

Viscoelastic properties of paper coatings: Relationship between coating structure—viscoelasticity and end-use performance

CHARLES. S. KAN, LINDA H. KIM, DO I. LEE, AND RONALD L. VAN GILDER

THE VISCOELASTIC PROPERTIES OF latex-based paper coatings affect the performance of the coated sheet. For example, in the coating process, the film-forming behavior of the latex and the coating's compressive response to calendering depend on the viscoelastic properties of the latex binder and the coating. There are also many parameters in the printing process—coating strength, rotogravure printability, stiffness, cracking resistance, folding endurance, blister resistance—that are affected by the viscoelastic properties of the latex and coating. Hagymassy *et al.* (1) studied the impact of polymer melt flow on the blister resistance of coated paper in web offset printing. Lee *et al.* (2) discussed the effect of varying the glass-transition temperatures (T_g) of the latex on rotogravure printability. Parpaillon *et al.* (3) used the torsional braid analyzer to study the effect of pigment on the T_g of the latex in paper coatings in an attempt to understand coating strength.

Many aspects of the viscoelastic properties of latex polymers have been studied using dynamic mechanical spectroscopy (DMS) (4–6). Zosel *et al.* studied the effects of varying the amount of carboxylic acid and the degree of crosslinking on the properties of acrylate latexes (7–9). Richard and Maquet (10, 11) studied the role of carboxyl functional groups at the latex interface on the viscoelastic properties of carboxylated styrene/butadiene latexes. The viscoelastic behavior of filled polymer systems has also been stud-

ied extensively and reviewed (12–14).

The viscoelastic properties of paper coatings, however, have not been studied in detail. Parpaillon *et al.* (3), Pettersson *et al.* (15), and Lepoutre and Hiraharu (16) determined the mechanical properties of paper coatings in their studies of coating strength. Ishikawa *et al.* (17) determined the DMS of paper coatings in a study of the role of coating compressibility in rotogravure printability. Hagen *et al.* (18) also studied the DMS of coated papers in an effort to understand pigment–latex interaction in the coating layer.

The present work also examines the viscoelastic properties of paper coatings as measured using DMS. However, the discussion here focuses on the correlation of viscoelastic properties with coating calenderability and coated-paper stiffness. A brief introduction to polymer viscoelasticity is also presented in the Appendix at the end of this article.

EXPERIMENTAL

Materials

Carboxylated styrene/butadiene (S/B) latexes were prepared using conventional emulsion polymerization. The pigments included two inorganic pigments—a kaolin clay (Hydrafine 90, Huber Inc.) and a ground calcium carbonate (Hydrocarb 90, Omya Inc.)—and an organic plastic pigment (Dow Chemical Co.).

Dynamic mechanical spectroscopy

The dynamic mechanical properties of unsupported coatings were deter-

COATING

ABSTRACT

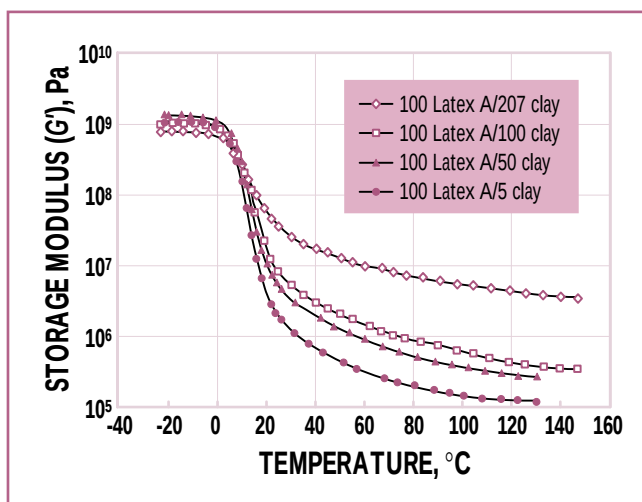
Viscoelastic properties of paper coatings affect the end-use performance of coated paper. This study focuses on the relationship between coating structure—viscoelasticity and (a) gloss improvement during calendering and (b) sheet bending stiffness. Viscoelastic properties were determined by dynamic mechanical spectroscopy for a range of latex-based paper coatings. Results suggest that the effect of calendering on gloss can be predicted based on the coating's elastic modulus. Sheet response to calendering decreased with increasing elastic modulus. Sheet bending stiffness showed the opposite trend and increased with increasing modulus.

Application: The viscoelastic properties of latex-based coating formulations can be manipulated to improve sheet stiffness and response to calendering.

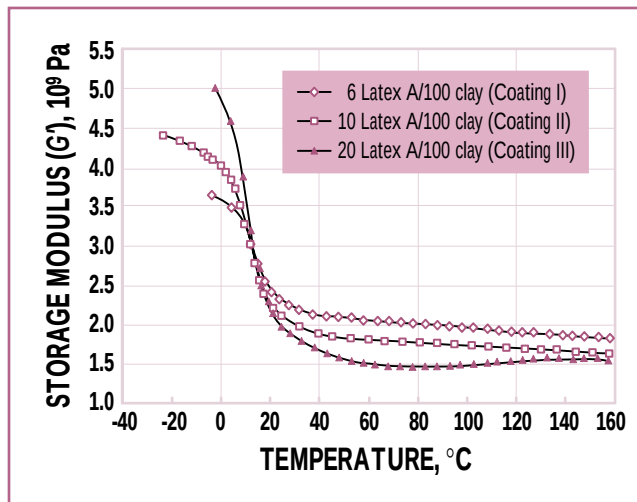
mined. Samples were prepared by mixing the latexes and pigment dispersions until they became homogeneous. The samples were then dried at 40°C in 12 mm x 70 mm Teflon molds for at least 24 h. The dried coatings were removed and cut to dimensions suitable for DMS experiments. Dynamic mechanical properties of the samples were determined using torsional rectangular geometry on a Rheometrics RDS-II instrument. The moduli of the coatings were determined as a function of temperature from a temperature below the $\tan \delta_{\max}$ (equivalent to glass-transition temperature, T_g ; see Appendix) of the latex polymers to approximately 150°C at a strain rate of 1 radian/s.

