Comparative Rheological Characteristics of Industrial Polyflavonoid Tannin Extracts

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ABSTRACT: Commercial, industrially produced mimosa, quebracho, pine, and pecan polyflavonoid tannin extracts water solutions of different concentrations were examined by rheometry by measuring dynamic moduli both as a function of strain amplitude and at varying frequency. The water solutions of these materials have been found to behave in general mainly as viscous liquids at the concentrations that are generally used for their main industrial applications. Clear indications of viscoelastic response are also noticeable, among these the crossover of the elastic and viscous moduli curves at the lower concentrations of the range investigated, with some differences being noticeable between each tannin and the others—pine and quebracho tannin extracts showing the more marked viscoelastic behavior. Other than pH dependence (and related structural considerations), the parameters found to be of interest as regards the noticeable viscoelastic behavior of the tannin extracts were the existence in the solutions of labile microstructures that can be broken by applied shear. This is supported by the well-known thixotropic behavior of concentrated, commercial polyflavonoid tannin extracts water solutions. Such microstructures appear to be due (1) to the known colloidal interactions of these materials already reported, or (b) to other types of secondary interactions between tannin oligomers and particularly between tannin and carbohydrate oligomers. The latter is supported by the dependence of this effect from both the average molecular masses of the tannin and of the carbohydrate oligomers. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1634–1642, 2001

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INTRODUCTION

Polyflavonoid tannin extracts have been produced and used industrially for many applications since the end of the 19th century.[1,2] Among these uses are the early ones as dyes for silk, and their predominant use today as tanning agents for the manufacture of leather[2] as well as their use as wood adhesives.[1] Considering the relevance of

their rheological characteristics on their main fields of industrial application, the literature is almost completely devoid of rheological studies on these materials. Recently, a study on the rheology of pine bark tannin extracts has been presented; unfortunately, these were extracted under conditions very different than what is used under industrially manufacturing.[3–5] Although interesting and valuable information was indeed obtained on the effects of pH and concentration, this study was limited only to pine bark tannin extract obtained under conditions rather distant from the almost standard conditions used for commercial

extraction of these tannins.[3–5] For example, the use of high temperature extraction with sodium hydroxide yielded solutions whose characteristic rheological behavior was predominantly that of a great excess of carbohydrate hydrocolloid gums obtained with such a method, in many cases masking completely the behavior of the tannin itself, and yielding some incorrect conclusion.[3–5] This caused, furthermore, the need to use in the study extract concentrations mostly lower than those used in their industrial applications, the two problems outlined yielding conclusions mainly inapplicable to industrial tannins and their applications.[3–5] It had the merit, however, due to the same preponderance of hydrocolloid gums, to clearly show the importance of secondary force associations between tannin and carbohydrate oligomers.[3–5] This study thus did not address the rheological characteristics of industrially manufactured tannin extracts of different types—hence of the tannin extracts that are indeed used in the industrial applications mentioned above.

In this article the rheological characteristics of four commercial polyflavonoid tannin extracts, extracted under standard conditions, and of industrial tannin extracts modified for different adhesive applications, are investigated and compared.

EXPERIMENTAL

Water solutions of commercial polyflavonoid tannin extracts of mimosa (*Acacia mearnsii*) bark, quebracho (*Schinopsis balansae*) wood, pine (*Pinus radiata*) bark, and Pecan (*Carya illinoensis*) nut membranes, the origin of which were respectively from Brazil, Argentina, Chile, and the USA, were prepared at four different concentrations— namely 20, 30, 40, and 50%. The tannin extracts are produced industrially by countercurrent extraction with just water at 95°C in the case of mimosa, by countercurrent extraction with respectively 5 and 2% sodium sulfite, and 100 and 70°C for quebracho and pine tannin extracts respectively, and by countercurrent extraction with 2–4% sodium sulfite and 0.4% sodium carbonate for pecan nut tannin extract. The industrially spray-dried tannin extracts were guaranteed at a percentage tannin (defined as the phenolic fraction of the extract containing trimers and higher oligomers as defined by the hide power test method) content of 75, 75, 72, and 80% for mimosa, quebracho, pine, and pecan respectively,

and all contained carbohydrate oligomers and monomers, although at different amounts.[1,6–13] Solutions of gum arabic of the same concentrations as the tannins were studied as a model of the carbohydrate oligomers also present in the extracts. Mimosa and quebracho tannins are mainly composed of mixtures of prorobinetinidins and profisetinidins, while pine tannin is almost exclusively composed of procyanidins and pecan nut tannin is composed of a very predominant part of prodelphinidins and some procyanidins.

