

Foaming of Recycled Crosslinked Polyethylenes via Supercritical Decrosslinking Reaction

Yong Jin Kwon,¹ Wan Yong Park,² Soon Man Hong,¹ Chong Min Koo^{1,3}

¹Nano Hybrids Center, Korea Institute of Science and Technology (KIST), Hwarangno 14-gil 5, Soeongbuk-gu, Seoul 136-791, Republic of Korea

²Youngbo Chemical Co. Ltd., 233 Taeseong-ri, Gangneung-myeon, Cheongwon-gun, Chungbuk, Republic of Korea

³Nanomaterials Science and Engineering, University of Science and Technology, 176 Gajung-dong, 217 Gajung Yuseong-gu, Daejeon, Republic of Korea

Received 15 July 2011; accepted 1 December 2011

DOI 10.1002/app.36617

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Foaming of decrosslinked crosslinked polyethylene (DCXLPE) was investigated to assess the feasibility of recycled crosslinked polyethylene for polyolefin foam applications. DCXLPE was recycled from irradiation-induced crosslinked polyethylene using the supercritical methanol process. As the concentration of crosslinking agents increased, the gel fraction and hardness of the DCXLPE foam sheets increased, while the expansion ratio and cell size decreased. The resulting foam products not

only revealed a viable foam structure and properties comparable with those of conventional polyethylene foam from virgin low-density polyethylene resin but also are expected to open new applications for recycled crosslinked polyolefin via supercritical decrosslinking reaction. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: forming; recycling; decrosslink; supercritical; LDPE

INTRODUCTION

Recycling of thermosetting polymers, such as crosslinked polyethylenes, has attracted great attention owing to the deep consideration given to environmental pollution and to resource conservation efforts around the world.^{1–6} A newly developed recycling technique using supercritical fluid was introduced to transform the crosslinked polyethylenes into thermoplasticized polyethylenes.^{2–5} In a previous article, we developed a kinetics model for the decrosslinking reaction of crosslinked polyethylenes on the basis of experimental results in which the decrosslinking reaction rate was linearly proportional to the gel concentration and related exponentially to the temperature.⁴

The crosslinked polyethylenes are widely used as polyolefin foams in automotive, construction, and sports and leisure markets owing to their inherent properties, such as novel toughness, flexibility, and resistance to chemicals and abrasion.⁷ The crosslinked polyethylene foams are made by complex processes designed by properly controlling the chemical cross-

linking and expansion sequence. The processes are characterized by three distinct steps: sheet formation, crosslinking, and foaming. Crosslinking is achieved either by a crosslinking agent such as dicumyl peroxide,^{8–10} or by high-energy radiation such as gamma, X-, and neutron rays.^{11,12} Foaming is controlled by the type of blowing agent and the process condition. Azodicarbonamide (ADCA) enjoys the most widespread use as a blowing agent in commercial crosslinked polyolefin foam production owing to its narrow decomposition temperature of ~200–210°C, slow gas release rate, gaseous composition, ease of dispersion, storage stability, low toxicity, and affordable cost.^{8,9,11}

In this work, we demonstrate that a foam sheet using the recycled decrosslinked crosslinked polyethylene (DCXLPE) has a viable foam structure and physical properties comparable with those of conventional neat low-density polyethylene (LDPE) foam sheet. To the best of our knowledge, this work is the first trial with recycled crosslinked polyethylene via supercritical decrosslinking reaction for foam applications. The DCXLPE was recycled from irradiation-induced crosslinked LDPE using supercritical methanol processing.

EXPERIMENTAL

Materials

LDPE with the trade name Lutene FB0300 was purchased from LG Chemicals. The density and melt

Correspondence to: C. M. Koo (koo@kist.re.kr).

