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The Effects of Additives for Deterioration of Ethylene Propylene Rubber by γ-ray Irradiation

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When polymer material is irradiated with γ-rays, it begins to deteriorate on account of various combined causes. To solve this deterioration problem, additive effects of aromatic oil, antioxidant, ultraviolet absorber and lead-based stabilizer, when added to EP rubber based on ethylene-propylene-diene terpolymer, have been studied. It has been found that lead-based stabilizers are not effective for improving radiation resistance, but that the other additives are effective although some differences in their effectiveness exist even among those with similar chemical structures. It has also been found that an increased amount of additive markedly improves the radiation resistance of EP rubber.

1. Introduction

Various polymer materials are used in nuclear-energy related facilities including nuclear power stations. In particular, materials with an extremely high radiation resistance are required for nuclear-fuel reprocessing plant. With the irradiation by γ-rays, polymer materials suffer various chemical changes such as the breakdown of their molecules, the generation of some decomposition gases and the formation of new bonds among their molecules (cross linking) and unsaturated bonds. These chemical changes lead to the gradual deterioration of the materials.[1] It is considered that in the deterioration of polymers by irradiation the effect of its oxidation plays an important role.[2] For that reason, the addition of various kinds of common antioxidants to polymer materials has been studied as the method of improving radiation resistance of polymers. In this work, a study has been made to examine the improvement in radiation resistance of EP rubber when aromatic oil, ultraviolet absorbers and lead-based stabilizers as well as those antioxidants are added to EP rubber, which is extensively used as the insulating material for electric wires and cables. Some effective additives have been selected from all the tested ones, and the effect of their amount has been examined.

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2. Experimental

2. 1 Preparation of samples

The additives listed in Table I were added for flame-resisting nonhalogen EP rubber compound. In the test for selecting additives, the percentage of additive amount was 4.5 wt% over compound. However, for those additives whose compatibility with EP rubber was poor and which caused bleeding or blooming, the percentage of additive amount was 1.5 wt%. On the other hand, in the test for examing the effect of added amount, the additive-content range of 7.0−23.0 wt% was employed. Compound was kneaded with additive, and then it was formed into a piece of press sheet with a thickness of about 1 mm.

2. 2 γ-ray irradiation

Sheet specimen was attached to the outside of a stainless drum (outer diameter is 400 mm) and fastened by bandaging glass tape. Using ^{60}Co (dose rate: 0.73−0.80 MR/h) as the radiation source, γ-rays were irradiated to these test specimens under the atmospheric condition (room temperature). In the test for selecting additives, the levels of irradiation dose were 2 and 5 MGy, while in the test for examining the effects of added amount they were 5, 7 and 10 MGy.

2. 3 Test items and test methods

Both test items and test methods used in this study were as follows:

1) Tenisile strength and elongation: JIS No.3 dumbbel shaped samples were cut out from the irradiated sheets, and the tensile strength and the elongation of the samples were measured. The tensile rate used was 200 or 500 mm/min (measuring temperature: 23±2°C).

2) Volume resistivity: Volume resistivity was measured in one minute after applying DC 500 V (measuring temperature: 23±2°C).

3) Alternating current breakdown voltage: AC breakdown voltage was measured by continuously increasing the voltage at a rate of 750 V/sec.

3. Results and Discussion

In the following description, the type of additive is expressed with symbols shown in Table I.

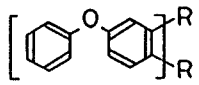
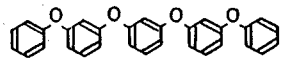
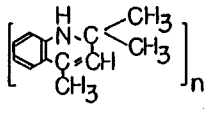
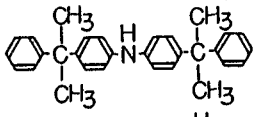
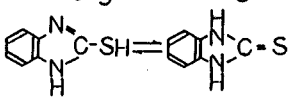
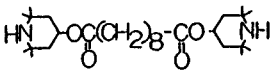
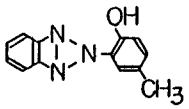
3. 1 Selection of additives

3. 1. 1 Tensile strength

Figures 1 a) and b) show the relationship between irradiation dose and tensile strength. As apparent from a), in case of specimen without any additive the γ-ray irradiaion caused no significant change regarding their tensile strength. However, for those specimens added with aromatic oil it was noticeable that their tensile strength tends to increase with increasing irradiation dose. Among those specimens

to which antioxidants were added, both B-1 and B-2 showed a decrease of tensile strength up to 2 MGy but an increase for higher doses. Though B-3 incerased up to 2 MGy, after that no more increase occurred. As apparent from b), the tensile strength of the specimen group containing ultraviolet absorbers did not change up to 2 MGy, but increased for higher doses. The tensile strength of the specimen group containing lead-based stabilizer was found to increase up to 2 MGy, but stabilized for higher doses. This fact indicates that the hardening of the specimens begins at a low level of irradiation dose.

