

## Evaluation of Surface-Active Additives in Highly Filled Composites by Mechanical Spectroscopy

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### Synopsis

The Rheovibron oscillatory viscoelastomer has been used to compare the rheological behavior of three composites at low temperature near the glass transition point. All three composites are highly filled materials containing 84-88% solids,  $\text{NH}_4\text{ClO}_4$ , and Al, in an elastomeric matrix. The main purpose of the measurements is to evaluate the efficiency of two surface-active agents: an aziridine polyester showing better adhesion properties between solid particles and the elastomeric binders than an amine polyester. Mixtures of both polyesters are shown to be even more efficient. The dynamic mechanical properties are qualitatively discussed in relation to the mechanism of actions of both surface-active compounds.

### INTRODUCTION

Effective adhesion between filler particles and polymeric matrices is a prerequisite for good mechanical properties of a majority of composite materials. Under strain, a weak bond at the binder-filler interface very often leads to dewetting of the binder from the solid particles, to formation of voids, and to deterioration of mechanical properties.

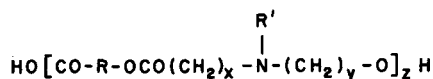
Special surface-active agents were synthesized to improve the binder-filler bond. The selection of these "bonding agents," however, was empirical because of the lack of experimental techniques to evaluate their action at the interface and to optimize their concentration in the composite material.

In a recent study,<sup>1</sup> Lepie and Adicoff submitted a highly filled polymer to sinusoidal stresses of various duration to induce dewetting. They related the extent of dewetting to the peak heights of  $\tan \delta$ , also known as the ratio of the loss modulus  $E''$  over the storage modulus  $E'$ . These peaks are located near the glass transition temperature  $T_g$ , where the mechanical absorption is at maximum. From this work of Lepie and Adicoff, it can be suggested to relate the peak height of  $\tan \delta$  to the differences in void concentrations,  $\Delta C$ , between composites 1 and 2 by the following equation:

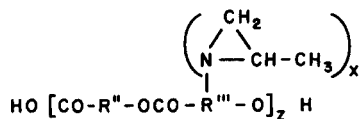
$$\ln \frac{(\tan \delta_1)}{(\tan \delta_2)} = -k\Delta C \quad (1)$$

in which  $k$  is a constant. Ferguson and his colleagues<sup>2</sup> also noted an increase in the maximum of  $\tan \delta$  at the apparition of spherulites in a block copolymer subjected to temperature variations.

From these results, it appeared that the efficiency of surface-active agents in preventing void formation at the interface should be inversely related to the peaks of  $\tan \delta$ . To verify this hypothesis and to obtain insights on the action of those additives, mechanical spectra were measured on highly filled thermosetting composites containing two surface-active agents of empirically known efficiencies: a N-methyl-di(2-hydroxyethyl)amine (amine polyester) (I) and a triaziridine polymerized with diacids (aziridine polyester) (II).



I



II

## EXPERIMENTAL

### Mechanical Properties

Dynamic mechanical properties were measured on a Rheovibron Dynamic Viscoelastometer Model DDV II (Toyo Measuring Instrument Co., Tokyo, Japan) from  $-100^\circ\text{C}$  to  $0^\circ\text{C}$ . The samples were cooled at a rate of  $1-2^\circ\text{C}/\text{min}$ . Sinusoidal oscillations were applied to samples 6 cm long, 0.5 cm wide, and 0.1 cm thick, machined on an automatic lathe.

