



Preparation of De-crosslinked Polyethylene from Waste Crosslinked High-Density Polyethylene Using Supercritical Twin-Screw Extrusion

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Abstract

This study examined a method for de-crosslinking high-density polyethylene (HDPE) for use in heating pipes using supercritical fluids and recycling them into polyethylene. Waste crosslinked HDPE is mostly incinerated because it is a thermosetting plastic and cannot be recycled. Therefore, there is an urgent need to develop new recycling technologies for crosslinked HDPE to prevent environmental pollution. Many experiments have been conducted under various subcritical and supercritical conditions using methanol as the supercritical solvent to recycle crosslinked HDPE. Consequently, PE can be prepared via a de-crosslinking reaction. To recycle crosslinked high-density polyethylene, we conducted experiments at three rotational speeds (80, 250, and 400 rpm) of the screw under the conditions of various temperatures (300–360 °C) by using methanol, ethanol, acetone, and water. As a result, we could prepare polyethylene with a linear structure at temperatures above 300 °C through the de-crosslinking reaction. This study evaluated the characteristics of recycled polyethylene based on the reaction conditions using Fourier transform infrared spectroscopy (FT-IR), gel permeation chromatography (GPC), X-ray diffraction (XRD), differential scanning calorimetry (DSC), and tensile strength analyses. In this study, samples with the same chemical and crystal structures were prepared under all conditions.

Keywords Crosslinked polyethylene (PEX) · De-crosslinking · High-density polyethylene (HDPE) · Supercritical fluid · Recycled polyethylene

Introduction

The recycling of plastic waste is important for solving global environmental problems. It creates recycled products by processing discarded waste and reusing them as a new energy source [1, 2]. Crosslinked high-density polyethylene (HDPE) is prepared through a ram extrusion process, using a crosslinking agent. Crosslinked HDPE, also known as PEX, is widely used for carrying hot water at high temperatures and cannot be reshaped because they do not melt under heat, owing to a crosslinked network structure with a crosslinking degree of more than 90% [3–7]. As a result, most PEX is incinerated. This is caused by the lack of proper treatment or recycling methods, and the insoluble and infusible nature of the intramolecular crosslinked network of polymer chains.

This study introduces an environmentally friendly supercritical fluid process for recycling discarded PEX [8–11]. A supercritical fluid is a substance in the supercritical phase region at a temperature and pressure above its critical point where distinct liquid and gas phases do not exist [12–17]. It is a reaction medium with various advantages including low surface tension, low viscosity, high gas diffusion rate, and excellent liquid solubility. It has been used to render harmful chemicals harmless or to treat plastic waste. Supercritical methanol has been shown to de-crosslink PEX above the critical point of methanol (513 K and 7.95 MPa) [18–21]. This study introduced a supercritical fluid process as a method to recycle crosslinked high-density polyethylene that cannot be recycled and selected a solvent that could decompose chemicals under high temperature and pressure. Moreover, it used a supercritical fluid process to de-crosslink the network structure of crosslinked high-density polyethylene. This study examined the cross-linking degree, structural and thermal properties, and physical properties of a prepared de-crosslinked and linear-structured recycled polyethylene. This study evaluated the structural, thermal, and physical

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characteristics of de-crosslinked recycled polyethylene by de-crosslinking the crosslinked structure of PEX using a supercritical fluid process (reaction solvent: methanol).

Experimental

Materials

PEX was fabricated by chemical crosslinking of HDPE (LG Chem, XL1800) using the ram extrusion method. The PEX had a crosslinking degree of 88% and was manufactured by Dongmyung Co., Ltd. The samples were crushed to particles less than 6 mm in size before the experiment. Methanol (Daejung chemical & Metals 99.5%), Ethanol (Daejung Chemicals & Metals, 99.5%), Acetone (Daejung Chemicals & Metals, 99.5%), Water (DI water) was used as the solvent. Xylene (Daejung Chemicals & Metals, 98.5%) and polymer additives (BASF, Irganox1150) were used to measure the degree of crosslinking. Trichlorobenzene (Merck, 99%) and butylated hydroxytoluene (Daejung Chemicals & Metals, 99.5%) were used to determine the molecular weights.

