Application of Dynamic Mechanical Testing to Characterize the Viscoelastic Properties of Powder-Filled Semisolids

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Abstract □ A nondestructive technique, dynamic mechanical testing, was used to characterize the viscoelastic properties of dispersions of powdered starch in anhydrous lanolin. The elastic shear modulus (G'), viscous shear modulus (G''), and loss tangent (damping; tan δ) were determined as a function of shear frequency, temperature, and the volume fraction of starch. The results of these studies show that constitutive mathematical models, derived to predict the mechanical behavior of solid-filled polymeric materials, can be applied to solid-filled semisolid pharmaceuticals. In particular, the Kerner equation was useful in describing the influence of starch on the G' of the dispersions. Even though the Kerner equation was unable to predict viscoelastic behavior at all shear frequencies, temperatures, and starch volume fractions, it proved beneficial in postulating mechanisms for starch–starch and starch–anhydrous lanolin interactions within the dispersions. In addition, damping was able to differentiate the influence of temperature. Data obtained from three temperature ranges, where anhydrous lanolin exists in three different structural states, shows that the influence of starch on damping is dictated by the structural state of anhydrous lanolin.

Keyphrases □ Dynamic mechanical testing—viscoelastic properties of powder-filled semisolids, starch–anhydrous lanolin model, Kerner equation □ Viscoelasticity—powder-filled semisolids, starch–anhydrous lanolin model, dynamic mechanical testing, Kerner equation □ Kerner equation—dynamic mechanical testing, application to the viscoelasticity of powder-filled semisolids, starch–anhydrous lanolin model

Pharmaceutical and cosmetic products are commonly heterogeneous dispersions of solid particles in liquid or semisolid vehicles. Usually, their rheology is studied with rotational, continuous shear viscometers (1–4). But unfortunately, continuous shear viscometers destroy the microcrystalline or amorphous three-dimensional networks that determine basic rheological properties and introduce the parameter of variation of structure with time. These viscometers are capable of determining the viscosity of Newtonian systems, but they are unable to determine fundamental viscoelastic parameters such as elastic or viscous moduli (5).

Semisolids in particular have been shown to exhibit complex rheological behavior and are generally classified as viscoelastic (6), *i.e.*, they exhibit spontaneously reversible deformation called elasticity and irreversible deformation called flow. To accurately characterize the viscoelasticity of a semisolid, the method of testing must minimize damage to structure that determines rheological properties. One such nondestructive method, dynamic mechanical testing, has been successfully used to characterize the viscoelastic properties of the heterogeneous semisolid anhydrous lanolin as a function of temperature and shear frequency (7, 8).

Because of the extensive use of solids suspended in ointments in the past and present, it would be invaluable to know the effect of suspended particles on the apparent viscoelastic properties of the ointment and to understand the phenomena associated with any observed changes. Despite the obvious importance of this type of information, there has been, up to now, a lack of information in the literature that examines the effects of powdered fillers on the viscoelastic properties of pharmaceutical semisolids.

This study was therefore initiated and showed that powdered fillers can have a significant influence on the viscoelastic properties of pharmaceutical semisolids. Data that relate temperature, shear frequency, and the volume fraction of starch to changes in viscoelastic moduli are presented for dispersions of starch in anhydrous lanolin. In addition, it is shown that mathematical models, which have been successfully used to predict viscoelastic moduli of powder-filled high polymers, can also be applied to powder-filled pharmaceutical semisolids to interpret changes in viscoelastic moduli in terms of interactions between the powder and the surrounding semisolid phase.

BACKGROUND

Unfortunately, the viscoelastic and mechanical properties of powder-filled pharmaceutical semisolids are not well understood, especially when the particles of powder interact among themselves or with the surrounding semisolid. Therefore, it is pertinent to this report that selected literature dealing with the rheological aspects and mechanical properties of suspensions of solid particles in nonaqueous media be reviewed first. In particular, emphasis will be placed on literature that deals with the mechanical properties of suspensions of solid particles in polymeric materials.

The flow behavior of suspensions of rigid particles in liquids is important because most theories of the moduli of composites have their origin in the theory of the viscosity of suspensions. Einstein's equation for the viscosity of a suspension of spherical particles is fundamental to the theory (9, 10):

$$\eta/\eta_1 = 1 + k_e\phi_2 \qquad \text{(Eq. 1)}$$

The apparent viscosity, η, is related to the viscosity of the suspending media, η_1, the Einstein coefficient, k_e, and the volume fraction of the suspended phase, ϕ_2[1]. When $\phi_2 \ll 1$ and the spheres are noninteractive, $k_e = 2.5$. Equation 1 holds only for very dilute suspensions. Attempts to extend the validity of this equation are numerous (11).