Contract grant sponsors: Ministry of Environment, Ministry of Knowledge Economy (MKE), Nano Hybrids Center of the Korea Institute of Science and Technology (KIST), Republic of Korea.

flow index of the LDPE were 0.921 g/cm³ and 0.3 g/10 min according to ASTM D1238. The molecular weight and molecular weight distribution (M_w/M_n) of the LDPE were 349,000 g/mol and 7.0. Irradiation-crosslinked LDPE (XLPE) was supplied from Youngbo Chemicals in South Korea. For the fabrication of XLPE, the irradiation was exposed to the LDPE using an electron beam generated by a Dynamitron accelerator [Nisshin high voltage (NHV)] with an acceleration voltage of 1 MeV at room temperature. The XLPE had a gel fraction of 65%. ADCA was purchased from Dong Jin Semichem, and Zinc oxide (ZnO) and dicumyl peroxide (DCP) from PJ Chem Tech. and Nippon Fat Chemicals, respectively. Each reagent had the purity higher than 99%. Methanol and xylene with a HPLC grade were purchased from Samchun Chemicals and Sigma-Aldrich, respectively. All chemicals were used as received.

Preparation of the DCXLPE

The DCXLPE were recycled from the XLPE using supercritical methanol as reported in our previous article.⁴⁻⁶ The supercritical decrosslinking of XLPE with 65% gel fraction was performed using a batch reactor made of stainless steel (SUS316) as described in a previous article.⁴⁻⁶ The reaction was carried out as follows: a 50 g piece of XLPE and 100 mL of methanol were charged in a 500-mL stainless steel reactor. Nitrogen was purged into the reactor to degas oxygen at room temperature. The reactor was heated up to the target reaction temperature to start the decrosslinking reaction, kept for 5 min at the target reaction temperature, and then cooled to room temperature by cold water to terminate the reaction. The pressure at the reaction temperature was far above the methanol supercritical point of 240°C and 7.93 MPa. After the supercritical reaction, the products were filtered and dried in a vacuum oven.

Preparation of the DCXLPE foam sheet

The foam sheet was prepared according to the sequence of Figure 1. The DCXLPE recycled from the XLPE using supercritical methanol at 365°C was used as a base resin. A mixture of DCXLPE, DCP, ADCA, and ZnO were sufficiently mixed via a Kneader with 1000-mL volume at 130°C. The composition ratio of DCXLPE, ADCA, and ZnO was fixed with 100, 2, and 1.6 phr, respectively. phr represents parts per hundred parts of resin on the basis of weight. The DCP ranged from 0.1 to 1.0 phr. The high-pressure foaming was performed in a hot press at 170°C and 140 bar for 10 min. For the comparison, the neat LDPE foam was prepared via the same process of DCXLPE foam except replacing DCXLPE with LDPE.

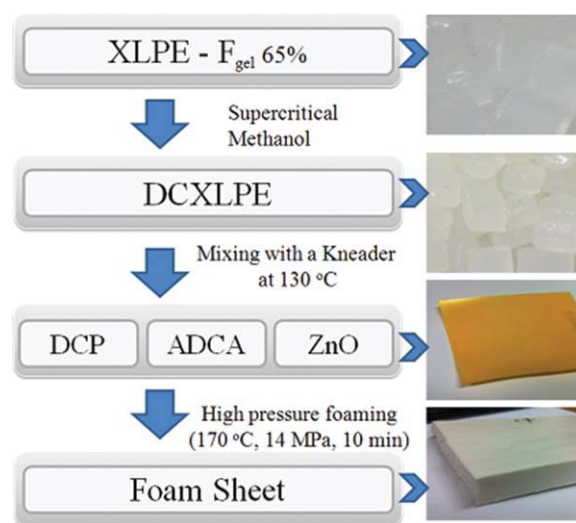


Figure 1 Schematic illustration of the fabrication process of foam sheets and the representative sample images in each step. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterizations

The gel fractions (F_{gel}) of the samples were evaluated as

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

where w_0 and w are the weight of the specimen before and after solvent extraction, respectively. Extraction was performed using a xylene medium at 110°C for 12 h. The molecular weight of the extracted were measured by a high-temperature GPC (Waters, Model 150C: Column Mixed B) with a polystyrene standard and trichlorobenzene solvent at 120°C. A Shore C hardness test of the prepared foams was performed using an ASKER type C, Kobushi Keiki under a load of 2 pounds. The density and expansion ratio were measured using a SD-200L, Alfa Miracle according to KSMISO 845. The morphology of the foams was observed using scanning electron microscopy (SEM) with a Hitachi S-2200C. The average cell sizes of the foams were analyzed using LEICA Application Suite software of LEICA Microsystems.

