

Rheological Behavior of Partially Hydrolyzed Poly(vinyl Acetate-Co-Ethylene)

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Synopsis

The rheological behavior of partially hydrolyzed poly(vinyl acetate-co-ethylene) (VAE) was investigated, using a Rheometrics Dynamic Mechanical Spectrometer. For the investigation, measurements of storage modulus (G'), loss modulus (G'') and loss tangent ($\tan \delta$) of the materials were recorded as functions of temperature at a fixed frequency (i.e., using temperature scans) and, also, as functions of frequency at a fixed temperature (i.e., using frequency scans). For the hydrolysis, three different grades of copolymer (containing 34, 47, 62 mol% of vinyl acetate) were used to yield poly(vinyl acetate-co-ethylene-co-vinyl alcohol) (VAEOH) with varying amounts of hydroxyl group. For comparison purposes, the viscoelastic properties of blends of VAE copolymer with poly(vinyl alcohol) (PVOH), having varying blend compositions, were also measured. The blends were prepared by first mixing a solution of VAE copolymer, which was dissolved in a toluene/dichloroethane mixed solvent, and an aqueous solution of PVOH, and then freeze drying the mixture to a constant weight. Also measured were the glass transition temperature (T_g) of the VAE copolymers and the T_g and melting point (T_m) of the VAEOH terpolymers, using a DuPont Thermal Analyzer equipped with a 910 DSC Module. It has been found that (1) introduction of hydroxyl group into the backbone of the amorphous VAE copolymer has made the resulting VAEOH terpolymer semicrystalline; (2) the T_m , T_g , G' , and the complex viscosity (η^*) of the VAEOH terpolymers increase with increasing amounts of hydroxyl group; (3) the physical blending of PVOH with VAE copolymer has not affected the T_g of the VAE copolymer; (4) the G' and η^* of the VAE/PVOH blends are found to increase with the amount of PVOH in the blend. The use of logarithmic plots of G' versus G'' has been found to be very useful for discerning the differences in the structure of the materials tested.

INTRODUCTION

Poly(vinyl acetate) (PVAc) is one of the most important of all the synthetic thermoplastic adhesives that are widely used today in industrial applications. However, because of the brittle nature of PVAc, a plasticizer is usually added to make it flexible and to achieve good adhesion characteristics. Nevertheless, due to the migration of the plasticizer, when applied to the surface of the substrate, the adhesive joints of the PVAc/plasticizer system become brittle. To overcome this drawback, copolymers of PVAc have been developed. One

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such copolymer that has met great commercial success is poly(ethylene-co-vinyl acetate) (EVA) or poly(vinyl acetate-co-ethylene) (VAE), which is obtained by introducing ethylene as a comonomer into vinyl acetate in the polymerization step. When the amount of vinyl acetate in the copolymer is less than 40 wt%, the copolymer is referred to as EVA, which is widely used as a melt adhesive. On the other hand, when the amount of vinyl acetate is more than 60 wt%, the copolymer is referred to as VAE, which is widely used in film laminating and packaging adhesives in the form of emulsions.¹

The flexibility of EVA or VAE copolymer is due to the flexible ethylene chains that are attached to the backbone of the vinyl acetate and, also, to the reduced frequency of vinyl acetate polar groups. Note that the ethylene molecules are permanently attached to the backbone of vinyl acetate and therefore may be considered as a permanent internal plasticizer. In the copolymerization process, one can vary the molar ratio of vinyl acetate and ethylene to obtain different properties of the resultant copolymers.

In recent years, the use of VAE emulsions has steadily increased. Various methods have been reported in the literature²⁻⁴ describing how the hydroxyl group may be introduced into VAE emulsions. A certain amount of poly(vinyl alcohol) (PVOH) may be grafted on the VAE copolymer during copolymerization. Also, an aqueous dispersion of PVAc may be modified by adding a small amount of alkali, which then forms stable films of the partially hydrolyzed VAE copolymer [i.e., films of poly(vinyl acetate-co-ethylene-co-vinyl alcohol) (VAEOH)], on the surface of the dispersed VAE droplets.³ Note that the VAEOH terpolymer thus formed has hydroxyl pendants on the backbone of the vinyl acetate. The VAE-based adhesive, however, has some serious drawbacks, in that it is very sensitive to water. The soft VAE copolymer has a solubility lower than the constituent homopolymers and thus can be readily attacked by solvents of low polarity (e.g., hydrocarbons). To overcome this drawback, it has been suggested that the hydroxyl groups in VAE emulsions be crosslinked with a curing agent (e.g., melamines).¹

It is a well known today that, when VAE or EVA copolymer undergoes hydrolysis, the replacement of the acetate groups by the hydroxyl groups gives rise to a change in thermal, physical, and mechanical properties by virtue of the hydrogen-bonding capabilities of the hydroxyl group.⁴⁻⁹ When the hydroxyl group is introduced into its backbone, the amorphous VAE copolymer is transformed from a rubbery material into a semicrystalline material, VAEOH terpolymer, having a higher glass transition temperature T_g . Since a strong intermolecular interaction can occur in the presence of the hydrogen bonding present in the vinyl alcohol groups, the linear additivity rule for predicting the T_g 's of many random vinyl copolymers has been found not applicable to predicting the T_g of VAEOH terpolymer.⁸ It has been observed, also, that the least number of vinyl alcohol units, necessary for one to detect the crystallinity in VAEOH terpolymer, increases as the vinyl acetate content in the parent VAE copolymer is increased.⁸

Very recently, we have investigated the rheological behavior of such partially hydrolyzed VAE copolymers. For comparison purposes, we have also prepared blends of VAE copolymer and PVOH, and measured their viscoelastic properties. In this paper, we report the highlights of our findings.

EXPERIMENTAL

Materials

Three different grades of VAE copolymer were kindly supplied to us by Dr. J. M. Hoyt of U.S.I. Chemical Company. They contained 34, 47, and 62 mol% of vinyl acetate, equivalent to 61, 72, and 83 wt%. It is believed that these materials were produced by the bulk copolymerization process. The VAE copolymers were used for preparing VAEOH terpolymers by hydrolysis, and also for preparing blends of VAE copolymer and PVOH. For the blends, partially acetylated PVOH (with 88 mol% vinyl alcohol and a molecular weight of 96,000) was purchased from Aldrich Chemical Company.

Preparation of VAEOH Terpolymers (Hydrolysis of VAE Copolymers)

The three different grades of VAE copolymer described above were hydrolyzed to obtain VAEOH terpolymers. For this, about 120 g of VAE copolymer was dissolved in about 240 mL of 1/1 toluene/methanol mixed solvent at 60°C. The hydrolysis reaction was conducted at 60°C for 1/2 h, with vigorous stirring, in the presence of a 0.25 N solution of sodium methoxide (prepared by dissolving metallic sodium in methanol) as catalyst, under a nitrogen gas atmosphere. The amount of catalyst used was varied to control the degree of partial hydrolysis. At the end of the hydrolysis reaction, the mixture was first neutralized with glacial acetic acid and then cooled by stirring in an ice water bath. The partially hydrolyzed VAE copolymer (i.e., VAEOH terpolymer) was precipitated in 5 L of distilled water, and the precipitate was then boiled in 4.5 L of distilled water three times, each time for about 1 h. The VAEOH terpolymer was finally dried at 50°C in a vacuum oven to a constant weight.

The amount of vinyl acetate in the VAE copolymers that were supplied to us, and the amount of hydroxyl group in the VAEOH terpolymers that were prepared by hydrolysis as described above, were determined by following the procedure described in the ASTM D1396-73. Table I gives sample codes and

TABLE I
Chemical Composition of the VAE Copolymers and VAEOH Terpolymers Investigated

Sample code	Ethylene	Composition, mol%	
		Vinyl acetate	Vinyl alcohol
A1 ^a	66	34	0
A2	66	20	14
B1 ^a	53	47	0
B2	53	41	6
B3	53	33	14
B4	53	25	22
B5	53	17	30
C1 ^a	38	62	0
C2	38	51	11

^aVAE Copolymer.

