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《**Original**》

Effect of Trifunctional Monomers and Antioxidants on the Crosslinking Reaction of Polyethylene

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폴리에틸렌의 가교반응에 미치는 삼관능성 단위체와 산화방지제의 영향

변형직 · 이영철 · 김길정 · 윤병목

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Abstract

The crosslinking reaction and oxidative stability of low-density polyethylene were studied in the presence of trifunctional monomers and antioxidants with electron beam.

The trifunctional monomers used in this study are Trimethylolpropane triacrylate(TMPTA), Trimethylolpropane trimethacrylate(TMPTM) and Triallyl cyanurate(TAC). And the antioxidants are Irganox 1010(Pentaerythritoltetrakis[3-(3, 5-di-t-butyl-4-hydroxyphenyl)-propionate]), Santonox R(4, 4'-Thio-bis(3-methyl-6-t-butylphenol)), Nocrac D(N-phenyl-β-naphthylamine) and Bisphenol A(4, 4'-Isopropylidene bisphenol).

Among the monomers, TMPTA is the best crosslinking agent and prvides polyethylene with oxidative stability.

Among the antioxidants, Nocrac D is the best antioxidant for polyethylene.

요 약

전자선을 이용하여 저밀도 폴리에틸렌을 가교시킬때의 삼관능성 단위체와 산화방지제의 효과를 검토하였다. 가교촉진제로서는 삼관능성 단량체인 Trimethylolpropane triacrylate(TMPTA), Trimethylolpropane trimethacrylate(TMPTM)과 Triallyl cyanurate(TAC)가 사용되었고, 산화방지제로서는 Irganox 1010(Pentaerythritol-tetrakis[3-(3, 5-di-t-butyl-4-hydroxyphenyl)-propionate]), Santonox R(4, 4'-Thio-bis(3-methyl-6-t-butylphenol)), Nocrac D(N-phneyl-β-naphthylamine)와 Bisphenol A(4, 4'-Iso-propylidene bisphenol)가 사용되었다. 삼관능성 단위체중에서 TMPTA가 폴리에틸렌의 가교도를 제일 크게 높였으며 또한 산화안정성도 부여했다. 산화방지제중에서 Nocrac D가 폴리에틸렌에 가장 적당한 것으로 나타났다.

I. Introduction

The purpose of this paper is to provide information for producing Class IE cable material. Definition[1,2] of Class IE is the safety classification of the electric equipment and systems that are essential to emergency reactor shutdown, containment isolation, reactor core cooling, and containment and reactor heat removal, or otherwise are essential in preventing significant release of radioactve material to the environment.

In order to meet IEEE Standard[1,3] for qualifying Class IE equiment for nuclear power generating stations, we must provide polyethylene (PE) with thermal stability, radiation resistance and oxidative stability. Crosslinking of PE yields several improvements in physical properties.[4,5] The major improvement is the increase in thermal stability, which permits service use at higher temperature. Though the melting point of low-density polyethylene(LDPE) is about 120°C, crosslinked LDPE retains its figure at higher temperature than melting point. Such termal stability is indispensible when PE is applied to cable material of nuclear power generating stations.

There are two kinds of process in crosslinking PE. One is thermal process[6] which is adding peroxides or other free radical-generating compounds to PE and crosslinking PE with heat. The disadvantages of the thermal process related to uniform incorporation of chemical catalysts into the base PE and the presence of residual catalyst fragments in the final product. The other is the radiation process[4,5,7] which crosslinks PE with high energy radiation such as γ-ray and electron beam. The radiation-crosslinking process for PE insulation of cables has following merits over the thermal process. Because of easy control at ambient temperature it is more economical than the thermal process. And there is no pollution problem.

Irradiation of PE causes reduction in its resistance to oxidation.[8] It is considered that this is caused by accumulation of free radicals, trans-vinylene double bonds and tertiary carbon atoms. So we studied effects of antioxidants on oxidative stability and crosslinking reaction of PE. And we also studied effects of trifunctional monomers on the enhancement of crosslinking reaction of PE.

