

The Influence of Intermolecular Hydrogen Bonding on the Flow Behavior of Polymer Melts

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Synopsis

The influence of hydrogen bonding on the flow behavior of polymer melts at high shear rates has been investigated using a capillary extrusion rheometer. The systems studied were copolymers of ethylene and acrylic or methacrylic acid. Hydrogen bonding was found to substantially enhance both flow activation energy and viscosity level, as well as the degree of dependence of viscosity on rate of shear. It was also found that hydrogen bonding does not influence the critical shear stress for onset of "melt fracture." The data support the view that hydrogen bonds act effectively as temporary (quasi-) crosslinks during the short time scales of deformation involved in flow at high shear rates.

INTRODUCTION

The flow behavior of high molecular weight polymer melts is ordinarily dominated by the effects of molecular entanglement. The entanglement structure of a polymer is in turn influenced by such molecular features as average molecular weight, molecular weight distribution, and the presence of long-chain branches, all of whose effects on flow behavior have been studied extensively.

Another aspect of structure which has received less attention as regards flow properties is the presence of strong secondary forces such as hydrogen bonds between polymer chains. Longworth and Morawetz¹ reported that intermolecular hydrogen bonding between carboxyl groups in styrene-methacrylic acid copolymers leads to an enhancement of melt viscosity and flow activation energy values at low shear rates. Their conclusions were disputed, however, by Fitzgerald and Nielsen,² who claimed that increases in viscosity and activation energy with increasing methacrylic acid concentration could be accounted for by the shift in glass transition temperature with copolymer composition alone. More recently, Boyce et al.³ investigated the flow behavior of a series of low molecular weight carboxyl-substituted polybutadiene and butadiene-acrylonitrile copolymers and reported that the introduction of polar groups enhanced both viscosity and activation energy.

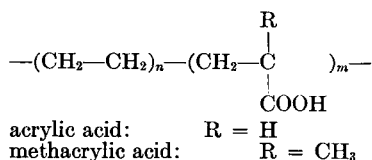
The present investigation was undertaken to elucidate the role played by intermolecular hydrogen bonding in determining flow behavior of polymer

melts of high molecular weight at rates of shear commensurate with processing operations.

MATERIALS

The materials chosen for study were copolymers of ethylene and either acrylic or methacrylic acid. These polymers are commercially available in a wide range of composition and molecular weight, and have been the subject of numerous investigations in the solid state.⁴⁻⁸

The chemical structure of the copolymers may be represented as follows:



The pendent carboxyl groups on the acid units can associate with one another forming hydrogen-bonded structures. The range of composition investigated in this study was from 1.3 to 8.8 mole-% acid, as determined by titration. For a random distribution of acid groups this interval corresponds to the average value of n ranging from 76 to 10 for $m = 1$. Conse-

TABLE I
Physical Properties of Polymers Investigated

Polymer	Supplier	Acid concentration, ^a mole-%	Melt index ^b	T_{β} , ^c °C	$\frac{\text{CH}_2}{100\text{C}}$ ^d
LPE	Phillips	0	0.2	—	—
BPE-I	du Pont	0	3	—	1.7
BPE-II	du Pont	0	250	—	—
EAA-1.3%	Union Carbide	1.3	4.8	-5	2
EAA-1.7%	Dow	1.7	5.3	—	—
EAA-3.1%	Dow	3.1	6.4	12	2
EAA-3.3%-I	Dow	3.3	0.5	—	—
EAA-3.3%-II	Dow	3.3	20	—	—
EAA-5.3%	Union Carbide	5.3	4.8	20	1.5-2.0
EAA-6.5%	Dow	6.5	6.9	24	1.5-2.0
EAA-8.8%	Union Carbide	8.8	300	—	—
EMA-3.2%	du Pont	3.2	3.8	—	—
EMA-4.5%	du Pont	4.5	6.6	—	—

^a Determined by titration.

^b ASTM D1238.

^c Determined by dynamic loss measurements at 100 cps; T_{β} is associated with the glass transition.

^d Determined by infrared measurements.

quently, the polymer chains are predominantly ethylenic, with a small number of acid groups scattered throughout.