Determination of coating gloss and the effect of calendering

Coating colors consisting of a series of S/B latexes and clay (6–20 parts binder/100 parts clay at 65% total



1. DMS showing storage modulus as a function of temperature for coatings containing Latex A at four levels of clay content



2. DMS showing storage modulus as a function of temperature for coatings containing Latex A at pigment (clay) concentrations above CPVC

solids) were coated onto 2-mil-thick clear polyester films using a No. 14 Meyer rod. Coatings were dried in a forced-air oven for 1 min at 80°C. The 75° gloss of the coatings was measured according to TAPPI T 480 (19). The coated polyester sheets were calendered sandwiched between another polyester sheet and a sheet of 20 lb/ream uncoated paper—with the coating facing the additional polyester sheet and the heated steel roll—at 1200 pli and temperatures ranging from 20°C to 100°C. The coatings were calendered as a sandwich to approximate the pressure experienced by the compressible paper. The sandwich of three sheets was removed as a unit as it exited the calender to prevent calender sticking and eliminate its effect on the coating gloss. Because of possible variation in gloss at various areas on the sheet, care was taken to measure the gloss of the calendered coatings at the same positions where the initial gloss measurements were taken.

Gurley stiffness of coated paper

Stiffness values for a series of two-side-coated papers were determined using a Gurley stiffness tester according to TAPPI T 543 (20). A 66-lb/ream base stock was coated with coating colors containing 15.3 parts binder/100 parts pigment to a coat weight of 9 lb/ream. The pigment

was 71 wt.% clay, 23 wt.% calcium carbonate, and 6 wt.% titanium dioxide. The coated papers were calendered at 65°C under various pressures to achieve a 75° gloss of 70. Calendering speed was 25 ft/min.

RESULTS AND DISCUSSION

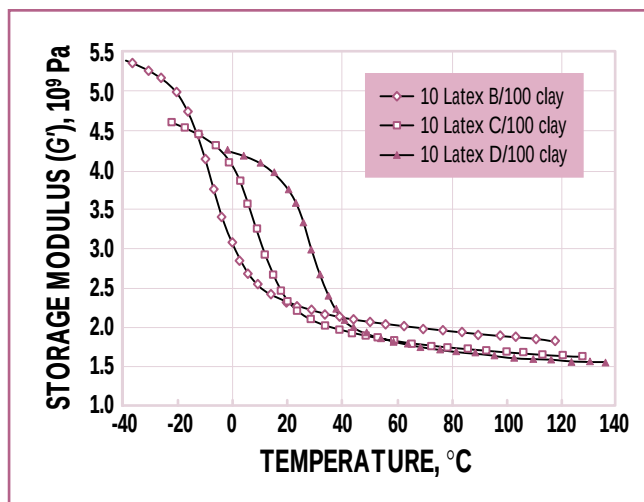
Dynamic mechanical spectroscopy of paper coatings

The effect of rigid fillers on the viscoelastic properties of polymers has been extensively studied and reviewed (12–14). Below the critical pigment volume concentration (CPVC) (21), the modulus of the composite can often be described using equations derived by Kerner (22), Nielsen (23), and others (24, 25).

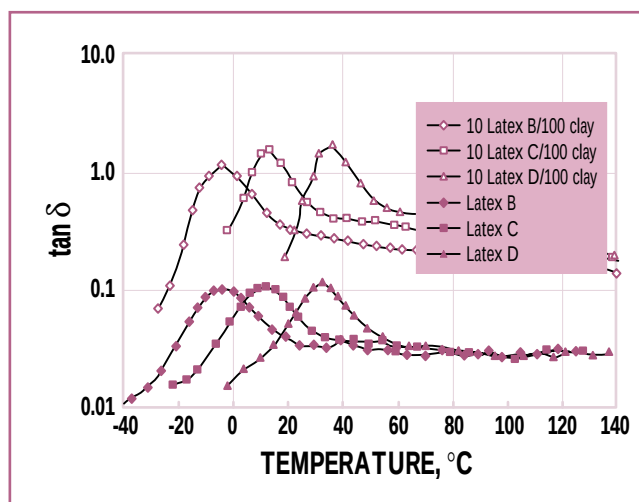
Figure 1 shows the effect of clay content on the storage modulus (or elastic modulus), G' , of Latex A (2200 Å, 50% solids, $T_g = 15^\circ\text{C}$). Clay content ranged from 5 parts to 207 parts by weight per 100 parts (or 2% to 45% by volume) of latex. As seen in Fig. 1, the moduli at temperatures below 0°C were in the range of 10^9 Pa. Storage moduli began to decrease within the range 0–20°C, the glass-transition regime. At temperatures above 20°C, the moduli decreased at a slower rate. The modulus of the coating increased as the pigment volume concentration (PVC) of clay increased from 2% (5 parts clay) to

28% (100 parts clay) in regimes both below and above the T_g of the latex. The increase was greater in the regime above T_g . For the coating with a calculated PVC of 45% (207 parts clay)—assuming that latex and clay are the only two phases—the modulus of the composite at the regime above the T_g of the latex was increased further. However, the modulus of the composite in the regime below T_g was less than for the lower-PVC composites. At a calculated PVC of 45%, the amount of pigment present was expected to be above the CPVC.

Composites with PVC above the CPVC are three-phase systems consisting of latex, pigment, and air voids. Floyd and Holsworth (26) suggested that a phase inversion occurs at the CPVC, with the system switching from polymer as the continuous phase to one where air is the continuous phase. The amount of pigment in paper coatings generally ranges from 65% to 90% PVC. For example, in Lee's study of coating gloss (27), the measured void volumes of paper coatings ranged from 30% to 40%. Groves *et al.* (28) studied the effect of latex level on coating porosity and found that the void volume decreased as the latex volume in the coating increased. The dynamic mechanical properties of paper coatings are dependent not only on the



3. DMS showing storage modulus as a function of temperature for coatings containing latexes with differing T_g (Latexes B, C, and D)



4. DMS showing $\tan \delta$ as a function of temperature for coatings containing latexes with differing T_g and for the three latexes alone (Latexes B, C, and D)

mechanical properties and volume fractions of latex and pigment but also on the void volume.