Experimental Apparatus and Procedure

This study was conducted under supercritical conditions by injecting ethanol into a co-rotating twin-screw extruder (screw diameter: 19 mm, L/D: 40) using a metering pump to test the de-crosslinking reaction of PEX. Figure 1 shows the supercritical extrusion apparatus. The PEX (raw material) was crushed to particles 6 mm or less in diameter and fed into the feeding unit of the supercritical extrusion apparatus to carry out the de-crosslinking reaction. The experiment was conducted while regulating the process temperature and rotational speed of the screws. The solvents of the supercritical fluid and the temperature and pressure of the critical

point were as follows: methanol (512.6 K and 8.09 MPa), ethanol (513.9 K and 6.14 MPa), acetone (508.1 K and 4.70 MPa), and water (647.3 K and 22.12 MPa). In the experiments, water was tested below its critical point. Crushed crosslinked high-density polyethylene is continuously fed into the extruder through the feeder section. Under various temperature conditions (300–360 °C) and screw rotation speeds (80, 250, and 400 rpm) inside the extruder, the crosslinked high-density polyethylene is pressurized and melted. De-crosslinking occurs by injecting supercritical fluid. The de-crosslinked linearly structured polyethylene is ejected through the die section of the extruder, cooled in a water bath, and cut by using a pelletizer to produce chip-shaped polyethylene.

Analytical Methods

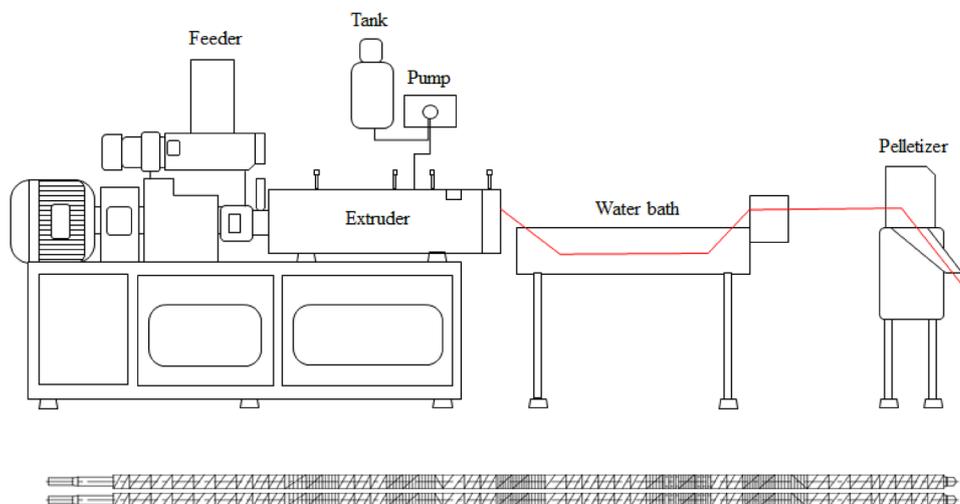
In this study, we measured the degree of crosslinking, molecular weight, and thermal properties to examine the properties of recycled polyethylene, a product of the de-crosslinking reaction, using infrared spectroscopy.

The degree of crosslinking was measured according to the ASTM D2765 standard. The crushed sample (300 mg, ≥ 30 mesh and < 60 mesh) was placed in a 120-mesh wire mesh bag. It was then added to a round flask containing 350 g xylene and 3.5 g irganox. The mixture was boiled at 1 atm and 110 °C for 12 h. The sample remaining in the wire mesh bag was collected and its weight was measured. The crosslinking content was calculated using the following formula:

$$F_{\text{gel}} = w/w_0 \times 100, \quad (1)$$

where F_{gel} is the degree of crosslinking (%), W is the amount of sample remaining after extraction (mg), and W_0 is the amount of sample before extraction (mg).

