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GAMMA IRRADIATION EFFECT ON THERMOSHRINK POLYETHYLENE TUBE: CASE STUDY

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Abstract

The production technology of heat shrinkable tubes is based on the industrial usage of so-called memory effect in some polymers. Many polymers can be rendered heat shrinkable, particularly polyolefins by introducing crosslinking in the polymer backbone. Heat shrinkable tubes and moulded parts provide mechanical and/or chemical and/or electrical protection. . In this work, irradiation from Co-60 was used to impart crosslinking in polymer and thus modify their mechanical and thermal properties. Heat shrinkable or thermoshrink polyethylene (PE) tube with diameter 6.4mm was selected to evaluate crosslinking behaviour from the gamma irradiation exposure at 5 different doses (120, 140, 160, 200 and 220kGy). The gel content (%), tensile properties and thermal behavior and stability of the tubes were measured using DSC and TGA. Tubes irradiated at 140 kGy and 160 kGy showed better tensile properties than those at 120, 200 and 220 kGy doses. Maximum percent of crystallization was observed at 160 kGy and temperature required to crystallize is lower than melting temperature due to changes in molecular orientation. Thermal decomposition of the irradiated tubes occurred at 430-450°C which is lower than the unirradiated sample. Gel content analysis for samples irradiated at 180-220 kGy yield up to 30 to 40% gel fraction. Although the gel fractions are higher than other dose, the samples are expected to experience chain scission presumably due to localized gel formation.

Keywords : thermoshrink tube, crosslinking, gamma irradiation, tensile strength and thermal decomposition

INTRODUCTION

Heat-shrinkable or thermoshrink products can be found in major markets, such as the automotive industries, electronics industries, appliances, communications and telecommunications, building and construction and many other markets.

Thermoshrink tubing is being used as a better alternative to standard approaches to insulation, such as taping or molding in place. The diameter of the tube can be expanded by air pressure above the melting temperature of the polymer, then the product is rapidly cooled to room temperature and the expanded diameter is frozen in. When the product is heated again above its melting temperature, a memory effect of the network results in shrinkage of the tube to its original diameter (Chodak, 1994). The shrinking process to conform to the size and shape of the underlying material would protect them from adverse environmental conditions.

Crosslinked polyethylene is normally preferred since large deformations can be stored and later recovered by heating the material. Heat shrinkable tube made of polyethylene is well known for its thermal stability properties and its resistance to electrical discharge, solvents, creep, and environmental stress-cracking. These products are commonly produced from low-density and high-density polyethylene (PE), and normally are crosslinked by two methods: high-energy (ionizing) irradiation or chemical reactions.

Nuclear Malaysia has been providing irradiation services to private shrinkable tube manufacturer at their Electron Beam Irradiation facility (known as ALURTRON). However, there were some request to look into gamma irradiation parameters to achieve crosslinking of this product as a backup plan should electron beam irradiation service become un-available. Data on both ionizing irradiation effect are important to predict the behavior of the irradiated product.

PE upon subjected to ionizing radiation (gamma ray or electron beam) either undergoes crosslinking or oxidative degradation (Suljovrujic, 2010). In general, the domination of one or the other of these competitive processes is determined by the structural peculiarities as well as the irradiation conditions (such as atmosphere, radiation dose, dose rate, sample thickness, irradiation temperature, antioxidant and anti-radiation agents, etc.) (Dole, 1972, 1973; Singh and Silverman, 1991). It is reported that oxidative degradation plays a major role during gamma irradiation, particularly at low dose rate gamma irradiation. However, there have been suggestions (Singh, 1999) that cross-linking may still be an important process during the low dose rate gamma irradiation and that peroxides can act as an initiator for radiation-induced crosslinking of PE.

In this paper, we report the effect of gamma irradiation on thermoshrink PE tube (product code TS-1000-4) manufactured commercially for corrosion prevention of automotives part. Gamma-ray irradiation, hopefully, will give a crosslinking effect and play the same role as electron beam in modifying the mechanical and thermal properties of PE. Thermal analysis technique, gel content test and tensile testing are used to characterize the gamma irradiated tubes and reported in this paper. Comparative evaluation on sample irradiated by gamma ray and electron beam will be elucidated.

