

《Original》

Applications of Irradiation to Polyethylene for Flame Retarded Wire and Cable Insulation

Young Kun Kong, Hoon Seun Chang and Chong Kwang Lee
Korea Advanced Energy Research Institute

Jae Ho Choi

Inha University
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방사선에 의한 폴리에틸렌의 난연성전선 및 케이블에 관한 연구

공 영 건 · 장 훈 선 · 이 종 광

한국에너지연구소

최 재 호

인하대학교
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Abstract

The properties of polyethylene materials exhibit good insulation and radiation resistance, but exhibit poor flame resistance. Flame retardant properties of the polyethylene were improved by the radiation induced grafting or crosslinking. When the various flame retardants were fixed onto polyethylene, the amount of fixation in grafting was increased with the increase of radiation dosages. In the case of grafting, it is necessary for high grafting yield that the polyethylene films were swelled before irradiation with γ -rays or electron beams. It is the suitable method for the fixation of flame retardant that polyethylene samples were blended with various flame retardants at 125°C and then blended polymers were crosslinked by the electron beams at room temperature.

요 약

고분자피복재 중 polyethylene은 전기적 절연성 및 내방사선성이 좋으나 난연성이 결여되어 있으

므로 이 단점을 해결하였다. 방사선을 이용하여 polyethylene에 여러 종류의 난연제를 고착시켰는데 grafting 방법과 blending후 crosslinking 방법을 사용하였다. 일반적으로 grafting시키는 경우 시료에 난연제가 고착되는 양은 방사선선량이 증가할수록 증가하였다. Grafting 방법으로 polyethylene에 난연제를 고착시킬 때 시료를 팽윤(swelling)시켜서 난연제를 grafting시켜야 한다. Blending 한 후 crosslinking시킨 경우 시료와 난연제의 양을 자유롭게 조절하여 blending하여 crosslinking시킬 수 있는 이점이 있다. 난연제를 고착시키는 2가지 방법중 blending 후 crosslinking시키는 방법이 가장 바람직하다.

1. Introduction

The high versatility and large volume applications of polyolefins are well known and strongly established. This growth has been principally with unmodified polymers or with limited modification to obtain stability or to change surface properties. One application area, which is rapidly growing and extending the range of commercial polyolefins, is especially fire retardant compounds. For many applications the thermoplasticity of polyolefins leads to serious temperature limitation and flammability. So it is necessary to convert the polymer from thermoplastic to the thermoset structure through crosslinking of the polymer chain. The principle advantage of irradiation is that it provides a means of imparting a crosslinked structure to a thermoplastic polyolefins without the application of heat. The crosslinked structure is a key to imparting to the insulation¹⁻⁵⁾ and mechanical properties such as abrasion resistance and resistance to flow or penetration at elevated temperatures.

It is difficult to assign "typical" properties to any broad class of irradiation crosslinked insulation compounds such as polyolefins, polyvinyl chloride, or other base polymers⁶⁻⁸⁾. Various additives are commonly utilized to alter thermal stability^{9,10)}, flammability^{1,2,11-16)}, radiation resistant¹⁷⁻¹⁹⁾ and processibility^{20,21)} which obviously

affect insulation properties. Add to this the variability in properties of the various polymers and copolymers themselves, together with the ability to effect control of crosslink density by control of exposure to radiation.

The purpose of the present work is to investigate the influence of crosslinking or grafting on flame retardancy. Ultimate objectives are to obtain electric wires and cable with excellent resistance to flame, heat deformation and radiation.

2. Experimental

2.1. Materials

Polyethylene 5301 Chip (PE) from Han Yang Chemical Corp. and polyethylene film (0.1mm thick) were used. Flame retardants such as Triallyl phosphate(TAPA), 2-chloroacrylic acid(2-CAA) and Fyrol 76 were obtained from Polyscience Co.(U.S.A.) and were not purified further. Trimethylol propane triacrylate(TMPT, crosslinking agent) and n-hexane(swelling agent) were E.P reagent grade and were not purified further.

Acrylic acid(AA) was purified by vacuum distillation(20mmHg, 56°C) and used immediately after distilling or stored below 0°C.