TABLE II
Chemical Composition of the VAE/PVOH Blends Investigated

Sample code	VAE Copolymer ^a (wt%)	PVOH (wt%)
D1	97.5	2.5
D2	95.0	5.0
D3	92.5	7.5
D4	90.0	10.0

^aSample B1.

the compositions of the VAE copolymers that were supplied to us and the VAE OH terpolymers that we have prepared. The terpolymers were later used for preparing specimens of shapes desired for various types of measurements described below. To prepare the specimens, either the VAE copolymers or the VAE OH terpolymers were dissolved in 1/1 ethanol/benzene mixed solvent, cast into the shape desired, and dried in a vacuum oven to a constant weight.

Preparation of the Blends of VAE Copolymer and PVOH

Various compositions of VAE/PVOH blends were prepared by first mixing an organic solution of VAE copolymer (Sample B1) with an aqueous solution of PVOH, forming an emulsion of VAE droplets. The emulsions were then quenched with liquid nitrogen and freeze-dried to a constant weight. For this, about 15 g of VAE copolymer was dissolved in 30 mL of 8/2 toluene/dichloroethane mixture, and a predetermined amount of PVOH, depending on the composition of the blend desired, was dissolved in 30 mL of distilled water. Table II gives sample codes and the compositions of the blends prepared.

Measurement of Thermal Properties

The thermal properties (specifically, the melting point and transition behavior) of VAE copolymers and VAE OH terpolymers were measured using differential scanning calorimetry (DSC), with the aid of a DuPont 1090 Thermal Analyzer equipped with a 910 DSC Module. Indium was used as the standard to determine the heat of fusion. The procedures used for sample preparation are described above. The dried samples had been kept in a desiccator after drying in a vacuum oven, and all the measurements were taken under the nitrogen atmosphere.

To investigate melting behavior, all the samples had the same thermal history, namely, (1) the samples were put in a vacuum oven kept at 90°C and then cooled down to room temperature by turning off the heater of the oven; (2) the samples were put in the DSC pan and heated up from room temperature to 130°C at the rate of 10°C/min. The peak temperature of the endothermic trace was taken as the melt temperature, and the heat of fusion was calculated from the area under the crystallization endotherm. The average of at least two measurements were taken for each sample.

For the investigation of transition behavior, specifically the glass transition temperature T_g , the sample was first heated up from room temperature to 60°C at the rate of 10°C/min, and then quenched down to -70°C with dry

TABLE III
 T_g , T_m , and the Heat of Fusion (ΔH_f) Determined from DSC Measurements for the
 VAE Copolymers and VAEOH Terpolymers

Sample code ^a	T_g (°C)	T_m (°C)	ΔH_f (J/g)
A1	-24.0	—	—
A2	-19.7	99.8	0.196
B1	-8.1	—	—
B2	-6.0	—	—
B3	-4.2	90.7	0.402
B4	1.5	93.6	1.580
B5	14.7	94.0	8.955
C1	16.1	—	—
C2	17.1	88.4	0.183

^aSee Table I for the composition of the VAE copolymers and VAEOH terpolymers.

ice. From this low temperature, the sample was heated up again to 60°C at the rate of 10°C/min. The T_g was taken as the midpoint in the step observed in the DSC trace.

Measurement of Rheological Properties

The Rheometrics Dynamic Mechanical Spectrometer was employed to measure the storage modulus (G'), loss modulus (G''), and loss tangent ($\tan \delta$) of the samples as a function of angular frequency (ω) at a fixed temperature, using the oscillatory shearing mode. Temperature scans were also conducted to follow the variation in G' , G'' , and $\tan \delta$ as a function of temperature at a fixed frequency. The peak value of $\tan \delta$ was taken as the glass transition temperature (T_g). Steps were taken to ensure that the samples had the same thermal history before measurements began. Measurements were conducted with VAE copolymers, VAEOH terpolymers, and VAE/PVOH blends.

RESULTS AND DISCUSSION

Melting and Glass Transition Temperatures

The melting point (T_m) and glass transition temperature (T_g) of VAE copolymers and VAEOH terpolymers, determined by DSC, are listed in Table III. It is seen in Table III that the greater the amount of vinyl acetate in the VAE copolymer and, also, the greater the amount of hydroxyl group in the VAEOH terpolymer, the higher the value of T_g . It has been reported¹⁰ that the T_g of many random vinyl copolymers may be expressed by a linear relationship with respect to the copolymer composition,

$$T_g = T_{g1}\Phi_1 + T_{g2}\Phi_2 \quad (1)$$

where T_{g1} and T_{g2} are the glass transition temperatures of the constituent components 1 and 2, and Φ_1 and Φ_2 are their volume fractions.

TABLE IV
Comparison of the T_g 's of VAE Copolymers Measured
With Those Predicted Using Eq. (1)

Sample code ^a	T_g (°C) measured	T_g (°C) predicted
A1	-24.0	-24.0
B1	-8.1	-7.0
C1	16.1	6.0

^aSee Table I for the composition of the VAE copolymers.

Table IV gives a summary of the comparison made between the measured and predicted values of T_g , in which Eq. (1) was used to predict the T_g 's of the VAE copolymers. It is seen that agreement is very good for the VAE copolymers containing less than 50 mol% vinyl acetate (Samples A1 and B1), but an appreciable difference exists for the VAE copolymers containing more than 50 mol% vinyl acetate (Sample C1). We speculate that the observed difference between the predicted and measured values of T_g for Sample C1 may be attributable to the increase in side chain branchings of vinyl acetate in the VAE copolymer. This speculation is based on the evidence¹¹ that a relatively large amount of chain transfer occurs during the polymerization of vinyl acetate, that the chain transfer to polymer occurs predominantly on the acetate methyl group in preference to the chain backbone, and that the copolymerization process of VAE copolymer, containing a large amount of vinyl acetate, may be considered to be close to the polymerization of vinyl acetate.

It is also seen in Table III that the T_g 's of the VAE OH terpolymers are higher than those of the parent VAE copolymers, and that T_g is increased as the amount of hydroxyl group in the VAE OH terpolymer is increased. Note that Eq. (1) is no longer valid for predicting the T_g of such terpolymers. This is believed due to the existence of strong intermolecular interactions that originate from the presence of hydroxyl groups that form hydrogen bonding.

In our investigation, no melting point was detected for Sample B2, i.e., the VAE OH terpolymer that contains 6 mol% of vinyl alcohol. This indicates that it is an amorphous polymer. It appears that 6 mol% of vinyl alcohol in the VAE OH terpolymer is not high enough to induce crystallinity. However, as the amount of hydroxyl group is increased in the VAE OH terpolymer, melting points were observed for Samples B3, B4, and B5 (see Table III). Earlier, MacKnight and co-workers⁸ reported similar observations.

Rheological Behavior of VAE Copolymers

Figure 1 gives plots of $\tan \delta$ versus temperature for the three VAE copolymers, Samples A1, B1, and C1. It is seen in Figure 1 that the peak value of $\tan \delta$ (hence T_g) increases as the amount of vinyl acetate in the material increases (see Table I for the compositions of the materials). The values of T_g determined from Figure 1 are -18°C for Sample A1, -2°C for Sample B1, and 23°C for Sample C1.

