

Studies of Some Peculiar Effects of Temperature on Molten High-Density Polyethylene Properties

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Synopsis

Many HDPE samples show peculiar behavior of melt viscosity at low shear rate and melt strength at constant extrusion rate in a temperature region of about 200° to 250°C. It was found that the degree of the peculiarity of the behavior was affected by temperature, residence time at a temperature, the temperature rise rate, and the kind and quantities of additives. It was concluded that the peculiar effects were due to the crosslinking that a chemical reaction produced. An attempt was made to express the different behaviors of temperature dependence of melt viscosity among many HDPE samples by some simplified equations. It is suggested that both the peculiar changes with temperature of the melt viscosity and those of the melt strength may be produced by the same mechanism. The similarity of the phenomena between HDPE samples exposed to high temperatures and those crosslinked by γ -rays was found. Finally, a possibility is discussed of predicting the processability of the resin and properties of final products before the processing operation.

INTRODUCTION

In the processing of polymer melts, the suitable selection of melt temperature is a very important matter. Firstly, melt temperature determines both the viscosity and the elasticity of polymer melts. These rheological properties are connected with the processability of the polymers. On the other hand, the processing temperature is one of the most important factors which influence the surface characteristics and mechanical properties of final products formed from melts.

Satisfactory understanding of these problems, however, is hindered and difficult in practice, because of the complicated manner in which melt temperature influences processability and the properties of final products. Many questions remain unsolved in this field. It is important that they are clarified from both the industrial and scientific points of view.

On performing various operations in processing of many high-density polyethylenes (HDPE) or rating physical properties of the products obtained, we have frequently met with apparently mysterious or undesirable phenomena and results. A few examples are described below:

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1. Extrusion coating of HDPE on metal was tried. Elevating the setting temperature of extruder to increase the fluidity of resin produced worse products at the higher temperature.

2. In blow molding, a slight change of the setting temperature of the extruder or the residence time of the resin varied some mechanical properties of final products.

3. Dependent upon the kind of stabilizers used in extrusion and blow molding, the skin appearance of the film and the bottle varied in quality over a wide range.

4. After passing through the extruder, the resin had a melt index which was considerably lower as compared with the original resin.

The primary factors responsible for these phenomena or results need to be found. It is very important to become capable of selecting more effective processing conditions or better polymerization processes. From this standpoint, we have attempted to measure temperature dependence of basic physical properties of HDPE melts over a wide temperature range.

These studies have already been done on poly(vinyl chloride) (PVC)¹⁻³ and polypropylene (PP)⁴ by some workers. Some reported that both PVC² and PP⁴ used in their studies showed one or more transitions in relationship between the logarithm of melt viscosity at constant shear rate or shear stress and reciprocal absolute temperature.

With HDPE, however, there have been few reports. Hori et al.⁵ found peculiar effects in the temperature dependence of the melt strength and the flow quantity per minute under a constant load of HDPE. They ascribed those effects to thermal degradation. The mechanism of this thermal degradation and its primary factors, however, were not clarified.

We have also found similar peculiar effects in many HDPE systems from the measurement of the temperature dependence of the melt viscosity at constant low shear rate and melt strength at constant extrusion rate. In this paper, we first introduce several examples of these peculiar effects, and then present a rough mechanism for the occurrence of the effects. An attempt to express the peculiar effects of the melt viscosity-temperature relationships of many HDPE's by a simplified equation is also described. Some similarities of the behaviors are also shown between γ -ray-crosslinked HDPE samples and those exposed to high temperature. Finally, the correlations of the peculiar effects of basic rheological properties of HDPE melts with the processability of resins and properties of final products are briefly discussed.

EXPERIMENTAL

Samples

HDPE samples used were Hizex (polymerized by the Ziegler method), Sholex (Phillips method), and Nissan (Wacker method). Basic physical properties of these samples are listed in Table I. Additives used as anti-oxidants and thermal stabilizers are BHT (4-methyl-2,6-di-*tert*-butylphenol);

TABLE I
Basic Physical Properties of HDPE Samples

Samples	Density ^a	MI_2 , ^b g/10 min	\bar{M}_v ^c $\times 10^{-4}$	$-\text{CH}_3/$ 1000 C ^d	$-\text{CH}=\text{CH}-/$ 1000 C ^e	$-\text{CH}=\text{CH}_2/$ 1000 C ^f	$>\text{C}=\text{CH}_2/$ 1000 C ^g	T_g , ^h ppm
Hizex A	0.9601	0.33	14.9	4.3	0.00	0.04	0.02	8
Hizex B	0.9520	0.35	13.9	3.9	0.12	0.40	0.06	64
Hizex C	0.9610	0.30	16.8	3.8	0.00	0.00	0.00	
Hizex D	0.9521	0.42	15.3	3.7	0.11	0.46	0.05	51
Sholex E	0.9636	0.53	13.8	2.0	0.00	0.79	0.00	
Nissan G	0.9533	0.79	15.2	4.3	0.05	0.63	0.06	9
Nissan H	0.9507	0.17	19.3	4.7	0.07	0.58	0.09	10

^a Obtained according to JIS K6760.

^b Obtained according to JIS K6760.

^c Calculated from the intrinsic viscosity in decalin at 135°C, by Chiang's equation.⁶

^d Obtained according to ASTM D 2238-64T, using infrared spectroscopy.

^{e,f,g} Obtained by infrared spectroscopy.⁷

^h Obtained by x-ray fluorescence analysis.

Yoshitomi Pharmaceutical Co., Ltd.), Ionox 330 (1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene; Shell Chemical Co., Ltd.), Ethyl 702 (4,4'-methylenebis(2,6-di-*tert*-butyl phenol); Ethyl Chemical Co., Ltd.), and Irganox 1010 (tetrakis[methylene-3-(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)propionate] methane; Chiba Geigy Co., Ltd.). Some samples contained calcium stearate (Ca-St), the scavenger of hydrogen chloride from the polymerization process.

Measurement of Melt Viscosity

For the measurement of melt viscosity, an Almighty Rheometer of Iwamoto Seisakusho Co., Ltd., was used as a cylindrical rotational viscometer. The outer cylinder used is 1.1 cm in radius and 7.1 cm in height. Two kinds of inner cylinders were used, one 0.8 cm and the other 0.9 cm in radius. After a sample was charged in the outer cylinder, usually at 170°C to 180°C, the equipment was immediately closed and deaerated under vacuum and filled with nitrogen to air pressure. The sample having melted, a inner cylinder was immersed slowly in the outer cylinder. For the exclusion of the end effect, immersing the inner cylinder to a position lower than 10 mm from the bottom of the outer cylinder was avoided. The measurement was begun after the resin temperature had become homogeneous in the gap between the inner and outer cylinder.

As the outer cylinder was rotated at constant angular velocity, the steady value of torque, which was imposed on the inner cylinder by the sample, was detected by a recorder, on the basis of which the apparent melt viscosity of the resin was calculated. The rotational angular velocity of the outer cylinder was usually fixed at about 1.53×10^{-3} rad/sec, a value corresponding to the values of the shear rate at the outer cylinder wall of about 9.30×10^{-3} sec⁻¹ and 6.70×10^{-3} sec⁻¹ in the inner cylinder radii of 0.9 cm and 0.8 cm, respectively. After the measurement at a temperature was over, the resin temperature was elevated by about 10°C for about 10 min, and the measurement of the melt viscosity was again done at that elevated temperature. In this way the measurement of the melt viscosity was done at about every 10°C usually over the temperature range of about 170°C to 280°C.

Measurement of Melt Strength

Melt strength was measured with a Melt Tension Tester of Toyo Seilki Seisakusho, Ltd. (Fig. 1). A resin melted in a reservoir of cylinder at a fixed temperature was extruded at constant rate with the piston from the orifice seen in Figure 1, the extruded resin being drawn into a filament by a winding roll. The strength of the resin in the filament state, or the melt strength, was determined by means of a strain gauge. The resin was usually extruded after 5 min of residence in the reservoir. To measure temperature dependence of the melt strength, the sample was charged newly at each temperature. The measurement was done without deaeration and subsequent admission of nitrogen, since this equipment is not devised to be closed up entirely.

