

# Rheological Characteristics of Proanthocyanidin Polymers from *Pinus radiata*. II. Viscoelastic Properties of Sequential Alkaline Extracts Based on Phenolic Acid Fraction

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## SYNOPSIS

Steady and dynamic oscillatory rheometry were used to characterize two members of the plant polyphenols from *Pinus radiata* bark, water-soluble proanthocyanidin polymers, and phenolic acids. The viscosity-controlling factor of the extracts could be revealed by examining the various extracts under different chemical and rheological environments. Water-extracted (100°C) bark was successively extracted with aqueous NaOH solutions of increasing alkalinity at 100°C and the rheological characteristics of the each fraction were examined in detail. The significant viscoelasticity of the 100°C aqueous NaOH sequential extracts suggests that this fraction can have a critical impact on the flow characteristics of overall extracts and arises from a major contribution of colloidal interactions involving the carbohydrate component. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

In an earlier communication,<sup>1</sup> it was pointed out that the viscosity changes upon addition of aqueous NaOH solution to solutions of the 100°C hot-water extracts (HWE) of *Pinus radiata* (*P.r.*) bark are due mainly to the dissolution of the phlobaphene fraction. These studies were confined to the rheological properties at very low extract concentrations. In an effort to further elucidate the factors controlling the complex flow properties of concentrated extracts of *P.r.* bark, the dynamic rheological properties of various extracts are investigated here, together with a study of the effect of the phenolic acid fractions on these flow properties.

Sequential extraction of the bark of most species of conifers and deciduous trees, using water followed by aqueous alkali, yields two fractions of polymeric polyphenols, respectively, referred to as proanthocyanidin polymers and phenolic acids.<sup>2</sup> Proanthocyanidin polymers are plant phenolic biopolymers that consist of flavanoid monomer units.<sup>2</sup> The water-

insoluble phenolic acid fraction can be isolated only by extraction with aqueous alkaline solutions or with sodium sulfite or bisulfite solutions at elevated temperatures and pressures. These materials react with formaldehyde or phenol-formaldehyde prepolymers to yield suitable resins for cold-setting waterproof adhesives for wood lamination or thermosets for exterior-grade plywood.<sup>3</sup>

It was previously shown that the aqueous extracts of the *P.r.* bark contains polyhydric phenols that are polyflavonoid in nature.<sup>4</sup> These polyflavonoid extracts, now being developed as wood adhesives,<sup>5</sup> have been hindered by limitations associated with the high chemical reactivity, relative instability, and excessive viscosity of the high-yield extracts. As a prerequisite for investigating and controlling the complex rheological characteristics, it is important to understand the contribution of each fraction of the extracts to the flow behavior.

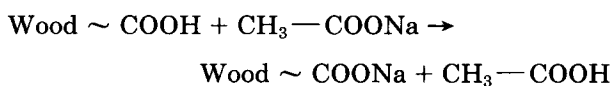
Yazaki and Hillis<sup>6</sup> reported a viscosity of 8.5 Pa-s for a 45% solution of the aqueous extract from *P.r.* bark. This is almost an order of magnitude higher than that expected on the basis of the pro-cyanidin content.<sup>7</sup> The material designated as "high molecular size" with molecular weights greater than 10<sup>6</sup> was removed either as a methanol-insoluble

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fraction or by ultrafiltration. The viscosities of the methanol-soluble portion and the ultrafiltered portions of this extract were 0.5 and 0.09 Pa-s, respectively. The former value is about that which may be expected for a proanthocyanidin polymer, while the latter indicates that most of the polymer fraction has been excluded by the filtration.<sup>7</sup> Yazaki and Hillis<sup>6</sup> showed that methanol insolubles contain some carbohydrate-type compounds and procyanidin polymers with a molecular size larger than that of a  $10^6$  molecular weight Dextran equivalent. When *P.r.* bark is extracted with sulfite-carbonate, the solution viscosities become much lower due to the partial depolymerization of proanthocyanidines,<sup>8</sup> although Pizzi and Stephanou recently showed that autocondensation and recombination occur.<sup>9,10</sup> Woo<sup>11</sup> reported a viscosity of 1.6 Pa-s for a 45 wt % solution of a commercial sulfite-carbonated tannin extract from *P.r.* bark. The rheological behavior of *P.r.* HWE has been studied by Yazaki<sup>12</sup> in a rotational viscometer at various concentrations, pH conditions, and temperatures. The apparent viscosity of extracts at 25°C varied between 2 Pa-s for 38% solids content to about 20 Pa-s at 50% solids content. Yazaki considered that hydrogen bonding was one of the factors involved in aggregation of the *P.r.* polyphenol extract. Hemingway et al.<sup>13</sup> showed that, under alkaline conditions, model procyanidin polymers are rapidly converted at ambient temperatures to species where most of the flavan-3-ol units contain a rearranged A-ring from which Porter<sup>7</sup> implied a greater degree of rigidity than that of the original polymer. However, these procyanidin results in alkaline solution vary considerably from those obtained by Weissmann<sup>14</sup> for alkaline extracts from *Pinus oocarpa* bark. On the basis of 30 wt % solutions at 20°C, the water-soluble material was found to have had a viscosity of 0.065 Pa-s, whereas the material soluble in 1% sodium hydroxide had a viscosity of 1.294 Pa-s. Weissmann<sup>14</sup> showed that the viscosity of the water-extract solution was dominated by the proanthocyanidins and that there are few accompanying polysaccharides. Hemingway and McGraw<sup>15</sup> showed that the alkaline extracts from southern pine contained phenolic acids and polysaccharides and recognized the difficulty of completely separating the carbohydrates from the polyphenols. Hergert<sup>16</sup> noted that, after their isolation, the phenolic acids were soluble in ethanol, while the ethanol-insoluble material was considered to be a polysaccharide. A possible structure for these phenolic acids has been related to catechinic acid rearrangement under alkaline conditions based upon model studies.<sup>13</sup> However, recent <sup>13</sup>C-NMR studies showed low proportions of

this rearrangement in actual procyanidin and prodelphinidin tannins.<sup>10</sup>

