COMPARISON BETWEEN DECROSSLINKING OF CROSSLINKED HIGH AND LOW
DENSITY POLYETHYLENES VIA ULTRASONICALLY AIDED EXTRUSION

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Abstract

Among various polymer wastes, management of crosslinked plastics is a major environmental problem requiring a solution. Among various crosslinked plastics, recycling of crosslinked polyethylenes is of a great importance due to the presence of a three-dimensional network. To solve this problem, novel environmentally friendly technologies for decrosslinking of the crosslinked polymers are developed based on ultrasonically assisted single (SSE) and twin screw (TSE) extruders. In particular, decrosslinking of peroxide crosslinked high-density polyethylene (XHDPE) and low-density polyethylene (XLDPE) by means of an ultrasonic SSE and TSE is investigated. Barrel pressure, die pressure and ultrasonic power consumption during extrusion are recorded. Swelling, rheological, thermal analysis and tensile tests are used to elucidate the structure-property relationships of decrosslinked XHDPE and XLDPE. The frequency dependencies of the storage and loss moduli, complex viscosity and tangent loss of XHDPE, XLDPE and their decrosslinked networks are described by the post critical gel model with its parameters correlated with gel fraction and crosslink density. The dynamic, thermal and tensile properties of the decrosslinked XHDPE and XLDPE are greatly affected by the type of preferential bond breakage. It was found that the decrosslinking of XLDPE is more difficult than that of XHDPE. An analysis based on the Horikx function reveals a highly preferential breakage of crosslinks during decrosslinking of XHDPE. In contrast to decrosslinking of XHDPE, the presence of long-chain branching in XLDPE is found to lead to the breakage of its main chains during decrosslinking. An improvement and a reduction in mechanical properties of decrosslinked XHDPE and XLDPE are, respectively, observed in comparison with those of virgin XHDPE and XLDPE. Such differences in behavior are due to the occurrence of a highly preferential breakage of crosslinks in XHDPE and the breakage of main chains in XLDPE during ultrasonic decrosslinking.

Keywords: Ultrasonic Decrosslinking, Crosslinked Polyethylenes, Structure, Rheology, Mechanical Properties.

Graphic Abstract

Stress-strain curves of HDPE, LDPE, XHDPE and XLDPE (a) and decrosslinked XHDPE (b) and XLDPE (c) by SSE and TSE with and without ultrasonic treatment.

Introduction

Among various kinds of PE, crosslinked PE (XPE) is used for rotational molding of various vessels, cable insulation, films, foams and many other applications. Due to the presence of three dimensional crosslinked network, XPE exhibits an improved toughness, environmental stress cracking resistance and creep resistance. However, recycling of XPE is very difficult. This is due to the fact that the presence of the crosslinked network of the XPE prevents its flow under pressure and heat. Therefore, it is necessary to develop a technology for decrosslinking of XPE to make it processable. Several studies are dedicated to decrosslinking of XPE using various technologies including supercritical fluid [1-3], mechanical milling [4, 5] and extrusion [6, 7]. Significant reduction of gel fraction of XPE was achieved using supercritical fluid [1-3] and mechanical milling [4,5]. In case of decrosslinking of silane crosslinked XPE (SXPE) whose crosslinks are siloxane groups, the decrosslinked SXPE is almost identical to the virgin PE due to the occurrence of the selective decomposition of crosslinks caused by the methanolysis reaction of siloxane groups. However, such a selective decomposition of crosslinks does not occur in case of decrosslinking of peroxide and irradiation XPE whose crosslinks are C-C bonds [2, 3]. Nevertheless, each of these aforementioned studies is devoted to only one particular XPE.

Ultrasonic devulcanization of various rubber vulcanizates are conducted by ultrasonically aided extrusion [8-11]. During ultrasonically aided extrusion of rubbers, the ultrasonic horn is in the direct contact with flowing rubbers. The longitudinal vibration of the horn generates ultrasonic waves in vulcanizates causing their devulcanization leading to an occurrence of a significant decrease of gel fraction and crosslink density. The mechanism of ultrasonic

devulcanization is due to the ultrasonic cavitation (rapid growth and contraction) of bubbles and voids present in rubber vulcanizates [11]. Due to the cavitation, the crosslink network around the oscillating bubbles is subjected to large deformations leading to the rupture of chemical bonds in the crosslinked network. The intensity of ultrasonically induced bubble cavitation is determined by the acoustic pressure which is proportional to the ultrasonic amplitude, and frequency. Thus, the effect of ultrasonic devulcanization increases with the ultrasonic amplitude and frequency. The ultrasonically devulcanized rubbers can be reprocessed as virgin rubbers and revulcanized leading to mechanical performance of vulcanizates affected by the chemical structure and type of rubbers [8-11]. The chemical structure of XPE is similar to that of rubber vulcanizates, therefore ultrasonic decrosslinking of peroxide-crosslinked HDPE was attempted by ultrasonically aided SSE [12]. However, a severe thermal degradation occurred due to significant ultrasonic energy dissipation in the ultrasonic treatment zone leading to inferior tensile properties of decrosslinked XHDPE. To overcome this problem, two novel ultrasonically aided extrusion systems with better controlled cooling of ultrasonic treatment zone are developed [13] and used to perform ultrasonic decrosslinking of XHDPE [14-17]. The effects of ultrasonic amplitude [14-17], flow rate [14, 15], extruder type [15], screw design [16] and degree of crosslinking [17] on ultrasonic decrosslinking of XHDPE are studied. It is found that the ultrasonically aided extrusion is a promising technology to obtain a melt processable decrosslinked XHDPE that exhibits good mechanical performance. The ultrasonic amplitude, screw design and degree of crosslinking of XHDPE are found to significantly affect the ultrasonic decrosslinking of XHDPE. However, the effect of branched structure of XPE on ultrasonic decrosslinking is not studied yet.

The present study is aimed to investigate the differences in ultrasonic decrosslinking of XHDPE and XLDPE using SSE and TSE. This will allow us to find effect of the branched

structure on decrosslinking. The process characteristics, structural, rheological and mechanical properties of these decrosslinked polymers are studied and compared. Also, the type of bond breakage during the ultrasonic decrosslinking is revealed. These findings further advance understanding the ultrasonic decrosslinking process leading to a possibility to obtain the decrosslinked XPE with superior mechanical properties.

Experimental

Figure 1 shows a process flow chart of preparation and decrosslinking of XHDPE (a) and XLDPE (b). The whole process included the homogenization of virgin PE and dicumyl peroxide, crosslinking of the mixture of virgin PE and dicumyl peroxide, crushing and extrusion of XHDPE and XLDPE. The details of each step are elaborated in the following three sections.

Figure 1. Process flow chart of preparation and decrosslinking of XHDPE (a) and XLDPE (b).

Materials

HDPE used was a rotational molding grade, 35 mesh powder (Paxon 7004, Exxon Mobil, Baytown, TX). LDPE used was a film blowing grade pellets (LD 100. BW, Exxon Mobil, Baytown, TX). Crosslinking agent was dicumyl peroxide in the pellet form (DC-40, Akrochem, Akron, OH). It contains 40 wt% peroxide and 60 wt% calcium carbonate as a carrier. Tetrakis [methylene (3,5-di-tert-butyl-4-hydroxyhydro cinnamate)] methane (Antioxidant 1010, Akrochem, Akron, OH) was used as a stabilizer during the swelling test. Xylene (mixture of isomers, ACS Reagent Grade, Sigma-Aldrich, WI) was used as a solvent for the swelling test.

The concentration of peroxide DC-40 pellets used to prepare XHDPE and XLDPE was 5%, corresponding to an active peroxide content of 2.0 wt%. The mixture of HDPE powder and DC-40 pellets were homogenized by a high speed mixer using the procedure employed earlier [9]. The mixture of LDPE pellet and DC-40 pellets were homogenized by using a TSE (PRISM US LAB 16, L/D=24, Thermo Electron Corporation, MA) equipped with a circular die with a diameter of 3 mm and a length of 11 mm. The schematic of extruder and screw configuration is shown in Figure 2. During the compounding, the LDPE and peroxide pellets were starve fed to the extruder using a 21 mm twin screw feeder (K2V-T2, K-Tron Corporation, Pitman, NJ) at a flow rate of 18 g/min and a high precision twin screws feeder (MT-2, Brabender Technologie GmbH & Co. KG, Germany) at a flow rate of 0.95 g/min, respectively. The screw speed of TSE was 200 rpm and the temperature profile of barrel and die of extruder were maintained at 120°C to avoid the occurrence of crosslinking reaction.

