Rheological Properties of Polyethylenes Modified with Dicumyl Peroxide

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Synopsis

Low- and high-density polyethylenes were modified using dicumyl peroxide. The modified polyethylenes were subjected to steady and oscillatory shearing flows. The viscous and elastic properties determined with a cone-and-plate rheometer are correlated to the molecular weight of the materials, which was determined with the aid of size exclusion chromatographic analysis. It was found that both the melt viscosity and elasticity increase with the amount of dicumyl peroxide used, and shear-thinning behavior becomes more intense. The Bueche master curve of viscosity is constructed by using a relaxation time based on the weight-average molecular weight for both virgin and modified resins.

INTRODUCTION

During the past decades, the plastics industry has used crosslinked polyethylene, especially crosslinked low-density polyethylene, in a number of commercial applications, such as in wire coating extrusion, rotational molding, foam extrusion, etc. Because of its complexity, the mechanism of crosslinking, especially chemical crosslinking, is not at present well understood, although some serious attempts[1-4] at elucidation were made in the past. Some investigators[5-7] have reported the thermal stability and mechanical properties of chemically crosslinked polyethylenes. However, there is no serious study which reports the rheological behavior of crosslinked polyethylene in the molten state. It should be pointed out that the study of Narkis and Miltz,[8] which was conducted more than a decade ago, discusses *only* the viscous behavior of chemically crosslinked low-density polyethylene, but nothing about its elastic behavior.

Today, it is a well-accepted fact that, from the point of view of polymer processing, the *elastic* behavior is equally as important as the *viscous* behavior of molten polymers, if not more so.[9] Information on the elastic behavior of a polymer often provides a better understanding of the molecular behavior of the polymer during its flow.

In this paper, we shall report the highlights of our recent investigation of both the viscous and elastic properties of low- and high-density polyethylenes, modified with dicumyl peroxide, subjected to steady and oscillatory shearing flows.

EXPERIMENTAL

The polymers used were two low-density polyethylenes (LDPE) (MN 714 and MN 710-20, U.S. Industrial Chemicals Co.) and two high-density polyethylenes (HDPE) (SDP 860 and SDP 750, ARCO/Polymers, Inc.). These polymers are

TABLE I
Molecular Characteristics of Polymers Used

Polymer	Sample code	Melt index[a]	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
MN 714	LDPE-A	70	0.75×10^4	9.39×10^4	12.5
MN 710-20	LDPE-B	22	1.07×10^4	11.50×10^4	10.7
SDP 860	HDPE-A	16	1.53×10^4	4.68×10^4	3.0
SDP 750	HDPE-B	12	1.23×10^4	6.83×10^4	5.6

[a] ASTM D1238, supplied by the resin manufacturers.

available in the form of powders. As a modifying agent, recrystallized dicumyl peroxide (Di-cup) (Hercules Chemical Co.) was used. Table I gives the number-average molecular weight ($\overline{M}_n$) and weight-average molecular weight ($\overline{M}_w$), and Figures 1 and 2 give molecular weight distribution curves for the polymers used. This information was obtained with the aid of size exclusion chromatographic analysis by Dr. R. Ranganath of U.S. Industrial Chemicals Co.

Approximately 400 g of polyethylene powder containing 0.1 wt % dicumyl peroxide (Di-cup) were first mixed by shaking the mixture in a large jar for 20 min, and then the mixture was ballmilled for 24 h. This mixture was used to prepare other mixtures of low Di-cup concentration by adding more polyethylene. We found that, with the exception of HDPE SDP 860, the polyethylene cured with Di-cup concentration greater than 0.1 wt % did not flow readily, giving rise to a great difficulty in gap setting the cone-and-plate rheometer. Therefore the highest Di-cup concentration used was 0.1 wt %. Table II gives the polyethylenes used, the Di-cup concentration for each polyethylene, and the melt temperature at which rheological measurements were taken.

In order to prepare samples for rheological measurement, a charge of approximately 20 g of premixed powder (resin and Di-cup) was placed directly into a multiple-cavity mold in the shape of a disk. The mixture was molded at 170°C under 2,000–2,400 psi for 30 min in a Preco hydraulic press. This molding condition was predetermined qualitatively by a DuPont 990 thermal analyzer equipped with a DSC cell.
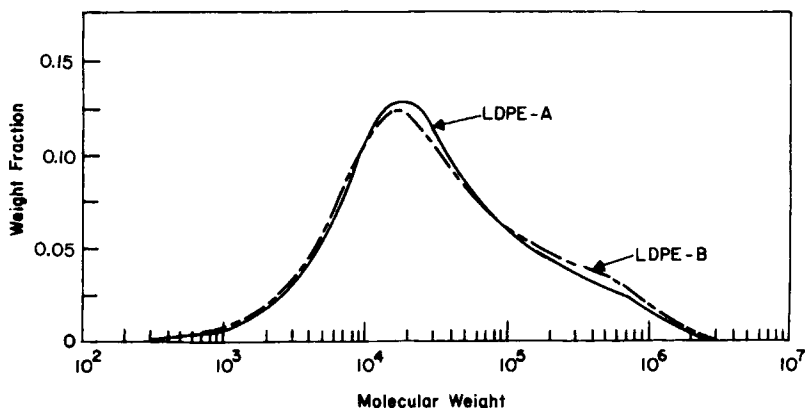

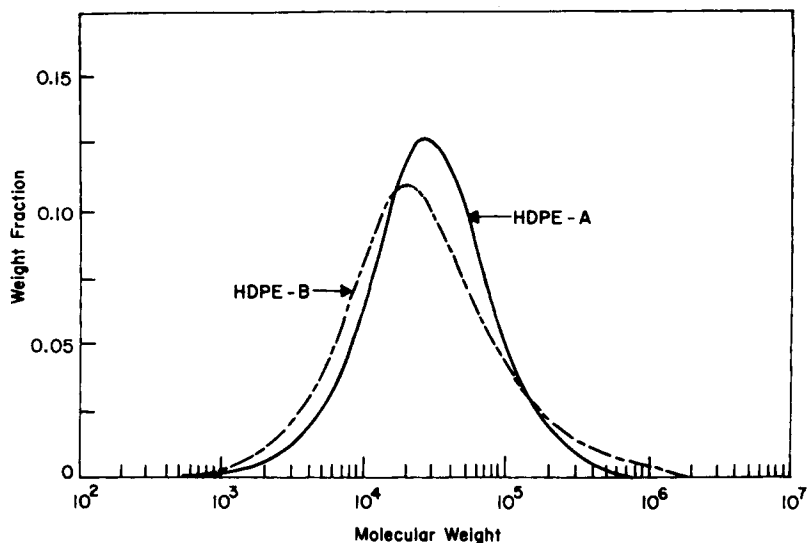Fig. 1. Molecular weight distribution curves for low-density polyethylenes used.

Fig. 2. Molecular weight distribution curves for high-density polyethylenes used.