TABLE I  
Mechanical Properties in Tension of Composites

Temperature, $^\circ\text{C}$	$\sigma_m$ , (dyn/cm <sup>2</sup> ) $\times 10^{-6}$	$\epsilon_m$ , %	$\epsilon_m$ , %	$E$ , (dyn/cm <sup>2</sup> ) $\times 10^{-7}$	Energy, (dyn-cm) $\times 10^{-7}$
Composite A					
-45.6	24.2	21.1	36.2	57.4	6.94
22.8	8.2	30.4	32.6	10.9	1.84
Composite B					
-53.9	24.6	10.6	20.7	50.9	7.01
-45.6	18.6	38.7	44.6	30.6	7.19
22.8	7.3	35.5	35.7	4.9	1.56
Composite C					
-53.9	36.2	23.0	36.3	54.9	9.43
-45.6	23.5	65.7	71.2	32.9	12.23
22.8	6.8	70.7	73.7	2.6	2.85

Mechanical properties in tension (Table I) were measured on an Instron apparatus at a cross-head speed of 5.08 cm/min, corresponding to a strain rate of  $0.741 \text{ min}^{-1}$  for the "dumbbell" specimen.

### Formulations

Composites were prepared as previously described.<sup>3</sup> Composite A contained 0.05% by weight of the amine polyester. Composite B contained 0.15% of the aziridine polyester, and composite C, 0.05% of the amine polyester plus 0.098% of the aziridine polyester.

The detailed formulations were as follows: composite A, 72%  $\text{NH}_4\text{ClO}_4$ , 12% Al, 3% diethylhexyl azelate (DEHA), and 12.95% of a binder prepared from an  $\alpha,\omega$ -dihydroxypolybutadiene cured with tolylene diisocyanate (TDI) in a NCO/OH ratio of 1.1 equivalent and catalyzed by 0.0003% ferric acetylacetonate (FeAA); composite B, 70%  $\text{NH}_4\text{ClO}_4$ , 18% Al, 2.25% isodecyl pelargonate (IDP), and 9.6% of a binder prepared from a similar prepolymer cured with a polymeric diisocyanate (DDI, General Mills Co.) in a NCO/OH ratio of 0.9; composite C, 68%  $\text{NH}_4\text{ClO}_4$ , 18% Al, 3.36% IDP, and 10% of the same binder as composite A. All three compositions were cured at  $60^\circ\text{C}$ .

### Calculation

Calculations of the complex modulus  $E^*$ , storage modulus  $E'$ , and loss modulus  $E''$  were done by computer using equations given in the instruction manual<sup>4</sup> of the instrument. Modulus values are given in  $\text{dyn/cm}^2$  or in Pa (1 Pa =  $10 \text{ dyn/cm}^2$ ).

## RESULTS

### Mechanical Spectra

The mechanical spectra of composite A at 110 and 3.5 Hz are given in Figure 1. To simplify this figure, results at 35 and 11 Hz are not included since they show the same trends as the two illustrated curves.

As the temperature decreases at 110 Hz, the storage modulus is seen to increase, and  $\tan \delta$  goes through a maximum indicative of the mechanical absorption of a given relaxation mechanism. The complex modulus  $E^*$  yields values slightly higher than  $E'$  but follows the same trend.

A diminution of the displacement frequency applied to the sample from 110 to 3.5 Hz shifts the  $E'$  curve and the maximum of  $\tan \delta$  to a lower temperature.

The mechanical spectra of composites B and C are similar to the spectrum of composite A, as shown respectively in Figures 2 and 3. However, by comparing those three spectra, differences in  $E'$  and  $\tan \delta$  are apparent.

At a given temperature,  $E'$  increases from composite A (amine polyester) to composite B (aziridine polyester) and finally to C (mixture of both polyesters). This can be seen by superposition of the three spectra or by com-

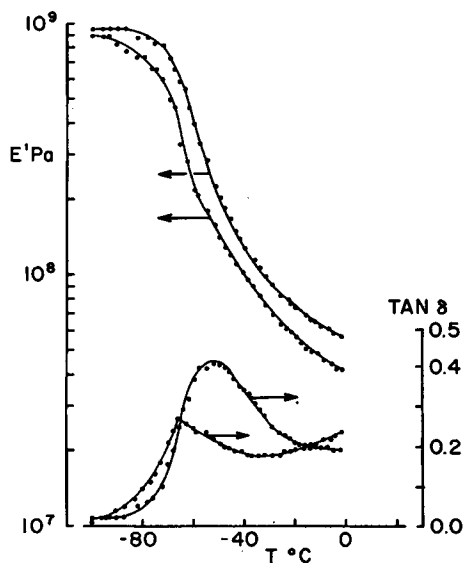


Fig. 1. Mechanical spectrum of composite A: (O) at 110 Hz and (●) 3.5 Hz.

