Journal of the Korean Nuclear Society
Volume 33, Number 2, pp.184~184, April, 2001

Characteristics of Heat Shrinkable High Density Polyethylene Crosslinked by γ-Irradiation

Phil Hyun Kang and Young Chang Nho
Korea Atomic Energy Research Institute
150 Dukjin-dong, Yusong-gu, Taejon 305-353, Korea
phkang@kaeri.re.kr

(Received August 2, 2000)

Abstract

The effects of γ-irradiation on the crosslinking of high density polyethylene (HDPE) was investigated for the purpose of obtaining a suitable formulation for heat shrinkable materials. In this study the HDPE specimens were prepared by blending with cross linking agents and pressed into a 0.2 mm sheet at 180℃. γ-irradiation was conducted at 40 to 100 kGy in nitrogen. The heat shrinkable property and thermal mechanical property of the HDPE sheets have been investigated. It was found that the degree of crosslinking of the irradiated HDPE samples were increased with irradiation dose. Compared with the HDPE containing triallylisocyanurate, the HDPE containing trimethylol propane triacrylate shows a slight increase in crosslinking density. The heat transformation and dimension change of HDPE decreased with increasing radiation dose. The heat shrinkage of the samples increased with increasing annealing temperatures. The thermal resistance of HDPE increased upon the crosslinking of HDPE.

Key Words : high density polyethylene; γ-irradiation; heat shrinkable property

1. Introduction

High density polyethylene (HDPE) is one of the most important thermoplastics, but its use is limited in certain applications by its low melting point, solubility in hydrocarbons and a tendency to be cracked when stressed. One large disadvantage in the use of thermoplastics such as HDPE comes from its tendency to thermoplastic flow or deformation at elevated temperature. Heat shrinkable uses can lead to excessive melting of HDPE during the manufacturing process of a heat shrinkable tube and a reduction in electrical and mechanical properties owing to the degradation of the HDPE molecules by heat. In order to solve these problems, the thermal properties of the present HDPE must be improved. Many investigators have tried to alter the properties of HDPE by changing the morphology. If a suitably crosslinked product is heat-extended and cooled in the extended state, it preserves its form at room temperature for a long time, however it "remembers" its original form and reassumes it upon heating. The tubes produced by that way (heat shrinkable tubes) can be used as electric insulators, casting materials used in orthopedics

and for protection against corrosion, mechanical stress and moisture. Cross linking can be induced by the γ-irradiation. This investigation of the γ-irradiation effects on HDPE is necessary to improve its commercial application. It is well known that γ-irradiation introduces free radicals into polyethylene. These free radicals can in turn lead to the crosslinking of the polymer.

Radiation cross linking has many advantages over other conventional methods. This technique has a broad range application in industry which led to the manufacture of many of high quality products such as crosslinked wire and cable insulation, crosslinked foam, heat shrinkable tubes and films, etc[1]. The technique involves crosslinking of a polymer by radiation. Such irradiated polymers exhibit elasticity above their crystalline melting point and the application of heat shrinks the material to its original dimensions. This phenomenon is referred to as the 'memory effect' or 'elastic memory' [2]. The improvement of radiation crosslinked polymer properties includes resistance to cold flow or creep, enhanced high temperature stability, resistance to attack by chemicals and solvents, high mechanical strength and superior electrical properties. These advantages, together with the heat shrinking property, make these products ideally suited for applications where a tight insulating cover is required over either a uniform or an irregularly shaped object. The treatment of polymers by an electron beam has been reviewed by various authors[3-5]. It is observed that, in general, rubbers can be crosslinked using an electron beam, whereas some plastics(like polypropylene and polyvinylchloride) have a tendency to degrade. The effect of electron beam radiation on the electrical and mechanical properties of polyethylene in the presence of various types of sensitizers has been reported[6-9]. The memory effect of electron beam-irradiated heat shrinkable low density polyethylene tubes has been discussed[10-13]. The literature survey reveals that scientific studies on the heat shrinkability of high density polyethylene crosslinked by γ-irradiation have not been reported. In the present work, HDPE was mixed with cross linking agents to obtain an efficient cross linking yield in spite of the low dose rate for a heat shrinkable tube. In this paper, attention is focused on the effects of γ-irradiation on the changes of shrinkage and thermo-mechanical properties of HDPE, irradiated at a dose of up to 100 KGy.

