

Improvement of Processability of Poly(ϵ -caprolactone) by Radiation Techniques

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ABSTRACT: Improvement of processability of Poly(ϵ -caprolactone) (PCL) was achieved by introduction of a branch structure using gamma-irradiation from a ^{60}Co source. Irradiated PCL has higher molecular weight by producing a branch structure. Hence, the irradiation at a lower dose, such as 3 Mrad, leads to a higher melt viscosity. The branched structure gave improved properties for dynamic viscoelasticity and elongational viscosity. High elongational viscosity was observed by entanglement due to branch chain formed during irradiation, and the elongational viscosity for 3 Mrad is higher than 1.5 Mrad. Due to a higher elongational viscosity, PCL foam can be produced by a molding process. Foam produced from irradiated PCL pellets at 3 Mrad has honeycomb-like structure, and the foam showed higher enzymatic degradation compared to film samples. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1815–1820, 1999

Key words: poly(ϵ -caprolactone); gamma-irradiation; melt flow index, elongational viscosity; dynamic modulus

INTRODUCTION

Poly(ϵ -caprolactone) (PCL) is a biodegradable synthetic aliphatic polyester that has been commercialized. It is thermoplastic with a relatively low melting temperature (60°C). Thermoplastics may be molded in a compression-molding machine or in the faster, more versatile and economical injection-molding machine. If sheets or films, rod, tube, or profiles of various lengths are desired, thermoplastics can be conveniently extruded.¹ In the latter cases, several factors, including melt viscosity, play an important role in the production of thermoplastic products. PCL has low

processability because melt strength reduces considerably during molding.² When these polymers are extruded or injection molded, they exhibit no strain hardening (an increase in resistance to stretching during elongation of the molten materials). A low melt flow index can be produced by introducing a branch structure or increasing the molecular weight. Stinson reported that the introduction of a multifunctional comonomer has been used to incorporate branching segments within a polycarbonate structure, which leads to properties that make the material more suitable for blow-molding applications, such as the fabrication of hollow items or panels.³

In current technology, such as the production of polyethylene and polypropylene foams, a blowing agent is kneaded into those polymers. To prevent flowing of the polymer during foaming at a

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high temperature, a high melt strength property of the polymer is required. Sufficiently high melt strength of polyethylene and polypropylene is achieved by adding a long branch structure into the main chains.^{4,5} More recently, high melt strength polypropylene was achieved by irradiating the polymer in the present of polyfunctional monomers.⁶ It was reported that among multifunctional monomers used, 1,4-butanediol diacrylate (BDDA) and 1,6-hexanediol diacrylate (HDDA) were the most effective for enhancing the melt strength of PP.

In the previous study, PCL was irradiated to produce a crosslinked network structure.⁷ When the polymer of a crosslinking type is irradiated by γ -rays or fast electrons below the gelation dose, linear polymers are converted to a higher molecular weight, leading to increasingly branched materials and ultimately to insoluble gel networks.^{8–10} Below the gel point, network formation is not complete, and the crosslinked polymer is amenable to solution and melt flow characterization.

The objective of the present study is to evaluate the melt flow, melt viscosity, dynamic mechanical properties, as well as foam preparation of irradiated PCL and enzymatic degradation of PCL foam.

EXPERIMENTAL

Material

Poly(ϵ -caprolactone), PCL-H7, which has a weight-average molecular weight of $\bar{M}_w = 1.63 \times 10^5$ and a number-average molecular weight of $\bar{M}_n = 9.26 \times 10^4$, was generously supplied by Daicel Chemical Industries Ltd., Japan. The samples were completely dried under vacuum at room temperature before used.

Irradiation of Sample

PCL pellets were irradiated using γ -rays generated from a ⁶⁰Co source with a dose rate of 1 Mrad/h using a plastic packaging vacuum at room temperature. After irradiation, a part of the sample was annealed at 55°C for 30 min, while another part of the sample was kept at room temperature.

Melt Flow Index (MFI) Measurement

Melt flow index was determined using an extrusion machine (Toyoseiki Co. Ltd, Japan). Certain

weights of pellets samples were introduced into the heated cell and MFI was estimated by measuring the weight of samples flowing for 10 min from the orifice of a 2.095-mm diameter under 2.16 kg static weight. MFI measurement was carried out according to Japanese Industrial Standards (JIS K 7210).