2.2. Grafting Technique

An electron accelerator(High Voltage Engineering Corporation) with a maximum beam current of 25mA and operated at

300,000V was used in this work. The samples were laid on a conveyor, so that the samples were irradiated by the suitable doses. The beam current and conveyor speed were varied from 0 to 15mA and 9.4 to 29.2cm/sec. respectively. The operation current-speed curve established¹⁴⁾ was used to calculate delivered dose for all experiments. Polyethylene films (2.5cm × 15cm × 0.01cm) were soaked in n-hexane for 30 hours and then dried in a vacuum oven at 55°C for 24 hours. Glass tubes containing polyethylene films and the mixed flame retardant solution were capped and then stood for at least 24 hours in the dark before irradiation with ⁶⁰Co gamma ray at room temperature. The gamma dose rate used was 1.67 × 10⁵rad/hr.

2.3. Preparation of Polymer Blends

Polyethylene having a melt index 0.3 and a density of about 0.924g/cm³ were blended together on a hot roll mill in the adjusted amounts. The hot roll mill temperature ranged from 120°C to 130°C. The flame retardants were then added to the blend. After the flame retardants have been completely added to the blend, milling was continued for about 4.5 minutes to disperse the flame retardants throughout the polymer blend. After the milling was out, the treated hot polymer blends were cooled and cut to the strips. The strips were pressed at 18,000 pounds for 3 minutes by the controlled hot plate, 300°C (Carver Laboratory Press Model C, U.S. A.). The sample size of polyethylene was 12cm × 15cm × 0.1cm. The samples were crosslinked by electron beams which ranged from 5 to 15 Mrad.

2.4. Separation of Homopolymer, Gel % and Graft %

The graft yield was determined after

the removal of the occluded homopolymer. For the AA and Fyrol 76 grafted films, homopolymer removal was done by soaking the films in hot NaOH solution of 24 hours. After this treatment the grafted films were vacuumdried at 50-55°C for 24 hours and they reached constant weight. The resulting weight increase was used to calculate the graft yield. In the case of blend polymer, gel formation was determined after 50 hours Soxhlet extractions with xylene at 130-135°C.

"Graft %" and "Gel %" are defined as follows:

$$\% \text{ Graft} = \frac{W_2 - W_1}{W_1} \times 100$$

$$\% \text{ Gel} = \frac{W_3}{W_2} \times 100$$

where W_1 is the initial weight of PE film, W_2 is the weight of grafted film, and W_3 is the weight of insoluble gel after xylene extraction.

3. Results and Discussion

3.1. Fixation of Flame Retardants by Grafting

When flame retardants (TAPA, Fyrol 76) were grafted onto PE film at room temperature, the percent of grafting was increased with irradiation dose (see Fig. 1). The treated film was irradiated at the dose rate of 8.94Mrad/sec. in air by electron beam.

It is considered that the more dense radical sites were generated in prepolymer (PE film) at high dose, the more grafting occurs with flame retardants. Grafting yield of flame retardant with TMPT was higher than that of flame retardants. It is supposed from such results that most of TMPT radicals were combined with the monomer radicals and rest radicals were partially crosslinked or grafted. It is alw-

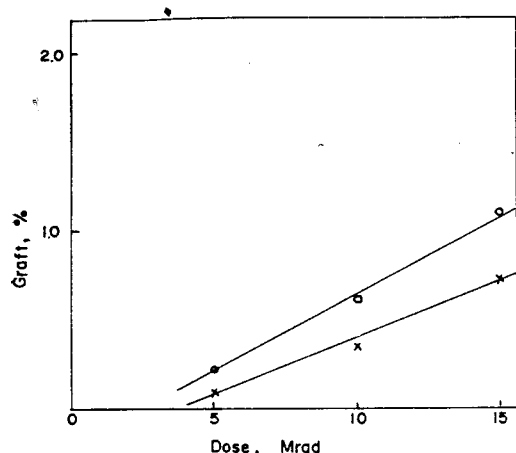


Fig. 1. Effect of Radiation Dosage on the Grafting of Flame Retardants on Polyethylene Film.
 × : TAPA/Fyrol 76=6/4 (by Vol.)
 ○ : TAPA/Fyrol 76/TMPT=5/4/1 (by Vol.)

ays reminded that PE is degraded at the extremely high dose.

Influence of acrylic acid on the grafting of flame retardants onto PE film is shown in Fig. 2. From Fig. 2, the percent of grafting was increased with increasing dose.