XHDPE and XLDPE slabs of 26 cm x 26 cm x 1.25 cm were produced by a compression molding press (Carver, Wabash, IN) at a hydraulic pressure of 50 MPa and a temperature of

Figure 2. Schematic of TSE (a) and its screw configuration (b) for compounding of dicumyl peroxide and LDPE.

180°C for 20 min and 25 min, respectively. The reaction time was determined by performing the curing test by means of the Advanced Polymer Analyzer (APA 2000, Alpha Technology, Akron, OH). The prepared XHDPE and XLDPE slabs were crushed by a grinder (WSL180/180, Weima, Fort Mill, SC) with a sieve having holes of a diameter of 4.5 mm. It was confirmed that the grinding process had no effect on the gel fraction of XHDPE and XLDPE.

Decrosslinking of XHDPE and XLDPE and extrusion of LDPE

A 25.4 mm ultrasonic SSE with $L/D=33$ equipped with a circular die of a diameter of 2 mm and a length of 60.5 mm was employed. The schematic design of the ultrasonic SSE and the photograph of the screw are given in Figure 3 (a) and Figure 3 (b), respectively. The SSE was equipped with two water-cooled ultrasonic horns operating at an ultrasonic frequency of 20 kHz connected to boosters and converters. Ultrasonic decrosslinking of the XHDPE and XLDPE by means of SSE was performed at a flow rate of 7.5 g/min and ultrasonic amplitudes of 5, 7.5 and 10 μm . The mean residence time in the ultrasonic treatment zone at this flow rate was 15.5 s. Also, decrosslinking of the XHDPE and XLDPE without imposition of ultrasound was

Figure 4. The schematic design of the ultrasonic TSE (a) and its the screw configuration (b).

imposition of ultrasound was also performed on the same TSE. Due to an excessive torque, decrosslinking of the XHDPE on TSE was only possible by imposition of ultrasound of amplitudes of 7.5, 10 and 13 μm . The die pressure and ultrasonic power consumption were recorded. All other procedures and equipment were same as in earlier study [14]. **It should be noted that the extrudates of decrosslinked XLDPE from TSE without treatment and with ultrasonic treatment at amplitudes of 5 and 7.5 μm was too fragile to form a continuous strand indicating a lack of flowability.**

The ultrasonic single- and twin-screws extrusion of virgin HDPE at various ultrasonic amplitudes and flow rates was reported earlier and no degradation of this HDPE was found [15]. The extrusion of virgin LDPE was carried out using ultrasonic SSE and TSE at the same processing conditions as those of XLDPE. These studies were done to see the effect of ultrasonic treatment on the molecular structure of HDPE and LDPE.

Preparation of Specimens and Their Characterization

The compression molded sheets of decrosslinked XHDPE and XLDPE of 34 cm x 16 cm x 0.185 cm were prepared at a temperature of 200°C and a pressure of 50 MPa for 20 mins. However, the decrosslinked XLDPE without and with ultrasonic treatment at amplitudes of 5 and 7.5 μm from TSE cannot be molded into a defect-free sheet due to its insufficient flowability, as mentioned earlier.

Swelling test of XHDPE, XLDPE, decrosslinked XHDPE and XLDPE were performed by following ASTM D 2765, test method C. The crosslink density of sample was determined by Flory-Rehner equation [18] as follows

$$v_e = - \frac{\ln(1 - v_{ro}) + v_{ro} + \chi v_{ro}^2}{v_1 \left(v_{ro}^{\frac{1}{3}} - \frac{1}{2} v_{ro} \right)} \quad (1)$$

where v_1 is the molecular volume of the solvent, χ is the Flory-Huggins interaction parameter, v_e is the crosslink density, and v_{ro} is the volume fraction of the polymer in the swollen network that is in equilibrium with the solvent. For xylene mixture of isomers at 110°C, $\chi = 0.28$ and $v_1 = 128.4 \text{ cm}^3/\text{mol}$ [19]. It should be mentioned that the crosslink density of decrosslinked XLDPE from TSE without and with ultrasonic treatment at an amplitude of 5 μm could not be measured due to the disintegration of sample during swelling test.

Small amplitude oscillatory shear (SAOS) test of XHDPE, XLDPE, decrosslinked XHDPE and XLDPE at a temperature of 160°C was performed by using a stress controlled Discover Hybrid Rheometer (DHR-2, TA Instruments, New Castle, DE) equipped with 25 mm parallel plates. A circular disk of a diameter of 25 mm was cut from the compression molded sheet. A gap of 2 mm was used for the test. By measuring dynamic properties at different gaps (2

mm and 1.5 mm), it was proven that no slippage occurred during the test [20]. The frequency sweep was in the range from 0.1 to 100 rad/s at a stress amplitude of 500 Pa. SAOS test of virgin and extruded LDPE with and without ultrasonic treatment were also performed at temperatures of 120, 140 and 160°C to calculate the activation energy for flow. The frequency sweep was in the range from 0.05 to 315 rad/s. The shear stress amplitude of SAOS test was 250 Pa.

Differential Scanning Calorimetry (DSC, Model Q200, TA Instruments, New Castle, DE) was used to investigate the thermal behavior of virgin HDPE, virgin LDPE, XHDPE, XLDPE, decrosslinked XHDPE and XLDPE. Samples were cut from tensile specimens by a stainless steel one sided razor blade. The cut samples of about 10 mg were sealed into the DSC hermetic pans (PS 1007, PS 1010, Instrument Specialist Inc., Twin Lakes, WI). To remove the thermal history, the heating-cooling-heating cycle at a rate of 10°C/min was applied in nitrogen environment. HDPE, LDPE, XHDPE, XLDPE and decrosslinked XHDPE and XLDPE were heated from 25 to 200°C, maintained at 200°C for 10 min, cooled from 200 to 25°C and equilibrated at 25°C, and finally heated from 25 to 200°C. The melting temperature and enthalpy were calculated from the second heating. The melting enthalpy of 282 J/g of the perfect linear PE crystal [21] was used to evaluate the crystallinity. The reported crystallinity and melting temperature are the average value of at least two measurements.

Tensile test was performed by using an Instron tensile tester (Mode 5567, Instron, Canton, MA) at a crosshead speed of 25 mm/min without an extensometer **following the ASTM D 1708 standard**. Dumbbell shape tensile test specimens were cut from the compression molded sheet of XHDPE, XLDPE, decrosslinked XHDPE and XLDPE by using a cutting die of a width of 5 mm and a gauge length of 23 mm. The stress-strain curves were recorded by a computer and used to

calculate the Young's modulus, yield stress, stress and strain at break. The error bars were calculated as the standard deviation of at least 5 test results.

Results and Discussions

Barrel pressure and ultrasonic power consumption

Figure 5 shows the barrel pressure before ultrasonic treatment zone in SSE (a) and die pressure in TSE (b) as a function of the ultrasonic amplitude during extrusion of XHDPE and XLDPE. It is seen from Figure 5 that the barrel pressure and die pressure decrease with the ultrasonic amplitude. The decrease of barrel pressure in SSE with the amplitude is due to the decrease of viscosity caused by thixotropic effect and permanent decrease of the gel fraction and crosslink density introduced by ultrasonic treatment [14]. The decrease of die pressure in TSE with the amplitude is due to the permanent decrease of viscosity caused by reduction of the gel fraction and crosslink density [16]. It is seen from Figure 5a that the barrel pressure in SSE during extrusion of XHDPE is slightly higher than that of XLDPE. This is due to the higher viscosity of decrosslinked XHDPE than that of decrosslinked XLDPE, as shown below. It is also seen from Figure 5b that the die pressure in TSE during extrusion of XHDPE is same as that of XLDPE at an amplitude of 7.5 μm and lower than that of XLDPE at amplitudes of 10 and 13 μm . This is also caused by the difference in viscosity of decrosslinked XHDPE and XLDPE.

