# Rheometry of Aging of Colloidal Melamine–Urea–Formaldehyde Polycondensates

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**ABSTRACT:** Aged and whitened melamine–urea–formaldehyde (MUF) resins in a colloidal state were tested with parallel-plate rheometry to determine the extent of their viscoelastic behavior. Only in advanced colloidal states, and so only when aggregated colloidal clusters occurred, did the resins present clear indications of viscoelastic responses, as illustrated by the crossover of elastic modulus and viscous modulus curves at lower strain percentages. These colloidal clusters were labile microstructures, which, broken by applied shear, justified the known thixotropic behavior of these resins sufficiently advanced by aging or other means. MUF resins already in the colloidal state, but for which colloidal clustering had not yet occurred, behaved exclusively as viscous liquids. Two different cases of physical gelation were observed, reversible physical gelation and irreversible physical gelation, underlying which a true gel situation possibly occurred. Physical gelation due to colloidal superstructures occurred in both, but the difference in the resin average molecular masses revealed if the physical gelation was reversible or irreversible and, therefore, if the liquid/cluster separation was defined as the terminal phase of physical gelation. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 655–659, 2005

**Key words:** adhesives; ageing; colloids; gelation; polycondensation; resins; rheology; viscoelastic properties

## INTRODUCTION

The wood-panel and resin-impregnated-paper industries rely heavily on the use of synthetic polycondensation resins. Among these resins, melamine resins, particularly melamine–urea–formaldehyde (MUF) resins, are very important for these applications. Recently, several low-cost additives have been shown to be capable of improving the performance of MUF resins or reducing their consumption.[1–9] Such an improvement in performance appears to be due particularly to the disruption of the colloidal state of these resins, as observed by low-angle laser light scattering (LALLS). All formaldehyde-based resins have been perceived for a long time to be in a colloidal state.[10–16] The aging of MUF resins has been shown to proceed from clear resins (molecular colloidal aggregation) to superclusters of whitened, thixotropic resins at the beginning of physical gelation to liquid/cluster separation, which is the terminal stage of physical gelation.[16]

Colloidal particle formation, followed by clustering, has been shown to be the normal path of aging of aminoplastic resins,[16] particularly MUF resins. Aging, or the further advancement of a resin by any other means, such as longer condensation times, causes the whitening of the resin. This is a macroscopic indication of the formation of colloidal particles and their clustering. Some clustering appears rather early in this process, even when most of the resin visually appears to be in a colloidal state, being transparent. However, it eventually progresses to a resin that is mostly in a colloidal, clustered state, and this is followed much later by a supercluster formation that involves the whole resin. A correspondence between increases in the molecular masses has been shown to exist by gel permeation chromatography (GPC), LALLS, and polarizing optical microscopy.

This article deals with the influence that the colloidal state has on the development of thixotropy and the viscoelastic behavior presented by some liquid-phase formaldehyde resins such as MUF resins.

## EXPERIMENTAL

Water solutions of two MUF resins, one a sequential formulation and the other a nonsequential formulation, prepared according to procedures already described,[7] were tested with a Rheometrics RS-500 (Rheometrics Inc., Piscataway, NJ) controlled-stress rheometer with parallel-plate geometry for all the measurements. Both MUF resins had (melamine + urea)/formaldehyde [(M + U)/F] molar ratios of 1:1.2 and melamine/urea (M/U) weight ratios of 47:53 (solid concentration = 55%). The rheometer plate diameter was 40 mm, and the gap between the parallel
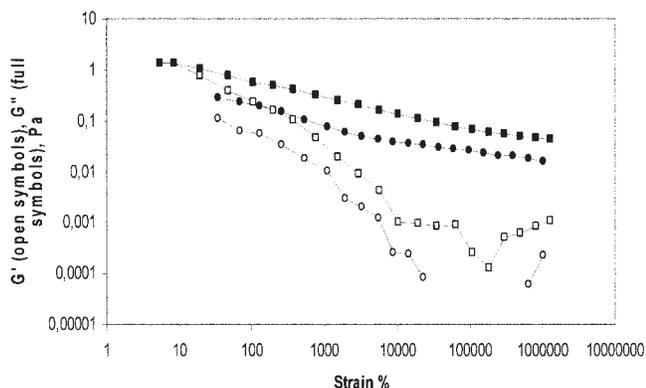
**Figure 1** Strain sweep at $\omega = 1$ rad s$^{-1}$ for a clear, colloidal, but unclustered nonsequential MUF resin [M/U = 47:53 w/w, F/(M + U) = 1.2 mol/mol] 18 months after preparation with (■,□) 54.2 and (●,○) 44% resin solid concentrations: (□,○) $G'$ and (■,●) $G''$ curves.