Figure 2 gives plots of G' versus temperature for the three VAE copolymers, Samples A1, B1, and C1. It is seen in Figure 2 that the G' value

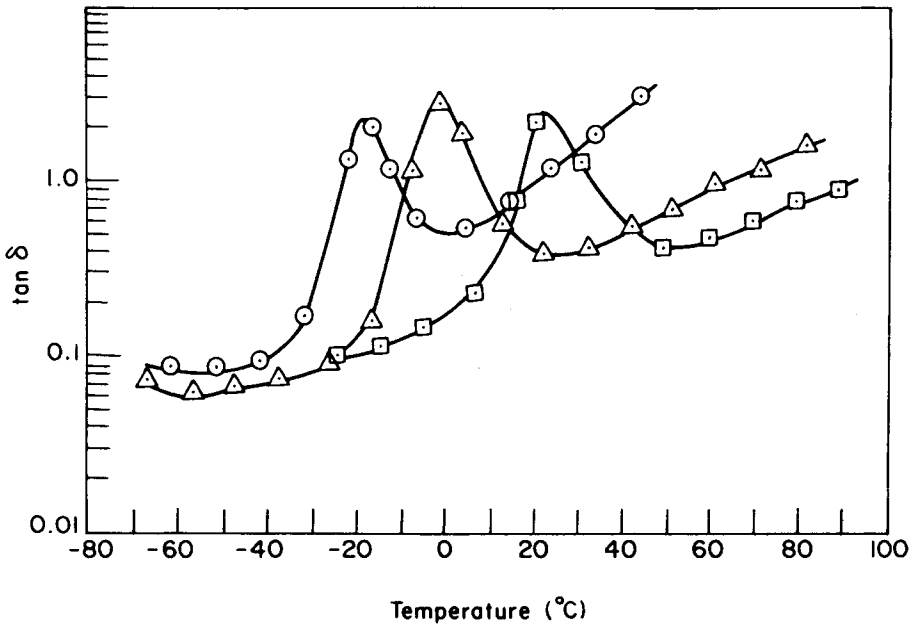


Fig. 1. $\tan \delta$ versus temperature for VAE copolymers. (\odot) Sample A1; (Δ) Sample B1; (\square) Sample C1.

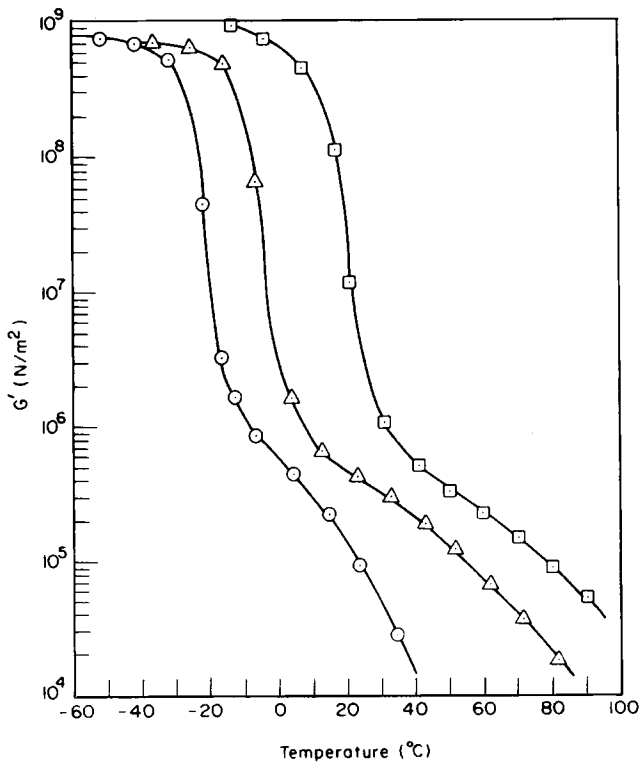


Fig. 2. G' versus temperature for VAE copolymers. Symbols are the same as in Figure 1.

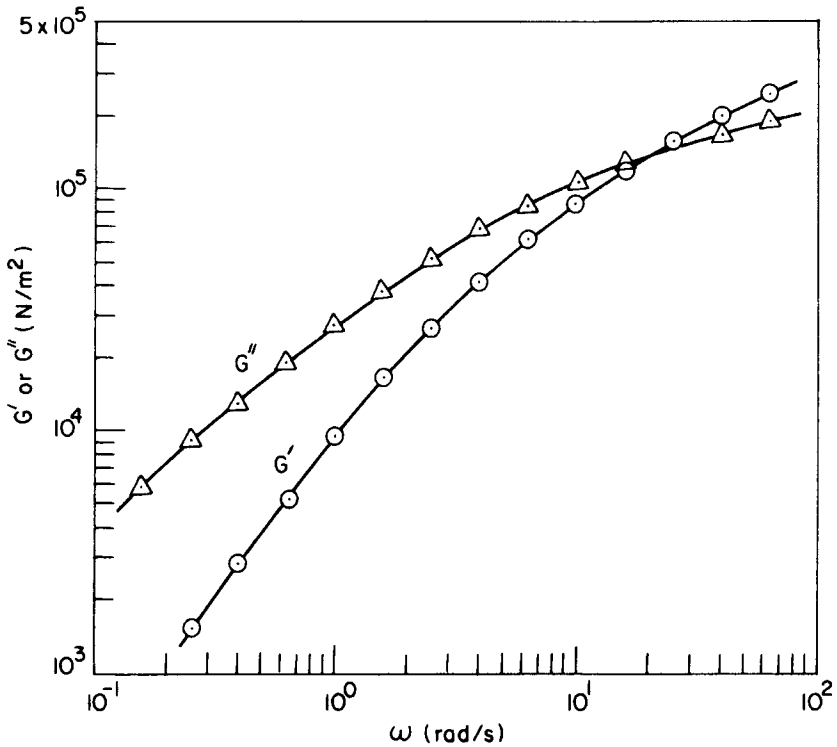


Fig. 3. Logarithmic plots of G' and G'' versus ω for Sample A1 at 25°C.

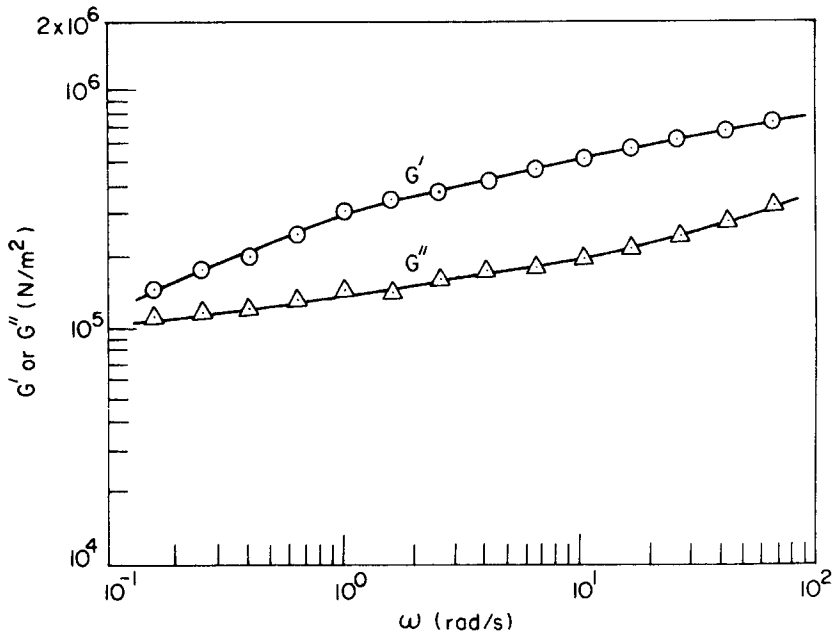


Fig. 4. Logarithmic plots of G' and G'' versus ω for Sample B1 at 25°C.