Fig. 1 Schematic of twin-screw extruder for supercritical fluid treatment



The molecular weight and molecular weight distribution were measured using gel permeation chromatography (Waters Corp. Model 150C: Column Mixed B). The recycled polyethylene specimen was dissolved in a solvent of 1,2,4-trichlorobenzene mixed with 0.01% butylated hydroxytoluene at 160 °C for 4 h. It was then filtered through a metal filter, and 300 mL was injected at a flow rate of 1.0 mL/min using a Mixed-B column. Infrared (IR) spectroscopy was performed using a Spectrum GX spectrometer (PerkinElmer). The recycled polyethylene film was scanned 18 times in the range of 800–4,500 cm^{-1} . The thermal properties were measured using differential scanning calorimetry (DSC 2950, Du Pont). Approximately 5 mg of polyethylene were placed in an aluminum pan and heated at a rate of 10 °C/min up to 180 °C under nitrogen gas to eliminate thermal history before measuring the thermal properties. X-ray diffraction analysis was performed using a Miniflex diffractometer (Rigaku). Recycled polyethylene in film form was measured at an angle of gyration (2θ) between 7° and 40°, and tensile strength specimens of de-crosslinked recycled polyethylene were prepared according to ASTM D638 using an injection molding machine (BOY 25E, Boy). The measurements were performed at room temperature using a Universal Testing Machine 5560 (Instron). The crosshead speed was determined from the mean of seven specimens at 10 mm/min.

Results and Discussion

Table 1 shows the characterization of recycled PEX prepared by de-crosslinking using 50 wt% ethanol in water, where methanol, ethanol, acetone, and water were used as co-solvents for the selection of supercritical solvents. The degree of crosslinking of the PEX is presented for comparison. The molecular weight and tensile strength of the initial PEX could not be measured because of the high degree of crosslinking.

The experiment was conducted at a reaction temperature of 300 °C, a screw rotation speed of 250 rpm (output: 216 g/min), and a solvent volume of 5 ml/min while changing solvents to select the supercritical fluid solvent. It was possible to fabricate partially de-crosslinked recycled polyethylene without using a supercritical solvent using a specially designed extruder for the de-crosslinking reaction. However, the recycled polyethylene had a high degree of crosslinking (7.2%), low molecular weight, and low tensile strength. In this study, various experiments were conducted to determine the process conditions that can produce a low degree of crosslinking, high molecular weight, and high tensile strength. In the solvent influence experiment, methanol showed the highest cross-linking degree of 4.4%, while water showed the lowest cross-linking degree of 1.5%. The de-crosslinking efficient water was higher than those of ethanol, methanol, acetone, and water + ethanol.

In testing the effects of different solvents, the product using methanol exhibited the highest degree of crosslinking (4.4%). When water was used, the degree of crosslinking was 1.5%, and the de-crosslinking reaction was the best optimal. The degree of crosslinking was 2.3% in the de-crosslinking reaction using ethanol and water, indicating a co-solvent effect. However, its molecular weight and tensile strength were low.

The critical point of methanol is lower than those of ethanol, water, and acetone, and the degree of crosslinking was 4.4%, indicating an overall good de-crosslinking reaction. In addition, the tensile strength of the de-crosslinked product was high (38.5 MPa), and its molecular weight was the highest (235,839). Therefore, methanol was selected as the solvent to fabricate recycled polyethylene through a de-crosslinking reaction under various supercritical conditions, and experiments were conducted under various conditions.

Figure 2 shows the change in the content of the crosslinking degree according to the change in the reaction temperature to quantitatively identify the degree to which the cross-linking reaction of crosslinked polyethylene treated with supercritical methanol. This study carried out the

Table 1 Characterization of PEX after supercritical fluid treatment with various solvents

Reaction temperature (°C)	Reaction pressure (bar)	Screw rotation speed (rpm)	Solvent	Amount of solvent (ml/min)	Gel content (%)	Molecular weight (Mw)	Tensile strength (MPa)
PEX	–	–	–	–	88.0	–	–
300	57	250	–	–	7.2	132,005	35.8
300	85	250	Methanol	5	4.4	235,839	38.5
300	91	250	Ethanol	5	4.2	157,297	39.1
300	91	250	Aceton	5	3.7	162,431	37.7
300	81	250	Water	5	1.5	161,535	34.6
300	84	250	Water + Ethanol	5	2.3	106,425	35.1