The rheological properties of the modified polyethylenes were determined with a Weissenberg rheogoniometer (Model R 16), fitted with a flat plate, and a 2.5-cm diameter, 4° cone. For each sample, three runs were made for steady shearing flow measurements and two runs were made of oscillatory shearing flow measurements. The average readings of two or three repeated runs were used to plot the data.

The compression molded specimens (in the form of thin sheet) were cut into small pieces and were then placed in a beaker containing orthodichlorobenzene (Fisher Chemicals) to yield approximately 10 wt % of resin in the solution. The solution was then heated with vigorous agitation, held at 160°C for 2 hr, and filtered at a particular desired temperature (namely, 155°C for LDPE and 175°C for HDPE). The filtrate was washed thoroughly several times with hot solvent. The content of insoluble material was determined by differential weighing after the material had been dried for 2 h at 100°C under 28-in. vacuum. Several runs were made for each sample, and the data were obtained by averaging the runs.

TABLE II
Concentration of Dicumyl Peroxide and Melt Temperature Employed for Rheological
Measurement

Sample code	Di-cup concn (wt %)	Test temp (°C)
LDPE-A	0.01; 0.05	140; 160; 180
LDPE-B	0.01; 0.02	140; 160; 180
HDPE-A	0.05; 0.10	160; 180; 200
HDPE-B	0.03; 0.05	160; 180; 200

RESULTS AND DISCUSSION

Solubility of Polyethylenes Modified with Dicumyl Peroxide

Table III gives the results of the gel content measurements. It may be concluded that over the range of dicumyl peroxide (Di-cup) concentration employed in the preparation of the specimens used for rheological measurements (see Table III), little, if any, insoluble gel particles were formed during the chemical reactions taking place between the virgin resins and dicumyl peroxide. In other words, the concentration of dicumyl peroxide used for modifying the LDPEs and HDPEs was too low to reach the threshold value (i.e., the lower limit of critical Di-cup concentration), at which insoluble gel particles begin to form. We have found that the threshold Di-cup concentration is about 0.05 wt % for the LDPE-A and 0.035 wt % for the LDPE-B.

It is worth pointing out that there is also an upper limit of peroxide concentration at and beyond which the gel content in a crosslinked polyethylene becomes constant. It is seen in Table III that the upper limit of Di-cup concentration for the LDPE-A is about 0.5 wt %. It should be mentioned that the threshold concentration of peroxide necessary for forming insoluble gel particles depends on the molecular structure and molecular weight of the polymer to be crosslinked.

In the past, some attempts[2,10] have been made at understanding the effect of organic peroxide concentration on the extent of the crosslinked portion of the polymer. They used a modified equation of Charlesby and Pinner,[11] namely

$$S + S^{0.5} = (p/q) + (1/2F\overline{M}_n [I]) \qquad (1)$$

in which S is the weight fraction of the soluble portion, p and q are fractions of the basic units of the polymer undergoing degradation and crosslinking, respectively, related to the total number of basic units, $\overline{M}_n$ is the number-average molecular weight of the polymer before crosslinking, F is the crosslinking efficiency given by the number of moles of crosslinks/mol of decomposed organic peroxide, and $[I]$ is the concentration of decomposed organic peroxide in mol/g polymer.

In the present investigation, we have not attempted to correlate our solubility data with the aid of eq. (1) because there were no insoluble gel particles present in our specimens employed.

TABLE III
Summary of Gel Content Measurement

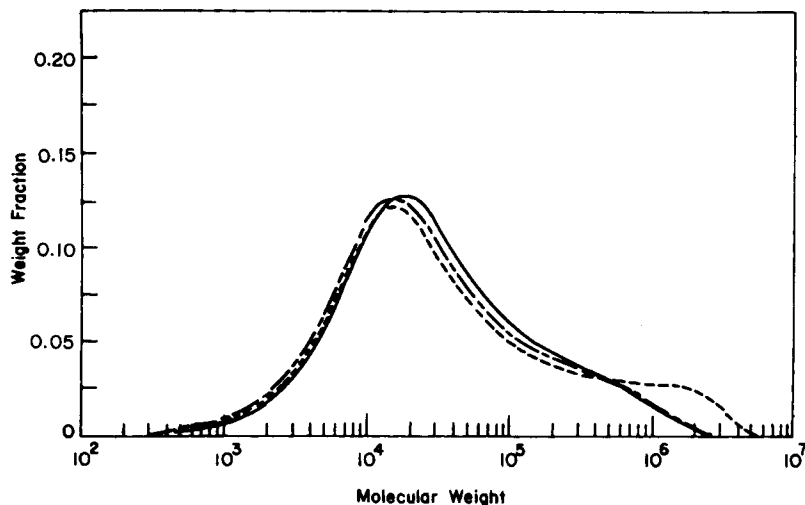| Di-Cup Concn (wt %)	Gel content (wt %)			
	LDPE-A	LDPE-B	HDPE-A	HDPE-B
0.000	0.00	0.00	0.00	0.00
0.010	0.00	—	—	—
0.020	—	0.00	—	—
0.050	0.00	2.7	0.00	0.00
0.075	17.1	38.6	—	—
0.100	34.6	63.0	0.00	0.00
0.500	74.5	—	—	—
1.000	75.2	—	—	—

Fig. 3. Molecular weight distribution curves for virgin and crosslinked LDPE-A (——); (—·—·—) LDPE-A/0.01% Di-cup; (- - -) LDPE-A/0.05% Di-cup.

Molecular Weight Distribution of the Polyethylenes Modified with Dicumyl Peroxide

Figure 3 gives molecular weight distribution (MWD) curves of the LDPE-A before and after reacting with dicumyl peroxide. The following observations may be noted in Figure 3: (1) the modified LDPE-A has more high molecular weight portions compared to the virgin resin. Also, as indicated in Table IV, both $\overline{M}_n$ and $\overline{M}_w$ increase with the amount of dicumyl peroxide used; (2) the position at which the maximum of the MWD curve occurs is shifted toward the left-hand side for the modified LDPE-A; (3) the modified LDPE-A has more low-molecular-weight portions compared to the virgin resin. These observations reveal the mechanism involved in the reactions between the virgin LDPE and dicumyl peroxide. First, the peroxide added to the polymer extended the polymer chains (especially, the long chain molecules) giving rise to larger molecules. There is also evidence, as may be seen in Table IV, that the degree of long-chain branching is increased in the presence of dicumyl peroxide free rad-

TABLE IV
Effect of Dicumyl Peroxide on Molecular Weights of Low-Density Polyethylenes Employed

Sample	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	LCB index[a]
Pure LDPE-A	0.75×10^4	9.39×10^4	12.5	0.53
LDPE-A/0.01 wt % Di-cup	0.89×10^4	10.50×10^4	11.8	0.49
LDPE-A/0.05 wt % Di-cup	1.32×10^4	17.30×10^4	13.1	0.49
Pure LDPE-B	1.07×10^4	11.50×10^4	10.7	0.49
LPDE-B/0.01 wt % Di-cup	1.01×10^4	15.10×10^4	15.0	0.46
LDPE-B/0.02 wt % Di-cup	1.14×10^4	17.20×10^4	15.1	0.46