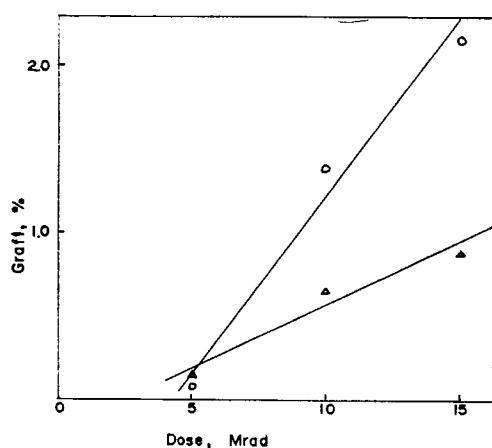


Fig. 2. Influence of Acrylic Acid on Radiation Grafting.
 △ : TAPA/Fyrol 76/AA=5/4/1 (by Vol.)
 ○ : TAPA/Fyrol 76/AA/TMPT=4/4/1/1 (by Vol.)

It is thought that the reason was similar to the case of Fig. 1. Comparing the Fig. 1 to Fig. 2, grafting % of flame retardant which was contained in AA, was higher than that of flame retardant only. It is supposed that AA was easily converted into AA radical by irradiation and thus AA radicals were participated in grafting or partially in crosslinking. In the case of Fig. 1 and Fig. 2, the graft yields were relatively low. It is interpreted that PE film was not swelled—PE film was so crystalline that monomers hardly could diffuse into it. The crystalline region were partially converted into the amorphous region by swelling agent. Therefore, it is possible that monomers are apt to react with polymer radicals—.

In the case of Fig. 3, PE film was swe-

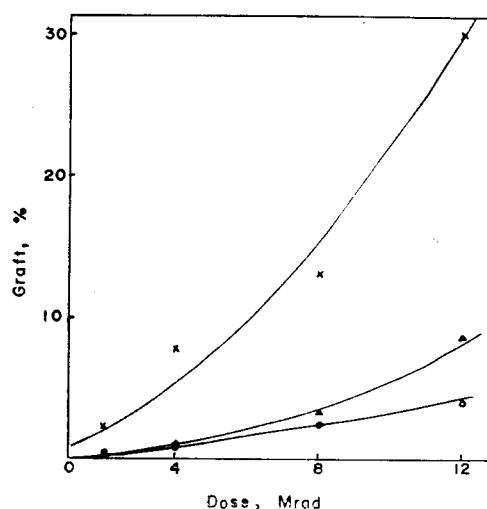


Fig. 3. Influence of Additives on Radiation Grafting.

Irradiation: Co-60, γ -ray

Swelling: 30°C, 24hrs in n-hexane

△ : TAPA/Fyrol 76/MeOH=30/20/2 (by Vol.)

× : TAPA/Fyrol 76/TMPT/MeOH=25/20/5/2 (by Vol.)

○ : TAPA/Fyrol 76/TMPT/AA/MeOH=20/20/5/5/2 (by Vol.)

lled and then stood in the flame retardants solution for 24 hours before irradiation with ^{60}Co γ -rays. It is shown from Fig. 3 that the flame retardants were grafted from 0.2% to 30.1%. The percent graft of flame retardants containing TMPT was rapidly increased with the irradiation dose, but the percent graft of flame retardants containing TMPT and AA was very slowly increased with the radiation dose. These experimental observations are explained that the reaction rate of TMPT in the mixed solution was slower than that of AA with TMPT in them, and thus such a fast reaction interfered with the grafting of flame retardants. Comparing the Fig. 1 with the Fig. 3, the percent graft in Fig. 3 was higher than the percent graft in Fig. 1. This result is considered as the swelling effect of PE film. It is necessary that PE film must be swelled before grafting.

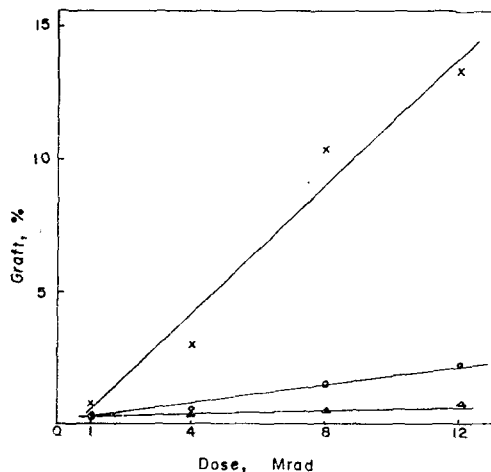


Fig. 4. Influence of Additives on Radiation Grafting.

