

## 극저밀도 폴리에틸렌의 분자Parameter와 열적, 유변학적 특성

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### Molecular Parameters, Thermal and Rheological Properties of Ultra Low Density Polyethylenes(ULDPE)

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**요 약 :** 폴리에틸렌계열 중에서 가장 최근에 상업화된 극저밀도폴리에틸렌(ULDPE)에 대한 구조적, 열적, 유변학적 그리고 분자 parameter적 특성을 검토하였다. ULDPE의 주용도가 일반 polyolefin과의 용융블렌딩을 통한 수지개질에 있는 점을 고려, 본보에서는 ULDPE의 용융유변특성을 비교적 자세하게 검토하였으며, 이러한 data는 ULDPE와 다른 수지와와의 용융블렌딩에 기본적인 data base가 되리라 본다.

**Abstract :** Ultra low density polyethylene(ULDPE), the newest and most recently commercialized member of polyethylene family, has been characterized in terms of structure, thermal, rheological properties, and molecular parameters. Since the prime use of the ULDPE is polyolefin modifier, emphasis is put on the melt rheology of the sample to provide data base for blending with other resins.

### INTRODUCTION

Polyethylene(PE) is a most widely encountered commodity resin satisfying about 1/3 of the total plastic market.<sup>1</sup> From the molecular point of view, PEs can be characterized by several parameters such as MW(molecular weight), MWD(molecular weight distribution), and chain branching.<sup>2</sup> These parameters are controlled primarily by the type of polymerization process and catalyst. On the other hand, for commercial application, the resin is spe-

cified by its density and MI(melt index) in addition to MW and MWD.

Ultra low density polyethylene(ULDPE) is the newest member of the PE family, and was commercialized by Mitsui in 1986.<sup>3</sup> The ULDPE, like linear low density PE(LLDPE), is PE copolymer having  $\alpha$ -olefin as comonomer unit. The type of comonomer, i. e., the length of branch, and the comonomer content primarily govern the product properties.

ULDPE is PE having the lowest density down

to approximately  $0.86 \text{ g/cm}^3$ , and offers improvements in strength, flexibility, optics, and sealability over the standard LLDPE.<sup>3</sup> Properties pertinent to ULDPE are mainly due to their low density, synonymous with low crystallization temperature, leading to low sealing temperature around  $25^\circ\text{C}$ . The sealability at low temperature plus hot tack finds application for film on its own. However, the prime use of ULDPE is for a resin modifier, particularly for high and low density PE (HDPE, LDPE) and polypropylene (PP) film and sheet. Addition of ULDPE to PE and PP improves impact strength, flexibility, tear strength, and low-temperature heat sealing characteristics of film.<sup>3-6</sup>

This paper characterizes five commercial ULDPE grades by means of IR (infrared spectroscopy), NMR (nuclear magnetic resonance spectroscopy), GPC (gel permeation chromatography), DSC (differential scanning calorimetry), X-ray diffractometer, melt indexer and RDS (Rheometrics dynamic spectrometer). Since the prime use of the ULDPE is for a resin modifier, an emphasis has been put on the melt rheology of the samples to provide data base for blending with other resins.

## EXPERIMENTAL

IR spectra of the samples were obtained from Perkin-Elmer 1330 spectrophotometer. Mn (number average molecular weight), Mw (weight average molecular weight), and MWD were determined from a GPC (Waters 150C) with Twin Shodex AT-80 M/S column, packed with crosslinked polystyrene gel. Solvent (trichlorobenzene) flow rate was  $1.0 \text{ ml/min}$ , and the column as well as the injector was kept at  $140^\circ\text{C}$ .

Thermal properties of the samples were measured using a DSC (Du Pont 1090B). Samples were heated to  $100^\circ\text{C}$  from room temperature, staying at that temperature for 10 min, and cooled down to room temperature. DSC thermograms were recorded during the second heating cycle. In all cases, temperature was programmed at  $20^\circ\text{C/min}$  to minimize reorganization to new crystal forms or

lamella thickness during the heating cycle.<sup>7</sup>

Crystalline structure of the samples were examined with a X-ray diffractometer (Rigaku) using a copper  $K_\alpha$  at 30kV, 20mA. Injection molded specimen was cut into slices, perpendicular to the length, and mounted for through direction.

