Improvement of Flame-Retardant Properties of Insulated Wires by Radiation Crosslinking

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Synopsis

Electric wires coated with polyethylene insulation crosslinked by a chemical method (gel fraction = 80%) and a jacket of self-extinguishing resin were produced. The jacket was crosslinked by irradiation with γ rays or accelerated electrons. Flame-retardant properties of the wire improved by γ-ray induced crosslinking up to ~60% gel fraction in the jacket. Beyond this point, however, the flame resistance rapidly decreased with increasing gel fraction. The flame resistance was also improved by irradiation with electrons, but the extent of the improvement was strongly dependent on the energy of incident electrons. This fact was attributed to the difference in the distribution of energy dissipation, i.e., crosslinks formed in the jacket. By introducing a double-layer structure to the jacket, in which the inner layer adjacent to the polyethylene insulation was crosslinked more densely than the outer layer, the wires were markedly improved in resistance to flame and heat deformation.

INTRODUCTION

Heat and flame resistance of plastics used as insulating or jacketing materials are very important properties for electric wires or cables. The radiation-induced crosslinking of polyethylene coatings on wire has been widely used to improve its resistance to heat deformation. However, polyethylene is combustible.

In order to impart self-extinguishing properties to coated wires, a process comprised of coating highly flame-resistant polymers like halogenated polyolefins or poly(vinyl chloride) over the combustible insulator has been proposed.[1] Gases generated through thermal decomposition of polyethylene lose their combustibility by reacting or mixing with flame-retardant compounds in passing through the layer of the jacket. Prolonged stay of the gases in the jacket layer will lower their combustibility. Since diffusion of gases in molten polymer mass is depressed by introducing network structure, crosslinking treatment on the jacket is a useful process for improving flame retardance.

The purpose of the present work is to investigate the influence of crosslinking on flammability. Ultimate objectives are to obtain electric wires with excellent resistance to flame and heat deformation.

EXPERIMENTAL

Structure and dimensions of an insulated wire sample are shown in Figure 1. A conductive copper piece was first coated with polyethylene containing dicumyl peroxide. It was put into a wire curing apparatus and heated for 30 min at 160°C

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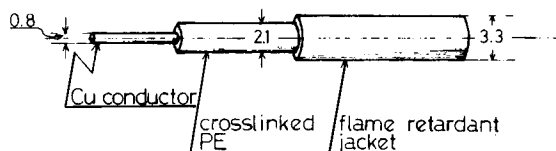
Fig. 1. Structure and dimensions of wire specimen (in units of mm).

for crosslinking of polyethylene up to a gel fraction (weight percentage of insoluble portion) ∼80% after extracting the soluble portion with boiling xylene for 20 hr. The crosslinked polyethylene was next covered with a 0.6-mm-thick layer of self-extinguishing resin having the following composition:

Polymer: Vinyl chloride (VCl)-grafted copolymer of ethylene (E) and vinyl acetate (VAC) (content of each monomer unit, VCl/E/VAC = 45/35/20 in weight ratio), 100 parts.

Flame Retardants: bisguanidinotetrabromophthalate, 12.5 phr; perchloropentacyclodecane, 12.5 phr; antimony trioxide, 5 phr.

Stabilizers: tribasic lead sulfate, 2 phr; lead stearate, 1 phr.

Antioxidant: 4,4′-thiobis(6-*tert*-butyl-*m*-cresol), 1 phr.

Carbon: 0.5 phr.

Dipropargyl maleate $(CH{\equiv}CCH_2OCCH{=}CHCOCH_2C{\equiv}CH$, DPM) and

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hexamethylene diacrylate $(CH_2{=}CHCO(CH_2)_6OCCH{=}CH_2$, HMA) were added

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to the resin composite as crosslinking accelerators. Radiation crosslinking treatment of the self-extinguishing resin was carried out using γ rays (dose rate = 5×10^5 rad/hr) from a ^{60}Co source or accelerated electrons (accelerating voltage = 0.27, 0.5, or 2.0 MeV) as radiations. The wire samples were irradiated from two parallel sides. The dose distribution is uniform throughout the jacket layer in the irradiation of γ-rays owing to their large penetration power. Boiling tetrahydrofuran was used for determining the gel fraction in the jacket.