There is some controversy at present as to whether the acid units in these copolymers exist in blocks or in acid-rich regions along the chain.^{9,10} The best information available indicates that the copolymers are essentially random,¹⁰ but as the concentration of acid is raised above 10 mole-%, doublets and higher-sequence lengths of acid units appear with increasing frequency.¹¹

The properties of the materials investigated in this study are listed in Table I. The polymers are designated by type (LPE for linear polyethylene, BPE for branched polyethylene, EAA for ethylene-acrylic acid copolymer, and EMA for ethylene-methacrylic acid copolymer) followed by acid concentration expressed in mole-%, where appropriate. Since the copolymers are prepared by a high-pressure free radical polymerization, they are characterized by both long- and short-chain branching and a broad molecular weight distribution. Patent information reveals that conversions are kept low to assure randomness and this would also tend to minimize long-chain branching. No molecular weight information is available at present for these polymers and intrinsic viscosity measurements have so far produced spurious results, even in solvents which should not permit interchain hydrogen bonding. Further work is being carried out to resolve these difficulties.

The intermolecular hydrogen bonds between carboxyl groups on neighboring chains is depicted schematically in Figure 1. Infrared measurements⁸ to determine the temperature dependence of the equilibrium constant for the association-dissociation reaction indicate that the hydrogen bonding equilibrium persists in the molten state. Figure 2 depicts the percentage of carboxyl groups tied up in hydrogen bonds as a function of temperature for some of the copolymers studied, calculated by extrapolating the data of Otocka and Kwei.⁸ The concentration dependence of the equilibrium exhibited by these data is probably a reflection of differences in the sequence distribution of acid groups among the copolymers. It is noteworthy that even at 210°C, the highest temperature employed in this study, some 10%-12% of the carboxyl groups are associated by hydrogen bonds.

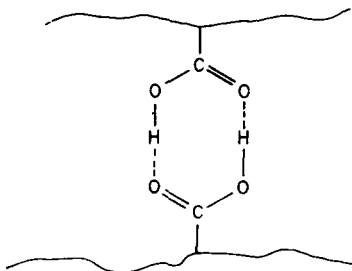


Fig. 1. Intermolecular hydrogen bonds between carboxyl groups.

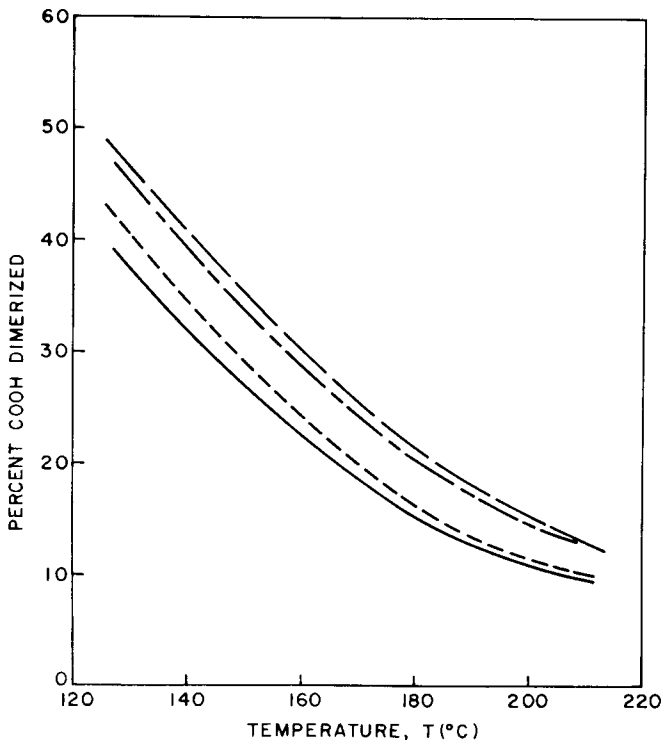


Fig. 2. Percentage of carboxyl groups dimerized vs. temperature for some ethylene-acrylic acid copolymers: (— —) EAA-5.3%; (- - -) EAA-6.5%; (- - -) EAA-3.1%; (—) EAA-1.3%.