[a] The smaller the value of LCB index, the greater the degree of long-chain branching.
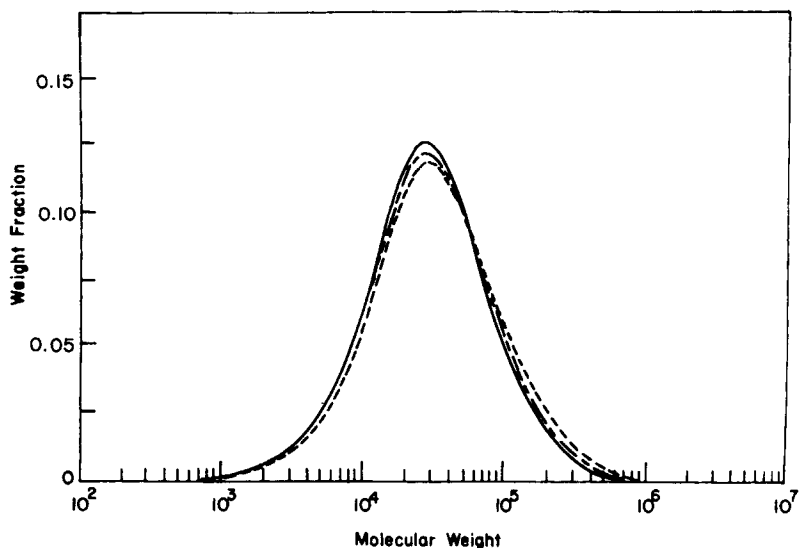
Fig. 4. Molecular weight dsitribution curves for virgin and crosslinked HDPE-A (——); (———)
HDPE-A/0.05% Di-cup; (- - -) HDPE-A/0.10% Di-cup.

icals. Second, when polymer chains are subjected to peroxide free radicals, dissociation of C—C bonds can occur simultaneously with crosslinking. The tendency toward degradation is related to the molecular structure of the repeating units.

Figure 4 gives MWD curves of the HDPE-A before and after reacting with dicumyl peroxide. It is seen that the entire MWD curve of the modified HDPE-A is shifted toward the right-hand side, indicating that polymer chains are extended in the presence of peroxide free radicals and little dissociation of C—C bonds has taken place. Table V gives information on the number- and weight-average molecular weights of the HDPEs.

Similar results were also obtained for LDPE-B and HDPE-B, but space limitations here do not permit us to present those results.

The little degradation of HDPEs observed, compared to the situation with LDPEs, may be explained by the fact that, when subjected to dicumyl peroxide free radicals, the tertiary carbon atoms present in the long- and short-chain branchings of LDPE are very susceptible to degradation compared to those in the straight chains.

TABLE V
Effect of Dicumyl Peroxide on Molecular Weights of High-Density Polyethylenes Employed

Sample	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
Pure HDPE-A	1.53×10^4	4.68×10^4	3.0
HDPE-A/0.05 wt % Di-cup	1.58×10^4	5.05×10^4	3.2
HDPE-A/0.10 wt % Di-cup	1.72×10^4	6.01×10^4	3.5
Pure HDPE-B	1.23×10^4	6.83×10^4	5.6
HDPE-B/0.03 wt % Di-cup	1.26×10^4	7.03×10^4	5.8
HDPE-B/0.05 wt % Di-cup	1.23×10^4	6.78×10^4	5.5
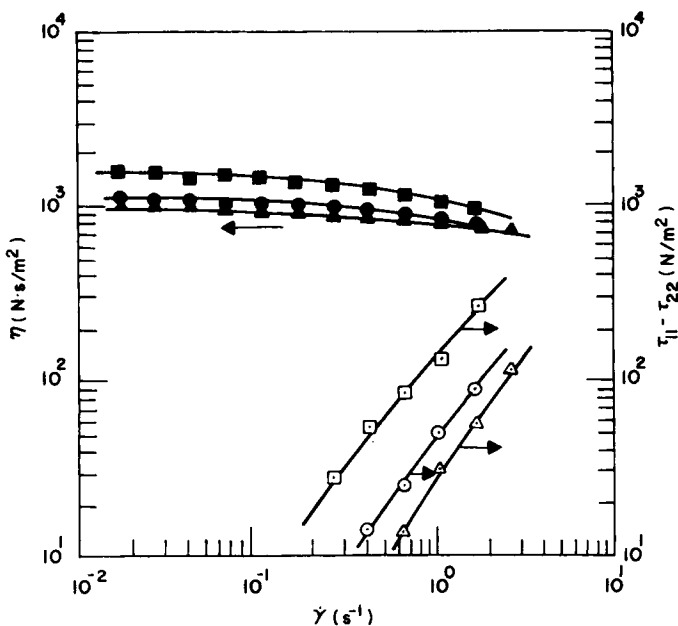
Fig. 5. η and $\tau_{11}-\tau_{22}$ vs. $\dot{\gamma}$ at 180°C: (▲,△) virgin LDPE-B; (●,⊙) LDPE-B/0.01 wt % Di-cup; (■,□) LDPE-B/0.02 wt % Di-cup.

Rheological Properties of the Polyethylenes Modified with Dicumyl Peroxide

Plots of viscosity (η) and first normal stress difference ($\tau_{11} - \tau_{22}$) versus shear rate ($\dot{\gamma}$) are given in Figure 5 for the LDPE-B at 180°C with and without dicumyl peroxide, and in Figure 6 for HDPE-B at 160°C with and without dicumyl peroxide. It is seen that both η and $\tau_{11} - \tau_{22}$ increase with the amount of Di-cup added. Interestingly enough, however, Figure 5 shows that at high shear rates the viscosity of the modified HDPE-B tends to be lower than that of the pure HDPE-B.

Figures 7 and 8 show the effect of melt temperature on η and $\tau_{11} - \tau_{22}$ for the modified LDPE-B and modified HDPE-B, respectively. Space limitations here do not permit us to present similar results for other materials. It is seen that, as the temperature is increased, both η and $\tau_{11} - \tau_{22}$ are decreased.

It is often very convenient to have rheological correlations which would become independent of temperature. Figures 9 and 10 give plots of reduced viscosity η/η_0 vs. $a_T\dot{\gamma}$ for virgin and modified LDPE-A and HDPE-B, respectively, in which η_0 is the zero-shear viscosity and a_T is a shift factor that is *empirically* obtained by shifting the viscosity curves at various temperatures to the viscosity curve at a reference temperature. It is quite evident that shear-thinning behavior becomes more intense as the amount of Di-cup is increased.