2. Experimental

2.1. Materials

The material used in this study was HDPE supplied by the Honam petroleum chemical corporation, S. Korea in pellet form. The molecular weight of HDPE was 400,000 (density : 0.96g/cm^3, melt index 0.4 g/10min). Trimethylol propane trimethacrylate (TMPTMA) and triallyl isocyanurate (TAIC) used as a crosslinking agent were obtained from Polyscience, Inc., USA.

2.2. Preparation of Samples

Radiation-crosslinking of HDPE was investigated for the purpose of obtaining a suitable formulation

Table 1. Blending Condition of HDPE and Crosslinking Agent

Sample	HDPE	TMPTMA(phr)	TAIC(phr)
1	100	0	0
2	100	5	0
3	100	10	0
4	100	15	0
5	100	0	5
6	100	0	10
7	100	0	15

for a heat shrinkable tube. As shown in Table 1 HDPE was compounded with various cross linking agents to evaluate their effects on radiation sensitivity, the heat shrinkable property and other thermal properties. Mixing of the HDPE and cross linking agent was accomplished by using a Brabender at 180℃. The prepared mixture samples were compression moulded between aluminium foils for 2 min at 180℃ and a pressure of 10 MPa in an electrically heated press. Specimens were irradiated with γ-rays at room temperature in a nitrogen atmosphere. ^{60}Co was used as the γ-irradiation source. Irradiation was conducted at doses of 40 kGy to 100 kGy.

2.3. Relative Crystallinity

The relative crystallinity of the specimen was measured using differential scanning calorimetry (DSC, DSC-7 Series Thermal Analysis System, Perkin Elmer). Heating runs were conducted from 50℃ to 200℃ at a rate of 10℃/min in nitrogen. Sample crystallinity was determined by comparing the heat of fusion for a fully crystalline polyethylene (288 J/g).

2.4. Percent Crosslinking Measurement

The percentage of cross linking was determined by the extraction method. Samples were extracted with boiling xylene for 24 hr, then washed with ethanol and were dried under vacuum at 80℃ to a constant weight.

2.5. Heat Shrinkability Experiment

As shown in Figure 1, crosslinked 10×80×0.2 mm thick films were stretched in propyleneglycol at 130℃. The samples were removed and cooled at 10℃ under tension. The shrinkage experiment was carried out by annealing at 80℃, 110℃, 120℃ and

