

Rheological Properties of Partially Hydrolyzed Ethylene-Vinyl Acetate Copolymers

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Synopsis

Studies have been made of steady-shear and dynamic viscosities for melts of two ethylene-vinyl acetate copolymers and their partially hydrolyzed derivatives using a Weissenberg rheogoniometer over the temperature range of 123–150°C with some tests at 160°C. The flow activation energy of all samples studied was essentially independent of shear stress. The introduction of hydroxyl groups in controlled concentrations, however, produced a complicated flow behavior. At low concentrations, there is a marked increase in Newtonian viscosity, flow activation energy, and shear dependence of viscosity. In contrast to previous reports, a further increase in all three functions was not observed with increasing vinyl alcohol concentration. Dynamic viscosities, in contrast, show monotonic increases with increasing hydroxyl group content, as do activation energies derived from the temperature dependence of the dynamic viscosity. These data may result from an increased chain cohesion due to hydrogen bonding of hydroxyl groups.

INTRODUCTION

It is of interest to study how the flow of high polymer melts is influenced by secondary forces, such as hydrogen bonding. Many workers¹⁻⁶ concerned with this subject have obtained results indicating that both viscosity and flow activation energy increase with increasing content of polar groups. Blyler and Haas³ suggest that intermolecular hydrogen bonds act as temporary (quasi) crosslinks during the short time scales of deformation and that the effect of increasing the number of hydrogen bonds is similar to increasing molecular weight. Similarly, Otocka and Blyler⁶ explained viscosity increases in polymers containing salt groups as due to an increase of apparent weight-average molecular weight caused by dipole bonding of ion pairs. Longworth and Morawetz⁴ derived, from rate process theory, a simple theoretical equation that expressed the relationship between reduced viscosity and the fraction of hydrogen bonds, which, however, they subsequently concluded was inadequate for representation of the data.

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TABLE I
Chemical Composition of Partially Hydrolyzed Ethylene-Vinyl Acetate Copolymers^a

Sample no.	Polymer composition, mole-%		
	Ethylene	Vinyl acetate	Vinyl alcohol
A1	75.4	24.6	0
A2	75.4	20.6	4.0
A3	75.4	13.5	11.1
A4	75.4	8.92	15.7
A5	75.4	5.03	19.6
A6	75.4	0.45	24.2
B1	59.1	40.9	0
B2	59.1	35.2	5.7
B3	59.1	20.9	20.0
B4 ^b	59.1	11.1	29.8
B5 ^b	59.1	4.67	36.2
B6 ^b	59.1	0.57	40.3

^a From references 11 and 12.

^b Viscosities are not reported since they increased continuously with time due to degradation.

TABLE II
Characterization of Partially Hydrolyzed Ethylene-Vinyl Acetate Copolymers^a
(from Reference 11)

	Copolymer A	Copolymer B
Molecular Weight (\bar{M}_n)	12,000 → 8,800	14,000 → 7,900
Change with Hydrolysis		
Molecular Weight Distribution	5.6 → 2.8	3.4 → 1.8
\bar{M}_w/\bar{M}_n Change with Hydrolysis ^b		
Monomer Distribution ^c	random	random
Branching at Ethylene Units ^c	none	none
Branching at Acetate Units ^c	none	<1.5 CH ₃ /1000 C
Branching at Chain Length ^c	0	>C12

^a From reference 11.

^b Determined by Monsanto Analytical Laboratory, Springfield, Massachusetts.

^c Determined by Dr. M. Wisotsky of Exxon, Linden, New Jersey.

Up to now, all studies¹⁻⁶ seem to conclude that both viscosity and flow activation energy increase with the introduction of polar groups. The influence of such secondary forces has been widely considered in terms of polymer viscoelasticity.⁷⁻¹² To further examine these concepts, the melt rheology of two random ethylene-vinyl acetate copolymers and their hydrolyzed derivatives has been investigated. Previously, thermal and mechanical properties of these polymers have been studied by differential scanning calorimetry (DSC) and by dynamic mechanical testing.^{11,12} It was found that the glass transition temperatures (T_g 's) increase with increasing hydroxyl group content in both series and that the highly hydrolyzed polymers are semicrystalline in nature. In this paper, we present both steady-shear and dynamic viscosity measurements as well as dynamic moduli for these two polymer series.