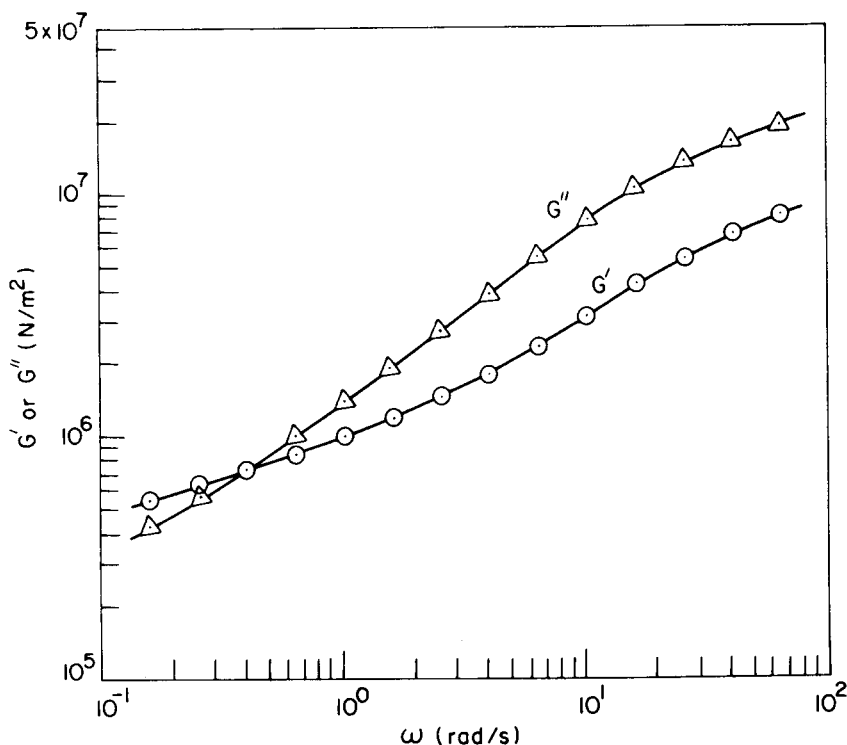


Fig. 5. Logarithmic plots of G' and G'' versus ω for Sample C1 at 25°C.

decreases with increasing temperature. A close examination of Figure 2, together with Figure 1, reveals that, until the material reaches its T_g , the dependency of G' on temperature is very similar among the three materials, but, above its T_g , Sample A1 exhibits a decrease in G' value at a rate much faster than Samples B1 and C1.

Logarithmic plots of G' and G'' versus ω are given in Figure 3 for Sample A1, Figure 4 for Sample B1, and Figure 5 for Sample C1, at 25°C. It should be pointed out that all three samples are amorphous, and that the temperature (25°C) at which the measurements were taken is above their T_g 's (see Table III as well Figure 1). The following observations are worth making: (1) for Sample A1 (see Fig. 3), G'' values are greater than G' values until the frequency reaches approximately 20 rad/sec, at which a crossover of G' and G'' occurs; (2) for Sample B1 (see Fig. 4), both G' and G'' increase with frequency at a relatively slow rate, compared to Sample A1, and no crossover of G' and G'' is observed over the entire range of frequencies tested; (3) for Sample C1 (Fig. 5), G' values are greater than G'' values until the frequency reaches approximately 0.4 rad/sec at which a crossover occurs, and then G'' values become greater than G' values. This behavior is quite opposite to that observed for Sample A1 (compare Fig. 5 with Fig. 3).

Figure 6 gives logarithmic plots of G' versus G'' for the three VAE copolymers investigated, at 25°C. It is seen that all three VAE copolymers (Sample A1, Sample B1, and Sample C1) follow a single correlation. In view of the fact that logarithmic plots of G' versus G'' are very sensitive to the

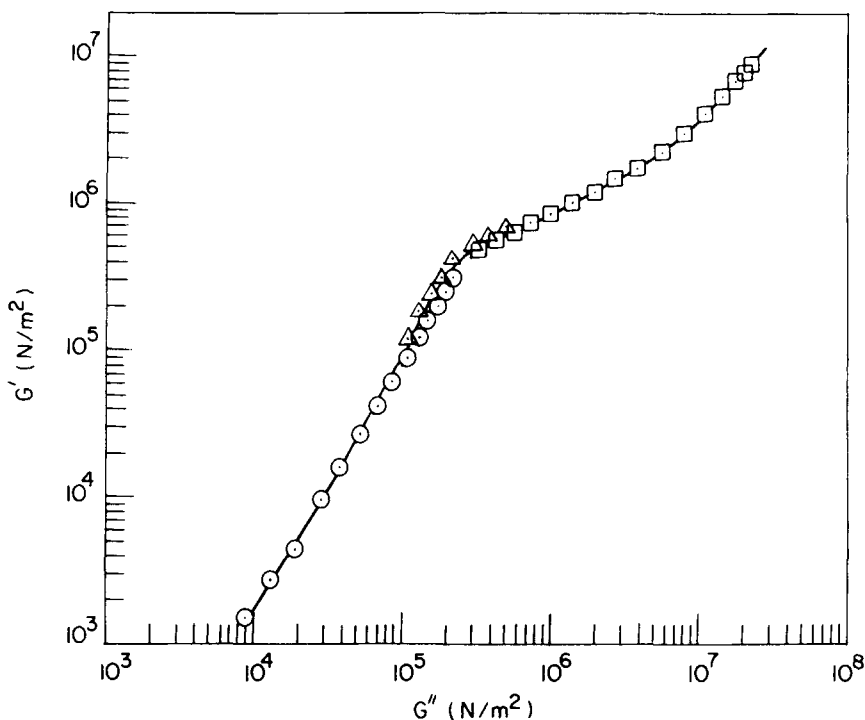


Fig. 6. Logarithmic plots of G' versus G'' for VAE copolymers at 25°C. Symbols are the same as in Figure 1.

chemical structure as well as to a difference in the morphological state among materials^{12,13} and that the three materials are very similar in their chemical structure and morphology, the correlation exhibited in Figure 6 is not surprising.

Figure 7 gives logarithmic plots of complex viscosity (η^*) versus ω for the three VAE copolymers at 25°C. It is seen that Sample A1 shows Newtonian behavior at low frequencies and then shear-thinning behavior at high frequencies, behavior typical of polymeric liquids. Sample B1 shows strong shear-thinning behavior over the entire range of frequencies tested, and Sample C1 also shows shear-thinning behavior over the entire range of frequencies tested, but with a trend toward flattening out in the range of frequencies, 1-10 rad/sec. It is of interest to observe in Figure 7 that the frequency dependency of η^* varies with the amount of vinyl acetate in the VAE copolymers.

Rheological Behavior of VAE OH Terpolymers

Figure 8 gives plots of $\tan \delta$ versus temperature, and Figure 9 plots of G' versus temperature, for the VAE OH terpolymers, Samples B2, B3, B4, and B5. It is seen in Figure 8 that the peak value of $\tan \delta$ (thus T_g) is increased with an increase in the amount of hydroxyl group in the VAE OH terpolymer (see, also, Table III). The values of T_g determined from Figure 8 are -5°C for Sample B2, 1°C for Sample B3, 11°C for Sample B4, and 19°C for Sample B5.