RESULTS AND DISCUSSION

Preparation of the DCXLPE

Figure 2 shows gel content and molecular weight of the DCXLPE using supercritical methanol at various reaction temperatures. The temperature was varied from 300 to 400°C. The reaction condition was much higher than the critical point of methanol, 240°C and

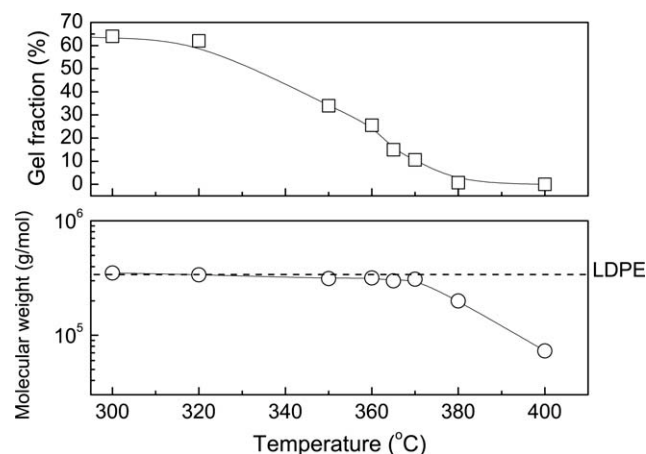


Figure 2 Gel content and molecular weight of DCXLPEs at various reaction temperatures.

7.93 MPa. The initial gel content of the XLPE was 65%. The residual gel content was maintained in excess of 60% up to 320°C and dropped steeply at around 360°C, and above 380°C, residual gel was no longer observed. A molecular weight analysis was carried out using the trichlorobenzene-extracted DCXLPE from the treated XLPEs. The molecular weights of the DCXLPEs were close to that of LDPE up to 370°C and then diminished with a further increase in the reaction temperature. This indicates that the XLPE was fairly selectively decomposed at the crosslink points up to 370°C and not at random sites due to the supercritical methanol treatment. The crosslink points in the XLPE must be more vulnerable sites in the thermal decomposition than other carbons, as the tertiary radicals produced from the quaternary carbons at the crosslink point are more stable than the secondary or primary radicals from other carbons.^{4,6}

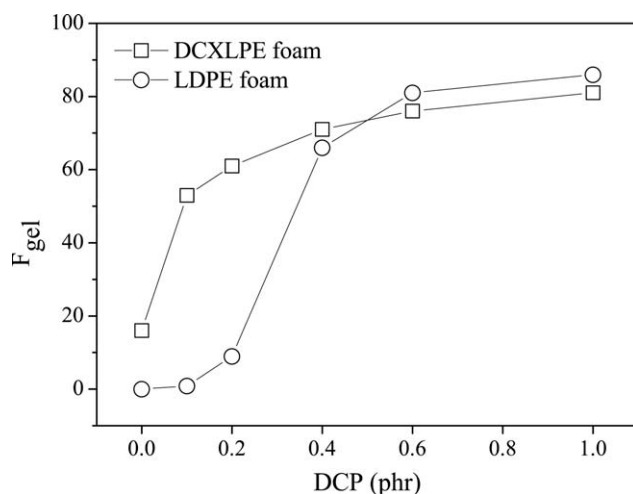


Figure 3 Gel fraction of DCXLPE and LDPE foam sheets as a function of DCP concentration.