EXPERIMENTAL

The viscous behavior of the ethylene-acrylic and methacrylic acid copolymers was investigated at several temperatures over approximately three decades of shear rate using a Sieglaff-McKelvey capillary extrusion rheometer, described elsewhere.¹² The capillaries employed had length-to-diameter ratios ranging from 26 to 83. For these capillaries entrance corrections were found to be negligibly small for all materials studied; consequently, the wall shear stress measurements required no correction. The true shear rate at the capillary wall, $\dot{\gamma}_w$, was calculated from the apparent value, $\dot{\gamma}_{wa}$, according to the Rabinowitsch equation¹³:

$$\dot{\gamma}_w = \dot{\gamma}_{wa} \left[\frac{3}{4} + \frac{1}{4} \frac{d \log \dot{\gamma}_{wa}}{d \log \tau_w} \right] \quad (1)$$

where τ_w is the wall shear stress. The fact that data obtained with different capillaries were superposable was taken as evidence that the results were not being influenced by viscous heat generation.

RESULTS AND DISCUSSION

Temperature Dependence

Typical flow curves ($\log \tau_w$ versus $\log \dot{\gamma}_w$) obtained for EAA-3.1% at four temperatures ranging from 130° to 210°C are shown in Figure 3. The curves are not well represented by the power law, $\tau_w = K\dot{\gamma}_w^n$, and resemble those of the branched polyethylene material, BPE-I, shown in Figure 4.

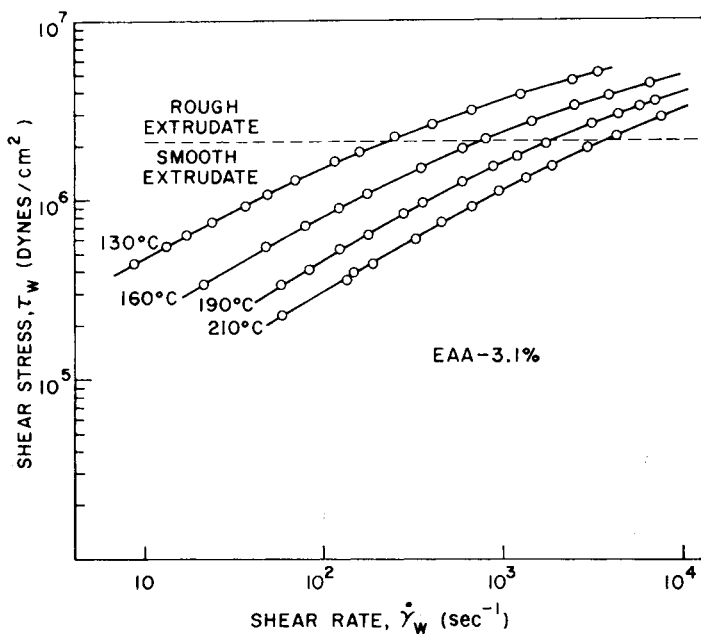


Fig. 3. Flow curves for EAA-3.1%.

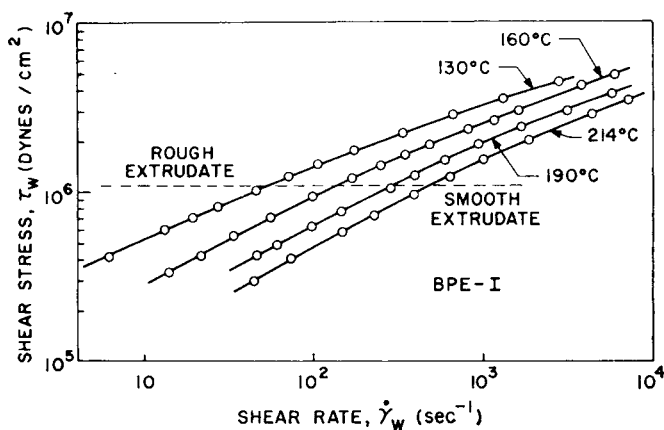


Fig. 4. Flow curves for BPE-I.