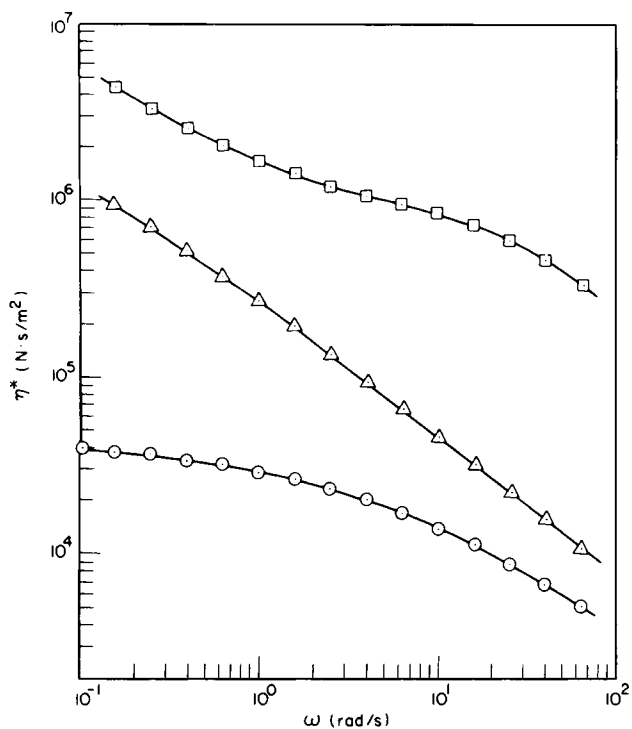


Fig. 7. Logarithmic plots of η^* versus ω for VAE copolymers at 25°C. Symbols are the same as in Figure 1.

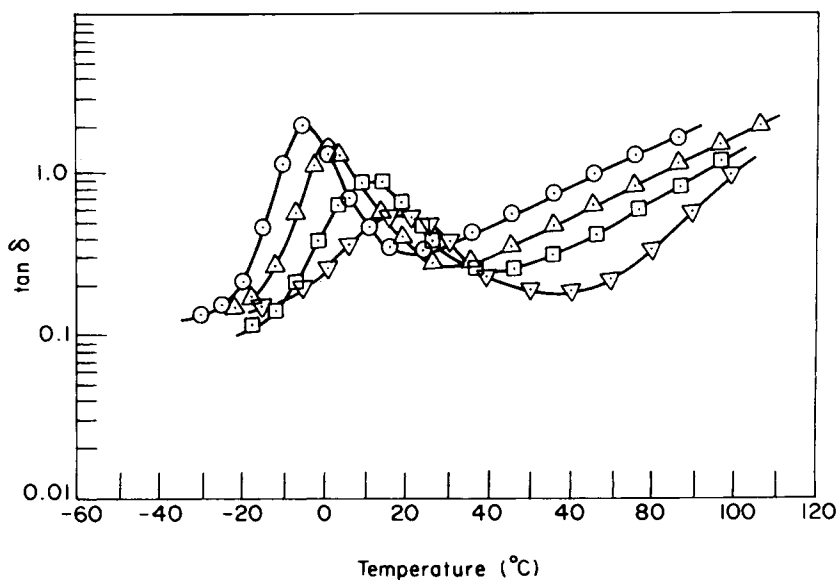


Fig. 8. $\tan \delta$ versus temperature for VAEOH terpolymers: (○) Sample B2; (△) Sample B3; (□) Sample B4; (▽) Sample B5.

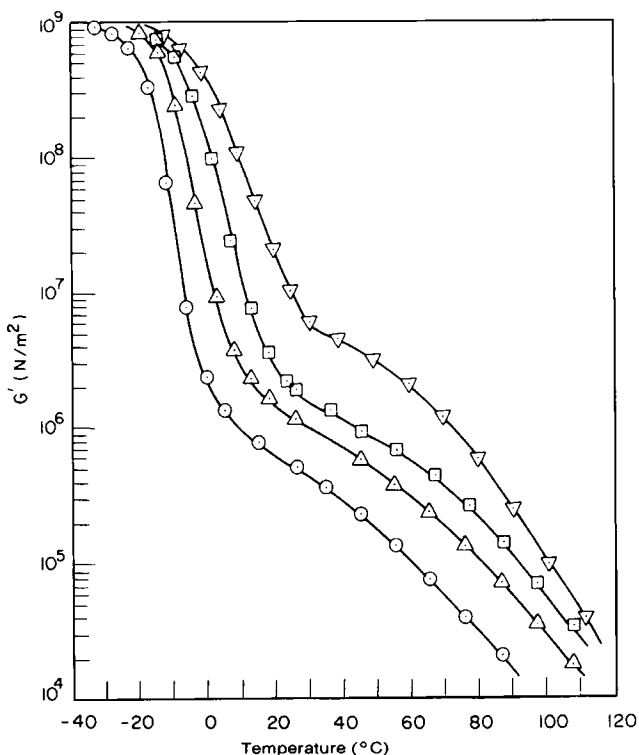


Fig. 9. G' versus temperature for VAEOH terpolymers. Symbols are the same as in Figure 8.

Note in Figure 9 that the temperature dependency of G' is very similar among the four samples investigated.

Figure 10 gives logarithmic plots of G' versus ω , and Figure 11 logarithmic plots of η^* versus ω , at 25°C. It is observed in Figure 10 that the frequency dependency of G' for Sample B5 (containing the largest amount of hydroxyl group among the four samples) is stronger than that for the other samples. It should be remembered that, among the four VAEOH terpolymers (Samples B2, B3, B4, and B5) investigated, Sample B2 is an amorphous polymer and the other three are partially crystalline polymers, and that the temperature (25°C) at which the rheological measurements were conducted is much lower than the melting point (T_m) of the crystalline phase in Samples B3, B4, and B5 (see Table III for the T_m values).

Figure 12 gives logarithmic plots of G' versus G'' for the four VAEOH terpolymers at 25°C. It is of interest to observe in Figure 12 that, at a given value of G'' , G' values increase with increasing amount of vinyl acetate. In view of the fact that logarithmic plots G' versus G'' are very sensitive to differences in the structure of polymers, as well as in their morphological states,^{12,13} it is not surprising to observe differences in the $\log G'$ versus $\log G''$ plots among the four materials investigated, because Sample B2 is an amorphous polymer and the other three materials (Samples B3, B4, and B5) have different degrees of crystallinity at 25°C, at which the rheological measurements were conducted (see Table III for the T_m values).

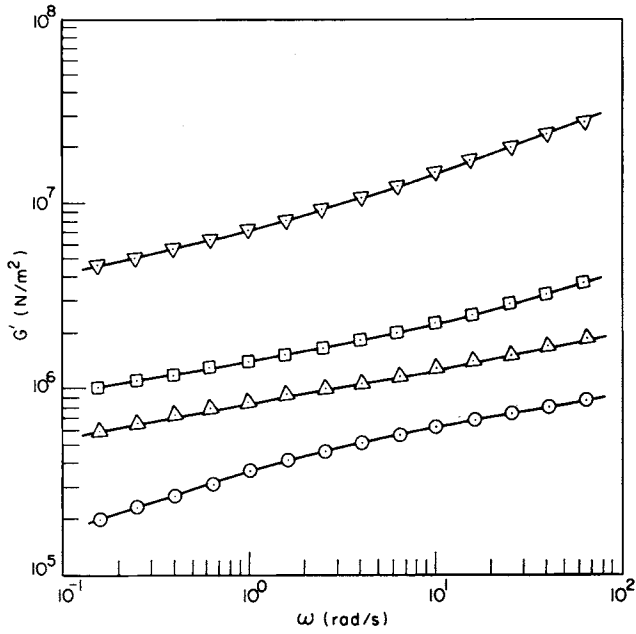


Fig. 10. Logarithmic plots of G' versus ω for VAE OH terpolymers at 25°C. Symbols are the same as in Figure 8.