In this study, HWE bark of *P.r.* was successively extracted with aqueous NaOH solutions of increasing concentration at 100°C and the rheological characteristics of the NaOH extracts was examined in detail. This sequential extraction process was carried out since the condensed tannin fraction will be coextracted with the phenolic acids under basic conditions. The effect of the various extract fractions on the flow characteristics at differing concentrations was investigated by both steady shear and dynamic oscillatory rheological measurements. Correlation of the resulting physical characteristics with the contribution of each extract fraction was obtained by considering the amounts of extractable and unextractable wood acids. This was achieved by the reaction of bark acids with aqueous sodium acetate as suggested by Subramanian.<sup>17</sup> The reaction of the bound, i.e., unextractable bark-carboxylic acid<sup>18</sup> can be written in a simplified form as follows:<sup>17</sup>



## EXPERIMENTAL

### Sample Preparation

The main isolation and purification methods used to extract the plant materials were similar as described previously.<sup>1</sup> The dried bark powder of *P.r.* (100 g) was extracted with 500 mL hot (100°C) water and 500 mL cold (20°C) water, respectively, to isolate procyanidins and their polymer and the bark residues were then dried at 105°C for 3 days. The pH values of the various extract solutions were determined together with the yields recorded on an oven-dry basis. The samples (100 g each) of the dried bark residue from 100°C water extraction was then reextracted at 100°C with 500 mL quantities of aqueous NaOH at concentrations of 0.1, 0.5, or 1*N*. The extraction procedures and the subsequent analyses conducted on the water-soluble proanthocyanidins and the phenolic acids are depicted in Figure 1 and Table I.

### Characterization

#### Rheological Measurements

Rheological parameters were measured at  $20 \pm 0.1^\circ\text{C}$  by using a Rheometrics Fluid Spectrometer RFS II

(Rheometrics, Piscataway, NJ) equipped with a parallel-plate geometry (plate diameter of 50 mm) and a concentric Couette geometry (cup radius: 17 mm; bob radius: 16 mm; bob length: 34 mm). Throughout the experiments, the torque sensitivity was varied by a decade by changing the mode of the force-rebalanced transducer. To minimize changes in composition for water evaporation during measurements, a humidification chamber was placed around the sample geometry.

During oscillatory rheological measurements, the shear was applied sinusoidally at a maximum strain amplitude ( $\gamma_{max}$ ) and angular frequency ( $\omega$ ) according to the standard relationship  $\gamma(t) = \gamma_{max} \sin(\omega t)$ . The amplitude of the shear stress ( $\tau$ ) and the phase difference ( $\delta$ ) between the stress and strain were monitored according to the relationship  $\gamma(t) = \tau_{max} \sin(\omega t + \delta)$ . From these measurements, in-phase (elastic modulus,  $G'$ ) and out-of-phase components (viscous modulus,  $G''$ ) were obtained via the following relationships:  $\tau(t) = \gamma_{max}[G' \sin(\omega t) + G'' \cos(\omega t)]$ . In the oscillatory mode, measurements were made as a function of strain amplitude to ensure linearity. Once the linear region was established, measurements were made as a function of frequency at a fixed amplitude. Finally, the steady-shear behavior was examined after full recovery time was given to the sample prior to the measurement.

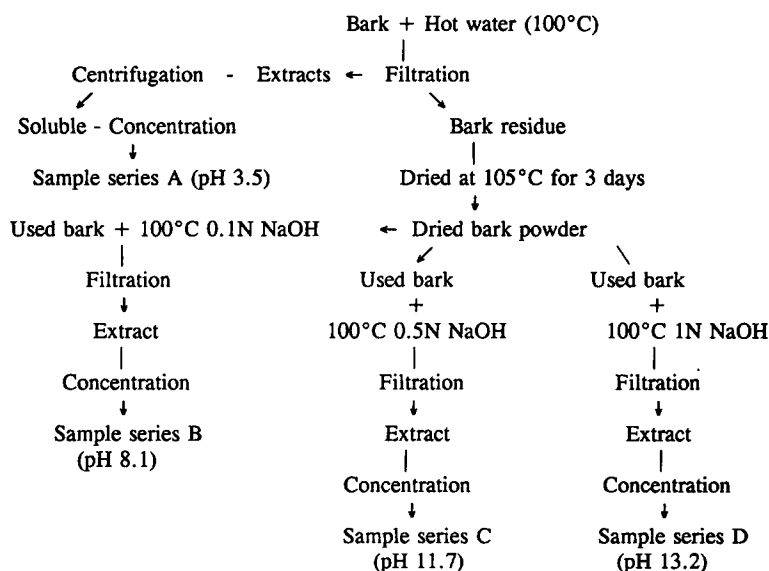
### Acidity of Extracts

Samples of *P.r.* bark powder (50 g) were added to 250 mL solutions of 0.5N sodium acetate solutions

