Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Melt Viscosity Characteristics of Ethylene-Acrylic Acid-Acrylamide Terpofymer

B. H. Clampitt[a]
[a] Gulf Research & Development Company Kansas City Laboratory, Merriam, Kansas

To cite this Article Clampitt, B. H.(1971) 'Melt Viscosity Characteristics of Ethylene-Acrylic Acid-Acrylamide Terpofymer', Journal of Macromolecular Science, Part A, 5: 8, 1317 — 1328
To link to this Article: DOI: 10.1080/00222337108061111
URL: http://dx.doi.org/10.1080/00222337108061111

J. MACROMOL. SCI.–CHEM., A5(8), pp. 1317-1328, December, 1971

Melt Viscosity Characteristics of Ethylene-Acrylic Acid-Acrylamide Terpolymer

B. H. CLAMPITT

Gulf Research & Development Company
Kansas City Laboratory
Merriam, Kansas 66202

SUMMARY

Melt index and melt viscosity measurements have been made on a series of ethylene-acrylic acid-acrylamide terpolymers. The terpolymers were prepared from a 2000 melt index ethylene-methyl acrylate copolymer and synthesis conditions were adjusted such that the polar groups varied from pure acid to pure amide to pure salt. Results of these measurements indicated the following order of melt viscosities at 190°C: 50% acid-50% amide $<$ 100% amide $<$ 100% acid $<$ $33\frac{1}{3}$% acid amide-salt $<$ 50% salt-50% amide $<$ 50% salt-50% acid $\ll$ 100% salt. This order apparently arises because of the complex inter- and intramolecular hydrogen bonding and ionic bonding forces that exist in these systems.

INTRODUCTION

Ethylene-acrylic acid-acrylamide terpolymers have been prepared by treating ethylene-methyl acrylate copolymers with caustic and ammonia in an aqueous environment at elevated temperatures and pressure [1]. The result is an aqueous dispersion which may be precipitated with an inorganic acid to yield a solid ethylene-acrylic acid-acrylamide terpolymer, or it may be precipitated with acetone to yield an ethylene-sodium acrylate-acrylamide terpolymer. By varying the amounts of caustic and ammonia charged to the reactor, it is possible to vary the relative amounts of acrylic acid and acrylamide in the terpolymer dispersion. Indeed, by suitably adjusting the reaction conditions and the precipitation techniques, it is possible to produce solid polymers of any desired acid-amide-salt ratio.

It is also possible to vary the acrylate content and the molecular weight of the starting ethylene-methyl acrylate copolymer, but the results presented in this paper will be mainly limited to a starting copolymer possessing 20 wt-% methyl acrylate and having a melt index of 2000. Some very limited data are also presented where the starting copolymer is 20% methyl acrylate, but it possesses a 2 melt index.

The objective of this research was to investigate how the acid, amide, and salt groups affect the melt flow characteristics of these polymers. Melt flow information was at first examined by means of melt index measurements. However, a more complete characterization of the melt viscosity of these polymers was gained by capillary rheometer measurements. The latter measurements allow the determination of the melt flow characteristics at several shear rates and, therefore, one obtains at least a qualitative indication of the non-Newtonian behavior of these systems.

EXPERIMENTAL

The polymer samples investigated were prepared according to the basic method described in Ref. 1 with suitable variation in the reactor charge and precipitation techniques to yield products where the original acrylate ester groups were converted to:

100% acid
100% amide
100% salt
50-50% acid-amide
50-50% acid-salt
50-50% amide-salt
$33\frac{1}{3}$% acid-amide-salt

Melt index values for the various products were determined at 190°C using the standard ASTM procedure [2] for polyethylene, condition E. Melt flow measurements under a variety of shear rates were obtained on an Instron capillary rheometer using a 2-in. die possessing an L/D of 67 and a 90°

entrance angle. Because of the widely different flow characteristics of the various forms of the polymer, it was not possible to make the measurements at uniform temperatures. The actual temperatures employed for a given resin were selected on the basis that shear stresses less than 1000 psi but greater than 10 psi were obtained for all the shear rates. Two or more temperatures were investigated for each resin system.