II. Experimental

II-1. Material

The polyethylene used in this study was grade No. 301 and 5301 of Korea Pacific Chemical Corp. And their properties are listed in Table 1.

Table 1. Polyethylene Specification

Grade No.	Melt Index*	Density*	Mv+
301	0.5	0.913	39,000
5301	0.25	0.924	59,000

* Data from catalog of Korea Pacific Chemical Corp.

+ Tested in p-xylene at 75°C

The tri-functional monomers were Trimethylolpropane triacrylate(TMPTA, Polysciences Inc.), Trimethylolpropane trimethacrylate (TMPTM, Polysciences Inc.) and Triallyl cyanurate(TAC, Wako Inc.).

The antioxidants were Irganox 1010(Pentaerythritol-tetrakis[3-(3, 5-di-tert butyl-4-hydroxyphenyl)-propionate], M.W. 1178, Ciba-Geigy), Santonox R(4, 4'-Thio-bis(3-methyl-6-t-butyl phenol), M.W. 359, Monsanto), Nocrac D(N-pheny-β-naphthylamine, M.W. 219, Daenaesh-inheung Inc.) and Bisphenol A(4, 4'-Iso-propylidene bisphenol, M.W. 228, Samjungdongup Inc.).

II-2. Preparation of Polyethylene Film

The samples were blended at 130°C, 300 RPM in a roll mixer which was made in KAERI for

10 minutes. And they were then pressed for 5 minutes at 125°C into 0.3mm thick sheets on a Carver hydraulic press. The pressure was released and then the films were quenched in running water. The films were kept in refrigerator before they were used. The samples were irradiated with a 300 KeV electron beam from ICT type electron accelerator. The irradiations were carried out at a dose rate of 6.0 Mrad sec^{-1} under ambient atmosphere.

II-3. Measurement of Gel Fraction and Oxygen Uptake

The gel fractions of the irradiated films were determined by Soxhlet extraction with boiling xylene for 48 hours followed by drying in a vacuum oven for another 10 hours at 50°C. Gel fraction(%) is defined as follows

$$\text{Gel fraction}(\%) = \frac{W_2}{W_1} \times 100$$

where W_1 is the initial weight of polyethylene film, W_2 is the weight of insoluble gel after xylene extraction.

One of the techniques for determining oxidative stability of polyethylene is oxygen uptake.[9~12] The oxygen uptake procedure is based on volumetric measurements of the rate at which oxygen combines with a polymer under isothermal conditions.

A modified apparatus suitable for this test is shown in Figure 1. The aging was carried out at 150°C.[13] The samples were exposed to oxygen atmosphere in a glass-reaction tube inserted in silicone oil bath. Above and below the reaction tube contained calcium oxide to absorb water

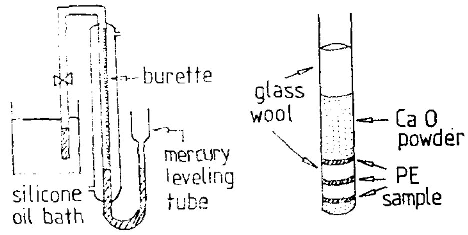

Fig 1. Schematic diagram of oxygen up take-apparatus.

and acidic oxidation products. The oxygen uptake was determined by means of a mercury burette connected to the reaction vessel. All data were corrected to 25°C and 1 atm, referred to 1 gram of the PE sample.

III. Results and Discussion

The PE films blended with each antioxidant and basic PE film were crosslinked by electron beam. The resulting gel fractions are shown in Figure 2-5. Antioxidants prohibit the crosslin-

