TEMPERATURE-INDUCED STRUCTURAL CHANGES IN STRAIN-HARDENING BEHAVIOUR OF SEMI-CRYSTALLINE POLYMER

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Abstract

Strain-hardening is essential in processing semi-crystalline polymers such as high-density polyethylene (HDPE). Although the behavior has been ascribed to the network density, its temperature dependence seems somewhat contradictory. This work aims to reveal the effect of temperature on HDPE’s strain-hardening behavior from the structural point of view. HDPE samples with different $M_w/M_n$ with almost identical $M_w$ are used to investigate the influence of the amorphous network. Dynamic response of polymer chains is detected by in situ Raman spectroscopy combined with step-cycle tests to monitor changes in the amorphous region and crystalline phase during strain-hardening. While the step-cycle response of the stress is more elastic for higher $M_w/M_n$ due to higher network density, the inter-crystalline motion above the $a_1$ relaxation region decreases pressure on the polymer chains. Thus, it is suggested that the inter-and intracrystalline relaxation is responsible for discrepancy from the prediction by Haward theory based on the amorphous network.

Keywords: high-density polyethylene, in-situ raman spectroscopy, strain-hardening behavior

INTRODUCTION

High-density polyethylene (HDPE) is a semi-crystalline polymer commonly used daily because of its high strength. It has hierarchical structures, from $10^{-10}$ m of polyethylene chain, a $10^{-9}$ m of a lamellar cluster, a $10^{-7}$ m of spherulite until a $10^{-6}$ m of HDPE film. The lamellar structure consists of the neatly ordered chain in crystalline phases and random chains in the amorphous region (Ward & Sweeney, 2013).

One of the origins of the strength of HDPE is strain-hardening behavior. The behavior describes the ability of the structure to resist applied stress. In processing HDPE, optimum strain-hardening behavior is desired to provide sufficient stretchability and bendability for the high-quality final product, avoiding any crack and macroscopically failure (Senden, Dommelen, & Govaert, 2010). Therefore, it is crucial to investigate the origin of strain-hardening behavior.

A tensile test can investigate Strain-hardening behavior. In the stress-strain curve, the tensile test result shows that the strain-hardening region covers the natural draw ratio until the breaking point. Here, strain-hardening behavior is measured as strain-hardening modulus $G_p$ based on Haward theory, Equation 1 (Haward, 1993), where $k$ is Boltzmann constant ($k = 1.38 \times 10^{-23}$ J.K$^{-1}$), $T$ is the temperature (K), and $\nu$ is network density. According to Haward, the strain-hardening modulus is proportional to the network density and temperature (Haward, 1993).

$$G_p = \nu \cdot k \cdot T$$  (1)

It has been reported for HDPE that a higher strain hardening behavior is observed for HDPE with wider molecular weight distribution (higher $M_w/M_n$). It is in fair agreement with the Haward theory because comprehensive $M_w/M_n$ provides a denser network in its amorphous
region (Kida, Hiejima, & Nitta, 2019). However, it has been reported that $G_p$ decreases with temperature (Na et al., 2007; Van Melick, Govaert, & Meijer, 2003), which is contradictory to Equation 1.

Because $G_p$ of HDPE is strongly dependent on the molecular weight distribution $M_w/M_n$ (Kida et al., 2019), in-situ Raman spectroscopy and the step-cycle tests were applied HDPE with different $M_w/M_n$ with almost identical $M_w$. The effects of temperature on structural changes in HDPE's strain-hardening behavior are investigated to shed light on the Haward theory's limitation.

**METHOD**

We used HDPE supplied by Japan Polychem Corporation. In order to clarify the effect of network density, we used HDPE6 ($M_w = 18.6 \times 10^4, M_w/M_n = 6$) and HDPE15 ($M_w = 17.0 \times 10^4, M_w/M_n = 15$). It is noteworthy that the polydispersity index ($M_w/M_n$) is doubled, whereas the weight-average molecular weight ($M_w$) is practically the same. The GPC curves confirm the characteristics of the molecular weight distribution in Fig 1.