Irradiation: Electron accelerator

Swelling: 30°C, 24hrs in n-hexane

△ : TAPA/Fyrol 76/MeOH=30/20/2 (by Vol.)

× : TAPA/Fyrol 76/TMPT/MeOH =25/20/5/2 (by Vol.)

○ : TAPA/Fyrol 76/TMPT/AA/MeOH =20/20/5/5/2 (by Vol.)

3.2. Fixation of Flame Retardant Blends by Crosslinking

Effect of phosphorus compound on gel formation in PE is shown in Fig. 5. It is

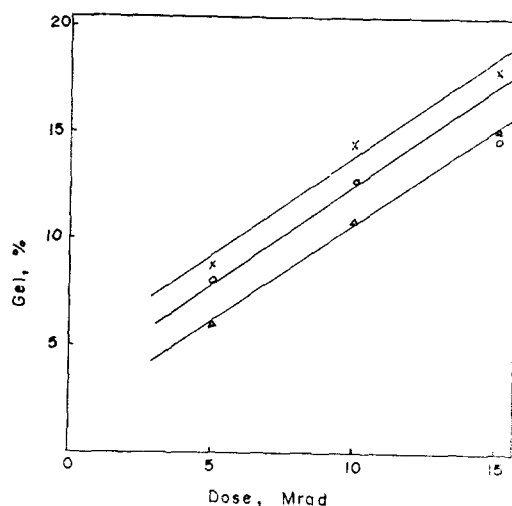


Fig. 5. Effect of Phosphorus Compound on Gel Formation in Polyethylene

△ : PE/TAPA/Shellac=100/5/10 (by Wt.)

○ : PE/TAPA/Fyrol 76=100/5/2 (by Wt.)

× : PE/TAPA/Shellac/Fyrol 76 =100/5/10/2 (by Wt.)

seen from the results that PE/TAPA/Fyrol 76 Blend was more crosslinked than PE/TAPA/Shellac, and the percent gel of PE/TAPA/Shellac/Fyrol76 Blend was higher than that of PE/TAPA/Fyrol 76 Blend. It is found from these observations that Fyrol 76 contains more double bonds than shellac, and thus the radicals which were produced from double bonds by irradiation had more opportunity to be crosslinked with the PE radicals. Fig. 6 illustrates the gel formation of Fyrol 76 mixture blends. As shown in Fig. 6, the increasing tendency to the degree of gel% was PE/Fyrol 76, PE/Fyrol 76/Shellac and PE/Fyrol 76/Shellac/TAPA orderly. The percent of PE gel was 9.6% and the percent

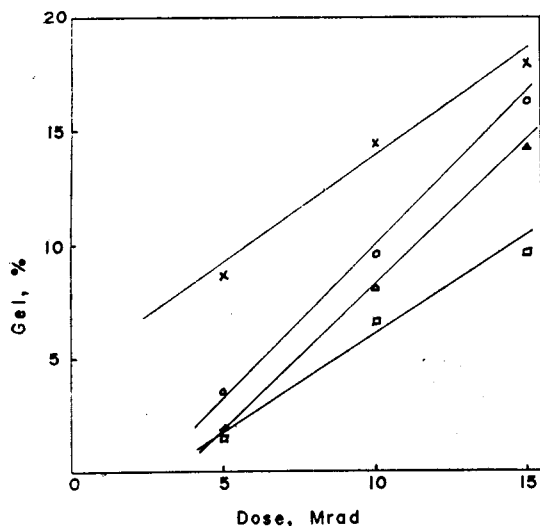


Fig. 6. Gel Formation of Fyrol 76 Mixture Blends.