MI was measured following the standard procedure described in ASTM-D1238L, viz. at  $190^\circ\text{C}$ , under 2.16 and 49.5 Kg loadings. Linear viscoelastic properties of the melt were measured using a RDS (Rheometrics, 7700) with a cone and plate geometry, at  $210^\circ\text{C}$  and 30% strain level.

## RESULTS AND DISCUSSION

Fig. 1 shows the typical IR spectra for the ULDPEs. Absorption peak at  $1375 \text{ cm}^{-1}$  corresponds to terminal- $\text{CH}_3$  group and is independent of the size of the branch. This peak appears in ULDPEs (Fig. 1), and is missing in HDPE.<sup>8</sup> In series P of UL-

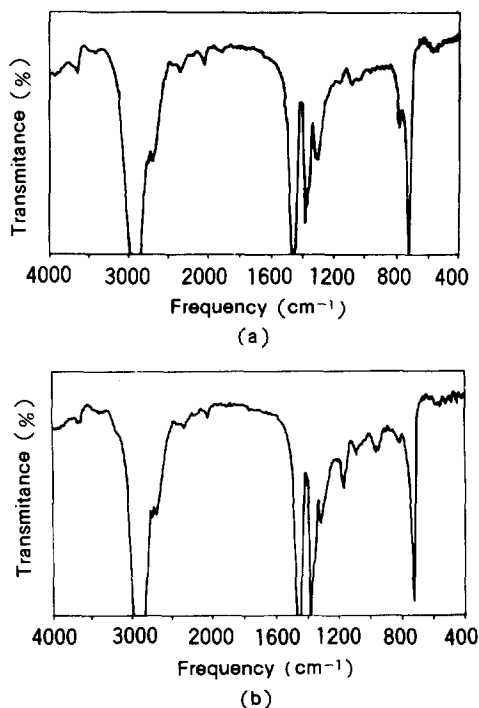


Fig. 1. I. R. spectra of ULDPEs : (a) A-4090, (b) P-0480.

DPE, additional absorption peak corresponding to isopropyl group is found at  $1170\text{ cm}^{-1}$ . Like in LL-DPE,<sup>9</sup> only one type of comonomer was found in the ULDPE.

Useful molecular parameters determined from GPC, together with density,  $T_m$ (melting peak temperature), and MI are given in Table 1. Densities of series A, containing butene-1 as comonomer, are slightly higher than those of series P, containing 4-methyl pentene-1 as comonomer. Mw of series A is  $4.78\sim 9.95\times 10^4$ , and is  $14.20\sim 17.21\times 10^4$  for series P. When compared with HDPE, the Mw of series A fall in lower end of molding grade, and Mw of series P in extension grade of HDPE.

MWD of the ULDPEs( $M_w/M_n=1.70\sim 1.86$  for series A, and  $1.94\sim 2.13$  for series P) is significantly narrower compared to that of commercial HDPEs( $M_w/M_n=5\sim 15$ ). In fact, such narrow MWD provides the ULDPE with new application of PE. In PE resin, narrow MWD gives good low temperature properties and high impact strength.<sup>6</sup>

MI is a rough guide to processability, especially at low rate of shear. MI values of the ULDPEs, except A-20090, range  $0.4\sim 3.9\text{ g}/10\text{ min}$  (under  $2.16\text{ Kg}$  loading) which is well within those of commercial HDPEs.