One of the most useful extensions is the Mooney equation (12):

$$\ln (\eta/\eta_1) = k_e\phi_2[1/(1 - \phi_2/\phi_m)] \qquad \text{(Eq. 2)}$$

where ϕ_m is the maximum volume fraction that the particles can attain when packed[2]. Equation 2 is a constitutive equation which adequately describes the viscosity of many kinds of suspensions over a wide range of concentrations.

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[1] ϕ_2 is equal to the volume occupied by the particles divided by the total volume of the suspension.

[2] ϕ_m is equal to the true volume of the particles divided by the apparent volume occupied by particles.
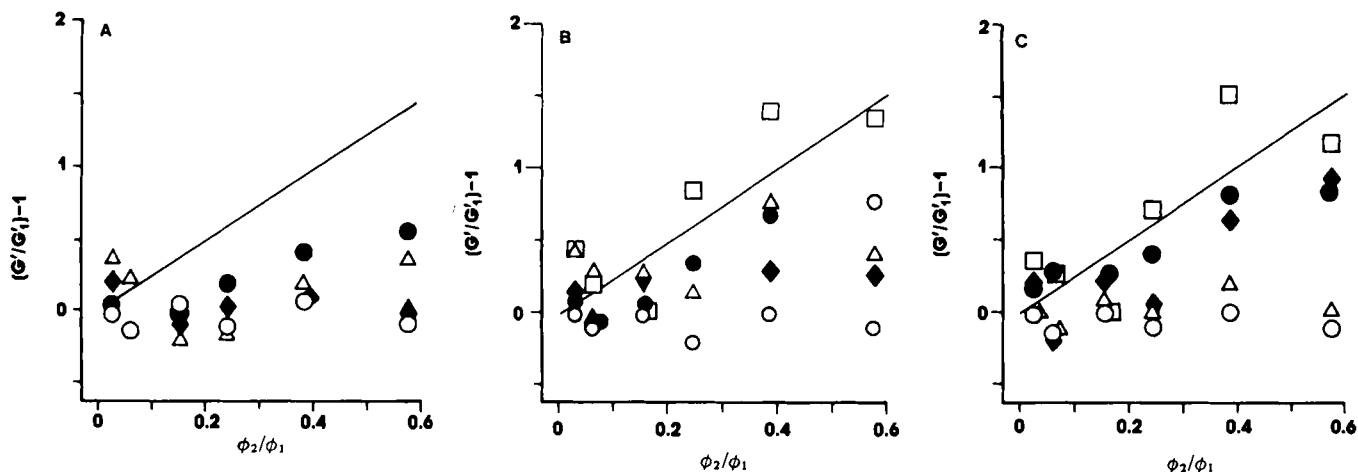
Figure 1—*Effect of the volume fraction of starch on the elastic moduli of starch-filled anhydrous lanolin USP dispersions, plotted on Kerner axes, at 3.54% strain and 0.0464 (A), 0.464 (B), and 4.64 (C) Hz. Key: (O) $0^c C$; (△) $10°C$; (◆) $15°C$; (●) $20°C$; (—) ideal Kerner equation prediction when $\mu_1 = 0.5$.*

Theoretically, ϕ_m is 0.74 for spheres in hexagonal close packing, but generally the value is much less because of irregularities in particle shape and particle-particle interactions. Viscosity generally increases rapidly with concentration and state of aggregation. The Einstein coefficient has been estimated for shapes other than nonagglomerated spheres, including roughly spherically shaped agglomerates of rigid spheres (13). Irregularities in shape generally increase k_e values.

With high concentrations of particles, suspensions become non-Newtonian and viscosity becomes a function of shear rate, $\dot{\gamma}$. For non-Newtonian suspensions that show a decrease in η with an increase in $\dot{\gamma}$, the Cross equation:

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)[1/(1 + \Omega\dot{\gamma}m)] \quad (Eq. 3)$$

often holds (14, 15). The constants Ω and m depend on the system, while η_0 is the viscosity at zero shear rate and η_∞ is the viscosity at high shear rates. It is generally assumed that the shear rate dependence of viscosity seen in these systems is due to structural changes in the suspension, such as the breaking up of agglomerates by shearing forces. Other shear-dependent theories have been proposed by Krieger and Dougherty (16) and Gillespie (17, 18).