- Δ : PE/Fyrol 76=100/2 (by Wt.)
 \bigcirc : PE/Fyrol 76/Shellac=100/2/10 (by Wt.)
 \times : PE/Fyrol 76/Shellac/TAPA=100/2/10/5 (by Wt.)
 \square : PE

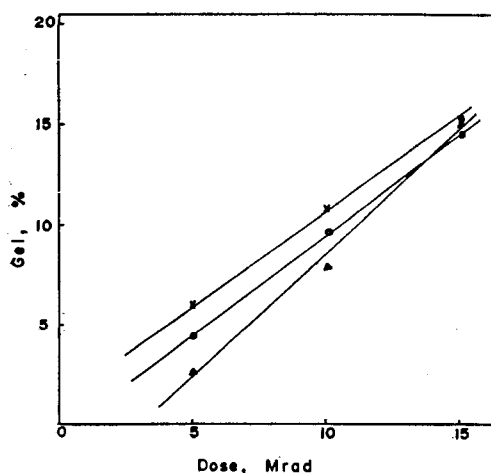


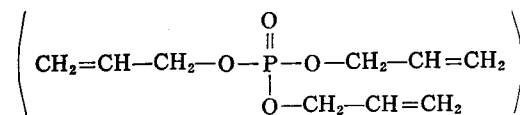
Fig. 7. Effect of Halogen Compound on Gel Formation in Polyethylene.

- Δ : PE/2-CAA=100/5 (by Wt.)
 \bigcirc : PE/2-CAA/Shellac=100/5/20 (by Wt.)
 \times : PE/TAPA/Shellac=100/5/10 (by Wt.)

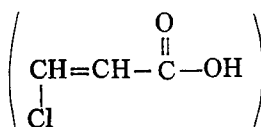
of PE gel treated with flame retardants was 18% at 15Mrad. It is supposed that the pure percent gel of flame retardants was 8.4% in this system.

When 2-CAA and/or shellac was crosslinked on the PE, the percent gel was increased with dose (see Fig. 7).

It is shown in Fig. 7 that the high dose made dense monomer radicals, and then those could be apt to react with PE radicals. Comparing 2-CAA with TAPA as gel effect, TAPA was more effective than 2-CAA. It is seen that TAPA



has three carbon double bonds, but 2-CAA



has one double bond.

The influence of various flame retardants

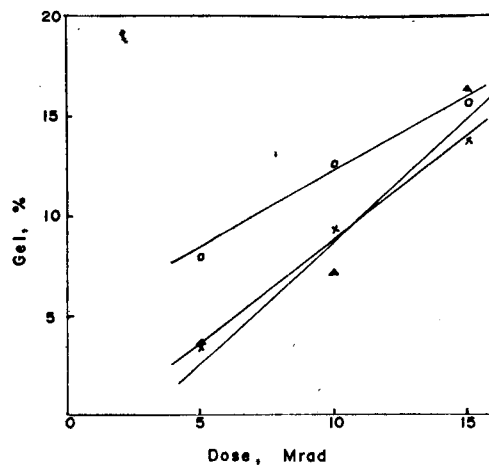


Fig. 8. Influence of Various Flame Retardants on Gel Formation

- Δ : PE/Fyrol 76/Shellac=100/2/10 (by Wt.)
 \bigcirc : PE/Fyrol 76/TAPA=100/2/5 (by Wt.)
 \times : PE/Fyrol 76/Glassfiber=100/2/10 (by Wt.)

nts on gel formation is shown in Fig. 8. It can be seen from the results that PE/Fyrol 76/TAPA was the highest gel% and PE/Fyrol 76/Glass fiber was the lowest gel%. It is considered that glass fiber could not be crosslinked and thus be attached into the network by physical bonding.

The effect of shellac mixtures on gel formation on polyethylene was shown in Fig. 9. From Fig. 9, it is said that PE/Shellac/Glass fiber/TAPA was the most effective combination in this system.

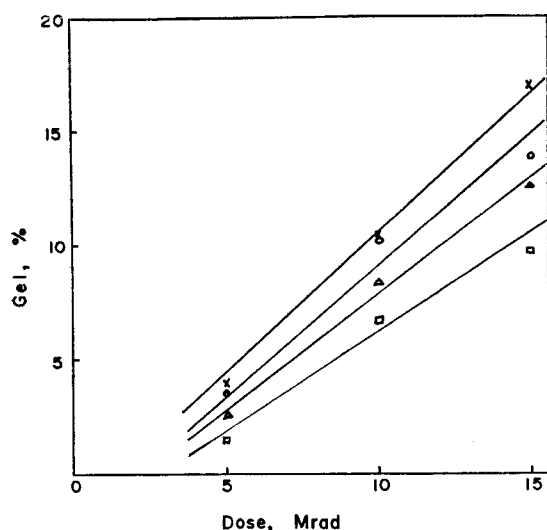


Fig. 9. Effect of Shellac Mixtures on Gel Formation on Polyethylene.

