# Polypropylene의 방사선멸균에있어 제 첨가제들에 의한 영향

강 길선○, 이 해방
생체의료고분자연구실, 한국화학연구소

# Radiation Effects on Polypropylene for Biomedical Application

Gilson Khang○, and Hai Bang Lee
Biomaterals Lab., KRICT, P.O. Box 107, Yusung, Taejon, 305-606, Korea

Studies on the formulations of the additives such as antioxidants, crosslinking agent, and *trans*-stilbeneoxide (StO) with polypropylene (PP) have been carried out to improve the resistance of gamma radiation sterilization. The irradiated PP and ethylene-propylene copolymers samples with control and additives were characterized by mechanical tester, colorimetry, and Fourier transform infrared spectroscopy with total attenuated reflectance mode (FTIR-ATR). Crosslinking agent and StO formulated PP showed remarkable radiation resistance and minimum discoloration. Also, radiation resistance of ethylene propylene copolymers with 3% of ethylene contents was better than that of PP homopolymers in the case of no additives. The proposed mechanisms of radiation stabilization with additives are also discussed.

## INTRODUCTION

Recently gamma irradiation for sterilization of polymeric medical devices has become increasingly important for industrial purpose due to both economic factors and ease of processability as substituents of ethylene oxide gas, and heat sterilization methods. When polymeric medical devices were exposed to gamma radiation, two basic structural changes were observed as (i) a chain scission and (ii) a crosslinking depending on the characteristics of the chemical structures[1~3].

Polypropylene (PP) has been finding wide use in number of medical application that take advantage of the relatively low cost, light weight, and chemical inertness[4]. However, PP degrades rapidly with irradiation of 2.5 Mrad dose[5~7]. There are two main degradation problems[1,3]: (i) discolorization which gives the devices an undesirable color tint as yellowing, and (ii) oxidative embrittlement causing loss of physical integrity. Moreover, the physical properties continue to deteriorate with time following irradiation, often leaving a product highly embrittled after a few months of normal aging. Since PP is a semi-crystalline materials, a high population of radicals remain in the crystalline regions which slowly migrate to the crystal surfaces where oxidation takes place causing even further degradation of the bulk properties of the materials[9].

In this study, the effects of some additives such as antioxidants, crosslinking agent, and stilbene oxide were studied to improve the resistance for gamma-radiation. Also, the effect of ethylene content of propylene ethylene copolymer (EPC) on the irradiation was investigated. Characteristic of oxidized irradiated-PP was observed by Fourier transform infrared spectroscopy with total attenuated reflectance mode (FTIR-ATR). The measurements of physical properties of irradiated PP were carried out colorimetry, and universal mechanical tester.

## EXPERIMENTAL

**Materials.** The materials used in this study are listed in Table I. PP homopolymers, EPC with 3 and 8% of ethylene contents and antioxidants are all commercially available grade. trans-Stilbene oxide (StO) and trimethylolpropantrimetacrylate (TMPTMA) were purchased from Jansen Chem. Co., and Tokyo Kasei Org. Chem., respectively. Chemical structure of StO is shown in Figure 1.

**Melt Mixing of PP with Additives.** Additive-free and additives with 0.1, 0.2, 0.5 and 1 parts per hundred resin (phr) were melt compounded into PP (4017 grade, Daehan Yuhwa Chem. Co. Ltd.) and EPC by Plasti-Corder R.E.O. 6 type (C. W. Brabender Instrument, USA) for 5 minutes at 200 °C, and 80 rpm rotor speed. Then additives free PP and EPC, and additives mixed-PP were pressed into stainless steel plate with 500 ± 50 μm cavity (10 × 10 cm, about 6.10~6.20 g) for 5 minutes at 200 °C by a heated laboratory press to fabricate sheet samples.

