

Protection Effects of Condensed Bromoacenaphthylene on Radiation Deterioration of Ethylene-Propylene-Diene Rubber

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Synopsis

As a continuation of a series of the studies on the flame and γ -radiation resistant modification of ethylene-propylene-diene rubber (EPDM), condensed bromoacenaphthylene (con-BACN) as a newly developed flame retardant was synthesized and its effects on the radiation resistance of EPDM were investigated. The radiation resistance evaluated by measuring tensile properties of irradiated sheets of 2 mm thick was found improved greatly by adding con-BACN together with ordinary rubber ingredients but decreased by decabromodiphenylether (DBDPE) that has bromins in aromatic rings as con-BACN. When EPDM sheets of 1 mm thick were irradiated in oxygen at a dose rate of 1×10^6 rad/h, the weight swelling ratio increased with increasing dose, indicating that oxidative main chain scission is predominant under the irradiation conditions. On the other hand, crosslinking was shown to be predominant in nitrogen. From the results of the swelling experiments with different additives, it was concluded that DBDPE accelerates both the main chain scission in oxygen and the crosslinking in nitrogen. In contrast to this, con-BACN reduced the chain scission in oxygen. This observation was accounted by the assumption that the influence of the oxidative chain scission is partly compensated by the concurrent crosslinking which takes place through additions of con-BACN to substrate polymers even in the presence of oxygen.

INTRODUCTION

In comparison with other hydrocarbon rubbers such as polybutadiene, polyisoprene, polybutene, copolymer of styrene and butadiene, etc., ethylene-propylene-diene rubber (EPDM) has known to have higher durability under radiation environments.^{1,2} It has acquired an important place as an insulation material for wires and cables in facilities for nuclear power generation plants, particle accelerators, and others where constant exposure to ionizing radiation is anticipated. It is usually modified into a flame retardant in practical use because of increased emphasis on safety against fire accidents. In practicing the flame-retardant modification, there are some problems associated with the use of flame-retardant reagents. One of those is that radiation resistance of the base rubber becomes lower when it is mixed with conventional flame retardants.

It is previously reported by the present authors that condensed bromoacenaphthylene acts as an excellent flame retardant for EPDM.³ In this paper as a continuation of a series of the studies on the flame- and radiation-resistant modification of hydrocarbon polymers, the effects of the newly developed flame retardant on the radiation-resistant properties of EPDM are reported.

EXPERIMENTAL

Synthesis of the condensed bromoacenaphthylene (con-BACN) was as described in the previous paper.³ It was a mixture consisting mostly trimers (average mol wt = 856, Br concn = 65.2%). Decabromodiphenylether (DBDPE), that is, one of popular flame retardants containing bromines in aromatic rings, and acenaphthylene (ACN) of reagent grade were used as reference materials in investigating radiation protection effectiveness of con-BACN. Both of them were purchased and used without further purification. EPDM (propylene concn = 34 wt %, I_2 value = 19.0) was supplied by courtesy of Japan Synthetic Rubber Co., Ltd.

Mixing of EPDM with the flame retardants and various rubber ingredients was first carried out on a hot roll at 120–150°C,³ and then with dicumyl peroxide (crosslinking agent) at about 40–50°C. The compound obtained was finally molded into sheets of appropriate thicknesses by pressing under a pressure of 100 kg/cm² at 160°C for 30 min. Irradiation of cobalt 60 γ -ray in air was carried out at room temperature with a dose rate of 5×10^5 rad/h. The irradiation under pure O₂ or N₂ atmosphere was carried out at a lower dose rate (1×10^5 rad/h). For measurements of tensile properties, the sheet samples were cut into dumbbells (JIS 3) before the irradiation. Strength and elongation at a break point at 25°C were recorded with Instron tensile tester, Model 1130 at a crosshead speed of 500 mm/min. To determine the amount of con-BACN and other additives extracted from EPDM films with boiling tetrahydrofuran (THF), GPC measurement was performed with a Waters ALC/GPC-202/R401 type gel permeation chromatograph. The detail of the measuring condition was reported previously.³