- △ : PE/Shellac=100/20 (by Wt.)
- : PE/Shellac/Glassfiber=100/20/5 (by Wt.)
- × : PE/Shellac/Glassfiber/TAPA=100/7.5/7.5/5 (by Wt.)
- : PE

3.3. The Flame Retardant Properties of the Modified PE

Gel % of PE/Fyrol 76/TAPE/Shellac(=100/2/5/10) v.s. Oxygen Index is depicted in Fig. 10. As shown in Fig. 10, the Oxygen Index of unmodified PE was 19 and the OI of modified PE was 26. Grafting yield of TAPA/Fyrol 76/TMPT/AA/MeOH

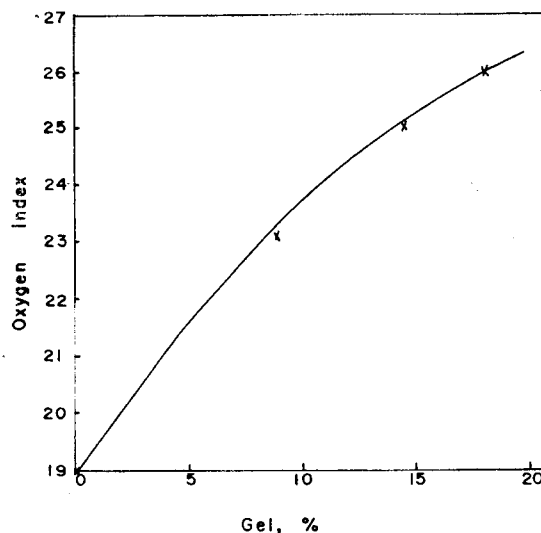


Fig. 10. Oxygen Index v.s. Gel % of PE/Fyrol 76/TAPA/Shellac Blend.

(20/20/5/5/2) v.s. Oxygen Index(OI) is shown in Fig. 11. The OI of PE film was 19

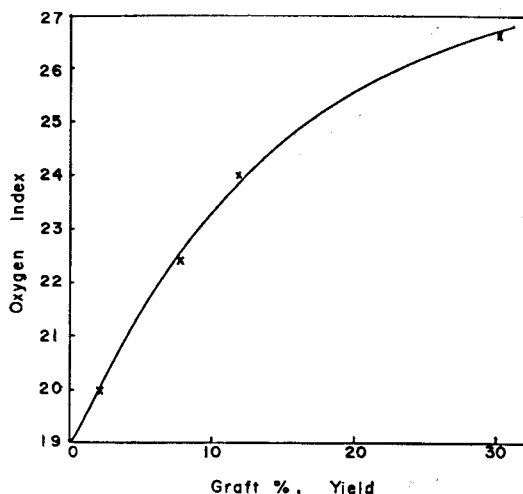


Fig. 11. Oxygen Index v.s. Flame Retardants Percent Grafting Yield.

but that of flame retardants(30%) grafted PE film was 26.7. The experimental data is reflected that the untreated samples were easily burned, but the modified sam-

ples had the considerable flame resistance in air.

In order to burn completely the modified sample, we must supply the oxygen. To mention the crosslinked PE, the OI of the crosslinked PE(at 15Mrad) was 19. Thus it had not character of flame retardancy. Fig. 12 is illustrated the thermogram of

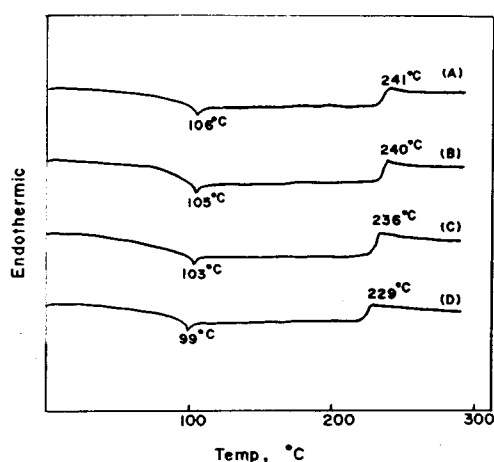


Fig. 12. Thermogram of Polyethylene Treated with Flame Retardants.