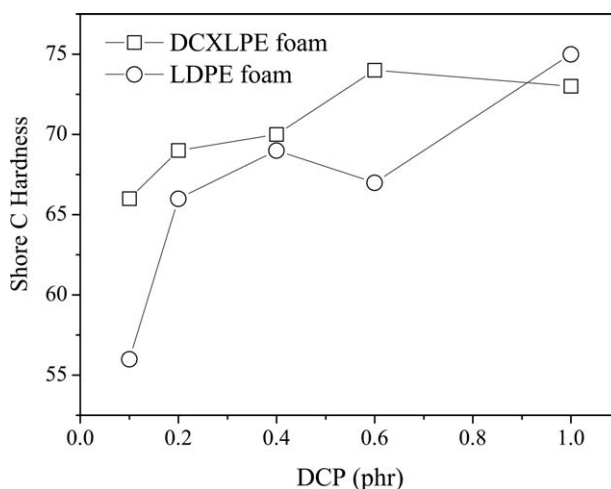


Figure 4 Shore C hardness of DCXLPE and LDPE foam sheets as a function of DCP concentration.

Preparation of the DCXLPE foam sheet

Figure 3 shows the gel fraction of the DCXLPE foam and LDPE foam sheets. The foam sheet was prepared via high-pressure foaming with a chemical crosslinking agent DCP and a blowing agent ADCA. For the DCXLPE foam sheet, the composition ratio of DCXLPE, ADCA, and ZnO was fixed at 100, 2, and 1.6 phr, respectively. The DCXLPE prepared using supercritical methanol at 365°C was used as a matrix resin. The DCXLPE had a 15% residual gel fraction. The DCP crosslinking agent ranged from 0.1 to 1.0 phr. The decomposition temperature of DCP with a 1-min half life was 171°C. The foaming was performed at 170°C and 140 bar for 10 min. A typical image of the DCXLPE foam sheet is presented in Figure 1. The gel fraction of the DCXLPE foam sheets were sharply increased with an increase in the DCP concentration at low DCP concentration and then saturated to the maximum gel fraction of around 80% at high DCP concentration. In contrast,

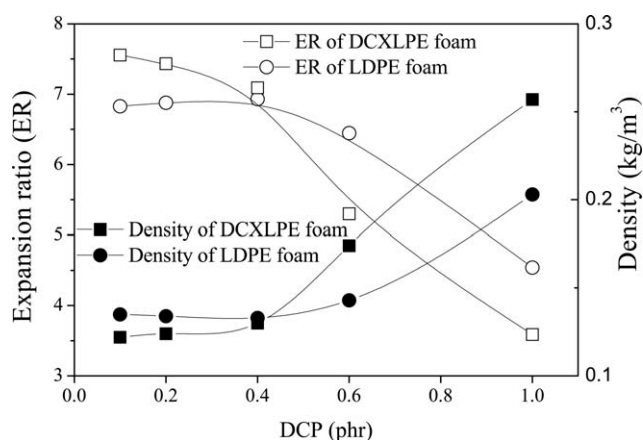


Figure 5 Expansion ratio of DCXLPE and LDPE foam sheets as a function of DCP concentration.