**Figure 2** Strain sweep at $\omega = 1$ rad s$^{-1}$ for a whitened, colloidal, and clustered sequential MUF resin [M/U = 47:53 w/w, F/(M + U) = 1.2 mol/mol] 17 months after preparation with (●,○) 54.9 and (■,□) 41% resin solid concentrations: (□,○) $G'$ and (■,●) $G''$ curves.

plates was 0.2 mm. The temperature was kept constant at $20 \pm 1°C$. A humidity cover and a solvent trap were used to prevent solvent evaporation. The resins, after being prepared, were aged for 1 month and then left in a deep freezer at $-5°C$ for 17–18 months; they were then defrosted and aged for 2 months in a refrigerator at $10°C$ and were aged even longer when liquid–solid separation due to aging was being studied. This procedure was adopted to slow down aging so that its different phases could be studied.

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

## RESULTS AND DISCUSSION

Figures 1 and 2 show plots of $G'$ and $G''$ for the two MUF resins with water solutions of various concentrations (30–60%). Dynamic oscillatory measurements were carried out to examine the shear-sensitive associations of the molecules and clusters at low deformations. The dynamic moduli ($G'$ and $G''$) of the two MUF resins were measured as functions of the strain
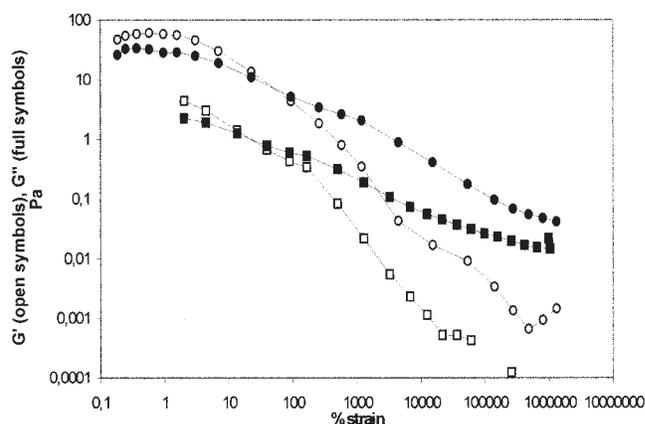
amplitude at a fixed frequency to determine the linear viscoelastic region. The strain sweep at various concentrations was measured at a frequency of 1 rad s$^{-1}$ (Figs. 1 and 2). Figure 1 shows that for the clear, nonsequential MUF resin, although it is colloidal in nature,[16] $G''$ is greater than $G'$, and so this resin behaves as a viscous liquid even at the higher (55%) concentration. This indicates that the clear resin, though in the early phases of a colloidal state, is still primarily composed of relatively short oligomers that do not appear to show the entanglement and elasticity of higher molecular weight polymers. This agrees well with GPC results already obtained for the number- and weight-average molecular masses of these resins.[16]

The plots in Figure 2 of $G'$ and $G''$ for the aged, white, sequential MUF resin present a different trend. The resin shows significant elastic properties ($G' > G''$) at low strain percentages, and this indicates the entanglement and elasticity of higher molecular weight oligomers, the presence of colloidal superclusters supported by the white and opaque appearance, or both. The molecular masses in Table I indicate that these are indeed higher in this resin but not enough to justify extensive entanglement. The inversion point of $G'$ and $G''$ is reached when associated colloidal superstructures start to part as they respond to external shear

**TABLE I**
**Number-Average Molecular Weight ($M_n$), Weight-Average Molecular Weight ($M_w$), and z-Average Molecular Weight ($M_z$) Values for the Two MUF Resins**

