

Title	Effect of thermal modification on rheological properties of polyethylene blends
Author(s)	Monchai Siriprumpoonthum; Nobukawa, Shogo; Satoh, Yasuo; Sasaki, Hiroko; Yamaguchi, Masayuki
Citation	Journal of Rheology, 58(2): 449-465
Issue Date	2014-02-26
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/14739
Rights	Copyright 2014 The Society of Rheology. This is the author's version of the work and posted here with permission of the Society of Rheology. Monchai Siriprumpoonthum, Shogo Nobukawa, Yasuo Satoh, Hiroko Sasaki and Masayuki Yamaguchi, Journal of Rheology, 58(2), 449-465 (2014). http://dx.doi.org/10.1122/1.4866345
Description	

Effect of Thermal Modification on Rheological Properties of Polyethylene Blends

**Monchai Siriprumpoonthum¹, Shogo Nobukawa¹, Yasuo Satoh²,
Hiroko Sasaki², Masayuki Yamaguchi^{1*}**

- 1) School of Materials Science, Japan Advanced Institute of Science and Technology,
1-1 Asahidai, Nomi, Ishikawa 923-1292 JAPAN**
- 2) Packing & Industrial Materials Laboratory, Prime Polymer Co., Ltd.
3 Chigusa-kaigan, Ichihara, Chiba 299-0108 JAPAN**

*** Correspondence to:**

Masayuki Yamaguchi
Japan Advanced Institute of Science and Technology
1-1 Asahidai, Nomi, Ishikawa 923-1292 JAPAN
Phone +81-761-51-1621, Fax +81-761-51-1625
e-mail m_yama@jaist.ac.jp

Synopsis

We examined the effects of thermal modification under flow field on the rheological properties of linear low-density polyethylene (LLDPE) with high molecular weight, low-density polyethylene (LDPE), and their blends, without thermal stabilizer. Although structural changes during processing are not detected by size exclusion chromatography or nuclear magnetic resonance spectroscopy (NMR), linear viscoelastic properties changed greatly, especially for the LLDPE. A cross-linking reaction took place, leading to, presumably, star-shaped long-chain branches. Consequently, the modified LLDPE, having high zero-shear viscosity, became a thermo-rheologically complex melt. Moreover, it should be noted that the drawdown force, defined as the uniaxial elongational force at a constant draw ratio, was significantly enhanced for the blends. Enhancement of elongational viscosity was also detected. The drawdown force and elongational viscosity are marked for the thermally-modified blend as compared with those for the blend of thermally-modified pure components. Intermolecular cross-linking reactions between LDPE and LLDPE, yielding polymers with more than two branch points per chain, result in marked strain-hardening in the elongational viscosity behavior even at small strain. The recovery curve of the oscillatory modulus after the shear modification is further evidence of a branched structure.

I. INTRODUCTION

Among conventional polymers, polyethylene has the widest variety of molecular structure with short- and long-chain branches and molecular weight distribution, which greatly affect its rheological behavior in the molten state. Consequently, various processing operations are available for polyethylene. For foaming and extrusion-coating, however, strong melt elasticity is required. Although some advanced methods have been proposed to increase the melt elasticity, including the enhancement of strain-hardening in the elongational viscosity [Yamaguchi and Miyata (2000); Mieda and Yamaguchi (2011); Yokohara *et al.* (2011)], intermolecular chemical reaction between polymer chains can also occur during foaming and extrusion-coating of polyethylene. According to previous reports, the rheological behavior of polyethylene, especially polyethylene without thermal stabilizer, is affected by the thermal history during processing. During processing, both chain scission and cross-linking reactions take place, the cross-linking reaction occurring more readily at relatively high temperatures, e.g., 250–320 °C. In these reactions, free radicals generated during processing play an important role. Kuroki *et al.* (1982) revealed that the rate of cross-linking reaction is 3–5 times larger than that of chain scission at temperatures below 350 °C. Andersson *et al.* (2004) found that the cross-linking reaction is dominant at temperatures below 325 °C during extrusion coating. The same result was obtained by Ono and Yamaguchi (2009a) for extrusion processing. Rangarajan *et al.* (1998), in contrast, reported that chain scission takes place randomly at temperatures between 450 and 490 °C. Because chain scission is generally not desired, various techniques are used to improve the cross-linking efficiency of polyethylene, such as irradiation [Rijke and Mandelkern (1971)], addition of peroxide compounds as free radical initiators, or addition of silane coupling agents. According to Ghosh *et al.* (1997), the addition of a proper amount of a peroxide compound results in the

acceleration of cross-linking reactions. This technique is applicable to control the shear viscosity and non-Newtonian behavior.

In the cross-linking reaction, macroradicals generated by the abstraction of a hydrogen atom in the chain, which often occurs at tertiary carbon atoms, show intermolecular reaction [Stockmayer (1944)]: X-type branch points are provided by the reaction of two macroradicals, whereas Y-type branch points result from the reaction between a macroradical and a double bond at the chain end (terminal vinyl) [Rijke and Mandelkern (1971); Peacock (1987); Smedberg *et al.* (1997)].

To our knowledge, however, most studies on the rheological changes resulting from thermal modification were restricted to a single component of polyethylene. Meanwhile, the marked elastic properties of LLDPE/LDPE blends, in which the LLDPE shows higher shear viscosity, have been reported by a number of researchers [Utracki and Schlund (1987); Wagner *et al.* (2004); Hussein and Williams (2004); Yamaguchi (2006a); Mieda and Yamaguchi (2007); Delgadillo-Velázquez *et al.* (2008); Mieda and Yamaguchi (2011)]. However, the thermal modification of LLDPE/LDPE blends has not been studied, even though the blends have been employed in industry. In this study, therefore, the effects of thermal history at high temperature on the rheological properties of LLDPE, LDPE, and their blends are studied. Because the mechanism of the anomalous rheological properties of the blends is still under discussion (as explained later), this study will also be valuable for understanding the molten structure of this interesting system.

II. EXPERIMENTAL

A. Materials and Sample Preparation

Commercially available LDPE, produced in an autoclave reactor, and LLDPE, synthesized by a metallocene catalyst, were used in this study. Neither sample contained thermal stabilizer. Molecular characteristics are summarized in Table I. The contents of unsaturated bonds at chain ends (terminal vinyl) and in the middle of chains (vinylene and vinylidene) were measured by proton nuclear magnetic resonance spectroscopy (^1H -NMR). The short- and long- ($\geq\text{C}_6$) chain branches per 1000 backbone carbon atoms were characterized by carbon nuclear magnetic resonance spectroscopy (^{13}C -NMR). The number of long- ($\geq\text{C}_6$) chain branches of LDPE is a typical one for conventional LDPE [Yamaguchi and Takahashi (2001); Wagner et al. (2003); Ono and Yamaguchi (2009a,b)]. Further, the molecular weights were evaluated by gel permeation chromatography (GPC) (Waters, Alliance GPC 2000) compared with a linear polyethylene standard, using TSK_{gel} GMH₆-HT and TSK_{gel} GMH₆-HTL, with ortho-dichlorobenzene at 140 °C as an eluant at a flow rate of 1.0 mL/min. The sample concentration was 0.15 wt.%.

TABLE I. Molecular characteristics of polyethylene used in this work

	GPC		^1H -NMR (per 1000 carbon atoms)			^{13}C -NMR (per 1000 carbon atoms)			
	Mn (Da)	Mw (Da)	terminal vinyl	vinylene	vinylidene	C2	C4	C5	C6 or more
LDPE	13,000	192,000	0.06	0.07	0.33	1	-	8	2
LLDPE	33,200	98,900	0.06	0.05	0.05	-	36	-	-

LDPE and LLDPE were melt-blended at various blend ratios in an internal batch mixer (Toyoseiki, Labo-plastmil) for 3 min at 280 °C to perform the thermal modification. The blade rotation speed was 30 rpm. Thermal stabilizers, such as pentaerythritol tetrakis(3-3,5-di-tert-

butyl-4-hydroxyphenyl propionate) (Ciba, Irganox1010) and tris(2,4-di-tert-butylphenyl)phosphate (Ciba, Irgafos168), were added after 3 min and further mixed for 30 s. The content of each additive was 5000 ppm. The same thermal history was also applied to pure LDPE and LLDPE. For reference, blend samples without thermal modification were prepared by melt-mixing at 130 °C with added thermal stabilizers.

The samples obtained were compressed into a flat sheet by a compression-molding machine at 230 °C under 10 MPa for 10 min. Then, the sample was cooled down to 30 °C. Because of the long annealing time in the compression-molding machine, the applied shear history, which has strong impact on the rheological properties of long-chain branched polymers, and is known as “shear modification” [Yamaguchi and Gogos (2001); Yamaguchi (2006b); Siriprumpoonthum *et al.* (2012)], was removed from the samples by Brownian motion. It was revealed that the rheological properties such as drawdown force and oscillatory modulus were not changed by prolonged annealing in the compression-molding machine. Consequently, the oscillatory modulus in the molten state was stable during the measurement, confirmed by repeat measurements of the frequency dependence of the oscillatory modulus.

B. Measurements

The frequency dependence of the oscillatory shear moduli was measured at 130, 160 and 190 °C in a rotational-type rheometer (TA Instruments, AR2000) under a nitrogen atmosphere using a cone-and-plate geometry. The time dependence of the oscillatory modulus at 0.01 Hz was also evaluated at 190 °C to confirm thermal stability. The cone angle and diameter were 4° and 25 mm, respectively. Further, the shear stress and primary normal stress difference under

steady-shear were measured at various shear rates at 190 °C using this rheometer. The measurements were performed three times to evaluate the experimental scatter.

Capillary extrusion was performed on a capillary rheometer (Yasuda Seiki Seisakusyo, 140 SAS-2002) at 190 °C to evaluate the steady-state shear viscosity and the appearance of the extruded strands. The molten polymer was extruded through a die of dimensions: 1 mm in diameter, 10 mm long and with an entrance angle of 180°. The swell ratio was measured by a laser detector fixed 5 cm below the die exit.

The drawdown force measurement was carried out at 190 °C with the capillary rheometer, equipped with a tension detector and a set of rotating wheels, as described previously [Siriprumpoonthum *et al.* (2012)]. The molten polymer was extruded through the same die used to evaluate the capillary extrusion properties. The draw ratio was 9.2, which was empirically chosen because it gave reliable values of force. Furthermore, the value is less sensitive to the draw ratio when the draw ratio is larger than 5 [Bernnat (2001); Ono and Yamaguchi (2009b)]. The shear rate at the die wall was 21.9 s^{-1} .

The growth curves of uniaxial elongational viscosity were evaluated at 160 °C on the rotational rheometer, equipped with a universal testing platform (Xpansion instruments, SER2-G). Flat sheet samples, 10 mm wide, 15 mm long, and 0.5 mm thick, were used.

The recovery behavior of the oscillatory modulus after applied shear modification was evaluated to obtain information about the branch structure. Under the applied hydrodynamic force, the long-chain branches become aligned to the main chain. The modulus recovery after the cessation of flow is a result of an increase in entropy around the branch points, as this alignment relaxes. Therefore, the process is sensitive to the branch structure. The samples were sheared at a stress level of 24.5 kPa by the cone-and-plate rheometer at 160 °C for 30 min. After cessation of

the shear flow, an oscillatory strain at 0.01 Hz was applied to the sample at 160 °C. Then, the growth curves of the shear storage modulus were evaluated as a function of the residence time in the rheometer. The details of this method were explained in a previous paper [Yamaguchi and Gogos (2001)].

III. RESULTS AND DISCUSSION

The molecular weights and their distributions for the samples before and after thermal modification are shown in Fig. 1. The GPC curves are barely changed by the thermal modification at 280 °C for 3 min in the internal mixer. Moreover, the contents of double bonds and the number of branches in the processed samples, evaluated by NMR, are the same as those in the original polymers within experimental error (data not presented here). Although the poor sensitivity (1/1000 carbon atoms for branches) has to be considered, these results indicate that the thermal history we have applied to the samples should not be severe enough to affect their primary molecular structure. This behavior was previously reported and well summarized by Janzen and Colby (1999). The result that thermal modification barely affects the number of short-chain branches is also well known for polyethylene [Suwanda and Balke (1993); Smedberg *et al.* (1997); Ono and Yamaguchi (2009a)].

[Fig. 1]

Prior to the measurement of the frequency dependence of the oscillatory shear modulus, the time dependence of the oscillatory shear modulus was evaluated at 190 °C to confirm the thermal stability during the measurement. As shown in Fig. 2, the shear storage modulus G' is

stable at 190 °C, suggesting that the samples are thermally stable, presumably as a result of sufficient added thermal stabilizers. Furthermore, the figures also demonstrate that the samples are free from shear history. It has been reported that the oscillatory moduli of a long-chain branched polymer are strongly reduced by applied shear history and increase with annealing time in the molten state without shear flow; this effect is known as shear modification [Yamaguchi and Gogos (2001); Yamaguchi (2006b); Yamaguchi and Wagner (2006); Siriprumpoonthum *et al.* (2012); Yamaguchi (2012)]. All the samples used in this study show constant values of both moduli irrespective of the residence time in the rheometer, demonstrating that the effect of the applied shear history was removed during the compression-molding at 230 °C for 10 min.