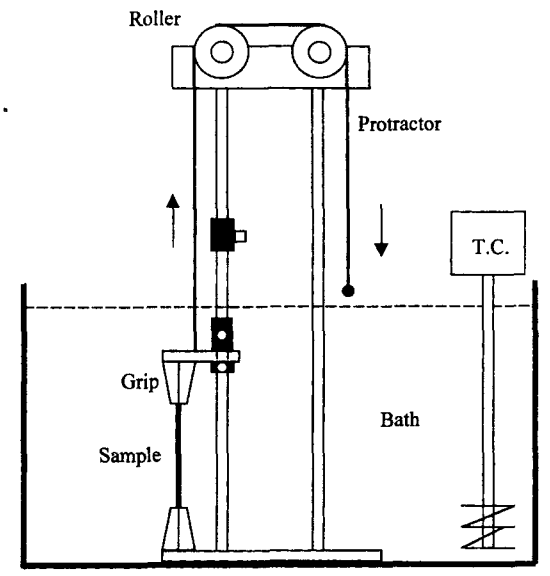

Fig. 1. Apparatus for Stretching and Annealing of HDPE

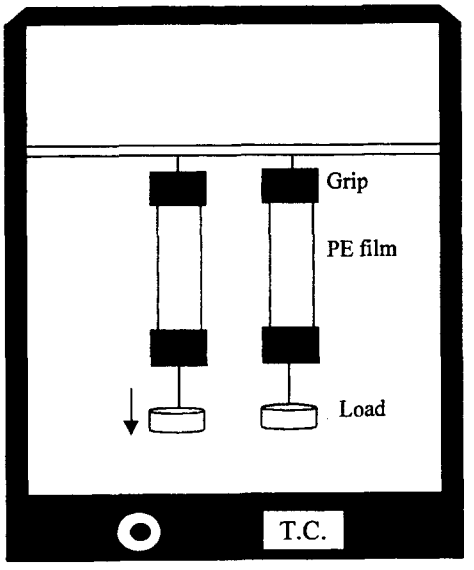

Fig. 2. Apparatus for Measurement of Heat Transformation of HDPE in an Oven

130℃ after the film was stretched. From the length of the two marks before and after shrinkage, the heat shrinkage (%) was calculated as follows :

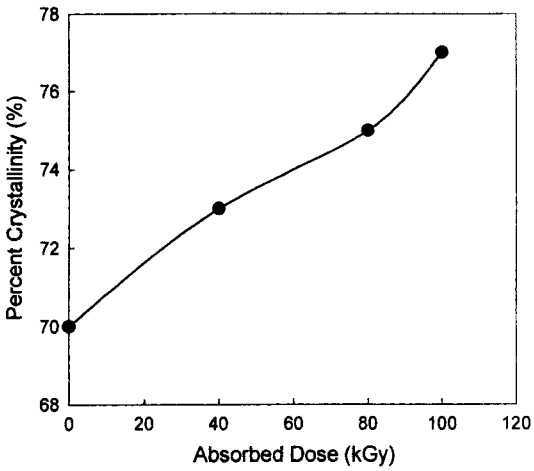

Fig. 3. The Effect of Irradiation dose on the Percent Crystalinity of HDPE

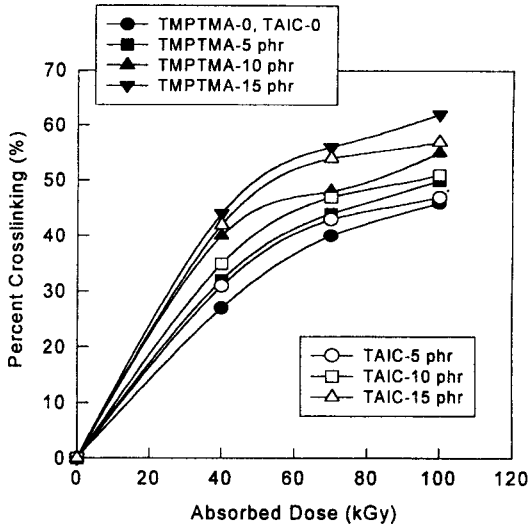

Fig. 4. The Effect of Irradiation dose on the Crosslinking for HDPE Using TMPTMA and TAIC as Crosslinking Agents

$$\text{Heat shrinkage (\%)} = (L\text{-}Lo)/L \times 100 \quad (1)$$

Where, L= length between the two bench marks before shrinkage as extended, and L_o = the length between marks after shrinkage.

2.6. Heat Transformation Experiment

The heat transformation test of irradiated HDPE films was conducted in an oven preheated at 140℃ (Figure 2.) Heat transformation was evaluated from the percent of the deformed length by pending a 15 g load for 5 min in an oven.

2.7. Thermal Mechanical Analysis

The thermal mechanical analysis was conducted on a TMA-943 system (Du-Pont model, USA). Temperature scans were from 30 ℃ to 150℃. A specimen of HDPE was studied using an expansion probe. The probe was lowered onto the samples and the initial height was recorded. The expansion was measured as 5℃/min in nitrogen.