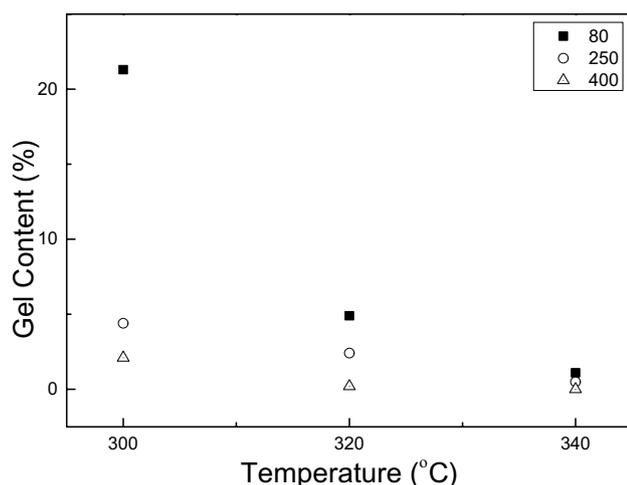


Fig. 2 Gel content of PEX after supercritical methanol treatment at various screw rotation speeds

depolymerization reaction under the screw rotation speed of 80 rpm and methanol injection at 5 ml/min. The error range of the measured crosslinking content is $\pm 3\%$, and the crosslinking content decreased with the increase in temperature. In particular, the de-crosslinking reaction hardly occurred until 280 °C, and the crosslinking content remained at 40% or higher. The crosslinking content decreased sharply at 300 °C and above, and the crosslinking content almost disappeared at 350 °C and above.

Figure 2 shows the change in crosslinked content according to the screw rotation speed. The crosslinking content, molecular weight, and tensile strength decreased as the screw rotation speed increased. It was confirmed that when the rotational speed of the screw for the de-crosslinking reaction was higher, the productivity of recycled polyethylene and the efficiency of the de-crosslinking reaction were higher. Moreover, when the rotational speed of the screw increased, the movement speed of the raw material increased, the extrusion efficiency decreased, and the pressure in the extruder decreased owing to decreased pressure

uniformity and energy loss. As the friction of the screw increased, the physical properties deteriorated.

Table 2 presents the molecular weight and molecular weight distribution of the crosslinked polyethylene treated with supercritical methanol in the temperature range where the crosslinking content changed significantly, as shown in Fig. 2. The molecular weight and molecular weight distribution of HDPE before crosslinking (the raw material for the crosslinked polyethylene) are also shown for comparison. Crosslinked high-density polyethylene had a high degree of cross-linking. Therefore, it was not possible to prepare tensile-strength specimens. Furthermore, due to the high degree of cross-linking, sampling for GPC analysis was not possible. Consequently, molecular weight could not be measured. The molecular weight of the de-crosslinked portion of polyethylene dissolved in high-temperature xylene decreased with increasing reaction temperature. It was not possible to measure the molecular weight and tensile strength of the polyethylene supercritically reacted at 300 °C, because 21.3% crosslinked content remained, and the weight-average molecular weight (Mw) and tensile strength of the de-crosslinked resin had a high degree of crosslinking.

At temperatures above 320 °C, the PEX was mostly de-crosslinked, with little crosslinked content. At 320 °C, the molecular weight decreased from 284,356 to 87,356. The molecular weight of the HDPE was approximately 261,272 before crosslinking. It was also confirmed that the de-crosslinked recycled polyethylene had a wider molecular weight distribution than the un-crosslinked HDPE before crosslinking.

Figure 3 shows the changes in crosslinked content with a change in reaction temperature to quantitatively determine the extent of the de-crosslinking reaction of PEX treated with supercritical methanol. In this study, the de-crosslinking reaction was performed while injecting methanol at 5 ml/min at a screw rotation speed of 80 rpm. The error range of the measured crosslinking content was $\pm 3\%$. The results showed that the crosslinking content decreased with increasing temperature. Noticeably, the de-crosslinking reaction

Table 2 Characterization of raw HDPE and PEX after supercritical methanol treatment at various temperatures

Reaction temperature (°C)	Reaction pressure (bar)	Screw rotation speed (rpm)	Solvent	amount of solvent (ml/min)	Gel content (%)	Molecular weight (Mw)	Tensile strength (MPa)
PEX	–	–	–	–	88.0	–	–
Raw HDPE	–	–	–	–	0	261,272	29.3
300	145	80	methanol	5	21.3	248,713	58.4
320	109	80	methanol	5	4.9	284,356	40.8
340	34	80	methanol	5	1.1	176,590	29.2
350	28	80	methanol	5	0.8	143,970	28.5
360	19	80	methanol	5	0	87,356	30.4