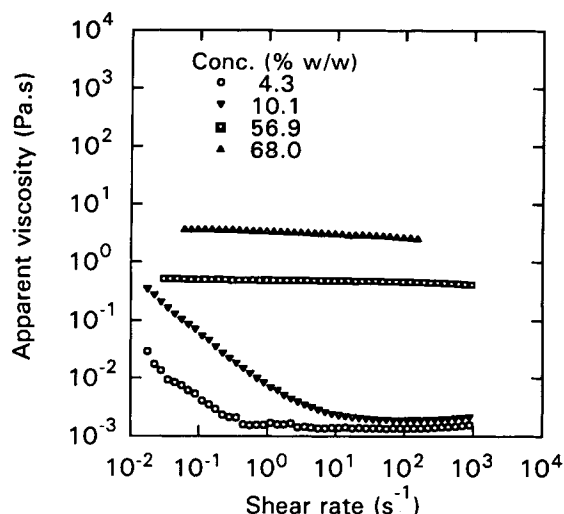
**Table I** A List of the Extracts Prepared for Rheological Study

| Extraction Method             | Sample I.D. | Extraction Yield (% w/w) | pH of Extract |
|-------------------------------|-------------|--------------------------|---------------|
| Cold (20°C)<br>water<br>(CWE) | A           | 5.95                     | 3.64          |
| Hot (100°C)<br>water<br>(HWE) | B           | 11.65                    | 3.52          |
| 0.1N NaOH<br>solution         | C           | 13.95                    | 8.14          |
| 0.5N NaOH<br>solution         | D           | 40.20                    | 11.71         |
| 1N NaOH<br>solution           | E           | 58.13                    | 13.24         |

at either 20 or 100°C, respectively, to liberate equivalent amounts of acetic acid. These suspensions were agitated vigorously for 10 min and then filtered using a Buchner funnel and No. 41 Whatman filter paper to remove insoluble materials. Subsequent pH titration gave the total acid content of the extract. The soluble acids were determined by water extraction and titration at 20 and 100°C, respectively. The total acid content minus the water-soluble acids gave the water-insoluble or bound acids content in the *P.r.* bark. Phlobaphenes were isolated by centrifugation at 4000 rpm for 30 min and the soluble fraction was then titrated in an identical method to de-



**Figure 1** Experimental scheme for HWE and NaOH sequential extracts at various alkalinities.



**Figure 2** Viscosity flow curves of the HWE at four different concentrations.

termine the acid content of the extract solution in the absence of phlobaphene.

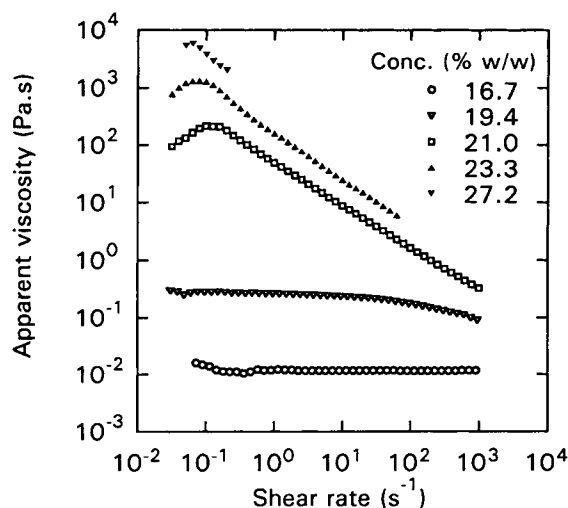
## RESULTS AND DISCUSSION

The apparent viscosity vs. shear-rate behavior of the HWE was initially examined at various concentrations (sample series A) as shown in Figure 2. The extracts show a shear-thinning response, with a high-shear limiting Newtonian regimes at low concentrations (4.3 and 10.1 wt %). This high-shear plateau indicates that any structure present in the extract was effectively broken by shear and that individual particle motion was attained at high rates of shear. With increasing concentration, shear-thinning became less significant (as observed in lin-log plot) with no high-shear Newtonian regimes over the shear-rate region examined. This relatively low value of viscosity at the very high concentration of 68% is very different from the result of Yazaki<sup>12</sup> (20 Pa-s at 50%).

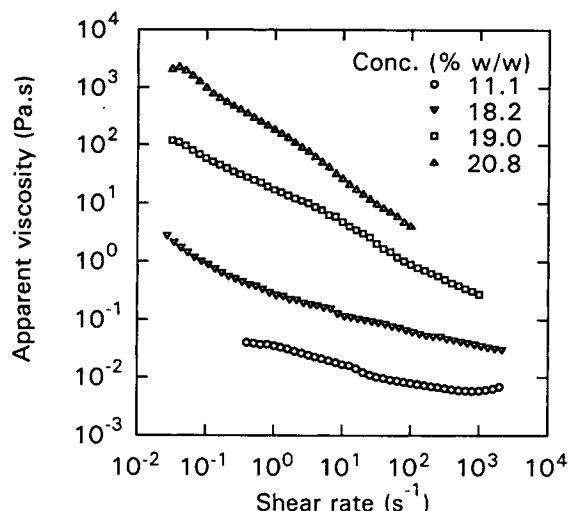
This low viscosity is due to the exclusion of all insoluble fractions by centrifugation after extraction. It was necessary to work only on the soluble fractions of HWE for rheological measurements since significant instability inhibited the measurement especially at concentrations as low as 10%. Thus, the low-viscosity value of this concentrated soluble fraction was similar to that (0.09 Pa-s at 45%) which had been demonstrated by the ultrafiltered HWE fractions ( $M_w < 10^6$ ) of Yazaki and Hillis.<sup>6</sup>

Figure 3 shows the steady-shear flow curves of the 100°C 0.1N NaOH sequential extracts at various concentrations (sample series B). Sample series B had a pH of 8.1. Figure 3 shows a significant increase in overall viscosity compared to the HWE (Fig. 2), with an apparent viscosity approaching  $10^4$  Pa-s at about 27% concentration. The progressive transition from Newtonian behavior to high shear thinning indicates an increasing association between many of the individual molecules, i.e., stronger intermolecular interaction and mechanical entanglements with its higher-energy dissipation, which is able to be progressively broken down by increasing the shear rate. This implies that the HWE (Fig. 2) has relatively smaller molecular flow units or a lower degree of molecular association.