EXPERIMENTAL

2.1. Sample preparation

The thermoshrink PE tube was supplied by Chemtube (M) Sdn. Bhd. It is made of low density polyethylene resin with a proprietary formula. Its outer diameter is 6.4 mm with wall thickness about 1.2-1.4 mm. About 1.5 meter sample was cut for each dose from 3 sampling reel #11, #16 and #30.

2.2. Gamma-ray irradiation

Irradiation was carried out at room temperature, in air, and at dose rate of 5 kGy/h using a ^{60}Co facility. The samples were irradiated for the absorbed dose ranging from 120kGy to 220kGy. Doses were measured with cellulose tri-acetate 'CTA-FTR-125' dosimeters from Fuji Film.

2.3. Tensile testing

Tensile properties was measured are according to ASTM D638 using INSTRON Tensio-meter machine. The load applied was 5kN. The speed of testing was 100 mm/min. For each sample, 5 replicates were tested ..

2.4. Differential scanning calorimeter (DSC)

DSC (Perkin Elmer, model DSC7 Pyris) was used to observe thermal behavior of the irradiated sample. Water baseline is used as the reference. Samples were heated from 50°C to 200°C under nitrogen flow at scanning rate of 20°C/ min. The areas under the endotherms were measured in accordance to ASTM D3417. The degree of crystallinity, in percent, was obtained by dividing the samples melting heat (ΔH) with the melting heat of 100% crystalline polyethylene, taken as 289.3 J/g (Suljovrujic, 2010).

2.5. Thermogravimetric analyses (TGA)

Thermogravimetric analyses were performed using TGA Pyris-Thermal Analyzer. It was carried out under nitrogen atmosphere at scanning rate of 20°Cmin^{-1}. Dynamic thermogravimetric study results indicated the thermal stabilities of control and irradiated samples. Range of heating was from 50°C to 700°C.

2.6. Determination of percentage of gel fractions

Gel content analysis is performed to determine the percentage of crosslink fraction in polymer. In this study, the gamma irradiated tubes were cut into small pieces and weighed and subsequently sealed in wire mesh (120 mesh). The wire meshes were labeled and heated up in a Soxhlet extractor with xylene as a solvent. The solvent was

fluxed through each sample for 8 hours, followed by drying the samples for 3 hours in a vacuum oven at 100°C. Gel percentages were calculated based on the following equation:

$$\%\text{Gel} = \frac{m}{m_0} \times 100\%$$

where m_0 and m are the mass of a sample before and after extraction, respectively.

RESULT AND DISCUSSION

Differential scanning calorimetry measurements

DSC thermograms obtained for the thermoshrink PE tube before and after gamma irradiation in air are shown in Fig. 1. Endothermic peaks appear in the 105-107°C range and the temperature of melting decreases as the sample exposed to irradiation. At lower irradiation dose applied, results show no significant change in the melting point i.e after irradiation from 120-220kGy. The decrease in melting point after irradiation is related to crystallinity of sample. The progressive decrease in the molecular chain length when the exposure to gamma rays is extended for longer periods and will cause changes in the temperature and shape of the peaks (Suarez, 2002). As a consequence, the endothermic peaks of irradiated samples are wider and the melting temperature decreases due to deterioration induced by the gamma exposure.

The scission process is important for the structural integrity of the polymer and, over time, the irradiation reduces the branching as chains are broken. The resulting shorter chains are able to pack together more easily, allowing the most of the branched segments to crystallize separately at lower temperatures.

The crystallinity of the sample improved with the gamma dose (Table 1). In this study, chain scission is dominant to crosslinking as it promotes new crystal formation and presents a higher crystallinity with the irradiation. The higher the percentage of crystal formed, the higher heat absorbed to melt the polymer.