As a material for undrawn specimens, adapted from a previous report (Kida et al., 2019), HDPE sheets were prepared. The pellets of HDPEs were melted at 483 K for 5 min. It was followed by degassing for 5 min, pressing at 20 MPa and 483 K for 5 min, and quenching in iced water for 5 min, sequentially. Annealing was conducted 5 hours at 333 K for HDPE6 and at 393 K for HDPE15 to obtain the thickness of 200 mm. The volumetric crystallinity was determined to be 59% for HDPE6 and HDPE15 by using the Archimedes method, where the crystalline and amorphous densities were assumed to be $\rho_c = 1000 \text{ kg.m}^{-3}$ and $\rho_a = 855 \text{ kg.m}^{-3}$ (J. Brundrup, E.H. Immergut, E.A. Grulke, A. Abe, 1999), respectively. The value of volumetric crystallinity is similar to crystallinity obtained by WAXD (wide-angle X-ray diffraction). Lamellar thickness was determined to be about 27 nm by SAXS (small-angle X-ray scattering) measurements. The similarity in the crystalline structure for both samples guarantees that the difference in the strain-hardening behavior is only originated from the network density. The HDPE sheets were cut into two types of dumb-bell shaped undrawn specimens. Type 1 has 10 mm of gauge length and 4 mm of width. This type was used for in-situ Raman spectroscopy. Type 2 has 4 mm of gauge length and width. This type was used for the step-cycle test. It is noticed that type 2 provides a broader area of unstretched specimens that prevent a slip during the trial.
To confirm whether the samples follow Haward’s relation that strain-hardening modulus $G_p$ has a linear correlation with temperature, uniaxial continuous tensile testing was conducted on undrawn specimens in different temperatures to determine $G_p$. The test was born with a strain rate of 1 min$^{-1}$ in 293 K and 333 K. It is noteworthy that the temperature applied were quite different to provide a wide possibility to find a distinguished response from HDPE structures during strain-hardening. Regarding a gaussian chain of HDPE, the strain-hardening modulus was calculated using Equation (2). Here, $\sigma_t$ is right to stress, $\lambda$ is draw ratio, and $\lambda_{NDR}$ is draw ratio at NDR (K. Nitta & Yamana, 2012).

$$\sigma_t = G_p \left\{ \left( \frac{\lambda}{\lambda_{NDR}} \right)^2 - \frac{\lambda_{NDR}}{\lambda} \right\}$$

To be focused on the strain-hardening region, drawn specimens were prepared as follows. First, the model was uniaxially-stretched up to and strain rate of 1 min$^{-1}$ by using INSTRON Model 4466 at room temperature. The drawing was terminated at the strain of natural draw ratio (NDR) $\varepsilon_{NDR}$. Secondly, the stretched specimen was fixed at the piece for 20 min. Finally, the sample was left at room temperature for 24 hours for complete relaxation.

As a continuous tensile test result, a curve is a sum of elastic and plastic deformation during the test, a step-cycle test as a dynamic mechanical test was performed. The test is conducted on drawn specimens with a strain rate of 1 min$^{-1}$ at 293 and 333 K. In the method, the HDPE specimen underwent loading and unloading processes until its broken point. Here, a cycle refers to one loading and one unloading process. HDPE was stretched up to a strain of 0.5 (loading process), followed by unloading until $\sigma = 0$ was reached. It is noteworthy that a piece of 0.5 was used to limit each cycle to prevent a large deformation. Elasticity is the focus of this test to represent the response of the network during strain-hardening. Thus, the analyzed parameters were elastic strain fraction and flexible energy fraction, a ratio of elastic strain and elastic energy toward a whole built pressure and strength for each step.

In an attempt to reveal the role of the crystalline phase of HDPE during strain-hardening behavior, in situ Raman spectroscopy was performed. A Raman spectrometer was previously applied to the-Raman measurements (Kida, Hiejima, & Nitta, 2016, 2017; Kida, Oku, Hiejima, & Nitta, 2015). A DPSS laser (RLK-640-200, LASOS) and a CCD camera equipped with a monochromator (PIXIS100 and SpectraPro 2300i, Princeton Instruments) were used as the light source and detector, respectively. The sample was a notched shape of drawn HDPE with 10 mm of length. It was subjected to a tensile test with a strain rate of 0.5 min$^{-1}$ at 293 and 333 K. The structure of its central portion was monitored by a Raman spectrometer. Each Raman spectrum was accumulated one time with an exposure time of 10 s. The range was fitted with the sum of Voigt functions using the nonlinear Levenberg–Marquardt method. The peak position of 1063 cm$^{-1}$ was determined accurately using the peak of 1298 cm$^{-1}$ as the internal reference—the height assigned to the anti-symmetric C-C stretching of the HDPE crystalline chain. Peak shift $\Delta \nu$ is defined as the deviation of the peak position during the tensile test, $\Delta \nu = \nu_t - \nu_0$. Here, $\nu_0$ is an initial peak position of the drawn specimen, and $\nu_t$ is a peak position during the tensile test. A peak shift provides information about changes in a crystalline phase of the HDPE chain. Negative and positive peak shifts are called red and blue dresses, respectively.