Flammability test for the wires was conducted according to UL subject 758 (flame test for AWM designated "FR-1," 1971) in a three-sided enclosure (Fig. 2). A wire specimen 18 in. long was supported with its longitudinal axis vertical in a center of the enclosure. A burner flame was directed to the specimen so that
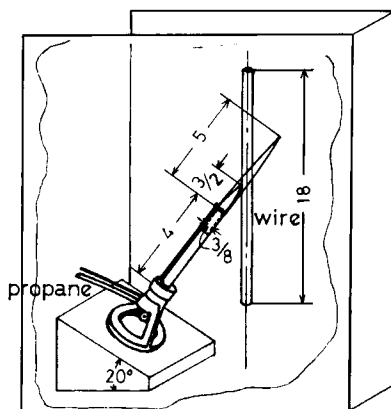

Fig. 2. Apparatus for flammability test.

the tip of the blue inner cone contacted the center of the wire. The test flame was applied six times (six rounds), in which the wire was heated for 15 sec with an interval of 15 sec between successive heatings. When combustion lasted for more than 15 sec after the removal of the test flame, the test flame was reapplied only after the flame went out. The shorter the burning time after the removal of the test flame, the better the self-extinguishing property of the wire.

RESULTS AND DISCUSSION

Figure 3 is a typical example of the effects of gel fraction in the jacket on the relation between flaming time and round number in a flammability test. The jacket was crosslinked by γ-ray irradiation at room temperature under an N_2 atmosphere. The burning time increased in round numbers until a maximum was reached at the third or fourth round (maximum round). Decrease in the burning time after the maximum round is due to consumption of combustible materials in the part exposed to the test flame. The maximum burning or flaming time (F_{max}) is decreased by moderate crosslinking (gel fraction = 58%), but F_{max} increases when the jacket is highly crosslinked (gel fraction = 80%). In the latter case, fairly large cracks were formed in the jacket during combustion in the maximum round.

Variation of F_{max} with gel fraction is shown in Figure 4. Values plotted in this figure were determined by taking an average from ten test pieces. The self-extinguishing property of the wire is independent of the amount of the cross-linkers added and is solely determined by the gel fraction in the flame-retardant layer. F_{max} is effectively decreased by crosslinking, which gives a gel fraction of about 60%. On the other hand, self-extinguishing properties decrease with increasing gel fraction above this point.

For wires irradiated in air with accelerated electrons, the variation of F_{max} with the gel fraction is shown in Figure 5. As was observed in the case of γ-ray irradiation, each class of samples gave a minimum point in F_{max}. In the case of 0.27-MeV electrons, the minimum point appeared at around 30% gel, in contrast to 60% for γ rays. Further, the increase in the flaming time after the minimum
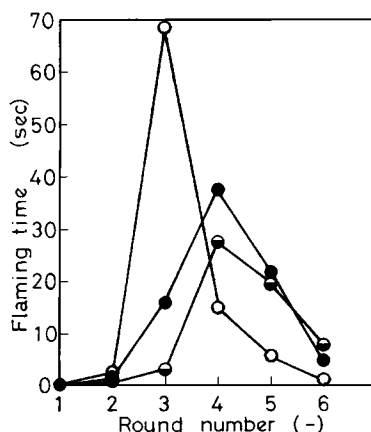

Fig. 3. Effect of crosslinking of flame-retardant jacket on relationship between flaming time and round number. Gel fraction (%): (●) 0; (◓) 58.5; (○) 80.2.
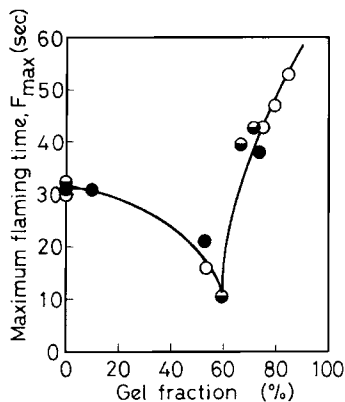
Fig. 4. Maximum flaming time F_{max} vs. gel fraction in case of γ-ray irradiation. Amount of crosslinkers (wt %): (●) 0; (◓) 0.5; (○) 3.0. DPM/HMA = $\frac{1}{2}$ (weight ratio).

point was less steep in the case of 0.5-MeV electrons when compared with those in the cases of 0.27 and 2.0 MeV. These differences in self-extinguishing behavior suggest that the combustion is influenced by the distribution of crosslinks in the jacket, which depends on the distribution of electron energy deposited in the flame-retardant layer and, hence, the penetration power of the electrons.