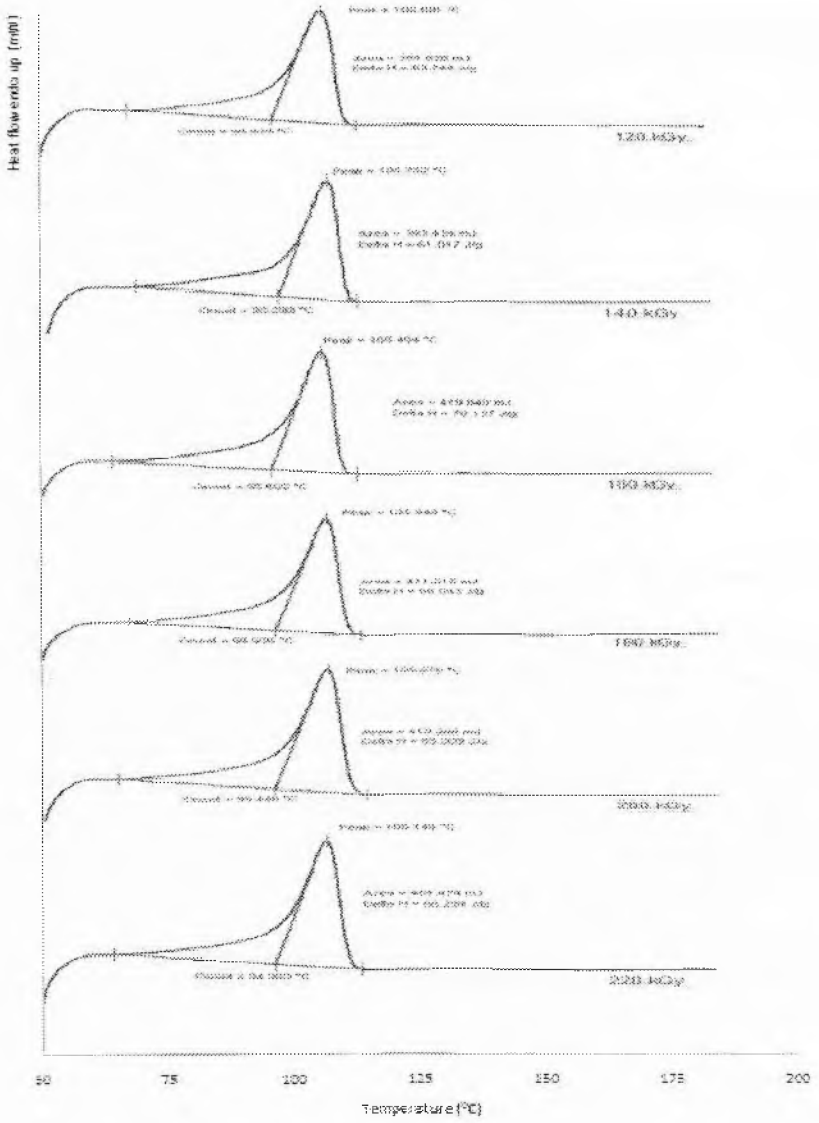

Figure 1. Calorimetric curves of heat shrink PE tube, after gamma irradiation

Table 1. Thermal properties of thermo shrink PE tube (TS-1000-4) and the percentage of crystallinity, before and after gamma irradiation.

Dose (kGy)	Melting temperature, T_m (°C)	Crystallization temperature, T_c (°C)	Decomposition temperature, T_d (°C)	Δ H (J/g)	Crystallinity %
0	106.818		465.24	38.710	13.4
120	105.691	92.175	448.26	63.744	22.0
140	105.752	92.549	449.51	61.017	21.1
160	105.404	92.638	446.61	70.137	24.2
180	105.948	92.616	-	66.043	22.8
200	105.876	92.305	445.62	65.009	22.5
220	105.148	91.488	431.44	66.294	22.9

Influence of gamma irradiation on the thermal stabilities of thermoshrink PE tube

Fig. 2 shows the dynamic TGA thermograms of controlled and irradiated thermoshrink PE tube, in nitrogen atmosphere. Table 1 presents detail thermal properties of these samples. The occurrence of chain scission is clearly demonstrated by the weight loss in TGA.