When the alkalinity of the extraction solvent is raised to 0.5N (sample series C), a increase of viscosity is observed which is accompanied by a rise in the degree of shear thinning even at low concentrations (11.1%), as shown in Figure 4. Ordering of the polymeric extracts by association to form a three-dimensional network structure is necessary to account for this significant shear-thinning flow behavior. Entanglement also appears likely because the polymer consists of linear chains of the flavan-3-ol units as discussed earlier. As the alkalinity of the extraction solvent is increased to 1N (sample series D shown in Fig. 5), a similar trend is observed but the concentration dependence of viscosity is now much less. Thus, this may be due to the early achievement of compact chain configurations at lower concentrations. The viscosity of extracts from *P.r.* bark is therefore governed primarily by the dis-



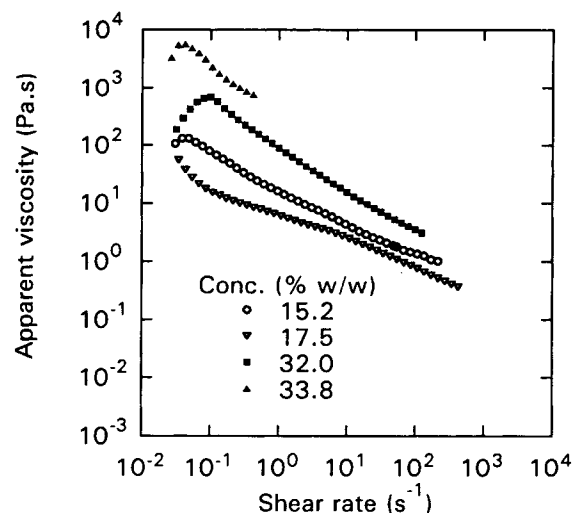
**Figure 3** Viscosity flow curves of the 0.1N NaOH sequential extracts at five different concentrations.



**Figure 4** Viscosity flow curves of the 0.5N NaOH sequential extracts at four different concentrations.

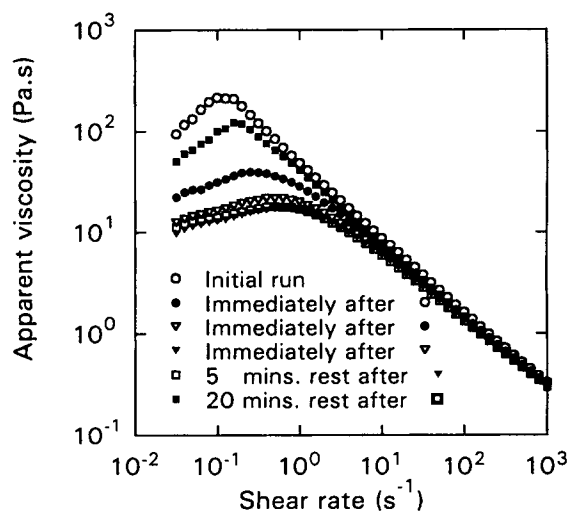
solution of phenolic acid fractions from bark which depends on the concentration of base in the extraction solvent.

In Figures 3 and 5, reversible shear thickening is observed at low shear rates for the most concentrated extract solutions. As the shear rate is increased, the viscosity passes through a maximum and then decreases. Further, this anomaly in viscosity in the low-shear region was found to be significantly time-dependent, as seen in Figure 6. Figure 6 demonstrates the effect of shear history and structural recovery upon the 21.0% 0.1N NaOH sequential extract. The extracts investigated here showed a time-dependent thixotropic response, indicating that these polymers contain segments that are capable of reversible association. The viscosity, especially at high concentrations, appears to diverge from power law behavior as shear rate approaches zero, preventing any estimate of the low-shear limiting viscosity. This divergence in viscosity at vanishing shear rate represents a solidlike response to the imposed flow field.<sup>19</sup> Increasing preshearing of the extract causes not only a decrease of solution viscosity, but also results in a decrease in the degree of shear thickening in the low-shear rate region. These effects may be caused by a change from primarily intramolecular to intermolecular associations, causing a lower distortion of the imposed flow field.<sup>20,21</sup> It has been suggested that this phenomenon in ionic polymers is caused by single-chain elongation as shear causes the breakup of intramolecular ion-pair associations and the formation of more intermolecular ion-pair associations.<sup>22</sup> Yemelyanov et al.<sup>23</sup> showed the transition from Newtonian to non-



**Figure 5** Viscosity flow curves of the 1N NaOH sequential extracts at four different concentrations.

Newtonian shear-thickening behavior of poly(acrylic acid) (PAA) polyelectrolyte solutions as the hydrophobicity of PAA molecules was increased. Here, it was suggested that this transition in flow character of the polyelectrolytes in aqueous medium was due to the presence of hydrogen bonds of the hydrophobic macromolecule interaction alongside those with strong polarity. The results in Figure 6 suggests that the rate-sweep measurements are influenced by time-dependent effects and, thus, full recovery time was given to the samples prior to the rheological measurements due to this limitation.