Fig. 2 shows the DSC thermograms of the ULDPEs. Complex and multimodal melting envelope of the ULDPE resin stands in sharp contradiction to those of HDPE, which is smooth and relatively sharp.<sup>7</sup> It would be expected that copolymers of ethylene with minor amounts of an  $\alpha$ -olefin homo-

geneously distributed over all molecular species would exhibit a smooth and well defined melting endotherm. The inhomogeneity of the distribution of the side groups along the chain is reflected in the DSC thermogram.<sup>9</sup> With unequal distribution of the  $\alpha$ -olefins along the chain, distribution of undisturbed chains exist, and this leads to lamella thickness distribution which eventually gives several peaks in DSC thermogram(Fig. 2). The mel-

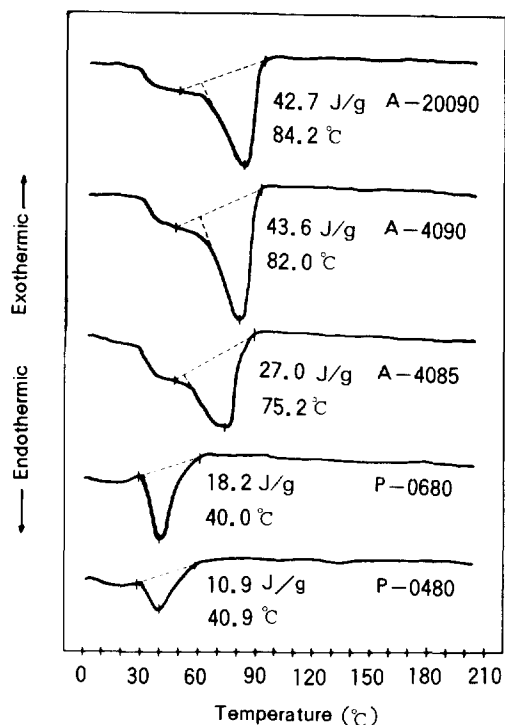


Fig. 2. DSC thermograms of ULDPEs.

Table 1. Characteristics of ULDPEs and HDPE

Sample	Density ( $\text{g}/\text{cm}^3$ )	$T_m$ ( $^{\circ}\text{C}$ )	MI ( $\text{g}/10\text{min}$ )*	$M_n$ ( $10^4$ )	$M_w$ ( $10^4$ )	Comonomer	$\text{C}_2$ units	Maker
A-4085	0.887	75.2	3.7/ 23.0	5.52	9.95	butene-1	86% mol	Mitsui
A-4090	0.893	82.0	3.9/ 24.0	3.75	6.99	butene-1	86% mol	Mitsui
A-20090	0.895	84.2	18.2/114.5	2.81	4.78	butene-1	86% mol	Mitsui
P-0480	0.865	40.8	1.0/ 6.6	6.66	14.20	4-methylpentene	76% wt	Mitsui
P-0680	0.867	40.0	0.4/ 3.1	8.88	17.21	4-methylpentene	76% wt	Mitsui
E308 (HDPE)	0.956	129	0.84/ 11.2	2.13	8.59	—	100% wt	Korea Petrochem.