Figure 2 shows the DMS of three paper coatings containing Latex A. Coating I consisted of 6 parts latex/100 parts clay; Coating II contained 10 parts latex/100 parts clay; and Coating III had 20 parts latex/100 parts clay. As seen in Fig. 2, Coating III (20 parts latex) had the highest modulus in the regime below the T_g of the latex, followed by Coatings II and I. However, in the regime above the T_g of the latex, Coating III had the lowest modulus, followed by Coatings II and I. This mechanical behavior can be explained by the variation of volume fractions of latex and voids in the paper coatings. The storage modulus of clay is approximately 8×10^9 Pa (29). The storage modulus of Latex A in the regime below T_g is in the same order of magnitude as that of clay. However, in the rubbery plateau region, the modulus of Latex A is approximately 1×10^5 Pa. Thus in the regime below the T_g of the latex, the modulus of the coating depends on the volume fractions of the pigment and latex. In the regime above the T_g of the latex, the modulus depends primarily on the volume fraction of the pigment only, since the modulus of the latex is approximately four orders of magni-

Coating	VOLUME, %		
	Clay	Latex	Void
I (6 parts binder)	58	8	34
II (10 parts binder)	55	15	30
III (20 parts binder)	48	34	18

*Coatings containing Latex A and 100 parts clay

I. Volume fractions of paper coatings depicted in Fig. 2*

tude lower than that of the pigment and does not contribute significantly to the overall modulus of the coating.

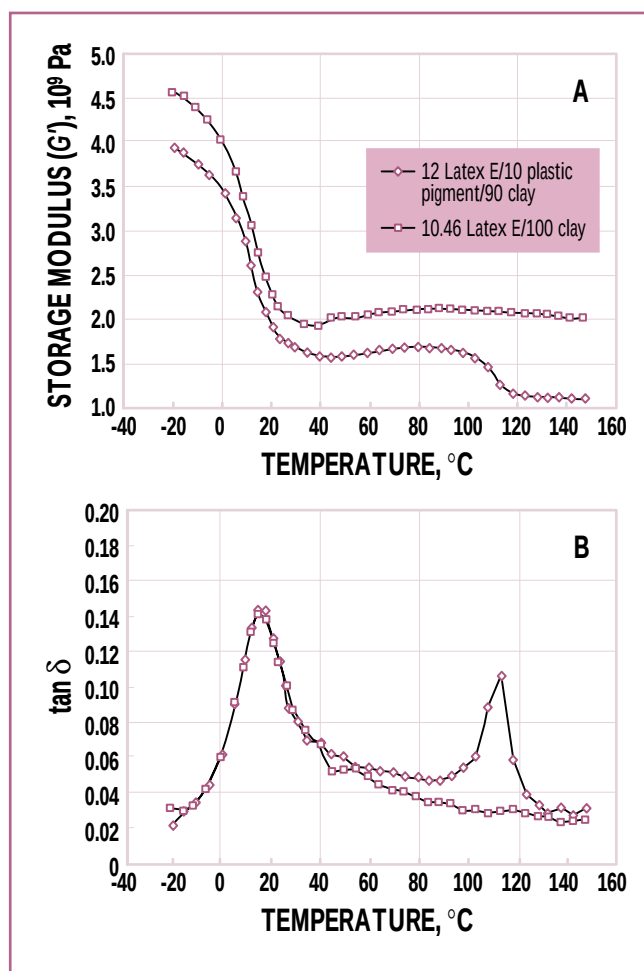
The volume fractions of clay, latex, and void determined by Groves and Lanham (28) for coatings of composition corresponding to Coatings I, II, and III are presented in Table I. These volume fractions provide a qualitative explanation for the modulus behavior observed here. The volume fraction of clay + latex increases from 66% to 82%, while the volume fraction of clay alone decreases from 58% to 48%. Therefore, comparing the moduli of Coatings I, II, and III, one would expect:

- In the regime below T_g , modulus should increase with increasing volume fraction of clay + latex, i.e., Coating III > Coating II > Coating I.

- In the regime above T_g , modulus should increase with increasing volume fraction of clay, i.e., Coating I > Coating II > Coating III.

This modulus dependency on composition was observed in general for all film-forming latexes studied to date.

Figure 3 shows the DMS of three paper coatings containing 10 parts of Latexes B, C, and D, respectively, per 100 parts clay. Latexes B, C, and D were similar to Latex A except in S/B ratio. The T_g values for Latexes B, C, and D were -12°C , 3°C , and 25°C , respectively, as measured by differential scanning calorimetry (compared with 15°C for Latex A). The coating containing Latex B had the highest modulus in the regimes above and below the T_g of the latex. The differences in the moduli of the coatings can be attributed to differences in



5. DMS showing (A) storage modulus and (B) $\tan \delta$ as functions of temperature for two coatings containing Latex E

void volume. Groves *et al.* (28) measured the void volume of paper coatings as a function of the butadiene content of the latex, and they found that the higher- T_g latexes have larger void volumes. Similar findings have been reported by others (30, 31). The coatings were prepared at 40°C, a condition above the minimum film-formation temperature of the latexes. Therefore, it is not expected that differences in the moduli of the coatings was due to incomplete latex film formation.

Figure 4 shows the $\tan \delta$ behavior of the same three coatings—and their base latexes—as a function of temperature. (See Appendix for definition of $\tan \delta$.) The maximum $\tan \delta$ ($\tan \delta_{\max}$) of the coatings occurred at the same temperatures as the base

latexes. (Note that $\tan \delta_{\max}$ occurs at T_g .)

Increases in the T_g of the polymers in filled systems have frequently been observed. These increases are interpreted in terms of interactions between the polymers and fillers (3), with fillers reducing the mobility and the flexibility of the polymer chains at the interfaces (12). However, in the present study, no detectable shift of the main $\tan \delta_{\max}$ of the S/B latexes in paper coatings was observed.

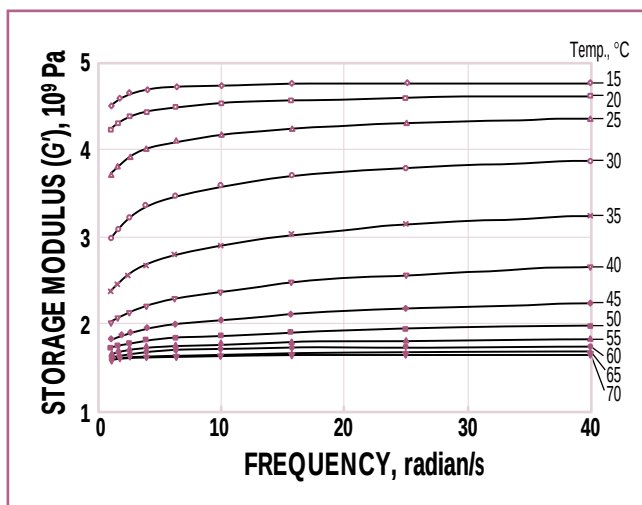
It has been reported (32) that the DMS of carboxylated S/B latex films showed two $\tan \delta_{\max}$. The main $\tan \delta_{\max}$ at the lower temperature was attributed to the S/B domain, whereas the minor $\tan \delta_{\max}$ at higher temperature was due to the carboxylate-rich interfacial polymer. It is

expected that the interfacial polymer interacted with the pigment and shifted the $\tan \delta_{\max}$ of the interfacial polymer to a higher temperature. However, the $\tan \delta_{\max}$ of the interfacial polymer was not easily detectable in paper coatings because of the small amount of latex present. Since there would be little interaction expected between the essentially nonionic S/B phase and the pigment, no perturbation of the main $\tan \delta_{\max}$ was anticipated.