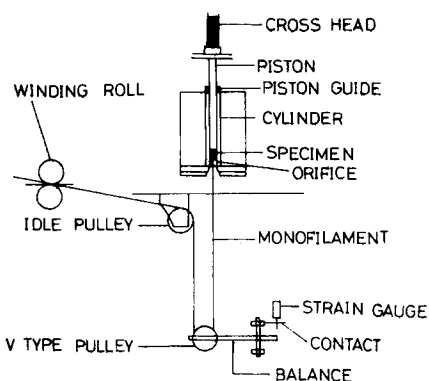


Fig. 1. Schematic diagram of the Melt Tension Tester.

The rate of extrusion was usually 20 mm/min. The orifice used is about 1.045 mm in radius and 8.004 mm in length. Under these conditions, the apparent shear rate at the wall of the orifice is about 27.6 sec^{-1} .

RESULTS AND DISCUSSION

Temperature Dependence of Melt Viscosity and Melt Strength

Peculiar Effects In Melt Viscosity-Temperature Relationship

In Figure 2, the temperature dependence of the melt viscosity at constant shear rate is shown for several Hizex samples. As seen in Figure 2, not all of the temperature-viscosity relations of these samples follow an Andrade-type relation

$$\eta = A \exp\left(\frac{E_a}{RT}\right)$$

where η is viscosity, E_a is activation energy, R is gas constant, and T is absolute temperature. Moreover, the aspects of those relations are not

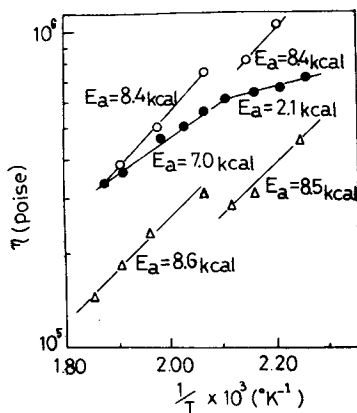


Fig. 2. Viscosity-temperature relations at constant shear rate of $6.70 \times 10^{-3} \text{ sec}^{-1}$ for various Hizex polyethylenes: (O) Hizex B; (●) Hizex C; (Δ) Hizex D.

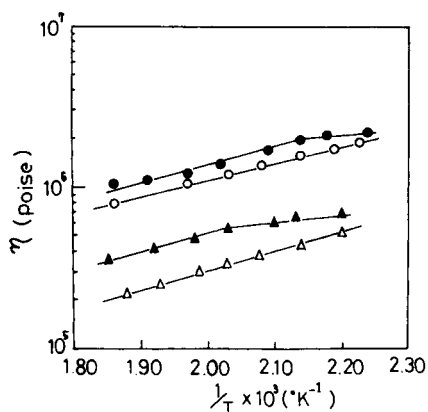


Fig. 3. Viscosity-temperature relations at constant shear rate of $9.30 \times 10^{-2} \text{ sec}^{-1}$ for Nissan polyethylene systems of additives and no additives: (○) Nissan H, 0.05 phr BHT and 0.07 phr Ca-St; (●) Nissan H, 0.07 phr of Ca-St; (△) Nissan G, 0.05 phr BHT and 0.07 phr Ca-St; (▲) Nissan G, no additives.

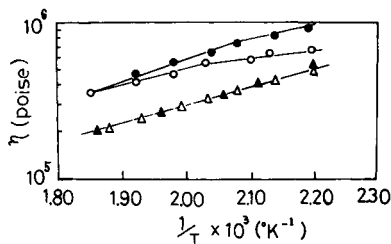


Fig. 4. Reversibility of temperature dependence of melt viscosity at constant shear rate of $9.30 \times 10^{-2} \text{ sec}^{-1}$ for various Nissan polyethylene systems: (○, ●) Nissan G, no additives (Nissan G-1); (△, ▲) Nissan G, 0.05 phr BHT (Nissan G-2); (○, △) measured raising temperature; (●, ▲) measured lowering temperature.

necessarily the same among all samples, for example, between B and C. With Nissan PE, the comparison of the types of temperature-viscosity relation between systems containing additives of known quantities and containing no additives gave results as shown in Figure 3. Though one Andrade-type relation was found with each of the systems containing BHT, each of the systems containing no BHT showed the existence of separate Andrade-type relations in the low- and high-temperature regions, respectively, and at the same time gave higher melt viscosity values than those containing BHT at all temperatures measured. From this, the complicated aspects of viscosity-temperature relation seen in Figure 2 may be due to a chemical reaction of polymer chains for which active species as radicals are responsible. (Henceforth, we shall call the discontinuity in the Andrade-type relation of the melt viscosity "melt transition" for brevity.)

Hori et al.⁵ used the expression "physical reversible crosslinking similar to entanglement" to explain peculiar changes of melt strength and flow quantity in the high-temperature region. In Figure 4, a disagreement of

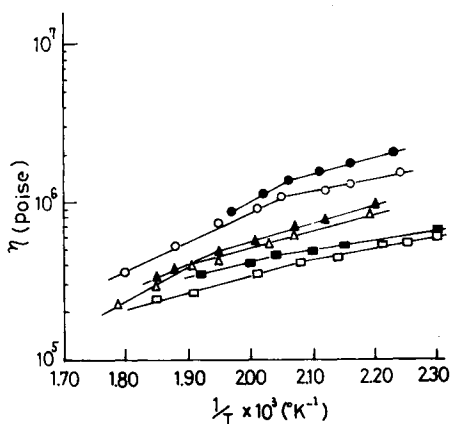


Fig. 5. Viscosity-temperature relations in nitrogen and oxygen at constant shear rate of $9.30 \times 10^{-3} \text{ sec}^{-1}$ for various HDPE: (○, ●) Hizex A; (△, ▲) Sholex E; (□, ■) Nissan G; (○, △, □) in nitrogen; (●, ▲, ■) in oxygen.

temperature dependence of the melt viscosity is, however, seen with systems showing the melt transition between raising temperature measured stepwise after the sample was charged at low temperature and lowering temperature again stepwise from the highest temperature attained by the preceding temperature rise measurement; while the system not showing the melt transition agreed very well between those two experimental conditions. The melt transition of HDPE thus appears to be due to a chemical reaction also from such an irreversible behavior which was found only in the system showing the transition.

From the behavior of D and B in Figure 2, it is found that the viscosity values given by the lines of the high-temperature region are higher than would be if viscosity followed the lines in the low-temperature region. On the other hand, the behavior of C gives a higher activation energy for the viscous flow in the high-temperature region than in the low-temperature region. In both cases, it is obvious that polymer melts were subjected to more resistance to the flow in the high-temperature region as compared with the low-temperature region. From these results, the thermal chemical reaction of polymer melts must have produced the crosslinking between polymer chains.

The degree of this crosslinking reaction can be thought to be affected by oxygen, the residue from the polymerization process, and the polymer structure (C=C double bond, branching, etc.). In Figure 5, all samples show higher values of melt viscosity in oxygen at all temperatures measured than in nitrogen. From this result, the crosslinking reaction of HDPE melts proves to be promoted by oxygen.

The more catalyst residues and points unstable to heat the polymer contains in the structure, the easier to degrade it will be. In Figure 2, the behavior of C having no C=C double bonds differs a little from that of B and D having many double bonds, though it is uncertain whether the

difference is truly due to double bonds. The effect of the catalyst residues on the degradation can be thought to depend upon the quantity of active catalyst residues rather than the apparent quantity. With PP, it was reported⁸ that the deactivated catalyst residues did not promote the thermal degradation of the polymer.

Peculiar Effects In Melt Strength-Temperature Relationship

The melt strength is the strength in the drawing direction of polymer melts in the filament state. This value is thought to reflect the elasticity as well as the viscosity of polymer melts.⁹ It can be used not only as an index of processability of the resin in the processing of filament, but also as an index of plastics processing generally. For example, it was found that a close correlation¹⁰ existed between the phenomenon of "neck-in" in extrusion coating and melt strength. Some relation was found also between the Barus effect, recognized as an elastic strain recovery phenomenon of polymer melts, and the melt strength.