The solutions were tested with a Rheometrics Controlled Stress Rheometer RS-500 with parallel plates geometry, which was used for all the measurements; the plate diameter used was 40 mm and the gap in between the parallel plates was 0.2 mm. Temperature was maintained constant at 20 ± 1°C. A humidity cover plus solvent trap was used to prevent solvent evaporation.

During oscillatory rheological measurements, the shear was applied sinusoidally at a maximum strain amplitude (γ_{max}) and angular frequency (ω) according to the standard relationship $\gamma(t) = \gamma_{max} \sin(\omega t)$. The amplitude of the shear stress (τ) and the phase difference (δ) between the stress and strain were monitored according to the relationship $\tau(t) = \tau_{max} \sin(\omega t)$. From these measurements the in-phase elastic modulus G' and the out-of-phase viscous modulus G'' were obtained via the relationship $\tau(t) = \gamma_{max} [G' \sin(\omega t) + G'' \cos(\omega t)]$. In the oscillatory mode, measurements were first made as a function of strain amplitude to try to ensure linearity. Once the linear region was established, measurements were made as a function of frequency at fixed amplitude.

RESULTS AND DISCUSSION

Figures 1–4 show plots of elastic modulus G' and viscous modulus G'' over various concentrations (20–50%) of water solutions of four natural polyflavonoid extracts—namely, mimosa, quebracho, pine, and pecan nut tannin extracts. 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 different extracts were measured as a function of strain amplitude at a fixed frequency to obtain the linear viscoelastic region. The strain sweep for the four natural extracts at various concentrations (20, 30, 40, 50%) measured at 1 rad s^{-1} frequency are shown in Figures 1–4. These figures show that in general $G'' > G'$
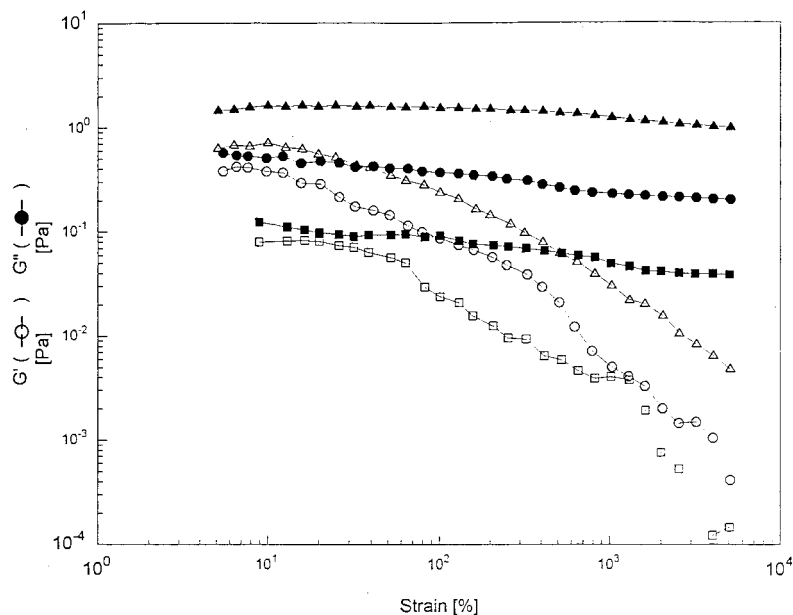
Figure 1   Strain sweeps at $\omega = 1$ rad s^{-1} for mimosa tannin extract solutions at different concentrations: (■) 30%, (●) 40%, and (▲) 50%. (○) G' curves; (●) G'' curves.