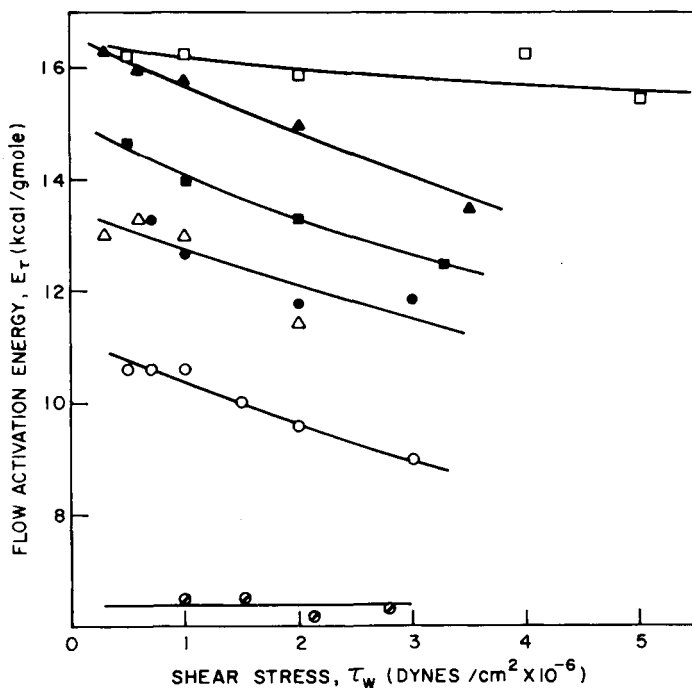


Fig. 5. Flow activation energy curves for several ethylene-acrylic acid copolymers of similar melt index (M.I.): (\square) EAA-6.5% (6.9 M.I.); (\blacktriangle) EAA-5.3% (4.8 M.I.); (\blacksquare) EAA-3.1% (6.4 M.I.); (\triangle) EAA-1.7% (5.3 M.I.); (\bullet) EAA-1.3% (4.8 M.I.); (\circ) BPE-I (3 M.I.); (\odot) LPE (0.2 M.I.).

As a general rule, the flow curves taken at different temperatures are not parallel for either the acid copolymers or branched polyethylene, and consequently they cannot be superposed by a horizontal shift along the $\log \dot{\gamma}_w$ axis. However, at any given value of τ_w , a set of shift factors, a_T , to account for changing temperature can be determined. These shift factors can be described by the Arrhenius expression:

$$a_T = A \cdot \exp [E_T/RT] \quad (2)$$

where A is a constant, E_T is the flow activation energy at constant shear stress, R is the gas constant, and T is absolute temperature. The flow activation energy determined in this manner is found to be independent of temperature, within experimental error, from 130° to 210°C, but dependent upon shear stress.

Figure 5 shows plots of activation energy against shear stress for several of the polymers of similar melt index (M.I.) investigated, including the linear and branched polyethylene materials. In contrast to the linear polyethylene sample, LPE, which has a constant activation energy of 6 kcal/g-mole, the branched polyethylene material, BPE-I, has a much higher E_T with a marked stress dependence. Further, as acrylic acid units are in-

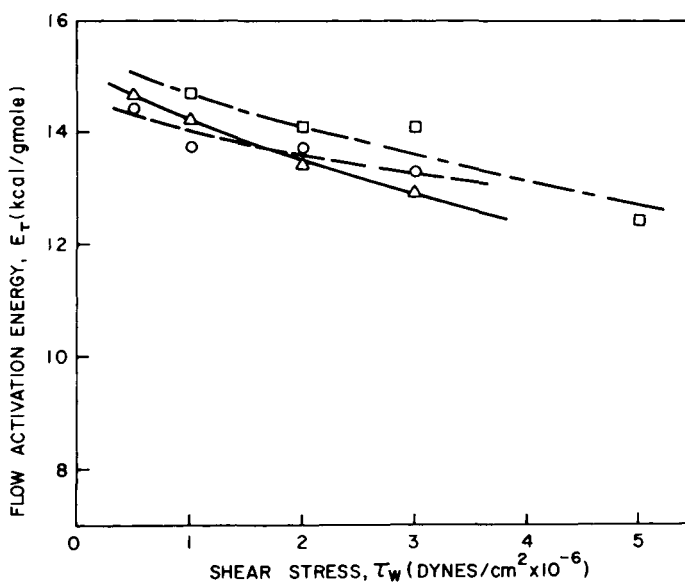


Fig. 6. Flow activation energy curves for copolymers of similar acid concentration but different melt index (M. I.): (\square) EAA-3.3%-I (0.5 M.I.); (Δ) EAA-3.1% (6.4 M.I.); (\circ) EAA-3.3%-II (20 M.I.).