**Irradiation of Mixed PP.** All irradiation work was carried out in a IR-149 $Co^{60}$ irradiator (Nordion, Canada) which is commercially operated by Greenpia Co. Ltd. (Yoeju, Korea). Samples were exposed to a dose of 1.5, 2.5 and 4.0 Mrads at a constant dose rate of 0.091 Mrads/hr, and ambient temperature. Changes of color, characterization of FTIR-ATR spectra and mechanical properties as tensile strength and elongation of irradiated-PP samples were evaluated after 3 months storage at room temperature.

**Measurements of Color.** Changes of color for irradiated-PP were measured by XL 20 colorimeter (Garner Instrument, USA). The standard color index of X, Y, and Z of standard white board were 82.4, 84.6 and 98.0, respectively. Yellow index (YI) were calculated as following equation:

$$YI = 100 \times \frac{1.28X - 1.06Z}{Y} \quad (1)$$

At least four measurements were taken on each samples and the mean values calculated.

**Measurements of Tensile Strength and Elongation.** Tensile strength and elongation of irradiated PP with different dosage samples were measured by Universal testing machine (Instron 1125, Canton, MA, USA) with a cross head speed of 10 cm/min according to ASTM procedure D 638-80. They were measured at least four specimens for each samples.

## RESULTS AND DISCUSSION

**Gamma Radiation on Additives-Free PP and EPC.** Figure 2 shows color changes of the irradiated PP and EPC with different irradiation dose. Yellow index (YI) *mildly increased with increased irradiation dose. It can be* proposed that the discoloration is due to the formation of colored radiolysis products such as ketone and aldehyde functional group derived from oxidation of polymer chain backbone. The formation mechanism of these functional group from gamma-irradiated deterioration of PP is suggested as follows, reactions (2)~(5),

$$PPH \xrightarrow{\gamma\text{-radiation}} PP\cdot \quad (2)$$

$$PP\cdot + O_2 \rightarrow PPO_2\cdot \quad (3)$$

$$PPO_2\cdot + PPH \rightarrow PPOOH + PP\cdot \quad (4)$$

$$PPO_2\cdot \rightarrow \text{non-radical products, e.g.} \sim COCH_3 \quad (5)$$

Elongations of the irradiated PP homopolymer samples were steeply decreased with increased irradiation dose, whereas no changes of the tensile strengths were observed as shown in Figure 3. These embrittlements are due to direct radiation induced PP chain scission and subsequent autooxidation of the active radical sites formed during irradiation process (reactions (2)~(5)). However, increased elongations of the irradiated EPC were observed on 3 and 8% of ethylene contents at 1.5 Mrad dose. It can be suggested that chain crosslinking on EPC of 3 and 8% of ethylene contents was more predominant than that of chain scission compared with PP homopolymers at 1.5 Mrad dose.

**Effects on Irganox 1010 and 1076 for Irradiation.** Irganox 1010 and 1076 are typical commercially available hindered amines antioxidants. Figure 4 shows the color changes of the irradiated PP homopolymers with the incorporation of Irganox 1010 and 1076 varied from 0.1 to 1.0 phr. YI increased with increased of formulated amount with Irganox 1010 and 1076. We proposed that hindered amines stabilizer as Irganox 1010 and 1076 were not suitable for stabilization of gamma-radiation.

**Effects on Crosslinking Agent for Irradiation.** Figure 5 shows that the YI changes of TMPTMA incorporated PP with different irradiation dose were lower than that of control PP. Also, Figure 6 shows the effect of TMPTMA on elongation of formulated PP with irradiation. At 0.1 phr of TMPTMA, the changes of the embrittlement with irradiation dose were similar that of control experiment. However, the augmentation of elongation in irradiation samples was observed at higher content of TMPTMA as 0.5, and 1.0 phr. In particular, the elongation of irradiated PP samples significantly increased from 28 % (control) to 242 % (0.5 phr) and 316 % (1.0 phr) at 2.5 Mrad as normal operating condition of sterilization.