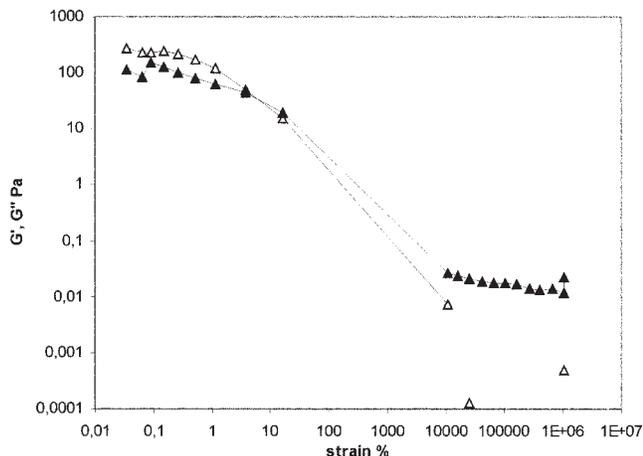|  | $M_n$ | $M_w$ | $M_z$ |
|---|---|---|---|
| MUF, nonsequential, clear | 437 | 666 | 1096 |
| MUF, sequential, white | 578 | 1021 | 1933 |

**Figure 3**  Strain sweep at $\omega = 1$ rad s$^{-1}$ for the nonsequential MUF resin of Figure 1 [M/U = 47:53 w/w, F/(M + U) = 1.2 mol/mol] diluted beyond its water tolerance point at a 41% resin solid concentration: ($\triangle$) $G'$ and ($\blacktriangle$) $G''$ curves.



**Figure 5**  $G'$ and $G''$ as a function of $\omega$ at a 1% strain for a whitened, colloidal, and clustered sequential MUF resin [M/U = 47:53 w/w, F/(M + U) = 1.2 mol/mol] 17 months after preparation at ($\blacksquare$,$\square$) 54.9 and ($\blacktriangle$,$\triangle$) 41% resin solid concentrations ($\tau = 0.2$ Pa): ($\square$,$\triangle$) $G'$ and ($\blacksquare$,$\blacktriangle$) $G''$ curves.

application. The microstructure of this MUF resin is significantly broken with applied shear, and this leads to a critical strain, after which a significant decline of $G'$ occurs. The associated colloidal superclusters present in the resin at rest are long enough to produce entanglement and, therefore, to justify $G' > G''$ at a low strain percentage. As these structures are broken, the resin becomes more fluid; this behavior appears to be reversible and hence related to the thixotropic behavior of the resin.

This confirms that ionic, colloidal interactions are likely to have an important impact on the resin and resin formulation behavior and on resin applications as wood adhesives. Beyond the $G' > G''$ crossover point, at a higher strain percentage, better substrate wetting will occur. This partly explains why lower colloidal formulations such as the nonsequential one used here can yield a better cured strength perfor-
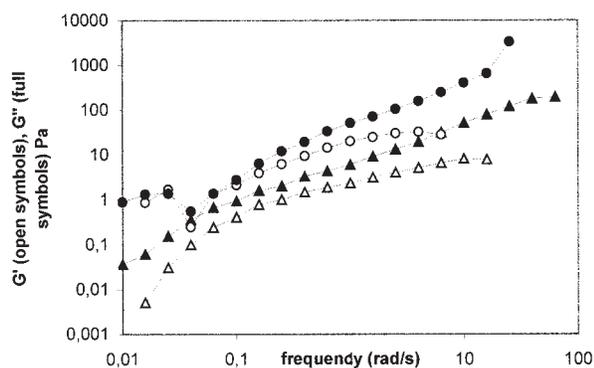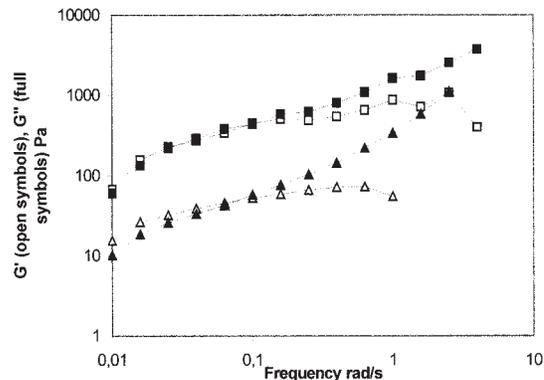
mance, at a lower melamine concentration, simply because both melamine and MUF resin waste decreases. The curves in Figure 2 also indicate that the collapse of the labile supramolecular colloidal clusters becomes easier the lower the solution concentration is of the resin (within the limits imposed to avoid resin precipitation). This is shown by the crossover of $G'$ and $G''$ occurring at a lower strain percentage when the concentration of the resin in solution is lower.