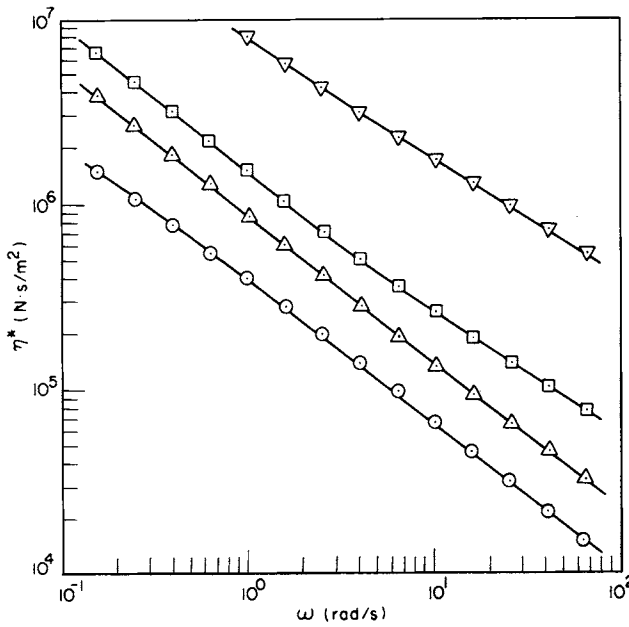


Fig. 11. Logarithmic plots of η^* versus ω for VAE OH terpolymers at 25°C. Symbols are the same as in Figure 8.

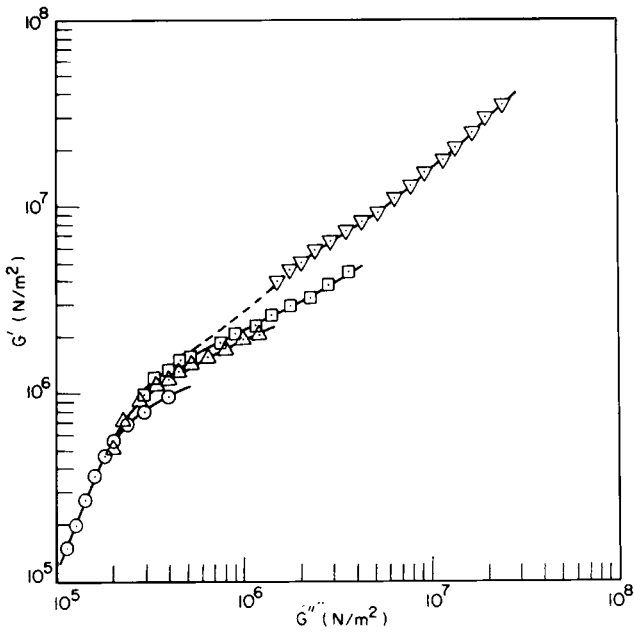


Fig. 12. Logarithmic plots of G' versus G'' for VAEOH terpolymers at 25°C. (○) Sample B2; (Δ) Sample B3; (□) Sample B4; (▽) Sample B5.

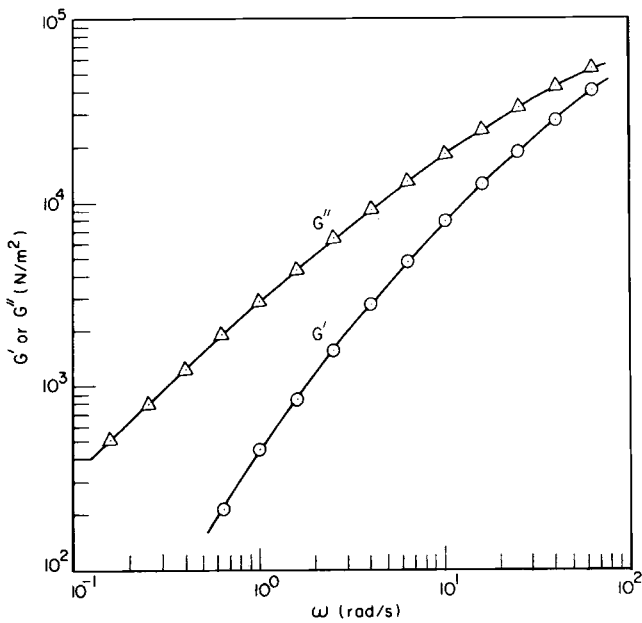


Fig. 13. Logarithmic plots of G' and G'' versus ω for Sample B2 at 100°C.

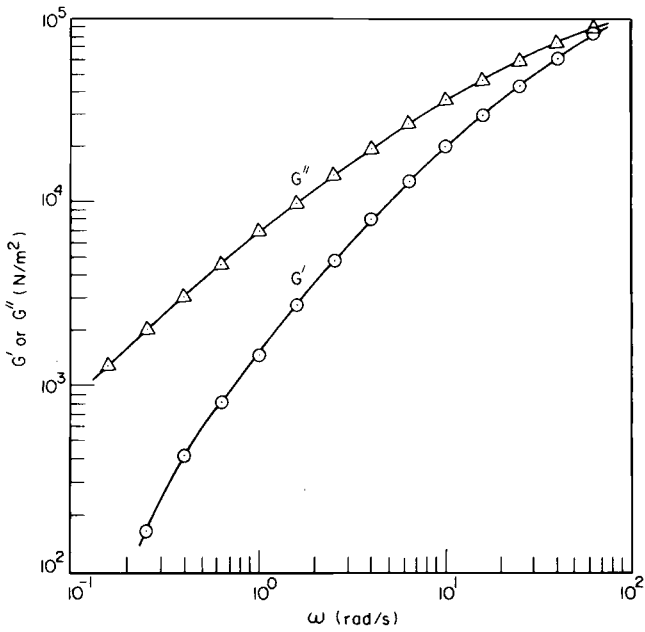


Fig. 14. Logarithmic plots of G' and G'' versus ω for Sample B3 at 100°C.

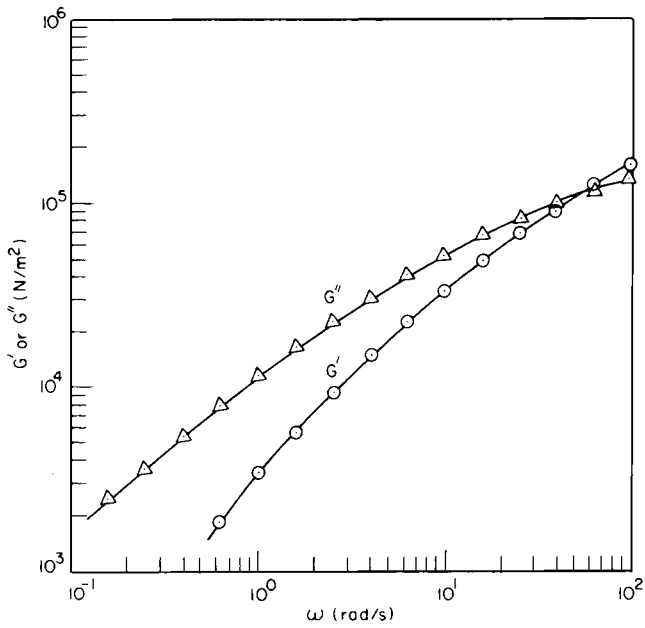


Fig. 15. Logarithmic plots of G' and G'' versus ω for Sample B4 at 100°C.

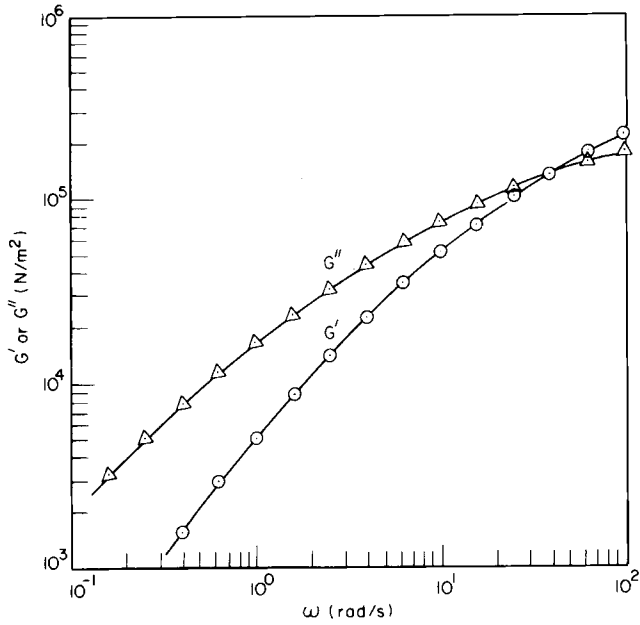


Fig. 16. Logarithmic plots of G' and G'' versus ω for Sample B5 at 100°C .

