoir des mouvements de parties locales telles des chaînes latérales, spécialement des groupes méthyliques qui n'ont pas réagi et des groupes aminés sur les résines phénoliques pour cette dispersion; il n'y a toutefois pas d'autres confirmations de cette supposition.

## Zusammenfassung

Die viskoelastischen Eigenschaften des Systems Phenolharz–Polyvinylbutyral wurde über einen grossen Temperaturbereich mittels der Stäbchenschwingungsmethode bei 50 Hertz und der dielektrischen Methode bei 60 Hertz untersuchte. Zwei mechanische, für Polyvinylbutyral im Mischungssystem charakteristische Dämpfungsmaxima treten bei 100 und 160°C auf und können leicht beobachtet werden, sie werden jedoch von der Behandlungstemperatur der Proben beeinflusst. Sie können für Systeme, die im Bereich von 180 bis 200°C behandelt wurden, leicht festgestellt werden, für solche, die unterhalb 170°C behandelt wurden, sind sie nicht beobachtbar. Der Einfluss der Behandlungstemperatur auf das Auftreten des dielektrischen Verlustmaximums bei ca 100°C für das System stimmt in der Tendenz mit dem auf das mechanische Dämpfungsmaximum im gleichen Temperaturbereich überein. Dieses Ergebnis scheint daher die Hypothese zu stützen, dass die polaren, funktionellen Gruppen des Systems eine wichtige Rolle für das Auftreten des Dämpfungsmaximums spielen. Eines dieser Dämpfungsmaxima bei ca 100°C stimmt mit dem höchsten Dämpfungsmaximum von Polyvinylbutyral in dem Mischungssystem gut überein, sodass man erwarten kann, dass dieses Maximum der Umwandlung zweiter Ordnung von Polyvinylbutyral, das in der Probe in heterogenem Zustand vorliegt, entspricht. Ein anderes, bei ca 160°C gefundenes Maximum kann der Bildung einer Graft- oder Vernetzungsstruktur zwischen Phenolharz und Polyvinylbutyral zugeschrieben werden, die bei der chemischen Reaktion der beiden Harze während des Behandlungsprozesses entsteht, wie die experimentellen Ergebnisse für das Mischungssystem Polyvinylbutyral—und dessen Derivate—Phenolharz zeigen. Auf Grund dieser Ergebnisse wurde ein Modell zur Erklärung des dispersen Zustandes der beiden Bestandteile in dem System vorgeschlagen. Schliesslich wird das Dämpfungsmaximum, das für das System bei −42°C auftritt, eindeutig dem Phenolharz selbst in der Mischung zugeschrieben und der zugrundeliegende, molekulare Mechanismus diskutiert. Aus den Ergebnissen der viskoelastischen und dielektrischen Messungen kann man die Bewegung lokaler Teile wie Seitenketten, besonders nichtreagierter Methylol- und Amingruppen in den Phenolharzmolekülen in der Dispersion annehmen; allerdings bestehen keine andersartigen Belege für diese Erwartung.