Figure 1 also indicates that in all strain regions, the moduli do not appear to be independent of the applied strain amplitude, as shown by the lack of a parallel trend of the two modulus curves. When the strain percentage increases, $G'$ starts to decrease even more significantly with respect to $G''$; this trend becomes slightly more evident at lower concentrations. This indicates that the resin has relatively low molecular masses. Furthermore, the $G'$ flat plateau limit appears to decrease somewhat with increasing concentration. This indicates that, notwithstanding the purely viscous liquid behavior of this MUF resin solution and its clear appearance, microstructures exist in solution. This fact is supported by the colloidal interactions for these materials already determined by other techniques[15] and already reported.[9–16] It indicates also that such microstructures are labile because they are significantly broken with applied shear, and this leads to a critical strain, after which a significant decline in $G'$ results. For the clear, nonsequential formulation, there was no case in which $G'$ was greater than $G''$, but $G'$ was equal to $G''$ for the plateau obtained at a low strain percentage.

Figure 3 indicates what happens to the resin shown in Figure 1 once it is diluted beyond its water tolerance point. Beyond their water tolerance point, all aminoplastic resins precipitate and remain in very finely dispersed suspensions. The rheometer response in Figure 3, at a low strain percentage, is that of an elastic



**Figure 4**  $G'$ and $G''$ as a function of $\omega$ at a 1% strain for a clear, colloidal, but unclustered nonsequential MUF resin [M/U = 47:53 w/w, F/(M + U) = 1.2 mol/mol] 18 months after preparation at ($\bullet$,$\circ$) 54.2 and ($\blacktriangle$,$\triangle$) 44% resin solid concentrations ($\tau = 0.2$ Pa): ($\circ$,$\triangle$) $G'$ and ($\bullet$,$\blacktriangle$) $G''$ curves.
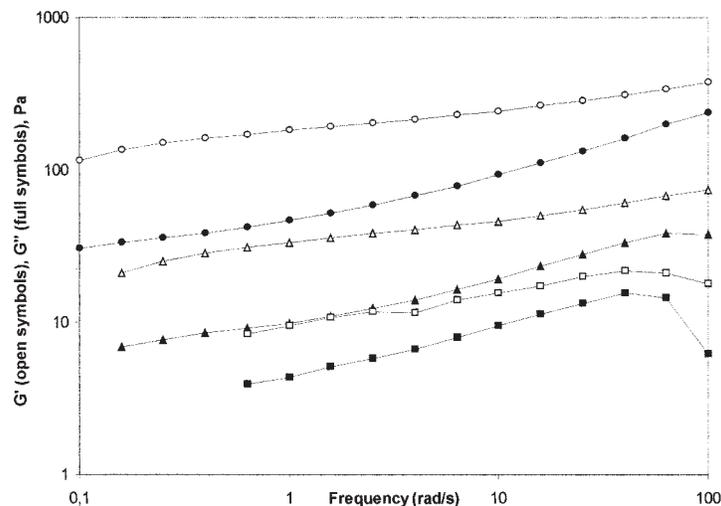
**Figure 6**  $G'$ and $G''$ as a function of $\omega$ at a 1% strain for the whitened, colloidal, and clustered sequential MUF resin of Figure 5 [M/U = 47:53 w/w, F/(M + U) = 1.2 mol/mol] aged long enough to be beyond its water tolerance point without any further water addition at (●,○) 54.9, (■,□) 47, and (▲,△) 41% resin solid concentrations: (○,□,△) $G'$ and (●,■,▲) $G''$ curves.

solid, this response being due to the nature of the colloidal polymer, which precipitates because of excess water. That this is the case is shown by the modulus value, which in Figure 1, for example, decreases at a 1% strain from 1 Pa for a 54.2% resin solid concentration to 0.3 Pa for a 44% resin solid concentration, as expected because of dilution. This increases markedly instead to 100–200 Pa for the resin diluted beyond its water tolerance point, as shown in Figure 3.Thus, beyond the water tolerance point, the rheometer reflects only the viscoelastic response of the colloidal polymer out of solution but still swollen by the solvent. This retention of solvent in the separated polymer and the still relatively low average molecular masses of the oligomers[16] are still sufficient to part associated colloidal superstructures as they respond to external shear application. For this reason, in precipitated resins at low strain percentages, $G'$ is greater than $G''$, whereas at a higher strain percentage, $G''$ is greater than $G'$; a crossover point in the particular case shown in Figure 3 is clearly visible at 50 Pa and 30% strain.