Molecular Weight Determination

Polymer molecular weights were determined by gel permeation chromatography (GPC), (HLC-802A, Tosoh Co. Ltd., Japan). The instrument was equipped with a series of four Tosoh gel columns and an RI-8 differential refractometer at 38°C. The eluent was chloroform, with a flow rate of 1 mL/min, and the polymer concentration was 1 mg/mL. The average molecular weights were calibrated using polystyrene standards.

Dynamic Mechanical Analysis (DMA)

To observe molecular motion of the sample in a range of the temperature, a rheometrics solids analyzer (RSA II) was used. Film samples 5×30 mm² and 0.5 mm thick were used to determine dynamic mechanical properties. The measurement was carried out at a frequency of 10 Hz over a temperature range of -150 to 300°C . The strain amplitude of the dynamic measurements was fixed at 5×10^4 .

Measurement of Elongational Viscosity

To measure elongational viscosity, an irradiated PCL rod with the size of 5 mm in diameter and 300 mm in length was mounted into the sample holder of a Melten rheometer-670 (Toyoseiki Co. Ltd., Japan). Rod-shaped samples for measurements were prepared using a single-screw extruder. Samples were completely relaxed in a silicone oil bath SRX 310 (Toray Dow Corning Ltd.) at 70°C for 10 min. Then uniaxial elongational viscosity was measured at 70°C. To calculate the actual strain rate, the sample diameter during elongation was monitored by a CCD camera. The setting strain rates were in the range of 0.001–0.5 s⁻¹.

Enzymatic Degradation of Irradiated PCL Foam

Enzymatic degradation of irradiated PCL foam was carried out using lipase AK enzyme at 50°C under different reaction times. A cylindrical sample with a diameter of 10 mm (about 15 mg) was

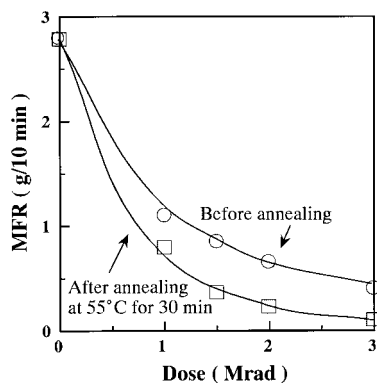


Figure 1 Change in MFR values of PCL by irradiation under vacuum and annealing after irradiation.

put into a test tube containing 6 mL of the enzyme solution in a buffer phosphate pH 7.4. The test tube was then put into the water bath at 50°C with shaking. For comparison, the films prepared from irradiated PCL pellets at 3 Mrad and unirradiated PCL by using compression molding at 120°C.

RESULTS AND DISCUSSION

Effect of Irradiation on MFI and Molecular Weight

The MFI measurement is useful to evaluate the processability for injection and extrusion molding of polymer materials. The MFI value is greatly dependent on the distribution of the molecular weight and branch structure of polymer materials. Generally, the higher the molecular weight of the polymer reflects lower MFI. Figure 1 shows the MFI of the irradiated PCL and annealed PCL after irradiation. It can be seen that MFI reduces remarkably up to 2 Mrad, followed by steady decreases in the MFI with increasing the dose. Postirradiation annealing has a lower MFI than without annealing for the same dose. The PCL structure consists of a crystalline part and an amorphous part. The crystalline part of the PCL has trapped radicals by irradiation. By annealing, the trapped radicals in the crystalline areas migrate to the crystal surface and cause a reaction to produce a branch structure. Accordingly, postirradiation annealing is effective in enhancing the melt viscosity.

In the previous article,⁷ PCL irradiated at room temperature was reported to form a gel at 15.2 Mrad. Crosslinks between the molecular chain do not form at a lower dose than 15.2 Mrad,

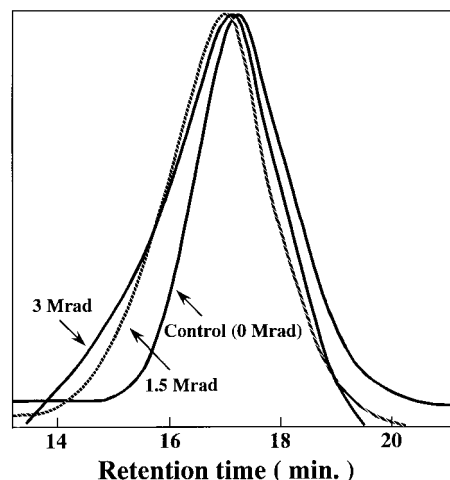


Figure 2 GPC chromatograms of irradiated PCL.

but the precursor for crosslinking is formed as branch and star-type structures.