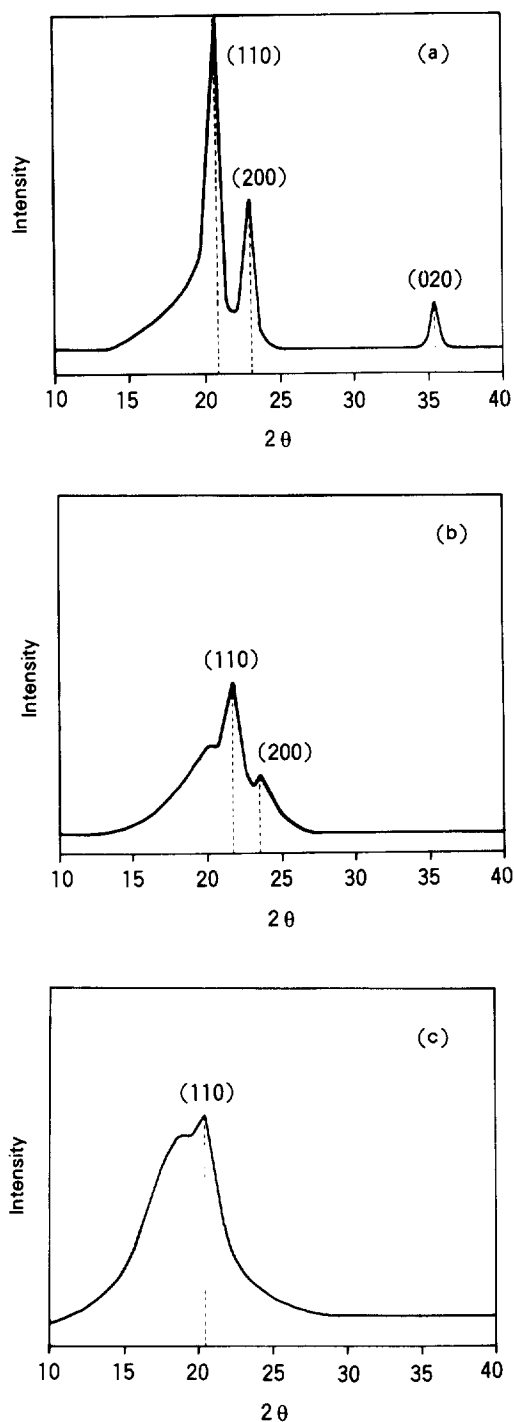


Fig. 3. X-ray diffraction profiles : (a) E-308(HDPE), (b) A-4090, (c) P-0480.

ting peak temperature of series A ranges approximately 75~84°C, and those of series P is around 40°C. Heats of fusion for the ULDPEs are about 27~43 J/g for series A, and 10~18 J/g for series P, and these values are significantly lower compared with those of commercial LDPE. Extremely low crystallinity and low melting temperature of the ULDPE grades respectively should give lower density and higher impact resistance, and heat sealability at lower temperature.

X-ray diffraction profiles for ULDPEs are shown in Fig. 3, together with that of HDPE for reference. The crystalline structure of PE is orthorhombic,<sup>10</sup> with lattice constants, at room temperature,  $a=7.39$ ,  $b=4.95$ ,  $c=2.54$  Å corresponding to  $2\theta=20.7^\circ$  (110),  $23.1^\circ$  (200) and  $35.4^\circ$  (020), respectively. Our X-ray profile for HDPE closely fit the cited data. The X-ray diffraction (XRD) profile for series A (shown for A-4090 only) shows a broad shoulder at  $2\theta=19.5^\circ$ , which corresponds to amorphous region diffraction of PE.<sup>5</sup> Essentially identical XRD patterns were obtained for other grades of series A. The XRD patterns for series P (Fig. 3(c), shown for P-0480 only) show broad and intense amorphous shoulder at  $2\theta=19.5^\circ$  over the series A due to the more amorphous nature of series P. Significant broadening of the ULDPE diffraction pattern relative to that of HDPE is apparently due to the unit cell distortions caused by the interruptive effect of the  $\alpha$ -olefin units.<sup>7</sup>

As mentioned earlier, since the ULDPE is largely used as a modifier of conventional PE and PP resins through melt blending, the melt properties of those grades will be discussed in relation to molecular parameters of the ULDPEs.

Fig. 4. shows the strain and time sweeps for the ULDPE(A-20090). The former test finds maximum strain level where the linear viscoelasticity of the sample is held, and the latter finds the stability during the measurement, which takes about 30 min for the frequency sweep in RDS measurement. Up to about 40% strain level, linear viscoelastic properties are kept constant, and this may be