In order to picture the change in the amount of energy deposited along a direction of thickness, the depth–dose distribution relationship was estimated for electrons of 0.27, 0.5, and 2.0 MeV. The results were given in Figure 6. The depth–dose relationship for polystyrene[2] was converted to that for the jacketing material by correcting for a difference in density. The penetration power of 0.27-MeV electrons is not enough for crosslinking the 0.6-mm-thick jacket. The irradiation is effective only in the outer half of the jacket. Hence, a real gel fraction of the crosslinked part could be double the observed value (averaged value). The shift of the minimum point of F_{max}, which was observed at ~60% in the case of γ-ray irradiation, to about 30% in the irradiation of 0.27-MeV electrons resulted from the fact that the averaged gel fraction was used (Fig. 6). On the other hand, with 0.5- and 2.0-MeV electrons, crosslinking may occur effectively in the whole part of the jacket. However, the dose distribution is not
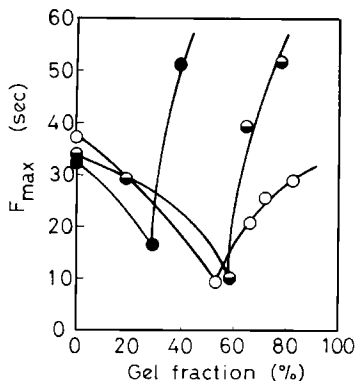

Fig. 5. F_{max} vs. gel fraction in case of accelerated electron irradiation. Energy of incident electrons (MeV): (●) 0.27; (○) 0.5; (◓) 2.0. Dose rate = 1 × 10^{5} rad/sec.
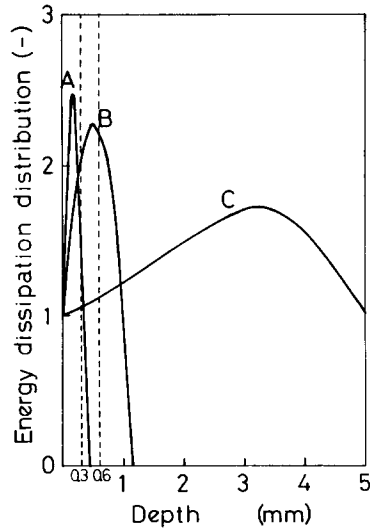
Fig. 6. Energy dissipation distribution of electrons. Energy of incident electrons (MeV): (A) 0.27; (B) 0.5; (C) 2.0.

uniform, even in the two cases. In contrast to the case of 0.27-MeV electrons, 0.5-MeV electrons produce the maximum dose point in the inner half, and, therefore, the inner part is probably more densely crosslinked than the outer half. Slow rise of F_{max} at high gel fraction has some relation to this type of heterogeneous distribution of crosslinks. Electrons of 2.0 MeV form more uniformly distributed crosslinks, since the difference in the energy dissipation distribution between the inner and outer halves is not as great. Almost the same curves were obtained in the relation between F_{max} and the gel fraction as those obtained by γ-ray irradiation.

In order to examine the effect of crosslink distribution on F_{max}, wires were molded so that the flame-retardant jacket was composed of two layers having different degrees of crosslinking (Fig. 7). Thus, the crosslinked polyethylene insulation was coated with two layers of the self-extinguishing resin which differed from each other in thickness and in the amount of crosslinkers (Table I). The wire was then exposed to γ rays up to 1.0, 2.5, or 5.0 Mrad. Since the two flame-retardant layers could not be separated, the gel fraction was measured for the entire jacket. The gel fraction of each layer can be estimated from the gel–dose relationship (Fig. 8), which was obtained for sheet samples molded separately and crosslinked under the same conditions used for the wire samples. The difference in the gel fractions between the two layers was 32.9, 16.9, and 18.7% at the dose of 1.0, 2.5, and 5.0 Mrad, respectively (Fig. 8).