3. Results and Discussion

The crystallinity can be easily measured by the use of differential scanning calorimetry. The peak temperature corresponds to the melting of the material and the area under the curve in the heat of fusion of the material. The heat of fusion (H_f) of a 100 percent crystalline polyethylene has been reported to be 288 joules per gram. Therefore, the crystallinity percentage can be calculated by the equation of (H_f of sample/288) × 100. It is known that the crystalline regions of any polymer form lamellae, which may organize further to form larger structures called spherulites. The lamellae of HDPE are composed of folded polyethylene chains. Following irradiation, the melting behavior was studied by differential scanning calorimetry. Figure 3 shows the percent crystallinity of the HDPE sheets irradiated to various doses in a

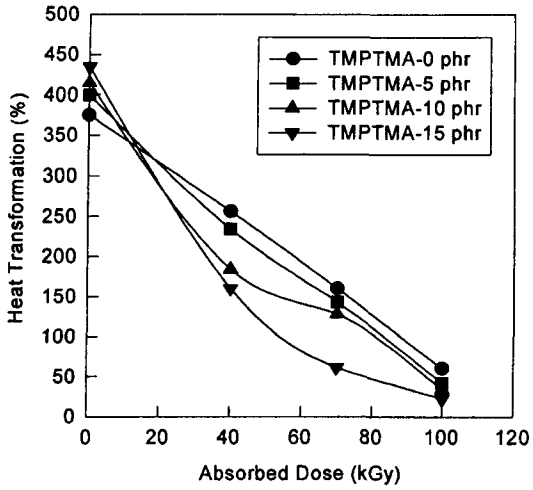

Fig. 5. The Effect of Irradiation dose on the Heat Transformation for HDPE Using TMPTMA as a Crosslinking Agents

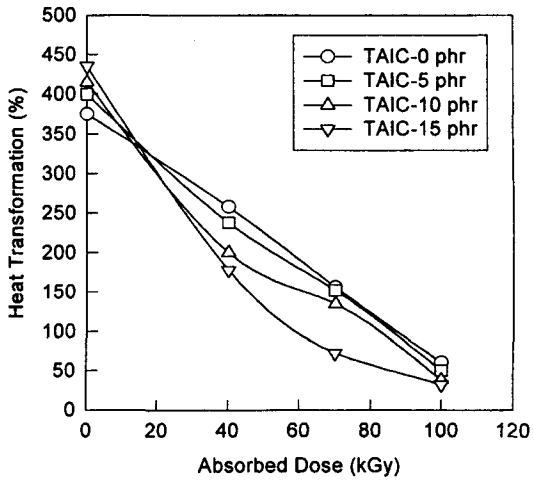

Fig. 6. The Effect of Irradiation dose on the Heat Transformation for HDPE Using TAIC as a Crosslinking Agents

nitrogen atmosphere. From the calorimetry, the crystallinty of the non-irradiated samples was 70%. It can be seen that the percent crystallinity of HDPE increases up to an irradiation dose of 100 kGy. This result was similar to the relation between crystallinity and irradiation of HDPE as described by Roe[14].

Figure 4 shows the effect of irradiation dose on the cross linking for HDPE containing TMPTMA and TAIC as crosslinking agents. Polyethylene, when exposed to high energy irradiation, is a crosslinking type polymer, and the formation of the intermolecular links is very common. These crosslinks are formed mainly in the amorphous region in the polymer, possibly the crystal fold surface and also in the crystallites. As shown in Figure 4, the degree of crosslinking, as measured by the gel fraction, remaining after boiling in a solvent like xylene, which can be achieved by a given radiation dose in the polymer, depends on the irradiation condition. Percent crosslinking of HDPE increased with radiation dose. Compared with the HDPE containing TAIC, HDPE containing TMPTMA shows a small increase in crosslinking. As the content of the crosslinking agent increased percent crosslinking increased with irradiation dose up to 100 kGy. The value of crosslinking depended on the content of the crosslinking agent and irradiation dose. An increase in crossliniking is due to the possibility of polymer chain rearrangement. Figs 5-6 show the results of heat transformation for HDPE containing TMPTMA and TAIC as crosslinking agents. It was found that heat transformation decreased with increasing radiation dose regardless of the crosslinking agent. The decreasing of heat transformation is due to the extent of HDPE crosslinking with radiation dose. Figs 7-8 show the TMA thermogram of HDPE with temperature. In polymeric materials the thermal transitions are accompanied by changes in the isobaric expansivity of the material. These changes are measured using thermo-mechanical analysis. TMA measures the change in length of a material over a temperature range. As shown in Figure 7, the value of the dimension change of the specimen is observed when increasing the temperature. The thermal expansion coefficient of