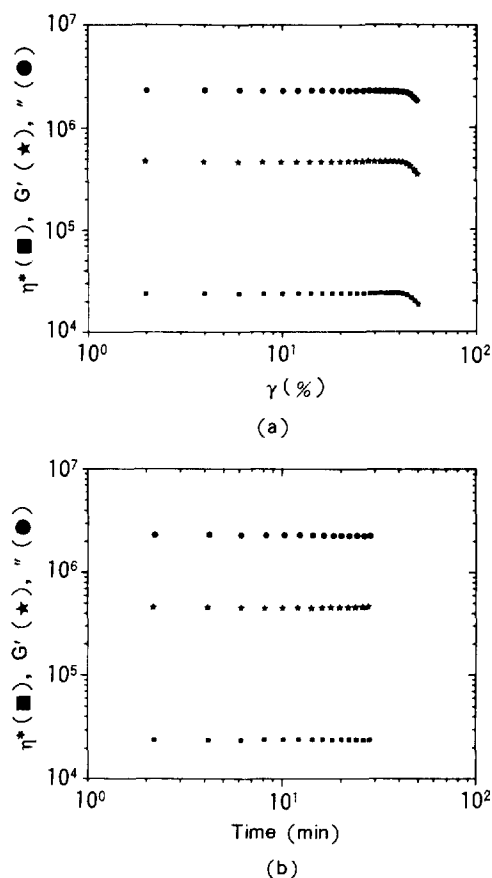


Fig. 4. Strain and time sweeps of A-20090 : (a) strain sweep(210°C, 100rad/s), (b) temperature sweep(20% strain, 100rad/s).

favorably compared with those of HDPE, which shows linearity up to about 25% strain level at the same conditions(not shown). The ULDPE grade is certainly strain stable. Time sweep again avoided the possibility of degradation during the measurement.

The complex viscosities of the ULDPE grades, measured at 210°C, are shown in Fig. 5. Also shown in the same figure are the complex viscosities of typical extrusion grade HDPE for comparison. Regardless of the type of grade, ULDPE shows limiting behavior at low frequencies, and gives Newtonian plateau, a clear indication of narrow MWD as summarized in Table 1. When the viscosity functions of the ULDPEs are compared

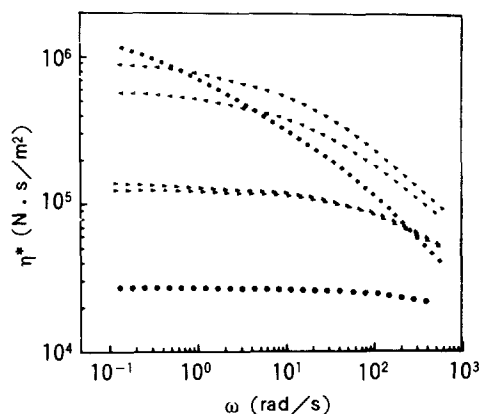


Fig. 5. Complex viscosities of ULDPEs and HDPE (210°C) : ( $\triangleleft$ ) P-0680, ( $\triangle$ ) P-0480, ( $\blacktriangleright$ ) A-4090, ( $\triangleright$ ) A-4085, ( $\bullet$ ) A-20090, ( $\blacksquare$ ) E308.

with that of the HDPE, a viscosity function crossover between the HDPE and ULDPE is observed, except A-20090. With a viscosity function crossover, the processability should be compared at a particular rate of shear encountered.

For example, the MI of P-0480(1.0) is higher than that of HDPE(0.84) under 2.16 Kg loading. However the order is reversed under 49.5Kg loading. This directly comes from the viscosity crossover between the two resins, i. e., the lower MI of HDPE corresponds to shear rate lower than the crossover frequency, and higher MI corresponds to shear rate higher than the crossover point, which is approximately 4 rad/s in the figure. When the ULDPE is blended with PE or PP, the existence of viscosity crossover is often favorably made use of to control the phase morphology. When, for example, A-4085 is melt blended with the equal amount of HDPE, A-4085 may possibly form continuous phase when blended at shear rate lower than the crossover frequency, and take dispersed phase when blended at shear rate higher than the crossover frequency,<sup>11,12</sup> which approximately is 250 rad/s in the figure.

Of interest to note is the viscosity function of A-20090, which shows an extended Newtonian plateau up to  $\omega = 10^2$ (rad/s). The extended Newtonian plateau often is observed for polymer melt

with serious thermal and/or shear degradations.<sup>13</sup> However, such possibilities are safely ignored from our temperature and strain sweep described above. Therefore, the viscosity function of A-20090 is pure resin characteristic of the grade, i. e., extremely narrow MWD.<sup>15</sup>

Storage modulus( $G'$ ) and loss modulus( $G''$ ) of the ULDPE grades are shown in Figs. 6 and 7.  $G'$  is energy stored, and  $G''$  is energy dissipated in a