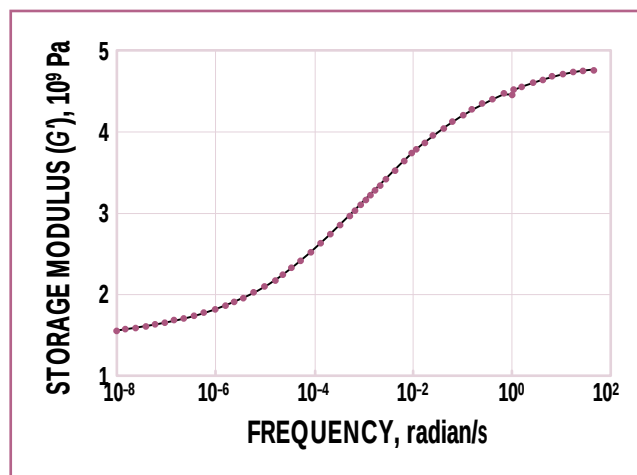
Polymeric pigments are commonly used in paper coatings. Figure 5 shows the DMS of a paper coating containing 12 parts Latex E, 10 parts of a 2250-Å polymeric pigment, and 90 parts clay. (Latex E is a 1500-Å latex.) The $\tan \delta$ peak at 15°C in Fig. 5b corresponds to the T_g of the S/B latex. The $\tan \delta$ peak at 112°C is attributed to the polymeric pigment. The viscoelastic behavior of this paper coating is compared with a control, a coating containing 10.46 parts Latex E and 100 parts clay. The volume ratio of binder/pigment is the same in both coatings. The storage modulus of the coating with the polymeric pigment is lower than that of the control, as seen in Fig. 5a, even though the modulus of the plastic pigment by itself in the temperature regime between the two $\tan \delta_{\max}$ is higher than that of the S/B latex. This again can be attributed to the higher void volume present in the coating containing polymeric pigment.

Relationship between coating structure-properties and end-use performance

The end-use performance of coated paper is affected by the coating process and the coating formulation. Efforts to develop a relationship between a single parameter—such as coating viscoelasticity—and end-use performance would be best served by keeping all other parameters constant. In practice, this is not always possible. In such cases, the



6. DMS showing storage modulus of paper coating as a function of frequency at temperatures of 15–70°C



7. Master DMS curve showing the fit of shifted modulus data (reference temperature = 25°C) for a paper coating using the WLF time-temperature superposition principle

contribution of other factors in the coating's end-use performance must be considered.

The viscoelastic properties of a paper coating affect many aspects of the coated paper's end-use performance, including the extent of gloss improvement and sticking during calendering, stiffness and crack/fold resistance, coating strength and blister resistance in offset printing, and rotogravure printability. The present work examines the effect of paper-coating viscoelasticity on (a) gloss response to calendering and (b) coated-paper stiffness.

WLF time-temperature superposition principle. Since the viscoelastic properties of a polymer are a function of both temperature and frequency (time), these properties must be determined at conditions that correspond to the end-use processes. However, some of the end-use processing conditions are not readily accessible with laboratory instruments. Instead, the WLF (Williams, Landel, Ferry) time-temperature superposition principle (33, 34) can be used to shift the viscoelastic properties observed at laboratory conditions to reflect the end-use conditions.

The time and temperature dependencies of the viscoelastic properties can be described by Eqs. 1 and 2.

$$\log a_T = -C_1(T - T_r)/(C_2 + T - T_r) \quad (1)$$

$$f_1 a_{T1} = f_2 a_{T2} \quad (2)$$

where

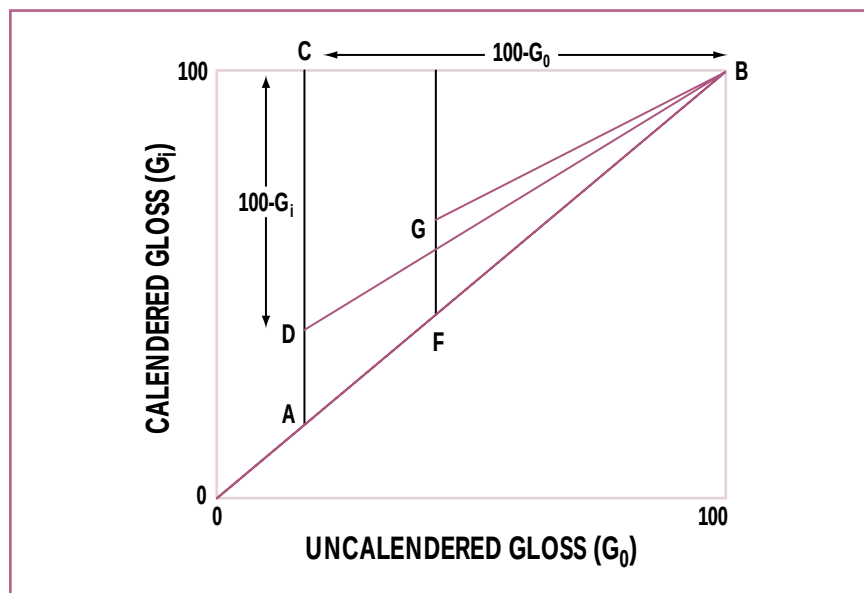
- a_T = shift factor at temperature T
- C_1 and C_2 = constants at a given set of conditions
- T_1 and T_2 = temperatures at conditions 1 and 2
- T_r = reference temperature at which a_T values are determined
- f_1 and f_2 = frequencies of deformation under conditions 1 and 2.