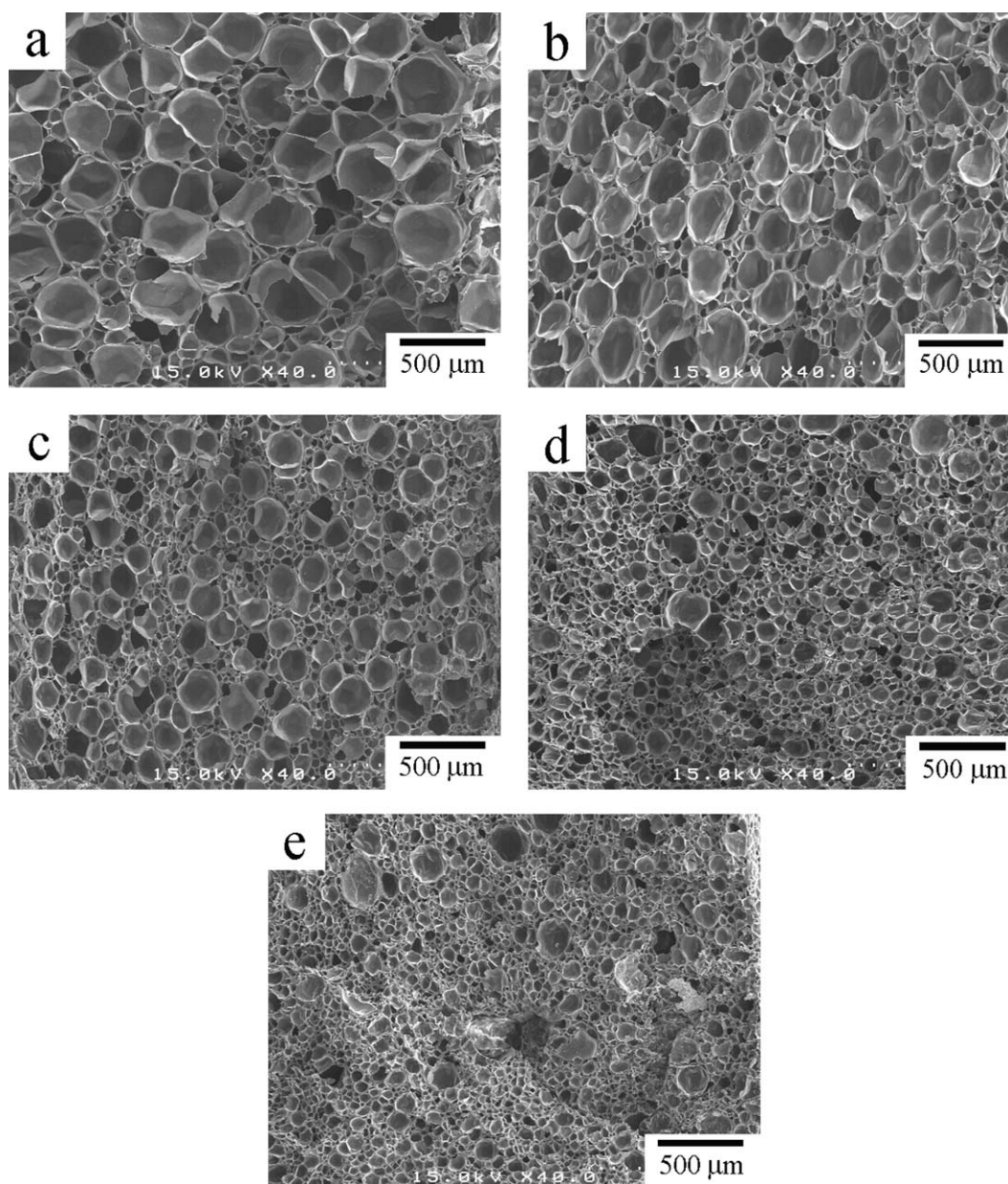


Figure 6 SEM images of DCXLPE foam sheets at various DCP concentrations: (a) 0.1 phr, (b) 0.2 phr, (c) 0.4 phr, (d) 0.6 phr, and (e) 1.0 phr.

as the DCP concentration increased, the gel fraction of the LDPE foam sheets slowly increased at a low DCP content, and sharply increased at 0.4-phr DCP and then reached the saturation gel level of about 80%.

Figure 4 shows the shore C hardness of the DCXLPE foam and LDPE foam sheets. The DCXLPE foam sheet with 0.2-phr DCP had a shore C hardness of 66 and the hardness of the DCXLPE foam sheets slowly increased with the DCP content. The LDPE foam sheet with 0.2-phr DCP had a shore C hardness of 56. The hardness of the LDPE foam sheets sharply increased with the DCP content up to

0.4-phr DCP and reached a plateau above that concentration. The hardness results were in good agreement with the gel fraction results. The gel fraction of the DCXLPE foam sheets more rapidly increased with the DCP content than those of the LDPE foam sheets because the crosslinking density enhanced the hardness of the material.