Fig. 3 Gel content of PEX after supercritical methanol treatment at various reaction temperatures

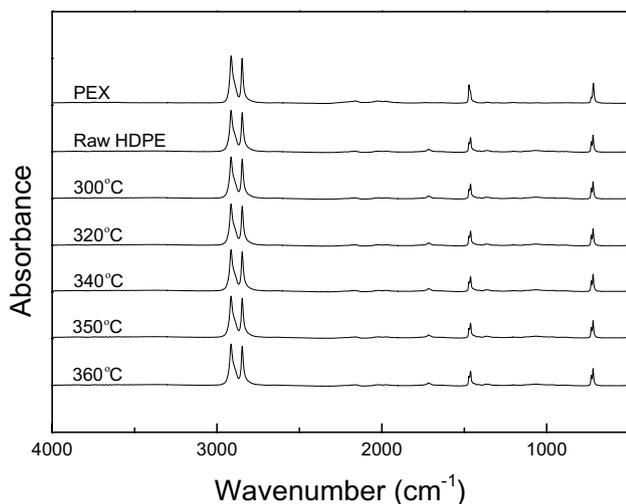
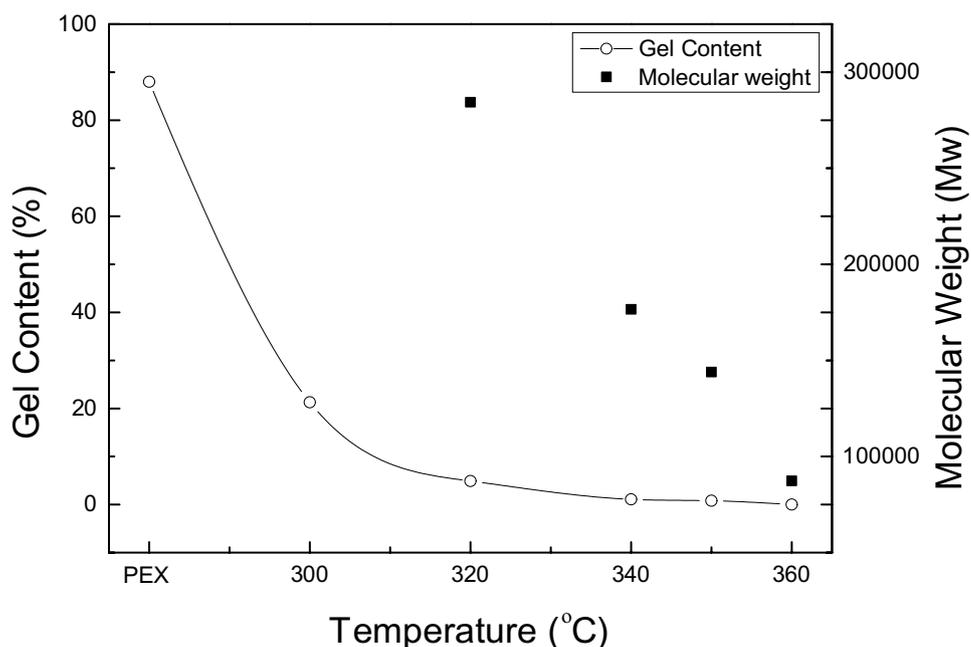


Fig. 4 FT-IR curves of raw HDPE and PEX before and after supercritical methanol treatment at various temperatures

hardly occurred below 280 °C, where the crosslinked content was above 40%. The crosslinked content decreased abruptly at 300 °C and above, and the crosslinked content approached zero at 350 °C