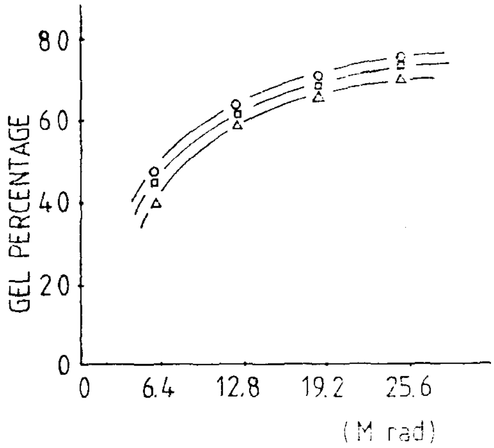

Fig. 2. Effect of Irganox 1010 concentration on gel fraction of PE-301.
○: PE 301 only □: 0.1 PHR
△: 0.5 PHR

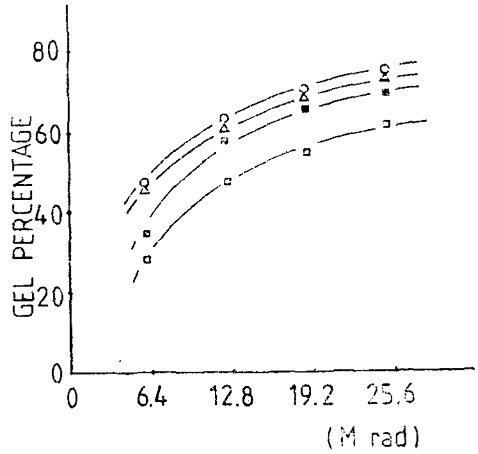

Fig. 3. Effect of Santonox R concentration on gel fraction of PE-301.
○: PE 301 only △: 0.02 PHR
■: 0.1 PHR □: 0.5 PHR

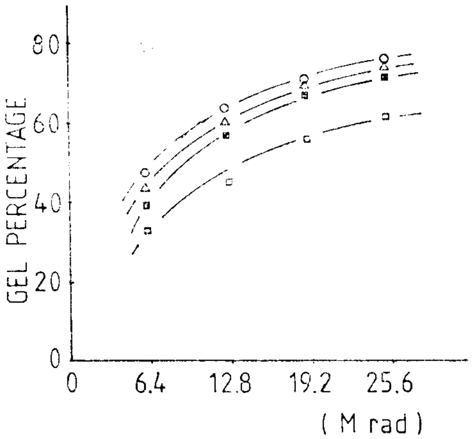

Fig. 4. Effect of Nocrac D concentration on gel fraction of PE-301.
○: PE 301 only △: 0.02 PHR
■: 0.1 PHR □: 0.5 PHR

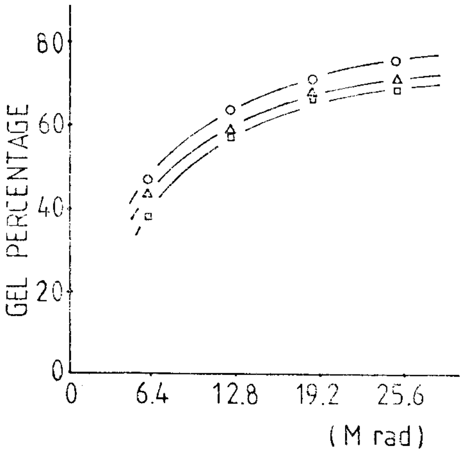

Fig. 5. Effect of Bisphenol A concentration on gel fraction of PE-301.
○: PE 301 only △: 0.1 PHR
□: 0.5 PHR

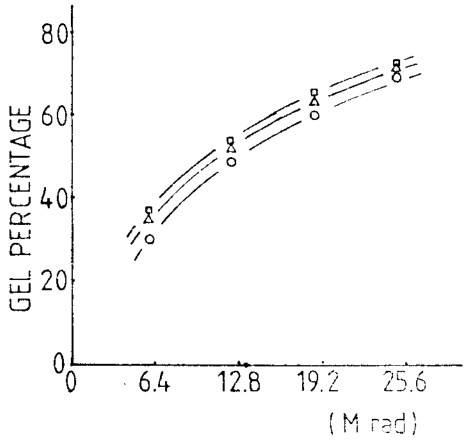

Fig. 6. Effect of TAC concentration and radiation dosage on gel fraction of PE-5301.
○: PE 5301 only □: 4m Mole/100g
△: 2m Mole/100g