**Effects on *trans*-Stilbeneoxide for Irradiation.** The radiation resistance of PP was examined as a function of the incorporated amount of StO. The chemical structure of StO consists of two phenyl rings and epoxide group which are strong functional group for irradiation as shown in Figure 1. Stabilities for irradiation of StO mixed PP are shown in Figure 7. The YI changes of StO mixed samples are significantly decreased with increased the incorporated amount. In the case of 1 phr mixed PP, especially, only a very few changes of YI were observed as from 7.4 at 0 Mrad to 8.9 at 4.0 Mrad compared with 5.3 at 0 Mrad to 14.2 at 4.0 Mrad of additives free PP. In Figure 8 the changes of elongation of StO formulated samples were greatly reduced, whereas that of tensile strengths were almost same (results are not shown).

**Effects on Co-formulation of Crosslinking Agent and *trans*-Stilbeneoxide for Irradiation.** Figure 11 shows the radiation effects on the co-formulation of TMPTMA and StO as the function of the YI changes. In the case of the co-formulation in the 0.2 phr of TMPTMA and 0.5 phr of StO, small changes of YI were observed. The elongation of the co-formulated PP against irradiation was increased from 90% to 370% as shown in Figure 10. It can be explained that the mechanisms of irradiation stabilization are the functionalities of double bond in TMPTMA and epoxide and aromatic ring in StO. We can conclude that the incorporation methods with crosslinking agent and StO proposed in this study are very useful to improve the resistance against the gamma radiation sterilization of PP on the purpose of medical products.

## CONCLUSIONS

Results on the improvement of gamma-radiation resistance of PP for the purpose of sterilization have been presented by means of incorporation methods with additives as crosslinking agent and *trans*-Stilbeneoxide. Significant improvement of irradiation resistance of PP homopolymer was observed by the formulation with above 0.5 phr of TMPTMA and above 0.5 phr of StO, receptively. The mechanism can be suggested that the functionalities of double bond in TMPTMA and epoxide and aromatic ring in StO stabilize effectively the processes of chain scission and subsequent autooxidation of PP by radiation. Increased elongations of ethylene-propylene copolymers with 3 % of ethylene contents were observed due to decreased with crystallinity and more predominant crosslinking reaction than chain decomposition reaction compared with PP homopolymers.

**Acknowledgements.** This work was supported by the Ministry of Science and Technology. This improved method for gamma radiation sterilization was partially filed Korea Patents (Korea Patent Filed Number, 085486(1995. 6. 07))

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Table I. Lists of Materials Used in This Study

| Materials | Description | Sources |
|---|---|---|
| H306F | PP-Homopolymer | Yukong Petro. Chem. |
| 4017 | PP-Homopolymer | DaeHan Yuhwa Chem. |
| SFC550 | 3% of Et in EPC | Honam Petro. Chem. |
| SB520 | 8% of Et in EPC | Honam Petro. Chem. |
| Irganox 1076[a] | Antioxidant | Ciba Geigy |
| Irganox 1010[b] | Antioxidant | Ciba Geigy |
| Stilbene Oxide | | Jansen |
| TMPTMA[c] | Crosslinking agent | Aldrich |

[a]:n-octadecyl-3-(4'-hydroxy-3',5'-di-tert-butylphenyl) propionate, [b]:tetrakis[methyl -3(3,5-di-tert-butyl-4-hydroxy-phenyl)propionate], [c]:trimethylolpropantrimetacrylate

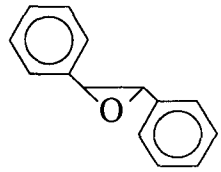

Figure 1. Chemical structure of *trans*-stilbene oxide.