Therefore, by knowing the temperature and frequency of deformation at the end-use condition, it is possible to calculate an equivalent temperature and rate of deformation that is accessible with DMS. Frequently, it is easier in an end-use application to determine the duration that the polymer experienced stress rather than the frequency of the stress. For example, the residence time of coated paper under the calender nip can be calculated easily from the speed of the moving web and the width of the nip. The time dependency of modulus can then be measured in a stress-relaxation experiment. Ferry (34)

noted that the stress-relaxation modulus, G_t , at time t (measured in seconds) is qualitatively equivalent to the storage modulus, G' , at frequency $f = 1/t$ (expressed as radian/s). Using this relationship, viscoelastic properties corresponding to the end-use condition—where the time rather than frequency is known—can also be obtained from the DMS.

For example, if the nip width and the linear speed of a calender were 0.64 cm and 18.6 cm/s, the residence time of a paper coating under the nip would be 0.034 s. The deformation frequency is thus calculated to be 29.4 radian/s. The C_1 and C_2 of Latex A were determined to be 16.3 and 62.2 at a T_r of 8°C. Using Eqs. 1 and 2, the temperature at a deformation frequency of 1 radian/s—the frequency of the DMS experiment—was calculated to be 47°C, corresponding to the calendering condition of 65°C and a residence time of 0.034 s.

The applicability of the WLF time-temperature superposition principle to paper coating is demonstrated as follows. The storage moduli of a paper coating were determined at various temperatures from 15°C to 70°C as a function of frequency from 1 radian/s to 40 radian/s, as shown in Fig. 6. If the WLF principle is applicable, then the



8. Schematic diagram illustrating the effect of calendering on gloss

modulus data can be shifted to form a master curve. **Figure 7** shows the master curve of the paper coating with 25°C as the reference temperature. It can be seen readily from the degree of fit in Fig. 7 that the WLF principle is operative in paper coating systems.

Gloss of paper coating. Gloss is an important coated-paper optical property that affects end-use performance. Coated papers are typically calendered to improve gloss. The factors affecting coated-paper gloss have been studied widely (27, 28, 35–37). Usually, the effect of calendering on gloss is quantified using ΔGloss , i.e., the difference between calendered gloss, G_i , and uncalendered gloss, G_0 . However, when comparing the gloss improvement for different coatings, ΔGloss is meaningful only if the initial uncalendered gloss values of the coatings are identical. This is because 75° gloss (19) has a maximum value of 100 for most clay-based coatings. Therefore, for a coating with low uncalendered gloss, the potential increase in gloss is larger than for a coating with high uncalendered gloss.

Conceptually, ΔGloss is zero for a coating with uncalendered gloss of 100, regardless of the coating's compressibility. Therefore, using ΔGloss

to measure the effectiveness of calendering can be misleading if the difference in uncalendered gloss is large.

Alternatively, the effect of calendering on gloss can be depicted as in **Fig. 8**, where calendered gloss is plotted against uncalendered gloss. If the data point falls on the 45° line AFB, calendering has no effect on gloss. In the hypothetical case where a data point falls on the line CB, calendering is 100% effective in increasing gloss to the maximum value of 100. In general, the data will fall somewhere within the triangle ABC. Coatings experiencing the same effect of calendering will fall on a straight line converging to a calendered gloss value of 100 at an uncalendered gloss of 100 as depicted by lines DB or GB. Qualitatively, the farther the line is from the 45° line, the more effective calendering is in increasing gloss. Therefore, coatings with gloss values on the line GB are more responsive to calendering than those described by line DB. It can also be seen from the figure that ΔGloss is not always a reliable measure of the effect of calendering. In **Fig. 8**, the ΔGloss of two coatings represented by AD and FG are the same. However, calendering has a larger effect on the coating with ΔGloss FG,

since the line GB is farther away from the 45° line than line DB. Again, if gloss values are used to measure the effect of calendering, ΔGloss must be compared at the same G_0 .

The effectiveness of calendering can be described by the quantity $(G_i - G_0)/(100 - G_0)$, where $(G_i - G_0)$ is ΔGloss and $(100 - G_0)$ is the potential for gloss improvement. The quantity $(G_i - G_0)/(100 - G_0)$ ranges from 0, where calendering has no effect on gloss, to 1, when G_i has increased to 100.

In this study, calenderability, κ , is defined as

$$\kappa = (100 - G_0)/(100 - G_i) \quad (3)$$

where

G_0 = uncalendered gloss

G_i = calendered gloss after i nips.

The value of κ ranges from 1, where calendering has no effect on gloss, to infinity. The quantity $(G_i - G_0)/(100 - G_0)$ is related to κ by Eq. 4.

$$(G_i - G_0)/(100 - G_0) = 1 - (1/\kappa) \quad (4)$$

The effect of binder level in paper coating on gloss and calenderability was studied by determining the G_0 and G_i of coatings containing 20 parts and 6 parts Latex E per 100 parts clay. Results are shown in **Table II**. The G_0 of the coating containing 20 parts latex is lower than the coating containing 6 parts latex, 45.1 vs 71.3. The lower gloss observed for the coating with the higher binder level is expected from Lee's study (35). After calendering, gloss increased to 67.7 and 80.6 for the two coatings, respectively. Values for κ are calculated to be 1.77 and 1.47, respectively, indicating that calendering is more effective at increasing the gloss of the coating containing the higher level of binder. To

illustrate the effect of this 0.3 increase in κ on gloss, consider a coating with $G_0 = 40$. An increase of κ from 1.47 to 1.77 would result in G_i increasing from 59 to 66.

The calenderability of coatings containing binders with different T_g values was studied using a series of latexes (B, C, and D). The viscoelastic properties of the latexes are similar except for a shift of T_g . The uncalendered and calendered gloss of coatings containing 20 parts latex/100 parts clay dried at 80°C are listed in **Table III**. The calenderability of the coating containing the lower- T_g latex, Latex B, was higher than that of the coatings containing the higher- T_g latexes, Latexes C and D, under the calendering conditions of the experiment.

The effect of calendering temperature on κ was also studied using a coating containing 20 parts Latex A/100 parts clay. Calendering was carried out with the calender at 20°C, 65°C, and 100°C. Results are shown in **Table IV**. The calenderability, κ , increased as calendering temperature was increased, as expected. However, note that calendering in the present experiment was carried out with no possibility of calendering sticking. Under actual conditions, a decrease in gloss might be experienced at high calendering temperatures because of calender sticking.