EXPERIMENTAL

Characterization data for series A, which is based on a 25 mole-% vinyl acetate copolymer, and series B, based on a 41 mole-% vinyl acetate copolymer, have been previously acquired and are assembled in Tables I and II.^{11,12} The details of the hydrolysis procedure are given in reference 10. Because of potential water sensitivity,¹¹ the samples were stored in a desiccator. Steady-shear viscosity measurements were made at 130°, 140°, and 150°C (some at 160°C) with a Weissenberg rheogoniometer (Model 17) under nitrogen gas. The temperature range is limited by the presence of crystallinity at lower temperatures and the occurrence of decomposition at higher temperatures. The highest melting point for these polymers is about 120°C.¹² Each sample was prepared in advance for cone-and-plate measurements by compression molding at 130°C and by drying in a vacuum oven to avoid effects of water on viscosity.

Oscillatory (dynamic) shear measurements were also carried out in the Weissenberg rheogoniometer. Each of the samples was tested at 123° and 142°C at seven frequencies: 9.48, 3.00, 0.948, 0.300, 0.0948, 0.0300, and 0.00948 Hz. The strain amplitude was limited to 0.02 radians to ensure linear viscoelastic behavior. The amplitude ratio of the stress to strain and the phase angle between them were measured by means of a Tronotec Phasemeter Model 702A. To exclude effects due to reaction of hydroxyl groups, measurements were limited to a maximum of 1 hr on each sample. Since the lower frequency reading required more time than the higher, the consequences of such possible reactions should be more apparent in the former.

RESULTS AND DISCUSSION

Table II shows that the number-average molecular weight (\bar{M}_n) and the molecular weight distribution both decrease on hydrolysis of the acetate groups in the two starting copolymers. An apparent decrease in \bar{M}_n on hydrolysis can simply result from the reduction in molecular weight caused by the replacement of acetate by hydroxyl groups. It is equally apparent, however, that the molecular weight distribution should remain unaltered as a result of this process. Therefore, it must be concluded that either the hydrolysis was not random or that some backbone degradation did accompany hydrolysis. The calculated decrease in \bar{M}_n was based on the \bar{M}_n of the starting copolymer and the chemical composition of the hydrolyzed derivatives. A random hydrolysis without degradation was assumed. It was also considered that all species, of whatever size, change molecular weight in the same proportion on hydrolysis. When this is done, a value of \bar{M}_n of 9035 is obtained from sample A6, in contrast to the observed value of 8800. Similarly, a value of 9351 is obtained for sample B6, in contrast to the observed value of 7900. The difference may be due to degradation which might result from the removal of any long-chain acetate branching by hydrolysis. However, on the basis of NMR results collected in Table II, no such branching could be detected. Nevertheless, such a process is in accord with the observed narrowing in molecular weight distribution, which is most pronounced at high de-

TABLE III
Steady-State Low Shear Newtonian Viscosities

Sample no.	Viscosity, poises			
	130°C ^a	140°C	150°C	160°C
A1	3.9×10^3	3.1×10^3	2.0×10^3	
A2	6.2×10^3	4.6×10^3	2.6×10^3	
A3	5.4×10^4	3.5×10^4	1.6×10^4	1.2×10^4
A4	2.8×10^4	1.9×10^4	1.2×10^4	8.9×10^3
A5	2.4×10^4	2.0×10^4	1.7×10^4	
A6	2.0×10^4	1.3×10^4	7.9×10^3	
B1	1.0×10^4	8.2×10^3	6.5×10^3	4.4×10^3
B2	2.4×10^4	1.4×10^4	8.3×10^3	
B3	6.2×10^4	4.4×10^4	3.1×10^4	

^a Test temperature.

degrees of hydrolysis, and the relatively good agreement between the calculated and observed \bar{M}_n 's. It might be possible that interactions of the hydrolyzed polymer in the gel permeation elutions may also produce this effect.

Table III is a collection of measured Newtonian viscosities at several temperatures. Assuming the generally accepted relationship between Newtonian viscosity η_0 and \bar{M}_w ,

$$\eta_0 = K\bar{M}_w^{3.4} \quad (1)$$

where K is a constant for a homologous series, it is predicted from values for the starting polymer that sample A6 should have an η_0 of 129 poises, instead of the observed value of 2.0×10^4 poises. Thus, the decrease in \bar{M}_w , which is most dramatic in the more highly hydrolyzed members, is more than compensated for by an increased interaction resulting from intermolecular hydrogen bonds between hydroxyl groups. The maximum in η_0 observed in the A series polymers may possibly be understood on the basis of two competing effects: an increase in η_0 caused by intermolecular hydrogen bonding, and the decrease in η_0 caused by the decrease in \bar{M}_w associated with the narrowing of the molecular weight distribution. In the absence of definitive data for the intermediate ranges of hydrolysis, it is not possible to independently evaluate the two effects. It can only be said that the effect of association is compensated for by the decreased \bar{M}_w at high degrees of hydrolysis, whereas the effect of association is more important than the \bar{M}_w decrease at low degrees of hydrolysis. The B series polymers are not a test of this effect, since it was impossible to obtain reliable data for the more highly hydrolyzed members of this series.