incorporated in the ethylene chain backbone in increasing concentration from 1.3 to 6.5 mole-%, the general character of the E_r curve remains essentially unchanged from that of the branched polyethylene material, but the curve is shifted to higher activation energies.

Activation energy curves for three materials of widely differing melt index, but approximately equal acid concentration, are shown in Figure 6. The activation energies are very nearly identical within experimental error, indicating that the influence of average molecular weight is minimal.

Activation energies at a stress level of 10^6 dynes/cm² are plotted against acid concentration for all polymers investigated, regardless of melt index, in Figure 7. Included in this plot are activation energies for two methacrylic acid copolymers, EMA-3.2% and EMA-4.5% (filled circles), which also fall on the curve. It is evident that the inclusion of very short branches (methyl groups) on the copolymer chain at the acid units does not influence E_r significantly, in agreement with results of other authors for ethylene polymers.¹⁴⁻¹⁶

When the flow of a polymer melt is considered as a thermally activated rate process, the activation energy is closely related to the energy required to create a hole in the liquid into which that portion of the polymer molecule comprising a flow unit can move. The regular increase in activation energy with increasing acrylic acid concentration in the copolymers might be explained simply on the basis that greater amounts of energy are required to create a hole in a liquid in which hydrogen bonds must be broken. How-

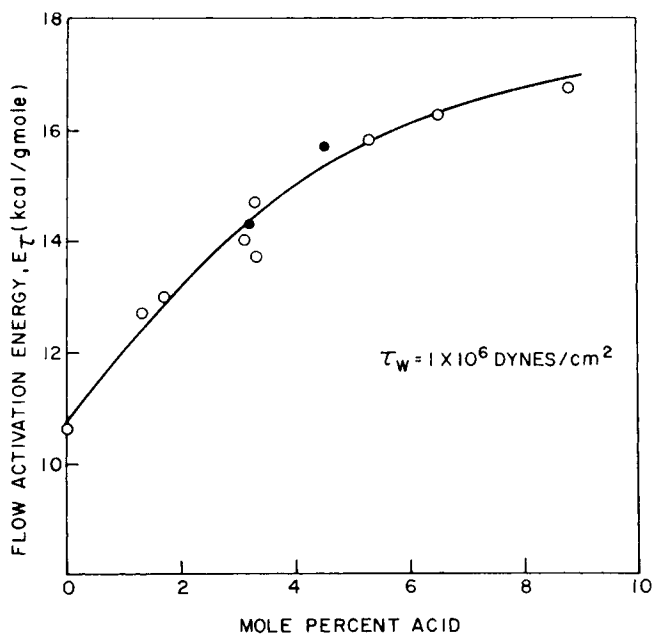


Fig. 7. Flow activation energy at a shear stress of 1×10^6 dynes/cm² vs. acid concentration for all copolymers investigated.

ever, some further reflection leads one to an alternative interpretation, particularly when the case of branched polyethylene is considered.

Experimental evidence¹⁴⁻¹⁶ indicates that long-chain rather than short-chain branching is responsible for the increase in activation energy of branched over linear polyethylene. Presumably the activation energy, a short-range property, is influenced by long-range interactions of long branches with other chains. Such interactions could lead to an increase in the effective size of the flow unit by hindering its orientation in the stress field, and hence to an increase in E_T . Support for this idea is seen in the stress dependence of the activation energy of branched polyethylene, for as stress is increased, flow unit orientation takes place to a greater degree and the effective size decreases, with a corresponding drop in E_T . Some caution must be exercised on this point, however, since the decrease in E_T with stress is most apparent in the region of observable extrudate roughness ("melt fracture"), where the flow mechanism is not well understood.