Correlation between calenderability and coating viscoelasticity. Paper coatings deform under the pressure and temperature of the calender, undergoing compression as the sheet passes through the calender nip. The compressive energy can be either stored or lost. When the compression is removed as the coating exits the nip, the coating will either (a) recover to its original state if it is elastic, resulting in little change in gloss or (b) permanently deform if the coating structure has rearranged or “flowed” to dissipate energy, thereby increasing its gloss. The stor-

Coating	Uncalendered gloss (G_0)	Calendered gloss (G_i)	Calenderability (κ)
6 parts binder	71.3 ± 1.1	80.6 ± 1.1	1.47
20 parts binder	45.1 ± 1.1	67.7 ± 1.5	1.77

*Coatings containing Latex E and 100 parts clay

II. Calenderability of paper coating*—effect of binder level

Coating	Uncalendered gloss (G_0)	Calendered gloss (G_i)	Calenderability (κ)	Latex T_g , °C
20 parts Latex B	45.1 ± 1.1	71.7 ± 1.8	1.96	-12
20 parts Latex C	47.4 ± 0.9	70.6 ± 1.6	1.79	3
20 parts Latex D	56.1 ± 2.2	73.8 ± 2.1	1.67	25

*Coatings containing 20 parts latex/100 parts clay

III. Calenderability of paper coating*—effect of binder glass-transition temperature

Calender temp., °C	Uncalendered gloss (G_0)	Calendered gloss (G_i)	Calenderability (κ)
20	43.5 ± 1.1	61.2 ± 1.1	1.46
65	43.4 ± 1.1	71.1 ± 1.2	1.96
100	43.5 ± 0.8	75.7 ± 2.0	2.33

*Coating containing 20 parts Latex A/100 parts clay

IV. Calenderability of paper coating*—effect of calendering temperature

Sample No.	Gurley stiffness, mgf ^a		Storage modulus (G'), ^b 10 ⁹ Pa
	MD	CD	
1	404	239	1.51
2	520	330	3.77
3	503	310	2.57
4	500	325	3.40
5	497	302	3.22
6	488	308	3.24

^aUnits for Gurley stiffness are milligrams-force

^bAt 25°C

V. Gurley stiffness of coated paper

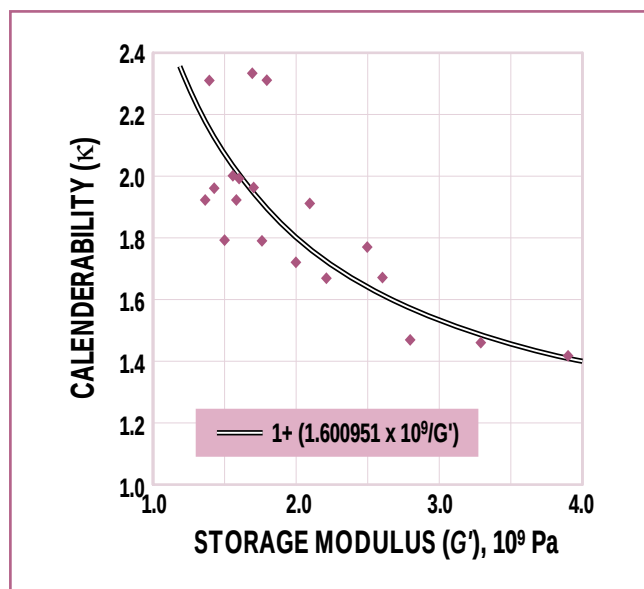
age modulus and $\tan \delta$ of the coating are indications of the elasticity. A $\tan \delta$ of low value indicates high elasticity, and vice versa. It is also possible that part of the compressive stresses can be temporarily stored in the coating and later contribute toward gloss reversal.

The calenderability of a series of coatings and the storage modulus,

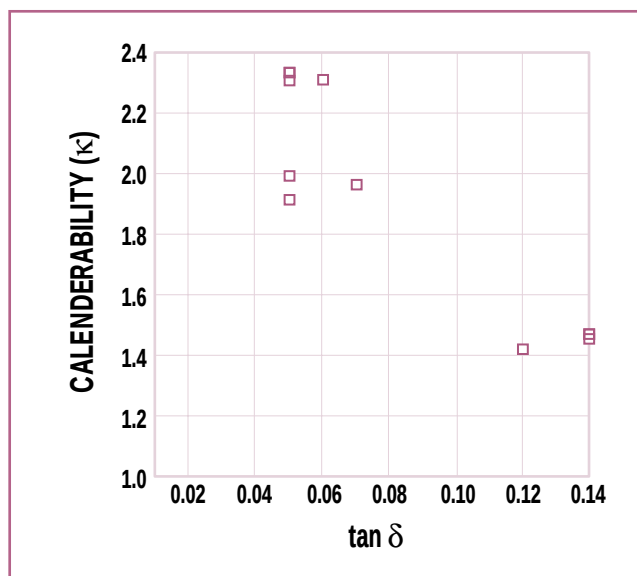
G' , corresponding to the calendering conditions were determined. Sheet calenderability is plotted against the storage modulus in **Fig. 9**. The data can be fitted with a curve (Eq. 5).

$$\kappa = 1 + (1.60 \times 10^9 / G') \quad (5)$$

A statistical analysis of these data is presented in the Appendix at the



9. Calenderability as a function of storage modulus of paper coating



10. Calenderability as a function of $\tan \delta$ of paper coating

end of this article.

A decrease in the modulus of the coating from 3×10^9 Pa to 2×10^9 Pa translates to a calculated increase of calenderability, κ , from 1.53 to 1.80. For a coating with G_0 equal to 40, this increase of κ corresponds to a change of G_1 from 61 to 67.

The calenderability of several coatings is also plotted against the $\tan \delta$ of the coatings at the calendering conditions in Fig. 10. If energy loss were important to increase gloss, then κ should increase with $\tan \delta$. This was found not to be the case in the present experimental conditions. Apparently, the energy loss of the coatings under the calender nip had reached a limit, and further increases in $\tan \delta$ did not produce an increase in gloss. Coated

papers are typically calendered using several nips to achieve the desired gloss, and the gloss improvement in successive nips decreases. For example, the calenderability of a coating containing 15 parts Latex A/100 parts clay decreased from 2.0 to 1.4 to 1.1 for successive nips. This decrease of κ can be interpreted as the result of consolidation of the coating, resulting in a decrease of void volume and, therefore, an increase in modulus.

Correlation between coated-paper stiffness and coating viscoelasticity. The stiffness of the coated paper is another important property that can be affected by coating viscoelasticity. The effect of coating viscoelasticity on coated-paper stiffness has not been studied extensively. Lepoutre and Rigdahl (38), however, have studied the effect of pigment type and coating structure on the elastic modulus of the coating and inferred its importance on stiffness.