Figure 5 shows the density and expansion ratio of the DCXLPE foam and LDPE foam sheets. The expansion ratio was calculated by the density of the sheet before foaming divided by the density of the sheet after foaming. The density of the foam sheets increased with an increase in the DCP concentration, while the

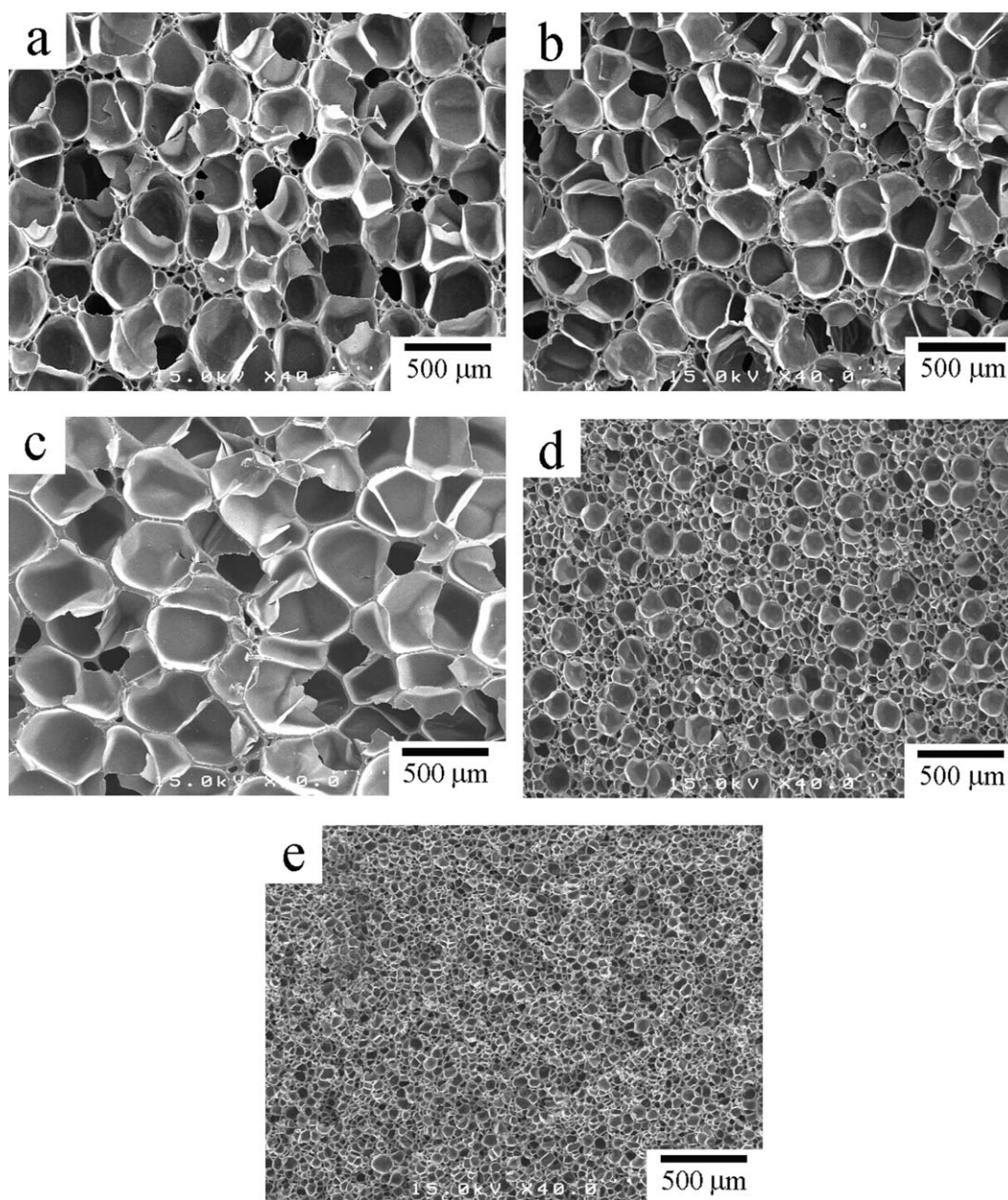


Figure 7 SEM images of LDPE foam sheets at various DCP concentrations: (a) 0.1 phr, (b) 0.2 phr, (c) 0.4 phr, (d) 0.6 phr, and (e) 1.0 phr.

expansion ratio decreased. The DCXLPE foam sheet with 0.2-phr DCP had an expansion ratio of 7.6 and the expansion ratio of the DCXLPE foam sheets monotonously decreased with an increase in the DCP concentration. The LDPE foam sheet with 0.2-phr DCP had an expansion ratio of 6.8. The expansion ratio of the LDPE foam sheets increased slightly with an increase in the DCP content up to 0.4-phr DCP and decreased with a further increase in the DCP concentration.