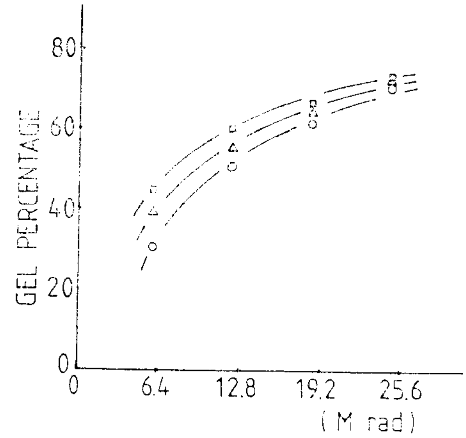

Fig. 7. Effect of TMPTA concentration and radiation dosage on gel fraction of PE-5301.
○: PE 5301 only □: 3m Mole/100g
△: 2m Mole/100g

king reaction. Because they react with active radicals which are produced by electron beam, leading to stable or inactive products. Namely antioxidants reduce the number of active radicals which are able to crosslink polyethylene chains. At 0.5 PHR(Parts per Hundred Resin) of each antioxidant, gel fraction decrease by 10~20%. Considering that antioxidants reduce th gel fraction of PE, it is necessary for PE to be blended with crosslinking agents which are promoting crosslinking reaction. Crosslinking agents[14,15] such as TAC, TMPTA and TMPT-M have been studied.

The PE films blended with each crosslinking agent were crosslinked by electron beam. The resulting gel fractions are shown in Figure 6-8. Gel-promoting effect of crosslinking agent at lower dosage is remarkable.[14] As the dosage increases, the gel-promoting effect of crosslinking agent decreases. Among three crosslinking agents TMPTA is the most active in gel enhancement.

The PE films blended with each crossli-

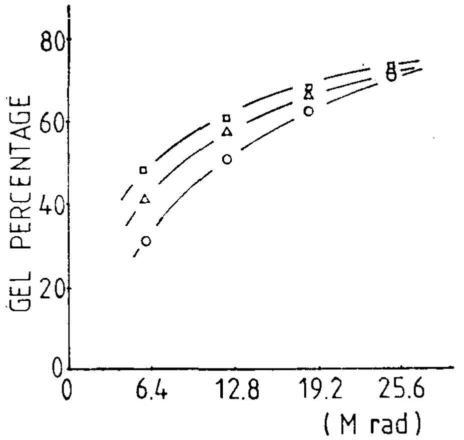

Fig. 8. Effect of TMPTM concentration and radiation dosage on gel fraction of PE-5031.
○: PE 5301 only □: 4m Mole/100g
△: 2m Mole/100g

nking agent and antioxidant were compared with basic PE film in gel fraction. The gel fractions at several dosages are shown in Table 2. In order to be easily compared with each other antioxidant, the concentrations of three antioxidants are modified.[16] Among various combinations, TMPTA is the most excellent in gel-promoting effect. According to Vagn Handlos,[17] the gel-promoting effect of three functional moers is due to the initial G(crosslinking) value of monomer. The initial G(crosslinking) value of TMPTM is 10.3, this quantity having been increased by a factor of 5 compared to pure PE. On the base of same antioxidants' functional group concentration, Nocrac D is the least

Table 2. Effect of Crosslinking Agents and Antioxidants on Gel Fraction of PE-5301. (unit: %)