[Fig. 2]

The angular-frequency dependence of the oscillatory moduli for LDPE and LLDPE is shown in Fig. 3. As indicated in Fig. 2, both moduli for LLDPE are greatly enhanced by the applied thermal history. Because the GPC curve, based on a linear polyethylene standard, is not changed by the history, the generation of only a small amount of long-chain branches must affect the rheological properties as shown later. Because the contents of double bonds in the original LLDPE are unchanged, the cross-linking reaction of two macro-radicals produced by the removal of a hydrogen atom in the backbone, which was revealed by Kriston (2010) in detail, could be the dominant mechanism to provide long-chain branches. A large number of short-chain branches in the LLDPE used in this study is responsible for the marked rheological change, because the hydrogen atoms attached to the tertiary carbon are easily abstracted. However, the effect of the applied thermal history on the linear viscoelastic properties is not obvious for LDPE,

suggesting that linear viscoelastic properties of LDPE are less sensitive to the applied thermal history. Because of the broad distribution of relaxation times of the original LDPE, as compared with the original LLDPE, prolonged relaxation mechanisms cannot be detected clearly. This is reasonable because a small amount of long-chain branches created by the thermal modification should have minimal effect on the linear viscoelastic properties of LDPE (Janzen and Colby, 1999). Even for LDPE, however, G' in the low frequency region is slightly enhanced, indicating that the characteristic time of the longest relaxation mechanism is prolonged. Moreover, GPC curves and dynamic mechanical properties indicate that chain scission by the applied mechanical force during the thermal history can be ignored for both samples.

The enhancement of G'' for pure LLDPE by thermal modification is of course associated with an increase in η_0 : from 19,000 [Pa s] at 190 °C for the original LLDPE to 190,000 [Pa s] for the modified LLDPE. Considering that there is almost no change in the weight-average molecular weight, this result also supports the generation of long-chain branches.

[Fig. 3]

The master curves in Fig. 3 are obtained by a simple horizontal shift without a vertical one. Strictly speaking, however, it is impossible to superpose all data for LDPE, because molten LDPE is known to be a thermo-rheologically complex material [Wagner *et al.* (2004); Delgadillo-Velázquez *et al.* (2008)]. With similar results, Keßner and Münstedt (2010) reported a metallocene-based LLDPE having long-chain branches.

The result is clear in the van Gurp-Palmen plot, i.e., phase angle δ plotted against absolute values of complex modulus $|G^*|$, for pure polymers, as seen in Fig. 4. Although all data are on a

single curve for LLDPE prior to thermal modification, the complex thermo-rheological behavior is clearly detected after thermal modification. Moreover, the data measured at low temperature are located below those at high temperature, as is also the case for LDPE. The phase angle becomes smaller as a result of the thermal modification, especially for LLDPE. This result is attributed to the broadening of the relaxation time distribution. Furthermore, the shoulder at $|G^*| = 10^4$ Pa in the modified LLDPE demonstrates that there is a long-time relaxation mechanism with a relatively narrow distribution of characteristic times, which is presumably attributed to the relaxation of the long-chain branches.

[Fig. 4]

The apparent flow activation energy E_a is calculated at the same level of the loss modulus G'' using an Arrhenius-type equation, as shown in Fig. 5. In the case of LDPE, it is found that E_a is almost unchanged by the thermal history. The high value at low modulus is attributed to the high E_a of the relaxation process associated with long-chain branches. In contrast, for LLDPE, E_a prior to the thermal modification is constant, irrespective of G'' . This is reasonable because a conventional LLDPE is thermo-rheologically simple, like other simple polymer melts. Exposure to the thermal history in the mixer, however, affects this thermo-rheological simplicity. After thermal modification, E_a increases with decreasing G'' , showing similar behavior to that seen for pure LDPE, indicating that long-chain branches are now present.

[Fig. 5]

Because G' is sensitive to the relaxation mechanism with a long characteristic time, the master curves of G' at 130 °C for the blends before/after the thermal modification are plotted in Fig. 6. Prior to modification, the blends exhibit higher G' values than those of the pure components in the low frequency region, as also seen in previous reports [Utracki and Schlund (1987); Wagner *et al.* (2004); Mieda and Yamaguchi (2007); Mieda and Yamaguchi (2011)]. According to the earlier reports, the oscillatory modulus is enhanced by the addition of high molecular weight linear polyethylene. Moreover, the blends exhibit marked melt elasticity, showing behavior such as strain-hardening in elongational viscosity. Some researchers concluded that the anomalous rheological behavior can be attributed to phase separation as summarized in references [Wagner *et al.* (2004); Delgadillo-Velázquez *et al.* (2008)], mostly based on thermal analysis. However, the melting and/or crystallization behavior of polyethylene blends have been known to induce segregation. Therefore, the miscibility in the molten state should not be discussed based on the results of characterization in the solid state (such as thermal analysis), although there has been controversial discussion on the miscibility of polyethylene blends [Alamo *et al.* (1997); Morgan *et al.* (1997)]. Moreover, one of the present authors reported that an advanced molecular model based on the molecular stress function (MSF) theory successfully predicts the rheological properties in the molten state, assuming phase separation [Wagner *et al.* (2004)]. Meanwhile, it was found that the enhancement of strain-hardening in elongational viscosity as well as in zero-shear viscosity was observed in blends of LDPE and linear polyethylenes, irrespective of the number of short-chain branches in the linear polyethylenes [Mieda and Yamaguchi (2007)]. Because the number of short-chain branches affects the miscibility, the anomalous behavior is not attributed to phase separation. The suggestion was made that the prolonged relaxation time of the linear chains surrounding a

branched polymer, which restricts dynamic tube dilation and constraint release, is responsible for the anomalous rheological behavior [Mieda and Yamaguchi (2011)]. Because similar results are obtained for the present blends prior to modification, the LDPE and LLDPE used in this study are assumed to be miscible in the molten state.

After the thermal modification, as shown in Fig. 6(b), enhancement in G' is detected, which becomes more pronounced with increasing LLDPE content. Consequently, LDPE shows the lowest values of all the samples.

[Fig. 6]

The zero-shear viscosity η_0 at 130 °C is calculated from G'' , as shown in eq.1, and is plotted as a function of the LLDPE content in Fig. 7. Prior to thermal modification, the values of the blends are higher than those of the individual components, consistent with previous papers [Yamaguchi (2006a); Mieda and Yamaguchi (2007); Delgadillo-Velázquez *et al.* (2008)]. Even after the thermal modification, the values are slightly greater than those expected from the log-additive rule, although η_0 increases monotonically with the LLDPE content. The result suggests that the anomalous behavior, i.e., enhancement of η_0 , is less distinct after thermal history, at least from the viewpoint of linear viscoelastic properties. In other words, the thermal history is the main factor affecting the zero-shear viscosity.

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega} \quad (1)$$

[Fig. 7]

Fig. 8 shows the shear stress σ and primary normal stress difference N_1 at 190 °C evaluated with the cone-and-plate rheometer. The measurements were carried out three times to confirm the results. In the figure, $|G^*|$ curves are plotted against the angular frequency ω , calculated from the oscillatory modulus. Prior to thermal modification, both LDPE and LLDPE show almost the same level of normal stress difference, although LDPE has long-chain branches. This is attributed to the difference in their molecular weights. In fact, the shear stress of the LLDPE, which has a higher molecular weight, is considerably greater than that of LDPE. The level of shear stress σ is almost the same as $|G^*|$, suggesting that the Cox-Merz rule is applicable to these systems. Furthermore, it is clearly seen that both shear stress and normal stress difference are enhanced by the thermal modification: the greatest enhancement is seen for the normal stress difference, and becomes more obvious with increasing LLDPE content.

Prior to modification, the shear stresses of the blends containing 50 or 75% LLDPE are similar to that of pure LLDPE. After thermal modification, however, LLDPE exhibits the highest shear stress, i.e., shear viscosity. Moreover, the shear stress increases with the LLDPE content, as do the linear viscoelastic properties. In contrast, the blends show still higher primary normal stress difference N_1 than the pure components even after the thermal modification. Although the detailed discussion should be carried out by steady-state compliance and recovery strain, the results demonstrate that the blends show higher melt elasticity than the pure components.

[Fig. 8]

Extrusion properties were evaluated by the capillary rheometer at 190 °C. The photographs of the extruded strands are shown in Fig. 9. The blends after thermal modification exhibit gross melt fracture at a lower shear rate than before modification, especially for LDPE/LLDPE (75/25), in which the onset shear rate greatly decreases from 1000 s^{-1} to 277 s^{-1} . As the LLDPE content increases, helical distortion, instead of chaotic distortion, is detected in the high shear rate region. In the case of pure LLDPE, shark-skin failure appears prior to gross melt fracture, irrespective of thermal modification. The onset shear stress is around 0.25 MPa, which seems to be independent of thermal modification and agrees with values reported previously (Koopmans *et al.*, (2010)). Further, the strand diameters became larger after thermal modification, as illustrated in Fig. 10. The enhancement of the Barus effect is clearly seen in LLDPE, which is consistent with the enhancement of the normal stress difference observed for this sample. The entrance flow will also have some influence as indicated by Mieda and Yamaguchi (2011).

[Fig. 9][Fig.10]

The origin of the gross melt fracture is believed to be the flow instability at the die entrance [Cogswell (1981); Kim and Dealy (2002); Kulikov (2005)]. Meller *et al.* (2002) stated that rupture occurs beyond the critical elongational stress generated by the contraction flow at the die entrance, whereas shark-skin failure takes place beyond the critical shear stress at the die exit. Therefore, a polymer liquid having marked strain-hardening in elongational viscosity, such as LDPE, is apt to show gross melt fracture even at a low output rate, as compared with a polymer melt without strain-hardening. The present result suggests that elongational viscosity is pronounced for the blend systems because of thermal modification, although the onset

elongational stress for gross melt fracture cannot be evaluated from the present results. Precise evaluation of the entrance angle is required to predict the elongational strain, and thus the elongational stress, at the die entry.

[Fig. 11]

To obtain information on the elongational stress of the samples, the drawdown force, i.e., the force required to stretch a strand [Bernnat (2001); Yamaguchi *et al.* (2003)], is evaluated as shown in Fig. 11. It is apparent that the drawdown force is greatly enhanced by the thermal modification, especially for the blends. It should be noted that enhancement of drawdown force is not so obvious for LLDPE, even though its linear viscoelastic properties and rheological properties under steady-state shear are greatly affected by thermal modification. The results suggest that the strain-hardening behavior, i.e., upwards deviation from the linear value, is not obvious for LLDPE, even after modification.

To evaluate the strain-hardening behavior in elongational viscosity directly, the growth curves of uniaxial elongational viscosity are measured (Fig. 12). The solid line in the figure represents three times of the growth curve of shear viscosity in the linear region $3\eta^+$, which is calculated by the approximate equation proposed by Osaki *et al.* (1976).

[Fig. 12]

As seen in the figure, the modified blend shows a steep curve of $3\eta^+$ and marked strain-hardening. Both these features are responsible for the enhanced drawdown force. Moreover, the

strain-hardening behavior, i.e., nonlinear response in elongational viscosity, also occurs at smaller strains, as demonstrated in Fig. 13. In the case of LDPE, strain-hardening is also pronounced, with a slight increase in $3\eta^+$, while the elongational strain required for strain-hardening is not changed greatly by thermal modification. Finally, the strain-hardening behavior is not clearly detected for LLDPE, even after the thermal modification; this will be explained later.

[Fig. 13]

It is well known that chain stretching in LDPE leads to strain-hardening in the elongational viscosity at lower strains, as demonstrated by advanced molecular models such as the MSF theory (Wagner *et al.* (2003)) and the Pom-pom model (Inkson and McLeish (1999)). This is reasonable because the chain segments between branch points are in a low entropy state as a result of chain stretching. Therefore, the present experimental results indicate that polymer chains having more than two branch points are generated in the blend.

In the case of LLDPE, a polymer chain has to be attacked by at least two macroradicals to become a comb-shaped branch chain. As demonstrated by the GPC curve against the linear polyethylene standard, however, the thermal history applied in this experiment is not so severe to change the molecular weight or its distribution. Moreover, the van Gurp-Palmen plot of the thermally-modified LLDPE indicates that the distribution of relaxation times associated with long-chain branches is not so broad. These results indicate that most branched chains generated by the thermal modification of LLDPE will have a star-shaped branch structure. For the blends, in contrast, intermolecular reaction between LLDPE and LDPE will take place, as well as the

reaction between two LLDPE molecules, because the cross-linking reaction occurs randomly when the blend is miscible. As a result, the number of branched polymers having more than two branch points in a chain will increase because of reaction of LLDPE with LDPE. Further, prolonged relaxation times of polymer chains surrounding the branched polymer will enhance the chain stretching. To confirm the intermolecular reaction between LLDPE and LDPE, another blend was prepared by mixing the thermally-modified pure components, i.e., modified LLDPE and modified LDPE, at 130 °C as a reference sample. After compression-molding at 230 °C, the rheological properties were evaluated. As indicated by x in Fig. 11, the drawdown force of the reference sample blended after the thermal modification is lower than that of the blend modified during mixing. Correspondingly, the upturn only occurs at a large elongational strain, and is smaller for the reference sample compared with that of the blend modified during mixing. In other words, the thermal modification during mixing is more effective at changing the elastic properties.

