

# LLDPE/LDPE Blends. II. Viscoelastic Properties in Solid State

MASAYUKI YAMAGUCHI, SHIGEHICO ABE

Yokkaichi Research Laboratory, TOSOH Corporation, 1-8 Kasumi, Yokkaichi, Mie 510-8540 Japan

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**ABSTRACT:** The effect of a small addition of a low density polyethylene into a linear low density polyethylene (ethylene-1-hexene copolymer; density =  $900 \text{ kg m}^{-3}$ ) on the linear and nonlinear viscoelastic properties in the solid state were studied. It was found that the addition of the low density polyethylene leads to a well-organized crystalline structure. Consequently, the location of  $\alpha$  relaxation process is shifted to higher temperature or longer time. Furthermore, the mechanical nonlinearity of the blend is found to be more prominent than that of the pure linear low density polyethylene. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3160–3164, 1999

**Key words:** linear low density polyethylene; low density polyethylene; polymer blend; viscoelastic property; nonlinear mechanical property

## INTRODUCTION

In the preceding study,<sup>1</sup> the linear low density polyethylene (LLDPE) (ethylene-1-hexene copolymer, density =  $900 \text{ kg m}^{-3}$ ) produced by the metallocene catalyst is found to be miscible in the molten state with the low density polyethylene (LDPE) obtained by chain-transfer reactions during free radical polymerization. Furthermore, the LDPE acts as the nucleating agent for the crystallization of the LLDPE. Consequently, the degree of crystallinity and the hardness of the LLDPE-LDPE (97.5/2.5) is much higher than those of the pure LLDPE, although the amount of the LDPE in the blend is fairly small. In this study, linear and nonlinear viscoelastic properties for the LLDPE and the LLDPE-LDPE (97.5/2.5) films are studied in detail for better understanding of the mechanical properties in the solid state.

Generally, the mechanical properties for crystalline polymers are complicated, because they

exhibit the marked departure from the linear viscoelasticity even in the small strain region.<sup>2–4</sup> It is, however, well known that the nonlinear relaxation modulus of some crystalline polymers with spherulitic structure, such as polyethylene and polypropylene, is expressed by the products of the linear relaxation modulus and the constant which expresses the degree of mechanical nonlinearity.<sup>5–9</sup> Ferry and Stratton<sup>10</sup> have considered that the degree of nonlinearity is decided by the change of the free volume fraction. Following that idea, Knauss and Emri,<sup>11</sup> and Popelar and Kenner<sup>8</sup> predicted the stress-strain curves of polyethylene. Furthermore, Nitta and Yamaguchi<sup>12,13</sup> have also proposed a nonlinear constitutive equation for crystalline polymers, in which anharmonicity of elasticity and plastic deformation are concerned. According to the constitutive equation,<sup>12</sup> Grüneisen constant,<sup>14</sup> which represents the anharmonicity of molecular potential, and the degree of plastic deformation decide the mechanical nonlinearity in the strain region below the yield point. In these studies, however, it has not been well elucidated what kinds of structural parameters affect the mechanical nonlinearity. The aim of this study was to clarify the relationship

Correspondence to: M. Yamaguchi (m\_yama@tosoh.co.jp).

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**Table I** Melting Point  $T_m$ , Density  $\rho$ , Volume Fraction of Crystallinity  $\chi_v$ , and Radius of Spherulites  $R_s$  for the LLDPE and the LLDPE-LDPE (97.5/2.5)

Sample	$T_m$ (K)	$\rho$ (kg m <sup>-3</sup> )	$\chi_v$ (vol %)	$R_s$ ( $\mu$ m)
LLDPE	370.3	903.1	33.2	6.5
LLDPE-LDPE (97.5/2.5)	372.5	904.8	34.3	0.7

between structure and mechanical nonlinearity for the LLDPE and the LLDPE-LDPE blend.

## EXPERIMENTAL

The experimental procedure for the preparation of sample films of the LLDPE and the LLDPE-LDPE (97.5/2.5) was described in the preceding article.<sup>1</sup> The characteristics of the sample films used are summarized in Table I. In the table, radii of spherulites were determined by small-angle light scattering measurements.