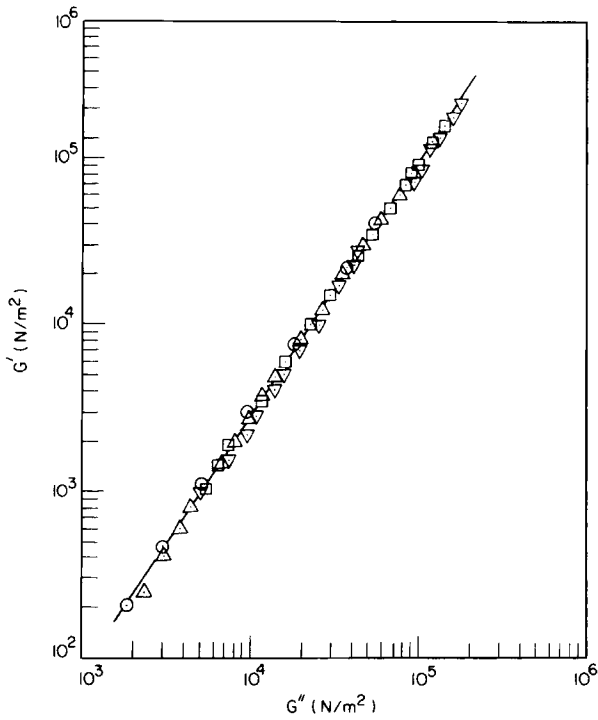


Fig. 17. Logarithmic plots of G' versus G'' for VAEHOH terpolymers at 100°C : (\odot) Sample B2; (Δ) Sample B3; (\square) Sample B4; (∇) Sample B5.

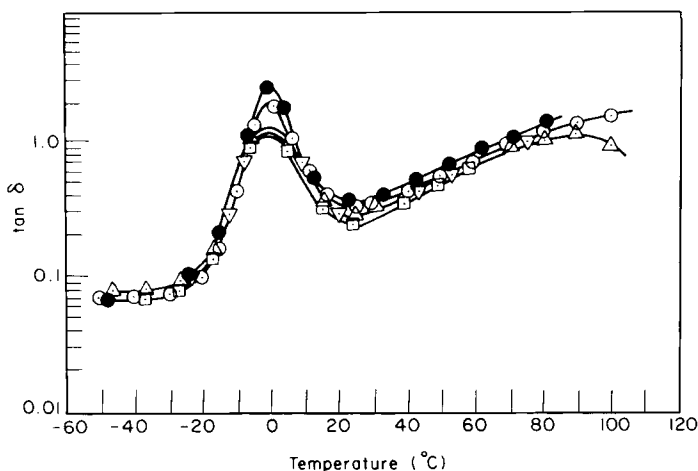


Fig. 18. $\tan \delta$ versus temperature for VAE/PVOH blends: (\odot) Sample D1; (Δ) Sample D2; (\square) Sample D3; (∇) Sample D4; (\bullet) Sample B1.

In order to observe if logarithmic plots of G' versus G'' would yield a single correlation when the crystallinity of Samples B3, B4, and B5 was destroyed by heating the materials, measurements of G' and G'' were made at 100°C which is higher than the melting points of the three VAE/OH terpolymers. Figure 13 gives logarithmic plots of G' and G'' versus ω for Sample B2 at 100°C. Similar plots are given in Figure 14 for Sample B3, in Figure 15 for Sample B4, and in Figure 16 for Sample B5. It is of interest to note in these figures that, over the range of frequencies investigated, values of G' are greater than values of G'' for Samples B2 and B3, but there is a crossover between G' and G'' for Samples B4 and B5. The frequency at which the crossover occurs is lower for Sample B5 than for Sample B4. Note that Sample B5 has a greater amount of hydroxyl group than Sample B4.

Figure 17 gives logarithmic plots of G' versus G'' for the four VAE/OH terpolymers, Samples B2, B3, B4, and B5. These plots were prepared by using the information in Figures 13 to 16. It is remarkable to observe in Figure 17 that the four materials indeed give rise to a single correlation, similar to that displayed in Figure 6. This observation reinforces our view that logarithmic plots of G' versus G'' are very useful for investigating rheological compatibility of polymer blends or heterogeneous polymer systems.¹⁴

Rheological Behavior of VAE / PVOH Blends

Figure 18 gives plots of $\tan \delta$ versus temperature for the VAE/PVOH blends, Samples D1, D2, D3, and D4. For comparison purposes, the plot for the VAE copolymer, Sample B1, is also given in Figure 18. It is seen that addition of PVOH to the VAE copolymer has hardly changed its T_g . Note that the T_g of PVOH is 85°C and the T_m of PVOH is 258°C.¹⁵ It is seen in Figure 18 that the blends containing PVOH equal to or greater than 5.0 wt% (Samples D2, D3, and D4) show peak values of $\tan \delta$ at a temperature around 90°C, which is close to the T_g of PVOH. Perhaps due to the small amount of

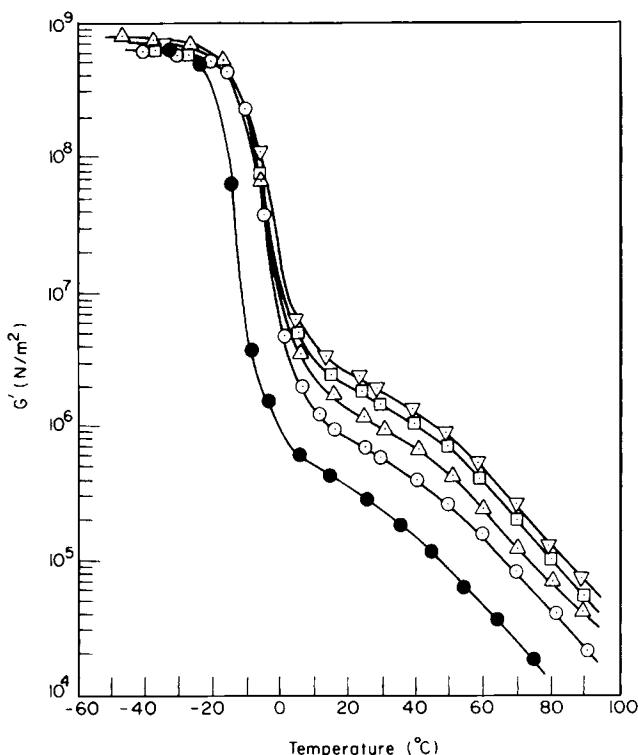


Fig. 19. G' versus temperature for VAE/PVOH blends. Symbols are the same as in Figure 18.

PVOH (2.5 wt%) present in Sample D1, no peak value of $\tan \delta$ is observed at around 90°C.

Figure 19 gives plots of G' versus temperature for the VAE/PVOH blends. It is of interest to observe in Figure 19 that, at temperatures below about 0°C, the G' values, while decreasing with increasing temperature, are almost the same for different blend compositions, whereas at temperatures above 0°C, the G' values increase as the amount of PVOH in the blend increases. This was not the case for the VAEOH terpolymers (see Fig. 9), in that the G' values increased with the amount of hydroxyl group in the VAEOH terpolymer over the entire range of temperatures scanned.