For a given instrument, the theoretical equations for shear viscosity and shear modulus should be of the same form for a given instrument geometry (19, 20). Therefore, shear strain in the modulus equation replaces shear rate in the viscosity equation. For a dispersion of a rigid filler in a viscoelastic matrix phase with a Poisson's ratio[3], μ, equal to 0.5, the relationship between relative viscosities and relative shear moduli can be expressed as:

$$\eta/\eta_1 = G/G_1 \quad (Eq. 4)$$

where G is the shear modulus of the disperse system and G_1 is the shear modulus of the unfilled matrix phase. Consequently, the same theory that is used to determine the viscosity of a disperse system can be used to estimate its shear modulus. For example, G/G_1 can be substituted for η/η_1 in Eqs. 1 or 2 to yield corresponding equations for the relative shear modulus. It should be noted that the correlation between the relative viscosities and relative shear moduli expressed by Eq. 4 breaks down when μ is <0.5. Fortunately, a theoretical equation has been developed which compensates for this condition (22). In addition, if the rigidity of the dispersed phase is not much greater than that of the matrix, Eq. 4 is not applicable, as the modulus ratio will be substantially less than the viscosity ratio. Actual moduli, lower than predicted, can occur because (a) the Poisson's ratio of the matrix is <0.5, (b) thermal stresses reduce the apparent modulus, or (c) the modulus of the filler is not significantly greater than the modulus of the matrix. On the other hand, when the matrix is a rigid material, the Mooney equation (Eq. 2) predicts shear moduli which are too high (23).

Another constitutive equation that can be used to predict the modulus of a dispersion is the Kerner equation (24). When the dispersed particles are more rigid than the bulk polymer and deformation occurs by shear, the Kerner equation can be written as:

$$\frac{G}{G_1} = 1 + \frac{15(1-\mu_1)}{8-10\mu_1} \cdot \frac{\phi_2}{\phi_1} \quad (Eq. 5)$$

where μ_1 is Poisson's ratio of the bulk phase and ϕ_1, the volume fraction of the bulk phase, equals $(1 - \phi_2)$. This equation assumes the particles dispersed in the bulk polymer phase are spherical and that there is good adhesion between the particles and the bulk polymer. Good adhesion between the dispersed phase and the matrix or bulk phase is assumed to exist if the externally applied stress does not exceed the frictional forces between the phases. In many cases where adhesion is poor, Eq. 5 holds because there is little if any relative motion across the dispersed particle-matrix interface. Viscoelastic response can vary dramatically from the case of perfect adhesion to that of no adhesion. Weak agglomerates which break under applied stress show many of the characteristics of poor adhesion.

According to theory, the elastic modulus of a composite system is independent of the size of the filler particles, but experimental data indicates that there is an inverse proportionality between particle size and modulus (23). When the dispersed phase volume fraction is held constant, an increase in the elastic modulus of the dispersion may be attributed to an increase in total particle surface area when particle size is reduced. As particle size decreases, the tendency for particle agglomeration increases, which causes a corresponding decrease in maximum packing volume and a resultant increase in the elastic modulus.

It has also been demonstrated that the distribution of particle sizes has an effect on the moduli and viscosity of suspensions (25-28). Dispersions of
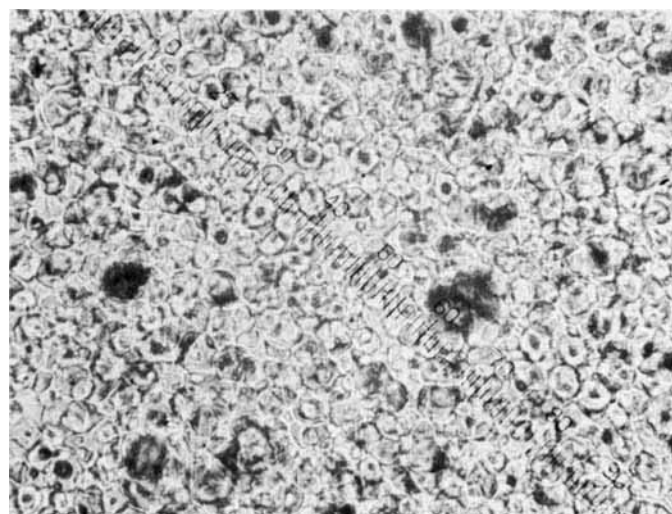
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[3] Poisson's ratio, μ, is an elastic constant which is defined for small elongations as the decrease in width of the specimen per unit width divided by the increase in length per unit length on the application of a tensile force. It can be shown that the relationship between μ and change in volume of the specimen, ΔV, can be expressed as: $\mu = 0.5 - (\Delta V/2\epsilon V_0)$, where V_0 is the original volume of the specimen and ϵ is the tensile force. When ΔV is sufficiently close to zero, the term $\Delta V/(2\epsilon V_0)$ is insignificant and equals 0.5. This condition holds for materials such as liquids and ideal rubbers. But when ΔV is positive, μ decreases to <0.5; and when ΔV is negative, μ increases to >0.5. Although the equation indicates that μ can be negative when the term $\Delta V/(2\epsilon V_0)$ is >0.5, this does not occur under conditions of small strain testing because ΔV is small compared to V_0 (21).