The linear and nonlinear viscoelastic properties in the solid state were measured using a dynamic mechanical analyzer (DVE V-4, Rheology Co., Ltd., Kyoto, Japan). The rectangular specimens, in which the width is 2 mm and the length is 20 mm, were cut from the films. The temperature dependence of tensile storage modulus  $E'$ , loss modulus  $E''$ , and loss tangent  $\tan \delta$  was measured at 10 Hz, and from 200 to 375 K at a heating rate of 2 K min<sup>-1</sup>. The frequency dependence of tensile moduli was measured in the frequency range of 0.1 and 200 Hz at temperatures between 298 and 333 K. The oscillatory moduli were obtained by vertical shifts as well as horizontal ones. Stress relaxation measurements were also performed at 298 K. The applied strain levels were below the yield strain. Initial strain was applied at a constant strain rate of  $2.85 \times 10^{-2} \text{ s}^{-1}$  and the time variation of the stress was monitored. In this study, the linear relaxation modulus  $E(t)$  was estimated from the master curves of oscillatory moduli using the following equation proposed by Schwarzl<sup>15</sup>:

$$E(t) = E'(\omega) - 0.560E''(\omega/2) + 0.200E''(\omega)|_{\omega=1/t}$$

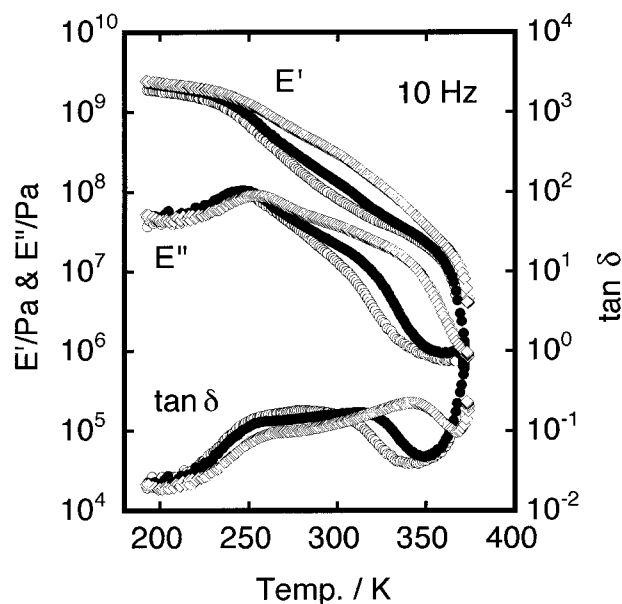
## RESULTS

### Characterization of Samples

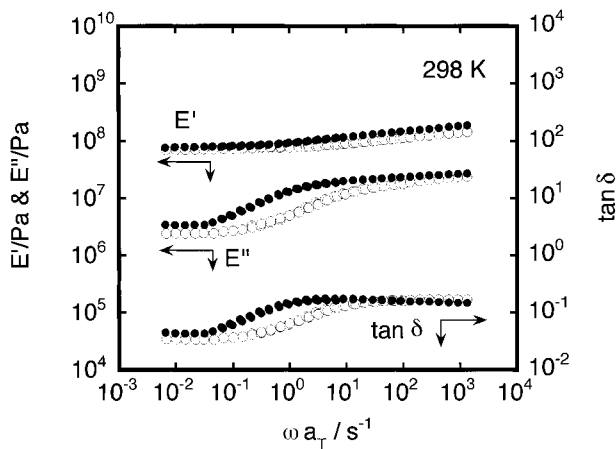
Table I summarizes the characteristics of the LLDPE and the blend [LLDPE-LDPE (97.5/2.5)]. In the table, volume fraction of crystallinity  $\chi_v$  is estimated from the density.<sup>1</sup> As described in the previous article, a small addition of the LDPE greatly enhances the crystallinity, such as melting temperature and degree of crystallinity. Moreover, the radius of spherulites of the blend is much smaller than that of the LLDPE, demonstrating that the LDPE acts as the nucleating agent for the crystallization of the LLDPE.