for the solutions of all the tannin and hence that the solutions of industrial polyflavonoid tannin extracts behave as viscous liquids even at the higher (50%) concentration. This indicates that commercial tannin extracts are primarily composed of relatively short oligomers that do not appear to show the entanglement and elasticity of higher molecular weight polymers. This is supported by measures of number and weight average molecular masses for the four tannins obtained by different techniques[14,15] showing that typical number average degree of polymerization (DP$_n$) of mimosa, quebracho, pine, and pecan industrial tannin extracts[14,15] are respectively 4.9, 6.7, 5.9, and 5.5. A level of entanglement is possible, however, for the higher molecular mass
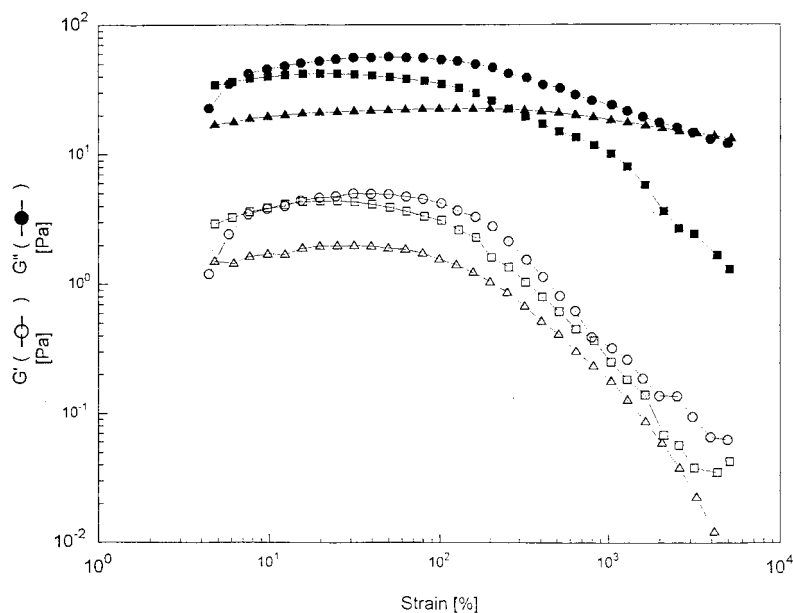

Figure 2   Strain sweeps at $\omega = 1$ rad sG'' for quebracho tannin extract solutions at different concentrations: (●) 30%, (●) 40%, and (▲) 50%. (○) G' curves; (●) G'' curves.
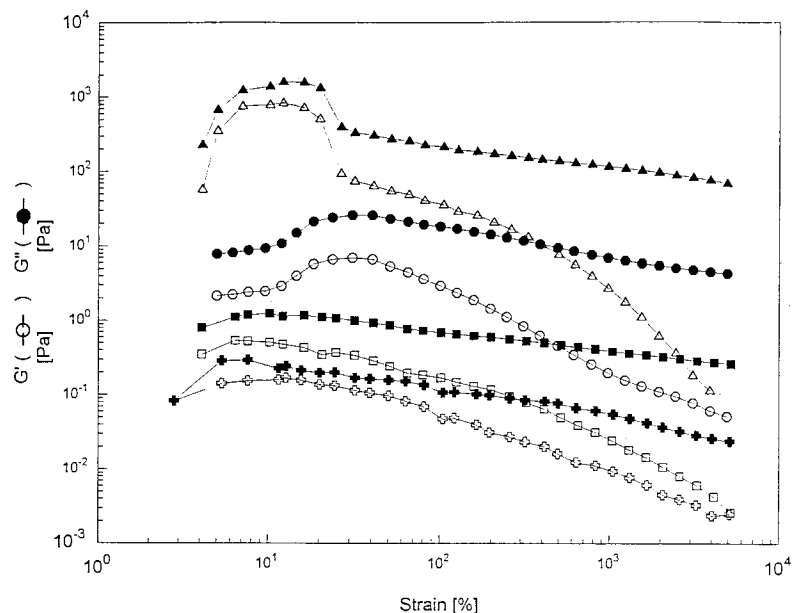
Figure 3 Strain sweeps at $\omega = 1$ rad s^{-1} for pine tannin extract solutions at different concentrations: (✚) 20%, (■) 30%, (●) 40%, and (▲) 50%. (○) G' curves; (●)G'' curves.

fractions of the tannins if one considers that typical values of the weight average degree of polymerization (DP$_w$) are respectively 8.8, 12.3, 10.9, and 9.5 for mimosa, quebracho, pine, and pecan tannins, and the great number of polar hydroxy groups present on these molecules.[14]