RESULTS AND DISCUSSION

Melt index values for the various compositions are given in Table 1. Melt index is usually thought to be related to the molecular weight of the polymer molecules, but the results in Table 1 clearly show that the functional groups present in a molecule greatly affect the melt index value. Indeed, all the derivatives of the 2000 melt index starting copolymer presumably have the same molecular weight, but melt index values range from 0.13 to 400. This wide range of melt index values must in some way be related to molecular association in the molten state. Indeed, the 100% salt form is thought to be cross-linked [3], which would imply that the whole macro-system is an approximation of the flow unit. At the other extreme, it is worth noting that all of the melt index values in Table 1 are considerably less than the base copolymer. Thus it appears that ester copolymers possess less association than any other type of copolymer system that has been investigated.

Table 1. Melt Index of Various Resin Forms

	Melt index	
Composition	2000 MI starting copolymer	2 MI starting copolymer
100% Acid	100	0.24
100% Amide	170	-
100% Salt	0.13	0.00
50% Acid-50% amide	400	-
50% Acid-50% salt	4.0	-
50% Amide-50% salt	7.8	-
$33\frac{1}{3}$% Acid-amide-salt	78.0	-

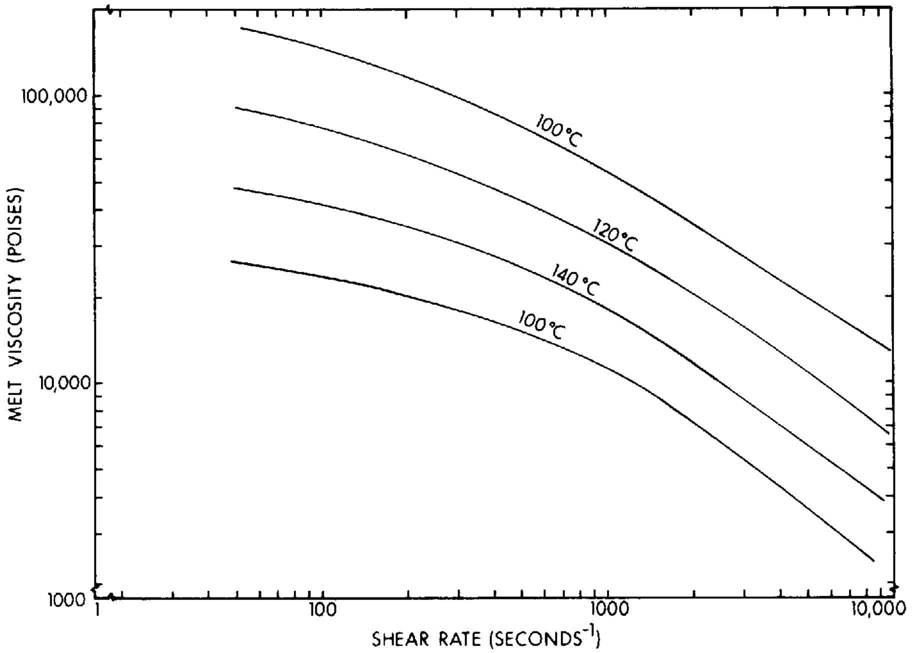

Fig. 1. Melt viscosity of 100% acid copolymer.