### Linear Viscoelastic Properties

Figure 1 shows the temperature dependence of tensile storage modulus  $E'$ , loss modulus  $E''$ , and loss tangent  $\tan \delta$ . In the figure, the oscillatory moduli for the LDPE were also plotted. As seen in the figure, the magnitude of  $E'$  decreases with increasing temperature and falls off sharply at the melting temperature. It was also found that the blend shows much higher moduli than the LLDPE, although the amount of the LDPE in the blend is only 2.5 wt %. Furthermore, there are two relaxation peaks in the  $\tan \delta$  curve for the



**Figure 1** Temperature dependence of oscillatory tensile moduli, such as storage modulus  $E'$ , loss modulus  $E''$ , and loss tangent  $\tan \delta$  for LLDPE ( $\circ$ ), LDPE ( $\diamond$ ), and LLDPE-LDPE (97.5/2.5) ( $\bullet$ ). The frequency used was 10 Hz.



**Figure 2** Master curves of oscillatory tensile moduli, such as storage modulus  $E'$ , loss modulus  $E''$ , and loss tangent  $\tan \delta$  for LLDPE (○) and LLDPE-LDPE (97.5/2.5) (●). The reference temperature is 298 K.

LDPE in the temperature range: the peak located at approximately 260 K is ascribed to  $\beta$  relaxation; and the other peak at approximately 350 K is ascribed to  $\alpha$  relaxation. On the other hand, there is an ambiguous broad peak in the temperature between 240 and 320 K for the LLDPE. The peak is composed of both  $\alpha$  and  $\beta$  relaxation. Moreover, the shape of the  $\tan \delta$  curve for the blend is much different from that for the pure LLDPE. In particular, the  $\alpha$  relaxation process for the blend is located in a much higher temperature than that for the LLDPE. It is well known that  $\alpha$  relaxation of crystalline polymers consists of at least two processes, referred to as  $\alpha_1$  and  $\alpha_2$  from lower temperature, respectively.<sup>2-4</sup> The  $\alpha_1$  process is pronounced in melt crystallized samples and is associated with the relaxation of grain boundaries, that is, mobility of crystalline fragments. The  $\alpha_2$  process is pronounced in single crystal mats and is ascribed to incoherent oscillations of the chains around their equilibrium positions in the crystalline lattice in which intermolecular potential suffers a smearing out. The  $\alpha$  relaxation in the present samples will be associated with the  $\alpha_1$  process because of the low degree of crystallinity.<sup>2,16</sup>

Figure 2 shows the master curves of the angular frequency dependence of oscillatory tensile moduli for the LLDPE and the blend. The reference temperature is 298 K. It was found that the magnitude of  $E''$  and  $\tan \delta$  greatly decreases with decreasing the angular frequency  $\omega a_T$  at approximately  $10^1 \text{ s}^{-1}$  for the LLDPE and at  $10^0 \text{ s}^{-1}$  for the blend. The difference demonstrates that the  $\alpha$

relaxation process for the blend is located at a much longer time than that for the LLDPE, which corresponds with the result of the temperature dependence of oscillatory moduli as shown in Figure 1. The shift of the location of the  $\alpha$  relaxation process to a longer time or higher temperature demonstrates that the mobility of crystalline fragments is suppressed. It is plausible because a well organized crystalline structure is formed in the blend by the blending of the LDPE, which acts as the nucleating agent for the LLDPE. The difference in the mobility of crystalline fragments will greatly affect the nonlinear mechanical properties in the preyield strain region.