Other correlations have also been suggested to obtain temperature-independent viscosity master curves.[12–16] We have attempted to test some of those correlations, using the data obtained in the present investigation. Figure 11 gives plots of reduced viscosity η/η_0 vs. $\eta_0\dot{\gamma}$, suggested by Vinogradov and Malkin,[12] for virgin and modified HDPE-B. We have prepared similar plots for other
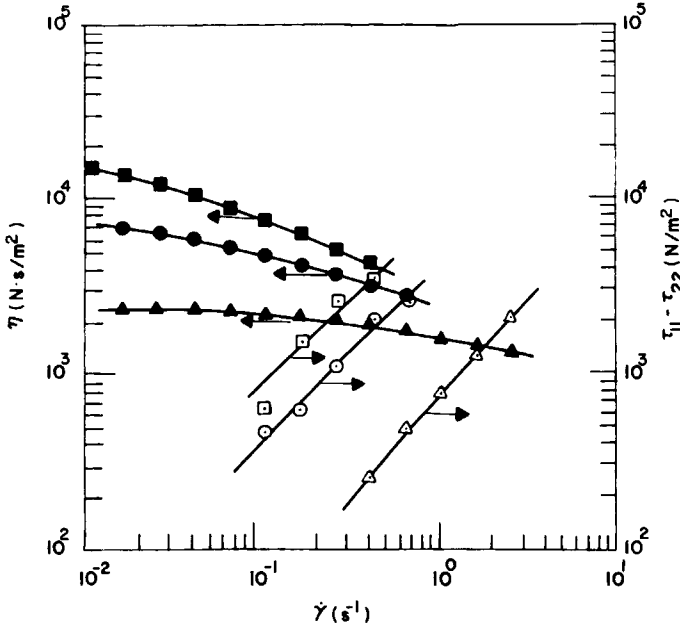
Fig. 6. η and $\tau_{11}-\tau_{22}$ vs. $\dot{\gamma}$ at 160°C: (▲,△) virgin HDPE-B; (●,○) HDPE-B/0.03 wt % Di-cup; (■,▢) HDPE-B/0.05 wt % Di-cup.

polymers (HDPE-A, LDPE-A, and LDPE-B), but space limitations here do not permit us to present those results.   It is seen that the correlations shown in Figure 11 are *not* as good as those shown in Figures 9 and 10.

We have also determined the shift factor a_T, defined by the Arrhenius relationship:

$$a_T = \exp\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right] \tag{2}$$
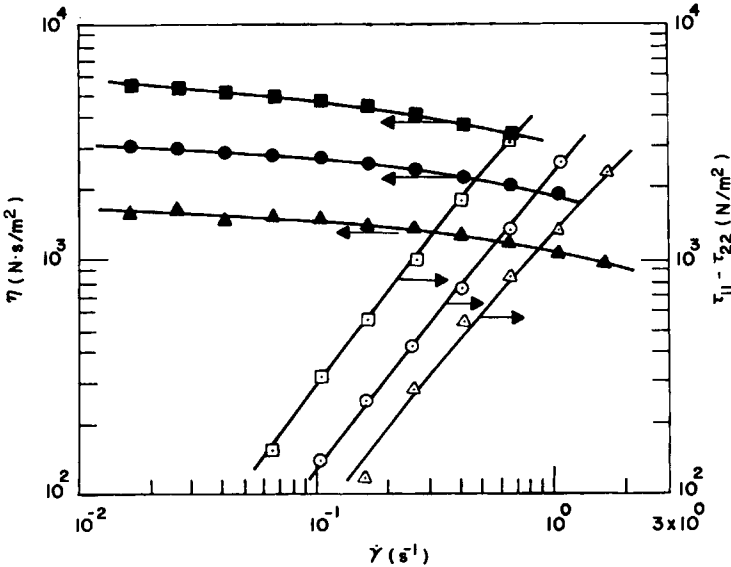
Fig. 7. η and $\tau_{11}-\tau_{22}$ vs. $\dot{\gamma}$ for LDPE-B/0.02 wt % Di-cup at various melt temperatures (°C): (▲,△) 180; (●,○) 160; (■,▢) 140.
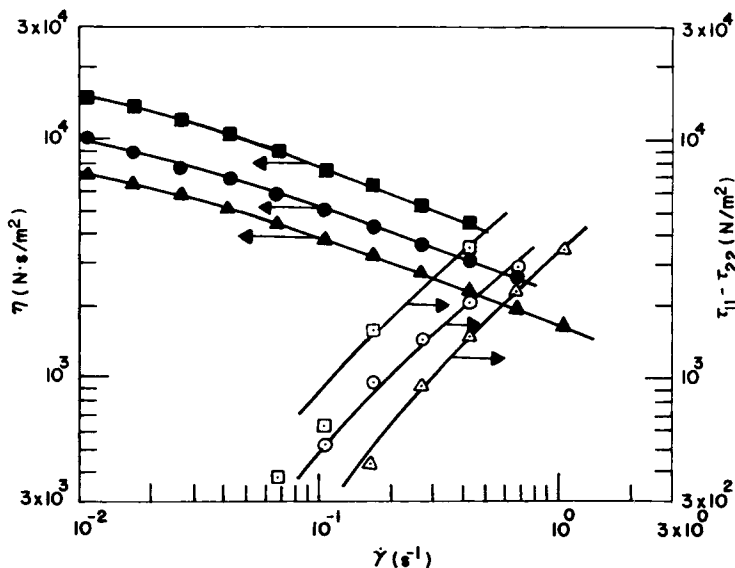
Fig. 8. η and $\tau_{11}-\tau_{22}$ vs. $\dot{\gamma}$ for HDPE-B/0.05 wt % Di-cup at various melt temperatures (°C): ($\blacktriangle,\triangle$) 200; ($\bullet,\circ$) 180; ($\blacksquare,\square$) 160.

in which E is the flow activation energy, R is the universal gas constant, T is absolute temperature, and T_R is a reference temperature. Mendelson[13] reported that the use of eq. (2) gave a good correlation when applied to his polyolefin data. However, when using eq. (2), the data we report in Figures 5–8 have *not* yielded as satisfactory correlations as those empirical correlations given in Figures 9 and 10. The scatter of data in the use of eq. (2) was about the same as that observed in the use of the Vinogradov–Malkin correlation (see Fig. 11).

We have attempted to test the usefulness of the Bueche theory[14]:

$$\frac{\eta}{\eta_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{N} \frac{\lambda_w^2 \dot{\gamma}^2}{n^2(n^4 + \lambda_w^2 \dot{\gamma}^2)} \left(2 - \frac{\lambda_w^2 \dot{\gamma}^2}{n^4 + \lambda_w^2 \dot{\gamma}^2}\right) \tag{3}$$
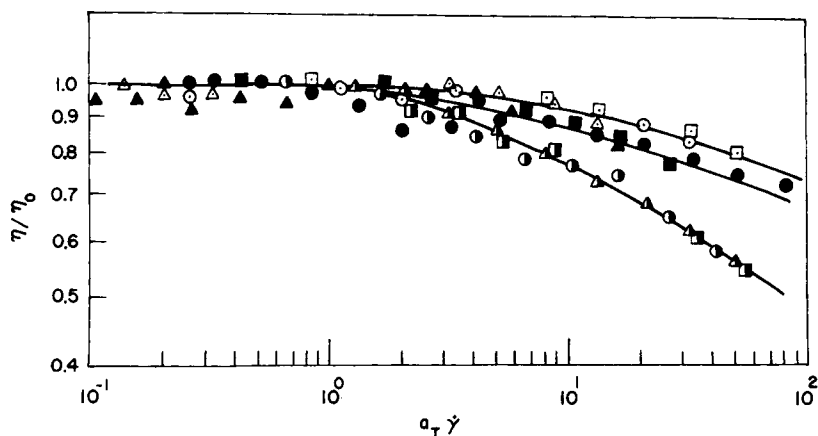
Fig. 9. η/η_0 vs. $a_T\dot{\gamma}$: (a) for virgin LDPE-A at 180°C ($\odot$), at 160°C ($\triangle$), and at 140°C ($\square$); (b) for LDPE-A/0.01 wt % Di-cup at 180°C ($\bullet$), at 160°C ($\blacktriangle$), and at 140°C ($\blacksquare$); (c) for LDPE-A/0.05 wt % Di-cup at 180°C ($\mathbf{O}$), at 160°C ($\blacktriangle$), and at 140°C ($\blacksquare$).

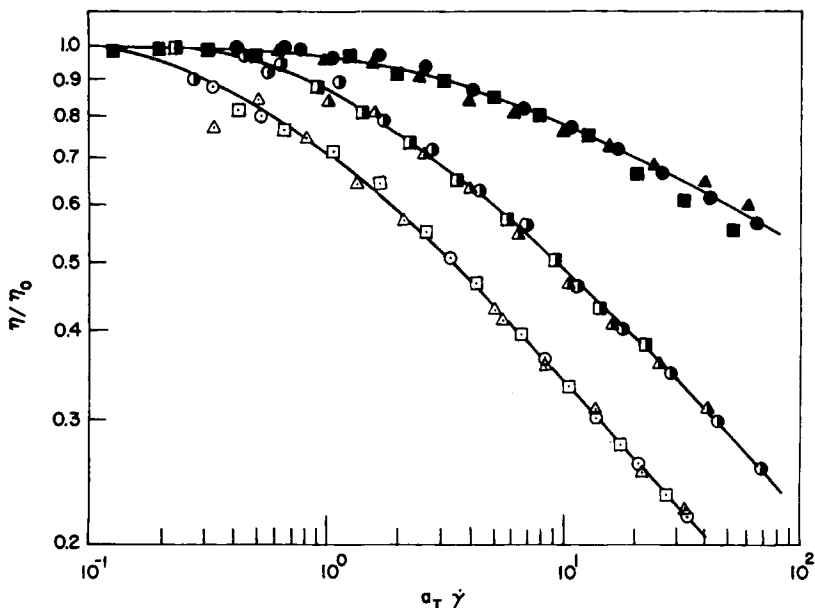Fig. 10. η/η_0 vs. $a_T\dot{\gamma}$: (a) for virgin HDPE-B at 200°C (●), at 180°C (▲), and at 160°C (■); (b) for HDPE-B/0.03 wt % Di-cup at 200°C (◐), at 180°C (▲), and at 160°C (◨); (c) for HDPE-B/0.05 wt % Di-cup at 200°C (⊙), at 180°C (△), and at 160°C (□).

where λ_w is the relaxation time defined by

$$\lambda_w = \frac{12\,\eta_0\overline{M}_w}{\pi^2\rho(T)RT} \tag{4}$$

Although the Bueche theory was developed for monodisperse polymers, we have used the weight-average molecular weight $\overline{M}_w$ in determining λ_w defined by eq. (4). Figures 12 and 13 give correlations obtained for LDPE-A and HDPE-B, respectively, before and after reacting with dicumyl peroxide. Earlier, Middleman[16] employed the number-average molecular weight $(\overline{M}_n)$ in using the Bueche theory.

In determining λ_w we have used the values of $\overline{M}_w$ given in Tables IV and V, and have calculated the density $\rho(T)$, using the following expression:

$$\rho(T) = \frac{28}{26.768 + 2.05 \times 10^{-2}\,T} \tag{5}$$

in which T is absolute temperature (°K). Note that eq. (5) was derived using the Simha–Boyer theory summarized in the monograph by Van Krevelen.[17] It is seen in Figures 12 and 13 that remarkably good correlations, independent of molecular weight and temperature, are obtained for all the resins tested.

In order to prepare a temperature-independent master curve of $\tau_{11} - \tau_{22}$, we have prepared plots of $\tau_{11} - \tau_{22}$ vs. shear stress τ_w, as suggested by Han.[9,18] Figures 14 and 15 give such plots for virgin and modified LDPE-A and HDPE-B, respectively. It is seen that such correlations are remarkably good. It can be concluded from Figures 14 and 15 that the resin becomes more elastic as the amount of Di-cup is increased. It should be noted that, earlier, plots of $\tau_{11} - \tau_{22}$ vs. τ_w were used by Han and co-workers[9,18-20] and White and co-workers,[21-24]

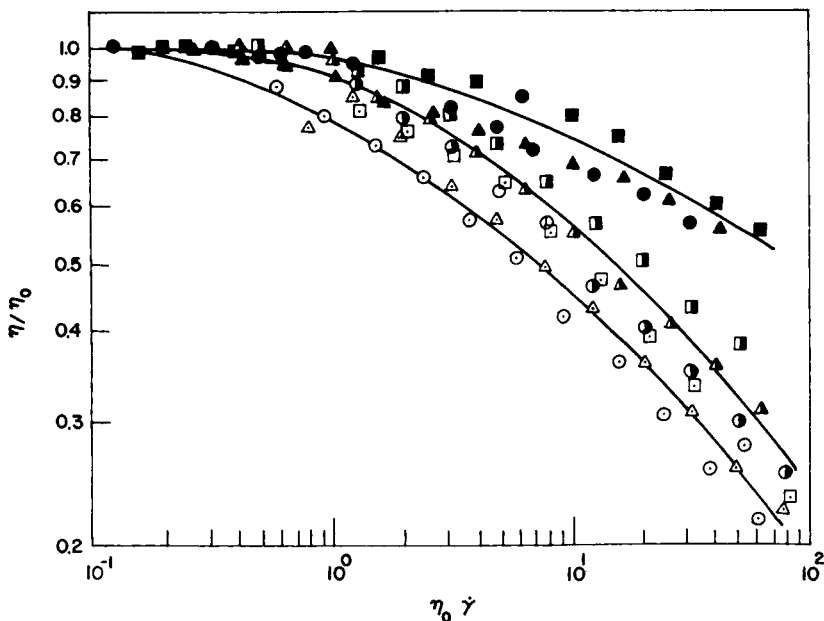Fig. 11. η/η_0 vs. $\eta_0\dot{\gamma}$: (a) for virgin HDPE-B at 200°C (●), at 180°C (▲), and at 160°C (■); (b) for HDPE-B/0.03 wt % Di-cup at 200°C (◑), at 180°C (▲), and at 160°C (▣); (c) for HDPE-B/0.05 wt % Di-cup at 200°C (⊙), at 180°C (△), and at 160°C (▫).

who dealt with homopolymers, polymer blends, highly filled thermoplastics and rubber-modified thermoplastics.