CROSSLINKING AGENT (m Mole/100g)		ANTIOXIDANT (m Mole/100g[a])	RADIATION DOSAGE (M rad)				
			6.4	12.8	19.2	25.6	38.4
		0	30.8	51.9	60.9	70.1	77.1
TMPTM	2	0	39.5	55.7	63.4	72.0	77.6
	4	0	44.9	60.0	64.7	72.3	—
	2	Irganox 1010	37.5	54.9	62.4	70.4	—
	2	Santonox R	36.8	54.7	59.5	69.2	—
	4	Irganox 1010	42.8	58.5	63.7	71.9	—
	4	Santonox R	37.9	56.4	62.7	70.9	—
	4	Nocrac D	—	59.0	—	71.0	76.5
TMPTA	2	0	41.6	57.8	65.2	71.9	—
	4	0	48.0	60.8	66.1	72.0	—
	2	Irganox 1010	41.6	56.4	64.3	70.8	—
	2	Santonox R	37.0	54.7	61.0	69.1	—
	4	Irganox 1010	44.6	59.1	65.6	70.9	—
	4	Santonox R	42.9	58.5	65.0	70.8	—
	4	Nocrac D	—	58.1	—	71.6	78.6
TAC	2	0	35.1	53.3	63.4	70.9	77.9
			31.4[b]	50.4[b]	62.9[b]	65.1[b]	
	4	0	36.8	53.7	66.2	71.6	78.3
			32.7[b]	50.9[b]	65.7[b]	67.4[b]	
	2	Irganox 1010	31.8	50.9	63.1	67.9	—
	2	Santonox R	27.5	46.7	59.9	64.4	—
	4	Irganox 1010	53.3	52.1	63.2	66.7	—
	4	Santonox R	25.0	51.4	61.5	64.4	—
	4	Nocrac D	—	52.9	—	70.2	77.8

a Irganox 1010: 8.5×10^{-2}: Santonox R: $2\times8.5\times10^{-2}$: Nocrac D: $4\times8.5\times10^{-2}$
b Samples were annealed

in gel-reducing effect. So TMPTA and Nocrac D are proved to be the best choice for crosslinking agent and antioxidant, respectively. The gel fractions of annealed PE films blended with TAC are also shown in Table 2.

The gel fraction of annealed PE film was smaller than that of quenched one. Because the annealed PE film has wider crystalline region than quenched one.[18] In series of papers, Patel and Keller[19] studied crosslinking in single crystalline PE. They found that no crosslinks were produced in the crystalline core of the single crystals.

Oxygen uptake curves of irradiated PE films are shown in Figure 9. The results of a study of irradiated PE at 150°C show that the oxidation rate of PE is only slightly affected by dosage. According as the dosage increases, the oxidative stability of irradiated PE decreases. The result seems to be due to increasing tertiary carbon atoms,[20] transvinylene[21] and conjugated double bonds[22] which are more susceptible to oxidation, Mechanisms of PE oxidation have been widely studied by Biggs,[23] Shelton[24], and DeJonge.[25]

Figure 10. shows oxygen uptake rate of irradiated PE containing crosslinking agent. Irradiated PE containing TMPTA is most stable to oxidation. It is explained by the fact that TMPTA is most stable to oxidation. It is explained by the fact that TMPTA has less tertiary carbon than TMPTM and more reactive double bonds than TAC. It has been reported[26] that there were so many unreacted double bonds in TAC-blended PE after irradiation. And in case of PE blended with TAC and TMPTA, it is more stable than pure PE. This unexpected oxidative stability may be explained by the fact[27] that TAC and TMPTA caused PE to be higer crosslinking density than pure PE. With increasing crosslinking density the mobility of radicals formed in the thermal degradation decreases.[28]

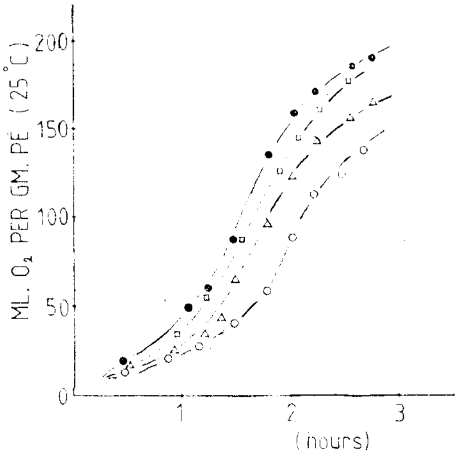

Fig. 9. Oxygen uptake of irradiated PE-5301 films at 150°C.
●: 38.3M rad □: 25.6 M rad
△: 12.8M rad ○: Non-irradiated