These figures also indicate that in the low percentage strain region both moduli appear to be fairly independent of the applied strain amplitude as shown from the almost parallel trend of the two moduli curves. However, when the percentage strain increases, the value of G' starts to decrease
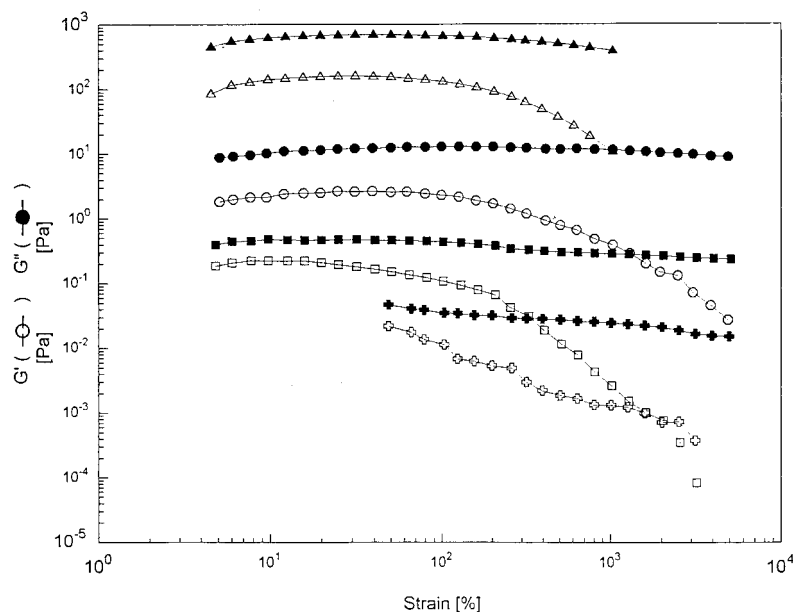

Figure 4 Strain sweeps at $\omega = 1$ rad s^{-1} for pecan tannin extract solutions at different concentrations: (✚) 20%, (■) 30%, (●) 40%, and (▲) 50%. (○) G' curves; (●)G'' curves.
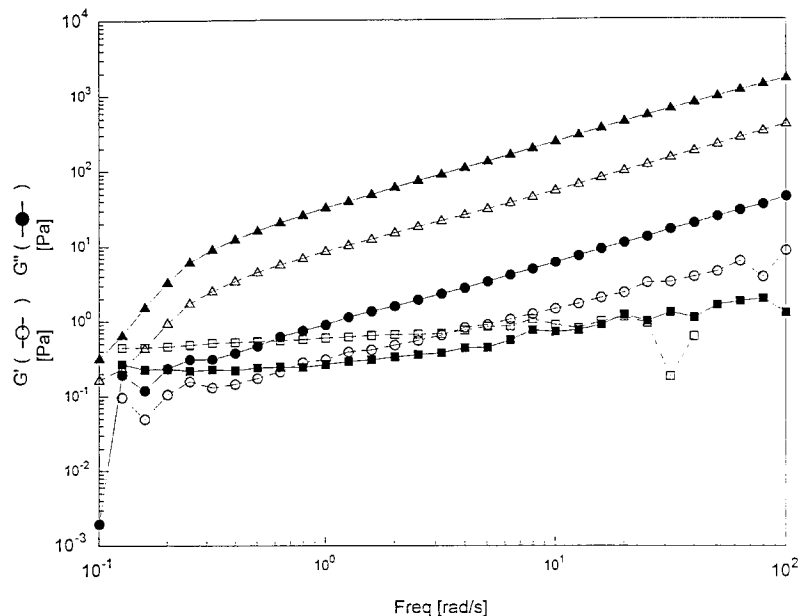
Figure 5   Elastic modulus (G') and viscous modulus (G'') as a function of frequency (ω) for mimosa tannin extract solutions at different concentrations: ($\blacksquare$) 30%, ($\bullet$) 40%, and ($\blacktriangle$) 50%. ($\bigcirc$)G' curves; ($\bullet$)G''curves, with 10% strain.