Figures 4 and 5 show the variation of $G'$ and $G''$ with the frequency for the two MUF resins. The lower the slope is of the curve, the closer the behavior of the MUF resins is to Newtonian behavior. The nonsequential, lower colloidal MUF resin in Figure 4 shows the tendency to almost (but not quite) settle into a rubbery plateau at higher frequencies, with $G'$ and $G''$ fairly independent of the frequency for the upper frequency range. $G'$ values are always smaller than $G''$ values and increase progressively with increasing frequency. The clear, nonsequential resin behaves essentially as a viscous liquid, and this suggests that the colloidal structures are small, rather stable, and well separated. In this resin then, there is little possibility of interaction

between the colloidal particles, which are however present,[15] resulting in smaller elastic contributions. This is supported by the relative values of the very low strain percentage plateau ends in Figures 1 and 2, which differ by a factor of approximately 30 between the two resins.

The behavior of the sequential MUF resin when the frequency of application to the resin solution (Fig. 5) is varied is different. Both $G'$ and $G''$ increase progressively with increasing frequency and are still fairly independent of the frequency for the upper frequency range. However, $G'$ values are higher than $G''$ values at lower frequencies, whereas $G''$ values becomes bigger than $G'$ values at higher frequencies. The crossover point is around 0.1 rad/s. This means that at a lower frequency, the resin behavior is viscoelastic, with the elastic character predominating. It starts to behave as a viscous liquid only at higher frequencies. This confirms the existence of labile structures in the sequential resins and its advanced thixotropic behavior.

As colloidal aggregation influences the stability of the MUF resins and complements what has already been found from the process of physical gelation[16] with resin aging, we found it interesting to examine the resin during a further step of its aging. Thus, in Figure 6 are reported the rheometry curves as a function of the variable frequency for the sequential MUF resin of Figures 2 and 5 after enough additional aging for the point to be reached at which its water tolerance is too low to even tolerate the water present in the liquid resin mix as originally prepared. The resin then precipitates and remains in a very finely dispersed suspension; this situation is similar to what is obtained by the addition of excess water to the resin in Figure 3, but in this case it is only reached by resin aging in

storage. Figure 6 shows that at all solid concentrations (54.9, 47, and 41%), the response of the resin at all frequencies is that of an elastic solid, this response being due to the nature of the colloidal polymer that has precipitated, with $G'$ values always bigger than $G''$ values throughout the whole range of frequencies used. Contrary to the case in Figure 3, however, the average molecular mass of the oligomers obtained by aging is higher,[16] and thus higher strains or higher frequencies and the water still present are not sufficient to destroy the colloidal superstructures of the resin and to make the resin behave again as a viscous liquid. Thus, no crossover points of $G'$ and $G''$ occur in this case. However, $G'$ and $G''$ both start to decrease at the highest frequencies used, this becoming progressively more evident the more diluted the resin suspension is. This is an indication that the colloidal superstructures of the resin start to separate and that the aggregates start to be destroyed, but the molecular mass of the resin oligomers is now so high that the resin behaves as a gel; indeed, it is a gel and cannot be liquefied anymore. The real gel point reached by the slow aging of the resin has now really been reached and defined in this manner. The structures of the two resins in Figures 3 and 6 obtained by precipitation, having reached their water tolerance point, are then very different. For the resin in Figure 3, the precipitate can still behave as a liquid at a higher strain percentage just by the destruction of colloidal superstructures because of the still low average molecular mass of the resin oligomers. For the resin in Figure 6, destruction of the colloidal superstructures can still occur, but the resin can never again behave as a liquid because of the much higher average molecular mass of its oligomers.

These two cases represent then two different cases of physical gelation: the former is a case of reversible physical gelation, and the latter is a case of irreversible physical gelation, underlying which a true gel situation also possibly occurs. The statement that liquid/cluster separation is defined as the terminal phase of physical gelation[14,16] is only valid in the latter of these two cases.

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