Sample Weight: 10mg

Inert Material: Al_2O_3

Atmosphere: Air

Sensitivity: $\pm 1000\mu\text{V}$

Heating Rate: $15^\circ\text{C}/\text{min}$

Sample Holder: GS 1307

Thermocouple: Pt-Pt-Rh10%

Sample: (a) PE/TAPA/Glass Fiber/Shellac Blend

(b) PE/Fyrol 76/TAPA/Shellac Blend

(c) PE/Fyrol 76/Shellac Blend

(d) PE

polyethylene treated with flame retardants. The flame retardants crosslinked PE had the high melting point and the improved glass transition temperature. The PE glass transition temperature was increased from 99°C to 106°C and its melting point was ranging from 229°C to 241°C at the same condition. According to such data, it

is found that the flame retardancy of the treated PE was increased.

4. Conclusion

To get a better flame retardance efficiency by the grafting of flame retardants onto PE film, PE film must be swelled in the n-hexane and then soaked in the flame retardant solution for 24 hours before irradiation. The composition of flame retardants, TAPA/Fyrol 76/TMPT/AA/MeOH = 20/20/5/5/2, exhibited the highest grafting yield (30.1%) among the various ratios of composition in its kind. The Oxygen Index of the grafted PE film was 26.7 and then the thermal stability of the grafted sample could be considerably high. The blending method has a merit of free control in mixing of flame retardants. Composition of PE, such as PE/Fyrol 76/TAPA/Shellac (=100/2/5/10) or PE/TAPA/Glass fiber/Shellac (=100/5/7.5/7.5) showed the high Oxygen Index value (~ 26). Such a modified PE shows not only the improved property of flame retardancy but also that of heat resistance.

References

1. M. Hagiwara et al., *J. Appl. Polymer Sci.*, **25**, 1541-1547 (1980).
2. M.F. Maringer et al., *Proc. Inst. Wire Cable Symp. 25th*, 350-355 (1976).
3. L. Spenadel, *Radiat. Phys. Chem.*, **14**, 683-697 (1977).
4. A. Barlow et al., *Plastic Engineering*, **32**(8), 42-45 (1978).
5. K.N. Venkatasubramaniam and K.P. Nanavaty, *Popular Plastics*, **20**, 6-9 (1975).
6. D.L. Schultz, *Rubber World*, 45-48, Nov. (1978).
7. N.M. Burns, *Radiat. Phys. Chem.*, **14**, 797-808 (1979).
8. 邊衡直 等, KAERI/347/AR-103/80 (1980).

9. E.W. Bennett, Jr., *Radiat. Phys. Chem.*, **14**, 947-951 (1979).
10. E.A. Abramyan and E.E. Finkel., *Radiat. Phys. Chem.*, **14**, 911-918 (1979).
11. R.J. Hovey, *Annu. Connector Symp. Proc.*, **10**, 259-272 (1977).
12. D.L. Buszard, *Fire Retard., Proc. Eur. Conf. Flammability Fire Retard., Ist*, 1977, 31-44 (1979).
13. P.G. Goavec, *Radiat. Phys. Chem.*, **14**, 61-67 (1979).
14. J.H. Choi et al., *J. Kor. Nuc. Soc.*, **12**(1), 1-8 (1980).
15. H. Braus and J.R. Woltermann, U.S. Patent 4,092,292 (1978).
16. J.D. Marshall and M.C. Kuklies, U.S. Patent 4,058,643 (1977).
17. J.B. Ardner et al., *J. Appl. Polymer Sci.*, **9**, 1585 (1965).
18. T. Nakagawa et al., *J. Appl. Polymer Sci.*, **15**, 747 (1971).
19. W.W. Tobin, "Modern Plastics Encyclopedia," 314 (1970-1971).
20. A. Barlow et al., *Radiat. Phys. Chem.*, **14**, 783-796 (1979).
21. S. Machi, *Radiat. Phys. Chem.*, **14**, 155-170 (1979).
22. G.L. Nelson, *Pap. Meet.-Am. Chem. Soc. Div. Org. Coat.. Plast. Chem.*, **36**(1), 217-223 (1976).