Figure 2—*Photomicrograph of a poured thin film of a starch-filled anhydrous lanolin USP dispersion, $\phi_1 = 0.802$. Original magnification 400X; 1 small division = 3.3 μm.*
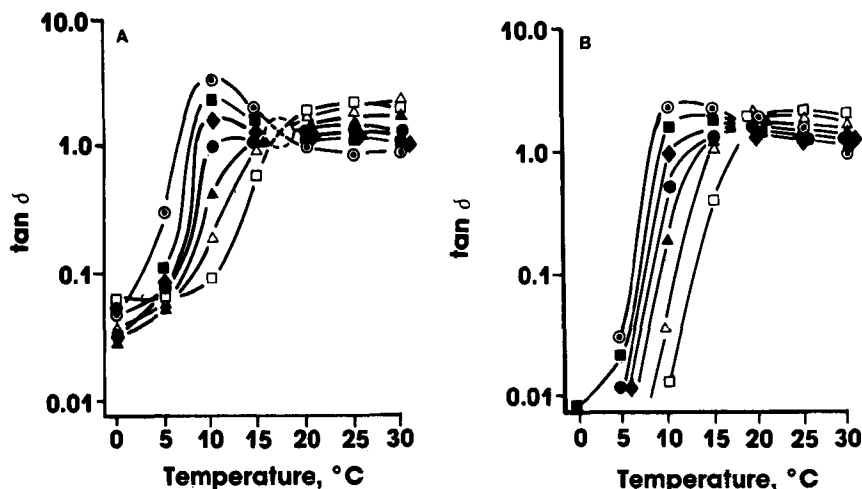
Figure 3—*Effect of temperature on the loss tangent of starch-filled anhydrous lanolin USP, at ϕ_1 equal to 0.802 (A) and 0.586 (B), and 3.54% strain. Key: (⊙) 0.0464 Hz; (■) 0.10 Hz; (◆) 0.215 Hz; (●) 0.464 Hz; (▲) 1.0 Hz, (△) 2.15 Hz; (□) 4.64 Hz.*

various particle sizes can pack more closely than monosized particles. Consequently, there is a larger maximum packing fraction and, hence, a lower modulus at a given concentration of dispersed phase.

In summary, the modulus of the disperse system (or composite) is dependent on the ratio of the moduli of the dispersed phase and matrix phase. The larger the modulus ratio, the greater is the modulus of the disperse system. This is especially true for high concentrations of particles.

EXPERIMENTAL

Materials—Anhydrous lanolin USP from the same production lot was used in all experiments[4]. It is a heterogeneous wax designated by the USP to contain not more than 0.25% water (25), the chemical composition of which has been examined extensively (26, 27). Potato starch[5], USP grade, was used to make the dispersions. When dispersed in anhydrous lanolin, 1 g of starch occupies an ~0.66-mL volume.

Apparatus—The viscoelastic properties of the starch dispersed in anhydrous lanolin were determined with a mechanical spectrometer, equipped with 50-mm cone and plate text fixtures[6]. Samples were oscillated sinusoidally by the output of a digital function generator and phase analyzer[7]. Temperature was controlled by enclosing the mounted sample in an environmental chamber[8]. A functional description of the apparatus, procedures for maintaining sample temperature and calculating the dynamic moduli, and data reproducibility have been previously given (7, 28).