The idea that long-range interactions of long branches might influence activation energy by hindering flow unit orientation can logically be extended to the case of ethylene-acrylic acid copolymers, if the hydrogen bonds are considered to act effectively as temporary (quasi-) crosslinks during the time scales of deformation involved in flow at high shear rates. Since such crosslinking would, in effect, create molecular entities resembling highly branched polymer chains, the enhancement of activation energy

with increasing acid concentration could be caused by a mechanism similar to that resulting from long branching in polyethylene.

The question as to whether hydrogen bonds are effective as crosslinks has been discussed in the literature for some time. Eldridge and Ferry¹⁷ explained the melting behavior of gelatin gels by proposing a crosslinking mechanism involving hydrogen bonds. Weisfeld et al.¹⁸ invoked a secondary crosslinking mechanism to describe dynamic modulus-temperature data for hydrogen-bonded urethane elastomers. On the other hand, Fitzgerald and Nielsen² concluded from a comparison of stress relaxation measurements on polystyrene and styrene-methacrylic acid copolymers that hydrogen bonds are very inefficient crosslinking members during long time scales. Tobolsky and Shen¹⁹ came to similar conclusions but also observed that hydrogen bonding appears to raise the relaxation modulus in the rubbery plateau region, an effect similar to that of primary crosslinking. Furthermore, Otocka and Kwei⁸ found that increases in glass transition temperature with increasing acid concentration in ethylene-acrylic acid copolymers are described more precisely by crosslinking equations than by copolymer relationships. Consequently, there exists some evidence which suggests that hydrogen bonds can act as secondary crosslinks if time scales of deformation are sufficiently short. However, the magnitude of the contribution such a mechanism might make toward enhancing flow activation energy in ethylene-acrylic acid copolymers cannot be assessed at this time.

Shear Dependence

Insight into the possible crosslinking action of hydrogen bonds in ethylene-acrylic acid copolymers can be provided by examining the influence of hydrogen bonding on the non-Newtonian viscosity, $\eta(\dot{\gamma})$. Because $\eta(\dot{\gamma})$ is influenced by many other aspects of molecular structure, in order to distinguish unambiguously the separate influence of hydrogen bonds it is necessary to carry out experiments on identical molecular structures having different degrees of intermolecular association present. This situation was achieved in two separate types of experiments, the first of which utilized the technique of blending polymers, while the second involved esterification of carboxyl groups to destroy hydrogen bonding.

The blending experiment is depicted in Figure 8, which shows the viscosity-shear stress curve of EAA-5.3% at 190°C. Also shown are similar curves at 190°C for two low molecular weight materials, one a branched polyethylene BPE-II (250 MI), the other EAA-8.8% (300 MI). These two polymers exhibit essentially the same viscosity curve. Two blends were prepared by mixing the molten polymers in a Brabender rheometer. Control samples were also run as a check against possible shear degradation. Blend A consisted of 60 parts by weight EAA-5.3% and 40 parts EAA-8.8%, yielding a 6.6% acid blend. Blend B was comprised of 60 parts EAA-5.3% and 40 parts BPE-II, yielding a 3.1% acid blend. In the absence of the complicating effects of intermolecular hydrogen bonding, the two blends would be expected to exhibit nearly identical viscosity curves at