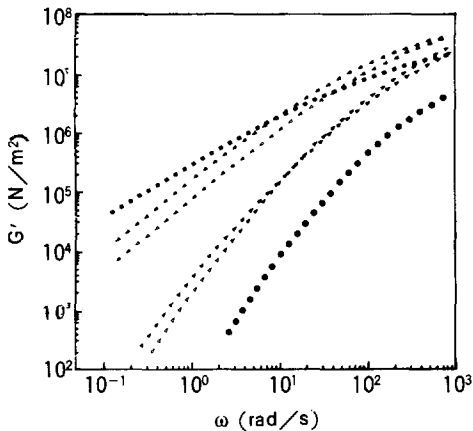


Fig. 6. Storage moduli for ULDPEs and HDPE(E308) : ( $\blacktriangleleft$ ) P-0680, ( $\triangleleft$ ) P-0480, ( $\blacktriangleright$ ) A-4090, ( $\triangleright$ ) A-4085, ( $\bullet$ ) A-20090, ( $\blacksquare$ ) E308.

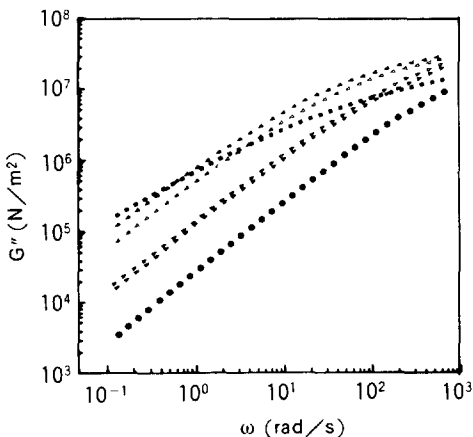


Fig. 7. Loss moduli for ULDPEs and HDPE(E308) : ( $\blacktriangleleft$ ) P-0680, ( $\triangleleft$ ) P-0480, ( $\blacktriangleright$ ) A-4090, ( $\triangleright$ ) A-4085, ( $\bullet$ ) A-20090, ( $\blacksquare$ ) E308.

cyclic deformation. Boltzmann superposition requires for any liquids at sufficiently low frequencies that  $G' \propto \omega^2$  and  $G'' \propto \omega$ , which in log-log plot give slope of 2 and 1, respectively.<sup>13</sup> For the ULDPEs tested,  $G'$  function shows limiting behavior only for series A, and  $G''$  for all of the samples tested. The latter, viz.  $G''$  behavior is consistent with the existence of Newtonian plateau in viscosity function. It is also noted that the melt elasticity of A-4090 is higher at low frequencies and lower at high frequencies compared to that of A-4085.

$G'$  is a useful parameter to determine the MW of the sample.<sup>13-17</sup> With increasing MW, the width of plateau value increases rapidly. In our experiment, the plateau does not appear at the highest frequency available. On the other hand, the shape of  $G''$  in terminal region strongly depends upon the MWD,<sup>15-19</sup> because chains of different size relax to equilibrium at different times. With narrow MWD, the terminal loss peak is sharply defined, and it is merely a broad shoulder with broad MWD. As the frequency further goes up, samples of different MW and MWD merge since the response depends only on the local chain motion.<sup>15</sup>

From these rheological properties, we may assess that the MWD of P-0680 is slightly broader than P-0480, and A-4085 than A-4090. This apparently makes contradiction with our GPC data, and the reason may be put in the following way. RDS measurement corresponds to fully viscoelastic state where the terminal zone relaxation, a long time response, occurs, and the relaxation is primarily governed by the high Mw tail of the sample. On the contrary in GPC measurement, the far end of high molecular weight tail is cut off in general, the case encountered in our experiment. The information on MWD would therefore be different depending on the characterization method. It should also be noted that the  $G''$  for A-4085 is higher than A-4090 throughout the frequency range, an agreement with viscosity function.