The molecular weight of the irradiated PCL with annealing was measured, and the results are shown in Figure 2. The higher molecular weight fraction increases with an increase of the dose. It is obvious that the molecular chains become larger due to irradiation. The number-average and weight-average molecular weights estimated from GPC curves are shown in Table I. It can be seen that the molecular weight increases upon increasing the dose. The \bar{M}_w of the PCL irradiated at 3 Mrad increases two times higher than that of the unirradiated PCL. From the polydispersity (\bar{M}_w/\bar{M}_n), it can be seen that distribution of the molecular weight becomes broader because of the increase of the high molecular weight fragment by irradiation.

Dynamic Mechanical Properties and Elongational Viscosity

To elucidate the melt behavior of irradiated PCL, dynamic viscoelastic properties were determined. Figure 3 shows dynamic modulus (E') as a function

Table I Molecular Weights of PCL at Different Doses

Dose (Mrad)	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	\bar{M}_w/\bar{M}_n
0	9.26	16.25	1.75
1.5	13.55	27.54	2.03
3.0	12.56	34.07	2.71

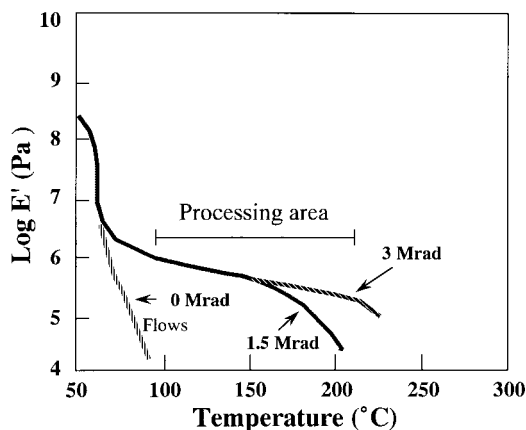


Figure 3 Dynamic modulus of PCL at various irradiation doses.

of temperature. It can be seen that E' dropped rapidly above the melting point, 60°C , for unirradiated PCL due to the melting of crystalline. On the contrary, irradiated PCL shows a steady decrease in E' up to 150 and 220°C for irradiation at 1.5 and 3 Mrad, respectively. A higher dynamic modulus of the irradiated PCL at an elevated temperature is probably due to the branch structures formed during irradiation. By such irradiation doses, the temperature range for molding is extended to keep a wider steady state at the higher temperature. Because the higher dynamic modulus is kept above the melting point, the melt down of the polymer during the blow process in the molding is prevented. Accordingly, the dynamic modulus measurement gives useful information for the processability of polymeric materials.

Elongational viscosity is also often measured to evaluate the processability of polymer materials. Elongational viscosity is the resistance of a fluid or semifluid substance to elongation. It is a melt property of a thermoplastic materials that can be determined by an instrument that measures the stress and strain of a specimen in the melt state when subjected to the tensile strain at a constant rate. Figure 4 shows the elongational viscosity of unirradiated and irradiated PCL at different strain rates at 70°C . The elongational viscosity of unirradiated PCL is substantially linear, and breaks at different times for various strain rates due to the straight chain molecular structure, while for the irradiated PCL, the elongational viscosity is nonlinear, and it increases rapidly before the break. For the faster strain rate (0.21488 s^{-1}) at 3 Mrad, elongational viscosity increases more rapidly at the earlier stage, fol-

lowed by the slower strain rates of 0.0937 and 0.0554 s^{-1} . The increase in elongational viscosity is due to entanglements by the branching segments formed during irradiation. Elongational viscosity of the irradiated PCL at 3 Mrad is higher than 1.5 Mrad. This is due to the formation of a longer branch or an increase of a branch number by irradiation. Similar results were reported for low-density polyethylene¹⁰ and polypropylene⁴ having a long branch structure. From these results, it can be concluded that irradiation at lower doses is effective in enhancing the processability of PCL.