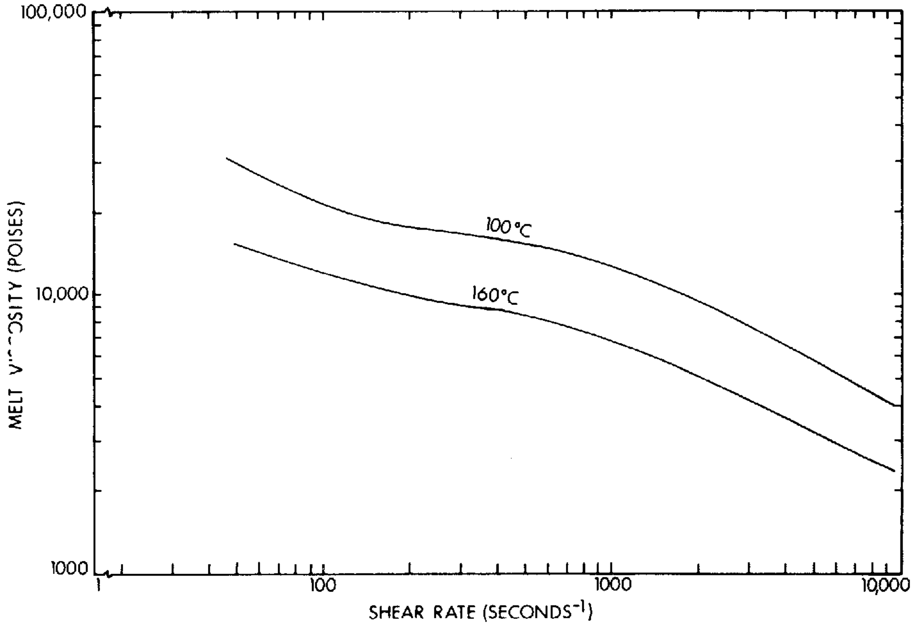

Fig. 2. Melt viscosity of 100% amide copolymer.

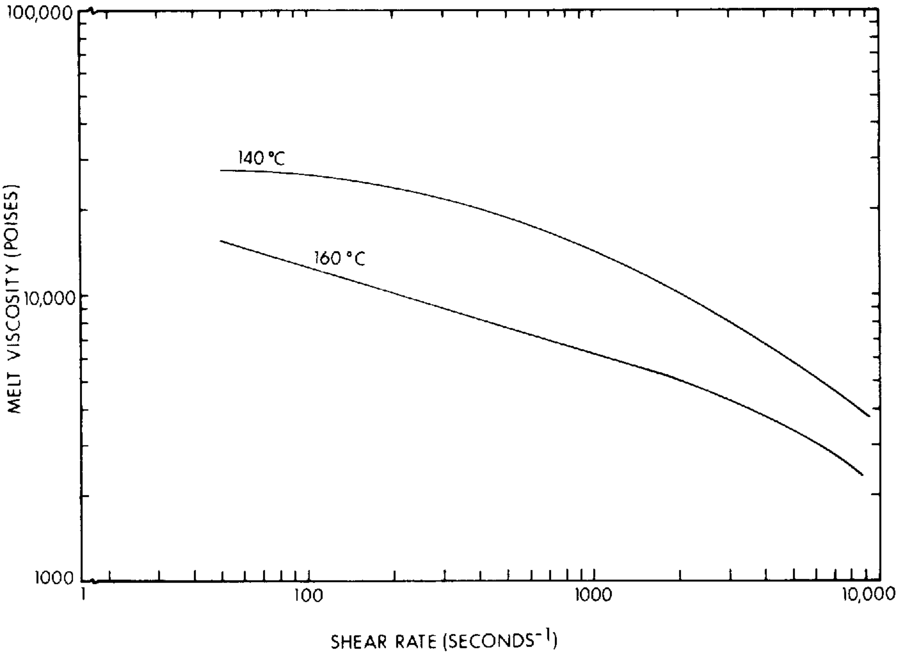

Fig. 3. Melt viscosity of 50% acid-50% amide copolymer.