The sudden decrement in the percent of weight loss of unirradiated and irradiated thermoshrink PE tube appeared at 468.2 °C and 431.4 to 449.5 °C, respectively. This result shows that irradiated thermoshrink PE tube decomposed at lower temperature than unirradiated sample by almost 20°C which corresponds to the reduction of its molecular weight.

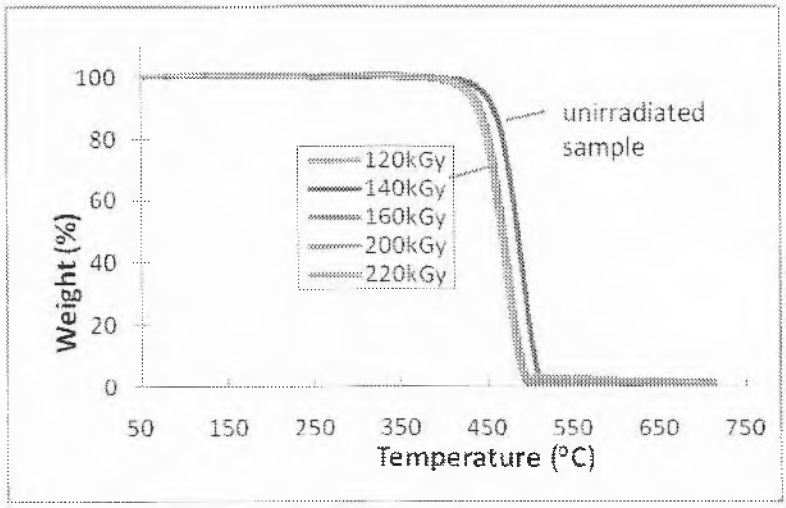

Figure 2. Thermal degradation of gamma irradiated thermoshrink PE tube at various doses.

Gel content analysis on thermoshrink PE tube

Gel content in polymers generally referred to degree of macromolecules crosslinking by means of covalent bonds. Many important properties of ethylene plastics usually vary with gel content changes. Hence, determination of the gel content provides a very important information and direct feedback that is vital in process control and the quality of finished products.

Gel extraction results are reported in Fig.3 as percent of gel at different dose of irradiation. The curve shows that amount of gel increases with dose for all irradiated samples. From this result, it is observed that the maximum gel fraction formed by gamma irradiation was about 40% (at 220 kGy). This is significantly low when compare to electron irradiation in which case 70% gel fraction can be achieved at lower dose of 155 kGy. It is clear that the overall gel formed by gamma irradiation is far less compared to samples irradiated by electron beam. These may be due to different in dose rate used in electron irradiation and gamma irradiation. As explained by Singh (1999); in air or in the presence of oxygen, oxidative degradation becomes a major process during gamma irradiation. In contrast, at the higher dose rates obtained with electron accelerators, oxidative degradation becomes negligible, except on the surface, and the crosslinking is the dominant process (Dole, 1972,1973; Feng and Ma, 1992; Singh et al., 1995).