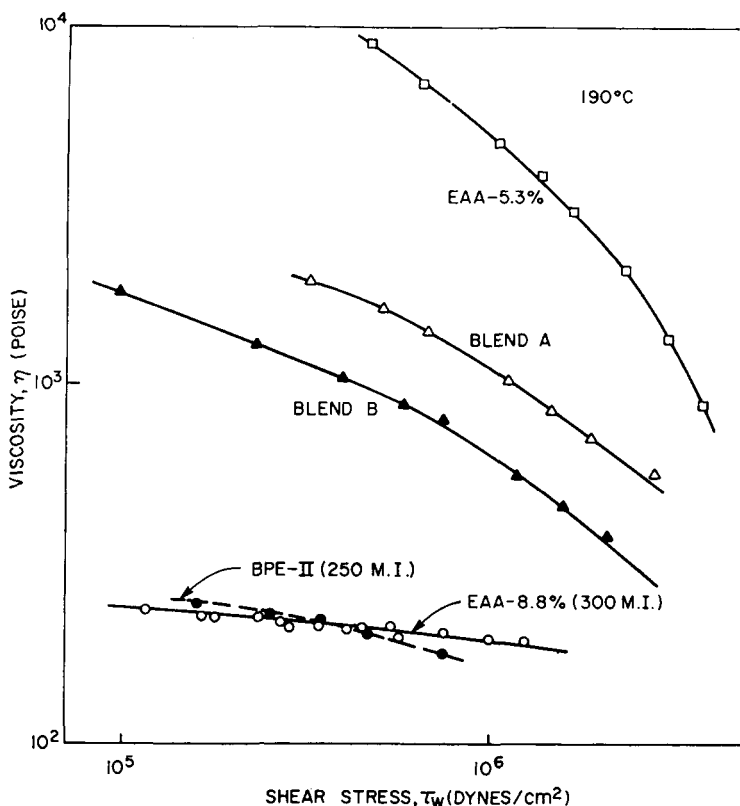
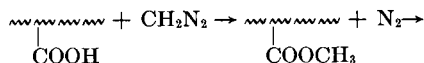


Fig. 8. Viscosity curves at 190°C for ethylene-acrylic acid copolymer blends. Blend A (6.6%): 60 parts EAA-5.3%, 40 parts EAA-8.8%. Blend B (3.1%): 60 parts EAA-5.3%, 40 parts BPE-II.

190°C. As seen in Figure 8, however, blend A has a much higher viscosity curve than blend B, demonstrating the synergistic effect of mixing copolymers of different acid concentration as opposed to "diluting" a copolymer with polyethylene. Because the higher acid concentration blend, blend A, behaves as if its molecular weight had been raised, the results indicate that hydrogen bonds do act effectively as temporary crosslinks when rates of deformation are high.

The second type of experiment performed involved esterification of the carboxyl groups to destroy hydrogen bonding in the original ethylene-acrylic acid copolymer, by reaction with diazomethane in xylene solution at 40°C. The reaction goes as follows:



This reaction was carried out on a sample of EAA-5.3%. After reaction the polymer was precipitated from solution and dried. Infrared measure-

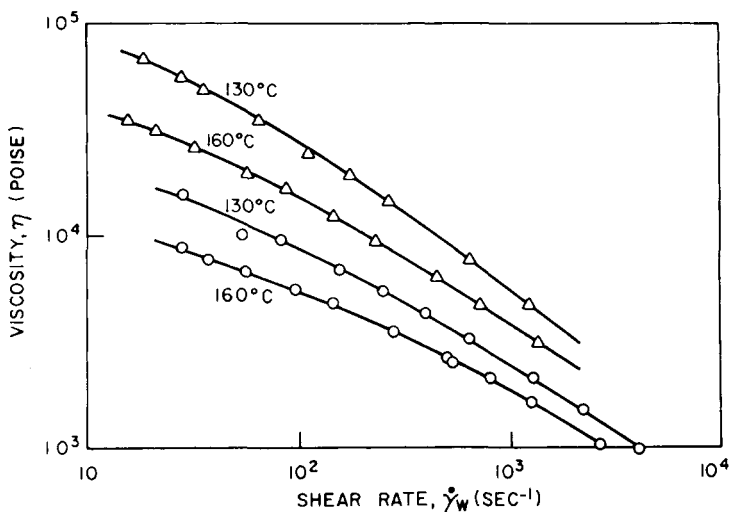


Fig. 9. Viscosity curves for EAA-5.3%, 85% ester, and EAA-5.3%, control at 130° and 160°C: (Δ) EAA-5.3%, control; (\circ) EAA-5.3%, 85% ester.

ments established that the esterification was 85% complete. In addition, a control sample was given the identical treatment as the reacted sample, except for the reaction step itself.