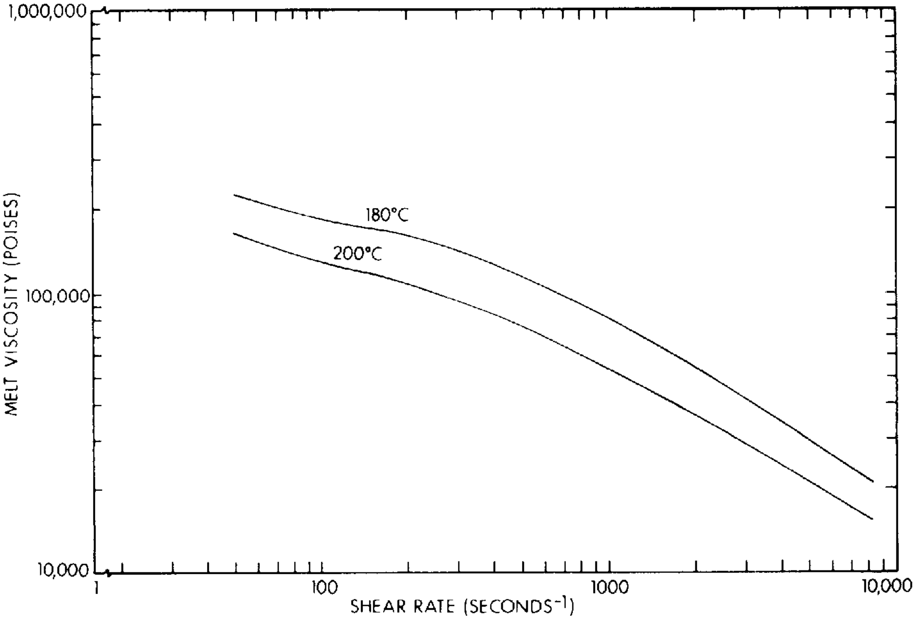

Fig. 4. Melt viscosity of 50% salt-50% acid copolymer.

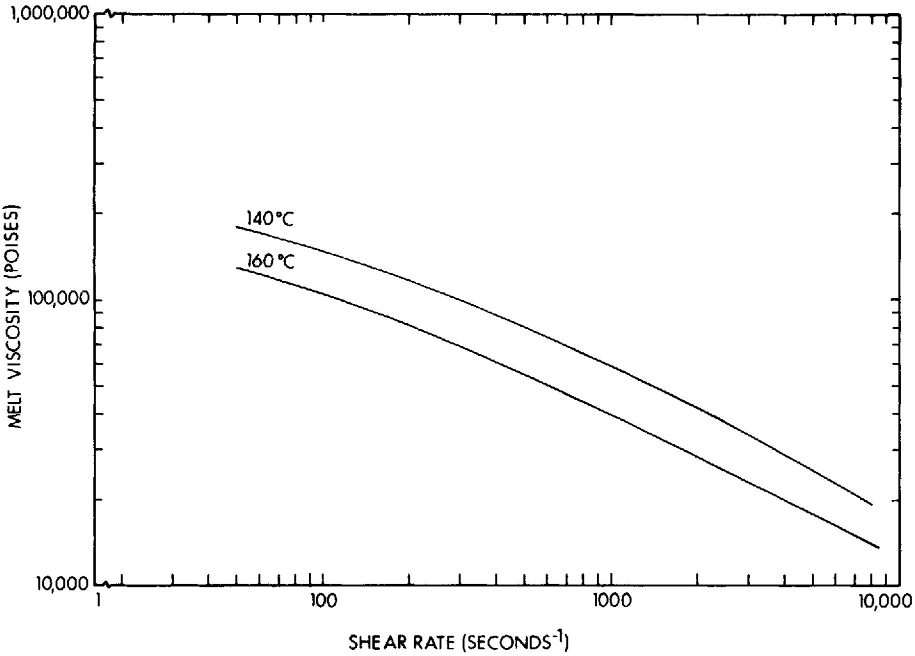

Fig. 5. Melt viscosity of 50% salt-50% amide copolymer.