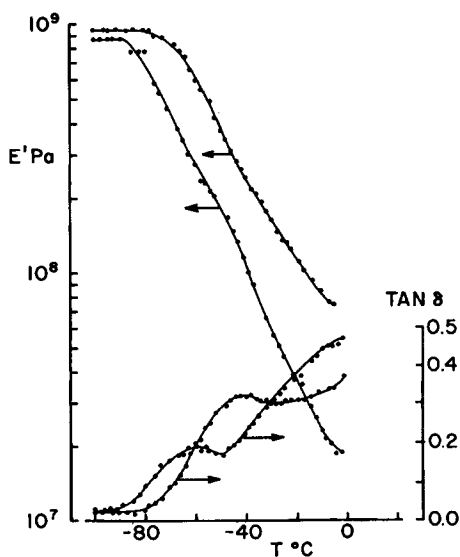


Fig. 2. Mechanical spectrum of composite B: (O) at 110 Hz and (●) 3.5 Hz.

paring  $E'$  at 110 Hz for a midrange temperature of  $-50^\circ$ ; the values are  $1.9 \times 10^9$ ,  $3.8 \times 10^9$ , and  $4.6 \times 10^9$  dyn/cm<sup>2</sup> for composites A, B and C, respectively. At temperature below the glass transition ( $T_g$ ),  $-80^\circ$  to  $-100^\circ\text{C}$ ,  $E'$  values attain a plateau near  $8.8$  to  $9.5 \times 10^9$  dyn/cm<sup>2</sup> depending on the applied frequency. This plateau is in accordance with the equivalence of state for all polymers below the  $T_g$ .

TABLE II  
Values of  $\tan \delta$  at the Maximum of the Mechanical Absorption Near  $T_g$

Composite	$\tan \delta$			
	110 Hz	35 Hz	11 Hz	3.5 Hz
A	0.41	0.46	0.31	0.26
B	0.32	0.29	0.21	0.20
C	0.17	0.16	0.15	0.11

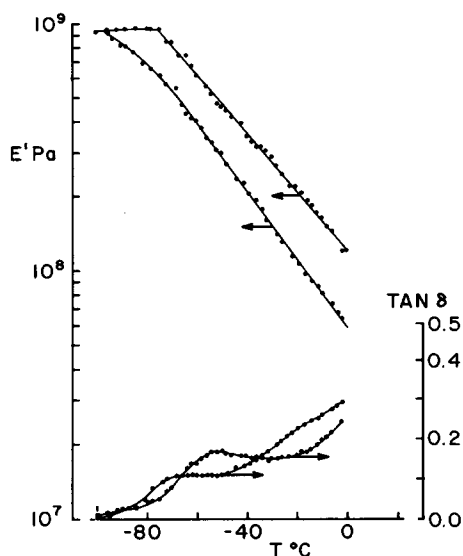


Fig. 3. Mechanical spectrum of composite C: (O) at 110 Hz and (●) 3.5 Hz.

The heights of the absorption peak for  $\tan \delta$  at 110 Hz decrease from 0.41 for composite A (Fig. 1) to 0.32 for composite B (Fig. 2) and 0.17 for C (Fig. 3). This trend is verified at the four applied frequencies, as demonstrated in Table II.