**Figure 6** Steady-rate sweep data for 21.0% (w/w) 0.1N NaOH sequential extract with various preshear history at 20°C.

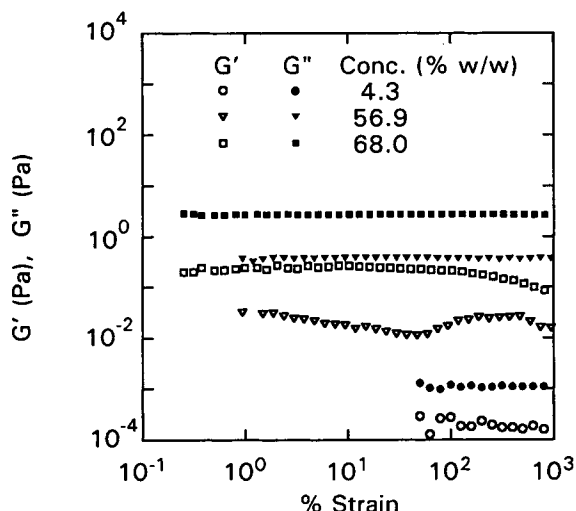


Figure 7 Strain sweeps for HWE at  $\omega = 1 \text{ rad s}^{-1}$ .

Further evidence for the above effect of the phenolic acid fractions on the microstructure and rheology of the solutions was obtained from plots of elastic modulus  $G'$  and viscous modulus  $G''$  over various concentrations. Dynamic oscillatory measurements were carried out in order to examine the shear-sensitive associations of molecules and clusters at low deformations. Dynamic moduli (storage modulus  $G'$  and loss modulus  $G''$ ) of the extracts were measured as a function of strain amplitude at a fixed frequency to obtain the linear viscoelastic region. The strain sweep for the HWE at various concentrations (sample series A) measured at  $1 \text{ rad s}^{-1}$  frequency is shown in Figure 7. Figure 7 indicates that both moduli are fairly independent of the ap-

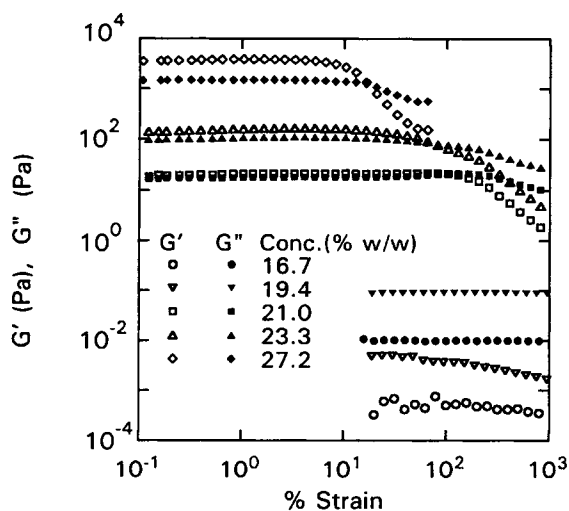


Figure 8 Strain sweeps for the 0.1N NaOH sequential extracts of five different concentrations at  $\omega = 1 \text{ rad s}^{-1}$ .

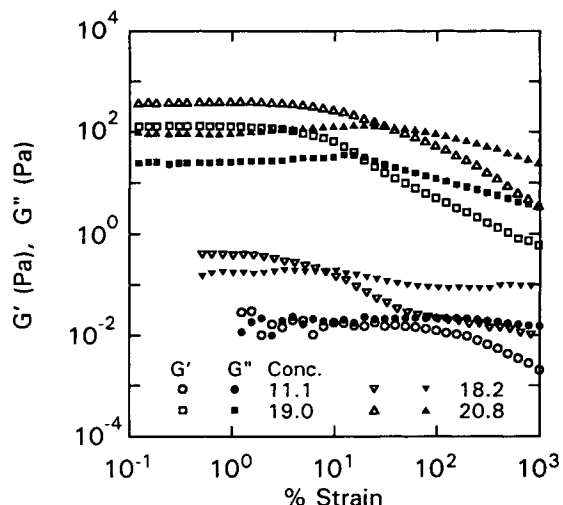


Figure 9 Strain sweeps for the 0.5N NaOH sequential extracts of four different concentrations at  $\omega = 1 \text{ rad s}^{-1}$ .

plied strain amplitude in the region studied. Figure 7 also indicates that the HWE appear to behave as viscous liquids even at concentrations as high as 68%. This has the implication that the HWE are primarily composed of relatively small proanthocyanidin oligomers, thus not showing the entanglement and elasticity of higher molecular weight polymers.

The strain dependence of the phenolic acid fractions obtained by sequential extraction with 0.1, 0.5, and 1N NaOH is also examined in Figures 8–10. Figure 8 shows that the moduli for the 0.1N extracts (sample series B) are fairly independent of the applied strain at low concentrations, while the moduli