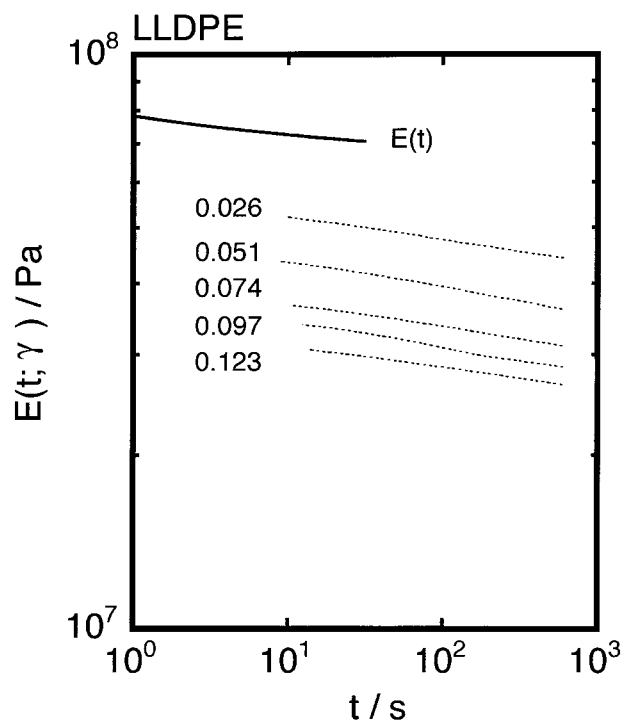
### Nonlinear Relaxation Modulus

Stress relaxation measurements under large strains were performed to clarify the mechanical nonlinearity. Figure 3 shows nonlinear relaxation moduli for the LLDPE and the blend at 298 K. In the figure, numerals denote the applied strain levels, and dashed lines and a solid line represent, respectively, the experimental values and the linear relaxation modulus  $E(t)$  calculated by the master curves of oscillatory moduli, shown in Figure 2, using eq. (1). The applied strains are below the yield point in which neither necking band nor stress-whitening is observed. In general, adiabatic deformation will lead the change of temperature of the sample. The temperature change under hydrostatic pressures is known to be given by the following equation<sup>17</sup>:

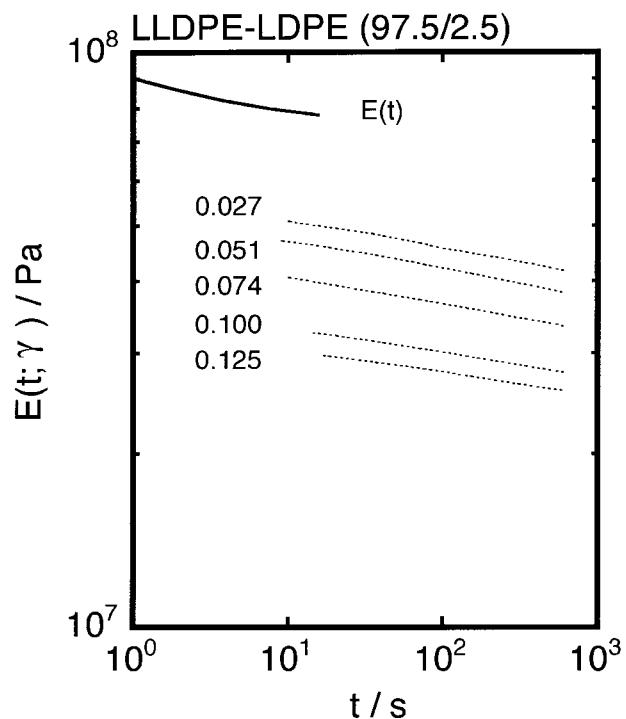
$$\left(\frac{\partial T}{\partial P}\right)_\theta = \frac{\alpha_v T_0}{\rho C_P} \quad (2)$$

where  $T_0$  is the reference absolute temperature,  $\alpha_v$ , the volume thermal expansion coefficient,  $C_P$ , the specific heat at constant pressure, and  $\rho$ , the density. Assuming that  $\alpha_v$  and  $C_P$  for the LLDPE are the same as those for LDPE,  $\alpha_v$  is  $5.1 \times 10^{-4}$  [Ref. 18] and  $C_P$  is  $1.916 \times 10^3$  [Ref. 19], the thermoelastic coefficient is estimated to be  $0.088 \text{ K MPa}^{-1}$ . The stress during the stress relaxation measurements in this study is below 10 MPa. Thus, the temperature change is within 1 K, which is negligible.

It was found from Figure 3 that the mechanical nonlinearity is prominent even when the strain level is approximately 0.03. The deviation from the linear relaxation curve is pronounced as the applied strain increases. Moreover, the degree of