significantly in relation to the value of G'', a trend that becomes slightly more evident the lower the concentration studied. Furthermore, the G' linearity limit appears to decrease somewhat with increasing concentration. This indicates the following, notwithstanding the purely viscous liquid behavior of these tannin extract solutions: (1) microstructures exist for these extracts in solution—a fact supported by the known colloidal interactions for these materials already reported[3–5,16–21]; and (2) such microstructures are labile as they are significantly broken with applied shear, leading to a critical strain, after which a significant decline in the elastic modulus results, a fact supported by the well-known thixotropic behavior of concentrated, commercial polyflavonoid tannin extract water solutions.[1,4,16,18] For the two higher concentrations used, and also for the 30% concentration, with only one exception, as the extracts were used at their natural pH, which is in the 4.2–5.1 range, there was no case where $G' > G''$ and no concentration occurred at which $G' = G''$, as this behavior has been associated with much higher alkalinity ranges.[4]

While these are general trends for all the four polyflavonoid tannins, some important difference between the tannins also exists, mainly based on their differences in viscosity. First, G' starts decreasing according to the different typical molecular masses of each tannin: to a higher molecular mass corresponds a later start in the decrease of

G'. The main difference occurs for pine tannin extract solutions where two plateaus for G' and G'' occur, with this becoming more evident the higher the tannin solution concentration. The existence of another transition at lower percentage strain also indicates the presence of another type of labile microstructure. Secondary force associations between tannin oligomers and oligomeric sugars, derived from degraded hemicelluloses that are always present in consistent proportions in these extracts, are well known.[1,4,14,15] They have often caused in the past the incorrect determination of absurdly high molecular masses for tannin oligomers due to the formation of ionic polymers between tannins and carbohydrate oligomers. This transition is particularly evident in Figure 3 for the pine tannin extract. It is not possible to conclude from the available data if this is the cause of the additional transition in pine tannin, or rather, if the affinity of carbohydrates for tannins is the transition that occurs for all the four tannins. The decrease of these secondary force associations at higher percentage strains will cause the system to appear to behave as composed of species of lower average molecular mass with the consequent trend observed for G' in Figures 1–4.

Figures 5–8 show the variation of G' and G'' with frequency for the four tannins each at four different concentrations. The lower the slope of
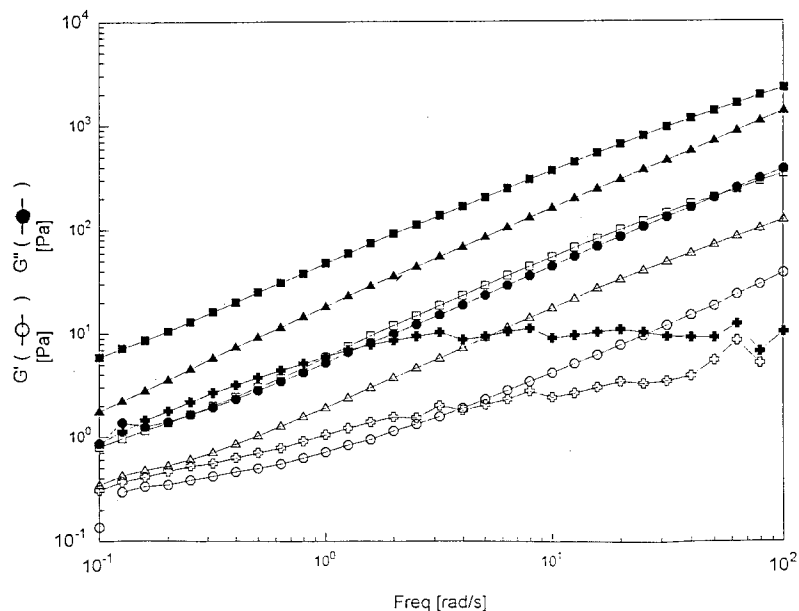
Figure 6 Elastic modulus (G') and viscous modulus (G'') as a function of frequency (ω) for quebracho tannin extract solutions at different concentrations: (✚) 20%, (■) 30%, (●) 40%, and (▲) 50%. (○)G' curves; (●)G'' curves, with 10% strain.