Foam Production of Irradiated PCL

As already mentioned, the melt viscosity of the polymer plays an important role in the production of

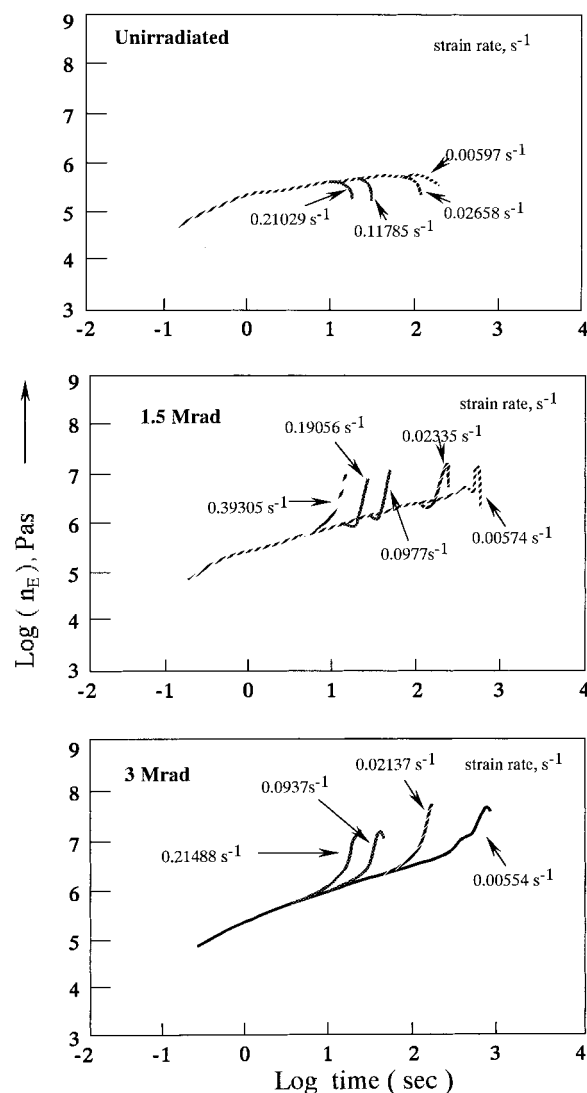


Figure 4 Elongational viscosity of PCL at 70°C .

foam material. In the production of polyethylene foams, the blowing agent, such as azodicarbonamide, is kneaded into the polymer subsequent to the polymer being irradiated to enhance the melt viscosity by crosslinking. After irradiation, the polymer is heated at a temperature higher than the decomposition temperature of the blowing agent, and a foam product is formed by making a lot of bubbles in the polymer. For PCL, the required melt viscosity to produce foam is achieved by formation of branch chains during irradiation at 3 Mrad. The foams prepared at 120°C have honeycomb structure, as can be seen in Figure 5. Because unirradiated PCL has a lower melt viscosity, the polymer break during the process or the foam product shrinks after blowing. Hence, it is difficult to produce foam for unirradiated PCL.

Enzymatic degradation results for PCL foam and film prepared from irradiated PCL pellets at 3 Mrad are presented in Figure 6. For film samples, enzymatic degradation of irradiated PCL at 3 Mrad gave the same degradation rate as 0 Mrad (unirradiated PCL). The weight-average molecular weight of irradiated PCL at 3 Mrad is about two times that of the unirradiated one, and the irradiated PCL has a higher polydispersity (see Table I). From these results, it is apparent that the molecular weight and polydispersity do not affect the enzymatic degradation of the PCL film. PCL foam and irradiated PCL at 3 Mrad have the the same molecular weight. However, enzymatic degradation of foam samples is higher than that of the unirradiated and irradiated (3 Mrad) PCL films. Degradation increases linearly at the initial stage, followed by a gradual increase