RESULTS AND DISCUSSION

Figure 1 shows the variation of the tensile strength and elongation at break as a function of irradiation dose. Composition of each sample was the same except that of the flame retardant and its synergist. Polymerized 2,2,4-trimethyldihydroquinoline (1.5 phr) as a heat stabilizer, stearic acid (1.0) as a lubricant, and sulfur (0.4) and ZnO (5) as coagents for crosslinking were added at 120°C. Sb₂O₃ (10–20 phr) as a flame-retardant synergist was also added to the specimens which have no flame retardant (BL). An important effect of the use of con-BACN is to reduce changes in the tensile properties due to the γ -ray irradiation. The ultimate strength is virtually constant up to a dose of 600 Mrad, while, in the cases of BL and DBDPE, it decreases first and increases with increasing dose after a minimum point at 100 Mrad. Every specimen used in this work was hardened and lost flexibility by the irradiation. The elongation, which gives a very useful measure for evaluating a degree of degradation, decreases continuously with increasing dose. When the elongation dropped to less than 50%, the irradiated sheets 2 mm thick became brittle and were easily broken by bending. Hence, the dose at which the elongation reaches 50% can be a measure for determining a radiation resistance (end point of useful life) of the rubber specimens used in the present work. It is apparent that the end point of the specimens containing con-BACN lies between 800 and 1000 Mrad, while that of those containing DBDPE, near 200 Mrad. With no flame retardant, the end point is at 600 Mrad. In this case, however, the surface of the irradiated sheet

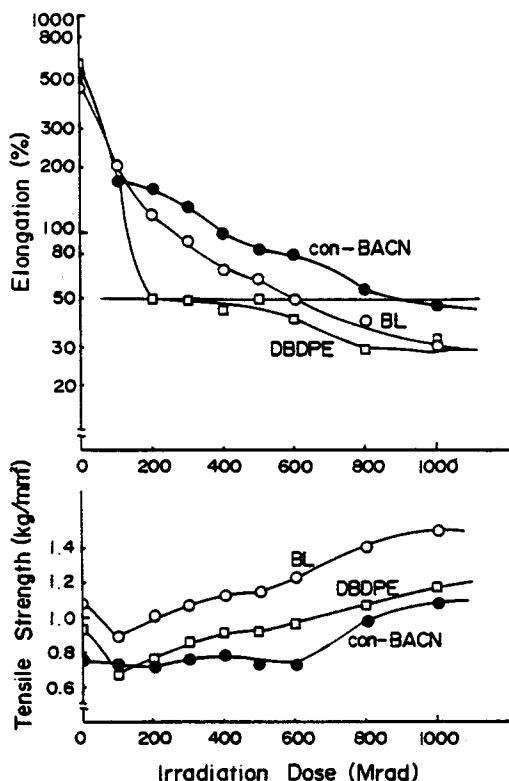


Fig. 1. Tensile strength and elongation of EPDM compounds as a function of radiation dose: con-BACN, 60 phr; DBDPE, 30 phr. Irradiation: ^{60}Co - γ -ray, 5×10^5 rad/h in air at RT.

had become very sticky owing to the degradation by oxidation far before that amount of dose was reached. Hence, it is apparent from these observations and the facts reported previously³ that con-BACN plays roles of an antiradiation reagent as well as a flame retardant.

When the irradiation is carried out to a thick sheet and/or at a high dose rate, the deterioration of EPDM proceeds by two different causes, degradation by oxidation in a surface part and crosslinking in an inner part. The ratio of two reaction zones varies, depending on the balance of rates of oxygen supply by diffusion and consumption by reaction. The samples used in the above experiments were too thick (2 mm) for the oxidation to prevail in a whole body of specimens when irradiated in open air at 5×10^5 rad/h. Under this condition, the boundary that separates two reaction zones was clearly observed by difference in color, which was thicker in the oxidized zone. The depth of the oxidized zone was about 0.345 mm. The decrease in the strength at low dose in the presence of DBDPE or in the absence of flame retardant is probably due to main chain scission by oxidation in the surface part. The gradual increase after the minimum point suggests that the influence of the crosslinking in the inner part exceeds that of the oxidative degradation at higher doses. Figure 2 shows changes in a gel fraction and a weight swelling ratio as a function of the dose. In both cases of DBDPE and BL, the gel fraction shows a significant decrease in the region between 200 and 600 Mrad. Low molecular weight polymers extractable with hot toluene might be produced as the result of the degradation in the surface