Stiffness values for sheets coated with formulations containing different latexes were determined using a Gurley stiffness tester according to TAPPI T 543 (20). The duration of the bending stress was approximately 2 s, equivalent to a deforma-

tion frequency of 0.5 radian/s. Using the WLF time-temperature superposition principle, the DMS temperature that is relevant to the stiffness testing is approximately 25°C at a frequency of 1 radian/s. Table V shows the Gurley stiffness in the machine direction (MD) and cross-machine direction (CD) along with the storage modulus (G'), of the coatings at 25°C.

Figure 11 shows plots of Gurley stiffness vs. G' in the MD and CD. Clearly, there is good correlation between Gurley stiffness and G' within the 95% confidence level. However, many other factors can also affect the stiffness of the coated paper, including variability in the stiffness of the base sheet and differences in moisture content of the coated papers. Nevertheless, the results of this study suggest that increasing the storage modulus of the paper coating at 25°C will increase the stiffness of the coated paper if all other parameters affecting stiffness remain constant.

SUMMARY

The viscoelastic properties of paper coatings are determined by (a) the viscoelastic properties of the binder and pigment and (b) the volume frac-

KEYWORDS

Bibliographies, calendering, chemical analysis, coated papers, coatings, gloss, mechanical properties, optical properties, paper grades, paper properties, properties, rheological properties, spectrochemical analysis, spectroscopy, stiffness, surface finishing, viscoelasticity.

tions of the binder, pigment, and void. The volume fractions become an important factor in coating viscoelasticity when the pigment volume concentration (PVC) in the coating exceeds the critical PVC (CPVC), which is generally the case for commercial coatings. For the latex binders used in this study, an increase in the volume fraction of binder increased the storage modulus (i.e., elastic modulus) of the coating in the regime below the glass-transition temperature and reduced the modulus in the regime above the latex's glass-transition temperature.

The viscoelastic properties of paper coatings were measured using dynamic mechanical spectroscopy (DMS). Laboratory results were translated to commercial end-use conditions using the WLF (Williams, Landel, Ferry) time-temperature superposition principle (33, 34).

Coating viscoelasticity showed correlation with (a) the compressive behavior of the coated paper during calendering and (b) the bending behavior as measured during Gurley stiffness testing. With knowledge of both the coated paper's uncalendered gloss and calenderability (from measurement of coating modulus), the effect of calendering on gloss can be predicted.

The results presented in this report help explain why coatings containing plastic pigments often have higher calendered gloss than coatings containing corresponding volumes of clay or calcium carbonate. Coatings with plastic pigments start off with a higher uncalendered gloss (because of less shrinkage during coating consolidation) and provide greater calenderability (because of the high void volume in the coating).

The laboratory method that was used to prepare the paper coatings for DMS differs from commercial coating operations, where the coating color experiences significant

shear. Furthermore, the rate of drying on a commercial machine is much faster. Finally, the coatings in this study were applied to polyester films and not to paper. Clearly, the different effects of coating consolidation on the viscoelastic properties of laboratory and commercial coatings should be considered in evaluating the results. Nevertheless, even with the expected difference of the coating consolidation on the DMS of paper coatings, the present study provides significant insight into the role of

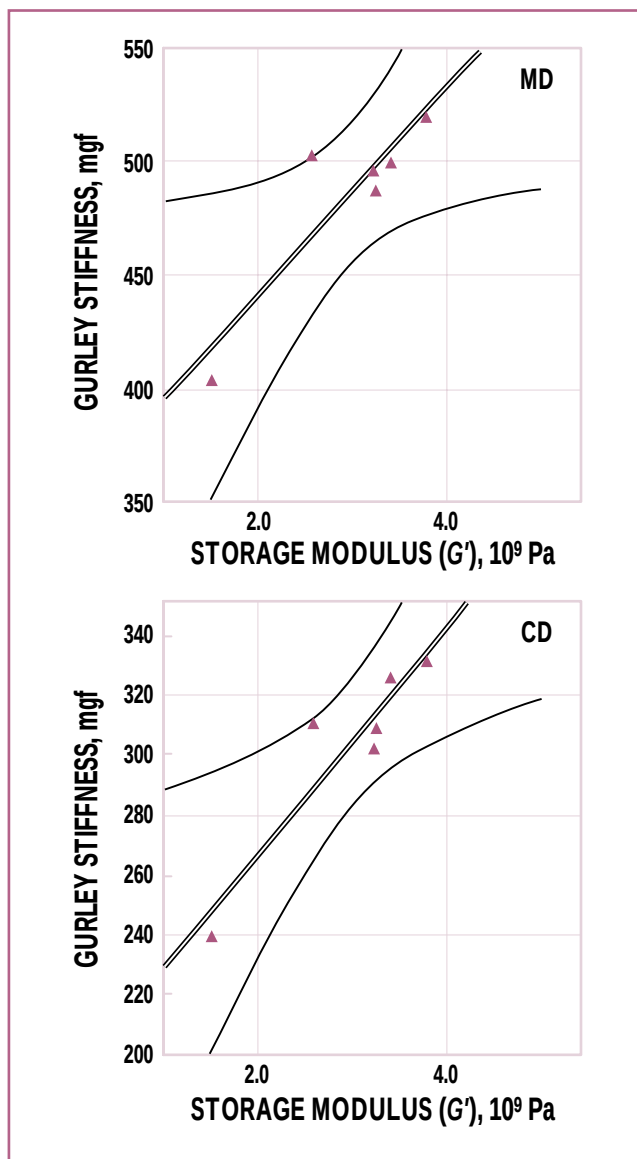
coating on the properties of coated paper. **TJ**

Kan, research associate, Kim, senior research engineer, Lee, research scientist, and Van Gilder, associate scientist, all work in emulsion polymers research at Dow Chemical Co., Midland, MI 48674.