The experimental results of both η and $\tau_{11} - \tau_{22}$ for the modified polyethylenes investigated here have prompted us to suggest that they might have formed rubberlike networks as well as somewhat flexible long-chain branchings. When modification yields gel particles (i.e., crosslinking occurs), discrete particles may be formed and dispersed in the matrix, as postulated by Narkis and Miltz.[8] In
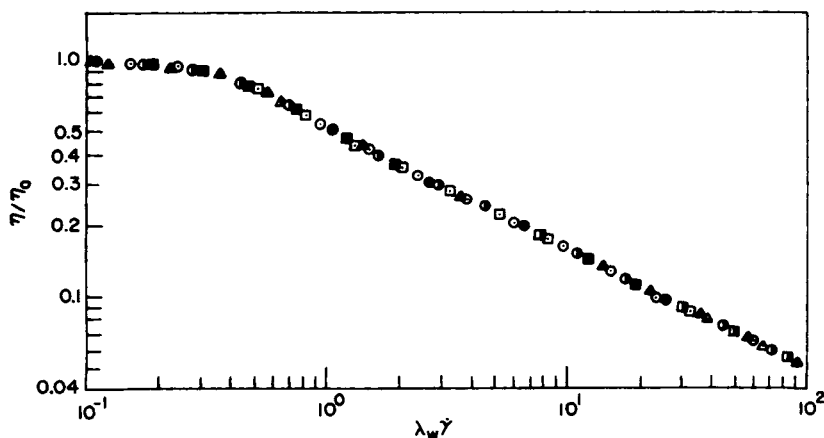
Fig. 12. η/η_0 vs. $\lambda_w\dot{\gamma}$: (a) for virgin LDPE-A at 180°C (⊙), at 160°C (△), and at 140°C (▫); (b) for LDPE-A/0.01 wt % Di-cup at 180°C (●), at 160°C (▲), and at 140°C (■); (c) for LDPE-A/0.05 wt % Di-cup at 180°C (◑), at 160°C (▲), and at 140°C (▣).
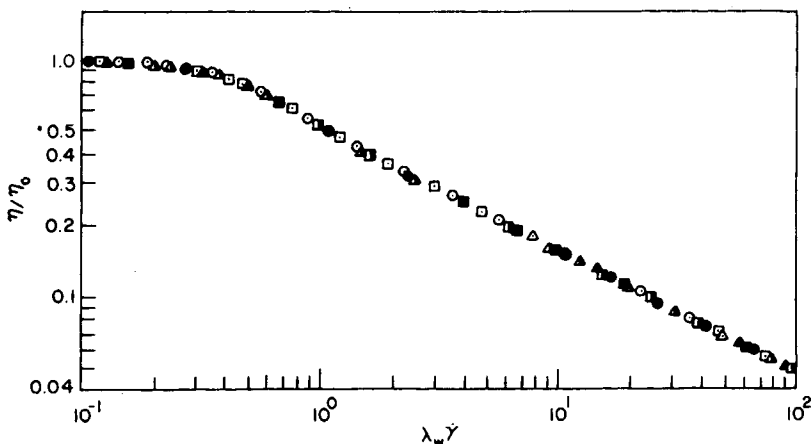
Fig. 13. η/η_0 vs. $\lambda_w\dot{\gamma}$:   (a) for virgin HDPE-B at 200°C ($\odot$), at 180°C ($\triangle$),and at 160°C ($\boxdot$); (b) for HDPE-B/0.03 wt % Di-cup at 200°C ($\ominus$), at 180°C ($\blacktriangle$), and at 160°C ($\boxminus$); (c) for HDPE-B/0.05 wt % Di-cup at 200°C ($\bullet$), at 180°C ($\blacktriangle$), and at 160°C ($\blacksquare$).

such an instance, the increase in normal stresses ($\tau_{11} - \tau_{22}$) observed here is not expected.   This is because the normal stresses of two-phase polymeric systems containing either rigid particles or barely deformable rubber particles (e.g., high-impact polystyrene), when plotted against τ_w, are expected to decrease as the amount of the discrete phase is increased.[9,23,24]

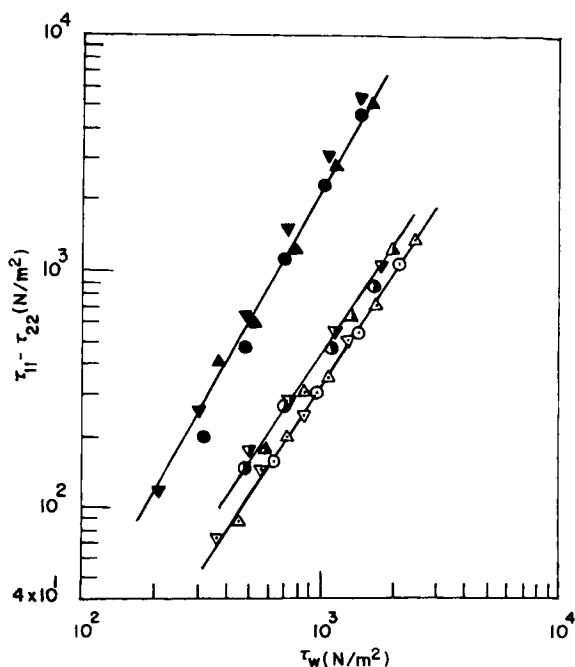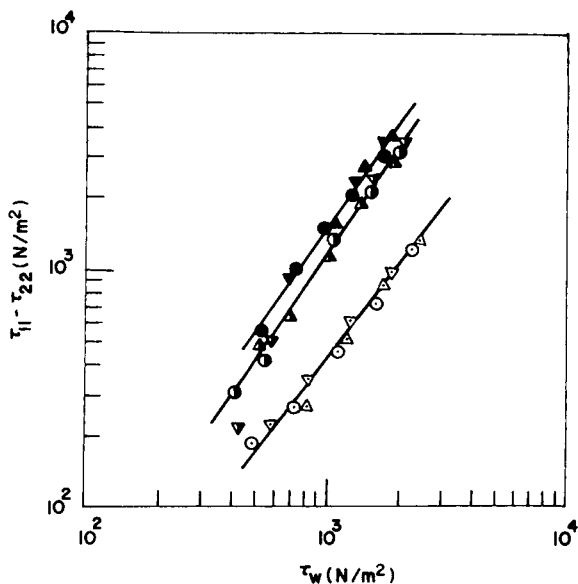Figures 16 and 17 give plots of dynamic viscosity (η') and storage modulus (G')

Fig. 14. $\tau_{11}-\tau_{22}$ vs. τ_w: (a) for virgin LDPE-A at 180°C ($\triangledown$), at 160°C ($\odot$), and at 140°C ($\triangle$); (b) for LDPE-A/0.01 wt % Di-cup at 180°C ($\blacktriangledown$), at 160°C ($\ominus$), and at 140°C ($\blacktriangle$); (c) for LDPE-A/0.05 wt % Di-cup at 180°C ($\blacktriangledown$), at 160°C ($\bullet$), and at 140°C ($\blacktriangle$).