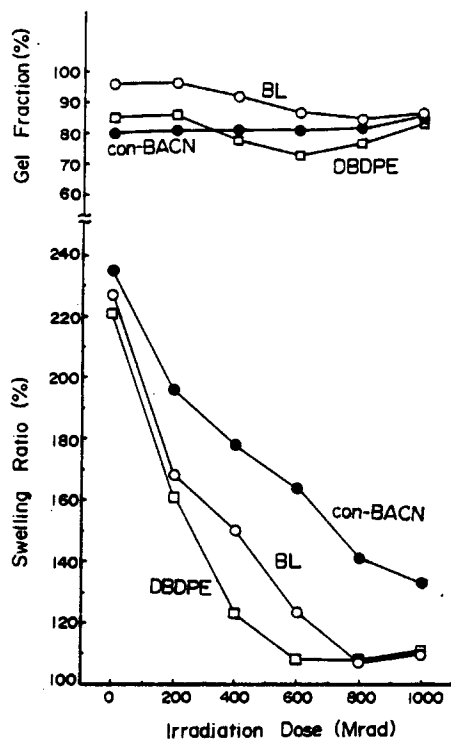


Fig. 2. Swelling ratio and gel fraction of EPDM compounds as a function of radiation dose: con-BACN, 60 phr; DBDPE, 30 phr. Irradiation: ^{60}Co - γ -ray, 5×10^5 rad/h in air at RT.

part. While in the presence of con-BACN, the gel fraction shows practically no change up to a dose of 600 Mrad and a slight increase between 600 and 1000 Mrad. This gel dose relationship implies that con-BACN inhibits the formation of low molecular weight polymers effectively even in the oxidation zone near the surface. The weight swelling ratio becomes smaller with increasing dose. This reduction is caused by the occurrence of crosslinking in nonoxidation zone. However, the data obtained with BL and specimens containing DBDPE at doses more than 400 Mrad include considerable errors because polymers degraded in the oxidation zone dissolved into toluene during the swelling experiment. The reduction of the swelling ratio, therefore, may not be directly related to the increase in crosslinking. Nevertheless, a very slow decrease in the ratio observed with con-BACN, especially in comparison with those with DBDPE, implies the occurrence of radiation protection due to con-BACN.

In order to elucidate the effects of the above additives on the degradation and crosslinking separately, thinner films (1 mm) of EPDM vulcanized by DCP after being mixed with con-BACN, DBDPE, or acenaphthylene (ACN) were irradiated under pure oxygen or nitrogen atmosphere at a dose rate of 1×10^5 rad/h. Under this condition, oxygen or nitrogen can diffuse throughout the film.⁴ ACN was used as a model compound to investigate the effect of fused aromatic rings in con-BACN, and each swelling ratio of nonirradiated EPDM was adjusted to fall to a similar level by controlling the amount of DCP. The results of the irradiation are listed in Tables I and II, and the relation between them is also plotted in Figure 3. As shown in Figure 3, the relative swelling ratios increase by the ir-

TABLE I
Swelling Ratio of EPDM Irradiated under Oxygen Atmosphere

Additive	Dose (Mrad)	Swelling ratio (%)	Relative swelling ratio	Number of crosslink points (mol/g)
BL (none)	0	345	1	1.33×10^{-4}
	21.5	455	1.32	0.90×10^{-4}
	46.5	656	1.90	0.59×10^{-4}
	66.5	1004	2.91	0.42×10^{-4}
ACN (15 phr)	0	352	1	1.29×10^{-4}
	21.5	394	1.12	1.10×10^{-4}
	46.5	398	1.13	1.10×10^{-4}
	66.5	426	1.21	0.99×10^{-4}
con-BACN (15 phr)	0	373	1	1.19×10^{-4}
	21.5	425	1.14	0.99×10^{-4}
	46.5	451	1.21	0.92×10^{-4}
	66.5	492	1.32	0.82×10^{-4}
DBDPE (15 phr)	0	351	1	1.3×10^{-4}
	21.5	530	1.51	0.75×10^{-4}
	46.5	895	2.55	0.45×10^{-4}
	66.5	1397	3.98	0.36×10^{-4}

radiation under oxygen, and decrease under nitrogen with increasing dose, irrespective of the kinds of the additives. From the plotted data it is apparent that DBDPE accelerates both the degradation in oxygen and the crosslinking in nitrogen. On the other hand, ACN retards both of them, and in the presence of con-BACN the degradation is retarded, but the crosslinking is accelerated.