Figure 6 shows temperature dependence of melt strength in several Nissan H samples different in the kind and quantity of additives contained. A sample having no additives shows a marked peak in a curve for melt strength change with temperature. Generally, it can be predicted that the melt strength decreases in a monotonic manner as temperature increases, because the slippage of entanglement becomes subjected to less resistance as temperature rises. However, the result of Nissan H-A in Figure 6 shows that the intermolecular forces of polymer chain grow rather

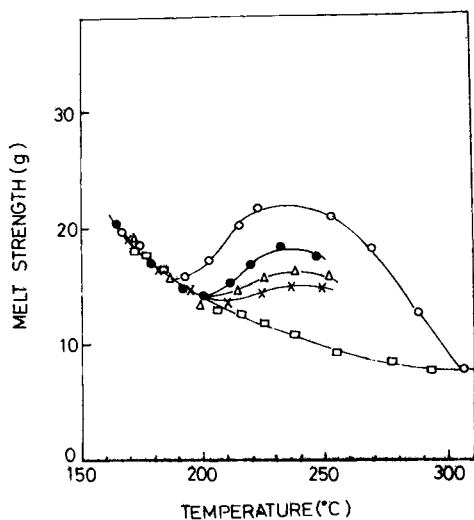


Fig. 6. Stabilizer effect on temperature dependence of melt strength at constant extrusion rate for Nissan H: (O) no additives (Nissan H-A); (●) Ca-St, 0.07 phr, Ionox 330, 0.005 phr (Nissan H-C); (Δ) Ca-St, 0.07 phr, Ionox 330, 0.01 phr (Nissan H-D); (×) Ca-St, 0.07 phr, Ionox 330, 0.03 phr (Nissan H-E); (□) Ca-St, 0.07 phr, BHT, 0.05 phr (Nissan H-B).

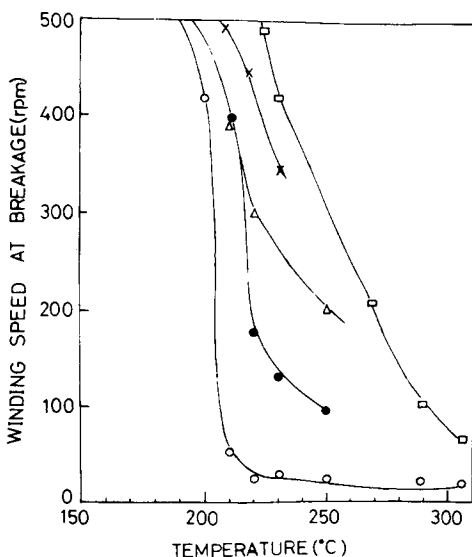


Fig. 7. Winding speed at breakage-temperature relations for various Nissan H systems of different kinds and quantities of additives; diameter of winding roll, 100 mm: (O) Nissan H-A; (●) Nissan H-C; (Δ) Nissan H-D; (X) Nissan H-E; (□) Nissan H-B.

stronger as temperature increases. This result is never normal. The height of the peak in the melt strength-temperature relation of Nissan H-A, however, becomes lower with increase in the quantity of additive Ionox 330 added to the sample. Finally, the sample BHT, 0.05 g per hundred g of resin (0.05 phr), shows no peak. Also from these facts with melt strength as well as melt viscosity, it can be concluded that HDPE produces crosslinking as the result of thermal reaction in a high-temperature region (200° to 250°C in both of these two rheological properties). From now on, this peculiar effect in melt strength-temperature relation will also be called "melt transition" for brevity.

In Figure 7, the winding speed values at breakage are plotted against temperature on each sample in Figure 6. The higher the peak of melt strength in Figure 6, the lower is the temperature at which the molten filament becomes susceptible to breakage in Figure 7. Without structure change in polymer melts, the molten resin will become apt to be drawn with temperature increase. The results in Figure 7 also show such a structure change in polymer melts as crosslinking appears in the high-temperature region. The winding speed at breakage is an important value that can be used as an index of processability of monofilaments. This value is, however, poor in reproducibility, as it is influenced obviously even by microquantity impurities.

In any case, many HDPE samples show melt transition in temperature dependence of the melt strength, while it is not seen in some HDPE systems or specific systems containing some additive.

Effect of Preheating Time in the Reservoir on Melt Strength

In Figure 6, the temperature–melt strength relation showed a marked peak in a temperature region except a system. The measurement was done at each temperature after resin residence for 5 min in the reservoir above the orifice of the melt tension tester. If the occurrence of the peak in the melt strength–temperature relation is due to a chemical reaction of polymer, we can suppose that the induction period of the chemical reaction becomes shorter as temperature increases until it becomes shorter than 5 min, and then the rise of melt strength with temperature is observed. If the residence time of the resin in the reservoir becomes longer than 5 min, at the lower temperature the peak in melt strength may be observed. Hence, we investigated the melt strength–residence time relation at constant temperature. In Figure 8, this relation obtained on Hizex A is shown for each of four temperatures, 180°C, 199°C, 219°C, and 230°C. (This sample also shows a peak in melt strength at about 230°C in case of the measurement after preheating for 5 min.)

At 180°C and 199°C, a rise in melt strength can be observed after some time lag, while at 219°C and 230°C it can be observed within 5 min. These results prove experimentally the supposition mentioned above that the occurrence of a peak in the melt strength–temperature relation at constant residence time (5 min) corresponds to the induction period of thermal reaction of HDPE less than 5 min near the peak temperature.

When a sample has an excellent thermal stability and has an induction period of thermal reaction of more than 5 min at all temperatures measured, the melt strength of the sample at constant residence time (5 min) must decrease with temperature increase over the whole temperature range measured. On the other hand, if a sample has an induction period for thermal reaction less than 5 min at all temperatures measured, in this case as well the melt strength at constant residence time (5 min) must decrease with temperature increase in the same manner as above. An ex-

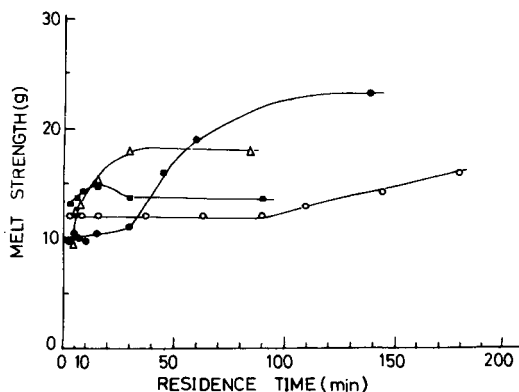


Fig. 8. Melt strength–preheating time relations at constant extrusion rate for various temperatures; resin, Hizex A: (○) 180°C; (●) 199°C; (△) 219°C; (■) 230°C.

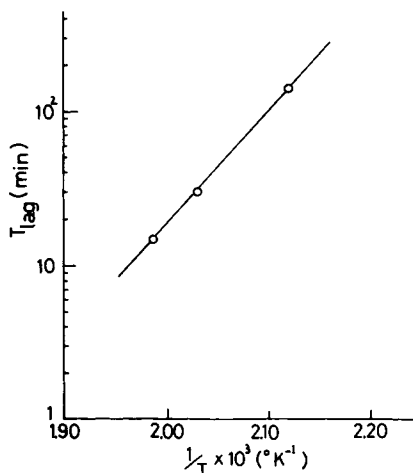


Fig. 9. Arrhenius plot of time lag for occurrence of the peculiar phenomena of HDPE melt; resin, Hizex A.

ample for the former is the result of Nissan H of BHT (0.05 phr) and Ca-St (0.07 phr) introduced already. The samples of little thermal stability may belong to the latter.

In Fig. 8, it takes a length of time after the sample has been charged to arrive at the maximum of the melt strength at each temperature. From now, this length of time will be called "time lag" (T_{lag}). The logarithm of T_{lag} is plotted against the reciprocal absolute temperature in Figure 9. In that figure, the result at 180°C is not plotted, since at that temperature the values of the melt strength have a tendency to rise still more in Figure 8. The time lag (T_{lag}) follows approximately an Arrhenius-type relation

$$T_{\text{lag}} = A \exp\left(\frac{E_a}{RT}\right)$$

E_a and A obtained from Figure 9, are 34.1 kcal and 5×10^{-32} min, respectively. These values may be used as an index of the thermal stability of resin.

Of course, the larger these values are, the more excellent the thermal stability of the resin must be.

MI₂ of Resin After Measurement of Melt Strength

The samples were collected after measurement of melt strength of Hizex A at several temperatures, and the MI₂ values were measured. Figure 10 gives these results together with the melt strength values. The fall of MI₂ is seen near the temperature of the peak of the melt strength. A similar relation between change in melt strength and that in MI₂ is seen in the residence time dependence of the melt strength at constant temperature (Fig. 11). These results may be considered to show that the

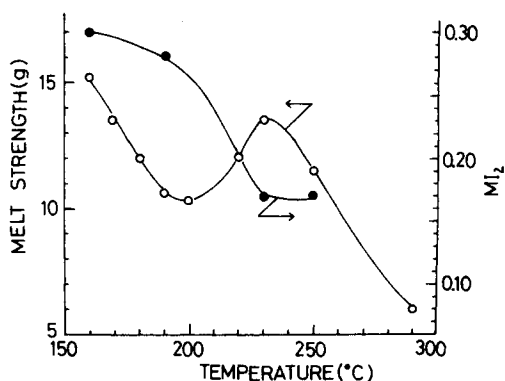


Fig. 10. Melt index of Hizex A after measurement of melt strength at several temperatures.