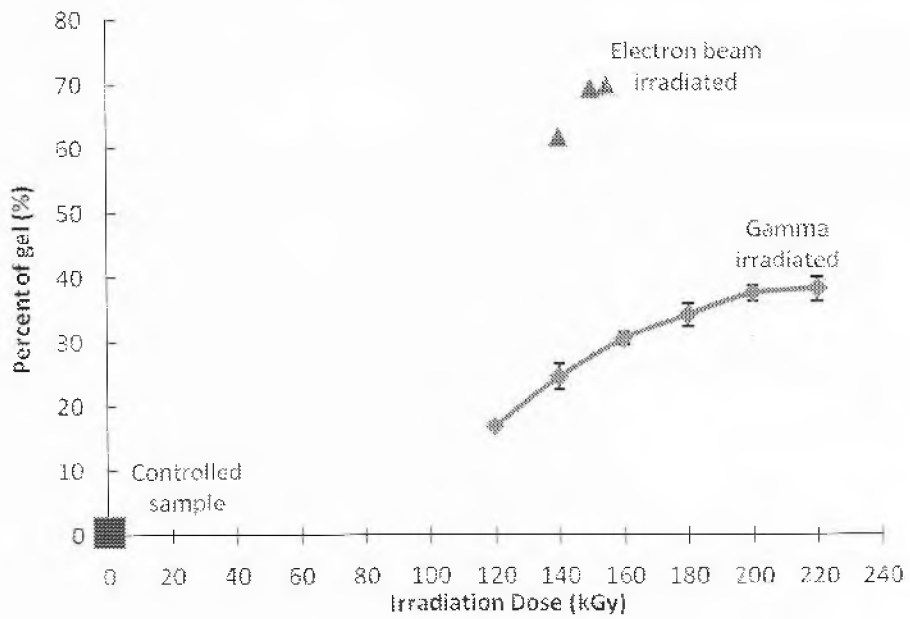

Figure 3. Percentage of gel content at different irradiation dose (gamma and electron beam) for thermoshrink PE tube

Tensile properties

The effects of irradiation on tensile behavior (tensile strength, elongation and elastic modulus) of thermoshrink PE tube irradiated by gamma are shown in Fig. 4, 5 and 6. With reference to Fig.4, the tensile behavior of tube irradiated at 120 kGy does not show any difference as compared to unirradiated thermoshrink tube. A significant change is observed as the thermoshrink tubes exposed to 140 and 160 kGy of gamma ray however, the tensile strength decreased when sample are exposed at over 180 kGy. Increase in tensile strength in the range of 140 to 160 kGy, means a higher degree of interchain interactions, which are introduced by covalent crosslinking or by non-covalent interactions such as those involved in the packing of crystalline domains. This finding is the similar as one observed by Al-Ali *et al*, 2003.

The similar behaviour is also shown in the modulus graph (Fig. 5). The measurement of the tube's stiffness proves that tube irradiated at 140 and 160kGy gamma dose can stand the tensile stress better than other dose. This probably due to an improvement in the crystal perfection as indicated in Table 1 for the greater crystallinity of the 160 kGy exposure. At these levels of irradiation, the major effect is the introduction of crosslink network and distribution of stress throughout the sample. For higher doses, degradation takes places and a small decrease in the modulus and a tendency to stabilization were observed.

The elongation at break of the tubes irradiated up to 220 kGy shows a little decrement less than 11% variation. There are two factors that contribute to the slight drop of elongation. At 140 and 160 kGy dose, the low in elongation was due to steric hindrance of chain segments by neighbouring linkages or known as crosslink. While at higher irradiation dose, chain degradation is predominant and thus lower down the ability to stand the stress.

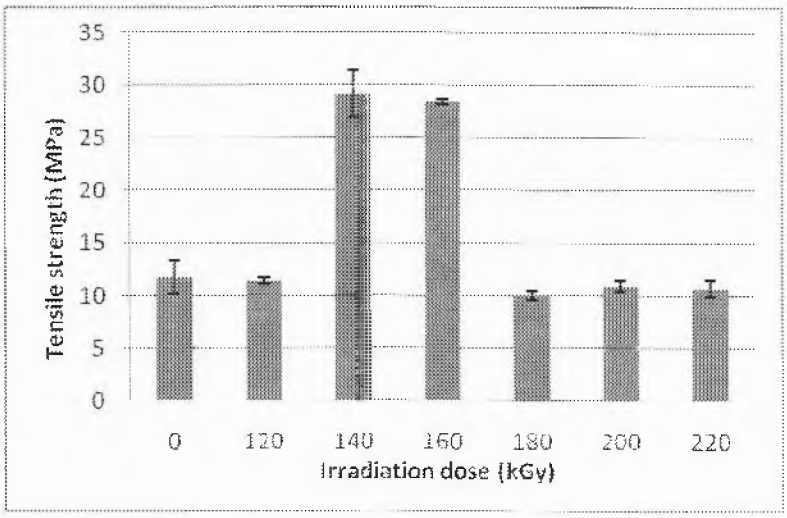

Figure 4. Tensile strength of thermoshrink PE tube.