Figures 6 and 7 show the SEM images of the DCXLPE foam and LDPE foam sheets, respectively. The average foam cell size of each sample is pre-

sented in Figure 8. Both DCXLPE and LDPE foam sheets had well developed closed sphere cells. The cell size distribution was quite broad. The average cell diameter was calculated from the observation of more than a thousand of cells to minimize the uncertainty. The cell size was significantly influenced by the DCP content. The average cell size of the DCXLPE foam sheet with 0.2-phr DCP was 250 μm. The cell sizes of DCXLPE foam sheets rapidly decreased with an increase in the DCP content up to 0.4-phr DCP and slowly decreased with a further increase in the DCP concentration. In contrast, the average cell size of LDPE foam sheet with 0.2-phr

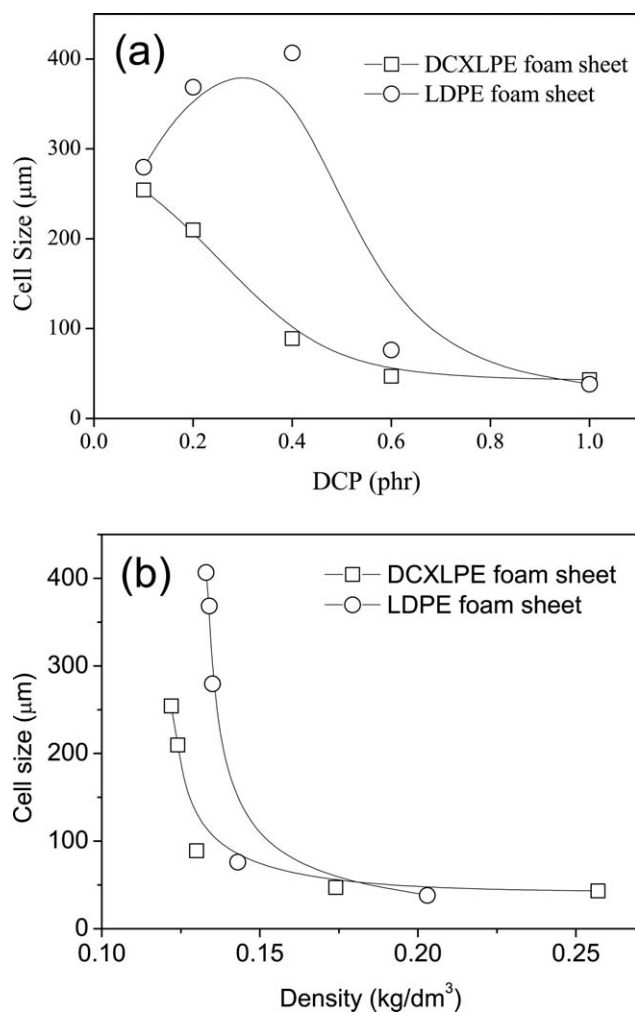


Figure 8 (a) Average cell sizes of DCXLPE and LDPE foam sheets as a function of DCP concentration and (b) average cell sizes versus density of DCXLPE and LDPE foam sheets.

DCP was 280 μm . The cell sizes of the DCXLPE foam sheets increased with an increase in the DCP content up to 0.4-phr DCP. The average cell size of the LDPE foam sheet with 0.4-phr DCP was 400 μm . At 0.6-phr DCP, the cell size abruptly decreased to 76 μm . The cell size slowly decreased with a further increase in the DCP concentration.