Figure 4 shows the FT-IR spectra of the regenerated polyethylene produced after de-crosslinking of the PEX resin at different temperatures. Un-crosslinked polyethylene is also shown for comparison. Regardless of the supercritical de-crosslinking reaction, all samples showed peaks in the 2800–3000 cm^{-1} region, representing sp^3 C–H stretching, and the 1,450 cm^{-1} peak, representing CH_2 bending. This indicates that the basic structure of polyethylene did

not change with the de-crosslinking reaction. In particular, the absence of sp^2 C–H (3,000–3,300 cm^{-1}), sp C–H (> 3,300 cm^{-1}), and C=C (1,600–1,650 cm^{-1}) peaks indicates that no double or triple bonds were formed during the supercritical reaction. We observed changes in the characteristic peak in the range of 1680–1780 cm^{-1} , which was attributed to the carbonyl group. When high-density polyethylene is treated at high temperatures, thermal oxidation may produce carbonyl (–C=O) functional groups. In addition, when ethanol and methanol are used as supercritical solvents, aldehyde compounds are produced while showing two peaks at 1700–1750 cm^{-1} and 2750–2850 cm^{-1} .

Figure 5 shows the DSC graph of the regenerated polyethylene produced after the de-crosslinking reaction of crosslinked PEX resin at different temperatures. All results were obtained during a secondary temperature elevation to obtain the melting temperature (T_m) without a thermal history and were compared to the pre-crosslinked polyethylene. In the case of PEX, T_m was 135.74 °C, which was the highest melting temperature, while that of polyethylene, a pre-crosslinked raw material, was 133.09 °C, which was a similar melting point of 133.48 °C at a reaction temperature of 300 °C. It was also confirmed that the higher the reaction temperature, the lower the melting temperature in general.

Figure 6 shows an XRD graph of the regenerated polyethylene produced after the de-crosslinking reaction of the PEX resin at different temperatures. It was confirmed to have (110) and (200) structures similar to that of polyethylene, and the area under the curve increased when the reaction temperature was higher. This confirms that when the crosslinking content decreases due to the de-crosslinking

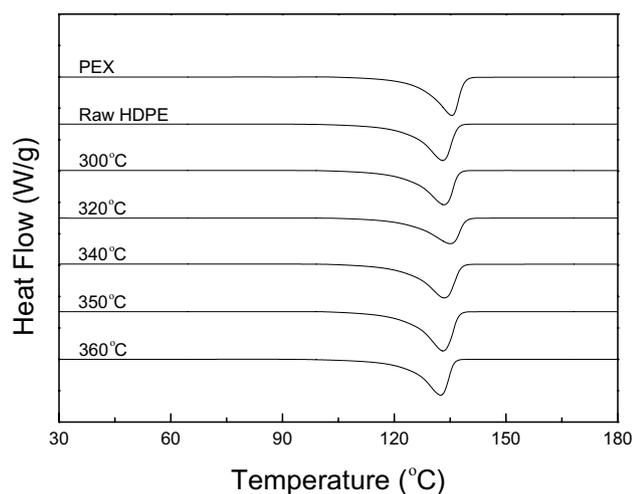


Fig. 5 DSC curves of raw HDPE and PEX before and after supercritical methanol treatment at various temperatures

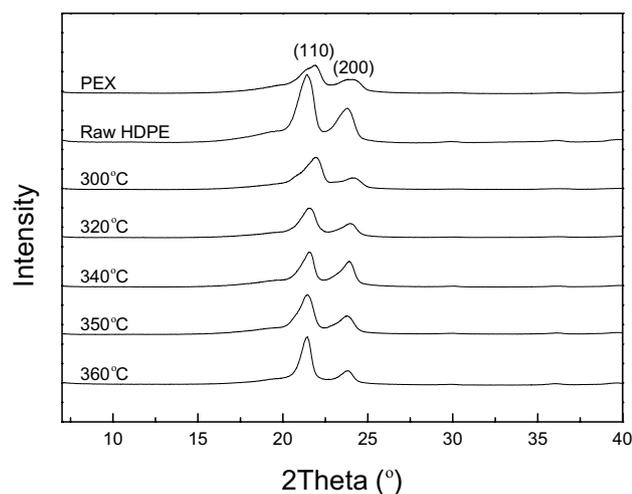


Fig. 6 XRD curves of raw HDPE and PEX before and after supercritical methanol treatment at various temperatures

reaction, the amorphous region becomes smaller and the crystallinity increases.

Conclusions

The following conclusions were obtained using a supercritical methanol treatment process for PEX resin.