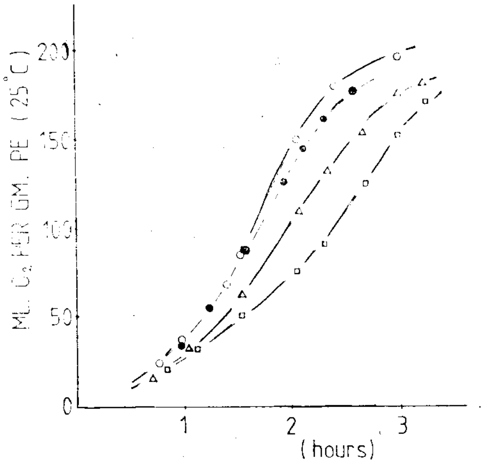

Fig. 10. Oxygen uptake of 25.6 M rad irradiated PE films containing crosslinking agent at 150°C.
○: TMPTM(4m Mole/100g PE)
△: TAC(4m Mole/100g PE)
□: TMPTA(4m Mole/100g PE)
●: Without any crosslinking agent

The relative effectiveness of the various antioxidants has been determined by direct measurement of the rate of oxygen absorption.[24,27,29] The induction period[30] in absorption of oxygen was used as a measure of the thermal oxidative stability of the PE. Effect of radiation dosage on induction period of PE films blended with antioxidant is shown in Figure 11. Induction period decreases according as radiation dosage

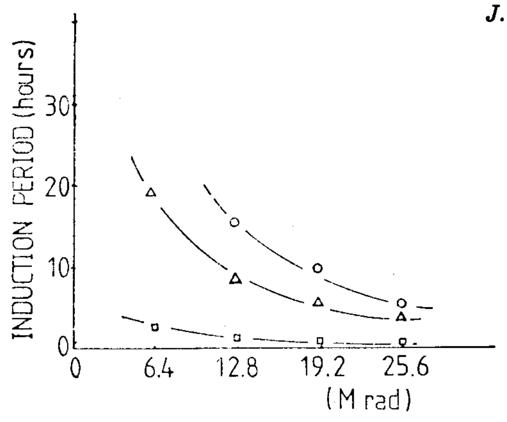

Fig. 11. Effect of radiation dosage and antioxidant on induction period of PE-5301 oxidation.
○: Santonox R, 0.1 PHR
△: Irganox 1010, 0.1 PHR
□: PE-5301 only

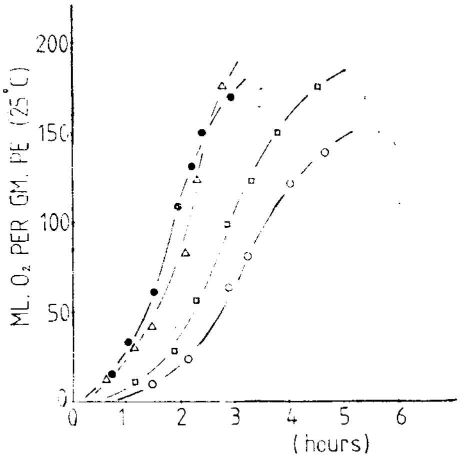

Fig. 12. Effect of antioxidant on oxygen uptake of 25.6Mrad irradiated PE-5301 films containing 4m Mole/100g TAC at 150°C.
△: Irganox 1010(0.085m Mole/100g PE)
□: Santonox R(0.17m Mole/100g PE)
○: Nocrac D(0.34m Mole/100g PE)
●: Without any antioxidant

increases.

These data enable us to preestimate the induction period of irradiated PE blended with Santonox R and Irganox 1010.

The effect of antioxidant on oxygen uptake of PE containing TAC is shown in Figure 12. The results show that Nocrac D enhanced oxidative stability of PE most greatly based on the same concentrative functional group such as amine and phenol group. And Nocrac D was reported[32] that it enhanced the radiative stability of PE.

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