Sample Preparation—Dispersions were prepared in 30-g lots. To prepare the dispersions, the appropriate weighed amounts of anhydrous lanolin and desiccator-dried starch were manually levigated together using a spatula and ointment tile. When the starch particles appeared to be completely coated, the mixture was transferred to a beaker and placed into a water bath at 50°C. After melting, the molten mixtures were gently stirred and placed into a desiccator. The desiccator was then evacuated by a filter pump, which acted to pull entrapped air from the molten mixtures. Deaerated samples were then gently stirred and poured onto the flat test fixture, while preventing air pocket formation. After 30 min at room temperature, the plate was mounted and the cone lowered to the preset gap. The extruded material was removed, and the sample was allowed to equilibrate at the test temperature for 15 min. Dispersions were made that contained the following volume fractions of starch (ϕ_2): 0.0295, 0.0604, 0.126, 0.198, 0.278, 0.366, and 0.414.

Description of Experiments—Samples were tested at 0°C, 5°C, 10°C, 15°C, 20°C, 25°C, and 30°C. At each T, all samples were oscillated over three decades of ν, 0.01–10.0 Hz, at a shear strain (γ) of 3.54%. The γ of 3.54% was the lowest obtainable strain with the equipment used (7). The moduli, G' and G'', and damping, tan δ, are calculated as a function of ν, T, and ϕ_2. In addition, photomicrographs[9] of thin poured films of the dispersions were taken to gain insight into the morphology of the dispersions.

RESULTS AND DISCUSSION

Kerner Equation Predictions—As previously discussed, many empirically derived equations are used to predict the viscoelastic behavior of powder-filled

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[4] Ruger Chemical Co., Irvington-on-Hudson, N.Y.
[5] J. T. Baker Chemical Co., Phillipsburg, N.J.
[6] Model RMS-7200; Rheometrics, Inc., Union, N.J.
[7] Model SA-2200; Rheometrics, Inc., Union, N.J.
[8] Model EC-1000; Rheometrics, Inc., Union, N.J.
[9] Olympus BH.

polymeric systems. Most of these equations are similar, but Kerner's equation is most useful (Eq. 5). For dispersions which undergo dynamic mechanical testing, the Kerner equation takes on the form:

$$\frac{G'}{G'_1} = 1 + \frac{15(1 - \mu_1)}{8 - 10\mu_1} \cdot \frac{\phi_2}{\phi_1} \qquad (Eq. 6)$$

where G' is the elastic modulus of the dispersion, G'_1 is the elastic modulus of the unfilled bulk phase, and ϕ_1 and ϕ_2 are the volume fractions of the bulk phase and filler, respectively. It generally holds when there is adhesion between the phases and the dispersed particles are nearly spherical. If Poisson's ratio, μ_1, equals 0.5, then the slope of the line predicted by a plot of $[(G'/G'_1) - 1]$ versus (ϕ_2/ϕ_1) is 2.5.

Deviations from a slope of 2.5 suggest that one or more assumptions on which the equation is based do not hold. For example, slopes of >2.5 could be due to strong interactions between particles, which causes an increase in elastic structure. In contrast, slopes of <2.5 could be caused by slippage at the particle-bulk phase interface, which gives an apparent loss in elastic structure. Other deviations from a slope of 2.5 could be due to irregularities in the shapes of the particles or variations in μ_1.

Experimentally determined elastic moduli, G', of starch-filled anhydrous lanolin dispersions are plotted on Kerner axes for three test frequencies, 0.0464, 0.464, and 4.64 Hz, in Fig. 1. These frequencies are representative of the three decades of shear frequency examined in these experiments. For comparison, a line equal to the "ideal" Kerner equation prediction (slope = 2.5) is presented in each plot.

An examination of the plots shows that at temperatures ≥10°C, an increase in ϕ_2 and ν causes an increase in G', up to a ϕ_2 of ~0.4. The plots also show that the effects of ϕ_2 on G' are enhanced as T and ν increase. An increase in G' occurs with increasing ν because the molecules of anhydrous lanolin do not have time to rearrange themselves within the time frame of straining.

An increase in G' with increasing T can also be explained in terms of particle interaction with anhydrous lanolin. The starch particles tie up anhydrous lanolin molecules by adhesion, thereby providing a more elastic structure. At $T = 0°C$, G' of the disperse systems do not change with ν and ϕ_2. Each dispersion has the same limiting elastic modulus, G_E, as unfilled anhydrous lanolin. The modulus contribution of the starch to the modulus of the dispersion is apparently shielded by the "frozen" structure of the anhydrous lanolin phase. The shielding action may result from a fluid component of the anhydrous lanolin, or air, adsorbing on the surface of the starch particles.