The viscosity curves of the esterified copolymer (EAA-5.3%, 85% ester) and the control sample (EAA-5.3%, control) are shown at 130° and 160°C in Figure 9, where it is apparent that hydrogen bonding has a substantial influence on the non-Newtonian viscosity and its temperature dependence. The control sample has a much higher viscosity, which exhibits a greater degree of shear dependence than the esterified sample. The effect of increasing hydrogen bonding present is therefore substantially similar to increasing molecular weight; consequently, one is again led to the conclusion that hydrogen bonds are effective crosslinking members during flow at high rates of shear.

The flow activation energy curves for the esterified sample and control are depicted in Figure 10. The control sample has an activation energy nearly twice that of the esterified sample, clearly demonstrating the substantial influence of hydrogen bonding on this property. The flow activation energy of the esterified sample is very close to that of BPE-I.

Unstable Flow

The dashed lines in Figures 3 and 4 indicate the point at which extrudate roughness or "melt fracture" is first apparent. The transition from stable to unstable flow is smooth for all materials studied and rather difficult to detect precisely. Nevertheless, careful observation revealed that the onset of "melt fracture" occurs at a critical value of shear stress, τ_c , independent of temperature for each polymer. This behavior has been reported

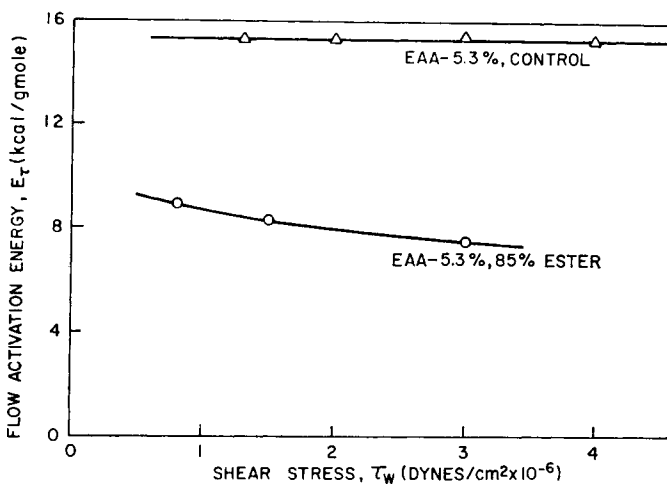


Fig. 10. Flow activation energy curves for EAA-5.3%, 85% ester, and EAA-5.3%, control.

for many polymer systems.²⁰ The critical shear stresses for the various polymers investigated are listed in Table II.

TABLE II
Critical Shear Stresses for Unstable Flow

Polymer	τ_{c1} dynes/cm ²
BPE-I	1.2×10^6
EAA-1.7%	2.5×10^6
EAA-3.1%	2.1×10^6
EAA-3.3%-I	1.4×10^6
EAA-3.3%-II	3.0×10^6
EAA-5.3%	3.1×10^6
EAA-6.5%	4×10^6
EMA-3.2%	1.8×10^6
EMA-4.5%	2.2×10^6

Since temperature shifts the hydrogen bonding equilibrium, the lack of dependence of critical shear stress on temperature strongly suggests that hydrogen bonding does not interfere with the mechanism giving rise to "melt fracture," except insofar as it influences the flow curve as a whole. The precise nature of the mechanism involved is not yet well understood, although there seems to be some consensus that "melt fracture" results from the elastic properties of polymer melt, by either a failure or an instability process.²¹⁻²³ It appears, therefore, that an independent determination of the influence of intermolecular hydrogen bonding on elastic properties of polymer melts might well shed some light on the "melt fracture" mechanism itself.

CONCLUSIONS

The presence of intermolecular hydrogen bonding in polymer melts leads to substantial increases in the activation energy for viscous flow, which depend upon the degree of hydrogen bonding possible. The viscosity is also enhanced, as well as its dependence on rate of shear. However, the critical shear stress for the onset of "melt fracture" is not influenced by hydrogen bonding. The experimental data indicate that intermolecular hydrogen bonds act effectively as temporary (quasi-) crosslinks during the short time scales of deformation involved in flow at high rates of shear.

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