Fig. 15. $\tau_{11}-\tau_{22}$ vs. τ_w: (a) for virgin HDPE-B at 200°C ($\triangledown$), at 180°C ($\odot$), and at 160°C ($\triangle$); (b) for HDPE-B/0.03 wt % Di-cup at 200°C ($\blacktriangledown$), at 180°C ($\oplus$), and at 160°C ($\blacktriangle$); (c) for HDPE-B/0.05 wt % Di-cup at 200°C ($\blacktriangledown$), at 180°C ($\bullet$), and at 160°C ($\blacktriangle$).

vs. frequency (ω) for virgin and modified LDPE-B and HDPE-B, respectively. The purpose of presenting these figures is to show the influence of dicumyl peroxide on both the viscous and elastic properties of the modified polyethylenes. Measurements were also taken at other temperatures, but space limitations here do not permit us to present those results. A close examination of Figures 16 and
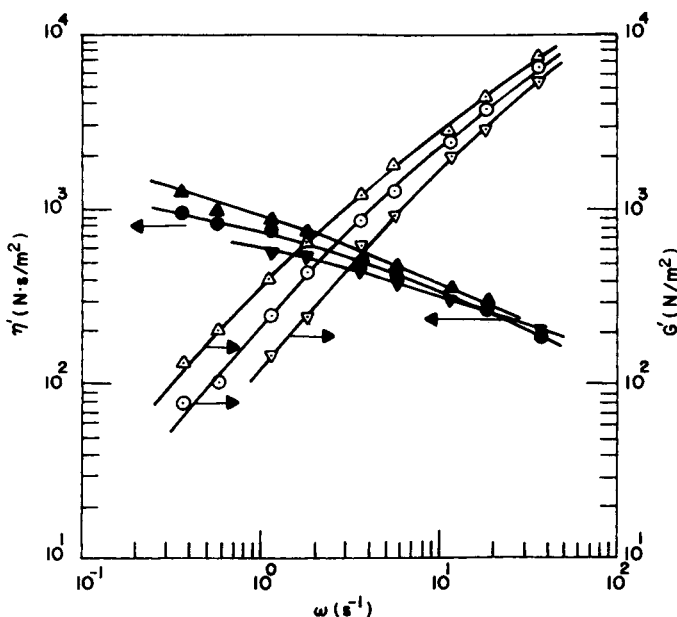

Fig. 16. η' and G' vs. ω at 180°C: ($\blacktriangledown,\triangledown$) virgin LDPE-B; ($\bullet, \odot$) LDPE-B/0.01 wt % Di-cup; ($\blacktriangle,\triangle$) LDPE-B/0.02 wt % Di-cup.
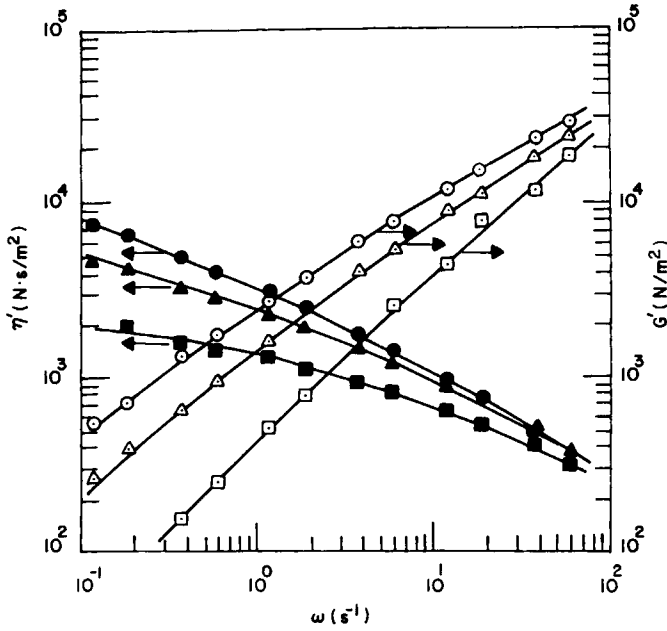
Fig. 17. η' and G' vs. ω at 160°C: (■, ▣) virgin HDPE-B; (▲,△) HDPE-B/0.03 wt % Di-cup; (●,○) HDPE-B/0.05 wt % Di-cup.

17 leads us to make the following observations: (1) at low values of ω, η' increases with the amount of peroxide used; (2) at high values of ω, the decrease in η' becomes greater as the amount of the peroxide used is increased; (3) G' increases
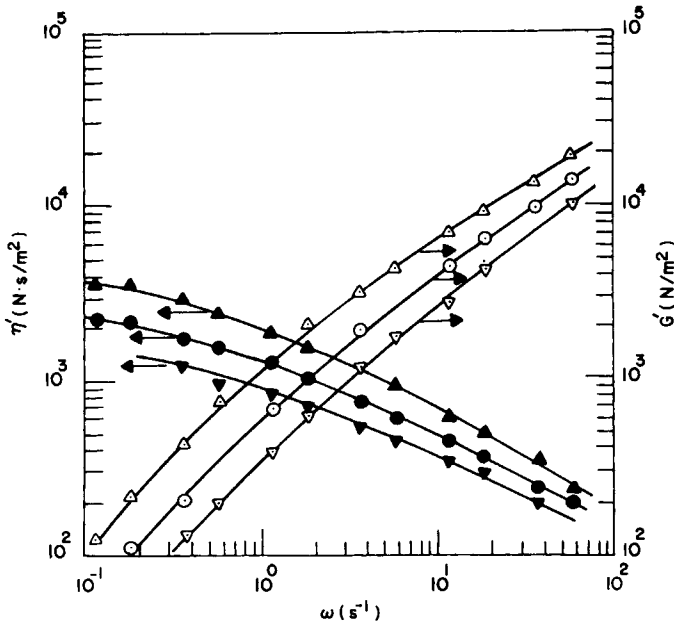