the curves the closer to a newtonian behavior is the behavior of the tannin extract solution. For all the tannins and for all the concentrations examined, G' values are smaller than G'', and all G' values are relatively low and increase progressively with increasing frequency. The tannin ex-

tracts behave essentially as a viscous liquid as discussed earlier, the only exceptions being the tannin extract solutions at 20% concentration where G' and G'' crossover points do indeed occur. For concentrations higher than 20%, this appears to suggest that the tannin oligomers are well sep-
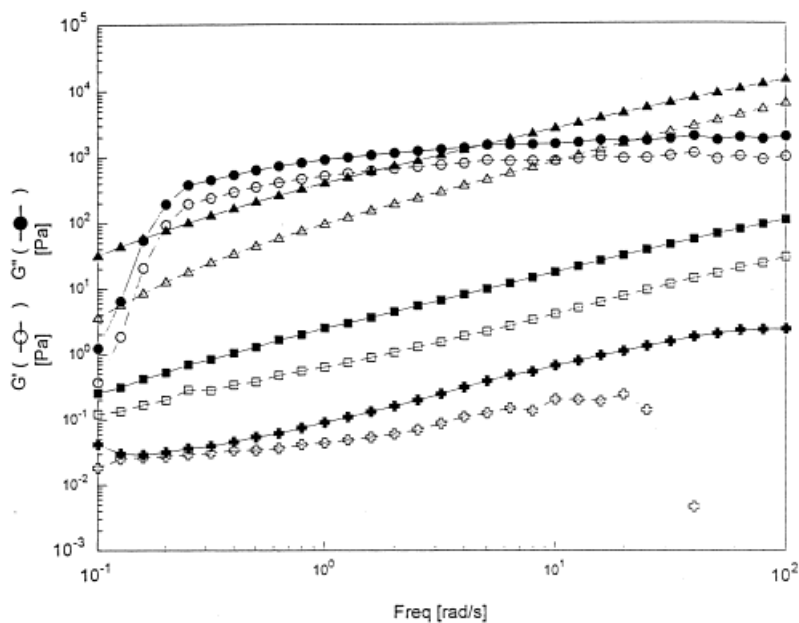
Figure 7 Elastic modulus (G') and viscous modulus (G'') as a function of frequency (ω) for pine tannin extract solutions at different concentrations: (✚) 20%, (■) 30%, (●) 40%, and (▲) 50%. (○)G'curves; (●)G''curves, with 10% strain.
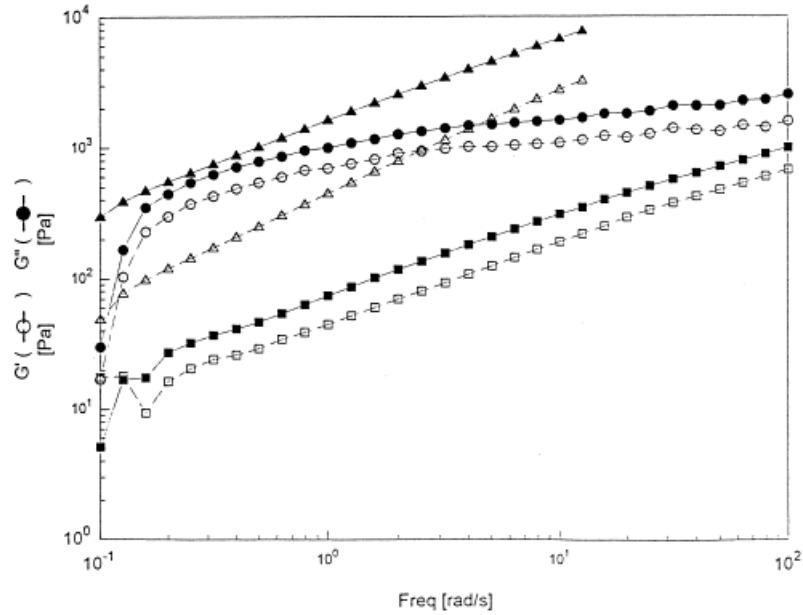
Figure 8 Elastic modulus (G') and viscous modulus (G'') as a function of frequency (ω) for pecan tannin extract solutions at different concentrations: (✚) 20%, (■) 30%, (●) 40%, and (▲) 50% concentration. (○)G' curves; (●)G'' curves, with 10% strain.