Finally, recovery curves of the shear storage modulus from the shear-modified state were evaluated to discuss the branch structure. Yamaguchi and Gogos (2001) found that the shear modification phenomenon, which is observed clearly for branched polymers, can be evaluated by examining the recovery process of the oscillatory modulus after cessation of shear flow. Furthermore, the degree of shear modification is determined by the applied shear stress, duration of shearing, and flow pattern. When the applied flow field is chaotic, the rheological properties are barely affected by the shear history [Yamaguchi *et al.* (2003)]. This is reasonable because the shear modification occurs by the alignment of branch chains along main chains. Therefore, the oscillatory modulus greatly decreases as a result of the shear flow in a cone-and-plate rheometer.

Moreover, the branch structure can be predicted from the recovery curves to some degree [Yamaguchi and Takahashi (2001); Mieda (2012)], because a longer branch will need a longer recovery time to return its equilibrium state.

Fig. 14 shows the recovery curves of G' and its normalized values, i.e., $G'(t)/G'(t=0)$, after removal of the shear stress at 24.5 kPa. As seen in the figure, G' increases with the residence time in the rheometer for all samples (except for LLDPE prior to modification). Although the G' change produced by the shear history is clear for the modified LLDPE, the modified blends require a longer time to recover to their plateau values, as does the modified LDPE. Because the recovery time is closely related to the length of long-chain branches [Yamaguchi (2012)], the thermally-modified blends have long or hierarchical branches compared with those of the thermally-modified LLDPE. This result also supports the idea that, in the blends, intermolecular crosslinking reactions between LLDPE and LDPE take place during the thermal modification. In contrast, depression of the initial G' , which is presumably attributed to the number of long-chain branches [Mieda (2012); Yamaguchi (2012)], is prominent for the thermally-modified LLDPE.

[Fig. 14]

Although the processability of the modified samples employed in this study has not been evaluated at actual processing operations, the rheological changes will affect aspects of the processability, including the level of neck-in at T-die extrusion [Kouda (2008)], the fine cell structure produced by foaming [Yamaguchi and Suzuki (2001)] and the uniformity of the wall thickness produced by blow-molding or thermoforming [Shinohara (1991); Yamaguchi and Suzuki (2002)].

IV. CONCLUSIONS

The effects of thermal history on the rheological properties of blends of LLDPE with high molecular weight and LDPE were examined. Because both polyethylenes contained no thermal stabilizer, the applied thermal history, i.e., 280 °C for 3 min in the internal mixer under shear, led to cross-linking reactions rather than chain scission.

The structural change significantly alters the rheological properties, although there are little or no changes to the molecular weights and their distributions (as evaluated by GPC) and the numbers of double bond and short-chain branches (as evaluated by NMR). Furthermore, the following results were obtained for the thermally-modified LLDPE; (1) the time-temperature superposition principle is not applicable, and the apparent flow activation energy increases with decreasing modulus; (2) the zero-shear viscosity greatly increases without any increase in the weight-average molecular weight; and (3) shear modification behavior is detected. These results indicate that long-chain branches have appeared in the main chains.

The zero-shear viscosity after thermal modification increases with LLDPE content, although, prior to modification, the blends show higher zero-shear viscosities than the individual pure components. The frequent cross-linking reaction of LLDPE owing to its large amount of tertiary carbon atoms is responsible for the rheological change. In contrast, the upwards deviation of the drawdown force from the linear additive rule was pronounced for the thermally-modified blends. Further, marked strain-hardening in elongational viscosity, even in the low elongational strain region, was detected, especially for the blends. Correspondingly, gross melt fracture was seen during capillary extrusion, even at low output rates, presumably caused by the

high elongational stress at the die entrance. The prolonged recovery of oscillatory modulus from the shear-modified state was also prominent for the blend. These results suggest that an intermolecular cross-linking reaction between LDPE and LLDPE, which provides branch chains having more than two branch points, occurs in the system during thermal modification. The intermolecular reaction is further confirmed by comparison of the rheological properties with those of a blend mixed from thermally-modified individual pure components.

References

- Ajji, A., P. Sammut and M. A. Huneault, "Elongational rheology of LLDPE/LDPE blends," *J. Appl. Polym. Sci.* **88**, 3070-3077 (2003).
- Alamo, R. G., W. W. Graessley, R. Krishnamoorti, D. J. Lohse, J. D. Londono, L. Mandelkern, F. C. Stehling and G. D. Wignall, "Small-angle neutron-scattering investigations of melt miscibility and phase segregation in blends of linear and branched polyethylenes as a function of the branch content," *Macromolecules* **30**, 561-566 (1997).
- Andersson, T., B. Stålborm and B. Wesslén, "Degradation of polyethylene during extrusion II: Degradation of low-density polyethylene, linear low-density polyethylene, and high-density polyethylene in film extrusion," *J. Appl. Polym. Sci.* **91**, 1525-1537 (2004).
- Bernnat, A., "Polymer melt rheology and the rheotens test," Ph.D. dissertation, University of Stuttgart, Stuttgart, Germany, 2001.
- Cogswell, F. N., "Polymer Melt Rheology," George Godwin, London, 1981.
- Delgadillo-Velázquez, O., S. G. Hatzikiriakos and M. Sentmanat, "Thermorheological properties of LLDPE/LDPE blends," *Rheol. Acta* **47**, 19-31 (2008).

- Doi, M., "Explanation for the 3.4-power law for viscosity of polymeric liquids on the basis of the tube model," *J. Polym. Sci., Part B: Polym. Phys.* **21**, 667-684 (1983).
- Ghosh, P., D. Dev and A. Chakrabarti, "Reactive melt processing of polyethylene: Effect of peroxide action on polymer structure, melt rheology and relaxation behavior," *Polymer* **38**, 6175-6180 (1997).
- Hussein, I. H. and M. C. Williams, "Rheological study of the influence of branch content on the miscibility of octane m-LLDPE and ZN-LLDPE in LDPE," *Polym. Eng. Sci.* **44**, 660-672 (2004).
- Inkson, N. J. and T. C. B. McLeish, "Predicting low density polyethylene melt rheology in elongational and shear flows with "pom-pom" constitutive equations," *J. Rheol.* **43**, 873-896 (1999).
- Janzen, J. and R. H. Colby, "Diagnosing long-chain branching in polyethylenes," *J. Mol. Struct.* **485-486**, 569-584 (1999).
- Keßner, U. and H. Münstedt, "Thermorheology as a method to analyze long-chain branched polyethylenes," *Polymer*, **50**, 507-513 (2010).
- Kim, S. and J. M. Dealy, "Gross melt fracture of polyethylene. I: A criterion based on tensile stress," *Polym. Eng. Sci.* **42**, 482-494 (2002).
- Koopmans, R., J. Doelder and J. Molenaar, "Polymer melt fracture," CRC Press, Boca Raton, 2010.
- Kouda, S., "Prediction of processability at extrusion coating for low-density polyethylene," *Polym. Eng. Sci.* **48**, 1094-1110 (2008).

- Kriston, I., “Some aspects of the degradation and stabilization of Phillips type polyethylene,” Ph.D. dissertation, Budapest University of Technology and Economics, Budapest, Hungary, 2010.
- Kulikov, O., “Novel processing aids for extrusion of polyethylene,” *J. Vinyl. Add. Tech.* **11**, 127-131 (2005).
- Kuroki, T., T. Sawaguchi, S. Niikuni and T. Ikemura, “Mechanism for long-chain branching in the thermal degradation of linear high-density polyethylene,” *Macromolecules* **15**, 1460-1464 (1982).
- Lentzakis, H., D. Vlassopoulos, D. J. Read, H. Lee and T. Chang, “Uniaxial extensional rheology of well-characterized comb polymers,” *J. Rheol.* **57**, 605-625 (2013).
- Meller, M., A. Luciani, A. Sarioglu and J. E. Manson, “Flow through a convergence, Part 1: Critical conditions for unstable flow,” *Polym. Eng. Sci.* **42**, 611-633 (2002).
- Mieda, N., “Effect of long-chain branches on non-linear rheological properties for polyethylene,” Ph.D. dissertation, Japan Advanced Institute of Science and Technology, Japan, 2011.
- Mieda, N. and M. Yamaguchi, “Anomalous rheological response for binary blends of linear polyethylene and long-chain branched polyethylene,” *Adv. Polym. Tech.* **26**, 173-181 (2007).
- Mieda N. and M. Yamaguchi, “Flow instability for binary blends of linear polyethylene and long-chain branched polyethylene,” *J. Non-Newtonian Fluid Mech.* **166**, 231-240 (2011).

- Milner, S. T. and T. C. B. MacLeish, "Reptation and contour-length fluctuations in melts of linear polymers," [Phys. Rev. Lett.](#) **81**, 725-728 (1998).
- Monchai, S., N. Mieda, V. A. Doan, S. Nobukawa and M. Yamaguchi, "Effect of shear history on flow instability at capillary extrusion for long-chain branched polyethylene," [J. Appl. Polym. Sci.](#) **124**, 429-435 (2012).
- Morgan, R. L., M. J. Hill, P. J. Barham and C. J. Frye, "Liquid-liquid phase separation in ternary blends of linear polyethylene with two ethylene-butene copolymers," [Polymer](#) **38**, 1903-1909 (1997).
- Ono K. and M. Yamaguchi, "Thermal and mechanical modification of LDPE in single-screw extruder," [J. Appl. Polym. Sci.](#) **113**, 1462-1470 (2009a).
- Ono K. and M. Yamaguchi, "Alternation in rheological properties of polyethylene by extrusion processing," [J. Japan Soc. Polym. Process.](#) **21**, 745-752 (2009b).
- Osaki K., A. Murai, N. Bessho, and B. S. Kim, "Linear viscoelastic relation concerning shear stresses at the start and cessation of steady shear flow," [J. Soc. Rheol. Jpn.](#) **4**, 166-169 (1976).
- Peacock, A. J., "The efficiency of crosslinking linear polyethylene by using dicumyl peroxide," [Polym. Commun.](#) **28**, 259-260 (1987).
- Rangarajan, P., D. Bhattacharya and E. Grulke, "HDPE liquefaction: Random chain scission model," [J. Appl. Polym. Sci.](#) **70**, 1239-1251 (1998).
- Rijke, A. M. and L. Mandelkern, "Irradiation of linear polyethylene partitioning between sol and gel," [Macromolecules](#) **4**, 594-599 (1971).
- Shinohara, M., "Uniaxial elongational viscosity of high molecular weight high density polyethylene melts," [J. Soc. Rheol. Jpn.](#) **19**, 118-124 (1991).

- Smedberg, A., T. Hjertberg and B. Gustafsson, "Crosslinking reactions in an unsaturated low density polyethylene," [Polymer](#) **38**, 4127-4138 (1997).
- Stockmayer, W. H., "Theory of molecular size distribution and gel formation in branched-chain polymers II: General cross linking," [J. Chem. Phys.](#) **12**, 125-131 (1944).
- Suwandam D. and S. T. Balke, "The reactive modification of polyethylene. I: The effect of low initiator concentrations on molecular properties," [Polym. Eng. Sci.](#) **33**, 1585-1590 (1993).
- Utracki, L. A. and B. Schlund, "Linear low density polyethylenes and their blends: Part 4. Shear flow of LLDPE blends with LLDPE and LDPE," [Polym. Eng. Sci.](#) **27**, 1512-1522 (1987).
- Wagner, M. H., M. Yamaguchi, and M. Takahashi, "Quantitative assessment of strain hardening of low-density polyethylene melts by the molecular stress function model," [J. Rheol.](#) **47**, 779-793 (2003).
- Wagner, M. H., S. Kheirandish and M. Yamaguchi, "Quantitative analysis of melt elongational behavior of LLDPE/LDPE blends," [Rheol. Acta](#) **44**, 198-218 (2004).
- Yamaguchi, M., "Anomalous rheological properties of polyethylene molecular composites," [Polym. Eng. Sci.](#) **46**, 1284-1291 (2006a).
- Yamaguchi, M., "Relationship between processing history and rheological properties during postprocessing annealing for anomalous polyethylene blends," [J. Appl. Polym. Sci.](#) **102**, 1078-1083 (2006b).
- Yamaguchi, M. "Rheological properties of molten polyolefins" in "Structure and properties of polyolefin materials," Transworld Research Network, Kerela, 2012.