From dynamic results, collected in Figures 1 and 2 at 123°C, it is apparent that complex dynamic viscosity η^* increases with increasing hydroxyl content for the A and B series and does not exhibit the maximum observed in η_0 . Thus, the association introduced by hydrogen bonding is the dominant factor determining the complex dynamic viscosity. In some cases, at lower frequencies and higher temperatures, anomalously high values of η^* were obtained for the higher members of both series. It is probable that this reflected a chemical change in the samples, possibly a crosslinking at the hydroxyl groups by etherification.

Table IV compares the values of η_0 and η^* for the first two members of each series. The agreement is excellent. Large deviations occur, however, for the higher members of each series, once again likely reflecting the influence of hydrogen bonding on the flow properties.

Table V gives flow activation energies E_{τ}^* calculated at constant stress, obtained from plots of $\log \eta_0$ versus $1/T^{\circ}\text{K}$. The E_{τ}^* values for A1 and B1 may be predicted from the corresponding values for polyethylene and poly(vinyl acetate), assuming simple additivity:

$$E_{\tau}^* = X_{\text{PE}}E_{\tau\text{PE}}^* + X_{\text{PVA}}E_{\tau\text{PVA}}^* \quad (2)$$

where E_{τ}^* is the flow activation energy for the copolymer, X_{PE} is the mole fraction of polyethylene, $E_{\tau\text{PE}}^*$ is the activation energy for polyethylene, X_{PVA} is the mole fraction of poly(vinyl acetate), and $E_{\tau\text{PVA}}^*$ is its activation energy.

Using the values of $E_{\tau\text{PE}}^* = 6-7$ kcal/mole for linear polyethylene and $E_{\tau\text{PVA}}^* = 12$ kcal/mole for PVA, and the values of X_{PE} and X_{PVA} of Table I, a value of E_{τ}^* of 8 ± 1 is calculated for A1 and 9 ± 1 for B1, compared to the experimental results of 12 ± 1 and 11 ± 1 , respectively. The change in E_{τ}^*

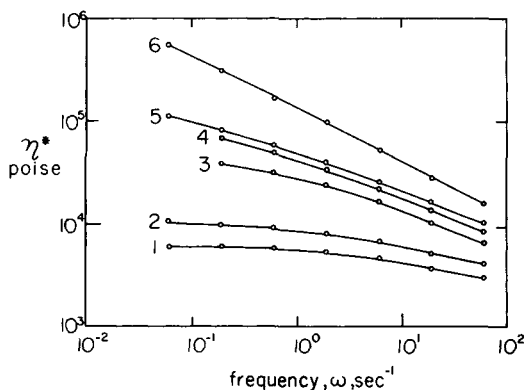


Fig. 1. Weissenberg rheogoniometer data for copolymer A and hydrolyzates at 123°C.

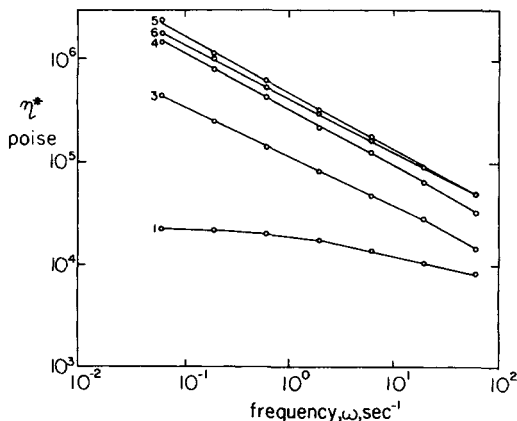


Fig. 2. Weissenberg rheogoniometer data for copolymer B and hydrolyzates at 123°C.