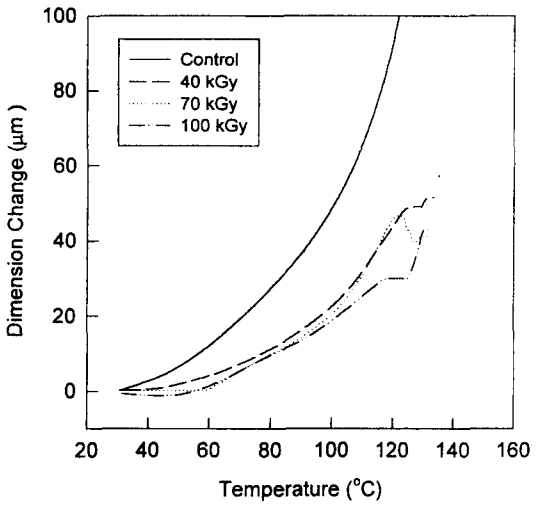

Fig. 7. MA Curves of Irradiated HDPE with TMPTMA as a Cross-linking Agent

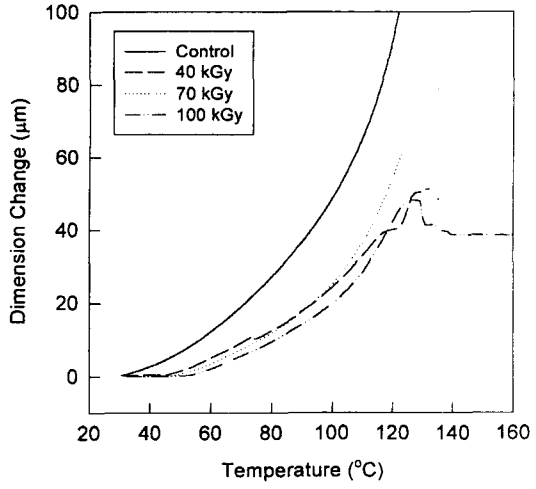

Fig. 8. TMA Curves of Irradiated HDPE with TAIC as a Cross-linking Agent

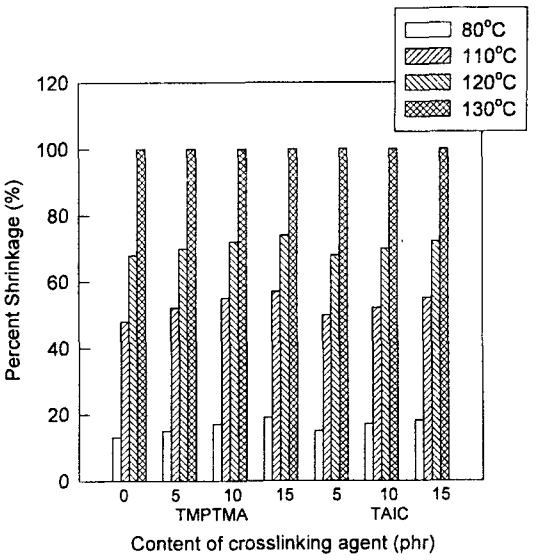

Fig. 9. Percent Shrinkage of Non-irradiated HDPE Film at Various Annealing Temperatures