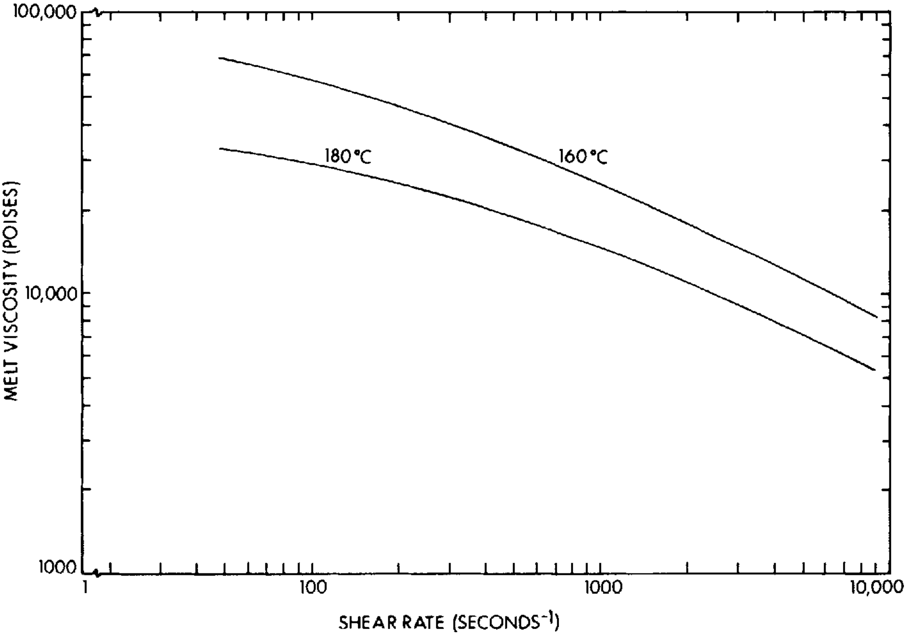

Fig. 6. Melt viscosity of 33 $\frac{1}{3}$% acid-amide-salt copolymer.

Attempts to measure melt index of polymer composition where the starting ester had a 2 melt index were disappointing since they are all very low. Results for the acid and salt forms of the resin are shown in Table 1, but because of their low values, they probably are not very accurate. Nevertheless, the results do indicate that if a given composition is desired of a given melt index, the product can be obtained by judicious selection of the starting copolymer ester.

Instron flow data for compositions derived from the 2000 melt index copolymer are shown in Figs. 1-6. No Rabinowitsch [4] corrections were applied to the experimental data and the melt viscosities given in Figs. 1-6 were computed by dividing the shear stress by the shear rate values obtained from the Instron. Regardless of the temperature employed, the 100% salt composition required excessive pressure to get it to extrude from the rheometer and a highly melt fractured strand was obtained. Therefore, melt flow curves for this form of the resin were not obtained. All other compositions gave reasonable flow curves with smooth extrudates.

Examination of Figs. 1-6 shows that the flow curves at different temperatures cannot be superposed by a shift along the shear rate axis. However, for any given shear rate, the variation of viscosity with temperature can be approximated by an Arrhenius equation:

$$\eta = A \exp [E/RT]$$

where A is a constant, E is the flow activation energy, R is the gas constant, T is the absolute temperature, and η is the melt viscosity. Shear rates of 1000 and 100 sec^{-1} were selected and constants for the Arrhenius equation determined for these shear rates. Values for A and E for the various compositions as well as the calculated melt viscosities at 190°C are shown in Tables 2 and 3. The relationship between melt viscosity and temperature at these shear rates is shown graphically in Figs. 7 and 8.

Melt viscosity data at 190°C indicate that the order of melt viscosities for the various composition is: 50% acid-50% amide $<$ 100% amide $<$ 100% acid $<$ $33\frac{1}{3}$% acid-amide-salt $<$ 50% salt-amide $<$ 50% salt-acid $\ll$ 100% salt. This order appears to be independent of shear rate and the same order is indicated in the melt index data given in Table 1.

The high melt viscosity of compositions containing salt groups suggests that a large amount of intermolecular bonding is occurring which gives rise to large melt flow units. The 100% acid and amide compositions would be expected to have large amounts of hydrogen bonding, but apparently this produces short-range order in these melts and leads to

Table 2. Melt Viscosities at a Shear Rate of 1000 sec^{-1}

Composition	Arrhenius constants		Melt viscosity at 190°C (P)
	Log A	E (cal/mole)	
100% Acid	-0.1643	8,400	6,000
100% Amide	-1.9601	11,500	2,750
50% Acid-50% amide	-3.7315	15,000	2,000
50% Acid-50% salt	+0.7317	8,700	65,500
50% Amide-50% salt	+1.1388	6,900	23,900
$33\frac{1}{3}$% Acid-amide-salt	-0.8271	10,400	11,400

Table 3. Melt Viscosities at a Shear Rate of 100 sec^{-1}

Composition	Arrhenius constants		Melt viscosity at 190°C (P)
	Log A	E (cal/mole)	
100% Acid	-0.5969	9,900	11,300
100% Amide	-1.3546	10,800	5,200
50% Acid-50% amide	-2.8344	13,800	4,400
50% Acid-50% salt	+1.6702	7,500	155,000
50% Amide-50% salt	+2.1172	5,800	69,300
$33\frac{1}{3}$% Acid-amide-salt	-1.9225	13,300	21,000

smaller flow units than those compositions which contain salt. This picture of long-range order in copolymers containing salt groups and short-range order in ethylene-acrylic acid copolymers is similar to the one proposed by Longworth and Vaughan [5] based on their x-ray study of ionomers.