Figure 6 shows the ultrasonic power consumption as a function of the ultrasonic amplitude during extrusion of XHDPE and XLDPE by SSE (a) and TSE (b). It is seen from

Figure 5. Barrel pressure before ultrasonic treatment zone in SSE (a) and die pressure in TSE (b) as a function of the ultrasonic amplitude during extrusion of XHDPE and XLDPE.

Figure 6 that the ultrasonic power consumption increases with the amplitude. This is due to the fact that ultrasonic power consumption increases with the acoustic pressure which in turn increases with the amplitude. It is also seen from Figure 6 that there is no clear dependence of ultrasonic power consumption on the type of XPE. According to the theoretical modeling of

Figure 6. Ultrasonic power consumption as a function of the ultrasonic amplitude during extrusion of XHDPE and XLDPE by SSE (a) and TSE (b).

ultrasonic power consumption during ultrasonic treatment of a bubble filled polymer [22], the ultrasonic power consumption increases with the sound velocity and longitudinal loss tangent of material at the ultrasonic frequency. The theoretical modeling also indicates that the power consumption increases with hydrostatic pressure due to the reduced volume fraction of bubbles at higher pressure [22]. To the best of our knowledge, there is no research on measuring the sound velocity and longitudinal loss tangent of XHDPE and XLDPE. However, study on the bulk rheology of linear and branched PS [23] and crosslinked polycyanurate of different crosslinked density [24] shows that there is insignificant dependence of bulk rheological

properties on chain architecture of polymer, i.e. linear, branched chain and crosslinked network. Thus, it is reasonable to expect that the sound velocity and longitudinal loss tangent of XHDPE and XLDPE are virtually same. Consequently, the difference between the ultrasonic power consumptions during extrusion of XHDPE and XLDPE is possibly due to the difference of the hydrostatic pressure in ultrasonic treatment zone.

Gel Fraction and Crosslink Density

Figure 7 shows the gel fraction (a) and crosslink density (b) of decrosslinked XHDPE and XLDPE as a function of the ultrasonic amplitude obtained by both SSE and TSE. The gel fraction and crosslink density of XHDPE and XLDPE are also indicated. It is seen from Figure 7 that XHDPE and XLDPE exhibit same gel fraction but different crosslink density. The lower crosslink density of XLDPE at the same concentration of peroxide (2 wt%) is due to a higher probability of formation of intramolecular linking during the crosslinking of LDPE than that of HDPE [25]. As shown in Figure 7, there is a significant decrease of gel fraction and crosslink density of decrosslinked XHDPE and XLDPE without the ultrasonic treatment. In particular, the crosslink density of decrosslinked XHDPE and XLDPE without the ultrasonic treatment drops from 0.121 to 0.024 kmol/m^3 and 0.084 to 0.015 kmol/m^3 , respectively. This indicates that the crosslinked network in XHDPE and XLDPE experiences the significant rupture caused by the shear stresses arising from the rotation of the screw. The gel fraction and crosslink density of decrosslinked XHDPE and XLDPE further decreases with the ultrasonic amplitude. Obviously, this is due to the increase of acoustic pressure with the amplitude. Since the ultrasonic decrosslinking is caused by the ultrasonic cavitation of bubbles, its intensity increases with the acoustic pressure leading to a decrease of gel fraction and crosslink density of decrosslinked XHDPE and XLDPE.

Figure 7. Gel fraction (a) and crosslink density (b) of decrosslinked XHDPE and XLDPE as a function of the ultrasonic amplitude obtained by both SSE and TSE. The gel fraction and crosslink density of XHDPE and XLDPE are also indicated.

It is also seen from Figure 7 that the gel fraction and crosslink density of the decrosslinked XHDPE obtained from SSE and TSE are significantly lower than those of the decrosslinked XLDPE. The previous study on decrosslinking of XHDPE of different levels of crosslink density [17] showed that the lower gel fraction and crosslink density of the decrosslinked XHDPE can be obtained in XHDPE of lower crosslink density. Thus, the lower gel fraction and crosslink density of decrosslinked XHDPE than those of decrosslinked XLDPE cannot be explained in terms of the crosslink density alone. Evidently, the branched structure is

an important factor. It is known that LDPE and XLDPE exhibit stronger strain-hardening during extensional deformation than HDPE and XHDPE due to the presence of long-chain branching. The strain-hardening behavior of polymers is due to a deviation of the end-to-end distance probability distribution function of polymer chains from Gaussian distribution at large strains leading to an increase of stress at a large strain before the occurrence of rupture. Since the decrosslinking of XHDPE and XLDPE is considered as a complex mechanochemical process causing the rupture of polymer chains and crosslinks, it is anticipated that a stronger strain hardening behavior of XLDPE enables its higher resistance to the rupture. This explains why decrosslinking of XLDPE is more difficult to achieve than that of XHDPE.

As shown in Figure 7, the decrosslinked XHDPE and XLDPE obtained by SSE exhibits a lower gel fraction and crosslink density than those by TSE. The observation can be explained as follows. It should be noted that the decrosslinking of XHDPE and XLDPE as a combination of two processes, namely mechanical and ultrasonic decrosslinking. By comparing the screws in SSE and TSE, it is reasonable to expect that SSE provides a stronger mechanical decrosslinking of XHDPE and XLDPE than TSE. This is due to the fact that the screws in SSE contains Union Carbide and melt star mixing sections whereas that in TSE contains only conveying elements. Also, it is seen that the dependence of the gel fraction of decrosslinked XHDPE and XLDPE vs. the ultrasonic amplitude by TSE exhibits a larger slope than that by SSE. At the same time, whereas the slope of crosslink density of decrosslinked XHDPE and XLDPE vs. the ultrasonic amplitude by TSE is virtually same with that by SSE. This indicates that the ultrasonic decrosslinking is more effective in TSE than SSE. The larger effect of ultrasonic decrosslinking in TSE is due to the fact that the ultrasonic frequency in TSE is 40 kHz and that in SSE is 20 kHz. Since the acoustic pressure is proportional to the ultrasonic frequency, the acoustic pressure in

TSE is higher than that in SSE at the same ultrasonic amplitude. Also, at a same residence time and a higher ultrasonic frequency in TSE a material would experience an ultrasonic treatment during larger number of ultrasonic cycles when the residence time is same. In fact, the mean residence time in SSE and TSE is 15.5 s and 17.5 s, respectively. Thus, XHDPE and XLDPE are subjected to an ultrasonic treatment at higher acoustic pressure during larger number of ultrasonic cycles in TSE than SSE. Consequently, a more intensive ultrasonic decrosslinking of XHDPE and XLDPE occurs in TSE than in SSE.

Since bonds in the crosslinks and main chains of XHDPE and XLDPE are all carbon-carbon bonds, spectroscopic determination of the type of bond breakage during decrosslinking of XHDPE and XLDPE is difficult. The type of bond breakage can be determined by analyzing the relationship between the gel fraction and crosslink density of decrosslinked XHDPE using the following Horikx functions [26]:

$$1 - \frac{\nu_{DXHDPE}}{\nu_{XHDPE}} = 1 - \frac{(1 - (1 - \zeta_{DXHDPE})^{1/2})^2}{(1 - (1 - \zeta_{XHDPE})^{1/2})^2} \quad (2)$$

$$1 - \frac{\nu_{DXHDPE}}{\nu_{XHDPE}} = 1 - \frac{(M_n \times \nu_{DXHDPE} + 2)(1 - (1 - \zeta_{DXHDPE})^{1/2})^2}{(M_n \times \nu_{XHDPE} + 2)(1 - (1 - \zeta_{XHDPE})^{1/2})^2} \quad (3)$$

where ν_{XHDPE} , ν_{DXHDPE} and ζ_{XHDPE} , ζ_{DXHDPE} are, respectively, the crosslink density and gel fraction of XHDPE and decrosslinked XHDPE, are, respectively and M_n is the number average molecular weight of the uncrosslinked HDPE. **It should be noted that the Horikx analysis is only applicable for decrosslinking of randomly crosslinked linear polymers. This is due to the statistical assumption in the Horikx functions during the derivation of the theory.** Since the value

of M_n is unavailable, the weight average molecular weight, $M_w=5.2\times 10^4$ g/mol [14], is used in calculation of Eq. (3). Eq. (2) is used to describe the relationship between the normalized gel fraction and the normalized crosslink density of decrosslinked XHDPE in the case when only the breakage of main chains occurs. Eq. (3) is used in case when only crosslinks are broken. Therefore, the type of preferential bond breakage during decrosslinking of XHDPE can be identified by using Horikx functions. Figure 8 shows the normalized gel fraction versus the normalized crosslink density of decrosslinked XHDPE and XLDPE. The normalized gel fraction