- Yamaguchi, M. and H. Miyata, "Strain hardening behavior in elongational viscosity for binary blends of linear polymer and crosslinked polymer," [Polym. J.](#) **32**, 164-170 (2000).
- Yamaguchi, M. and C. G. Gogos, "Quantitative relation between shear history and rheological properties of LDPE," [Adv. Polym. Tech.](#) **20**, 261-269 (2001).
- Yamaguchi, M. and M. Takahashi, "Rheological properties of low density polyethylenes Produced by Tubular and Vessel Processes," [Polymer](#) **42**, 8663-8670 (2001).
- Yamaguchi, M. and K. Suzuki, "Rheological properties and foam processability for blends of linear and crosslinked polyethylenes," [J. Polym. Sci., Part B: Polym. Phys.](#) **39**, 2159-2167 (2001).
- Yamaguchi, M. and K. Suzuki, "Enhanced strain-hardening in elongational viscosity for HDPE/crosslinked HDPE blend: 2. Processability of thermoforming," [J. Appl. Polym. Sci.](#) **86**, 79-83 (2002).
- Yamaguchi, M., D. B. Todd and C. G. Gogos, "Rheological properties of LDPE processed by conventional processing machines," [Adv. Polym. Tech.](#) **22**, 179-183 (2003).
- Yamaguchi, M. and M. H. Wagner, "Impact of processing history on rheological properties for branched polypropylene," [Polymer](#) **47**, 3629-3635 (2006).
- Yokohara, T., S. Nobukawa and M. Yamaguchi, "Rheological properties of polymer composites with flexible fine fiber," [J. Rheol.](#) **55**, 1205-1218 (2011).

Figure Captions

FIG. 1. GPC curves of LDPE and LLDPE; (dotted lines) before and (solid lines) after thermal modification

FIG. 2. Time dependence of shear storage modulus G' at 0.01 Hz at 190 °C for the samples (open symbols) before and (closed symbols) after thermal modification; (circles) LDPE and (diamonds) LLDPE.

FIG. 3. Master curves of frequency dependence of (circles) shear storage modulus G' and (diamonds) loss modulus G'' at 130 °C for (a) LDPE and (b) LLDPE; (open symbols) before and (closed symbols) after thermal modification.

FIG. 4. van Gurp-Palmen plots for the samples (open symbols) before and (closed symbols) after thermal modification; (circles) LDPE at 130 °C, (diamonds) LDPE at 160 °C, (squares) LDPE at 190 °C, (triangles) LLDPE at 130 °C, (inverted triangles) LLDPE at 160 °C and (right triangles) LLDPE at 190 °C.

FIG. 5. Relation between shear loss modulus G'' and flow activation energy E_a for (circles) LDPE and (diamonds) LLDPE; (open symbols) before and (closed symbols) after thermal modification

FIG. 6. Master curves of frequency dependence of shear storage modulus G' at 130 °C for LDPE/LLDPE blends (a) before and (b) after thermal modification; (closed circles) LDPE, (open circles) LDPE/LLDPE (75/25), (closed diamonds) LDPE/LLDPE (50/50), (open diamonds) LDPE/LLDPE (25/75) and (closed triangles) LLDPE.

FIG. 7. Zero-shear viscosity η_0 at 130 °C for LDPE/LLDPE blends (open circles) before and (closed circles) after thermal modification

FIG. 8. Steady-state properties such as (closed symbols) shear stress σ and (open symbols) primary normal stress difference N_1 plotted against shear rate $\dot{\gamma}$ at 190 °C for the samples (a) before and (b) after thermal modification; (circles) LDPE, (diamonds) LDPE/LLDPE (75/25), (triangles) LDPE/LLDPE (50/50), (squares) LDPE/LLDPE (25/75) and (right triangles) LLDPE. The solid lines denote the shear stress predicted by the Cox-Mertz rule.

FIG. 9. Optical photographs of extruded strands at 190 °C through a circle die with L/D = 10/1 (mm): (a) LDPE, (b) LDPE/LLDPE (75/25), (c) LDPE/LLDPE (50/50), (d) LDPE/LLDPE (25/75) and (e) LLDPE. The numerals in the figure represent the applied shear rate $\dot{\gamma}$.

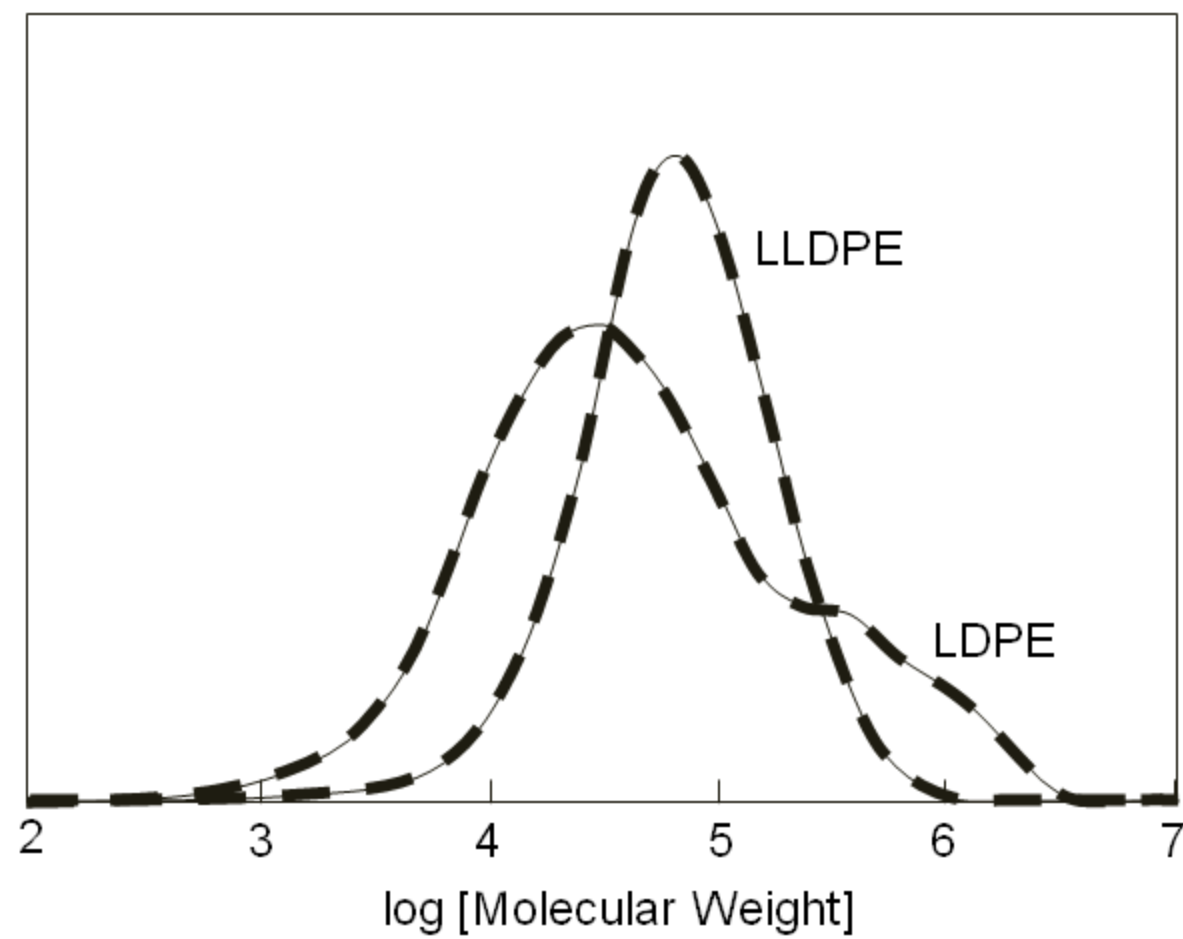
FIG. 10. Swell ratio plotted against shear rate $\dot{\gamma}$ at 190 °C for (circles) LDPE, (triangles) LDPE/LLDPE (50/50) and (diamonds) LLDPE; (open symbols) before and (closed symbols) after thermal modification.

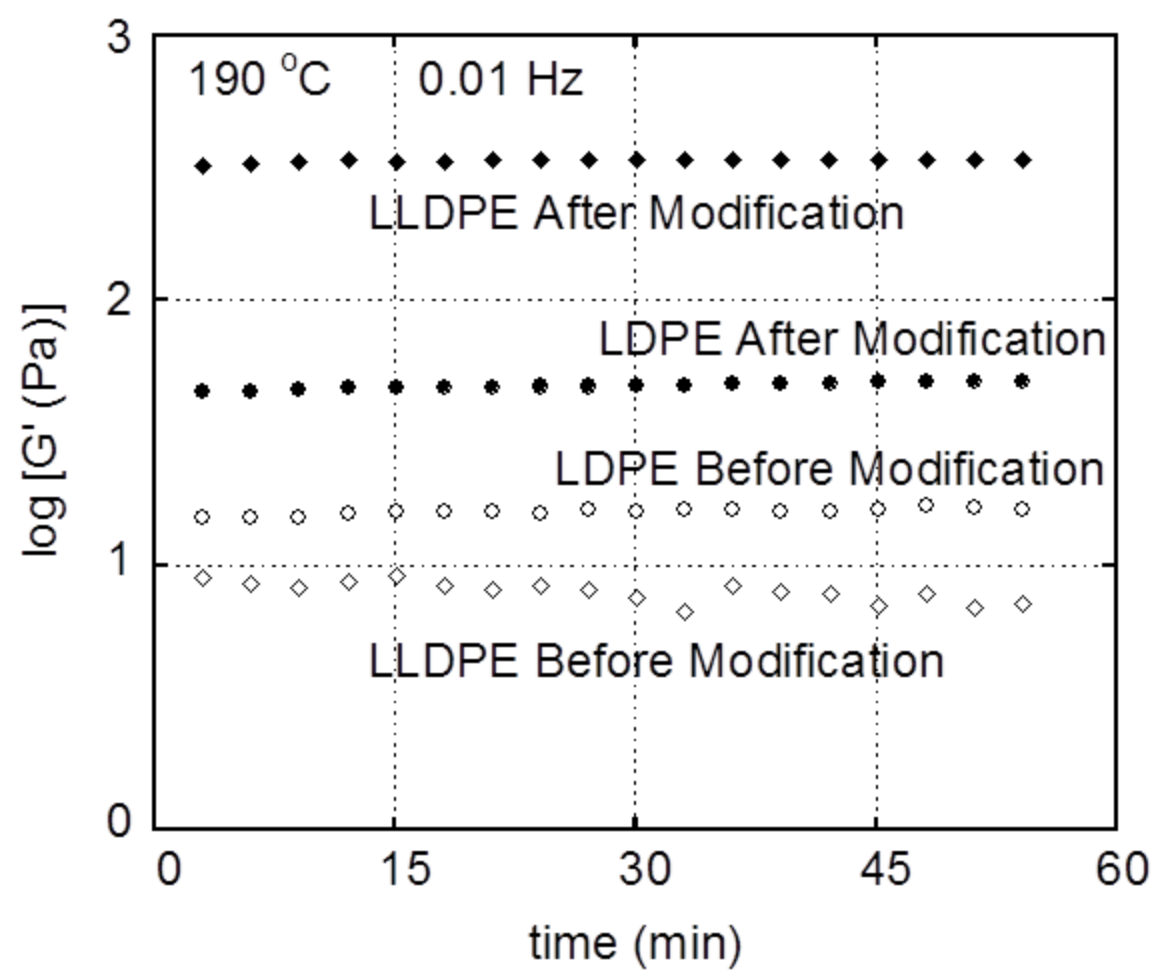
FIG. 11. Drawdown force at 190 °C for LDPE/LLDPE blends; (open circles) before and (closed circles) after thermal modification. In the figure, (x) denotes the drawdown force of the LDPE/LLDPE (50/50) blend prepared by mixing the thermally-modified pure components.