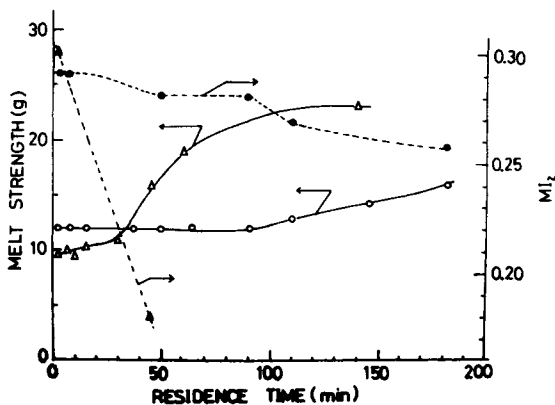


Fig. 11. Melt index of Hizex A after measurement of residence time dependence of melt strength: (O, ●) 180°C; (Δ, ▲) 199°C.

increase of the melt strength with temperature in a temperature region corresponds to the enlargement of the flow unit as made clear by the decrease in MI_2 . For example, the peak value of the melt strength at 230°C in Hizex A may have been produced by the change in flow unit that corresponds to that of MI_2 from 0.30 to 0.17 g/10 min.

Effect of the Kind of Additives on Melt Viscosity and Melt Strength

The temperature dependence of melt strength and melt viscosity of three systems with additives and one system with no additives was measured. Each of the former systems contained 0.05 phr of one of three kinds of additives as the antioxidant, BHT, Ethyl 702, Irganox 1010, and 0.07 phr of Ca-St. HDPE sample used is Nissan G. The results are shown in Figures 12 and 13. Among the three systems, it is possible to compare the extent to which the melt transition of the HDPE melts are repressed. In Figures 12 and 13, the system with BHT does not show as marked a transition as the other systems. It can be also observed that the

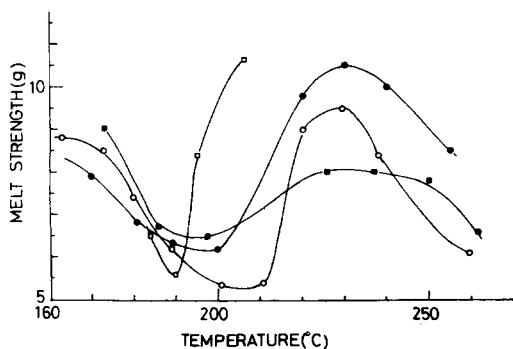


Fig. 12. Melt strength-temperature relations at constant extrusion rate for Nissan G systems of different kinds of additives and no additives: (□) no additives; (●) Irganox 1010, 0.05 phr, Ca-St, 0.07 phr; (○) Ethyl 702, 0.05 phr, Ca-St, 0.07 phr; (■) BHT, 0.05 phr, Ca-St, 0.07 phr.

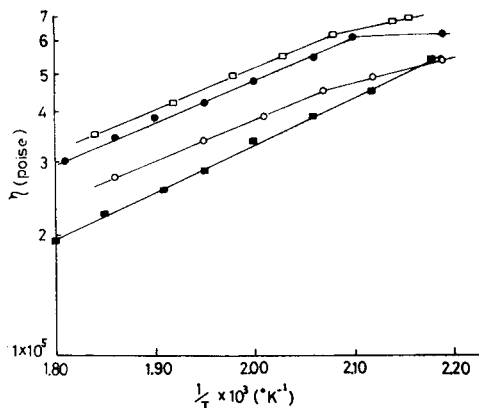


Fig. 13. Viscosity-temperature relations at constant shear rate of $9.30 \times 10^{-3} \text{ sec}^{-1}$ for Nissan G systems of different kinds of additives and no additives: (□) no additives; (●) Irganox 1010, 0.05 phr, Ca-St, 0.07 phr; (○) Ethyl 702, 0.05 phr, Ca-St, 0.07 phr; (■) BHT, 0.05 phr, Ca-St, 0.07 phr.

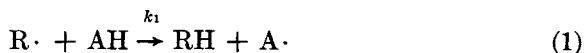
melt transition of the system containing Ethyl 702 is lower than Irganox 1010 and the system of no additives shows the most marked melt transition. At temperatures higher than 210°C , measurement of melt strength was impossible in the system of no additives, because of the continual breakage of the extruded strand of HDPE melts. The additives used here are all the phenolic antioxidant and deactivate the generated radicals by donating the hydrogen of the $-\text{OH}$ group. They differ in molecular weight and the number of functional groups ($-\text{OH}$) per molecule, hence under the same weight addition, the total number of functional groups differs among the three systems with additives. They may differ, too, in mobility because of the considerable difference in molecular weight. After all, the radical scavenging power differs among the four systems in Figures 12 and

13. From these figures, what kind of antioxidant is added to the processing proves to be a very important matter.

Effect of Thermal History on Melt Viscosity

Measurement of temperature dependence of melt strength was usually done by charging a fresh sample at each temperature. On the other hand, temperature dependence of melt viscosity was measured by raising the temperature stepwise after the sample initially had been charged at the lowest temperature. This difference of in the thermal history between the physical values should never be neglected when comparing temperature dependence.

It was attempted to observe the effect of the way of raising the temperature on melt viscosity of a resin. The resin used is again Nissan G. In a preliminary experiment, Ethyl 702 was selected as a thermal stabilizer, and the melt viscosity was measured charging the sample newly at each of three conditions of setting temperature of the oil bath, 180°C, 200°C, or 250°C. The result is shown in Figure 14. The "time" in the abscissa refers to the time passed after the sample was charged. Surprisingly, an increase in melt viscosity with temperature can be observed. In Figure 13, all systems show a melt viscosity decrease with temperature increase over the whole temperature region measured, though a difference among them is seen in the way the melt viscosity decreased. The discrepancy between Figure 13 and Figure 14 is perhaps due to the difference in thermal history between both. The possible mechanism that can be accepted may be as follows: By the addition of a certain antioxidant (AH), the reactive species (R·) to produce the crosslinking must be deactivated.



On the other hand, the reactive species must interact with each other or attack the weak points in the polymer chains, and produce the products of the reaction:

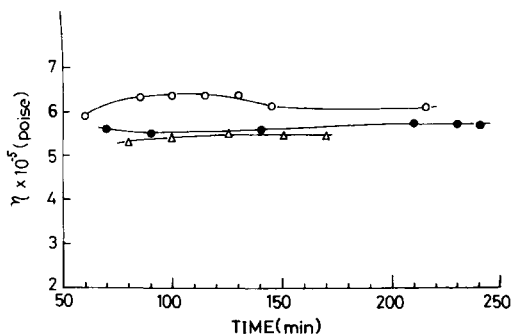


Fig. 14. Effect of temperature rise rate on viscosity values; resin, Nissan G; additive, Ethyl 702, 0.05 phr: (O) 250°C; (●) 200°C; (Δ) 180°C.

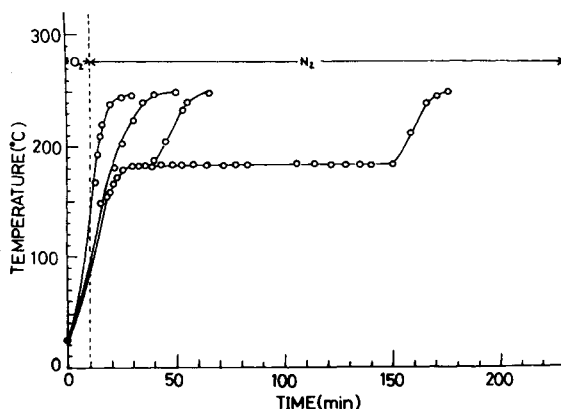


Fig. 15. Various curves for temperature rise toward 250°C of sample.

We suppose that below a certain temperature, k_1 is larger than k_2 , and above the temperature, k_1 is smaller than k_2 . We also suppose that the reactive species are comparatively stable even under exposure to the high temperature, once they are deactivated.