Figure 8. Normalized gel fraction versus the normalized crosslink density of decrosslinked XHDPE and XLDPE. Lines represent Horikx function fits for decrosslinked XHDPE to Eqs. (1) and (2).

and crosslink density of decrosslinked XHDPE and XLDPE are defined with respect to the values of XHDPE and XLDPE, respectively. The dotted and dashed lines in Figure 8 are drawn for cases when only the breakage of main chains and crosslinks occurs according to Eqs. (2) and (3), respectively. To the best of our knowledge, there is no statistical theory applicable to determine the type of bond breakage during decrosslinking of XLDPE. Due to this reason curves

for XLDPE are not calculated. It is seen from Figure 8 that all decrosslinked XHDPEs except for one by TSE at an amplitude of 13 μm lies between the main chain breakage and crosslink breakage curves and exhibits a similar type of bond breakage. The data point representing the decrosslinked XHDPE by TSE at an amplitude of 13 μm lies close to the main chain breakage curve. It can be inferred that substantial amount of the main chain breakage takes place during the decrosslinking of XHDPE by TSE at an amplitude of 13 μm . It is also seen from Figure 8 that the data points representing decrosslinked XLDPE by TSE at amplitudes of 10 and 13 μm corresponding to lower values of normalized crosslink density lies beneath those for decrosslinked XLDPE by SSE. Monte-Carlo on the normalized gel fraction versus normalized crosslink density of degraded crosslinked polymer [27] suggests that for two decrosslinked polymers with same crosslink density but different gel fraction, a higher preferential breakage of crosslinks occurs in the decrosslinked polymer of a higher gel fraction. Unlike Horikx function analysis, this simulation study [27] is applicable for both crosslinked linear and branched polymers. Possibly, a higher preferential breakage of crosslinks occurs during the decrosslinking of XLDPE by SSE than TSE as indicated in Figure 8.

Dynamic Properties

The frequency dependences of the storage modulus (Figure 9), loss modulus (Figure 10), complex viscosity (Figure 11) and loss tangent (Figure 12) of decrosslinked XHDPE obtained by SSE (a) and TSE (b) and decrosslinked XLDPE obtained by SSE (c) and TSE (d) without and with ultrasonic treatment at various amplitudes at a temperature of 160°C are measured. The dependences for XHDPE and XLDPE are also indicated in these figures. It is seen from Figures 9 to 11 that the storage and loss moduli and complex viscosity of XHDPE, XLDPE, decrosslinked XHDPE and XLDPE as a function of the frequency exhibit the behavior close to a

Figure 9. Frequency dependences of the storage modulus of XHDPE and decrosslinked XHDPE obtained by SSE (a) and TSE (b) and XLDPE and decrosslinked XLDPE obtained by SSE (c) and TSE (d) without and with ultrasonic treatment at various amplitudes at a temperature of 160°C. Dotted lines are drawn by fitting to post critical gel model, Eq. (3).

Figure 10. Frequency dependences of the loss modulus of XHDPE and decrosslinked XHDPE obtained by SSE (a) and TSE (b) and XLDPE and decrosslinked XLDPE obtained by SSE (c) and TSE (d) without and with ultrasonic treatment at various amplitudes at a temperature of 160°C. Dotted lines are drawn by fitting to post critical gel model, Eq. (4).

Figure 11. Frequency dependences of the complex viscosity of XHDPE and decrosslinked XHDPE obtained by SSE (a) and TSE (b) and XLDPE and decrosslinked XLDPE obtained by SSE (c) and TSE (d) without and with ultrasonic treatment at various amplitudes at a temperature of 160°C. Dotted lines are drawn by fitting to post critical gel model, Eq. (5).

Figure 12. Frequency dependences of the loss tangent of XHDPE and decrosslinked XHDPE obtained by SSE (a) and TSE (b) and XLDPE and decrosslinked XLDPE obtained by SSE (c) and TSE (d) without and with ultrasonic treatment at various amplitudes at a temperature of 160°C. Dotted lines are drawn by fitting to post critical gel model, Eq. (6).

power-law behavior. Also, the loss tangent of XHDPE, XLDPE, decrosslinked XHDPE and XLDPE shows a relatively weak dependence on the frequency. Such a behavior is typical for so-called “critical gel” [28-33] and “post critical gel” [34]. The post critical gel model fitting of XHDPE, XLDPE, decrosslinked XHDPE and XLDPE is also indicated in Figures 9 to 12 by dotted lines. The following equations are used for this fitting [34]:

$$G' = \Gamma(1-m) \cos\left(\frac{m\pi}{2}\right) S \omega^m + G_e \quad (4)$$

$$G'' = \Gamma(1-m) \sin\left(\frac{m\pi}{2}\right) S \omega^m \quad (5)$$

$$|\eta^*| = \frac{\sqrt{\left[\Gamma(1-m) \cos\left(\frac{m\pi}{2}\right) S \omega^m + G_e \right]^2 + \left[\Gamma(1-m) \sin\left(\frac{m\pi}{2}\right) S \omega^m \right]^2}}{\omega} \quad (6)$$

$$\tan \delta = \frac{\Gamma(1-m) \cos\left(\frac{m\pi}{2}\right) S \omega^m}{\Gamma(1-m) \sin\left(\frac{m\pi}{2}\right) S \omega^m + G_e} \quad (7)$$

where Γ is the gamma function, S is the gel stiffness, m is the relaxation exponent, and G_e is the equilibrium modulus. The post critical gel model parameters of XHDPE, XLDPE, decrosslinked XHDPE and XLDPE are tabulated in Table 1. It is seen from Figures 9 to 12 that Eqs. (4) to (7) are adequate to describe the dynamic properties of XHDPE, XLDPE, decrosslinked XHDPE and XLDPE. An obvious similarity between the storage and loss moduli and complex viscosity of decrosslinked XHDPE and XLDPE is seen in Figures 9 to 11. However,

Table 1. Gel fraction, crosslink density, post critical gel model parameters for XHDPE, XLDPE, decrosslinked XHDPE and XLDPE

Material	Type of Extruder	Amplitude, μm	ζ	ν	S , $\text{Pa}\cdot\text{s}^m$	m	G_e , Pa
XHDPE	None	None	0.93	0.121	2.75×10^5	0.1092	3.64×10^5
XLDPE	None	None	0.93	0.084	6.42×10^4	0.1981	2.65×10^5
Decrosslinked XHDPE	SSE	0	0.64	0.0150	1.98×10^5	0.1500	1.14×10^4
		5	0.65	0.0163	2.03×10^5	0.1449	7.91×10^3
		7.5	0.60	0.0093	1.47×10^5	0.1699	4.16×10^3
		10	0.56	0.0076	1.20×10^5	0.1816	4.62×10^3
	TSE	7.5	0.67	0.013	2.12×10^5	0.1402	1.45×10^4
		10	0.59	0.011	1.58×10^5	0.1624	0
		13	0.27	0.0068	3.55×10^4	0.2833	0
Decrosslinked XLDPE	SSE	0	0.80	0.023	8.88×10^4	0.1843	1.34×10^5
		5	0.75	0.019	7.28×10^4	0.1843	9.37×10^4
		7.5	0.75	0.018	7.29×10^4	0.1909	6.96×10^4
		10	0.69	0.014	5.44×10^4	0.2018	4.39×10^4
	TSE	0	0.82	N.A.	7.96×10^4	0.1694	9.66×10^4
		5	0.83	N.A.	7.83×10^4	0.1727	1.02×10^5
		7.5	0.81	0.024	7.33×10^4	0.1780	9.08×10^4
		10	0.72	0.021	6.74×10^4	0.1906	5.33×10^4
		13	0.61	0.013	4.42×10^4	0.2100	1.76×10^4