TABLE IV
Comparison of Steady-Shear and Complex Dynamic Viscosities of Ethylene-Vinyl Alcohol-Vinyl Acetate Terpolymers

Sample no.	η_o^* at 142°C, $\omega \rightarrow 0$, poises	η_a at 140°C, $\tau \rightarrow 0$, poises
A1	3.0×10^3	3.1×10^3
A2	4.8×10^3	4.6×10^3
B1	9.3×10^3	8.2×10^3
B2	1.5×10^4	1.4×10^4

with hydrolysis is depicted in Figure 3 for both series. The data may be uncertain, the behavior is complex and affords no simple interpretation. Significantly, however Table V reveals that E_τ^* is essentially independent of the shear stress τ over the range studied. This is in contrast to the behavior observed in the cases where a significant amount of long-chain branching is present¹⁴ and provides additional evidence for the essentially linear nature of the copolymers. This result also suggests that viscosity data at different temperatures will superimpose to form master curves of fractional viscosity changes as a function of $\tau/T^\circ\text{K}$. This superposition is carried out for samples A5 and B3 in Figure 4, resulting a smooth master curves.

E_ω^* values were obtained from plots of η^* versus $1/T^\circ\text{K}$ at constant values of the dynamic shear stress ($\eta^*\omega$) as shown in Table VI. The observed behavior is in considerable contrast to that derived from steady shear measurements. In the A series, at high values of ($\eta^*\omega$), there is a monotonic increase in E_ω^* with increasing hydroxyl group content. This result is accord with those previously reported for other hydrogen-bonded systems as mentioned in the introduction.¹⁻⁶ In the case of samples B4-B6, E_ω^* appears to decrease with decreasing ($\eta^*\omega$). This may be considered to result from irreversible chemical crosslinking in these samples. It is to be emphasized that the E_ω^* for samples A1 and B1 correspond reasonably to the E_τ^* for these copolymers. However, as the hydroxyl content increases in each series, little or no correspondence exists between E_ω^* and E_τ^* . At this time, the reason for this behavior remains obscure.

Figures 5 and 6 present the angular frequency dependencies of the real part of the complex dynamic modulus G' and viscosity, η' for series A and B at 123°C. Qualitatively, all these plots are very similar. The increase of G' with increasing ω becomes much smaller with increasing hydroxyl group content, as is true for the decrease of η' with increasing ω . This behavior is consistent with the idea that the hydrogen bonding introduced by the hydroxyl groups leads to a more elastic material. The dynamic data for B1 also exhibit good superposability and master curves of η' and G' . For example, data at 146°C superimpose well on the corresponding data at 123°C, as given in Figure 6.

CONCLUSIONS

Steady-state shear viscosity measurements for the copolymers studied yield results which are not interpretable as simple dependencies on the con-

TABLE V
 Flow Activation Energy E_{τ}^*

Sample no.	Shear stress $\times 10^{-3}$, dynes/cm ²	E_{τ}^* , kcal/mole
A1	Newtonian	12 + 1
	2.0	12
	15	12
	30	12
	50	12
A2	Newtonian	16
	2.0	16
	10	16
	30	16
	50	16
A3	Newtonian	23
	10	23
	30	23
	100	23
	200	23
A4	Newtonian	17
	6.0	17
	20	16
	50	15
	100	15
A5	400	15
	Newtonian	7.4
	10	7.4
	70	7.3
	150	7.8
A6	500	9.1
	Newtonian	17
	10	17
	30	17
	100	18
B1	300	18
	Newtonian	11
	1.0	11
	10	11
	30	12
B2	70	14
	Newtonian	19
	10	19
	40	19
	100	19
B3	300	19
	Newtonian	12
	10	12
	40	12
	100	12
	300	13
	600	14

centration of hydrogen bonding of hydroxyl groups. Changes in molecular weight and distribution occur simultaneously with hydrolysis. These overlapping effects may be partially responsible for the observed anomalous behavior.