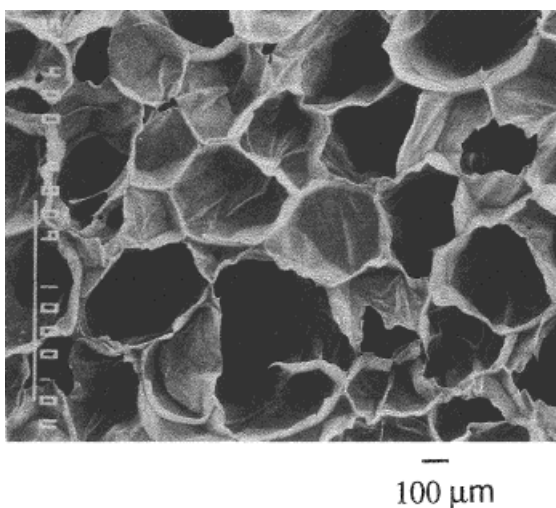


Figure 5 SEM photograph of PCL foam prepared from irradiated PCL at 3 Mrad.

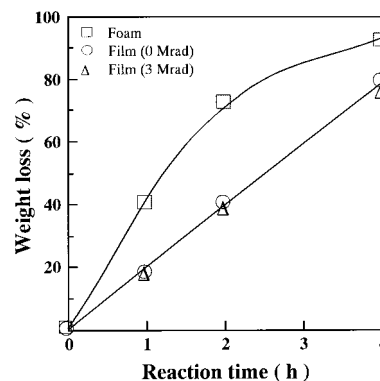


Figure 6 Enzymatic degradation of PCL foam and film as a function of time. Foam is prepared from irradiated PCL at 3 Mrad.

with the increase of the reaction time for the foam sample, while it was linear with time for both the PCL films. PCL foam consists of many holes, with a diameter ranging from 200 to 550 μm , leading to a higher surface area compared to the unirradiated film. Enzymatic degradation of the PCL proceeds via a surface erosion of sample; therefore, such degradation is highly affected by the surface area of sample. From these results, it is clear that the degradation rate of the PCL foam is higher than that of the unirradiated PCL film due to a higher surface area of the PCL foam.

CONCLUSIONS

Insulation cable and dry rubber are often irradiated to improve heat stability and green strength, respectively. A required dose for such modifications are more than 10 Mrad. In the case of PCL, processability is improved by enhancing the melt viscosity in irradiation at a lower dose: 1.5 to 3 Mrad.

One of the disadvantages of the PCL was overcome by irradiation at such lower doses. It was confirmed that radiation is useful even for improvement of the processability of polymeric materials. It is expected that these findings will extend the application fields of PCL.

REFERENCES

1. Jone, R. J.; Chandy, K. T. In *Handbook of Industrial Chemistry*; Kent, J. A., Ed.; Van Nostrand Reinhold Co., Ltd.: New York, 1974, p. 238.
2. Ito, M. Daicel Chemical Company, Japan, private communication.

3. Stinson, S. C. *Chem Eng News* 1990, May 7, 55.
4. Scheve, B. J.; Mayfield, J. W.; Denicola, A. J. U.S. Pat. 4,916,198, C.A. 105: 19185 e, Himont Incorporated, Wilmington, DE.
5. Bradley, M. B.; Philips, E. M. *Plast Eng* 1991, 82.
6. Yoshii, F.; Makuuchi, K.; Kikukawa, S.; Tanaka, T.; Saitoh, J.; Koyama, K. *J Appl Polym Sci* 1996, 60, 617.
7. Darwis, D.; Mitomo, H.; Enjoji, T.; Yoshii, F.; Makuuchi, K. *J Appl Polym Sci* 1998, 68, 107.
8. Woods, R. J.; Pikaev, A. K. *Applied Radiation Chemistry, Radiation Processing*; John Wiley & Sons: New York, 1994.
9. Chapiro, A. *Radiation Chemistry of Polymeric Systems*; Interscience Publishers: New York, 1962.
10. Wilson, J. E. *Radiation Chemistry of Monomers, Polymer and Plastic*; Marcel Dekker, Inc.: New York, 1974, p. 371.
11. Bradley, R. *Radiation Technology Handbook*; Marcel Dekker, Inc.: New York, 1984, p. 91.
12. Kojima, K.; Ishizuka, O. *J Polym Sci Part B* 1989, 27, 297.
13. Billmeyer, E. W. *Textbook of Polymer Science*; John Wiley & Sons: New York, 1984, p. 341.