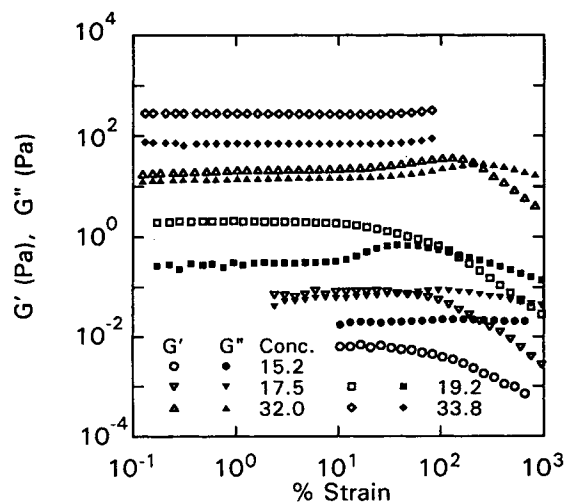
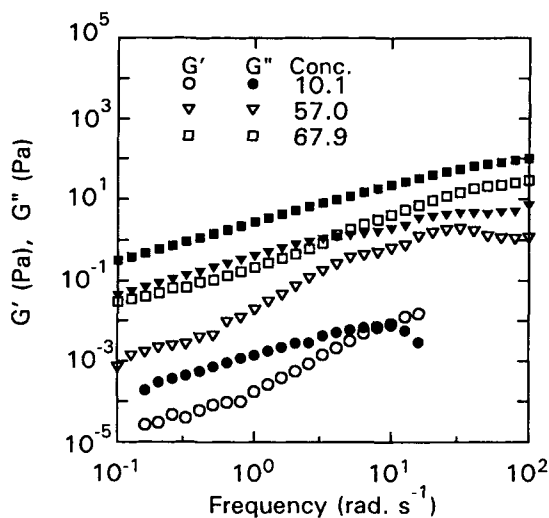


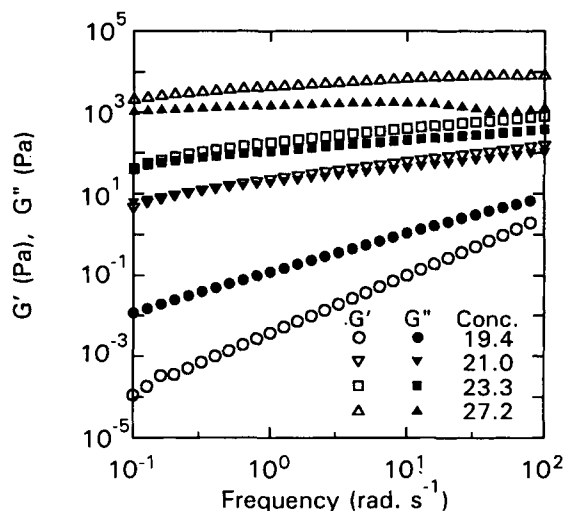
Figure 10 Strain sweeps for the 1N NaOH sequential extracts of five different concentrations at  $\omega = 1 \text{ rad s}^{-1}$ .

of concentrated extracts initially remain independent of the strain but start to decrease significantly at certain strains as the concentration increases. Notably, the linearity limit decreases with increasing concentration. This indicates that the microstructure of these extracts at high concentrations is significantly broken with applied shear, leading a critical strain after which the significant decline in the elastic modulus results, whereas the HWE at similar concentrations (Fig. 7) behave as viscous liquids. The elastic modulus becomes dominant with  $G'$  crossing over  $G''$  at concentrations above approximately 20%.

Figure 9 shows the strain sweeps for 0.5N extract (sample series C) over various concentrations. The rheology of the system is similar to that obtained from 0.1N extracts. However, the system is becoming more elastic in its behavior at lower concentrations. The dominance of elastic modulus in the low-strain region was already achieved at a concentration of 11%. It is interesting to note that the linearity limit increases slightly with increasing concentration which is contrary to the 0.1N sequential extracts. Similar behavior was shown from the strain sweeps for 1N sequential extracts (sample series D). Again, the linearity limit increases with increasing concentration. The crossover concentration ( $C_{G'=G''}$ ) was inversely proportional to the normality of aqueous NaOH extraction solutions, which indicates that the highly polymerized materials are progressively extracted as the alkalinity of the solvent increases. Previous studies<sup>18</sup> indicate that a major part of this component (NaOH soluble) consists of pro-



**Figure 11** Elastic modulus ( $G'$ ) and viscous modulus ( $G''$ ) vs. frequency ( $\omega$ ) for the HWE of various concentrations.

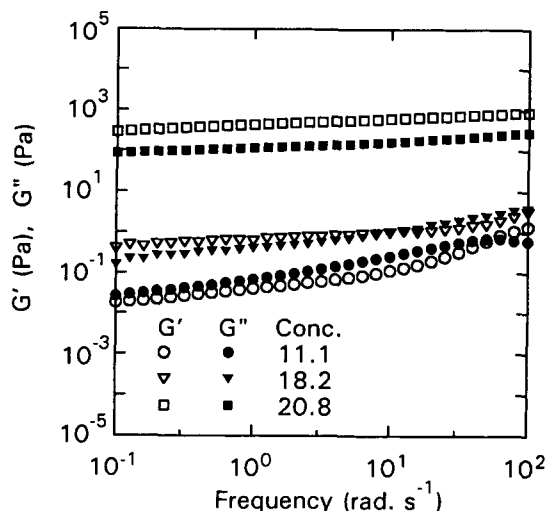


**Figure 12** Elastic modulus ( $G'$ ) and viscous modulus ( $G''$ ) vs. frequency ( $\omega$ ) for the 0.1N NaOH sequential extracts at various concentrations.

cyanidin polymers and aliphatic long-chain dicarboxylic acids. Yazaki and Aung<sup>18</sup> presumed that these aliphatic dicarboxylic acids are generated by base hydrolysis of the crosslinked cutin structure present in bark. Thus, the high degree of viscoelasticity shown by these samples may be attributed to colloidal interactions involving the carbohydrate component.