An increase in G' would also be expected from increasing particle-particle contact. A representative photomicrograph of a starch-filled anhydrous lanolin

Table I—Experimentally Determined Loss Tangents of Unfilled Anhydrous Lanolin USP at 3.54% Strain

Shear Frequency, Hz	$(G''/G')_1$ Unfilled Anhydrous Lanolin[a]		
	0°C	10°C	20°C
0.0464	0.0478	2.67	0.785
0.100	0.0337	2.20	0.827
0.215	0.0247	1.63	0.884
0.464	0.0220	1.09	0.985
1.00	0.0118	0.613	1.13
2.15	0.0139	0.184	1.32
4.64	0.0101	0.075	1.49

[a] ϕ_1 equals 1.00.

Table II—Theoretically Predicted and Experimentally Determined Loss Tangents of Starch-Filled Anhydrous Lanolin USP at 3.54% Strain

| Shear Frequency, Hz | $(G''/G')_1 \cdot \phi_1$ Starch-Filled Anhydrous Lanolin[a] | | | | | |
| | 0°C | | 10°C | | 20°C | |
	Theory[b]	Exp.[c]	Theory	Exp.	Theory	Exp.
0.0464	0.0383	0.0448	2.14	3.30	0.630	1.08
0.100	0.0270	0.0399	1.76	2.41	0.663	1.01
0.215	0.0198	0.0348	1.30	1.62	0.709	1.08
0.464	0.0176	0.0540	0.874	0.969	0.790	1.16
1.00	0.00946	0.0310	0.492	0.517	0.906	1.30
2.15	0.0111	0.0358	0.148	0.208	1.05	1.48
4.64	0.00810	0.0559	0.060	0.091	1.19	1.64

[a] ϕ_1 equals 0.802. [b] Calculated using Eq. 7 and data in Table I. [c] Experimentally determined.

dispersion shows a packed network of starch particles (Fig. 2). Two physical mechanisms can be postulated to explain the increase in G' from increasing particle-particle contact. The first is a phenomenon known as bridging. Bridging occurs when the ends of molecules in the disperse phase interact with the surfaces of suspended particles, linking different particles together. As the volume fraction of starch increases, particle density and the probability of particle-particle contact increase. Therefore, it is probable that anhydrous lanolin molecules will bridge more particles, provide more structure, and increase G' because the particles are generally closer to one another. This phenomenon is well illustrated by the interaction of rubber with suspended particles of carbon black (29).

The second mechanism that could cause an increase in G' with increasing particle-particle contact is volumetric dilation. As particle density increases, suspended particles are forced past one another during shear. In the process, there is a dilation in the volume of the dispersion. Resistance to volumetric dilation appears as an increase in G'. The degree of dilation and resultant increase in G' is, therefore, proportional to ϕ_2. This postulate is supported by the Kerner equation (Eq. 6). In this equation, μ_1 compensates for changes in volume of the matrix phase. When there is no change in volume, $\mu_1 = 0.5$, but when volumetric dilation occurs, μ_1 decreases[3]. Therefore, a decrease in μ_1 would be reflected as an increase in G'.

The Kerner equation has proved beneficial for postulating a general mechanism for the influence of starch particles on the elastic modulus of dispersions of starch in anhydrous lanolin, but it must be emphasized that the "ideal" Kerner prediction does not correlate with experimentally determined moduli at all ν and T. As evidenced by Fig. 1, the "ideal" Kerner prediction is approximated only at $\nu \geq 0.464$ Hz and $T = 30°C$. One would intuitively expect ν and T to affect G'/G'_1 because of their demonstrated influence on the viscoelastic properties of anhydrous lanolin. The shapes of the Kerner plots presented in this study may be due to nonlinear viscoelastic behavior. Nonlinear behavior results from testing at strains in excess of that necessary for linear viscoelasticity. The effects of ν and T on G' will subsequently be discussed further in this report. To further study the effects of powdered starch on the viscoelastic properties of anhydrous lanolin, it was decided to examine energy dissipation (7) by measuring damping, tan δ, as a function of volume fraction.

Energy Dissipation Considerations—Like the Kerner equation, the ratio of G'' to G', tan δ, is also an indicator of structural changes. To illustrate, the damping curves for the two volume fractions of starch used in these experiments, 0.198 and 0.414 ($\phi_1 = 0.802$ and 0.586, respectively), are presented in Fig. 3. When the shapes of these curves are compared with those of unfilled anhydrous lanolin in Fig. 4, noticeable differences occur at 0°C, 5°C, 10°C, and 20°C. Essentially, at these temperatures the range of tan δ obtained from 4.64 to 0.464 Hz is narrower for the starch-filled anhydrous lanolin dispersions, which indicates that the internal structure created by the starch tends to dominate the contribution of the anhydrous lanolin.