If the above assumption is correct, it can be predicted that little crosslinking is formed under mild temperature rise. On the other hand, it may be probable that a rapid temperature rise condition makes the action of antioxidant ineffective and produces many chances to form crosslinking. If in a polymer system exposed to heat, k_1 is larger than k_2 , the system can be said to be thermally stabilized. In the reverse case, the polymer system is said to be unstable to heat. The result of Figure 14, an increase of melt viscosity with temperature, is thus never unaccountable as based on this mechanism of thermal stabilization. If the result of Figure 14 was produced according to the mechanism described above, the system residing for a length of time at a lower temperature before the temperature rise to 250°C can be predicted to have more excellent thermal stability than without that treatment and not to show the behavior of Figure 14.

This prediction is based on the assumption that the system may be given more chances to deactivate the reactive species by residing at the lower temperature. Using the same four systems as selected to obtain the results of Figures 12 and 13, the melt viscosity values at 250°C were compared among a variety of conditions distinguished by the different temperature rise rates up to 250°C. The sample was initially charged at the setting temperature of the oil bath at 185°C and resided at that temperature for a length of time before the temperature rise toward 250°C. The temperature rise rate toward 250°C was adjusted by changing the residence time (T_7) at the oil bath temperature of 185°C. The curves for variable temperature rise rates are shown in Figure 15. The deaeration was always done within 10 min after the sample was charged, and the nitrogen was immediately introduced.

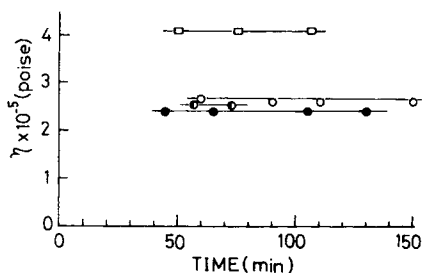


Fig. 16. Effect of temperature rise rate on viscosity at 250°C; for Nissan G. shear rate, $9.30 \times 10^{-3} \text{ sec}^{-1}$; additive, BHT, 0.05 phr, Ca-St, 0.07 phr: (□) $T_r = 0$ min; (○) $T_r = 30$ min; (●) $T_r = 15$ min; (●) $T_r = 215$ min.

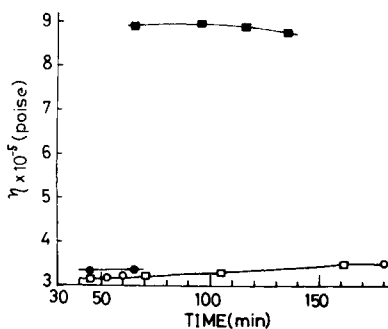


Fig. 17. Effect of temperature rise rate on viscosity at 250°C for Nissan G; shear rate, $9.30 \times 10^{-3} \text{ sec}^{-1}$; additives, Irganox 1010, 0.05 phr, Ca-St, 0.07 phr: (■) $T_r = 0$ min; (●) $T_r = 30$ min; (○) $T_r = 35$ min; (□) $T_r = 80$ min.

The melt viscosity values at 250°C of the resins adjusted the thermal history in the way as described above are shown in Figures 16, 17, 18, and 19. The "time" in the abscissa refers to the lapsed time after the change from 185°C to 255°C of the oil bath temperature, which is equal to the lapsed time after the sample was charged as T_r is added. Because of the final dissimilarity by about 5°C between the oil bath temperature and resin temperature usually observed, the former was set at 255°C to obtain the latter of 250°C.

The results in Figures 16 to 19 clearly present the dependence of the melt viscosity on T_r . The resins residing at the oil bath temperature of 185°C for a length of time show lower values of melt viscosity as compared with those at T_r equal to 0, that is, temperature is raised at an extremely rapid rate. Furthermore, in each of Figures 16 to 19, the melt viscosity values show a tendency to fall to a minimum value. These results seem to justify our view on the mechanism of thermal degradation of polymers already described. Now we select T_a , the time lapsed till temperature of the resins reaches 240°C after they were charged, as a measure of temperature rise rate. (Because the time lapsed till the resin temperature reaches 250°C is difficult to determine accurately, 240°C is selected instead of that temperature.)

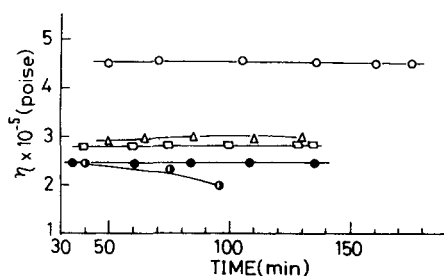


Fig. 18. Effect of temperature rise rate on viscosity at 250°C for Nissan G; shear rate, $9.30 \times 10^{-3} \text{ sec}^{-1}$; additives, Ethyl 702, 0.05 phr, Ca-St, 0.07 phr: (○) $T_r = 0$ min; (△) $T_r = 15$ min; (□) $T_r = 40$ min; (●) $T_r = 130$ min; (●) $T_r = 225$ min.

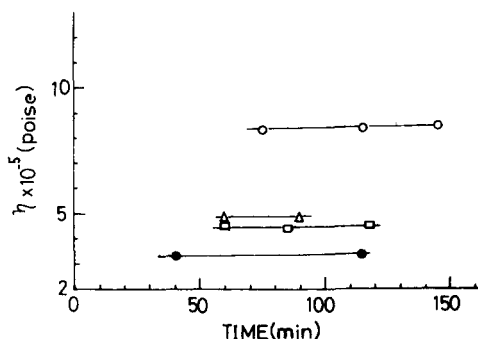


Fig. 19. Effect of temperature rise rate on viscosity at 250°C for Nissan G; shear rate, $9.30 \times 10^{-3} \text{ sec}^{-1}$; no additives: (○) $T_r = 0$ min; (△) $T_r = 17$ min; (□) $T_r = 30$ min; (●) $T_r = 90$ min.

In Figure 20, the melt viscosity values at 250°C are plotted against T_a . All the melt viscosity values are those at the shortest time measured in the abscissa, in each of several T_r values in Figures 16 to 19. The effect of the kind of additives and the thermal history on the melt viscosity values can be clearly observed in Figure 20. The systems with BHT and Ethyl 702 show a tendency to give a constant melt viscosity value at T_a values more than about 30 to 40 min. The system with Irganox takes about 50 min to reach an equilibrium value of melt viscosity, which is higher than the above two. This length of time may be recognized as a value inversely proportional to the rate constant k_1 . The longer the value is, the slower the action of antioxidant must be. Accordingly, it can be concluded that Irganox is inferior to BHT and Ethyl 702 as radical scavenger at the same weight addition.

It is of interest that the effect of thermal history on the melt viscosity values can be observed also in the system with no additives. From this, it may be inferred that the reactive species can be also deactivated by other processes than process (1). Provided that the catalyst residue is deactivated to some extent under the mild temperature rise condition and some restraint of the crosslinking formation results, the phenomenon of

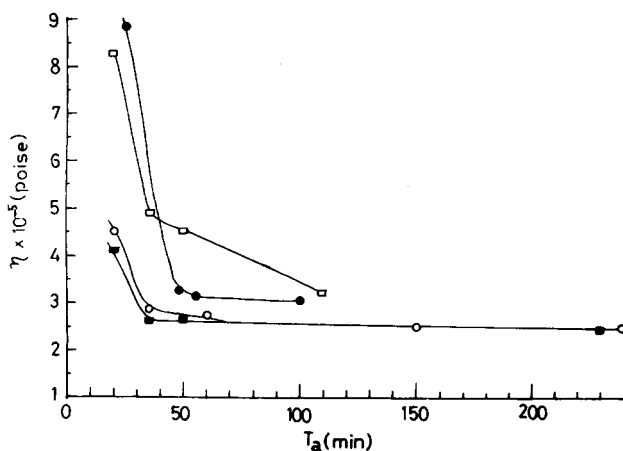


Fig. 20. Effect of temperature rise rate on the viscosity at 250°C for several Nissan G systems; shear rate, $9.30 \times 10^{-3} \text{ sec}^{-1}$: (●) Irganox 1010, 0.05 phr, Ca-St, 0.07 phr; (□) no additives; (○) Ethyl 702, 0.05 phr, Ca-St, 0.07 phr; (■) BHT, 0.05 phr, Ca-St, 0.07 phr.

the system with no additives in Figure 20 may be understandable. In Figure 20, it can be also observed that the system of no additives does not yet reach the equilibrium value of melt viscosity at T_a of about 110 min. This result can be clearly distinguished from the results of the systems of additives. Without additive, a satisfactory thermal stabilization of polymers cannot be attained even under mild temperature rise conditions.