the frequency dependence of loss tangent of the decrosslinked XHDPE and XLDPE are different, as shown in Figure 12. Therefore, the processing-dynamic property relationship of decrosslinked XHDPE and XLDPE will be discussed by analyzing the dependence of post critical gel model parameters of decrosslinked XHDPE and XLDPE on the ultrasonic amplitude, type of extruder and molecular structure of uncrosslinked precursor. The relaxation modulus of a post critical gel after small step strain is given as [34]:

$$G(t) = St^{-m} + G_e \quad (8)$$

where $G(t)$ is the relaxation modulus, t is the time. It is clear from Eq. (8) that the physical interpretation of post critical gel can be considered as a critical gel and an elastic solid are

assembled in parallel. Thus, the value of S increases with the gel fraction, crosslink density, rubbery plateau modulus and molecular weight of uncrosslinked precursors [28]. The m decreases with the gel fraction and crosslink density [28] and increases with crosslinked network defects, i.e. dangling chains and looping [35]. The value of G_e increases with the gel fraction and crosslink density. Indeed, it is seen from Table 1 that the values of S and G_e of decrosslinked XHDPE and XLDPE are, respectively, lower than those of XHDPE and XLDPE, whereas the values of m of decrosslinked XHDPE and XLDPE are, respectively, higher than those of XHDPE and XLDPE. This is caused by a decrease of the gel fraction and crosslink density during extrusion of XHDPE and XLDPE. The dependence of the values of S , m and G_e of the decrosslinked XHDPE and XLDPE on the ultrasonic amplitude and type of extruder can be explained by correlating these material parameters with the gel fraction and crosslink density. It is seen from Table 1 that values of S , m and G_e of the decrosslinked XHDPE and XLDPE show a very good correlation with the gel fraction and crosslink density of decrosslinked XHDPE and XLDPE. Namely, values of S and G_e increase with the gel fraction and crosslink density and value of m decreases with them. However, the dependence of the values of S , m and G_e of decrosslinked XHDPE and XLDPE on the molecular structure of the uncrosslinked PE cannot be explained by the gel fraction and crosslink density alone. In fact, it is seen from Table 1 that the value of S of the decrosslinked XHDPE is higher than that of the decrosslinked XLDPE. This is in contradiction with the gel fraction and crosslink density of the decrosslinked XHDPE and XLDPE, but can be explained by considering the rubbery plateau modulus of HDPE and LDPE. It is known that the rubbery plateau modulus of HDPE, due to its linear structure, is higher than LDPE. Therefore, the higher value of S of the decrosslinked XHDPE

than that of the decrosslinked XLDPE is due to the higher rubbery plateau modulus of HDPE. Also, the value of m of the decrosslinked XHDPE is lower than that of the decrosslinked XLDPE, except for the decrosslinked XHDPE by SSE at an amplitude of 10 μm . This is also in contradiction with the gel fraction and crosslink density of the decrosslinked XHDPE and XLDPE, but can be possibly explained by the crosslinked network defects. It is known that the network defects decrease with the fractal dimension of the polymer chains in a crosslinked network. A theoretical study [35] showed that the fractal dimension of polymer chains in network can be correlated to the value of m as:

$$m = \frac{d(d + 2 - 2d_f)}{2(d + 2 - d_f)} \quad (9)$$

where d is the dimensionality of sample which is 3 in this study, d_f is the fractal dimension of polymer chains in the crosslinked network. It is inferred from Eq. (9) that the value of m decreases with that of d_f . Since the value of m of the decrosslinked XLDPE is lower than that of the decrosslinked XHDPE, it is very likely that the decrosslinked XLDPE has more crosslinked network defects than decrosslinked XHDPE. It is difficult to quantify the crosslinked network defects in the decrosslinked XHDPE and XLDPE. However, due to a lower probability of intramolecular linking reaction during crosslinking of HDPE, XHDPE contains a less amount of crosslinked network defects than XLDPE. Also, a higher preferential breakage of crosslinks occurs during decrosslinking of XHDPE than that of XLDPE which will be discussed in the later section, is due to the effect of long-chain branching of LDPE. Thus, it can be inferred that the amount of crosslinked network defects in the decrosslinked XHDPE is less than that in the decrosslinked XLDPE.

In our previous studies [14-17], the activation energy for flow of the soluble fraction of the decrosslinked XHDPE has been investigated and indicated the presence of the branched structure in it. This information was used to infer the type of bond breakage during decrosslinking. If a preferential breakage of crosslinks occurs during decrosslinking, the activation energy for flow of the soluble fraction of the decrosslinked XHDPE should be close to that of HDPE. However, such an analysis is not applicable to find type of bond breakage during decrosslinking of XLDPE, since both type of the bond breakage lead to the soluble fraction of a highly branched PE. In this scenario, the activation energy of soluble fraction cannot provide information on type of bond breakage. However, the effect of ultrasonic treatment on the molecular structure of LDPE may shed light on understanding the effect of branched structure on type of bond breakage. Let us consider the possible structural changes in an ultrasonically treated LDPE. The ultrasonic treatment of LDPE may lead to either breakage of backbone or branched structure. In both cases, the viscosity of the ultrasonically treated LDPE should decrease in comparison with that of the virgin LDPE. Also, the activation energy of ultrasonically treated LDPE should not be affected significantly, if only breakage of main chains occurs, and decreased if the breakage of branched structure, especially that of long-chain branching, occurs. Thus, the activation energy of the ultrasonically treated LDPE can be used to determine the type of bond breakage.

Figure 13 shows the frequency dependence of the complex viscosity of the virgin and extruded LDPE obtained by SSE (a) and TSE (b) with and without ultrasonic treatment at a temperature of 120°C. It is seen from Figure 13 that there is a strong non-Newtonian behavior of the virgin and extruded LDPE due to their high molecular weight and long-chain branching. The complex viscosity of the ultrasonically extruded LDPE by SSE is insignificantly affected by the

Figure 13. Frequency dependences of the complex viscosity of virgin and extruded LDPE obtained by SSE (a) and TSE (b) with and without ultrasonic treatment at a temperature of 120°C. However, the complex viscosity of the ultrasonically extruded LDPE by TSE decreases with the ultrasonic amplitude indicating an occurrence of ultrasonic degradation of LDPE due to higher ultrasonic frequency used in TSE.

Figure 14 shows the frequency dependence of the complex viscosity of the virgin LDPE (a) and ultrasonically treated LDPE by TSE (b) at an amplitude of 13 μm at temperatures of 120, 140 and 160 °C. Cross model [36] fits are also indicated by lines in Figure 14 based on the following equations:

$$|\eta^*| = \frac{\eta_o^*(T)}{1 + \left[\frac{\eta_o^*(T)\omega}{\tau} \right]^{1-n}} \quad (10)$$

$$\eta_o^*(T) = A \exp\left(\frac{T_b}{T}\right) = A \exp\left(\frac{E}{RT}\right) \quad (11)$$

Figure 14. Frequency dependences of the complex viscosity of the virgin LDPE (a) and ultrasonically treated LDPE by TSE (b) at an amplitude of 13 μm at temperatures of 120, 140 and 160°C Dashed lines represent Cross model fits to Eqs. (9) and (10).

where, A , T_b , τ and n are fitting parameters. The function of $\eta_o^*(T)$ is the temperature dependency of the zero-frequency viscosity by the Arrhenius equation, where T is the temperature, E is the activation energy of flow and R is the gas constant. It is seen from Figure 14 that the Cross model is adequate to fit the complex viscosity at different temperatures. The

Cross model is also used to fit the complex viscosity of other ultrasonically treated LDPEs at temperature of 120, 140 and 160°C, but not shown here due to their similarity. The Cross model parameters of virgin and extruded LDPE are tabulated in Table 2. It is seen from Table 2 that the activation energies of the untreated and ultrasonically treated LDPE differ insignificantly. This indicates that the untreated and ultrasonically treated LDPE exhibits a similar branched structure. As discussed earlier, the occurrence of decrease of complex viscosity without significant change of activation energy of ultrasonically treated LDPE is due to the breakage of backbone rather than branched structure of LDPE. Therefore, it is possible to suggest the molecular mechanism of the ultrasonic degradation of LDPE. Obviously, the ultrasonic degradation of LDPE is caused by the ultrasonic cavitation of bubbles in LDPE melt. The latter causes a strong biaxial deformation on LDPE molecules around the bubbles. According to the classical molecular description of polymer dynamics [37], due to the presence of long-chain branching, the reptation of backbone of LDPE is not likely without the complete retraction of the long-chain branches from its tube. Since the ultrasonic frequency is very high, it is very likely that the retraction of long-chain branches is difficult. Thus, the backbone of LDPE is possibly subjected to a very