Changes in the dynamic mechanical properties of polymers as a function of ϕ_2 are often most evident in damping (30). The change in tan δ of solid-filled polymers can be approximated by a volume averaging relation (31, 32):

$$(G''/G') = (G''/G')_1 \cdot \phi_1 + (G''/G')_2 \cdot \phi_2 \qquad (\text{Eq. 7})$$

where $(G''/G') =$ tan δ, the damping of the filled polymer; $(G''/G')_1$ and $(G''/G')_2$ are the damping of the pure polymer and pure filler, respectively; and ϕ_1 and ϕ_2 are the volume fractions of the pure polymer and pure filler, respectively. Since the damping of most rigid fillers is very small compared with that of the polymeric bulk phase, the term $(G''/G')_2 \cdot \phi_2$ is almost zero and can be neglected.

Experimentally determined damping values of unfilled anhydrous lanolin, at 0°C, 10°C, and 20°C, are given in Table I. These data represent three temperature ranges where anhydrous lanolin is in three different viscoelastic states (7). The glassy state of anhydrous lanolin is represented by 0°C, while 10°C is within the transition zone from a glassy to a rubbery state, and 20°C is within the region just beyond the transition zone. In Tables II and III, theoretical and experimentally determined damping values of two starch-filled anhydrous lanolin dispersions, $\phi_1 = 0.802$ and 0.586, respectively, are given. The theoretically predicted values were calculated by substituting the values from Table I into Eq. 7.

It is apparent that predicted damping does not equal that determined experimentally. In Table II, where $\phi_1 = 0.802$, it can be seen that the presence of starch increases damping over the temperature range of 0-20°C and over the entire test frequency range. The increases are probably caused by newly introduced damping mechanisms that are not present in anhydrous lanolin alone. The new damping mechanisms may include (a) particle-particle friction, where particles touch each other as in weak agglomeration, (b) particle-anhydrous lanolin friction, where there is little or no adhesion at the interface, and (c) excess damping in anhydrous lanolin near the interface because of induced thermal stresses or changes in anhydrous lanolin molecular conformation. Each of these mechanisms cause the elastic modulus to decrease and the viscous modulus to increase, which both independently give higher damping. An increase in damping indicates that these damping mechanisms cause an increase in energy dissipation during deformation of the dispersion.

In Table III, where $\phi_1 = 0.586$, the presence of starch increases or decreases damping of anhydrous lanolin depending on the temperature. At 0°C, where anhydrous lanolin exists in the glassy state, the experimentally determined damping of this dispersion is lower than that predicted by Eq. 7. At 10°, where anhydrous lanolin is in the transition zone from a glassy to a rubbery state, results are mixed. At low ν, experimental results are higher, while at higher ν experimental results are lower. At 20°C, a temperature just above the transition zone, experimental results are higher at all ν. Damping values lower than those predicted by Eq. 7 can be explained in terms of particle-particle interactions and particle-bulk phase interactions that result in a structure that is not easily deformed or broken by applied stress. These interactions result in increased elasticity and a consequent increase in G'. The viscous modulus, G'', also increases but not as greatly as the rate of increase in G'. Hence, the net result of changes in G' and G'' is a lower tan δ (the ratio of G'' to G').

For dispersions of starch in anhydrous lanolin, it would be appropriate to modify Eq. 7 to the form:

$$(G''/G') = (G''/G')_1 \cdot \phi_1 + (G''/G')_2 \cdot \phi_2 + \text{Interaction Term} \qquad (\text{Eq. 8})$$
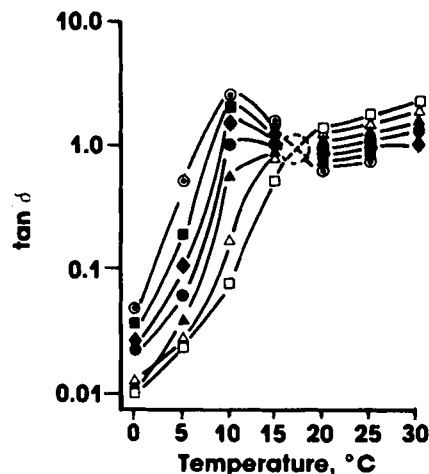

Figure 4—*Effect of temperature on the loss tangent of unfilled anhydrous lanolin USP, at 3.54% strain. Key: (○) 0.0464 Hz; (■) 0.10 Hz; (◆) 0.215 Hz; (●) 0.464 Hz; (▲) 1.0 Hz; (△) 2.15 Hz; (□) 4.64 Hz.*