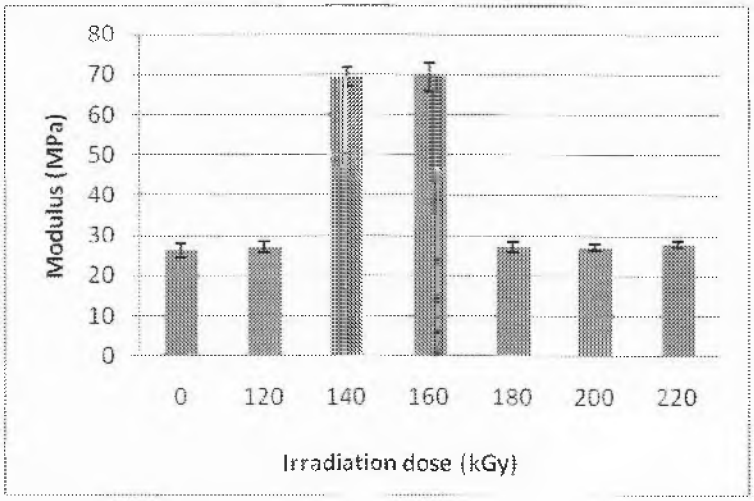

Figure 5. Modulus of thermoshrink PE at different irradiation dose

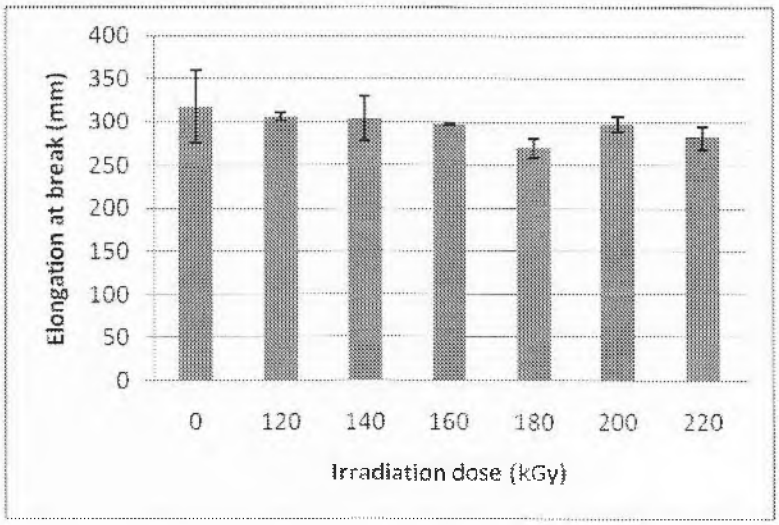

Figure 6. Elongation of thermoshrink PE tube at break

CONCLUSION

The experimental data suggest that exposure of thermoshrink PE tube to gamma rays induces chemical crosslinking. The gel content increased as the dose was increased. However, the value that give indication to crosslinking density occurs in polymer is much lower than that achieved from electron beam irradiation. This result can be further improved if the irradiation is performs in inert or vacuum condition to prevent photo-oxidative degradation.

Thermal analysis done in this study proves that crystallinity of PE tube is increased after irradiation. The highest percent of crystallinity recorded was at 160kGy (24%). This suggests that sample irradiated at this dose experiences molecular crosslinking and packed closely to crystallize. High gel content presented at doses up to 220kGy may be due to formation of gel as localized crosslinking that promotes inhomogeneity and thus reflected in decrease of the tensile properties.

The gamma irradiation in air induces molecular crosslinking and chain scission, simultaneously. The present results indicate that gamma irradiation of the thermoshrink PE tube in the air modifies the molecular structure of the material and changed its tensile properties. Gamma doses at 140 kGy and 160 kGy exhibits the highest tensile strength and modulus. Higher exposure yields no significant impact to the strength and modulus properties. Percent of elongation at break decreases proportionally to the radiation exposure and indicates the alteration to the molecular orientation that attributes stiffness to the samples.

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