Table 2. Cross model parameters and activation energy for flow of virgin and extruded LDPE

Material	Extruder	Amplitude, μm	A, Pa*s	T_b , K	τ , Pa	n	E, kJ/mol
Virgin LDPE	No	No	0.0190	6075	9.7×10^3	0.38	50.5
Extruded LDPE	SSE	0	0.0210	6113	9.1×10^3	0.37	50.8
		5	0.0516	5784	8.4×10^3	0.38	48.1
		7.5	0.0959	5492	9.0×10^3	0.38	45.7
		10	0.0543	5737	8.2×10^3	0.37	47.7
		0	0.0087	6414	9.9×10^3	0.38	53.3
	TSE	5	0.0273	5964	1.07×10^4	0.37	49.6
		7.5	0.0409	5768	9.6×10^3	0.37	48.0
		10	0.3727	6113	9.3×10^3	0.38	50.8
		13	0.0044	6042	8.7×10^3	0.41	50.2

large stretch due to its limited ability to change configuration. In this scenario, it is possible that the backbone of LDPE between two branch points becomes overstrained. Accordingly, its length is being extended over its contour length, leading to the degradation of LDPE. Similarly, the long-chain branching in XLDPE may have a similar effect on decrosslinking of XLDPE, enhancing the breakage of main chains by reducing its ability to change configuration when the XLDPE network is subjected to a strong biaxial deformation caused by the ultrasonic cavitation of bubbles. This will cause an excessive breakage of the main chains during decrosslinking of XLDPE affecting the mechanical performance of the decrosslinked XLDPE, as shown later.

DSC Analysis

Figure 15 shows the DSC traces obtained during the second heating of the HDPE, XHDPE and decrosslinked XHDPE (a) and LDPE, XLDPE and decrosslinked XLDPE (b), and the first cooling of the HDPE, XHDPE and decrosslinked XHDPE (c) and LDPE, XLDPE and decrosslinked XLDPE (d) by SSE and TSE with and without ultrasonic treatment. It is seen from Figure 15 that the XHDPE and XLDPE exhibits broad melting and crystallization peaks and small melting and crystallization enthalpies than HDPE and LDPE, respectively. The melting and crystallization peaks of decrosslinked XHDPE and XLDPE resemble peaks of XHDPE and XLDPE, rather than those of HDPE and LDPE. This is mainly due to the presence of the crosslinked network in gel of the decrosslinked XHDPE and XLDPE. However, the melting peak of the decrosslinked XLDPE by TSE at an amplitude of 13 μm exhibits more similarity to that of LDPE than that of XLDPE.

Figure 16 shows melting temperature (a) and crystallinity (b) of decrosslinked XHDPE and XLDPE as a function of the ultrasonic amplitude along with values for HDPE, LDPE,

Figure 15. DSC traces obtained during the second heating of the HDPE, XHDPE and decrosslinked XHDPE (a) and LDPE, XLDPE and decrosslinked XLDPE (b), and the first cooling of the HDPE, XHDPE and decrosslinked XHDPE (c) and LDPE, XLDPE and decrosslinked XLDPE (d) by SSE and TSE with and without ultrasonic treatment.

XHDPE and XLDPE. As seen from Figure 16, the melting temperature and crystallinity of HDPE due to its linear structure is significantly higher than that of LDPE. The melting temperature and crystallinity of XHDPE and XLDPE are lower than those of HDPE and LDPE, respectively. This is due to the presence of crosslinks in the gel of XHDPE and XLDPE hindering the formation of the PE crystal [38]. It is also seen from Figure 16 that the melting temperature and crystallinity of the decrosslinked XHDPE and XLDPE are generally higher than those of XHDPE and XLDPE, respectively, and increases with the ultrasonic amplitude but still lower than those of HDPE and LDPE. This is due to the decrease of gel fraction and crosslink

Figure 16. Melting temperature (a) and crystallinity (b) of decrosslinked XHDPE and XLDPE as a function of the ultrasonic amplitude. The values for HDPE, LDPE, XHDPE and XLDPE are also indicated. Some data points are shifted horizontally for clarity.

density of the decrosslinked XHDPE and XLDPE with the amplitude. As shown in Figure 16, the increase of crystallinity and melting temperature of the decrosslinked XLDPE is, respectively, mild and significant. Such difference in the melting temperature and crystallinity is caused by the difference in types of bond breakage during decrosslinking of XHDPE and XLDPE. The significance of this effect on the melting temperature and crystallinity of the decrosslinked

XHDPE is emphasized earlier [14-17]. This is due to the fact that the breakage of main chains creates a soluble fraction containing branched structures impeding the growth of PE crystal. Thus, there are two competing effects on the melting temperature and crystallinity, namely, a decrease of the gel fraction and crosslink density and an increase of the branched soluble fraction. Consequently, an insignificant and significant increase of the melting temperature and crystallinity of the decrosslinked XHDPE during decrosslinking of XHDPE of low (0.015 kmole/m^3) and high (0.44 kmole/m^3) crosslink density and intermediate crosslink density (0.121 kmole/m^3) in SSE is, respectively, observed [17]. This is due to the absence and presence of a preferential breakage of crosslinks in the former and latter case, respectively. A significant increase of the melting temperature and crystallinity of the decrosslinked XHDPE with the amplitude, seen in Figure 16, is a result of highly preferential breakage of crosslinks in both SSE and TSE. Therefore, it is reasonable to expect a similar dependence of the melting temperature and crystallinity of the decrosslinked XLDPE on the preferential breakage of crosslinks. It is inferred that a significant breakage of main chains occurs during decrosslinking of XLDPE due to the presence of long-chain branching. Thus, a mild increase of melting temperature and crystallinity of decrosslinked XLDPE with the amplitude is most likely caused by less preferential breakage of crosslinks during decrosslinking of XLDPE. Indeed, the melting temperature and crystallinity of the decrosslinked XLDPE by TSE at an amplitude of $13 \text{ }\mu\text{m}$ is virtually same as that of LDPE. However, this is not caused by the preferential breakage of crosslinks but due to the significant decrease of the gel fraction and crosslink density.

The dependences of the melting temperature and crystallinity of the decrosslinked XHDPE and XLDPE on type of extruder are different. It is seen that at same amplitude the melting temperature and crystallinity of the decrosslinked XHDPE by SSE is generally higher

than that by TSE. This is due to the fact that at same amplitude the gel fraction and crosslink density of the decrosslinked XHDPE by SSE is lower than that of the decrosslinked XHDPE by TSE. Although the gel fraction and crosslink density of the decrosslinked XHDPE by TSE at an amplitude of 13 μm is significantly lower than that at lower amplitudes, there is no significant increase of its melting temperature and crystallinity. This is due to the significant breakage of main chains during decrosslinking of XHDPE by TSE at an amplitude of 13 μm , as indicated by Figure 8. The dependences of the melting temperature and crystallinity of the decrosslinked XLDPE on type of extruder are insignificant. This is caused by less preferential breakage of crosslinks during decrosslinking of XLDPE.