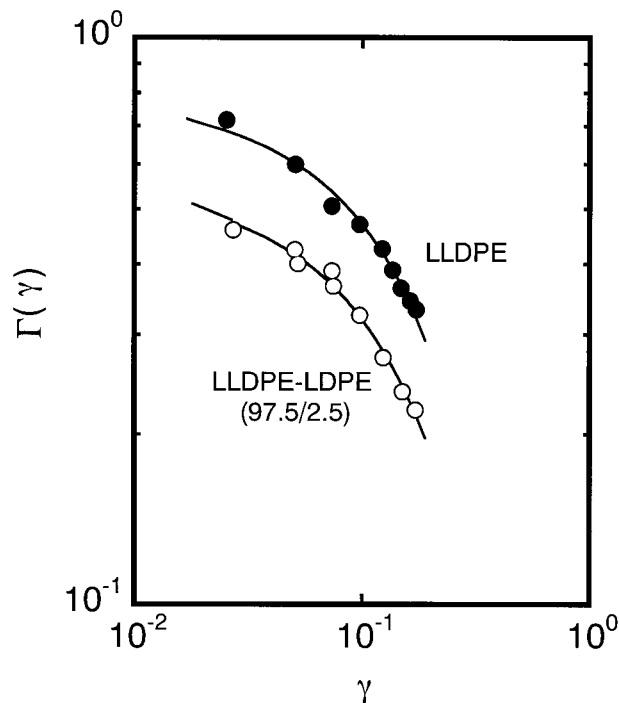


(a)



(b)

**Figure 3** Nonlinear relaxation moduli  $E(t; \gamma)$  at 298 K: (a) LLDPE and (b) LLDPE-LDPE (97.5/2.5). Numerals in the figures denote the applied strain levels, the bold solid line the linear relaxation modulus  $E(t)$  calculated by eq. (1).



**Figure 4** Applied strain dependence of nonlinear parameter  $\Gamma(\gamma)$  for LLDPE (●) and LLDPE-LDPE (97.5/2.5) (○).

deviation from the linear relaxation modulus for the blend is larger than that for the LLDPE. Furthermore, the nonlinear relaxation moduli can be superposed onto each other in the experimental range from the phenomenological point of view. According to numerous studies,<sup>5-9,12,13</sup> the nonlinear relaxation modulus  $E(t; \gamma)$  is often described by the following relation:

$$E(t; \gamma) = E(t)\Gamma(\gamma) \quad (3)$$

where  $\Gamma(\gamma)$  represents the degree of mechanical nonlinearity. The applicability of eq. (3) also has been reported for polyethylene and polypropylene with spherulitic structure.<sup>5-9,12,13</sup>

Assuming that eq. (3) is also applicable in the present study, the nonlinear parameter  $\Gamma(\gamma)$  is estimated as a function of the applied strain. Figure 4 shows the strain dependence of  $\Gamma(\gamma)$ . The nonlinear parameter is unity at the strain of 0.00025, which is the applied oscillatory strain during the measurements of oscillatory moduli. As seen in the figure, the magnitude of  $\Gamma(\gamma)$  decreases rapidly with increasing the applied strain, that is, the mechanical nonlinearity is enhanced near the yield point. Furthermore, the

magnitude of  $\Gamma(\gamma)$  of the blend is much lower than that of the LLDPE, indicating that the blend shows marked nonlinearity of the mechanical behavior. In the preyield strain region, the following four processes of deformation are considered to take place dominantly by rheo-optical studies and so on<sup>3,20,21</sup>: 1. orientation of the amorphous chain; 2. affine or pseudo affine deformation of spherulites; 3. rearrangement of crystalline fragments because of the bending, twist, or slippage in lamellae; and 4. plastic deformation such as void opening and dislocation of crystalline defect. As increasing in the strain, mechanisms 3 and 4 have a large effect on the mechanical nonlinearity.<sup>3,20,21</sup> Moreover, in the case of the samples with a well organized crystalline structure, rearrangement of crystalline fragments and plastic deformation take place dominantly instead of affine deformation of spherulites,<sup>3,20,21</sup> because the mobility of crystalline fragments is suppressed. Also in the present study, the magnitude of mechanical nonlinearity corresponds to the mobility of crystalline fragments, that is, the blend, in which the mobility of crystalline fragments is lower than that in the pure LLDPE, shows a marked nonlinearity.

## CONCLUSIONS

The effect of a small addition of LDPE into LLDPE on the linear and nonlinear viscoelastic properties in the solid state was studied. The  $\alpha$  relaxation process of the LLDPE-LDPE blend, in which the amount of the LDPE is only 2.5 wt %, is more prominent than that of the LLDPE, indicating that a well organized crystalline structure is formed. Furthermore, the nonlinear relaxation moduli for the blend were found to deviate greatly from the linear relaxation modulus, demonstrating that the blend shows the marked mechanical nonlinearity. It is attributed to the depression of the mobility of crystalline fragments.

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