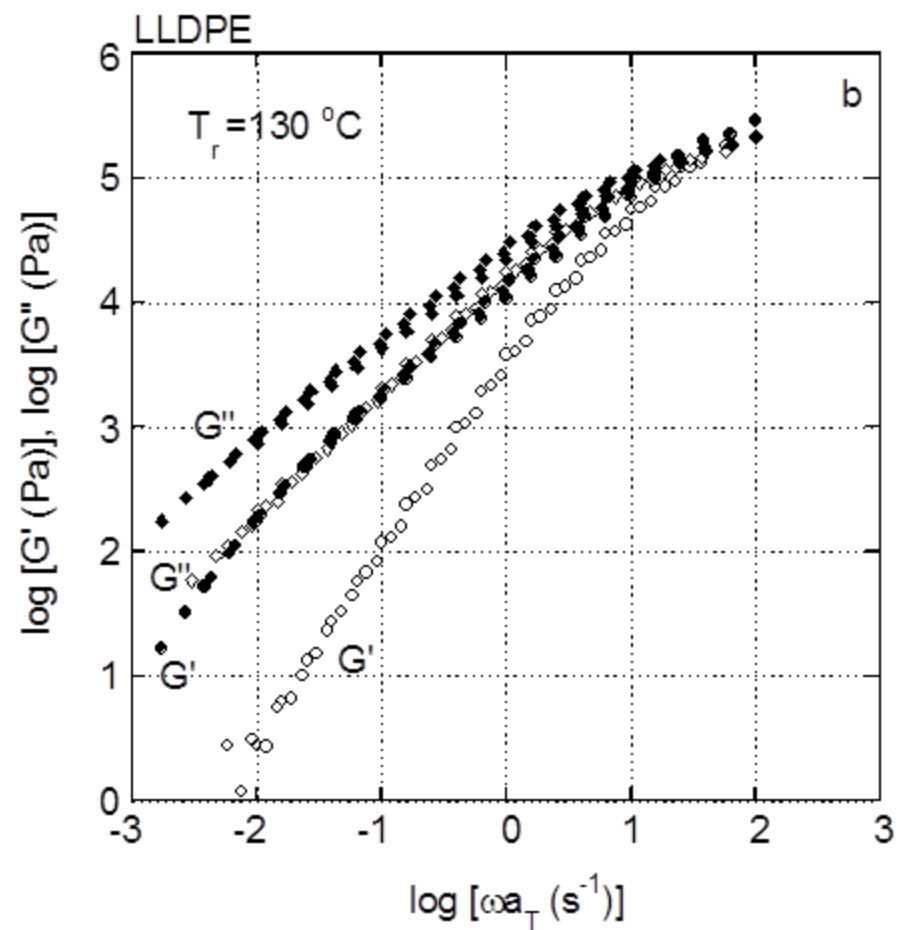
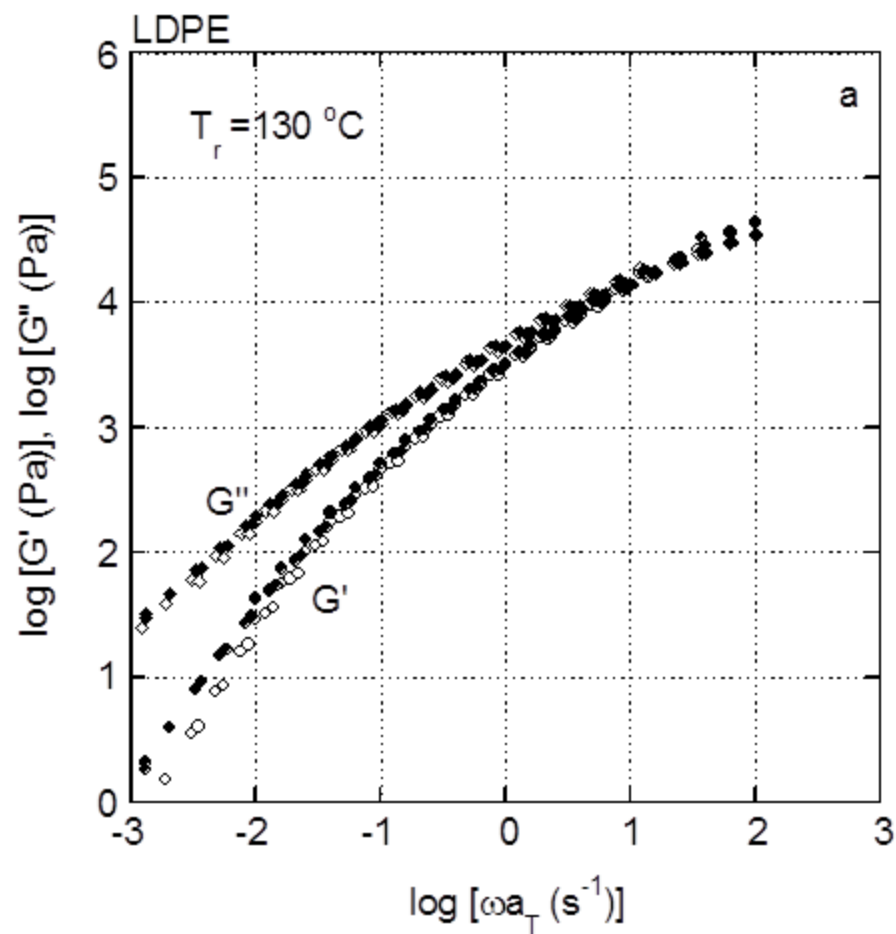
FIG. 12. Growth curves of uniaxial elongational viscosity $\eta_E^+(t, \dot{\epsilon})$ at 160 °C; (a) LDPE, (b) LDPE/LLDPE (50/50) and (c) LLDPE; (open symbols) before and (closed symbols) after thermal modification at various strain rates, (circles) 0.1 s^{-1} , (squares) 0.2 s^{-1} , (diamonds) 0.4 s^{-1} and (triangles) 0.8 s^{-1} . The solid line denotes the growth curve of elongational viscosity at a low strain rate asymptote $3\eta^+(t)$.

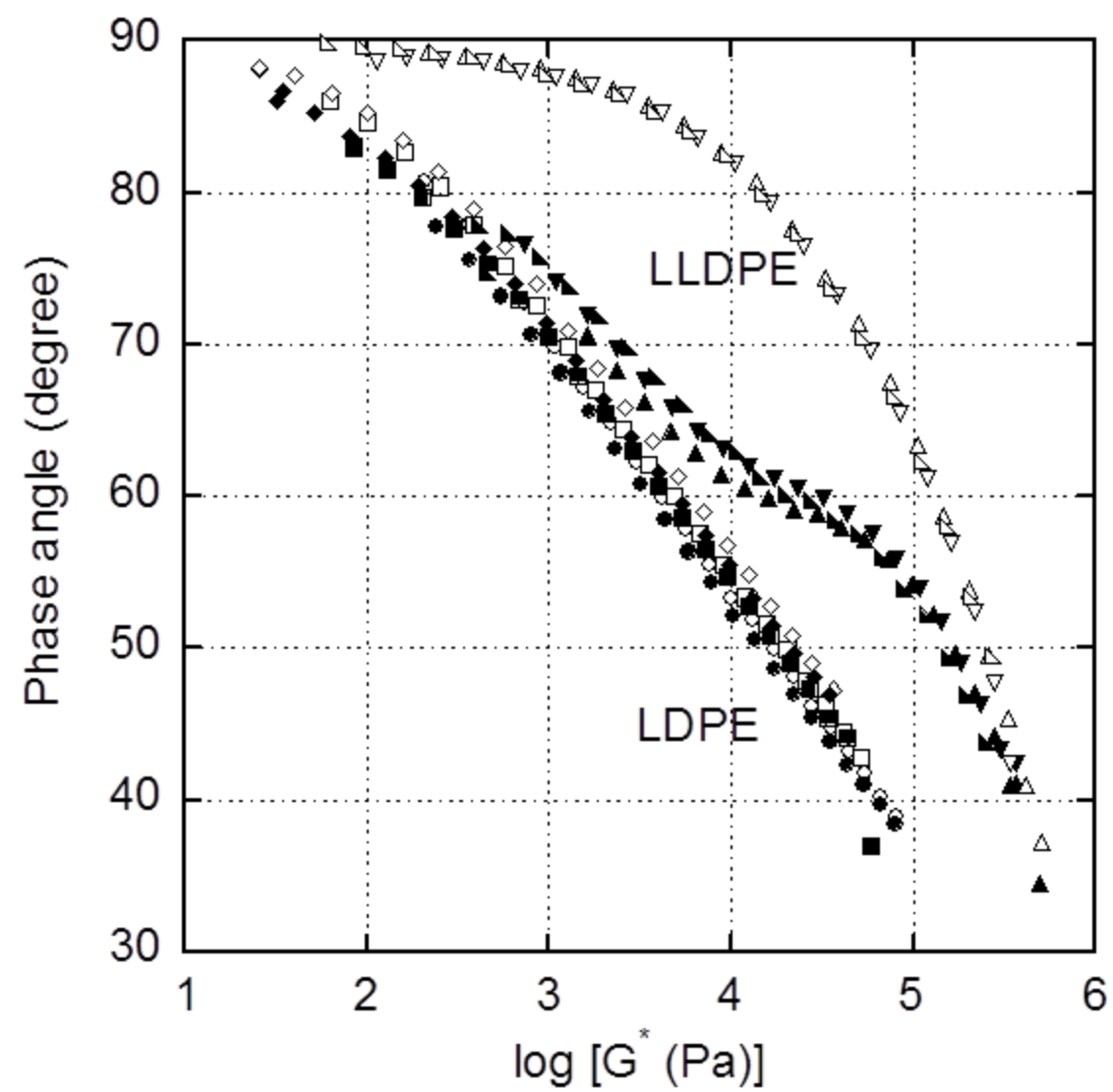
FIG. 13. Ratio of uniaxial elongational viscosity $\eta_E^+(t, \dot{\epsilon})$ to that at the low strain rate asymptote $3\eta^+(t)$ as a function of elongational strain ϵ at a strain rate $\dot{\epsilon}$ of 0.2 s^{-1} for (a) LDPE and (b) LDPE/LLDPE (50/50); (open circles) before and (closed circles) after thermal modification. The closed diamonds represent the data of the LDPE/LLDPE (50/50) blend prepared by mixing the thermally-modified pure components.

FIG. 14. Time dependence of (circles) shear storage modulus G' and (diamonds) its normalized values $G'(t)/G'(t=0)$ at 0.01 Hz after the removal of shear stress (24.5 kPa for 30 min) at 160 °C; (open symbols) before and (closed symbols) after thermal modification for (a) LDPE, (b) LDPE/LLDPE (50/50) and (c) LLDPE.