As a peak shift describes a load-sharing mechanism, tie molecules are suggested to be involved (Kida et al., 2016). The tie molecule analysis was conducted with Equation (3), based on the Huang-Brown model. It was used to predict the number of tie molecules that bind a certain
number of lamellar layers (Nilsson, Lan, Gkourmpis, Hedenqvist, & Gedde, 2012). Here, \( f_n(M) \) is the number-averaged molecular weight distribution, and \( f_t \) is the tie molecule fraction for one single molecular chain.

\[
F_t = \frac{\int_0^{\infty} f_t(M) dM}{\int_0^{\infty} f_n(M) dM}
\] (3)

Temperature dependence of HDPE viscoelasticity was evaluated using DVE-V4 (UBM Co., Ltd., Kyoto, Japan) from 123 to 423 K at 10 Hz. The dimension of specimens was 5 mm in width and 10 mm in length.

**RESULT AND DISCUSSION**

Fig 2 shows normalized stress-strain curves resulted from a continuous tensile test of undrawn specimens based on Equation (2). Calculated values of \( G_p \) are presented in Table 1. It is found that HDPE15 exhibits a more robust strain-hardening behavior than HDPE6 irrespective of temperature, which is consistent with the previous work (Kida et al., 2019). The higher \( M_w/M_n \) gives higher \( G_p \) supports the Haward theory, where a denser network leads to higher strain-hardening (Haward, 1993). However, \( G_p \) becomes much smaller at high temperatures; \( G_p \) of HDPE6 decreases by 50% from 293 to 333 K, which is contrary to the Haward theory (Haward, 1993).

![Normalized stress-strain curves of HDPE6 and HDPE15 at (a) 293 and (b) 333 K.](image)

Table 1. Strain-hardening modulus of undrawn specimens.

<table>
<thead>
<tr>
<th>Temperatures (K)</th>
<th>( G_p ) (MPa)</th>
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<tbody>
<tr>
<td></td>
<td>HDPE6</td>
</tr>
<tr>
<td>293</td>
<td>56.4 ± 1.3</td>
</tr>
<tr>
<td>333</td>
<td>25.59 ± 0.24</td>
</tr>
</tbody>
</table>

Fig 3 shows a typical result for step-cycle tests for HDPE15 at 333 K. The upper envelope of the step-cycles curve successfully reproduces the stress-strain curve of the tensile tests for the drawn specimen as also reported by previous reports (Bartczak, 2005; Humbert, Lame, Chenal,
Seguela, & Vigier, 2012). It proves that the step-cycle test is a reliable method to reveal changes in elasticity of drawn HDPE during strain-hardening behavior.

Fig 4 shows the cycle dependence of the elasticity profile of HDPE is stronger than temperature dependence. Here, elasticity is represented by elastic strain and elastic energy fraction. The elastic strain was defined by a ratio of the recovered strain to the applied strain after a loading and unloading process. The elastic energy is the recovered energy after the procedure (Patlazhan, Hizoum, & Rémond, 2008). Similar values of elastic strain and flexible strength are discovered in the fourth cycle at all HDPE temperatures. It indicates no significant changes in the amorphous region at low cycles. For HDPE15 at 333 K, elasticity of markedly enhanced. The increase of elasticity at higher processes is explained by a pull-out chain mechanism, where crystalline chains are pulled out and fill the amorphous region (Blumenfeld, 2000). For HDPE 6 at 333 K, its elasticity is almost constant beyond the fourth cycle, indicating no improvement in the amorphous chain’s entanglement. The more oriented undeveloped chain is suggested for this phenomenon, as found in previous reports on stretched ultra-high molecular weight polyethylene in high temperature (Zhu et al., 2017).
of HDPE15 is appreciably more extensive than that of HDPE6. Based on the load sharing mechanism (Kida et al., 2016), the larger red shift of HDPE15 is explained that wider $M_d/M_n$ provides a denser network chain in the amorphous region. Note that the amorphous network plays the role of stress-transmitter. At 333 K, the red shift's overall level is smaller than at 293 K owing to lower stress exerted on the crystalline chains.