arated and that, once the interactions with the carbohydrate are eliminated or minimized, there is little possibility of molecular interaction and entanglement, even at the higher concentration. Thus, is there little interaction in the tannin extracts, resulting in smaller elastic contribu-

tions—or must one consider also other parameters? In this respect there are some differences in the curves of the four natural extracts. From Figure 9, which compares the elastic and viscous moduli curves for the four tannins, but for one single concentration (40%) and one fixed strain
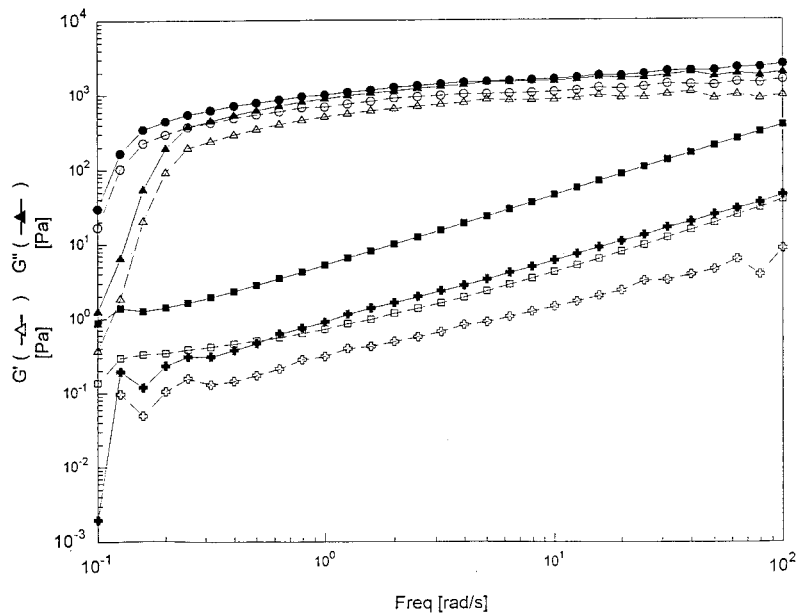

Figure 9 Elastic modulus (G') and viscous modulus (G'') as a function of frequency (ω) for the four tannin extracts: (▲) pine, (●) pecan, (■) quebracho, and (✚) mimosa at a concentration of 40% and a strain of 10%. (○)G'curves; (●) G'' curves.

(10%), it can be noticed that the value of the two moduli are quite different, passing from one tannin to the other: pecan ≅ pine ≫ quebracho > mimosa. Pine and pecan tannin extracts appear to have a similar behavior: with a rubbery plateau at higher frequencies, G' and G'' fairly independent of the frequency for the upper range of frequency, and also relatively high values of both moduli compare to the other tannin extracts. Mimosa and quebracho present much lower values of G' and G'', and both moduli are quite dependent of the frequency, increasing frequency yields to increase G' and G'' too. Considering, for example, the mimosa tannin extract (Fig. 5), which shows the lowest values of both moduli compared to the other three tannin extracts, it can be noticed that since the 20% solution of mimosa tannin extract was too viscous to obtain stable curves of G' and G'', the lowest concentration used was 30% and the crossover point $G' = G''$ occurs for this 30% solution at high frequencies. Another interesting behavior can be observed for the quebracho tannin extract solutions (Fig. 6). The expected increase of values of both moduli, while increasing the concentration, does not occur. In fact, at low frequencies, G' and G'' values of the 30% solution are bigger than respectively the values of the 50, 40, and 20% solutions, while at higher frequencies, the order of the moduli values is 30 > 50 > 20 > 40%. This unusual behavior of the two lower concentrations (20 and 30%) can be explained by the almost immediate formation of clusters on the rheometer plates when applying the sample for analyses. Indeed, the rheological properties measured in the case of 20 and 30% quebracho tannin solutions are those of the clusters (which have locally a much higher concentration) and not those from a homogeneous solution of 20 or 30%, since the formation of these clusters is immediate and cannot be avoided.

Figures 5–8 also indicate that G' and G'' present pronounced frequency dependence for mimosa and quebracho tannin extracts, as indicated by the sharper slope of the moduli curves. The same figures indicate that G' and G'' present instead little or no frequency dependence for pine and pecan tannin extracts.