$\tan \delta$  as a function of  $\omega$  is shown in Fig. 8.  $\tan \delta$ , by definition, is the ratio of energy dissipated via viscous action, to energy stored elastically,

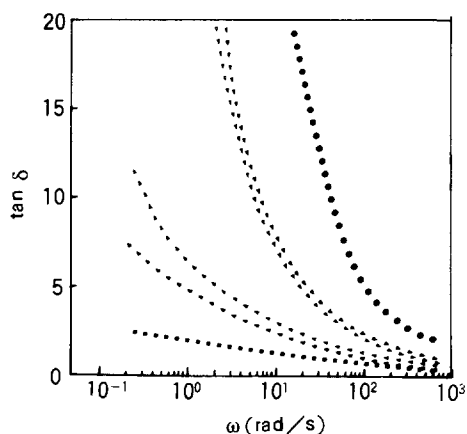


Fig. 8. Loss tangent for ULDPEs and HDPE(E308) : (◄) P-0680, (◁) P-0480, (►) A-4090, (▷) A-4085, (●) A-20090, (■) E308.

in a cyclic deformation. The  $\tan \delta$  values of the ULDPEs are significantly higher than that of HDPE due mainly to the lower MW of the ULDPEs. A close comparison between the HDPE ( $M_w = 180000$ ) and P-0680 ( $M_w = 172100$ ) reveals that melt elasticity ( $G'$ ) is also controlled by MWD ( $M_w/M_n = 8.6$ , and  $1.94$  for HDPE and P-0680, respectively). With broad MWD, higher melt strength is indicated.<sup>20</sup>

The relaxation spectrum, calculated using  $G''$  data in Ninomiya-Ferry's first order approximation<sup>21</sup> is given in Fig. 9. A-4085 and A-4090 show essentially identical relaxation time distribution, but the distribution of P-0680 is greater than that of P-0480 at longer relaxation times. In addition, the ULDPEs relax much faster than the HDPE due to the smaller distribution in high molecular weight tail of the MWD. Short relaxation times of the ULDPEs make the melt processing easy, and lead to effective hot melt.

Finally the Cole-Cole plots for the ULDPEs are shown in Fig. 10. The plots for the series A define semicircle. In pure resin other than blend, drift from semicircle is found with bimodal MWD having two discrete relaxation time distributions.<sup>22,23</sup> However, our GPC trace exhibited a unimodal type MWD (not shown), and the relaxation time distri-

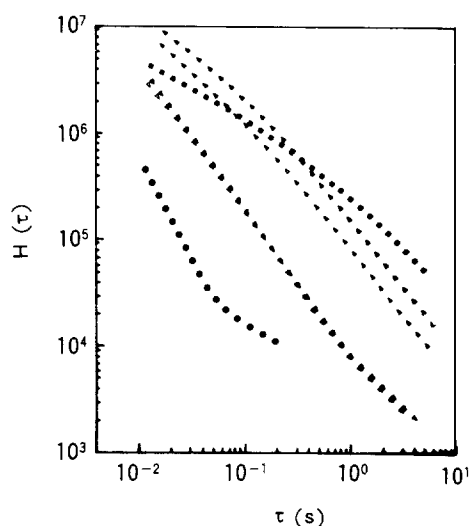


Fig. 9. Relaxation spectra for ULDPEs and HDPE(E308) : (◄) P-0680, (◁) P-0480, (►) A-4090, (▷) A-4085, (●) A-20090, (■) E308.

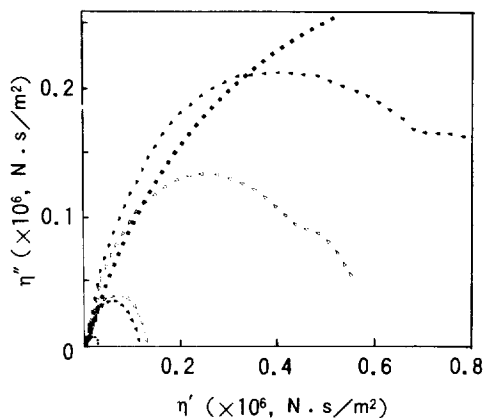


Fig. 10. Cole-Cole plots for ULDPEs and HDPE(E308) : (◄) P-0680, (◁) P-0480, (►) A-4090, (▷) A-4085, (●) A-20090, (■) E308.

bution was also of uniform for series P. We are not aware of anything precisely for the nature of the drift except that the series P contains relatively longer side chains (4-methyl pentene-1) than series A (butene-1).

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