In Figure 9 F_{max} was plotted against the observed (averaged) gel fraction. The
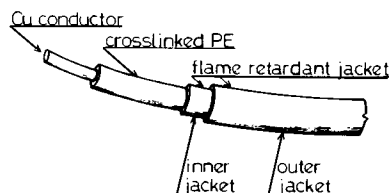

Fig. 7. Structure of wire having double-layer jacket of self-extinguishing resin.

TABLE I
Thickness of Layers of Double-Layer Flame-Retardant Jacket and Amount of Crosslinkers
Added[a]

	Outer jacket		Inner jacket	
Cable	Thickness, mm	Crosslinkers, wt %	Thickness, mm	Crosslinkers, wt %
A	0.4	0.5	0.2	3.0
B	0.3	0.5	0.3	3.0
C	0.2	0.5	0.4	3.0
D	0.4	3.0	0.2	0.5

[a] Crosslinkers: DPM/HMA = $\frac{1}{2}$ (weight ratio).

self-extinguishing property of the double-jacketed wire was remarkably improved, particularly in the region above 60% gel fraction, when the inner layer has a higher gel fraction than the outer layer (wires A, B, and C). It should be noted, however, that the highly crosslinked inner layer should be kept thinner than the outer layer because F_{max} tends to increase with increasing thickness of the inner layer. When the outer layer was more densely crosslinked than the inner layer (wires D), improvement in the self-extinguishing property was not obtained. Every specimen (wires D) produced cracks during combustion.

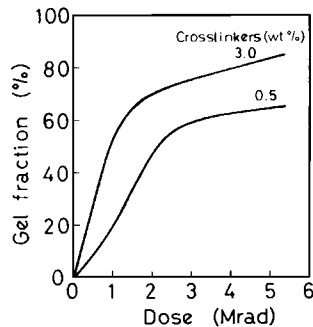Polymer flammability reactions occur in the gas phase, at the surface and in

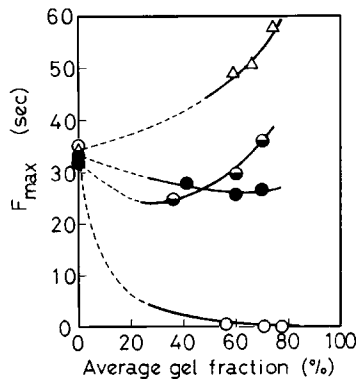Fig. 8. Gel fraction–dose relationship of resin used for the double-layer coating.

Fig. 9. Effects of double-layer jacket on self-extinguishing property of the wires. Structure of the wires (Table I): (O) A; (●) B; (◓) C; (△) D.

solid polymer. In the present case, when the wire is exposed to a flame, the self-extinguishing resin and the polyethylene melt and decompose. In passing through the jacket, combustible gas is mixed and/or reacts with flame-retardant compounds to form a self-extinguishing mixture. When the flame-retardant jacket becomes too thin owing to the flow of molten resin, it does not serve as a barrier to prevent the combustible gases from diffusing to the surface. On the other hand, since crosslinked polymer shows little flow even in the molten state, the diffusion of combustible gases will be reduced. Improvement of the self-extinguishing property of the wire by crosslinking (gel fraction up to about 60%) should be interpreted in the light of these considerations.

Other effects should be considered for highly crosslinked polymers. Since polymers lose their flexibility by excessive crosslinking, even small internal stresses may cause the formation of cracks. In the case of wires D, cracking might be caused by the excessive crosslinking in the outer layer which is under pressure from expansion of evolved gas and deformation of the loosely crosslinked inner layer. The cracks thus formed lower the self-extinguishing property of the wire by functioning as shortcuts for combustible gas to diffuse to the atmosphere. On the other hand, the outer layer crosslinked moderately in the cases of wires A, B, and C is rigid but flexible enough to prevent the formation of cracks. It might serve as a backup covering for the highly crosslinked inner layer.

Moreover, the wires show excellent resistance against heat deformation when the jacket has a gel fraction (averaged) of more than 70%.

References

1. P. O. Nicodemus, *U.S. Pat.* 3,546,014 (1970).

2. L. V. Spencer, *Energy Dissipation by Fast Electrons,* NBS Monograph 1, National Bureau of Standards, U.S. Department of Commerce, Washington, D.C., 1959.