Table III shows the amount of additives which reacted during the treatment for vulcanization of EPDM and the subsequent irradiation. ACN reacts completely in EPDM matrix already during the vulcanization process and shows no change by the irradiation. This can be attributable to dimerization or polymerization⁵⁻⁷ of ACN induced by heating in the presence of DCP. Almost half of the con-BACN is reacted during the vulcanization stage, and the amount of

TABLE II
Swelling Ratio of EPDM Irradiated under Nitrogen Atmosphere

Additive	Dose (Mrad)	Swelling ratio (%)	Relative swelling ratio	Number of crosslink points (mol/g)
BL (none)	0	330	1	1.42×10^{-4}
	19.2	284	0.86	1.79×10^{-4}
	45.8	248	0.75	2.21×10^{-4}
	97.8	200	0.61	3.15×10^{-4}
ACN (15 phr)	0	341	1	1.36×10^{-4}
	19.2	307	0.90	1.59×10^{-4}
	45.8	290	0.85	1.73×10^{-4}
	97.8	239	0.70	2.37×10^{-4}
con-BACN (15 phr)	0	351	1	1.3×10^{-4}
	19.2	293	0.83	1.71×10^{-4}
	45.8	244	0.695	2.29×10^{-4}
	97.8	205	0.58	3.03×10^{-4}
DBDPE (15 phr)	0	351	1	1.3×10^{-4}
	19.2	254	0.72	2.14×10^{-4}
	45.8	204	0.58	3.06×10^{-4}
	97.8	157	0.45	4.7×10^{-4}

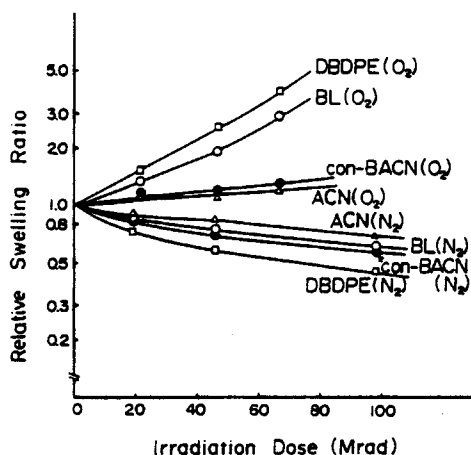


Fig. 3. Change in relative swelling ratio by irradiation under oxygen or nitrogen atmosphere: additive, 15 phr. Irradiation: ^{60}Co - γ -ray, 1×10^5 rad/h at RT.

reacted con-BACN increases gradually with increasing dose. Although it is less reactive than that of acenaphthylene, con-BACN has also polymerizable double bonds. The increase in the unextractable con-BACN indicates that they combine with EPDM. It is interesting to note that the reaction of con-BACN proceeds with almost the same rate in oxygen as in nitrogen. As pointed out earlier on the basis of the data given in Figure 3, con-BACN retarded the degradation in oxygen, but accelerated the crosslinking in nitrogen. If the combination of con-BACN with EPDM results in the formation of crosslink irrespective of the atmosphere, the effect of the main chain scission under oxygen can be cancelled to a certain extent by the concurrent crosslinking. In other words, the apparent retardation of the oxidative degradation in the presence of con-BACN is thought to be due to the occurrence of the reaction that has opposite influences. As

TABLE III
Conversion^a of Additives during Molding and γ -Ray Irradiation

Additive	Conversion			
	0	21.8 Mrad	66.4 Mrad	93.2 Mrad
ACN ^b	100%	—	100%	—
con-BACN ^c	49%	64.5%	69%	71%
DBDPE ^d	0.0%	3.6%	7.4%	8.0%

Additive	Conversion			
	0	19.2 Mrad	65.4 Mrad	97.8 Mrad
ACN ^b	100%	—	100%	—
con-BACN ^c	52%	60%	70.5%	76%
DBDPE ^d	0.0%	0.7%	3.2%	—

^a EPDM compounds were immersed in boiling THF for 24 h. Unreacted additive was determined by GPC measurement.

^b ACN was detected at 338 nm (UV).

^c Con-BACN, 340 nm (UV).