Figure 11 shows the variation of  $G'$  and  $G''$  with frequency ( $\omega$ ) for the HWE at various concentrations. For all extract concentrations examined,  $G'$  values are smaller than  $G''$  values and all  $G'$  values are relatively low and increase progressively with increasing frequency, i.e., the extracts are behaving essentially as a viscous liquid, as discussed earlier. This suggests that the macromolecules are well separated and that there is little molecular interaction or entanglement, even at higher concentrations (67.9%). Thus, there is little "connectivity" in the extracts, resulting in the small elastic contribution.

Significant differences in the general viscoelastic properties were observed among the aqueous NaOH sequential extracts for different concentrations and frequencies as shown in Figures 12–14. The elastic modulus (Fig. 12) for 0.1N aqueous NaOH sequential extracts (sample series B) reflect Maxwellian behavior in which the universal low-frequency limit is supplemented with a plateau region at high frequencies. The relaxation frequency, which characterizes the transition region between the two limits, decreases with increasing concentration. At 19.4%,  $G'$  values are smaller than are  $G''$  values and  $G'$  shows a pronounced frequency dependence, i.e., behavior

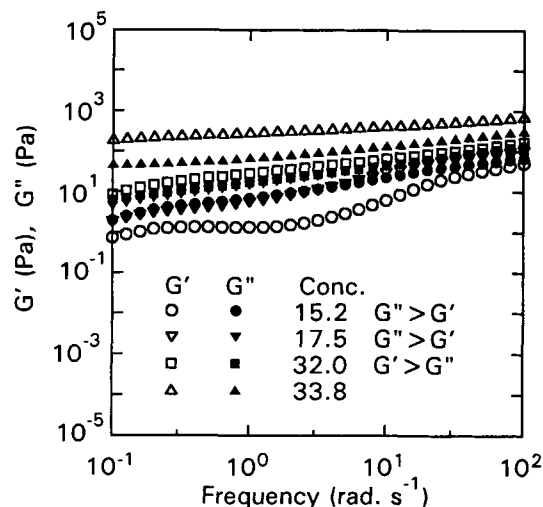


**Figure 13** Elastic modulus ( $G'$ ) and viscous modulus ( $G''$ ) vs. frequency ( $\omega$ ) for the 0.5N NaOH sequential extracts at various concentrations.

characteristic of a viscous liquid. With a further increase in concentration to 21.0%,  $G'$  crosses over  $G''$  at about  $3 \times 10^{-1}$  rad  $s^{-1}$  and becomes considerably less frequency-dependent, and the modulus values are all approximately three orders of magnitude greater than at 19.4%. As the concentration is increased further to 23.3%, the crossover now occurs at  $10^{-1}$  rad  $s^{-1}$ . Thus, the transition from a viscous liquid to a viscoelastic material occurs for the 0.1N NaOH extract over a very narrow concentration range spanning about 20%. At higher concentrations (27%), the behavior is highly viscoelastic.

Both the elastic and the loss modulus increased as the alkalinity of the extraction solvent increased from 0.1N (sample series B) to 0.5N (sample series C) as shown in Figure 13. Here, both moduli are approaching frequency independence at a concentration of 11.1% with a low-frequency crossover concentration of about 15 wt %. Here, the 20.8% extract has a distinct rubberlike plateau with  $G' = 300$  Pa. It is noteworthy that the gel structure of the sample was extremely rigid throughout the high concentrations examined. A further increase in alkalinity of the extraction solvent to 1N (sample series D) resulted in a similar behavior as shown in Figure 14, but the transition concentration to a viscoelastic material was delayed to much higher concentration (30 wt %).

The complexation of the long-chain high molecular weight proanthocyanidins with a polysaccharide fraction of the aqueous NaOH sequential extracts<sup>18</sup> at high concentration may result in a dominance of the elastic modulus over the whole frequency range



**Figure 14** Elastic modulus ( $G'$ ) and viscous modulus ( $G''$ ) vs. frequency ( $\omega$ ) for the 1N NaOH sequential extracts at various concentrations.

examined which was not observed with the HWE shown in Figure 11. This significant difference in behavior of the aqueous NaOH sequential extracts from those obtained by HWE suggests that the pronounced viscoelasticity of sodium hydroxide sequential extracts is primarily due to colloidal interactions<sup>1,24</sup> and autocondensation and recombination<sup>9,10</sup> to longer-chain polymers involving the carbohydrate component, although alkali has been shown to convert water-insoluble polyphenols to lower molecular weight fractions by acting as a nucleophile during alkali extraction.<sup>25</sup> Hemingway and McGraw<sup>15</sup> showed that for southern pine the alkaline extracts contain not only phenolic acids but also polysaccharide components without phenolic character which act as contaminants in adhesive formulations and commented on the difficulty of completely separating the carbohydrates from the polyphenols. The significant viscoelasticity of the alkali-

**Table II** Acid Content at Different Extraction Temperatures

| Water Extraction (°C) | Acid Content (Equivalents/50 g Dry Bark) |                    |                              |
|-----------------------|--|--------------------|------------------------------|
|                       | Water Soluble                            | Total <sup>a</sup> | Water Insoluble <sup>b</sup> |
| 20                    | 1.08                                     | 3.49               | 2.41                         |
| 100                   | 2.58                                     | 4.64               | 2.06                         |

<sup>a</sup> By sodium acetate extraction.

<sup>b</sup> By difference.



**Table III Acid Content in HWE With and Without Phlobaphenes**

| Extracts         | Acid Content<br>(Equivalents/50 g Bark) |                    |                                     |
|------------------|---|--------------------|-------------------------------------|
|                  | Hot Water<br>Soluble                    | Total <sup>a</sup> | Hot Water<br>Insoluble <sup>b</sup> |
| With phlobaphene | 2.58                                    | 6.50               | 3.92                                |
| No phlobaphene   | 2.10                                    | 4.64               | 2.54                                |

<sup>a</sup> By sodium acetate extraction.<sup>b</sup> By difference.

soluble materials observed here show that these components have a critical impact on the flow characteristics of the extracts themselves.