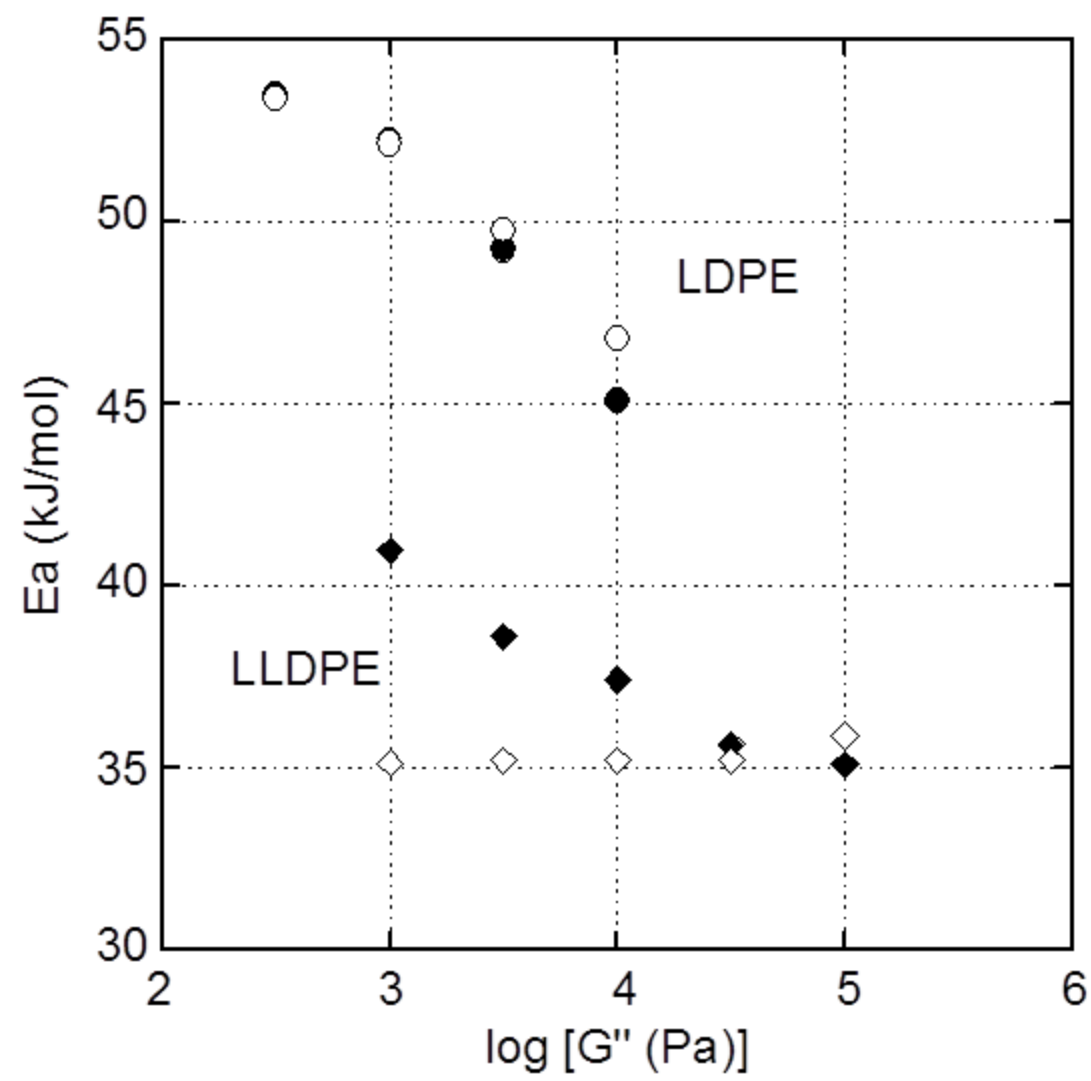


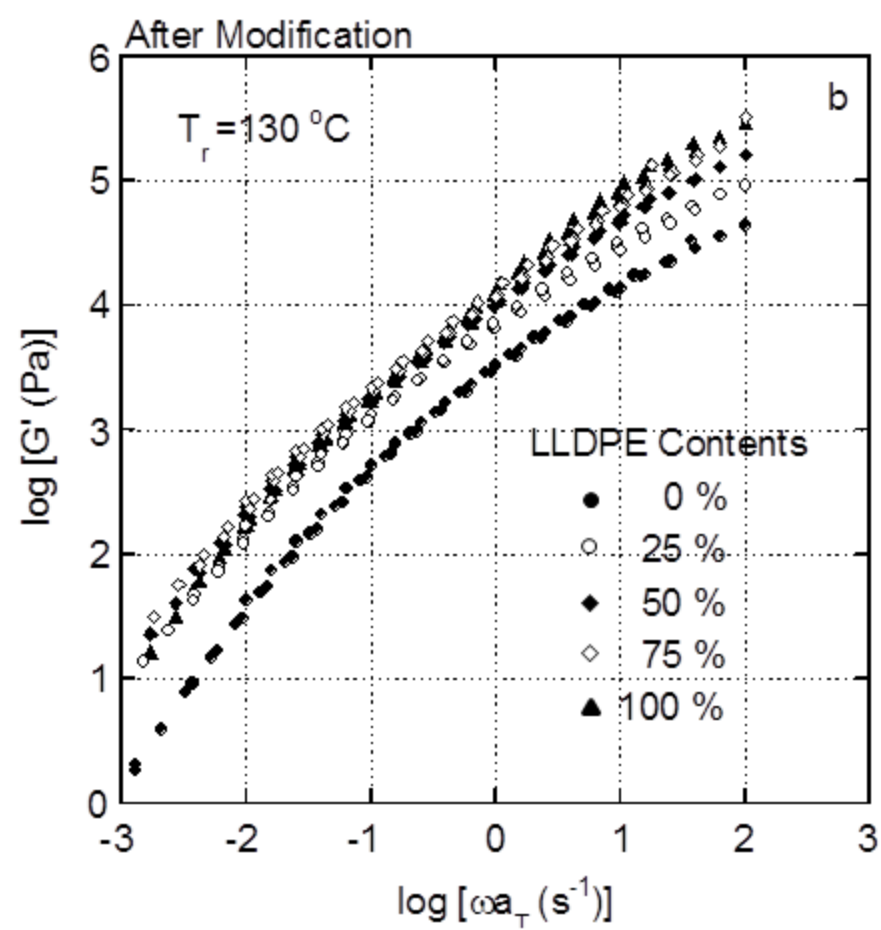
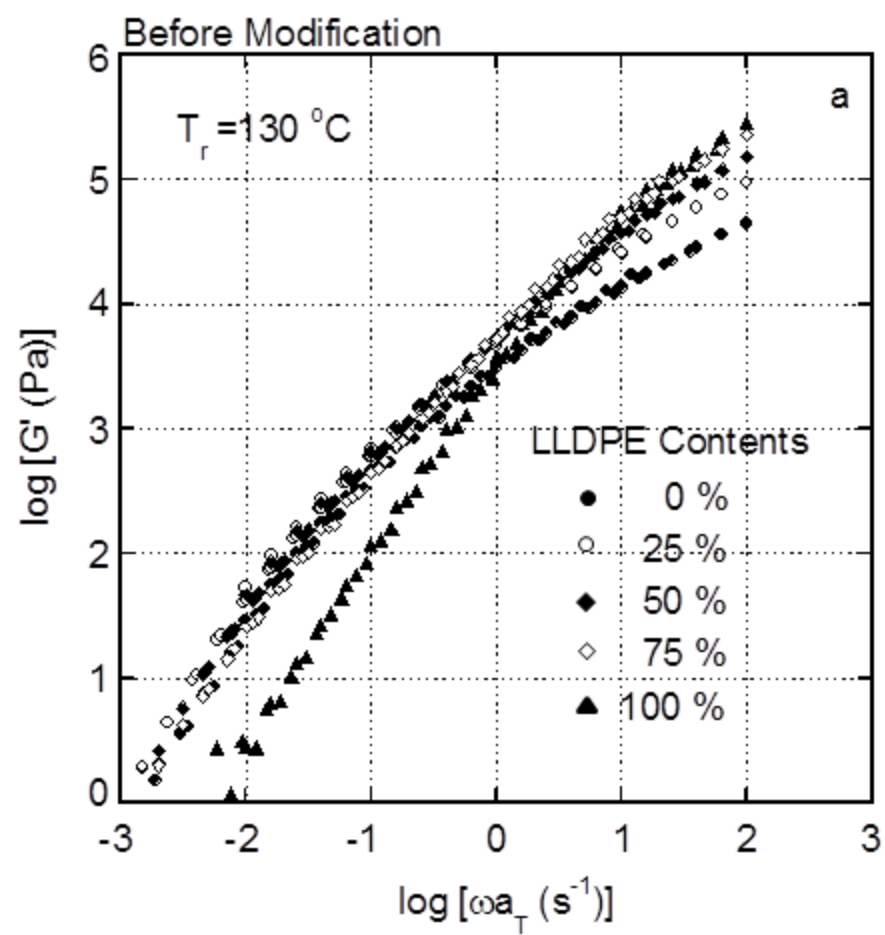


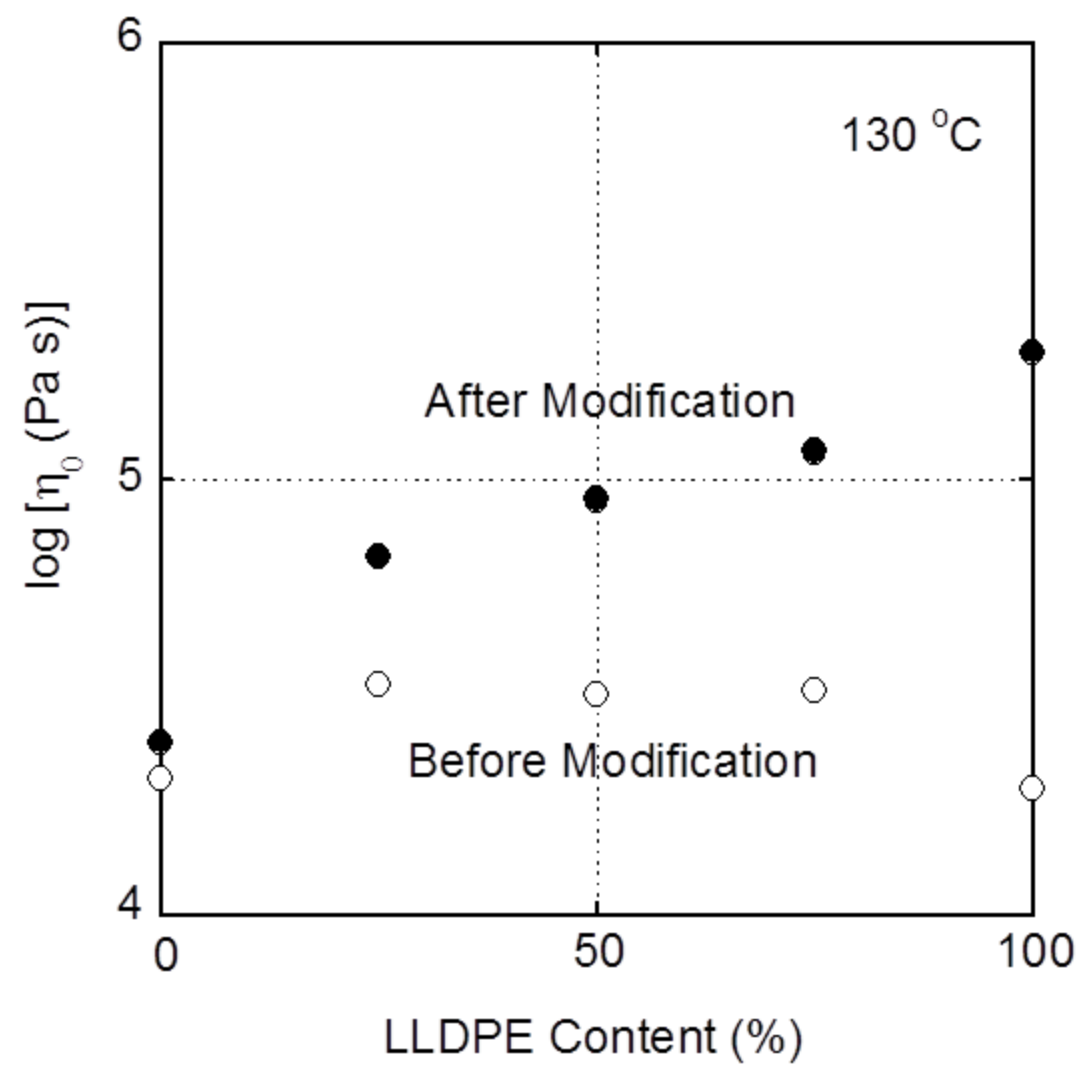


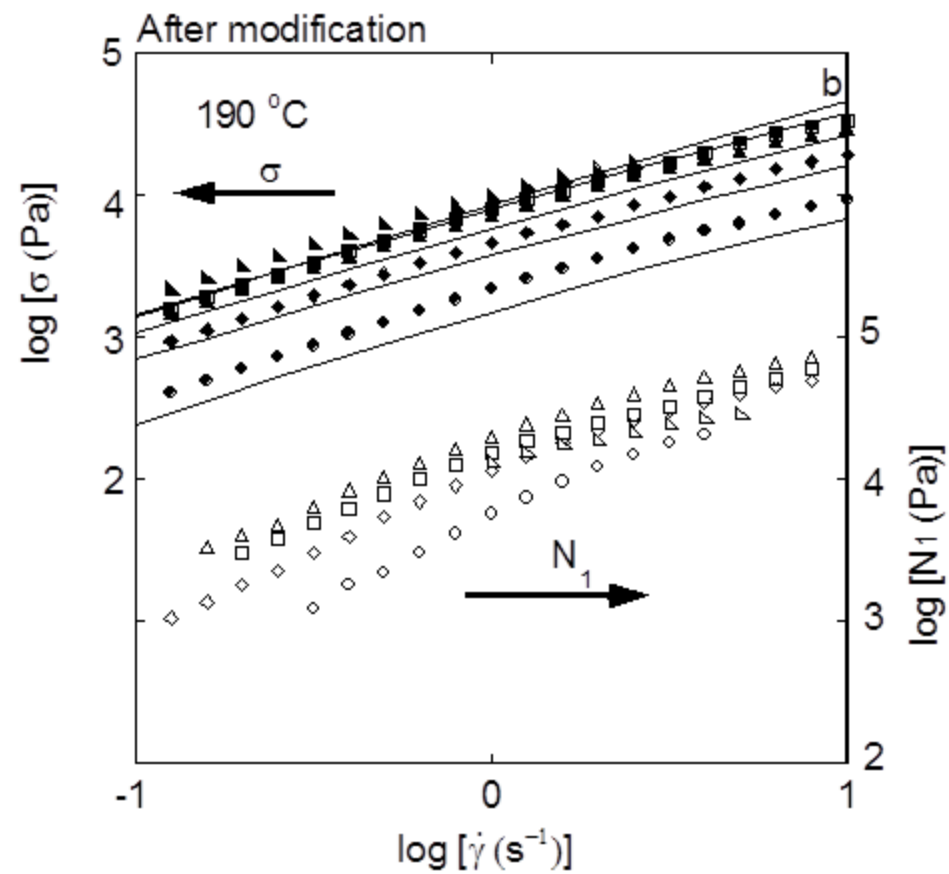
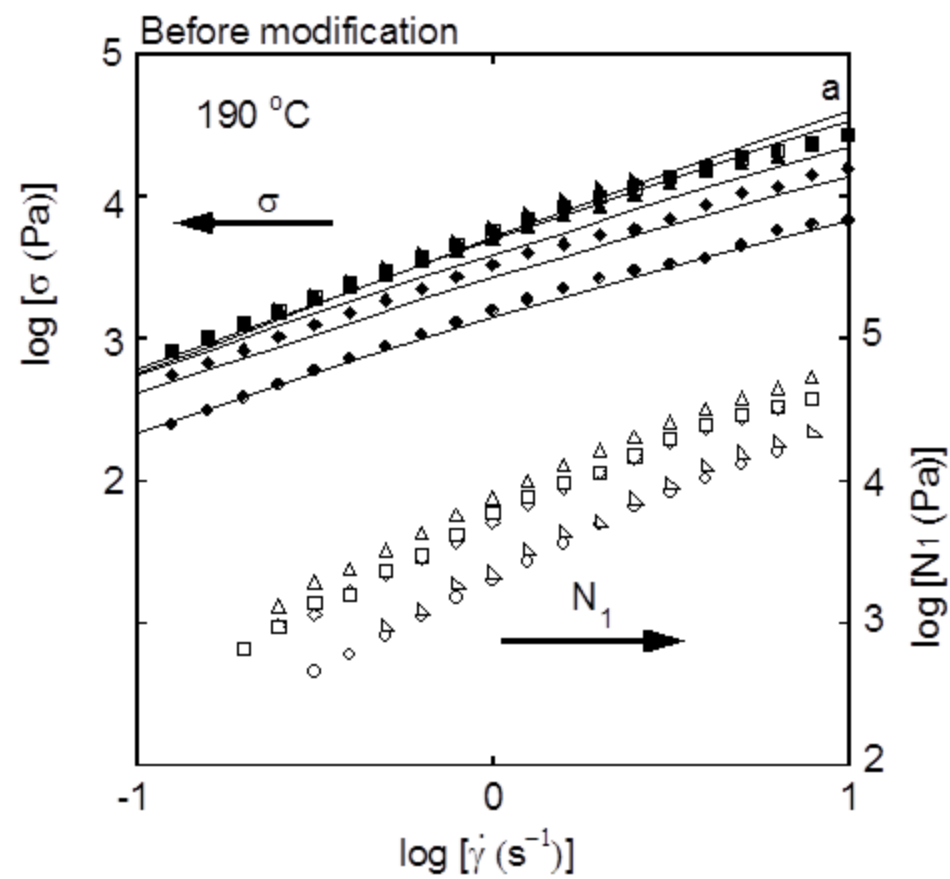