(1) It is possible to de-crosslink crosslinked polyethylene resin using a supercritical methanol reaction. (2) The effects of the de-crosslinking reaction temperature and screw rotational speed are significant in supercritical methanol. When the reaction temperature increased, the crosslinking reaction and physical properties could be regulated. (3) The de-crosslinking reaction in supercritical

methanol did not involve any side reactions except for the breakage of some main chains. The de-crosslinked recycled polyethylene had the same chemical structure as the raw material, (un-crosslinked polyethylene resin), and showed similar physical properties. In the experimental results, at conditions of 320°C and 109 bar, the gel content remained at 4.9%. However, the molecular weight was 284,356 Mw, and the tensile strength was 40.8 MPa, confirming that the properties of molecular weight and tensile strength were superior in the recycled polyethylene compared to the Raw polyethylene resin.

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References

1. H. Nishida, *Polym. J.* **43**, 435 (2011)
2. S.M. Hong, H.K. Cho, C.M. Koo, J.H. Lee, W.Y. Park, H.S. Lee, Y.W. Lee, *Korean Chem Eng Res* **46**, 63 (2008)
3. G. Brunner, *Supercrit Fluid Sci Technol.* **5**, 511 (2014)
4. H. Hirabayashi, A. Iguchi, K. Yamada, H. Nishimura, K. Ikawa, H. Honma, *Mater. Sci. Appl.* **4**, 497 (2013)
5. U.W. Gedde, M. Ifwarson, *Polym. Eng. Sci.* **30**, 202 (1990)
6. S.M. Tamboli, S.T. Mhaske, D.D. Kale, *Mater Total Joint Arthrop.* **11**, 133 (2015)
7. C.M. Koo, Y.J. Cho, B.G. Cho, S.M. Hong, *J Korean Inst Resour Recycl.* **23**, 71 (2014)
8. H.K. Cho, S.M. Hong, K.Y. Baek, H.S. Lee, Y.W. Lee, C.M. Koo, *Macromol. Res.* **17**, 950 (2009)
9. B.K. Baek, Y.H. La, A.S. Lee, H.S. Han, S.H. Kim, S.M. Hong, C.M. Koo, *Polym. Degrad. Stab.* **130**, 103 (2016)
10. H.S. Lee, J.H. Jeong, S.M. Hong, C.M. Koo, H.K. Cho, Y.W. Lee, *Korean Chem Eng Res* **50**, 88 (2012)
11. G.C. Hwang, K.H. Kim, S.Y. Bae, S.C. Yi, H. Kumazawa, *Korean J. Chem. Eng.* **18**, 396 (2001)
12. G.N. Sapkale, S.M. Patil, U.S. Surwase, P.K. Bhatbhave, *Int. J. Chem. Sci.* **8**, 729 (2010)
13. H.S. Lee, J.H. Jeong, G.Y. Hong, H.K. Cho, B.K. Baek, C.M. Koo, S.M. Hong, J.H. Kim, Y.W. Lee, *Ind. Eng. Chem. Res.* **52**, 6633 (2013)
14. H.K. Cho, J.S. Lim, *Korean Chem Eng Res* **55**, 220 (2017)
15. H.K. Cho, J.S. Lim, *Int. J. Thermophys.* **38**, 175 (2017)
16. J.H. Yim, W.S. Kim, J.S. Lim, *J. Supercrit. Fluids* **82**, 168 (2013)
17. D.E. Kwon, M.G. Aregay, B.K. Park, Y.W. Lee, *Korean J. Chem. Eng.* **38**, 2560 (2021)
18. I. Okajima, A. Kajima, A. Katsuzaki, T. Goto, T. Yamazaki, T. Sako, *J. Chem. Eng. Jpn.* **43**, 231 (2010)
19. Y.J. Kwon, S.M. Hong, C.M. Koo, *J. Polym. Sci., Part B: Polym. Phys.* **48**, 1265 (2010)
20. S.D. Yoon, H.S. Byun, *Clean Technol.* **18**, 123 (2012)
21. F. Sun, J. Guo, Y. Li, S. Bai, Q. Wang, *R Soc Open Sci.* **6**, 1 (2019)

22. T. Goto, S. Ashihara, T. Yamazaki, I. Okajima, T. Sako, Y. Iwamoto, M. Ishibashi, T. Sugeta, *Ind. Eng. Chem. Res.* **50**, 5661 (2011)

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