The following two refutations of our interpretations of the results of Figures 16 to 20 are never impossible to present. One is an explanation that the scission of polymer chains is promoted and the melt viscosity decreases as T_a increases, because the increase of T_a prolongs the length of time for which the polymer is exposed to the large thermal energy. The other is that the disentanglement of polymer chains by heat proceeds more fully and the melt viscosity becomes lower under the mild temperature rise conditions as compared with the conditions of rapid temperature rise. However, these two opinions in opposition can be denied from the facts that the melt viscosity values are almost independent of time in the abscissa at each T_r in Figure 16 to 19 and the effect of the kind of additives is observed in Figure 20.

The result of Figure 20 seems to prove experimentally the rough mechanism for the thermal stabilization or degradation of polymers described in the beginning of this section and shows to us how the transition appears in the melt viscosity-temperature relation of many HDPE melts. It is of interest to investigate the identity of reactive species that produces the result of Figure 20 by a method other than rheological, such as ESR.

Effect of Thermal History on Melt Index

Melt index of HDPE samples smashed after being pressed at high temperature (for example, 250°C) has been observed to drop considerably as

TABLE II
 MI_2 of Samples of Different Thermal History

Samples	MI_2	T_r , min
A-1 ^a	0.79	— ^b
A-2 ^a	0.35	0
A-3 ^a	0.40	40
A-4 ^a	0.55	70
B-1 ^c	0.79	— ^b
B-2 ^c	0.26	0
B-3 ^c	0.27	40

^a Nissan G containing 0.03 phr BHT and 0.07 phr Ca-St.

^b Original sample before compression molding.

^c Nissan G containing 0.05 phr Irganox 1010 and 0.07 phr Ca-St.

compared with the original. For instance, the melt index of the sample from the sheet of Nissan G (no additive) pressed for 10 min at 250°C was observed to drop from the original 0.86 to 0.12. This phenomenon is understandable from the explanation presented on the thermal history dependence of melt viscosity. The fall in melt index (MI_2) can also be thought to be produced by the fact that the stabilization process is overcome by the other process leading to the crosslinking. If so, the large fall in MI_2 as mentioned above may be avoided by adjusting the temperature rise rate in the compression molding at high temperature. To prove this idea, Nissan G systems were selected which contained 0.03 phr BHT and 0.07 phr Ca-St or 0.05 phr Irganox 1010 and 0.07 phr Ca-St. The experiment was done in the following way. First, two presses were set at separate temperatures. One was at 180°C and the other at 250°C. A compression was given to a sample with the press at 180°C (preheating time was 3 min and pressure, 100 kg/cm²). After a length of time, the sample was transferred to the press at 250°C, and immediately pressed for 13 min and then cooled to room temperature with a cooling press. By changing the residence time (T_r) at 180°C press, the way of donating heat to the sample was adjusted.

The pressed sample of about 1 mm in thickness thus obtained was smashed and was used for the measurement of MI_2 . The results of MI_2 are presented in Table II. The system of Irganox 1010 shows little difference between 0 min and 40 min of T_r . However, the MI_2 of the BHT system increases and tends to approach that of the original as T_r increases. This result is plotted in Figure 21. The insufficiency of recovery of MI_2 value with increase of T_r as compared with the melt viscosity may be due to oxygen effect from the molding process of sample without deaeration. In any case, it is of interest that MI_2 depends upon the thermal history and the fall in MI_2 of the sample pressed at a high temperature can be restrained to some extent by an appropriate selection of thermal history, even if finally at the same temperature. Also, the results of Figure 21 appear to prove a universality of the rough mechanism on the thermal stabilization of HDPE melts already presented.

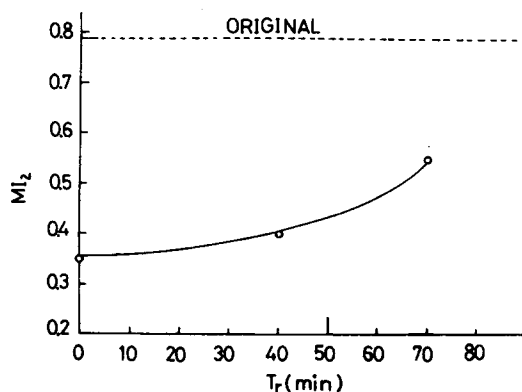


Fig. 21. Effect of thermal history on MI_2 values; resin, Nissan G; additives, BHT, 0.03 phr, Ca-St, 0.07 phr.

Expression of Peculiar Phenomena of Melt Viscosity-Temperature Relation by a Simplified Equation

We attempted to treat the complicated phenomena of melt viscosity in a general way by a simplified equation. For this purpose, we refer to Bueche's idea for the viscosity¹¹ and assume the HDPE sample to be monodisperse in molecular weight.

The viscosity of polymer is equivalent to the self-diffusion phenomenon of polymer chains and is in an inverse proportion to the diffusion coefficient D :

$$\eta \propto \frac{1}{D}. \quad (3)$$

In eq. (3) η is viscosity, D is diffusion coefficient, and the former is limited to values at very low shear rate. D is related to friction coefficient per molecule f , Boltzmann constant k , and absolute temperature, in the following manner:

$$D = \frac{kT}{f}. \quad (4)$$

In the polymer chain, f should be substituted by frictional coefficient per segment f_0 multiplied by the number of segments N , because polymer chains move not as molecules but as segments:

$$D = \frac{kT}{f_0 N}. \quad (5)$$

From eqs. (3) and (5),

$$\eta = K \frac{f_0 N}{kT} \quad (6)$$

where $K = \text{constant}$. In eqs. (5) and (6), N is the number of segments that move cooperatively as a polymer chain moves. Accordingly, this

number is not always equivalent to the molecular weight of polymer, but can be thought to contain the entanglement effect and crosslinking effect. N may be thought to depend on temperature, since both the slippage of entanglement and the rate of crosslinking formation are affected by temperature. The difference between $N^*(T)$, the values of N reached as the consequence of crosslinking, and $N(T)$, the values of N without the crosslinking, can be thought to be proportional to k' , the rate constant of chemical reaction that produces the crosslinking:

$$N^*(T) - N(T) \propto k' = A \exp\left(-\frac{E_{a1}}{RT}\right) \quad (7)$$

where $A = \text{constant}$, $E_{a1} = \text{apparent activation energy for the chemical reaction that produces crosslinking}$, and $R = \text{gas constant}$. From eq. (7),

$$N^*(T) = N(T) + A' \exp\left(-\frac{E_{a1}}{RT}\right) \quad (8)$$

where $A' = \text{constant}$.

On the other hand, f_0 , from which both the entanglement and crosslinking effects are excluded, must decrease monotonously with temperature increase. Temperature dependence of f_0 is thus expressed in the following manner:

$$f_0 = B' \exp\left(\frac{E_{a2}}{RT}\right) \quad (9)$$

where $B' = \text{constant}$ and $E_{a2} = \text{apparent activation energy for jump frequency of segments}$. In this way, eq. (6) can be rewritten in the form of eq. (10), if the crosslinking reaction occurs:

$$\eta^* = K \frac{f_0 N^*(T)}{kT} \quad (10)$$

where $\eta^* = \text{viscosity of crosslinked polymer}$. By using eqs. (8) and (9), eq. (11) can be obtained from eq. (10):

$$\eta^* = \beta \exp\left(\frac{E_{a2}}{RT}\right) + \delta \exp\left(\frac{E_{a2} - E_{a1}}{RT}\right) \quad (11)$$

$$\beta = \frac{KB'N(T)}{kT} = \text{constant}, \quad \delta = \frac{KA'B'}{kT} = \text{constant}$$

If E_{a1} is infinitely large, that is, a chemical reaction in which crosslinking does not occur at all, the second term in eq. (11) then becomes negligible and the melt viscosity must follow an Andrade plot against temperature (① in Fig. 22). On the other hand, when E_{a1} is zero, that is, the thermal reaction of HDPE melts proceeds at infinitely rapid rate, eq. (11) can be rewritten in the following form:

$$\eta^* = (\beta + \delta) \exp\left(\frac{E_{a2}}{RT}\right). \quad (12)$$

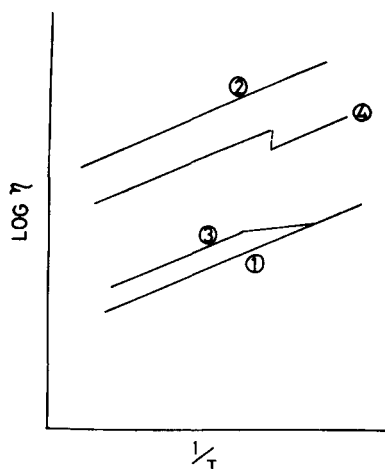


Fig. 22. Typical viscosity-temperature relations for HDPE melts.