Table III—Theoretically Predicted and Experimentally Determined Loss Tangents of Starch-Filled Anhydrous Lanolin USP at 3.54% Strain

Shear Frequency, Hz	$(G''/G')_1 \cdot \phi_1$ Starch-Filled Anhydrous Lanolin[a]					
	0°C		10°C		20°C	
	Theory[b]	Exp.[c]	Theory	Exp.	Theory	Exp.
0.0464	0.0285	0.00681	1.59	2.25	0.468	1.34
0.100	0.0201	0.00797	1.31	1.58	0.493	1.28
0.215	0.0147	0.00677	0.971	0.964	0.527	1.27
0.464	0.0131	0.00294	0.650	0.508	0.587	1.30
1.00	0.00703	0.00498	0.365	0.207	0.673	1.38
2.15	0.00828	0.00288	0.110	0.0370	0.787	1.56
4.64	0.00602	0.00291	0.0447	0.0128	0.888	1.68

[a] ϕ_1 equals 0.586. [b] Calculated using Eq. 7 and data in Table I. [c] Experimentally determined.

where the interaction term accounts for deviations from idealized behavior. The interaction term would be negative when experimentally observed damping is lower than that predicted by Eq. 7. Conversely, the interaction term would be positive when experimentally observed damping is higher than that predicted by Eq. 7.

As previously mentioned, Figs. 3 and 4 illustrate the relationships between tan δ, T, and ϕ_2 for starch-filled and unfilled anhydrous lanolin. A comparison of Fig. 3 to Fig. 4 shows the maxima in the damping curves at the lowest ν all occur at 10°C. Overall, there appears to be no significant difference between Fig. 4 and Fig. 3A. This is a good indication that starch, up to $\phi_2 = 0.198$, does not shift the mechanical transition temperature (analog of T_g) of anhydrous lanolin. There also appears to be no significant shift in the crossover region of the damping curves. But when ϕ_2 reaches 0.414, there is a significant difference in appearance in the damping curves, as evidenced by a comparison of Figs. 4 and 3B. Even though the damping curve generated by a ν of 0.0464 Hz has its maximum at 10°C, its magnitude has been reduced, as is also the case at each ν at $\leq$10°C. At >10°C, the curves are closer together and most noticeably, the crossover region has shifted from 17°C to ~20°C. These plots suggest that the degree of influence on the transition temperature of anhydrous lanolin is proportional to the volume fraction of starch.

CONCLUSION

Dynamic mechanical testing has been shown to be a sensitive tool to examine the effects of a powdered filler on the viscoelastic properties of a pharmaceutical semisolid. Viscoelastic parameters give insight into fine structural changes of the dispersions that cannot be observed with conventional steady shear rheometers. Even though the widely used Kerner equation was unable to predict the elastic moduli of starch-filled anhydrous lanolin dispersions at all ν, T, and ϕ_2, it did prove useful in postulating mechanisms of interaction between the filler and the bulk phase. One probable reason for the limited applicability of the Kerner equation is the nonlinear viscoelastic effects caused by the introduction of starch into anhydrous lanolin. It must be noted, however, that damping was an effective indicator of the degree of influence starch had on the mechanical transition of anhydrous lanolin from the rubbery state to the glassy state.

APPENDIX: Glossary

G = shear modulus (dyne cm^2 or Pa: N m^2)
G_1 = shear modulus of the unfilled matrix phase
G' = dynamic shear storage modulus (same units as G)
G'' = dynamic shear loss modulus (same units as G)
G_E = limiting value of G'
T = temperature
V_0 = original volume of test specimen
ΔV = change in volume of specimen
T_g = glass transition temperature
k_e = Einstein coefficient
ϵ = tensile force
m = exponent of shear rate in Cross equation
δ = phase angle between stress and strain vectors
γ = strain
$\dot{\gamma}$ = rate of strain
η = shear viscosity (Poise: dyne s cm^{-2} or Pascal seconds: N s m^{-2})
η_0 = shear viscosity at zero shear rate
η_1 = shear viscosity of the suspending media
η_∞ = shear viscosity at very high shear rates
μ = Poisson's ratio (dimensionless)
μ_1 = Poisson's ratio of the bulk phase

ϕ_1 = volume fraction of bulk phase
ϕ_2 = volume fraction of dispersed phase
ϕ_m = volume fraction of maximally packed particles
ν = shear frequency (Hz)
Ω = constant in the Cross equation

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