Tensile Properties

Figure 17 shows the stress-strain curves of HDPE, LDPE, XHDPE and XLDPE (a) and decrosslinked XHDPE (b) and XLDPE (c) by SSE and TSE with and without ultrasonic treatment. It is seen from Figure 17a that HDPE exhibits typical characteristics of ductile polyethylene including the strong yielding peak at a low strain, a necking plateau at intermediate strains and strain hardening behavior at high strains. The stress-strain curve of LDPE also exhibits similar characteristics but significant differences are seen. To be specific, the yielding peak of LDPE is weak in comparison with that of HDPE. Also, the magnitude of stress of necking plateau of LDPE is lower than that of HDPE. However, a stronger strain-hardening behavior is seen in LDPE than in HDPE. The later is due to the presence of long-chain branching in LDPE. As shown in Figure 17a, the stress-strain curves of XHDPE and XLDPE are, respectively, different with those of HDPE and LDPE due to the structural change after their crosslinking. In particular, XHDPE exhibits a low yield stress, a low stress in its necking plateau

Figure 17. Stress-strain curves of HDPE, LDPE, XHDPE and XLDPE (a) and decrosslinked XHDPE (b) and XLDPE (c) by SSE and TSE with and without ultrasonic treatment.

and a strong strain hardening behavior in comparison with HDPE. This is due to the presence of crosslinked network. XLDPE does not exhibit a yielding peak due to the significant distortion of

its crystalline structure caused by the presence of the crosslinked network. Due to this network, XLDPE shows a significant enhancement of strain hardening at high strains than LDPE. By comparing Figure 17a and Figure 17b, it is found that the stress-strain curve of the decrosslinked XHDPE is similar to that of XHDPE but shows a higher yield stress and weaker strain hardening behavior, except for the decrosslinked XHDPE by TSE at an amplitude of 13 μm . Due to the excessive breakage of main chains, the decrosslinked XHDPE by TSE at an amplitude of 13 μm ruptures without showing a strain hardening following its necking plateau. As seen from Figure 17c, the stress-strain curve of the decrosslinked XLDPE is similar to that of the XLDPE but shows a lower strain at break. This is clearly due to the excessive breakage of main chains during the decrosslinking of XLDPE. Also, the decrosslinked XLDPE by SSE with and without ultrasonic treatment does not exhibit yielding at low strains whereas the decrosslinked XLDPE by TSE at amplitudes of 10 and 13 μm exhibits a weak yielding at low strains.

Figure 18 shows the Young's modulus (a), yield stress (b), strain at break (c) and stress at break (d) of decrosslinked XHDPE and XLDPE as a function of the ultrasonic amplitude. The values for HDPE, LDPE, XHDPE and XLDPE are also indicated. The Young's modulus and yield stress of HDPE is higher than those of the decrosslinked XHDPE which in turn is higher than those of XHDPE. This correlates with the increasing order in the crystallinity of XHDPE, decrosslinked XHDPE and HDPE. A similar behavior is seen for the Young's modulus of LDPE, decrosslinked LDPE and XLDPE and the yield stress of LDPE and decrosslinked XLDPE. It is seen from Figures 18a and 18b that an increase of the ultrasonic amplitude leads to an insignificant increase of the Young's modulus and yield stress of the decrosslinked XHDPE obtained at various conditions, except for the decrosslinked XHDPE by TSE at an amplitude of 13 μm . This observation cannot be correlated to the crystallinity of the decrosslinked XHDPE. In

Figure 18. Young's modulus (a), yield stress (b), strain at break (c) and stress at break (d) of decrosslinked XHDPE and XLDPE as a function of the ultrasonic amplitude. The values for HDPE, LDPE, XHDPE and XLDPE are also indicated. Some data points are shifted horizontally for clarity.

our previous studies of the decrosslinking of XHDPE [14-17], comprehensive literature review on the dependence of the Young's modulus and yield stress of PE on its structure are given based on the extensive studies on structure-tensile property relationship of PE [39-45]. The Young's modulus and yield stress do not solely depend on the crystallinity of PE, but is also greatly affected by the morphology of the crystalline structure of PE which is very sensitive to its molecular structure. Since the decrosslinked XHDPE is a composite of lightly crosslinked gel particles and branched soluble fraction, its molecular structure is very complicated. The insignificant effect of the amplitude on the Young's modulus and yield stress of the

decrosslinked XHDPE is most likely due to its complex molecular structure. However, the significant increase of the Young's modulus of the decrosslinked XHDPE by TSE at an amplitude of 13 μm is probably caused by the significant morphological change of its crystalline structure due to its very low gel fraction (27%). The effect of ultrasonic amplitude on the Young's modulus of the decrosslinked XLDPE is insignificant at amplitudes of 5 and 7.5 μm but noticeable at amplitudes of 10 and 13 μm . This is most likely caused by the increase of crystallinity, as seen from Figure 16, and the decrease of gel fraction and crosslink density of the decrosslinked XLDPE at amplitudes of 10 and 13 μm , as seen from Figure 7. As shown in Figure 18a and Figure 18b, the Young's modulus and yield stress of the decrosslinked XHDPE by TSE are higher than those of the decrosslinked XHDPE by SSE. Since the dependence of the Young's modulus and yield stress of the decrosslinked XHDPE on type of extruder cannot be explained in terms of their crystallinity alone, this dependence is most likely due to the difference of the morphology of the crystalline structure of the decrosslinked XHDPE by different extruders.

The strain at break of virgin HDPE and LDPE is 1250 and 540%, respectively. HDPE due to its linear molecular structure shows the highest strain at break among all the samples, as seen from Figure 18c. The strain at break of XHDPE and XLDPE is, respectively, lower than that of HDPE and LDPE. This is due to the presence of crosslinks impeding the slip motion of polymer chains. The strain at break of the decrosslinked XHDPE by SSE is higher than that of XHDPE and increases with the ultrasonic amplitude. This is due to the highly preferential breakage of crosslinks during the decrosslinking of XHDPE by SSE. The strain at break of the decrosslinked XHDPE by TSE reaches a maximum at an amplitude of 10 μm and then decreases significantly at an amplitude of 13 μm . This is due to the fact that a highly preferential breakage

of crosslinks occurs during decrosslinking of XHDPE at amplitudes of 7.5 and 10 μm , but significant breakage of main chains takes place at an amplitude of 13 μm . The effect of type of extruder on the strain at break of the decrosslinked XHDPE can be understood by correlating the gel fraction and crosslink density with the strain at break. Decrosslinking of XHDPE causing the preferential breakage of crosslinks can be roughly considered as the reverse reaction of crosslinking of HDPE. It is known that the strain at break of XHDPE decreases with the gel fraction and crosslink density [17]. Accordingly, the strain at break of the decrosslinked XHDPE decreases with the gel fraction and crosslink density. Since at same ultrasonic amplitude the gel fraction and crosslink density of the decrosslinked XHDPE by TSE is higher those by SSE, the decrosslinked XHDPE by TSE exhibits a lower strain at break than that by SSE. A significant increase of the strain at break of the decrosslinked XLDPE by both of SSE and TSE with the amplitude is seen in Figure 18c. This correlates with the increase of soluble fraction of the decrosslinked XLDPE with the amplitude. The decrosslinked XLDPE is a composite of gel particles and branched soluble fraction. Since the interaction of gel particles is weak, the load transfer in decrosslinked XLDPE at high strains is accomplished by having the soluble fraction forming a continuous phase, even at highest soluble fraction being as low as 0.39.

The stress at break of ductile PE is determined by the strain at break and the strain hardening behavior at high strains. As shown in Figure 18d, the stress at break of HDPE is higher than that of XHDPE. However, the stress at break of LDPE is lower than that of XLDPE. As shown in Figure 17a, crosslinking of HDPE and LDPE leads to an enhancement of the strain hardening behavior and a decrease of the strain at break. These are two competing factors. In particular, the decrease of the strain at break is more important for HDPE and XHDPE, whereas the strain hardening is more significant for LDPE and XLDPE. It is seen from Figure 18d that

the effect of the ultrasonic amplitude on the stress at break of the decrosslinked XHDPE by SSE is insignificant. This can also be explained in terms of two competing effects, namely the increase of the strain at break and the weakening of strain hardening. As seen from Figure 17b, the strain hardening behavior of the decrosslinked XHDPE by SSE slightly decreases with the ultrasonic amplitude. However, the strain at break of the decrosslinked XHDPE by SSE increases with the amplitude. In case of the decrosslinked XHDPE by SSE, the effects of these two competing factors lead to an insignificant change of the strain at break of decrosslinked XHDPE. The stress at break of the decrosslinked XHDPE by TSE reaches a maximum at an amplitude of 10 μm and then decreases significantly at an amplitude of 13 μm . It is known that the stress at break of XHDPE decreases with the gel fraction and crosslink density [17]. The decrosslinking of XHDPE by TSE at amplitudes of 7.5 and 10 μm can be approximately considered as the reverse reaction of crosslinking of HDPE. Thus, the decrosslinked XHDPE by TSE at an amplitude of 10 μm having lower gel fraction and crosslink density, exhibits a higher stress at break in comparison with that by TSE at an amplitude of 7.5 μm . The significant decrease of stress at break at an amplitude of 13 μm is caused by the excessive breakage of main chains. In case of decrosslinked XLDPE, an increase of the amplitude also leads to a decrease of the strain hardening behavior and an increase of strain at break. For the decrosslinked XLDPE by SSE, an increase of the amplitude leads to the significant increase of the strain at break but a slight decrease of the strain hardening behavior, as seen from Figure 18c and Figure 17c, respectively. Thus, the stress at break of these samples increases with the ultrasonic amplitude. The insignificant change of stress at break of decrosslinked XLDPE by TSE at an amplitude of 13 μm in comparison with that at an amplitude of 10 μm is due to the above mentioned

competing factors. The effect of the type of extruder on stress at break of the decrosslinked XLDPE can also be explained by these competing factors.