Equation (12) tells to us that the melt viscosity shows the same temperature dependence in both cases of different extreme values of E_{a1} , though the melt viscosity values themselves differ from each other (① and ② in Fig. 22). As an intermediate case between the above two, we can consider a positive E_{a1} value that is larger than E_{a2} . In that case, the second term increases in eq. (11) with temperature, while the first term shows an opposite temperature dependence. The change in melt viscosity with temperature then gives a gentler slope in the Andrade plot than the above two cases. However, if the reactive species that produce the crosslinking is exhausted at some temperature, temperature dependence of the melt viscosity is again controlled by E_{a2} . This behavior of the melt viscosity in the third case can be expressed by eqs. (13), (14), and (15) (visualized by ③ in Fig. 22):

$$T < T_{c1} \quad \eta^* = \beta \exp\left(\frac{E_{a2}}{RT}\right) \quad (13)$$

where T_{c1} = critical temperature initiating reaction.

$$T_{c1} \leq T \leq T_{c2} \quad \eta^* = \beta \exp\left(\frac{E_{a2}}{RT}\right) + \delta \exp\left(\frac{\Delta E_a}{RT}\right) \quad (14)$$

where T_{c2} = critical temperature completing reaction, $\Delta E_a = E_{a2} - E_{a1}$

$$T_{c2} < T \quad \eta^* = \beta \exp\left(\frac{E_{a2}}{RT}\right) + \delta \exp\left(\frac{\Delta E_a}{RT_{c2}}\right). \quad (15)$$

Under mild temperature rise conditions, the thermal reaction of HDPE melts begins to proceed slowly in the temperature region near about 180°C and results in a gentler slope in the Andrade plot of the melt viscosity than when stabilized to heat. The gentle slope usually remains unchanged up to a temperature region of about 210° to 230°C at which the reactive species are almost exhausted, and then the melt viscosity decreases again with temperature increase according to the temperature dependence of

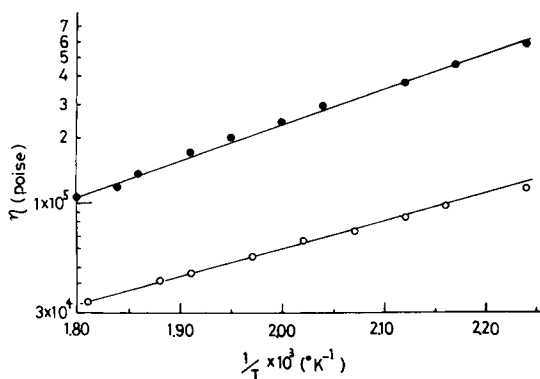


Fig. 23. Viscosity-temperature relations at constant shear rate of $9.30 \times 10^{-3} \text{ sec}^{-1}$ for two Nissan HDPE systems consisting of the same resin, different in kind of additives added; resin, Nissan HDPE ($MI_2 = 0.98$): (●) Ca-St, 0.07 phr; (○) BHT, 0.05 phr, Ca-St, 0.07 phr.

segmental Brownian motion of polymer chains. In a specific case, it is probable that the degree in which the second term in eq. (11) increase with temperature exceeds the degree in which the first term decreases even if under mild temperature rise conditions. The result ④ in Figure 22 can be observed in such cases, concrete examples of which are the results of Hizex B and D in Figure 2. Figure 23 shows a characteristic difference between the melt viscosity-temperature relations of two samples consisting of the same resin, different only in the kind of additives, and gives concrete examples for ① and ② in Figure 22. The behavior ③ in Figure 22 was observed for many HDPE samples. Hizex A is one of those, and gave a melt viscosity-temperature relation as shown in Figure 24, if the measurement was started from temperature of about 150°C . ⑤ in Figure 24 is almost parallel to ③, and the former can be thought to be equivalent to eq. (13). On the other hand, ⑥ in Figure 24 must be equivalent to eq. (14), hence the difference between η^* , the melt viscosity value given by ⑥ at a certain temperature, and η , the melt viscosity value at the same temperature given by extended ⑤, must produce the following relation:

$$\eta^* - \eta = \delta \exp\left(\frac{E_{a2} - E_{a1}}{RT}\right) \quad (16)$$

The Andrade plot of $(\eta^* - \eta)$ against the reciprocal absolute temperature is shown for Hizex A in Figure 25, from which $(E_{a2} - E_{a1})$ can be obtained. There are two separate slopes in Figure 25, and the lower one is equivalent to -14.6 kcal ($E_{a2} - E_{a1}$) and the higher, to -25.0 kcal . Using an E_{a2} value of 8.5 kcal , E_{a1} is 23.1 kcal in the former and 33.5 kcal in the latter. Apparent activation energy of Hizex A for the thermal reaction that produces crosslinking proves to be about 20 to 30 kcal, and is almost equal to the E_a value of 34.1 kcal in Figure 9. This approximate equality between two activation energy values from the measurement of each of the peculiar phenomena of different rheological properties may be thought

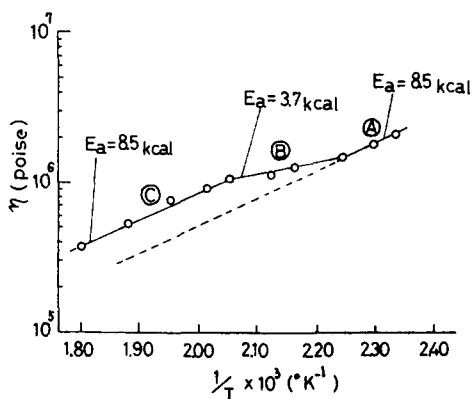


Fig. 24. Viscosity-temperature relation at constant shear rate of $9.30 \times 10^{-3} \text{ sec}^{-1}$ for Hizex A.

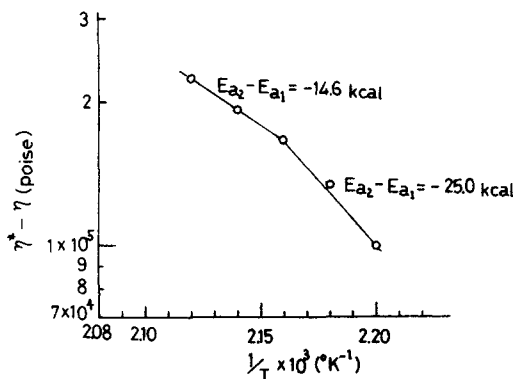


Fig. 25. Andrade plot of $(\eta^* - \eta)$ for Hizex A.

to show that the two peculiar phenomena are produced by the same mechanism. Concretely, it may be concluded that the discontinuity in the temperature dependence of melt viscosity seen even in nitrogen atmosphere is produced by the microquantity oxygen remaining in polymer dye to imperfect deaeration, since oxygen must be a main factor in the peak in temperature dependence of melt strength always measured without deaeration.

Comparison with Slight Crosslinking by Radiation

It is a problem to investigate whether the crosslinking of many HDPE melts by heat changes the solid structure of the polymers or not. An example of results obtained by such an investigation is shown in Table III. The results of Table III show that the crosslinking reaction does not proceed up to such extent that it affects the solid structure of the polymer, but occurs in only a slight quantity. This result is similar to that of crosslinking by γ -ray irradiation at room temperature, under vacuum. In Table IV, basic properties of three Nissan HDPE samples are shown at

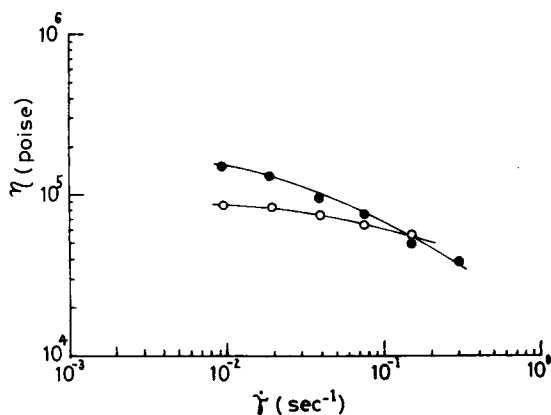


Fig. 26. Shear rate dependence of viscosity at 190°C for γ -ray-irradiated and non-irradiated samples; resin, Nissan HDPE ($MI_2 = 2.76$): (O) nonirradiated; (●) irradiated.