### $E'$ Master Curves

The relation between the storage modulus and frequencies at different temperature is shown in Figure 4. This family of curves can be reduced to a master curve using the WLF shift factor.<sup>5</sup> The  $T_g$  was taken as constant at  $-78^\circ\text{C}$  for all three composites, and the master curves of Figure 5 were obtained from measurements at  $-14^\circ$ ,  $-37^\circ$ ,  $-52^\circ$ ,  $-60^\circ$ ,  $-70^\circ$ ,  $-74^\circ$ ,  $-78^\circ$ , and  $86^\circ\text{C}$  at each one of the four frequencies. These master curves give superposable results for composites A and B, showing that the difference in  $E'$  spectra is a consequence of a temperature shift of similar viscoelastic relaxations. Composite C master curve is definitely higher than A and B curves.

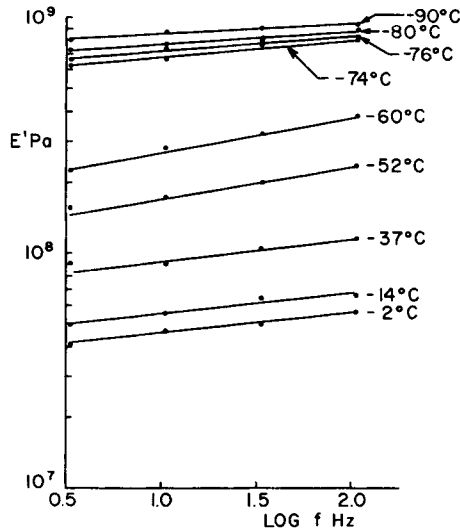


Fig. 4. Storage modulus of composite A at different temperatures.

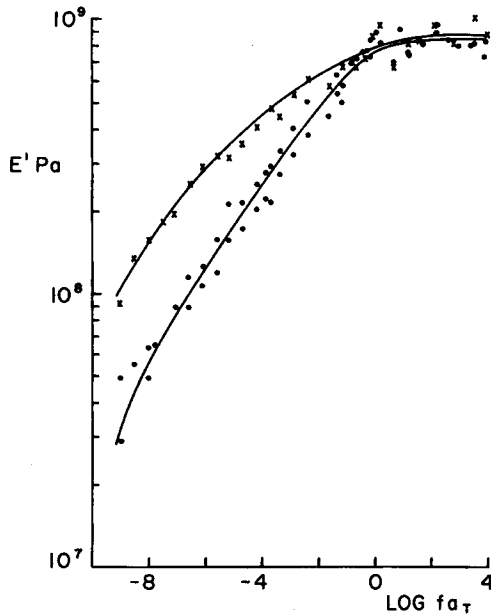


Fig. 5. Reduced storage modulus spectrum of composites A(O), B(●), and C(×).

### Loss Modulus

Loss moduli  $E''$  are calculated from  $\tan \delta$  measurements and  $E'$  values. Variations of  $E''$  with temperature for the three composites are given in Figure 6 at 3.5 Hz and in Figure 7 at 110 Hz. The  $E''$  value at the maximum of the absorption peak follows the same trend as  $\tan \delta$  (Table II), which is  $E''(A) > E''(B) > E''(C)$ . The maximum loss modulus values at the four applied frequencies are summarized in Table III.

TABLE III  
Maximum Loss Modulus

Composite	Maximum loss modulus $E''$ , (dyn/cm <sup>2</sup> ) $\times 10^{-9}$			
	110 Hz	35 Hz	11 Hz	3.5 Hz
A	1.55	1.50	1.15	1.10
B	1.25	1.25	0.84	0.76
C	0.94	0.95	0.80	0.61