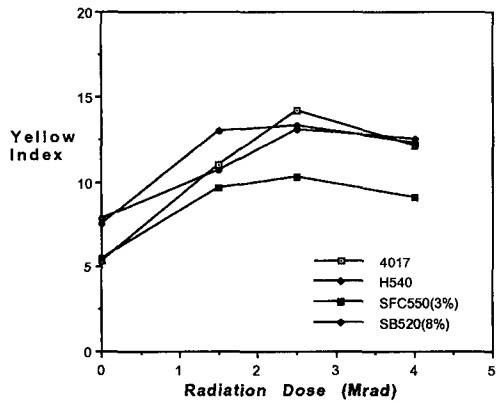


Figure 2. Color changes of the irradiated PP (4017, H540) and EPC (SFC550 (3% of ethylene contents), and SB520 (8% of ethylene contents)) with different irradiation dose.

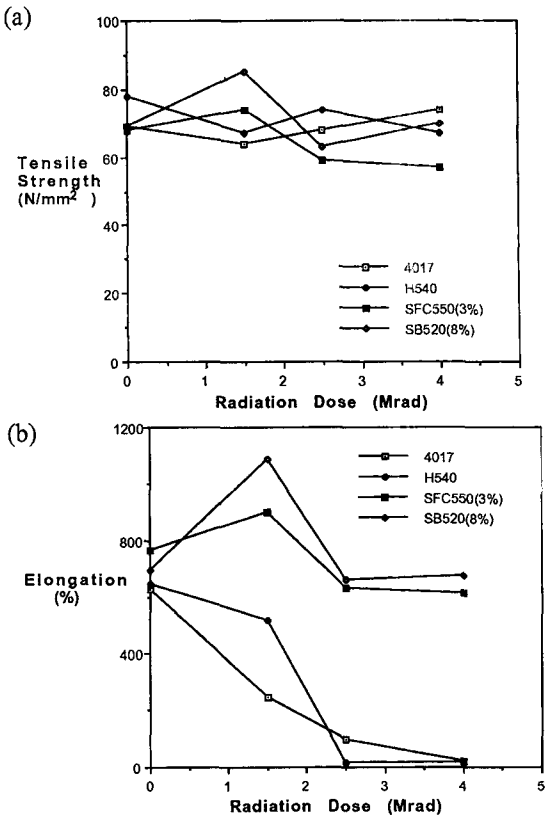


Figure 3. Tensile strength and elongation of the irradiated PP and EPC samples. (a) Tensile strength, and (b) Elongation.

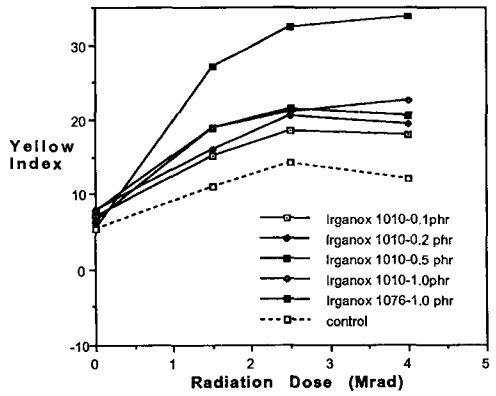


Figure 4. Color changes of the irradiated PP with the incorporation of Irganox 1010 and 1076 varied from 0.1 to 1.0 phr.

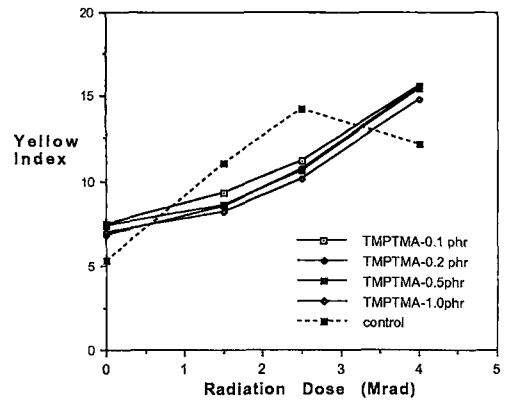


Figure 5. YI changes of crosslinking agent as TMPTMA incorporated PP.