The structural picture of ethylene copolymers of this type presented by these authors is that short-range order exists in the systems that do not contain metal ions because of crystallinity and hydrogen bonding forces. The introduction of metal ions alters the structure such that long-range Coulombic interactions come into play. This gives rise to clusters of ions

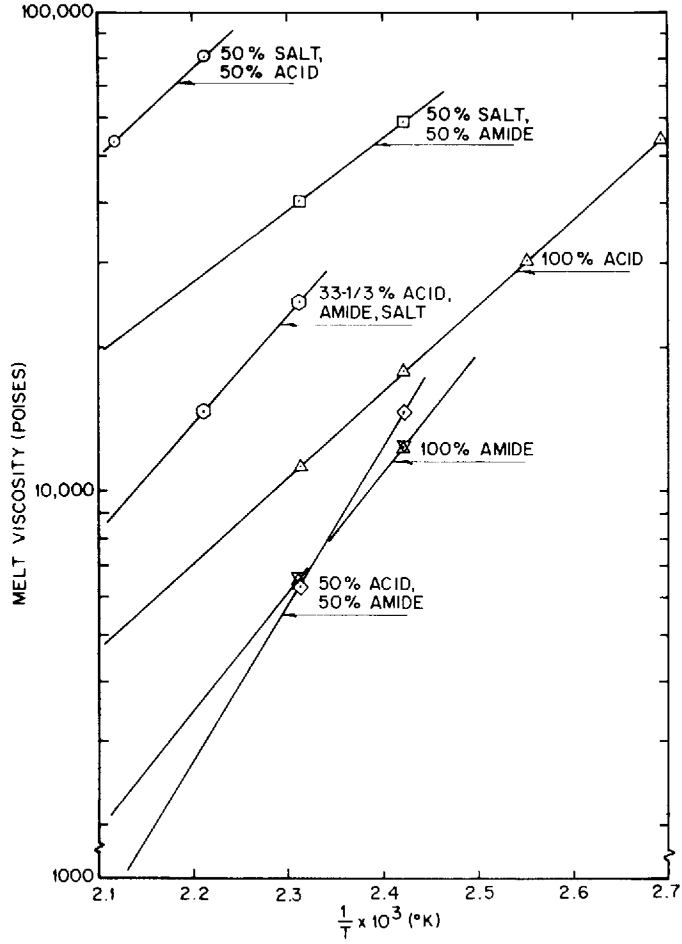

Fig. 7. Arrhenius plots at 1000 sec^{-1} shear rate.

that are arranged in regular fashion of relatively large size and these are interspersed with small miscellar regions of short-range ordered molecules. While the Longworth and Vaughan model was based on studies of these systems in the solid state, the present study would suggest that the same structural parameters apply to systems in the molten state.

The fact that the acid-amide composition has a lower melt viscosity at 190°C than either the pure acid or pure amide is somewhat surprising. The high flow activation energy for this composition indicates a highly