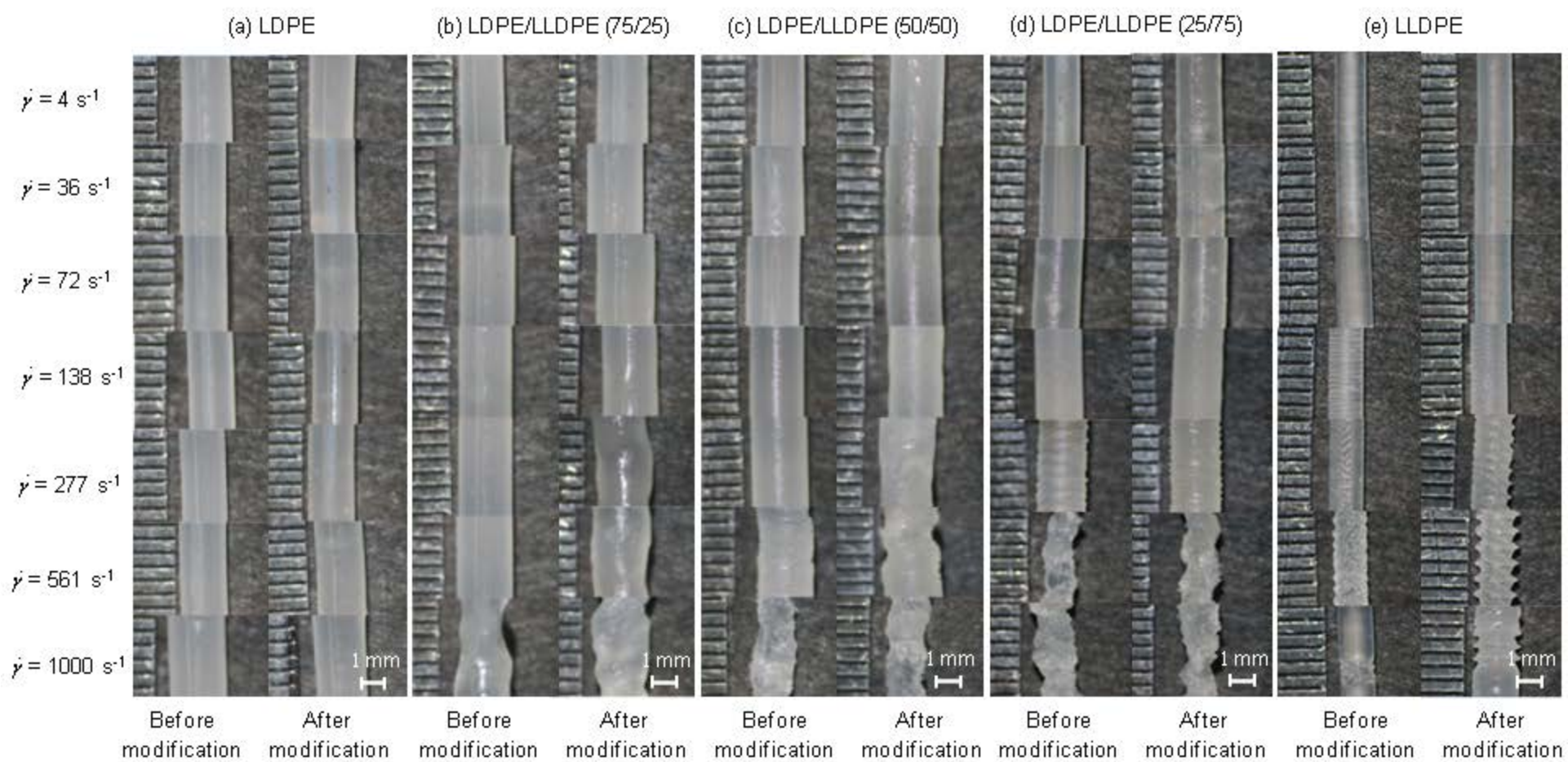
Siriprumpoonthum et al., Figure 4

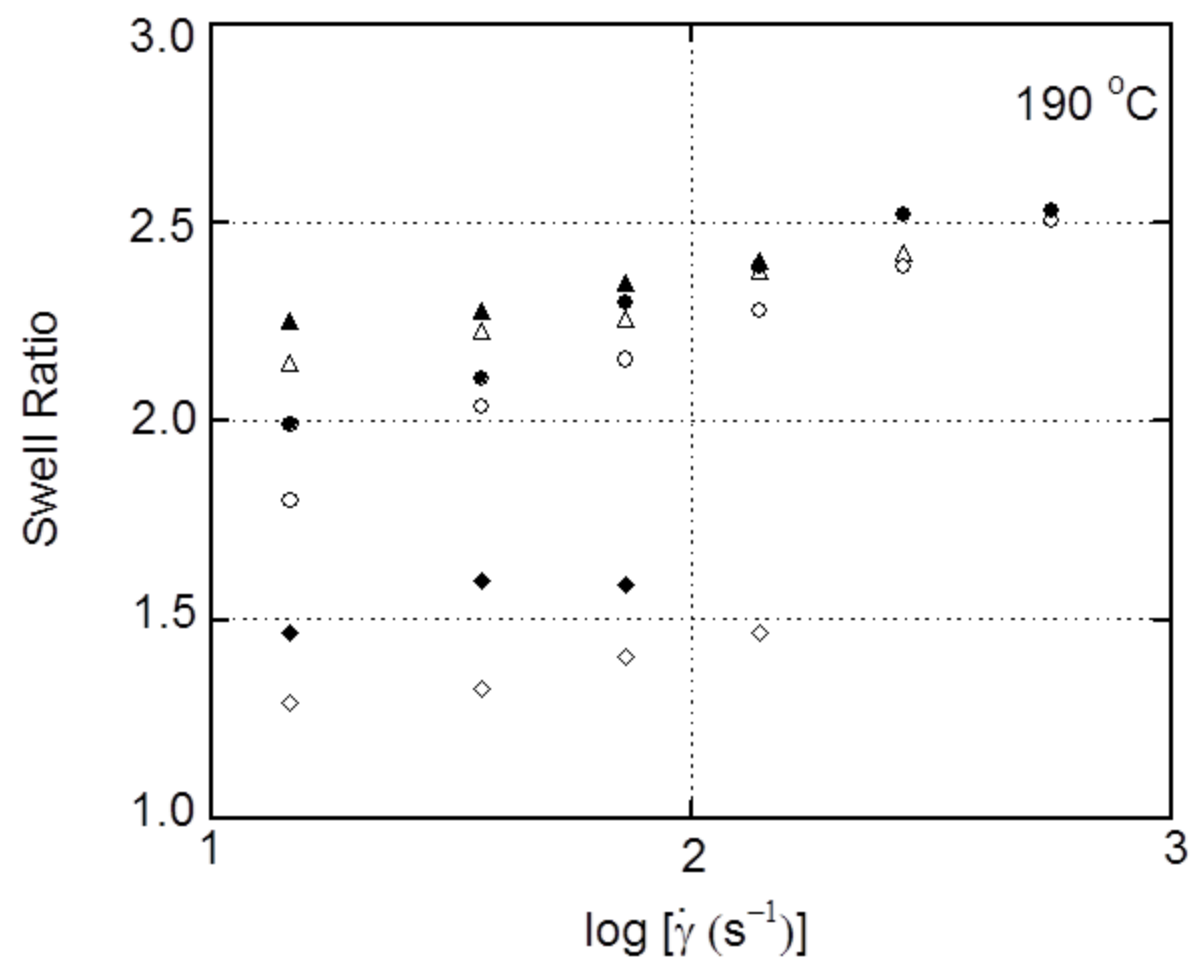


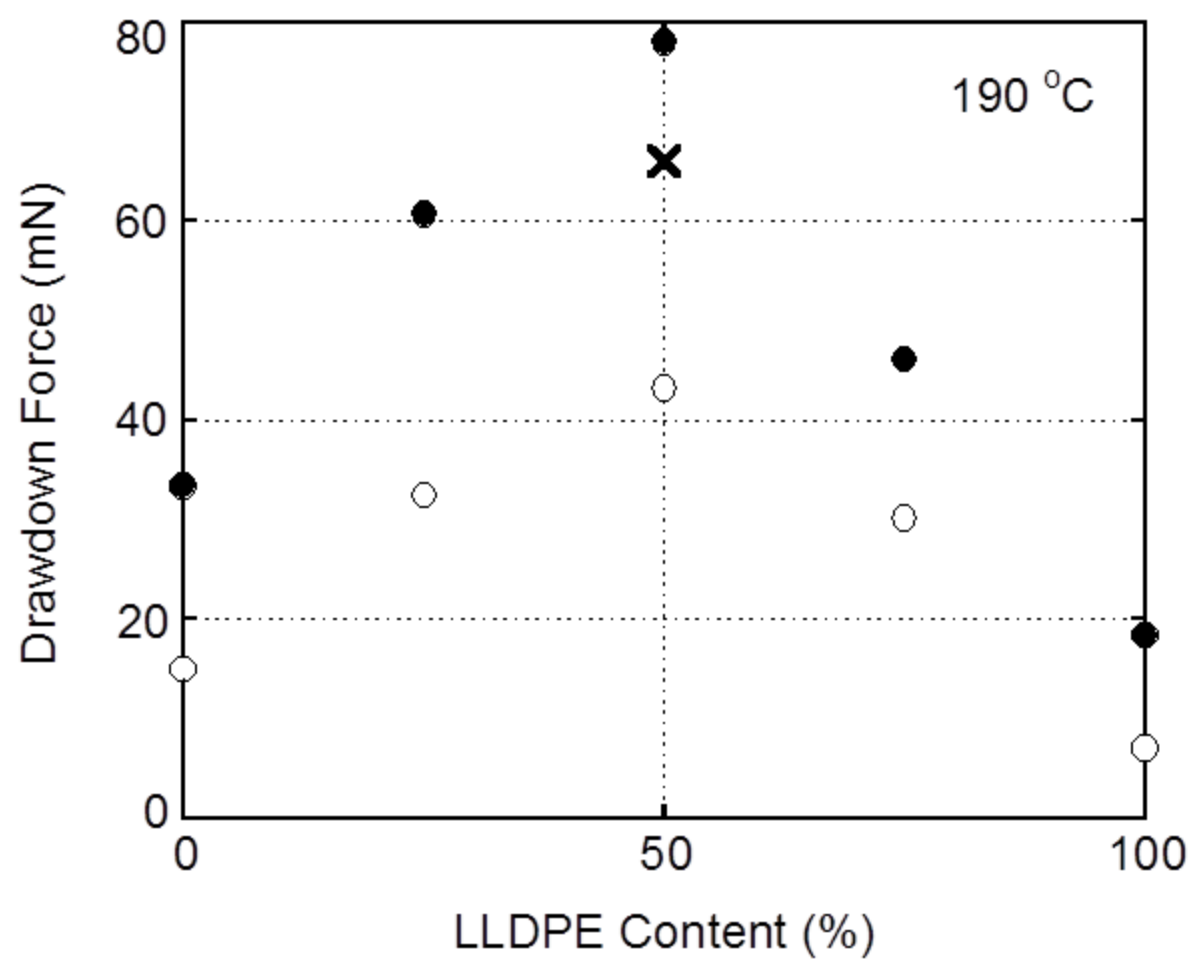


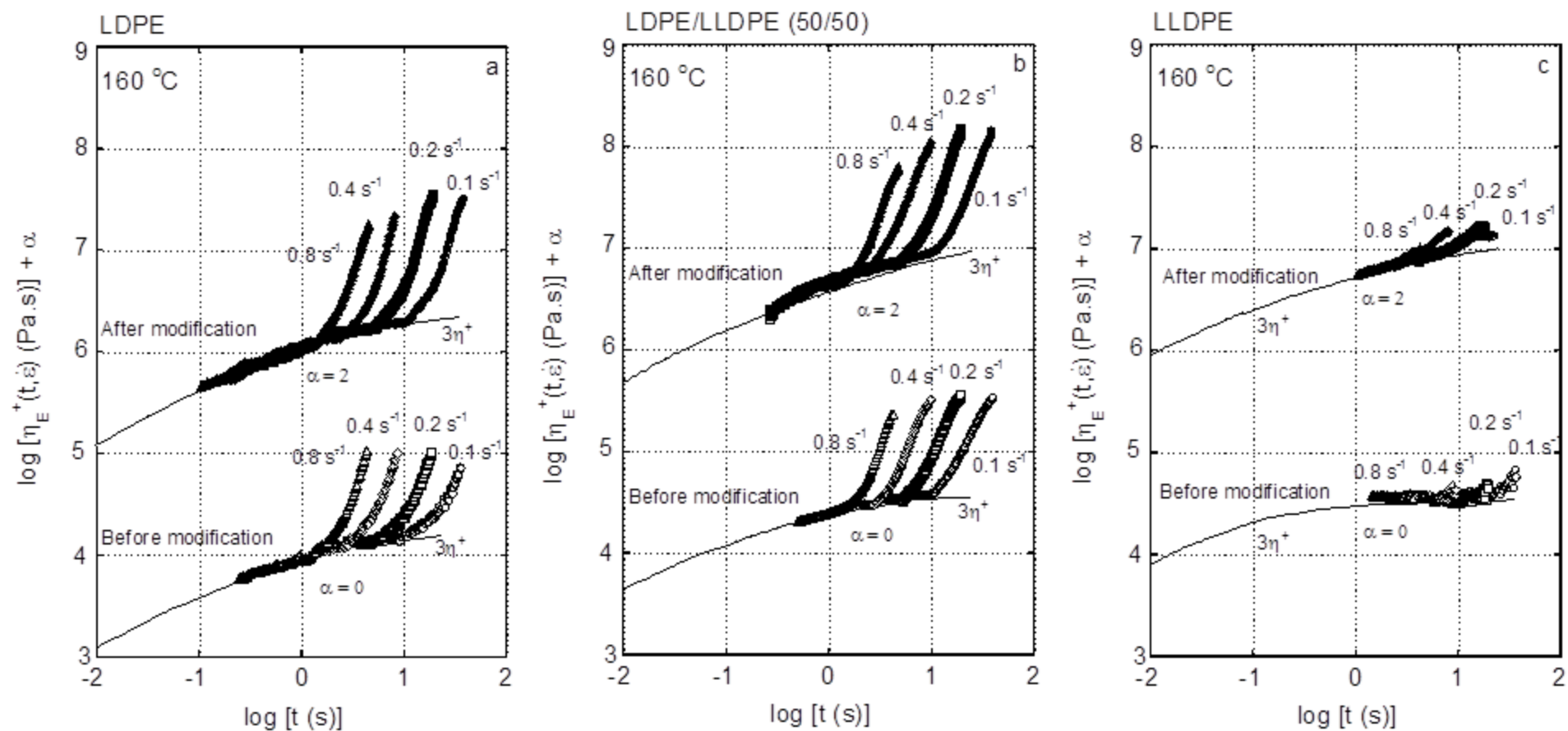