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11. Stiffness of coated paper as a function of storage modulus of paper coating in (top) machine direction and (bottom) cross-machine direction

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APPENDIX

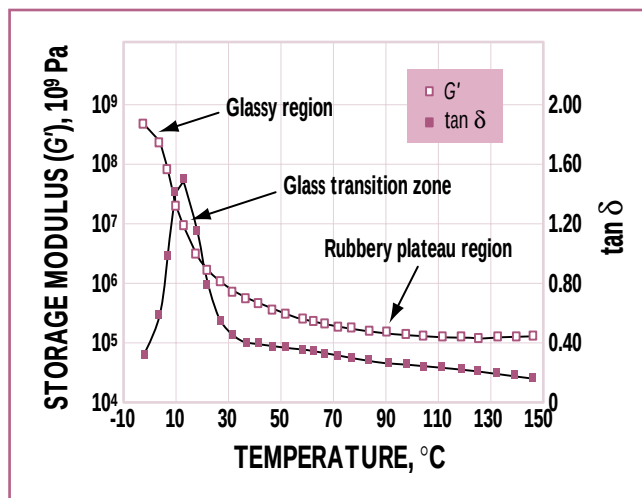
A brief introduction to polymer viscoelasticity

The response of polymers and coatings to deformation can be characterized by their viscoelastic behavior. The elasticity of a material refers to its ability to store deformation energy and then resume its original configuration after the deformation stress is removed. The viscosity of a material refers to its ability to dissipate or lose the deformation energy through flow. Materials that exhibit both elastic and viscous behaviors are classified as viscoelastic. When a viscoelastic material is subjected to a deformation stress, a portion of the

deformation energy is stored, with the rest of the energy lost. When the deformation stress is removed, the stored elastic energy is released. Since a portion of the deformation energy is lost through viscous flow, the material undergoes permanent deformation and does not regain its original configuration completely.

The viscoelastic properties of polymers can be measured in a dynamic mechanical experiment by subjecting the material to sinusoidal strain deformation. The storage or elastic modulus, G' , and loss or viscous modulus, G'' , are calculated from the stress exhibited by the material.

The storage modulus is a measure of the stiffness of the material. The ratio $\tan \delta, G''/G'$, is a measure of the energy loss to energy stored. Qualitatively, G' is a measure of the force needed to deform the material to a certain strain. The larger the G' , the stiffer is the material, and the higher the force needed to deform the material. If the material is elastic, then it returns to a configuration similar to its original shape when the deforming force is removed, little energy is lost, and $\tan \delta$ is small. On the other hand, materials with large $\tan \delta$, showing a significant energy loss, will retain the geometry of the deformed state.



A-1. DMS showing storage modulus and $\tan \delta$ as functions of temperature

The viscoelastic properties of polymers depend on the temperature and frequency of the deformation. Therefore, the viscoelastic properties are frequently determined as a function of temperature at some frequency (or as a function of frequency at a given temperature). In a constant-frequency experiment, in the temperature regime where the polymer is glassy, the G' is high, in the range of 10^9 to 10^{10} Pa, as seen in Fig. A-1. At this point, $\tan \delta$ or G'' is low. When the temperature is increased, G' decreases sharply, and $\tan \delta$ or G'' increases, indicating the polymer is in the glass-transition region, until $\tan \delta$ reaches a maximum. The temperature at which $\tan \delta$ is maximum is often referred to as the glass-transition temperature, T_g . As temperature increases further, G' continues to decrease, but at a slower rate. This regime is referred to as the rubbery plateau region. Depending on the molecular structure of the polymer, $\tan \delta$ usually reaches a minimum and then starts to increase slowly.

For noncrosslinked polymers, G' decreases sharply as temperature is increased. This is referred to as the terminal zone, where polymer melting occurs. The temperature at which the polymer starts to melt

depends on the molecular weight of the polymer. Concurrently, $\tan \delta$ or G'' also starts to increase, indicating that deformation stress is dissipated by polymer flow. For crosslinked polymers, the terminal zone is absent, and G' and $\tan \delta$ remain relatively constant. The magnitude of G' , referred to as the equilibrium modulus, reflects the crosslink density.

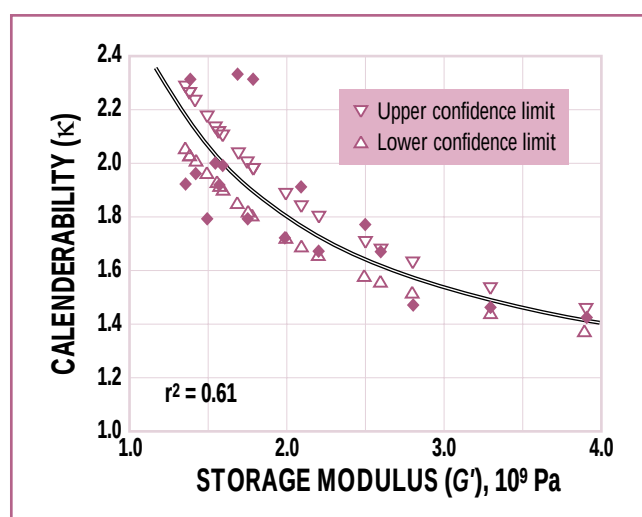
As mentioned before, the viscoelastic properties of polymers and coatings are functions of both temperature and deformation frequency (i.e., time). The relationship of temperature and frequency/time often can be described using the Williams, Landel, Ferry (WLF) time-temperature superposition theory (33, 34). Quantitatively, the relationship between temperature and frequency is described using the WLF equations,

$$\log a_T = -C_1(T - T_r)/(C_2 + T - T_r) \quad (\text{A-1})$$

$$f_1 a_{T1} = f_2 a_{T2} \quad (\text{A-2})$$

where the variables are defined as earlier in the text.

This relationship is useful in translating polymer and coating viscoelastic properties as measured



A-2. Calenderability as a function of storage modulus of paper coating with upper and lower 95% confidence boundaries

with DMS at a given deformation frequency to the frequency of the end-use application. Qualitatively, if the application frequency is higher than the DMS frequency, the moduli corresponding to the application are at a lower temperature than that obtained with DMS. For example, using the general WLF equations, the modulus for printing at 20°C with an ink-film thickness of 1.5×10^{-3} cm at 300 cm/s can be calculated to correspond to the DMS modulus at 4°C at 1 radian/s for a polymer with a T_g of 10°C.

Statistical analysis of the relationship between calenderability and coating modulus

A statistical analysis of the data in Fig. 9 was carried out. Figure 9 has been replotted here as Fig. A-2, showing the 95% confidence level. The analysis of variance and the parameter tables are presented in Eq. A-1 and A-2, respectively. The coefficient of determination, r^2 , was calculated to be 0.61, indicating a significant amount of scatter in the data. It is believed that the variability in preparing the drawdowns greatly contributed to the uncertainty of the results. Nevertheless, despite the scatter in the data, it is clear that the coating modulus affects the calenderability of the coating.