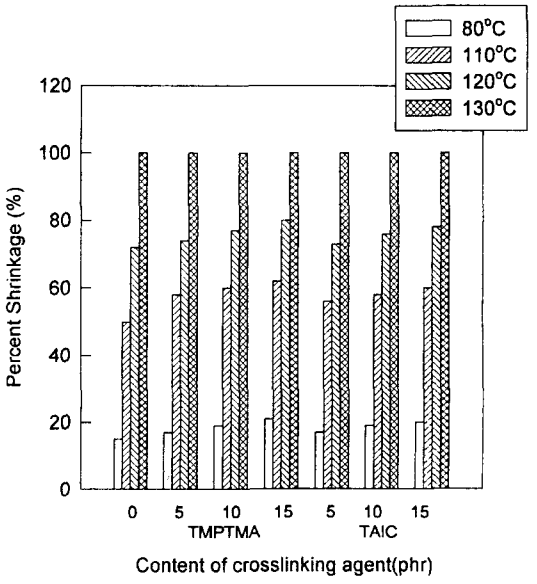

Fig. 10. Percent Shrinkage of Irradiated(40kGy) HDPE Film at Various Annealing Temperatures

the specimen decreased with increasing irradiation dose. The difference in expansivity of the sample at the same temperature can be described by the crosslinking network of the polymer caused by the irradiation effect. This result was similar to that of the heat transformation shown in Figs 5-6. Figs 9-12 show the percent shrinkage of irradiated HDPE film. When the linear polymer chains are subjected to mechanical deformation by stretching, molecular chains usually tend to align themselves

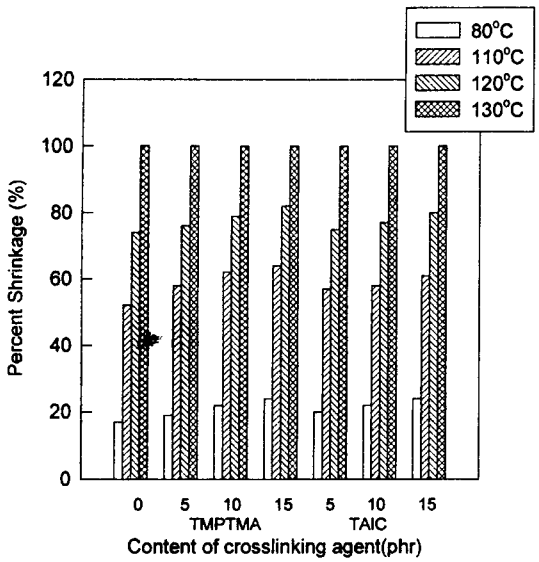

Fig. 11. Percent Shrinkage of Irradiated(70kGy) HDPE Film at Various Annealing Temperatures

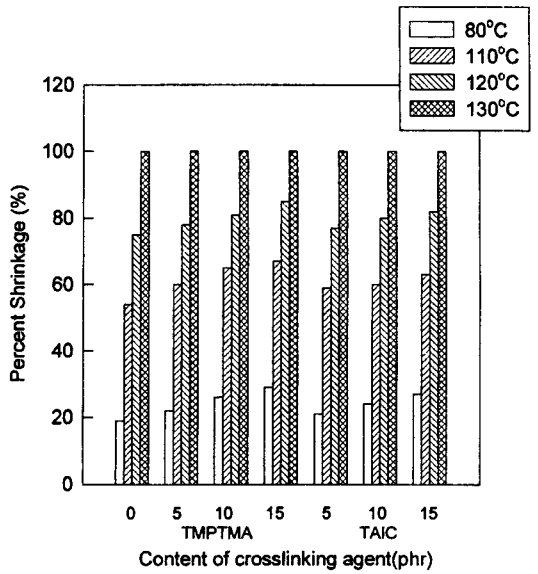

Fig. 12. Percent Shrinkage of Irradiated(100kGy) HDPE Film at Various Annealing Temperatures

parallel to the direction of deformation, i.e. the chains become oriented. This orientation is a function of the elongation as well as the level of irradiation dose. As soon as the polymer is heated up to 130℃ the chains recoil and shrink. On heating, the chains that have a higher orientation would shrink to a greater extent, as expected. Heat shrinkage of HDPE was quite varied with annealing temperature. Percent shrinkage was increased remarkably as annealing temperature increased. It was found that all samples examined exhibit a "memory effect" after drawing at 130℃. Heat shrinkage of HDPE did not vary much with radiation dose and the types of crosslinking agents, but it increased remarkably with increasing annealing temperature.