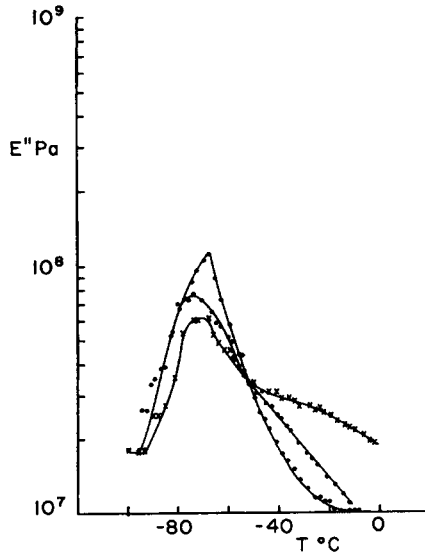


Fig. 6. Loss modulus spectrum of composites: A (O), B (●), and C (×) at 3.5 Hz.

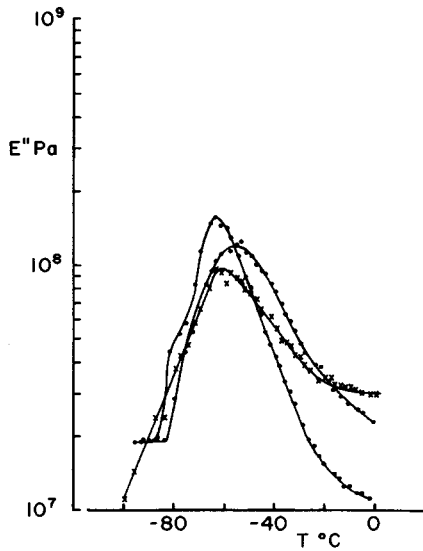


Fig. 7. Loss modulus spectrum of composites A(O), B (●), and C (×) at 110 Hz.

### Activation Energy

The frequency  $f_m$  and the temperature  $T$  of the maximum loss modulus is characteristic of a given viscoelastic relaxation phenomenon and permits the calculation of the activation energy  $\Delta H_a$  of the transition using the equation

$$\Delta H_a = -Kd(\ln f_m)/d(1/T)$$

where  $K$  is the Boltzman constant. The temperatures corresponding to the maximum loss modulus at each frequency and the calculated activation energies are given in Table IV. The value of 58 kcal/mole for composite A is normal for an  $\alpha$ -transition at a temperature slightly above the  $T_g$ ,<sup>6</sup> while the values of 16 and 26 kcal/mole for composites B and C, respectively, are very low for the  $\alpha$ -type of transition.

TABLE IV  
Temperature of Maximum Absorption

Composite	Temperature, °C				$\Delta H_a$ , kcal/mole
	3.5 Hz	11 Hz	35 Hz	110 Hz	
A	-68	-68	-65	-64	58 ± 15
B	-75	-66	-64	-57	16 ± 3
C	-72	-69	-67.5	-61	26 ± 5

In the same table, the average least-squares deviation was calculated for the slope of the curve relating the logarithm of the applied frequency to the inverse of the absolute temperature. At 20–25%, the deviations of  $\Delta H_a$  are quite important.

### DISCUSSION

For the purpose of the discussion, the experimental results can be summarized under three topics. First,  $\tan \delta$  and  $E''$  values follow the same trend  $A > B > C$ . Second, the activation energies of the transition give a higher value for composite A (amine polyester) than for both composites B (aziridine polyester) and C (mixture of both polyesters). Finally, the reduced  $E'$  curve is higher for composite C than for both A and B.

#### Tan $\delta$ and Loss Modulus

In considering the peak heights of  $\tan \delta$  and the hypothesis which inversely relates these maxima to the efficiency of the surface-active additives, it may be deduced that the mixture of both polyesters is more efficient than the aziridine polyester, which is more efficient than the amine polyester. This should lead to the following scale of final composite properties: composite C > composite B > composite A.

The conventional mechanical properties by uniaxial tension tests (Table I) confirm this trend and show that composite C gives the best properties of



the three samples, with a stress  $\sigma_m$  comparable to both A and B, a strain  $\epsilon_m$  doubled in value, and definitely higher network energy. Differences in strain between composites A and B are not very obvious at room temperature; but at low temperature composite B exhibits better properties than composite A, specially at  $-45.6^\circ\text{C}$ .