Figure 20 gives logarithmic plots of G' versus ω , and Figure 21 logarithmic plots of η^* versus ω , for the VAE/PVOH blends at 25°C. It is seen in Figures 20 and 21 that both G' and η^* increase as the amount of PVOH in the blend increases. The reasons for the observed increase in both G' and η^* for the VAE/PVOH blends differ from those for the VAEOH terpolymers (see Figs. 10 and 11).

It should be remembered that the introduction of sufficient hydroxyl groups into the VAE copolymer has transformed an amorphous polymer into a semicrystalline polymer and that the temperature 25°C, at which the measurements were taken, is above the T_g , but below the T_m , of the VAEOH terpolymers (Samples B3, B4, and B5) investigated (see Table III). It can be concluded, therefore, that the presence of the crystalline phase in the VAEOH

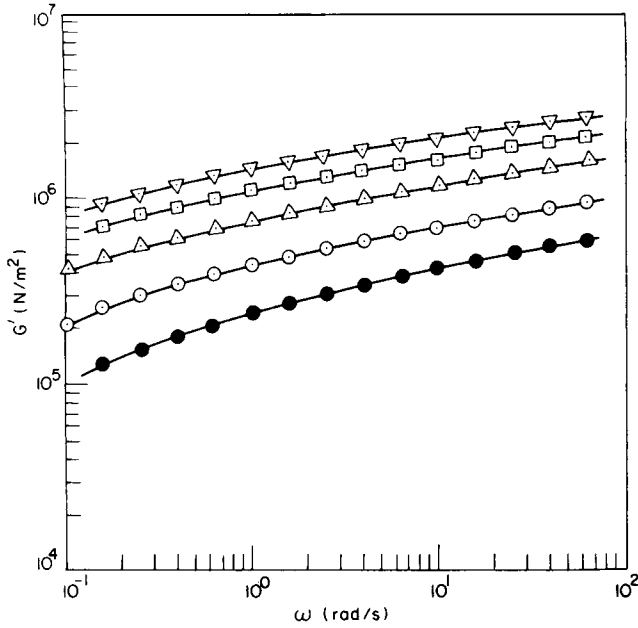


Fig. 20. Logarithmic plots of G' versus ω for VAE/PVOH blends at 25°C. Symbols are the same as in Figure 18.

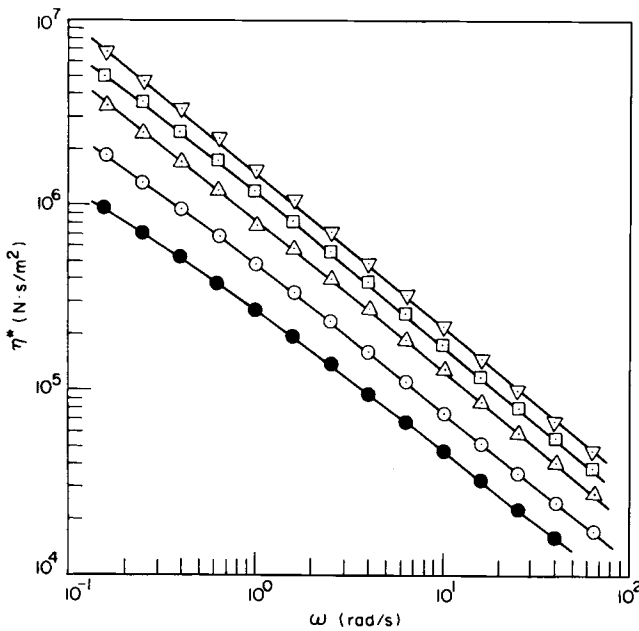


Fig. 21. Logarithmic plots of η^* versus ω for VAE/PVOH blends at 25°C. Symbols are the same as in Figure 18.

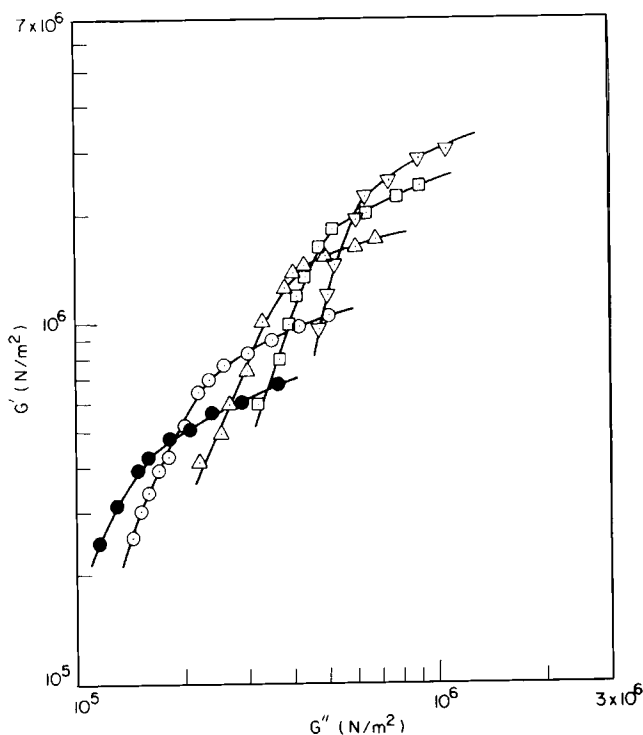


Fig. 22. Logarithmic plots of G' versus G'' for VAE/PVOH blends at 25°C: (○) Sample D1; (△) Sample D2; (□) Sample D3; (▽) Sample D4; (●) Sample B1.

terpolymer has contributed to the observed increase in G' and η^* . Note that the size of the crystalline phase is very small.

On the other hand, the observed increase of G' and η^* , as the amount of PVOH in the VAE/PVOH blends increases, may have the following physical causes. Note that the VAE/PVOH blends at 25°C form two phases, of which the PVOH is the discrete phase suspended in the continuous phase (i.e., amorphous VAE copolymer). The T_g of PVOH is 85°C, which is considerably higher than the temperature at which the rheological measurements were taken, and the T_g of the VAE copolymer (Sample B1) is about -2°C (see Fig. 18), which is considerably lower than the measurement temperature. Hence the VAE/PVOH blend may be considered as a two-phase system, in which the dispersed particles of PVOH are suspended in the very viscous rubberlike materials that form the continuous phase. The size of the suspended particles is expected to be of the order of a micron. Therefore, the increase of G' and η^* as the amount of PVOH in the VAE/PVOH blends increases, observed in Figures 20 and 21, is due to the increase in the number of PVOH particles suspended in the mixture as the amount of PVOH in the blend is increased. This conclusion is consistent with the results shown in Figure 18 that addition of PVOH to the VAE copolymer (Sample B1) has not affected the T_g of the VAE copolymer itself. This is a clear indication that the VAE/PVOH blends form two phases.

Figure 22 gives logarithmic plots of G' versus G'' for the VAE/PVOH blends at 25°C. It is seen that each blend shows a separate curve, very similar

to that for the partially crystalline VAE OH terpolymers at 25°C which is below their melting points (see Fig. 12), but quite different from those correlations observed for the amorphous VAE copolymers (see Fig. 6) and the partially crystalline VAE OH terpolymers at 100°C which is above their melting points (see Fig. 17). This is another clear indication that the VAE/PVOH blends form two phases. Each blend has a different amount of discrete phase and may also have different domain sizes, contributing to different rheological responses. It should be noted that Han and co-workers¹²⁻¹⁴ have previously investigated the rheological behavior of both compatible (homogeneous) and incompatible (heterogeneous) polymer blends using logarithmic plots of G' versus G'' .

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