TABLE VI
Flow Activation Energy for Complex Viscosity of Ethylene-Vinyl Acetate-Vinyl Alcohol Terpolymers Between 123° and 142°C

Sample no.	Vinyl alcohol, mole-%	$(\eta^*\omega)$, dynes/cm ²						
		1×10^3	5×10^3	1×10^4	5×10^4	1×10^5	2.5×10^5	5×10^5
A1	0	12.4	12.1	12.8	12.5	12.1		
A2	4.0	13.1	13.3	13.5	14.3	13.9		
A3	11.1			14.2	16.6	15.9	13.3	
A4	15.7			13.3	12.7	13.0	13.7	
A5	19.6				14.5	15.7	16.6	
A6	24.2				31.1	31.7	31.8	
B1	0	14.9	14.8	14.9	14.7	14.3		
B2	5.7							
B3	20.0					14.9	18.4	20.9

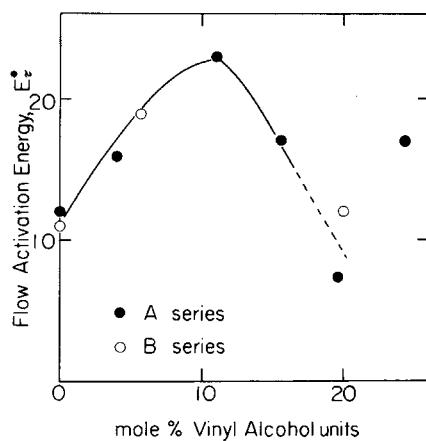


Fig. 3. Change of E_{τ}^* with vinyl alcohol content for copolymers of A and B.

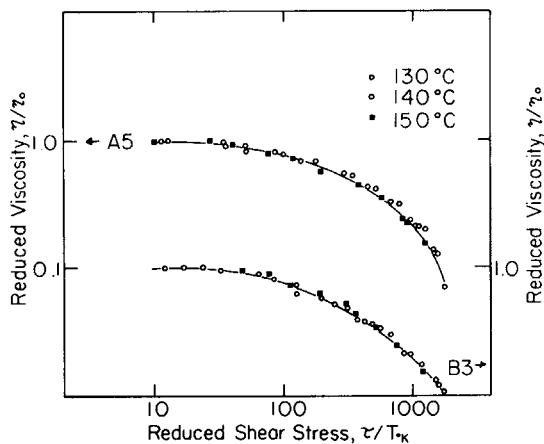


Fig. 4. Viscosity changes with shear. Reduced plots for terpolymers.

The trends of dynamic measurements for the complex viscosity, on the other hand, are interpretable in a straightforward manner as resulting from increases in cohesion brought about by hydrogen bonding due to hydroxyl groups.

Both the steady-shear and dynamic measurements obey the time or frequency-temperature superposition principle, and data may thus be treated to

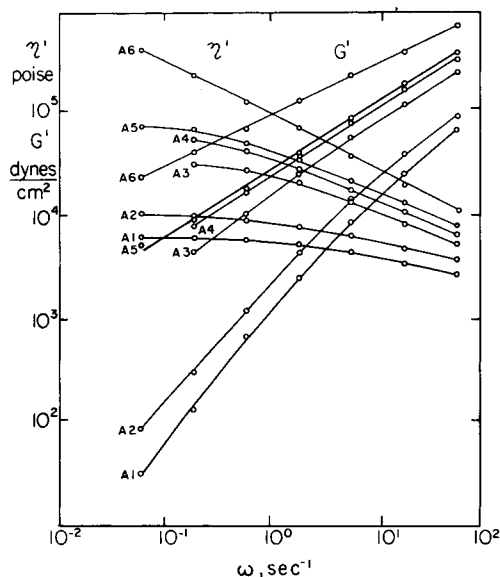


Fig. 5. Viscoelasticity of the A series copolymers at 123°C.

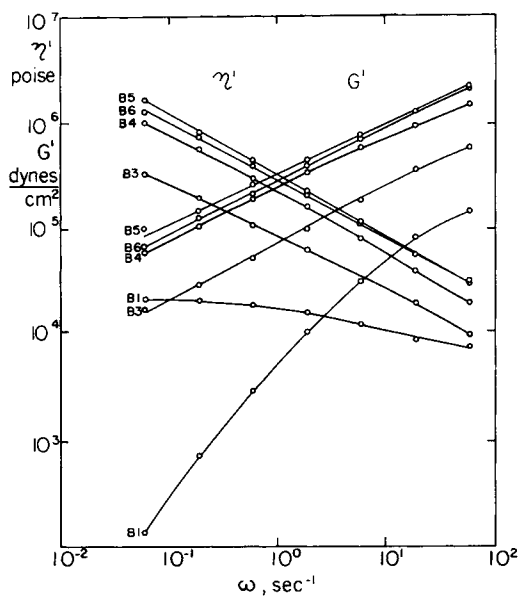


Fig. 6. Viscoelasticity of the B series copolymers at 123°C.

give master curves at a reference temperature over extended time or frequency scales.

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