4. Conclusions

Maximum heat shrinkage of HDPE was observed at 130℃ when the samples were irradiated at 100kGy. It was found that the percent crosslinking of the irradiated HDPE samples were increased with irradiation dose. The heat transformation and dimension change of HDPE were decreased with increasing radiation dose. The heat shrinkage of the samples increased with increasing annealing temperature. The thermal resistiance of HDPE increased upon crosslinking of HDPE. From these experimental results, we expect that these data are useful for the application of heat shrinkable material such as a casting material used in orthopedics, heat shrinkable sleeves and cable joints.

Acknowledgement

The present work was supported by the Nuclear R&D Program from Ministry of Science & Technology, Korea.

References

1. P. E. Jacobs, "The effect of electron beam radiation on film properties of film and extrusion coating resins," Tech, Pop. Reg. Tech. Conf.-Soc. Plast. Eng.(Plasty. Prog. Process. May 5-8), p. 675(1980).
2. D. H. Morton Jones and J. W. Ellis, "Polymer Products-Design Materials and Processing," Chapman & Hail, London.(1986).
3. M. Aoshima, T. Jinno and T. Sassa, "Electron beam crosslinking of ethylene-propylene rubber," Kautschuk Gummi Kunststoff" **45**, p.644(1992).
4. G. G. A. Bohm and J. O. Tveekrem, "The radiation chemistry of elastomers and its industrial application Rubber Chem. Technol," **55**, p.575(1982).
5. L. P. Nethsinghe and M.Gilbert, "Structure property relationships of irradiation crosslinked flexible PVC," *Polymer*. 29, p.1935(1988).
6. T. K. Chaki, R.S. Despande, A.B. Majali, V.K. Tikku and A.K. Bhowmick, "Electron beam initiated grafting of methyl methacrylate onto polyethylene, structure and properties," *Die Angew. Makromol. Chem* **61**, p217 (1994).
7. T. K. Chaki, D. Roy, A. B. Majali, V. K. Tikku, and A. K. Bhowmick, "Dynamic mechanical relaxations in irradiation crosslinked polyethylene grafted with methyl methacrylate," *J. Polym. Eng.* **13**, p.17(1994).
8. T. K. Chaki, S. Roy, R. S. Despande, A.B. Majali, V.K. Tikku and A. K. Bhowmick, "Electron beam initiated grafting of triallyl cyanurate onto polyethylene: structure and properties," *J. Appl. Polym. Sci.* 53, p.141(1994).
9. V.K. Tikku, G.Biswas, R.S. Despande, A.B. Majali, T.K.Chaki, and A.K.Bhowmick, "Electron beam initiated grafting of trimethyrol," *Radiat. Phys. Chem.* 45, p.829(1995).
10. J. Dobo, P. Forgacs, A. Somogi and M. Roder, " Some properties of radiation crosslinked polyethylene and ethylvinyl acetate copolymer," *Proc. Tihany Symp. Radiat. Chem.*, Vol. 4, p. 359 CA 08812074814G (1977).
11. T. N. Gordiichuk and V.P. Cordienko, "Effect of accelerated electrons on polyethylene containing ethylene-vinyl acetate copolymer," Kompoz, Polim. Mater., 38, 33. CA.01 1910): 76669k(1988).
12. G. C. Odian and B. S. Bernstein, "Memory effect in irradiated polyethylene," *J. Appl. Polym. Sci*, **8**, p.1853(1964).
13. R. W. Waldron, H. F. McRae,and J. D. Madison, "The effects of various monomers on crosslinking efficiency," *Radiat, Phys. Chem.* **25**, p.843(1985).
14. R. J. Roe, E. S. Grood, R. Shastri, C. A. Gosselin, and F. R. Noyes, "Effect of radiation sterilization and aging on ultrahigh molecular weight polyethylene," *J. Biomedical Materials Research*, **15**, p209(1981).