^d DBDPE, 310 nm (UV).

shown in Table III, the reaction of DBDPE scarcely occurs. The enhancement by DBDPE of both the crosslinking in nitrogen and the degradation in oxygen implies the radiation sensitive nature of halogen-substituted hydrocarbons. Bromine atoms ejected from DBDPE attack surrounding polymers to form radicals which undergo oxidation in the presence of oxygen or crosslinking in nitrogen.

From the swelling data given in Tables I and II, the number of crosslink points [τ (mol/g)] can be calculated using Flory's equation as below⁸:

$$\tau = -\frac{1}{2} \frac{\ln(1-\nu) + \nu + \mu\nu^2}{V\rho(\nu^{1/3} - \nu/2)} + \frac{1}{\bar{M}_n}$$

where ν is volume fraction of the swollen polymer, μ is Huggins' coefficient which was assumed to be 0.4 reported for atactic polypropylene-toluene,⁹ $\rho = 0.85$ g/cc is density of EPDM, \bar{M}_n is the number average molecular weight of original EPDM ($\bar{M}_n = 34,000$), and V is the molar volume of toluene (106 cc/mol). As seen in Figure 4, plots of the number of crosslinks against the dose in a logarithmic scale give straight lines. From the viewpoint of radiation protection, it is desirable that the additives can reduce radiation reactions like the crosslinking and the main chain scission to a degree as low as possible, which usually influence mechanical properties seriously. Though their complete inhibitions are very difficult, it is possible to control ratio of frequency of their occurrences. When they occur with an equal frequency, a line with zero slope is obtained. The positive slope of the lines indicates that the crosslinking takes place more frequently than the main chain scission, and the negative slope, vice versa. Using the slopes of the lines plotted in Figure 4, the excess frequency of a dominant reaction of two concurrent ones under a certain atmosphere can be calculated and the results are listed in Table IV as in a form of excess G values. ACN is very effective in reducing the excess G values, irrespective of the irradiation atmosphere. This fact suggests the reduction of absolute G value of each reaction itself. As is well established, certain aromatic compounds protect substrate polymers by acting as energy transfer agents to dissipate energy absorbed by irradiated systems.^{10,11} The same function can be expected to be possessed by

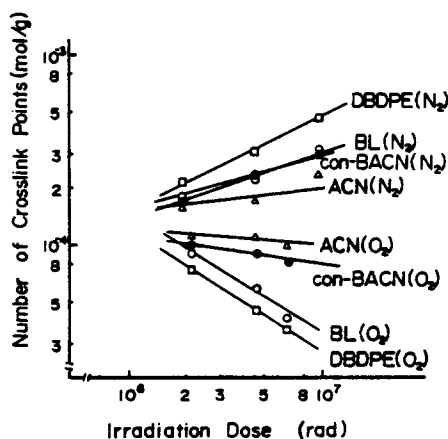


Fig. 4. Change in crosslink points by irradiation under oxygen or nitrogen atmosphere: additive, 15 phr. Irradiation: ^{60}Co - γ -ray, 1×10^6 rad/h at RT.

TABLE IV
Effects of Irradiation Atmosphere on Excess G_x and G_s of EPDM Compounds

Additive	Irradiation atmosphere	
	O ₂	N ₂
	Excess G_x value ^a (0–46.5 Mrad)	Excess G_x value ^b (0–45.8 Mrad)
BL	1.6	1.8
ACN	0.4	0.85
con-BACN	0.6	2.2
DBDPE	1.9	4.0

^a $G_s - G_x$.

^b $G_x - G_s$.

the aromatic rings in ACN. Detailed studies on roles of ACN in the energy transfer process are now being carried out in our laboratory.

In spite of the fact that it contains bromines as DBDPE, con-BACN reduces effectively the excess G_s in oxygen atmosphere. As postulated in the foregoing discussion, if the combination of con-BACN with the substrate polymers leads to the formation of a crosslink, it serves to cancel the effects of the concurrent chain scission in oxygen on the one hand, but, on the other hand, it should enhance those of the crosslinking in nitrogen. This situation is revealed by the fact that the excess G_x (under nitrogen) becomes larger in the presence of con-BACN than in the absence of the additive (BL). The compensation effect in oxygen atmosphere seems very important characteristics of con-BACN for radiation stabilization of EPDM. Smaller excess G_x in the case of con-BACN than DBDPE may result from a dissipating energy transfer associated with fused aromatic rings in con-BACN.

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