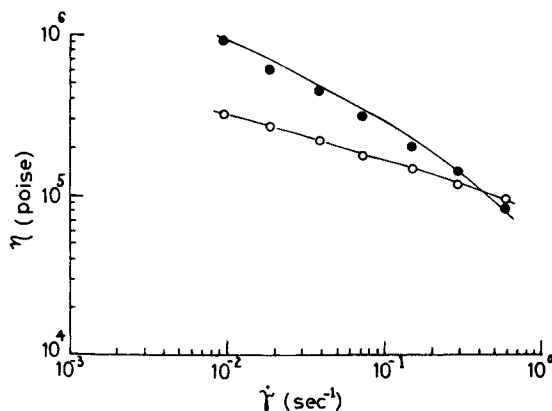


Fig. 27. Shear rate dependence of viscosity at 250°C for Nissan G in two cases different in thermal history: (●) T_r (residence time at 180°C) = 0 min; (O) $T_r = 40$ min.

several radiation doses. (We entrusted γ -ray radiation to Japan Atomic Energy Research Institute, Takasaki, Japan). With increase in radiation dose, a marked decrease in MI_2 is observed, which suggests crosslinking formation, while the density, number of branching, C—C double bonds, and η_{sp}/c show no marked changes. The γ -radiation at room temperature is generally said not to affect the crystal structure of the sample radiated; hence, it can be thought to produce crosslinking structure to only a slight extent. From the similarity between Table III and Table IV, the peculiar phenomena at high temperature of many HDPE samples presented in this study can be thought to be equivalent to the property changes of the sample by γ -ray crosslinking at room temperature, with slight radiation dose.

In Figure 26, the shear rate dependence of the melt viscosity of γ -ray-sample is compared with that of nonradiated sample. The crosslinked

TABLE III
 MI_2 and Solid Structure of Samples of Different Thermal History

Sample	Pressing temp., ^b °C	MI_2	Density	$-\text{CH}_2/$ 1000 C	$-\text{CH}=\text{CH}-/$ 1000 C	$>\text{CH}=\text{CH}_2/$ 1000 C	$>\text{C}=\text{CH}_2/$ 1000 C
Nissan G ^a	180	0.86	0.9533	4.1	0.09	0.66	0.08
Nissan G	200	0.40	0.9534	4.2	0.09	0.68	0.11
Nissan G	250	0.12	0.9534	4.1	0.10	0.68	0.09

^a No additive, smashed from sheets pressed at each temperature.

^b Preheating time 3 min, pressing time 10 min, pressure 100 kg/cm².

TABLE IV
 Effect of Radiation Doses on HDPE Properties

Samples	Radiation doses, Mrad	Density	MI_2 , g/10 min	η_{sp}/c^a , dl/g	$-\text{CH}_2/$ 1000 C	$-\text{CH}=\text{CH}-/$ 1000 C	$>\text{C}=\text{CH}_2/$ 1000 C	$>\text{C}=\text{CH}_2/$ 1000 C
Nissan-A	0.0	0.9466	0.26	2.66	5.5	0.15	0.46	0.17
	0.1	0.9464	0.15	2.76	5.2	0.13	0.43	0.18
	0.2	0.9466	0.072	2.72	5.1	0.13	0.43	0.14
Nissan-B	0.5	0.9457	0.016	2.85	5.7	0.15	0.41	0.12
	0.0	0.9532	0.23	2.54	4.5	0.06	0.63	0.05
	0.1	0.9533	0.13	2.61	4.5	0.06	0.61	0.09
Nissan-C	0.2	0.9532	0.12	2.63	4.4	0.08	0.65	0.06
	0.5	0.9515	0.0078	2.77	4.5	0.07	0.53	0.08
	0.0	0.9531	2.76	1.56	4.8	0.11	0.75	0.05
	0.1	0.9530	1.81	1.75	4.6	0.11	0.74	0.05
	0.2	0.9529	1.29	1.77	5.0	0.11	0.74	0.05
	0.5	0.9516	0.32	1.78	4.6	0.12	0.65	0.04

^a Obtained from a solution of polymer concentration 0.1 g/100 ml, in decalin, at 135°C.

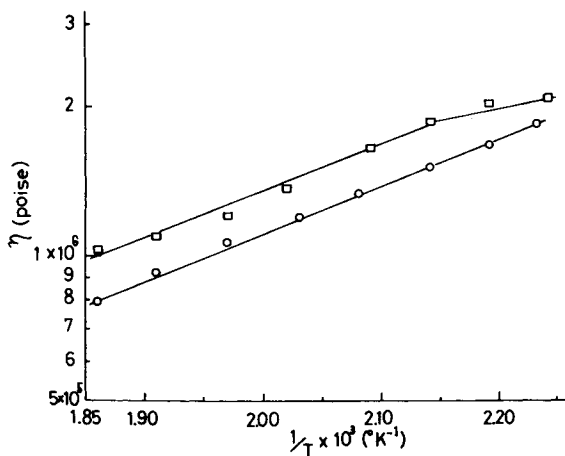


Fig. 28. Viscosity-temperature relations at constant shear rate of $9.30 \times 10^{-3} \text{ sec}^{-1}$ for samples obtained from two bottles of different mechanical properties; resin, Nissan HDPE ($MI_2 = 0.19$): (\square) pinch-off welding, bad; (\circ) good.

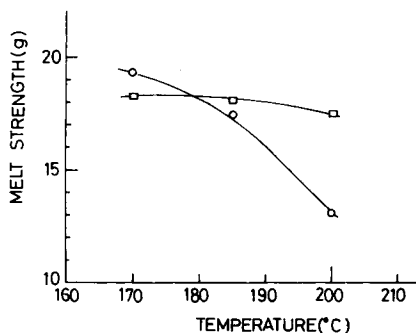


Fig. 29. Melt strength-temperature relations at constant extrusion rate for samples obtained from two bottles of different mechanical properties; resin, Nissan HDPE ($MI_2 = 0.19$): (\square) pinch-off welding, bad; (\circ) good.

sample has a more striking shear rate dependence of the melt viscosity than the original. In Figure 27, the shear rate dependences of the melt viscosity at 250°C are shown for two systems consisting of the same resin different in thermal history. One system that reached 250°C with a rapid temperature rise rate and might be unsatisfactory in heat stabilization shows a behavior similar to that of the γ -ray-crosslinked samples in Figure 26, as compared with the other system reaching 250°C under mild temperature rise conditions. Generally, it is known¹² that the crosslinked sample is more striking in shear rate dependence of melt viscosity than the crosslinked sample.

Processability and Properties of Final Products

Some of the peculiar phenomena in the temperature dependence of the melt properties of many HDPE samples described in this study can be, of course, thought to be closely related to the processability of the resins and

the physical properties or appearance of final products. The increase in melt viscosity with temperature in some cases tells us that the rise in temperature does not necessarily result in improved fluidity of the resin. The widening of distribution of flow units of polymer melts by the cross-linking may possibly affect the skin appearance of the final products. From the results of Figures 12 and 13, it can be predicted that the processability of resins depends greatly on the quantity and kind of additives. A detailed description of these necessitates many pages. To describe the following one example is all that we intend to do now.

In blow molding, one of two bottles from the same resins different in kind and quantity of additives was very satisfactory in the pinch-off welding, and the other was unsatisfactory. Samples were smashed from these bottles, the melt viscosity and melt strength being measured at several temperatures. Figures 28 and 29 show the results. It can be predicted that the delayed parison inflation after the weld has been formed gives weak seals and may even cause the weld to part on full inflation. The degree of crosslinking must affect strongly the pinch-off welding, since the parison inflation is a reflection of elastic properties of polymer melts. In Figures 28 and 29, the sample with weak seal shows the same behavior as the peculiar phenomena of many HDPE samples described in this study, while the sample of satisfactory pinch-off welding does not show such behavior. This correspondence between the problem met in processing and the peculiar phenomena of the basic physical properties leads us to expect that it becomes possible to predict the processability of resins and properties of final products before the processing operation.

Based on some peculiar phenomena of many HDPE samples that this paper has presented and their interpretation, it may be possible to some extent to explain the apparently mysterious phenomena which we have frequently encountered on processing or pelletizing. However, at present our knowledge is very poor on the identity of reactive species that produce these peculiar phenomena. This is for the future to solve.

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