In this work, for the first time, the foaming of the DCXLPE was investigated. DCXLPE was recycled from XLPE using the supercritical decrosslinking reaction. Foaming of the DCXLPE was compared with that of the neat LDPE. For both DCXLPE and LDPE form sheets, as the concentration of DCP crosslinking agent increased, the gel fraction and shore C hardness increased, and the expansion ratio and cell size decreased. This is the expansion ratio and cell size reduced with an increase in the crosslinking density of polyethylene. It was caused by the fact that excessive crosslinking restricted the foam

expansion.⁷ For the cell growth of the foams, the foam gas cell nucleated from each ADCA dispersion in a matrix should be expanded by itself or be combined with adjacent gas cells. However, as the crosslinking density increased, viscoelasticity of the polymer (DCXLPE or LDPE) increased. The strong viscoelasticity restricted the foam cells not only from expanding to higher size but also from combining the neighbor gas cells.

Interestingly, the expansion ratio and cell size of the DCXLPE foam sheets more rapidly decreased with an increase in DCP content than those of the LDPE foam sheets. These resulted from the fact that the gel fraction and the shore C hardness of the DCXLPE foam sheets more rapidly increased with an increase in the DCP concentration than those of the LDPE foam sheets. Generally, the chain decomposition reaction of saturated aliphatic chain at high temperature causes to produce the byproducts like double bonds or other many functional groups.¹³ In this study, such byproducts must be a minor portion because FTIR did not measure the presence of these groups as shown in the previous literature.⁵ However, the minor population of double bond and the functional groups in the DCXLPE seems to help the DCXLPE foam sheet to be crosslinked more easily than the neat LDPE, resulting that the DCXLPE form sheet had higher gel fraction and higher shore C hardness than the LDPE form sheet. As a result, the DCXLPE produced smaller cell diameter and smaller expansion ratio than the LDPE.

CONCLUSIONS

In this work, foaming of the DCXLPE recycled using supercritical methanol was compared with that of neat LDPE. The DCXLPE had higher gel fraction and smaller foaming cell diameter than the LDPE at the same crosslinking agent level, resulting that the DCXLPE produced smaller expansion ratio and smaller foaming cell diameter than the LDPE, due to the delicate difference in the molecular structures like the presence of double bonds in the DCXLPE. Nevertheless, the DCXLPE foam sheet showed a viable foam structure and physical properties comparable with those of the LDPE foam sheet.

References

1. Watanabe, S.; Komura, K.; Nagaya, S.; Morita, H.; Nakamoto, T.; Hirai, S.; Aida, F. *Proc Int Conf Pro Appl Dielectr Mater* 2003, 7, 595.
2. Goto, T.; Yamazaki, T.; Sugeta, T.; Okajima, I.; Sako, T. *J Appl Polym Sci* 2008, 109, 144.
3. Goto, T.; Yamazaki, Y. *Hitachi Cable Rev* 2004, 24, 24.
4. Lee, H. S.; Jeong, J. H.; Cho, H. K.; Koo, C. M.; Hong, S. M.; Kim, H.; Lee, Y. W. *Polym Degrad Stab* 2008, 93, 2084.

5. Cho, H. K.; Lee, H.; Lee, Y. W.; Hong, S. M.; Koo, C. M. *Macromol Res* 2009, 17, 950.
6. Kwon, Y. J.; Hong, S. M.; Koo, C. M. *J Polym Sci Polym Phys* 2010, 48, 1265.
7. Klemperer, D.; Frisch, K. C. *Handbook of Polymeric Foams and Foam Technology*; Hanser, Munich, 1991.
8. Zakaria, Z.; Ariff, Z. M.; Sipaut, C. S. *J Vinyl Add Tech* 2009, 15, 120.
9. Marcilla, A.; Garcia-Quesada, J. C.; Beltran, M. I.; Ruiz-Femenia, R. *J Appl Polym Sci* 2008, 107, 2028.
10. Abe, S.; Yamaguchi, M. *J Appl Polym Sci* 2001, 79, 2146.
11. Youssef, H. A.; Senna, M. M.; Eyssa, H. M. *J Polym Res* 2007, 14, 351.
12. Sagane, N.; Harayama, H. *Radiat Phys Chem* 1981, 18, 99.
13. Cowie, J. M. G.; Arrighi, V. *Polymers: Chemistry and Physics of Modern Materials*, 3rd ed.; CRC Press: Scotland, 2008.