Very little molecular characterization has been carried out on the polyphenolic acid fractions even though most species of bark contain similar fractions.<sup>2</sup> It can be seen from Table II that the acidity of extracts can be varied by changing the extraction temperatures. The acid content of the HWE was also determined in the absence of the phlobaphene fraction in order to characterize the nature of this fraction. The significant increase in the acidity through the inclusion of phlobaphenes in Table III suggests that phlobaphene fractions are associated with significant amounts of carboxylic acid containing carbohydrates.

## CONCLUSION

Hot-water-extracted bark of *Pinus radiata* was successively extracted with aqueous NaOH solutions at various alkalinity to liberate hot-water insolubles and these alkaline extracts showed an increasing viscoelastic behavior that was not shown at any concentration by the hot-water soluble fractions. The crossover concentration ( $C_{G'=G''}$ ) of aqueous NaOH sequential extracts was inversely proportional to the normality of aqueous NaOH extraction solutions, which indicates that the highly polymerized materials are progressively extracted as the alkalinity of the solvent increases. This significant viscoelasticity of the base-soluble extracts from *P. radiata* bark shows that these could have a critical impact on the flow characteristics in the formulation and application of wood adhesives. Such complex flow behavior arises from contributions from colloidal interactions involving the carbohydrate component. The amounts of extractable and unextractable phenolic acid fraction from *P. radiata* bark was

examined by the reaction of bark acids with aqueous sodium acetate. The significant increase of acidity arising through the inclusion of phlobaphenes suggests that phlobaphene fractions may be associated with a significant amount of carboxylic acid containing carbohydrates.

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## REFERENCES

1. S. Kim and D. E. Mainwaring, *J. Appl. Polym. Sci.*, **56**, 905 (1995).
2. H. L. Hergert, *Adhesives in Renewable Resources*, R. W. Hemingway, A. H. Conner, and S. J. Branham, Eds., ACS Symposium Series 385, American Chemical Society, Washington, DC, 1989, Chap. 12, pp. 155-171.
3. F. W. Herrick and R. J. Conca, *Forest Prod. J.*, **July**, 361-368 (1960).
4. R. W. Hemingway, in *Proceedings of Complete Tree Utilization to Southern Pine Symposium*, New Orleans, April 17-19, 1978.
5. E. von Leyser and A. Pizzi, *Holz Roh Werkstoff*, **48**, 25-29 (1990).
6. Y. Yazaki and W. E. Hillis, *Holzforchung*, **34**, 125-130 (1980).
7. L. J. Porter, in *Adhesives in Renewable Resources*, R. W. Hemingway, A. H. Conner, and S. J. Branham, Eds., ACS Symposium Series 385, American Chemical Society, Washington, DC, 1989, Chap. 13, pp. 172-184.
8. L. Y. Foo, G. W. McGraw, and R. W. Hemingway, *J. Chem. Soc. Chem. Commun.*, 672 (1983).
9. A. Pizzi and A. Stephanou, *Holzforch. Holzverwert.*, **45**(2), 30-33 (1993).
10. A. Pizzi and A. Stephanou, *J. Appl. Polym. Sci.*, **51**, 2109-2124 (1994).
11. J. K. Woo, Paper presented at the *International Symposium on Adhesion and Adhesives for Structural Materials*, Washington State University, Pullman, WA, Sept. 28-30, 1982.
12. Y. Yazaki, *Holzforchung*, **38**, 79-84 (1984).
13. P. E. Laks, R. W. Hemingway, and A. H. Conner, *J. Chem. Soc. Perkin Trans.* **1**, 1875 (1987).
14. G. Weissmann, *Int. J. Adhes. Adhes.*, **3**, 31-35 (1983).
15. R. W. Hemingway and G. W. McGraw, *Appl. Polym. Symp.*, **28**, 1349-1364 (1976).
16. H. L. Hergert, *The Chemistry of Flavonoid Compounds*, Part 17, T. A. Geissman, Ed., Macmillan, New York, 1962, p. 553.

17. R. V. Subramanian, in *The Chemistry of Solid Woods*, R. Rowell, Ed., American Chemical Society, Washington, DC, 1984, Chap. 9, pp. 323–348.
18. Y. Yazaki and T. Aung, *Holzforschung*, **42**(6), 357–360 (1988).
19. A. J. Hopkins and L. V. Woodcock, *J. Chem. Soc. Faraday Trans.*, **86**(12), 2121–2132 (1990).
20. P. Bradna and O. Quadrat, *Colloid Polym. Sci.*, **262**, 189–196 (1984).
21. T. A. Witten, Jr. and M. H. Cohen, *Macromolecules*, **18**, 1915–1918 (1985).
22. M. J. Ballard, R. Buscall, and F. A. Waite, *Polymer*, **29**, 1287–1293 (1988).
23. D. N. Yemelyanov, B. V. Myasnikov, and L. I. Myasnikova, in *Proceedings of the Third European Rheology Conference and Golden Jubilee Meeting of the British Society of Rheology*, D. R. Oliver, Ed., Elsevier, London, 1990, pp. 519–521.
24. A. Pizzi and A. Stephanou, *J. Appl. Polym. Sci.*, **51**, 2125–2130 (1994).
25. P. E. Laks and R. W. Hemingway, *J. Chem. Soc. Perkin Trans. I*, 465–470 (1987).

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