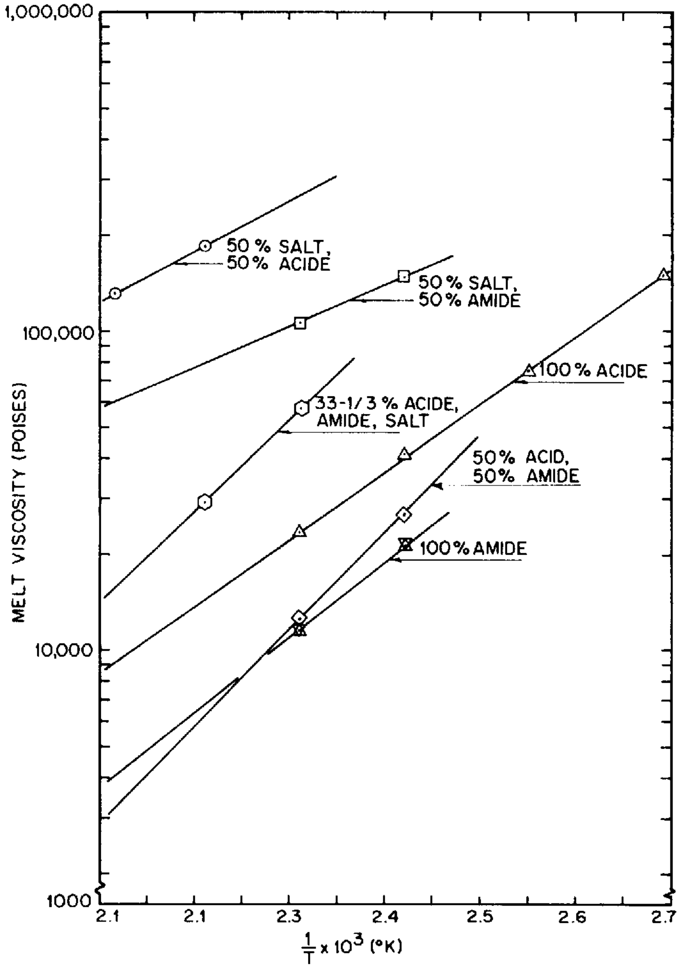

Fig. 8. Arrhenius plots at 100 sec^{-1} shear rate.

associated condition [6]; however, the low melt viscosity would indicate a small amount of association. Therefore, one must conclude that the association which exists in this system leads to smaller melt flow units than the other compositions. One possibility that would explain this paradox is that intramolecular hydrogen bonding occurs between the acid and amide groups leading to melt flow units more nearly spherical than the other compositions. Another possibility is that intermolecular association occurs which produces dimer molecules, and these dimer flow units would have a hydrocarbon exterior which would have low internal friction between them. The possibility of dimers in ethylene acrylic acid copolymer melts can be inferred from certain infrared measurements [7], and the presence of amide groups in the molecule would be expected to enhance this possibility [8]. There are probably other explanations for the low melt viscosity of the acid-amide composition, but with the limited data that are available, it is difficult to decide what is the true picture of the molecular flow units.

The temperature dependence of the melt viscosity of these systems is quite complex. By comparing Figs. 7 and 8 it will be seen that the flow activation energy depends upon both the shear rate and the composition. There does not appear to be a simple relationship between flow activation energy and composition or melt viscosity at a given temperature. Indeed, it will be noted that by variation of temperature it is possible to alter the order of melt viscosities of the various compositions. This is a further indication of the complex nature of the changing short-range and long-range order phenomena in polymer melt composition of this type.

CONCLUSIONS

As a result of the study of melt index and Instron melt rheometry data of ethylene-acrylic acid-acrylamide terpolymers, it appears that:

(1) All of the copolymers show non-Newtonian melt flow behavior.

(2) Melt index of ethylene copolymers is not a function of molecular weight alone, but depends upon the functional groups that are present.

(3) Of the compositions that were investigated, the ethylene-sodium acrylate copolymer has the highest melt viscosity.

(4) Of the compositions that were investigated, the 50% acid-50% amide copolymer has the lowest melt viscosity at 190°C.

(5) Temperature dependence of the melt viscosities is complex and is not related to composition.

(6) The inter- and intramolecular hydrogen bonding and ionic bonding forces existing in these systems greatly alter the melt flow units that exist in the various compositions.

REFERENCES

[1] B. H. Clampitt (to Gulf Research & Development Company), U.S. Patent 3,511,799 (1970).

[2] ASTM-D-1238-65T, “Measuring Flow Rates of Thermoplastics by Extrusion Plastometer.”

[3] H. P. Brown, *Rubber Chem. Technol.*, **30**, 1347-1386 (1957).

[4] B. Rabinowitsch, *Z. Phys. Chem.*, **A145**, 1 (1929).

[5] R. Longworth and D. J. Vaughan, *Nature*, **218**, 85 (1968).

[6] L. L. Blyler, *Rubber Chem. Technol.*, **3**, 823 (1969).

[7] E. P. Otocka and T. K. Kwei, *Macromolecules*, **1**, 244 (1968).

[8] P. J. Kmeger and D. W. Smith, *Can. J. Chem.*, **45**, 1611 (1967).

Accepted by editor June 11, 1971
Received for publication July 6, 1971