![Graph](image)

**Fig 5.** Peak shifts of HDPE6 and HDPE15 at (a) 293 and (b) 333 K.

The probability to form a tie molecule is estimated by Equation (1) and plotted against the number of lamellae connected by the tie molecule in Figure 6. It is clearly shown that tie molecules of HDPE 15 are always more extensive than that of HDPE6, irrespective of the number of lamellar layers. The longer chains are likely to acts as tie molecules that bind several lamellae together, building lamellar cluster units (Kida et al., 2019; Lagarón, Capaccio, Rose, & Bert, 2000; Xiong, 2016).

Fig 7 shows $a_1$ relaxation temperature of HDPE is at around 333 K. At this temperature, an interlamellar slip process and motion in the inter-crystalline region occur (K. H. Nitta & Tanaka, 2001). As the value of $a_1$ relaxation, the temperature is the same for both HDPE, the motion is suggested to be the leading cause of temperature dependences.
Fig 6. Tie molecules analysis; HDPE15 possesses a doubled number of tie molecules of which HDPE6.

Fig 7. Dynamic mechanical properties of HDPE6 and HDPE15 reveals structural motion along with temperatures.

Fig 8. Model for strain-hardening behavior at 293 K.
During the tensile test, macroscopic stress applied on HDPE is accepted by the amorphous chain and transmitted to crystalline as a load. Below $a_1$ relaxation temperature, as shown in Fig 8, with the absence of inter-crystalline motion, a crystalline phase has an unnegligible contribution in supporting amorphous chain resisting stress. Having a denser network in the amorphous region and more tie molecules, HDPE 15 can transmit more macroscopic stress to the crystalline phase than HDPE 6, so that with the same applied stress level, HDPE 15 produces less strain than HDPE 6. In other words, HDPE 15 has more strength to resist stress, and it results in a higher strain-hardening modulus.

Considering elasticity, because the crystalline chain actively releases energy from transmitted load in its stretching, the difference of the amorphous chain in storing energy is not too large between HDPE 6 and HDPE 15. It results in a small difference of $G_p$ between HDPE 6 and HDPE 15.

At $a_1$ relaxation temperature, inter-crystalline motion is activated. In Fig 9, at given stress, the strain is more extensive than shown in Fig 8. The macroscopic focus from the tensile test is not effectively transmitted to the crystalline phase because it is not steady. In that way, the crystalline phase's function in supporting amorphous resisting stress is reduced and results in reduced strain hardening modulus from which at below $a_1$ relaxation temperature.

At $a_1$ relaxation temperature, as a consequence of less contribution from the crystalline phase in governing strain-hardening, the amorphous chain effect on strain hardening is observed clearer. The undeveloped chain is more active in resisting stress and storing energy. HDPE 15, with more tie molecules and denser network density, can withstand more pressure and keep more life. Energy is stored in the amorphous chain's entanglement (Bartczak, 2005; Bartczak & Kozanecki, 2005; Kida et al., 2019; Pawlak, 2019). It is detected by a significant difference in $G_p$ and elasticity between HDPE 6 and HDPE 15 at $a_1$ relaxation temperature.

**CONCLUSION**

In this work, a controversy on Haward's theory about the temperature dependence of strain-hardening behavior is discussed. Two kinds of HDPE with different $M_w/M_n$ is subjected to various temperature to show typical strain-hardening behavior. The red shift of *in situ* Raman spectra and the step-cycle tests suggest that the failure of the Haward theory is caused by inter-crystalline relaxation, which suppresses the stress transmission between the lamellar cluster units. The pull-out chain mechanism also interprets the enhancement of elasticity for more extensive $M_w/M_n$ observed by the step-cycle tests.
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REFERENCES