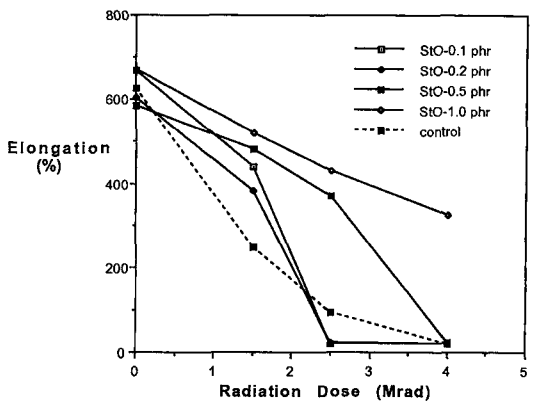


Figure 8. Changes of elongation of StO formulated samples with irradiation.

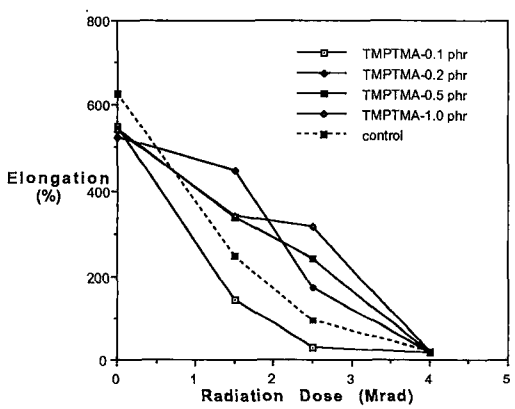


Figure 6. Effect of TMPTMA on elongation of formulated PP with irradiation.

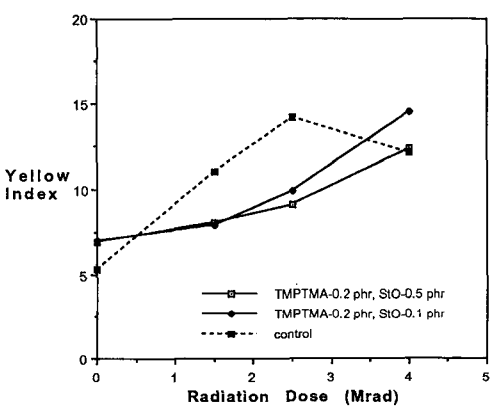


Figure 9. YI changes of the co-formulation of TMPTMA and StO with irradiation.

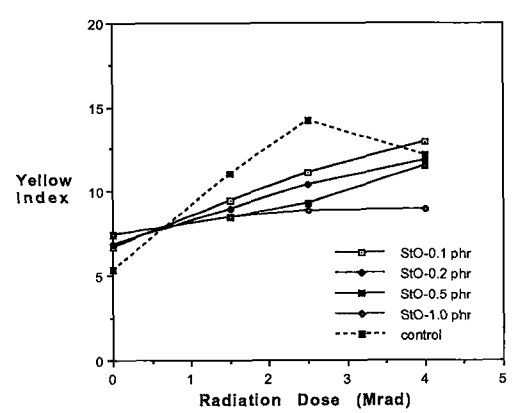


Figure 7. YI changes of StO mixed PP with irradiation.

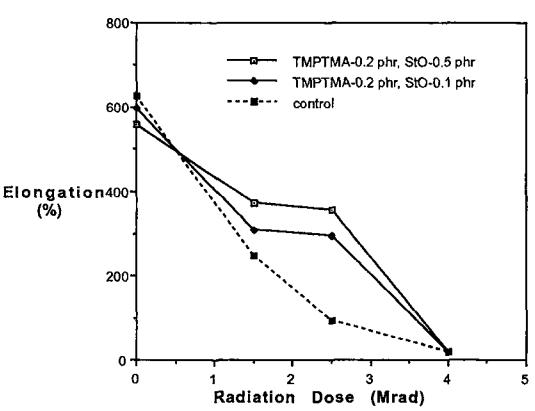


Figure 10. Changes of elongation and of the co-formulated PP with TMPTMA and StO after irradiation.