Conclusion

Extrusion of XHDPE and XLDPE is performed by means of an ultrasonic SSE and TSE without and with ultrasonic treatment. The barrel pressure, die pressure and ultrasonic power consumption are recorded during the extrusion. Swelling test, SAOS, thermal analysis and tensile test are employed to determine the gel fraction, crosslink density, dynamic properties, melting temperature, crystallinity and tensile properties of HDPE, LDPE, XHDPE, XLDPE, decrosslinked XHDPE and XLDPE.

The barrel pressure in SSE and die pressure in TSE decrease and ultrasonic power consumption increases with the amplitude. The mechanical shear during the extrusion of XHDPE and XLDPE leads to a significant decrease of the gel fraction and crosslink density of the decrosslinked XHDPE and XLDPE with a larger decrease seen in case of XHDPE. The ultrasonic treatment further decreases the gel fraction and crosslink density of the decrosslinked XHDPE and XLDPE. SSE generates a strong mechanical decrosslinking of XHDPE and XLDPE since its screws contains UCM and melt star mixing section. TSE generates a strong ultrasonic decrosslinking of XHDPE and XLDPE due to the higher ultrasonic frequency. It is found that decrosslinking of XLDPE, due to the presence of the long-chain branching, is more difficult than that of XHDPE. The analysis based on the Horikx function indicates the occurrence of the preferential crosslink breakage during decrosslinking of XHDPE.

The frequency dependence of dynamic properties of XHDPE, XLDPE, decrosslinked XHDPE and XLDPE is fitted to the post critical gel model. The dependence of dynamic

properties of the decrosslinked XHDPE and XLDPE on the ultrasonic amplitude, type of extruder and branched structure is explained by the post critical gel model parameters of the decrosslinked XHDPE and XLDPE. The complex viscosity and activation energy of the ultrasonically treated LDPE indicates its ultrasonic degradation caused by the breakage of its polymer backbone. This reveals that the long-chain branching in XLDPE enhances the breakage of main chains during decrosslinking of XLDPE. The melting temperature, crystallinity and tensile properties of the decrosslinked XHDPE and XLDPE are significantly affected by the type of preferential bond breakage during decrosslinking. The decrosslinked XHDPE exhibits a better mechanical performance than XHDPE, whereas the decrosslinked XLDPE exhibits lower mechanical properties than XLDPE. By comparing the decrosslinking of XHDPE and XLDPE via ultrasonically aided SSE and TSE, it is found that decrosslinking of the XLDPE without breakage of main chains is difficult.

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Table captions

Table 1. Gel fraction, crosslink density, post critical gel model parameters for XHDPE, XLDPE, decrosslinked XHDPE and XLDPE.

Table 2. Cross model parameters and activation energy for flow of virgin and extruded LDPE.

Figure Captions

Figure 1. Process flow chart of preparation and decrosslinking of XHDPE (a) and XLDPE (b).

Figure 2. Schematic of TSE (a) and its screw configuration (b) for compounding of dicumyl peroxide and LDPE.

Figure 3. The schematic design of the ultrasonic SSE (a) and the photograph of the screw (b).

Figure 4. The schematic design of the ultrasonic TSE (a) and of its the screw configuration (b).

Figure 5. Barrel pressure before ultrasonic treatment zone in SSE (a) and die pressure in TSE (b) as a function of the ultrasonic amplitude during extrusion of XHDPE and XLDPE.

Figure 6. Ultrasonic power consumption as a function of the ultrasonic amplitude during extrusion of XHDPE and XLDPE by SSE (a) and TSE (b).

Figure 7. Gel fraction (a) and crosslink density (b) of decrosslinked XHDPE and XLDPE as a function of the ultrasonic amplitude obtained by both SSE and TSE. The gel fraction and crosslink density of XHDPE and XLDPE are also indicated.

Figure 8. Normalized gel fraction versus the normalized crosslink density of decrosslinked XHDPE and XLDPE. Dotted and dashed lines represent Horikx function fits to Eqs. (2) and (3), respectively.

Figure 9. Frequency dependences of the storage modulus of XHDPE and decrosslinked XHDPE obtained by SSE (a) and TSE (b) and XLDPE and decrosslinked XLDPE obtained by SSE (c) and TSE (d) without and with ultrasonic treatment at various amplitudes at a temperature of 160°C. Dotted lines are drawn to by fitting to post critical gel model, Eq. (4).

Figure 10. Frequency dependences of the loss modulus of XHDPE and decrosslinked XHDPE obtained by SSE (a) and TSE (b) and XLDPE and decrosslinked XLDPE obtained by SSE (c) and TSE (d) without and with ultrasonic treatment at various amplitudes at a temperature of 160°C. Dotted lines are drawn to by fitting to post critical gel model, Eq. (5).

Figure 11. Frequency dependences of the complex viscosity of XHDPE and decrosslinked XHDPE obtained by SSE (a) and TSE (b) and XLDPE and decrosslinked XLDPE obtained by SSE (c) and TSE (d) without and with ultrasonic treatment at various amplitudes at a temperature of 160°C. Dotted lines are drawn to by fitting to post critical gel model, Eq. (6).

Figure 12. Frequency dependences of the loss tangent of XHDPE and decrosslinked XHDPE obtained by SSE (a) and TSE (b) and XLDPE and decrosslinked XLDPE obtained by SSE (c) and TSE (d) without and with ultrasonic treatment at various amplitudes at a temperature of 160°C. Dotted lines are drawn to by fitting to post critical gel model, Eq. (7).

Figure 13. Frequency dependences of the complex viscosity of virgin and extruded LDPE obtained by SSE (a) and TSE (b) with and without ultrasonic treatment at a temperature of 120°C.

Figure 14. Frequency dependences of the complex viscosity of the virgin LDPE (a) and ultrasonically treated LDPE by TSE (b) at an amplitude of 13 μm at temperatures of 120, 140 and 160 °C Dashed lines represent Cross model fits to Eqs. (10) and (11).

Figure 15. DSC traces obtained during the second heating of the HDPE, XHDPE and decrosslinked XHDPE (a) and LDPE, XLDPE and decrosslinked XLDPE (b), and the first cooling of the HDPE, XHDPE and decrosslinked XHDPE (c) and LDPE, XLDPE and decrosslinked XLDPE (d) by SSE and TSE with and without ultrasonic treatment.

Figure 16. Melting temperature (a) and crystallinity (b) of decrosslinked XHDPE and XLDPE as a function of the ultrasonic amplitude. The values for HDPE, LDPE, XHDPE and XLDPE are also indicated. Some data points are shifted horizontally for clarity.

Figure 17. Stress-strain curves of HDPE, LDPE, XHDPE and XLDPE (a) and decrosslinked XHDPE (b) and XLDPE (c) by SSE and TSE with and without ultrasonic treatment.

Figure 18. Young's modulus (a), yield stress (b), strain at break (c) and stress at break (d) of decrosslinked XHDPE and XLDPE as a function of the ultrasonic amplitude. The values for HDPE, LDPE, XHDPE and XLDPE are also indicated. Some data points are shifted horizontally for clarity.