A case apart appears to be the 20% concentration case for the three tannins for which such a concentration was also used (mimosa was not used at 20% concentration). A G' and G'' crossover point ($G' = G''$, and then at increasing frequency $G' > G''$) occurs for all the three tannin extracts, as also occurs for mimosa tannin solutions at 30% concentration—in all four cases at the extreme

range of the frequency used (Figures 5–8). This again confirms that on top of the effect of the pH,[4] the viscoelastic response of the tannin extracts obtained in these cases is due to intermolecular associations. It is a very clear indication that molecular associations between tannin molecules, and particularly between tannin molecules and carbohydrates to form labile structures of greater apparent molecular mass by either colloidal or other interactions, do indeed occur. An example of the behavior of a solution of a polymeric carbohydrate, such as gum arabic, at the same four concentrations and the same strain (10%) used for the tannins (Fig. 10) indicates both significant elastic properties ($G' > G''$) at the two higher concentrations (40 and 50%); the temporary network structure is strong enough. And also, at the two lower concentrations (20 and 30%), $G' = G''$ crossover points occur; $G' > G''$ at low frequencies, but increasing frequency yields to a breakdown of the more brittle temporary network structure that is formed in these less concentrated solutions of gum arabic. This again confirms the participation of carbohydrate oligomers in imparting, under certain conditions, viscoelastic behavior to tannin extract solutions, a purified tannin without any carbohydrates rather behaving as a viscous liquid only.[19–21]

CONCLUSION

Commercial, industrially produced mimosa, quebracho, pine, and pecan polyflavonoid tannin extract water solutions of different concentrations were examined by rheometry by measuring dynamic moduli both as a function of strain amplitude and at varying frequencies. The water solutions of these materials have been found to behave in general mainly as viscous liquids at the concentrations generally used for their main industrial applications.[1,2,7] Clear indications of viscoelastic response are also noticeable, among these the crossover of the elastic and viscous moduli curves at the lower concentrations of the range investigated, with some differences being noticeable between each tannin and the others, pine and quebracho tannin extracts, showing the more marked viscoelastic behavior. Other than pH dependence (and related structural considerations), the parameters found to be of interest as regards the noticeable viscoelastic behavior of the tannin extracts were the existence in the solutions of labile microstructures that can be broken by applied shear. This is supported by the well-known thixotropic behavior of concentrated, commercial
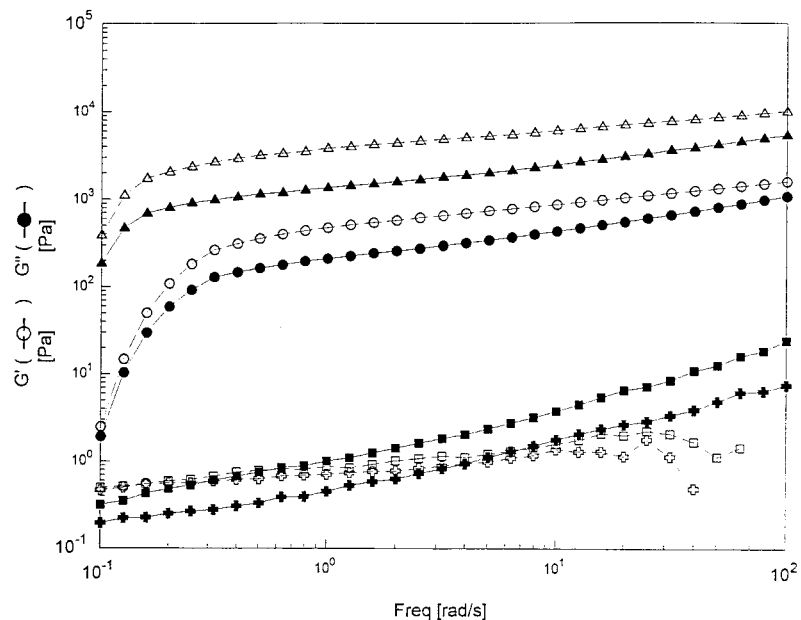
Figure 10 Elastic modulus (G') and viscous modulus (G'') as a function of frequency (ω) for gum arabic solutions at different concentrations: (✚) 20%, (■) 30%, (●) 40%, and (▲) 50%. (○)G' curves; (●)G'' curves, with 10% strain.

polyflavonoid tannin extract water solution.[1,4,16,18] Such microstructures appear to be due (1) to the known colloidal interactions of these materials already reported,[1,4,6,16,17,19–21] or (2) to other types of secondary interactions[17,19–21] between tannin oligomers and particularly between tannin and carbohydrate oligomers. The latter is supported by the dependence of this effect from both the average molecular masses of the tannin and of the carbohydrate oligomers.

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