The same trend is also confirmed by the ratio of the elongation at rupture  $\epsilon_r$ , over the elongation at maximum  $\epsilon_r/\epsilon_m$  at low temperature, which is sometimes empirically considered as an index of dewetting in those highly filled unreinforced composites. At  $-45.6^\circ\text{C}$ , the  $\epsilon_r/\epsilon_m$  ratios are, respectively, 1.70, 1.15, and 1.08 for composites A, B, and C (a ratio of 1.00 indicating a perfect interface efficiency).

Using eq. (1), which is similar to the one suggested by Lepie and Adicoff, it is possible to calculate that composites B and C would respectively contain in volumic fraction  $0.007 \pm 0.002$  and  $0.018 \pm 0.003$  fewer void formation resulting from the application of a low sinusoidal stress of 3.5 to 110 Hz than composite A, arbitrarily taken as the reference.

The loss modulus follows the same trend as the  $\tan \delta$  absorption. If  $\tan \delta$  in eq. (1) is replaced by  $E''$ , the following equation is obtained:

$$\ln E_1''/E_2'' = -k\Delta C \quad (2)$$

Then, the calculated  $\Delta C$  values between composites A and B or A and C are respectively  $0.005 \pm 0.002$  and  $0.010 \pm 0.002$ , using the same constant  $k$  as in eq. (1), which is surprisingly close to the value obtained with  $\tan \delta$ . These results tend to indicate that the efficiency of the surface-active agent is also inversely proportional to the height of the  $E''$  peak at the point of mechanical absorption slightly above  $T_g$ .

### Activation Energy of the Transition

The large difference between the  $\Delta H_a$  of composite A (amine polyester: 58 kcal/mole) and composite B (aziridine polyester: 16 kcal/mole) reflects a difference in the mechanism of action at the interface. It was hypothesized<sup>8</sup> that the amine polyester was forming an ionic bond at the surface of the ammonium perchlorate through its tertiary amine groups. The aziridine polyester can form a similar ionic bond through its amine groups or can homopolymerize at the surface to encapsulate the solid particles.<sup>7</sup> The differences in  $\Delta H_a$  would thus favor the homopolymerization mechanism over the ionic bond formation. The mixture of both polyesters gives an intermediary value as expected.

### Reduced Storage Modulus

The obtention of superposable reduced  $E'$  curves for composites A and B is an indication that those surface-active agents react at the surface of filler particle without interfering with the bulk of the binder. The higher reduced  $E'$  curve obtained for composite C would indicate that the mixture of both polyester affects the binder in such a way as to increase its modulus. The two main mechanisms that would explain such a behavior are: the

reinforcement of the matrix by the solids through the surface-active compounds, or the increased crosslinking density of the binder. However, when used separately, both polyesters act at the interface without noticeable effect on the binder.

### CONCLUSIONS

This study on three composite materials highly filled with solids (84–88%) led to the following conclusions:

1. The efficiency of surface-active agents was found to be inversely proportional to the peak height of the loss tangent and loss modulus near the glass transition point.
2. Composite C, containing a mixture of two surface-active agents (aziridine and amine polyesters), yielded the best properties. Composite B (aziridine polyester) was second and composite C (amine polyester) was last.
3. The activation energy near the glass transition point was higher for composite A than for composites B and C.
4. The reduced curve for the storage modulus of composite C was higher than that of composites A and B. The two reduced curves for composites A and B were superposable.
5. The viscoelastomer technique appears very promising for evaluation of surface-active agents in elastomeric composite materials highly filled with solids.

Dynamic mechanical properties on the Rheovibron were skillfully measured by Mr. Y. Boucher. The composites were prepared by the Process Engineering Group.

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Received August 31, 1973

Revised October 30, 1973