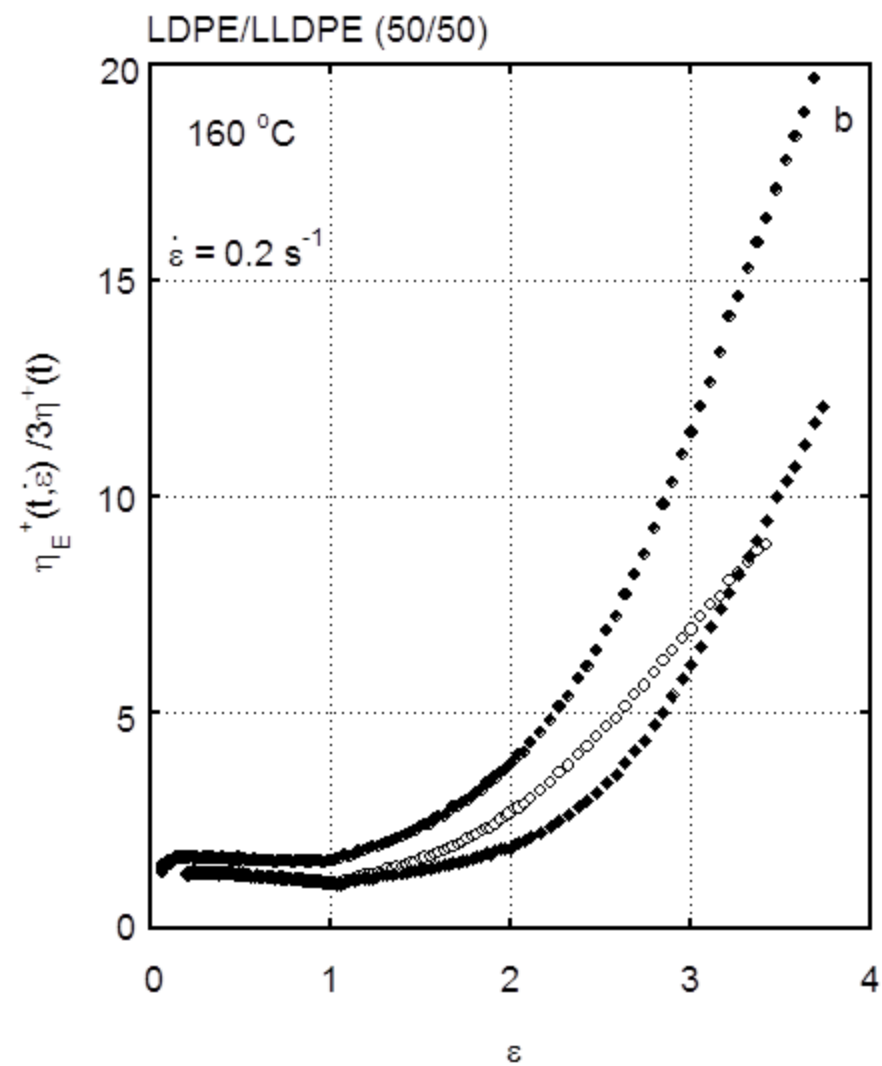
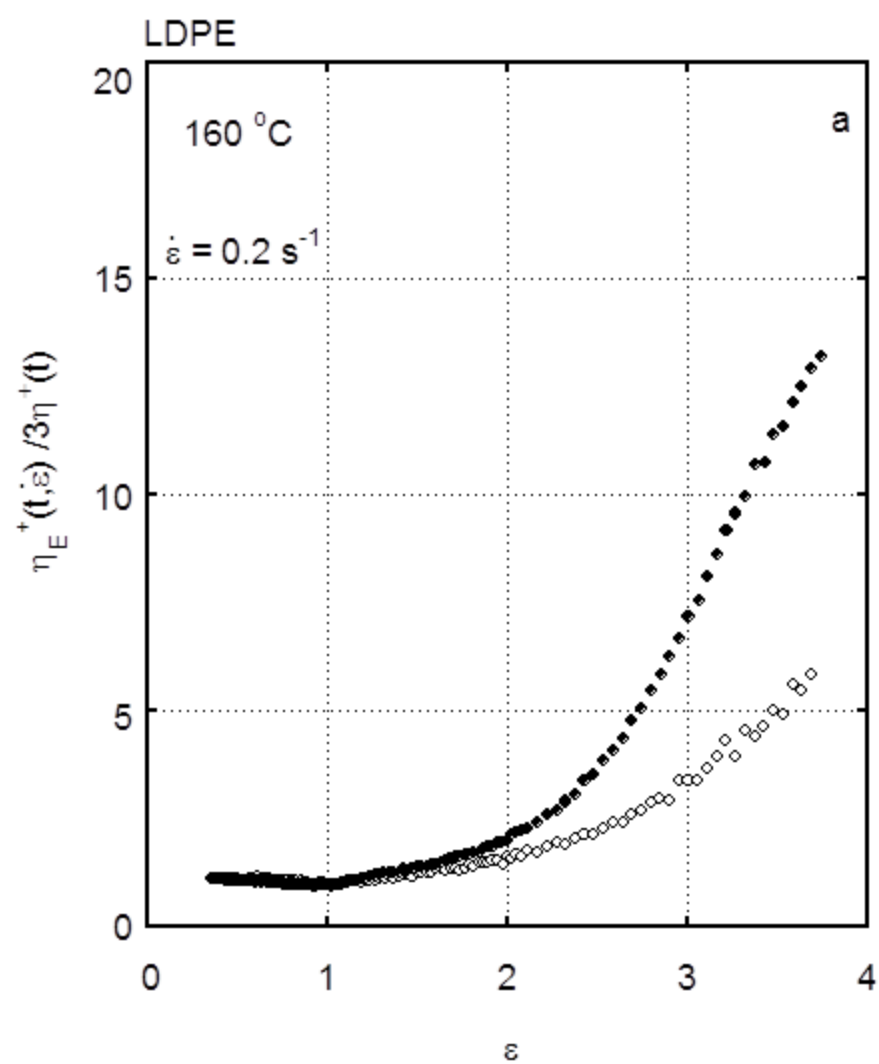


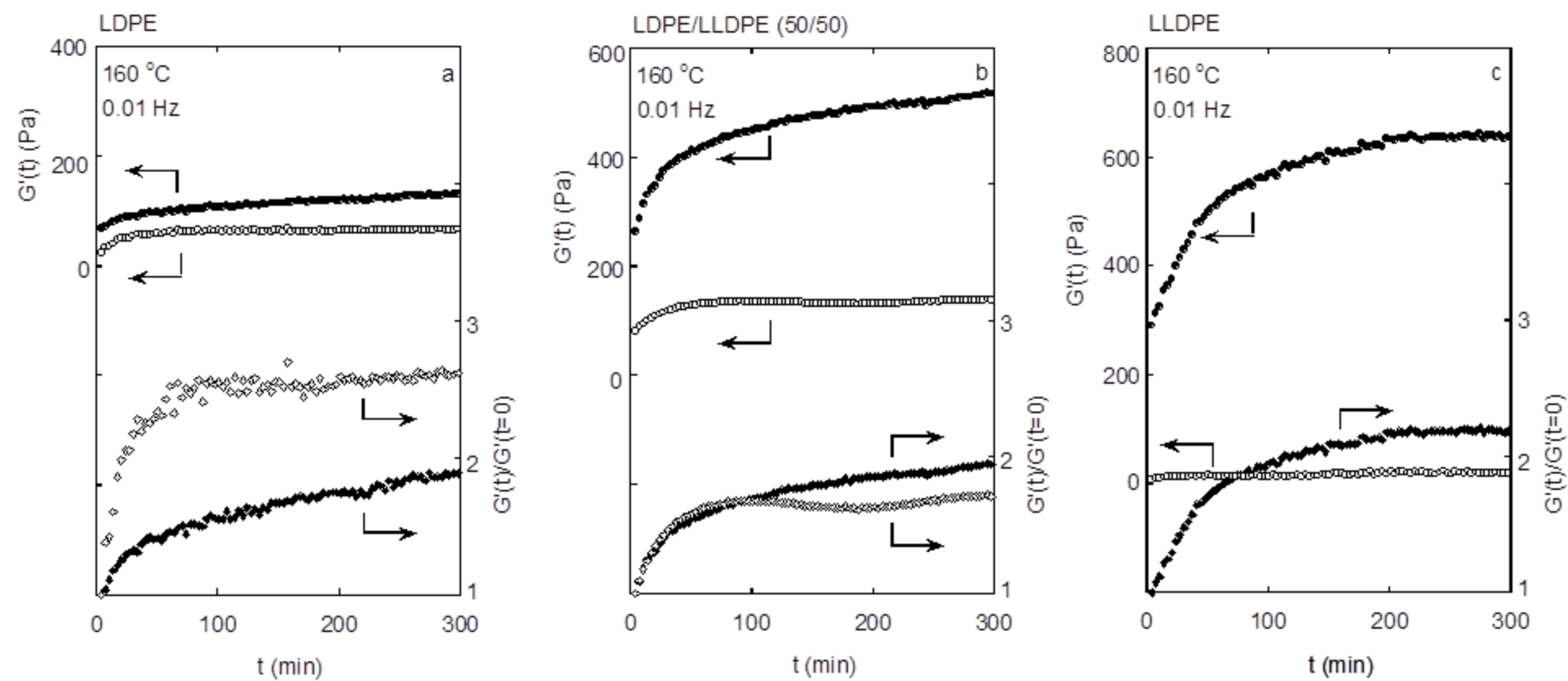






Siriprumpoonthum et al., Figure 12





Siriprumpoonthum et al., Figure 14