Fig. 18. η' and G' vs. ω for LDPE-B/0.02 wt % Di-cup at various melt temperatures (°C): (▼,▽) 180; (●,○) 160; (▲,△) 140.
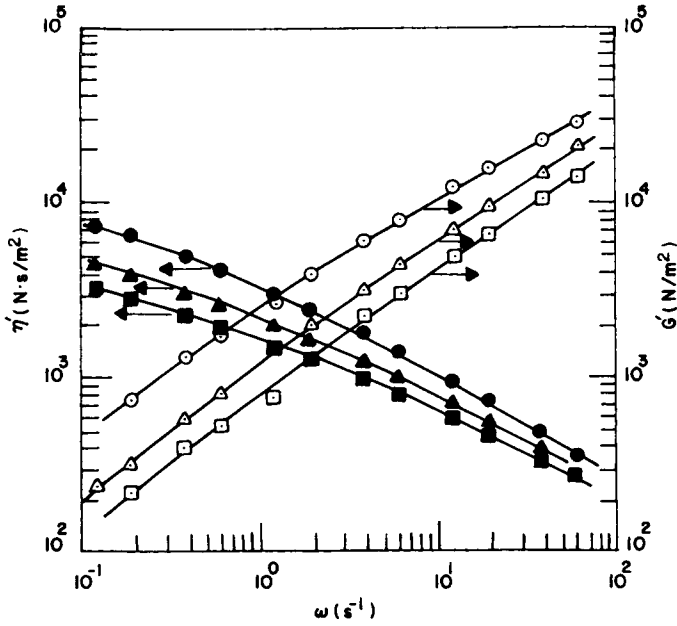
Fig. 19. η' and G' vs. ω for HDPE-B/0.05 wt % Di-cup at various melt temperatures (°C): (■,◻) 200; (▲,△) 180; (●,○) 160.

with the amount of the peroxide used. These observations are in agreement with those based on steady shearing flow measurements discussed above (see Figs. 5 and 6).
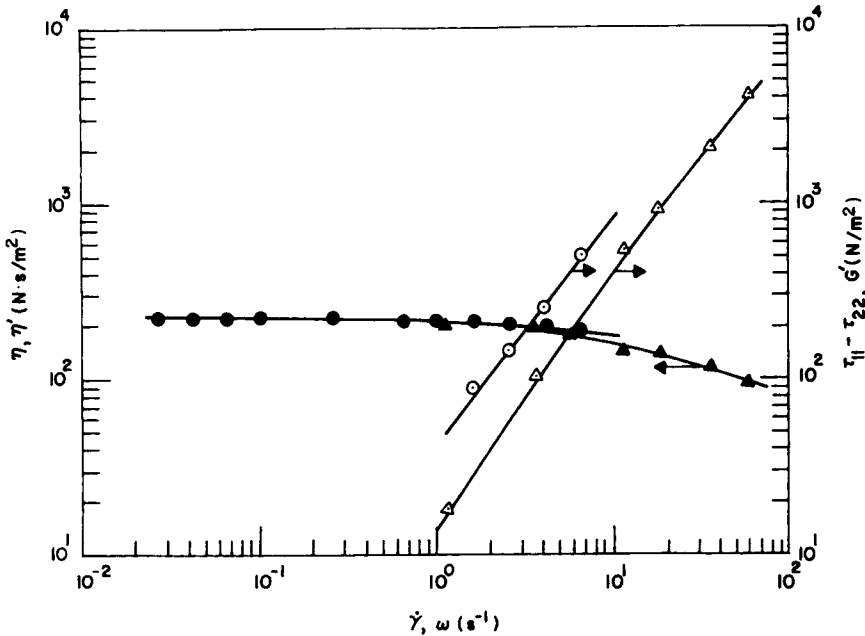

Fig. 20. η and $\tau_{11}—\tau_{22}$ vs. $\dot\gamma$ and η' and G' vs. ω for virgin LDPE-A at 180°C: (●,○) steady shearing flow data; (▲,△) oscillatory shearing flow data.
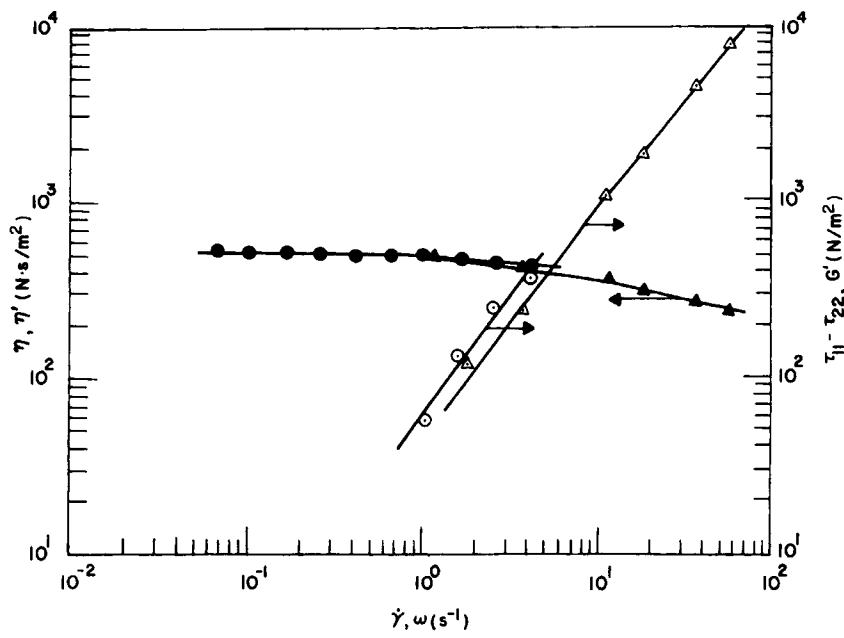
Fig. 21. η and $\tau_{11}-\tau_{22}$ vs. $\dot{\gamma}$ and η' and G' versus ω for virgin HDPE-A at 180°C: ($\bullet$,$\odot$) steady shearing flow data; ($\blacktriangle$,$\triangle$) oscillatory shearing flow data.

Figures 18 and 19 show the effect of melt temperature on η' and G' for modified LDPE-B and modified HDPE-B, respectively. Again space limitations here do not permit us to present similar plots for other materials tested. It is seen that, as the temperature is increased, both η' and G' are decreased. This trend is in agreement with that based on the steady shearing flow measurements discussed above (see Figs. 7 and 8).

It is worth mentioning that, although some attempts were made in the past to relate the rheological data obtained in oscillatory shearing flow to that obtained in steady shearing flow, there exists no rigorous theory that relates the two, except at extremely low shear rates or frequencies, that is,

$$\lim_{\omega \to 0} \eta'(\omega) = \lim_{\dot{\gamma} \to 0} \eta(\dot{\gamma}) \tag{6}$$

$$\lim_{\omega \to 0} G'(\omega)/\omega^2 = \lim_{\dot{\gamma} \to 0} (\tau_{11} - \tau_{22})/2\dot{\gamma}^2 \tag{7}$$

Figures 20 and 21 give both steady and oscillatory shearing flow data for virgin polyethylenes, which seem to support the theoretical predictions given by eqs. (6) and (7).

CONCLUDING REMARKS

It has been demonstrated in this paper that, by controlling the amount of organic peroxide used in modifying polyethylenes, one can obtain new resins which may be less viscous (especially at high shear rates) and yet more elastic than the virgin resin. The concentration of dicumyl peroxide used in the present investigation was low enough not to yield insoluble gel particles in the modified resins.

Therefore, the new resins produced in the present investigation may be considered to have resulted from chain extension, rather than from crosslinking. The usefulness of such modified resins in improving the physical/mechanical properties of virgin resins is yet to be investigated. Polymer processing operations, such as wire coating extrusion, rotational molding, blow molding, and foam extrusion may be worth investigating with the concept developed in this paper.

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