Table 1 Classification of additive

Classification	Sym.	Chemical names	Structural formula
Aromatic oil	A-1	Alkyl diphenyl ether	
	A-2	Pentaphenyl ether	
Antioxidants	B-1	Polymerized trimethyl dihydroquinoline	
	B-2	4, 4' (α ,α-Dimethyl benzyl) diphenylamine	
	B-3	2-Mercaptobenzoimidazole	
Ultra-violet light absorbs	C-1	Bis (2, 2, 6, 6,-tetramethyl-4-piperidil) sebacate	
	C-2	2-(2'-Hydroxy-5'-methyl phenyl)-benzotriazole	
Stabilizers of lead	D-1	Tribasic lead sulphate	$3PbO \cdot PbSO_4 \cdot H_2O$
	D-2	Litharge	PbO

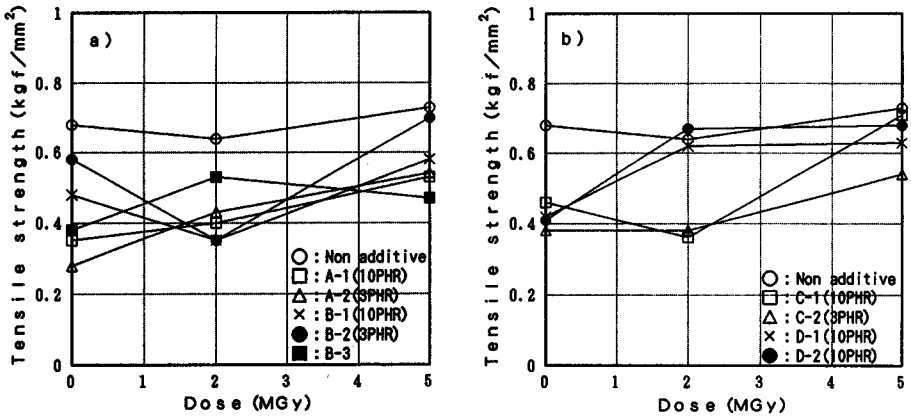


Fig.1 Dose-tensile strength (for selection of additives).

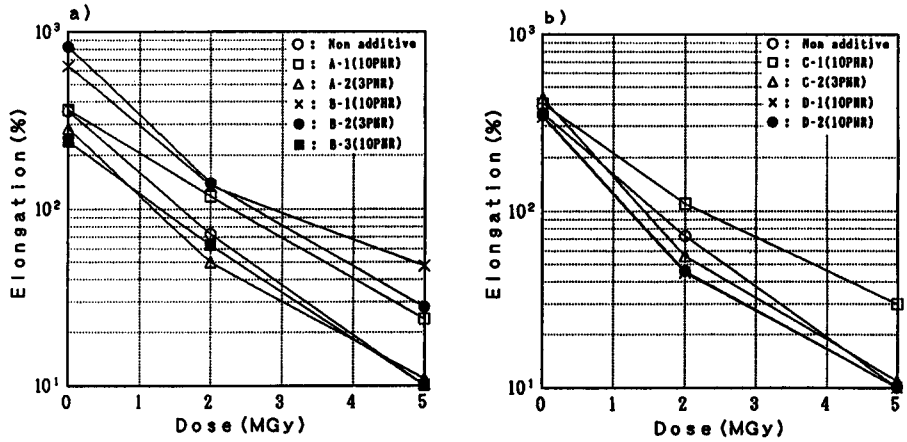


Fig.2 Dose-elongation (for selection of additives).

3. 1. 2 Elongation

To estimate the life of vulcanized rubber, the elongation value is commonly used and its end point is considered[3] to be 50 %. Figures 2 a) and b) show the relationship between irradiation doses and elongation values. It can be seen that the elongation value of specimens without additive dropped below 50 % at the dose of 2-3 MGy and below 10 % at 5 MGy.

Among those specimens added with aromatic oil, A-2 showed a decrease of elongation value more than the specimens without additive, indicating that the addition of A-2 has no effect for inhibiting deterioration. However, A-1 showed an elongation value of about 24 % even at 5 MGy, indicating that the addition of A-1 was effective in improving its radiation resistance. When the equal amounts of these two types of aromatic oil were added respectively to EP rubber (so as to become 4.5 wt% for each type), A-2 caused bleeding, and its added amount was reduced to 1.5 wt%. It is not clear therefore that this improving effect of radiation resistance is due to the differences in chemical structure of additive or its added amount.

Among those specimens added with antioxidant, elongation of irradiated B-3 was almost equal to that of the specimen without additive, that is, no effect for improving radiation resistance was noticeable. However, both B-1 and B-2 showed an improvement of radiation resistance. In particular, B-1 showed a large value of about 50 % even at 5 MGy.

In the case of those specimens added with ultraviolet absorber, C-1 showed an improvement of radiation resistance. This is considered to be caused by the fact that the ozone generated under γ-ray irradiation was consumed to oxidize, $>C=O$, thereby suppressing the oxidation of EP rubber.

With regard to specimens added with lead-based additive, no improvement was found for any of them.

3. 1. 3 Volume resistivity and alternating-current breakdown voltage

Figures 3 a) and b) show the relationship between irradiation dose and volume resistivity, while Figs. 4 a) and b) show the relationship between irradiation dose and alternating-current breakdown voltage. Neither volume resistivity nor alternating-current breakdown voltage was found to be affected significantly by γ-ray irradiation.

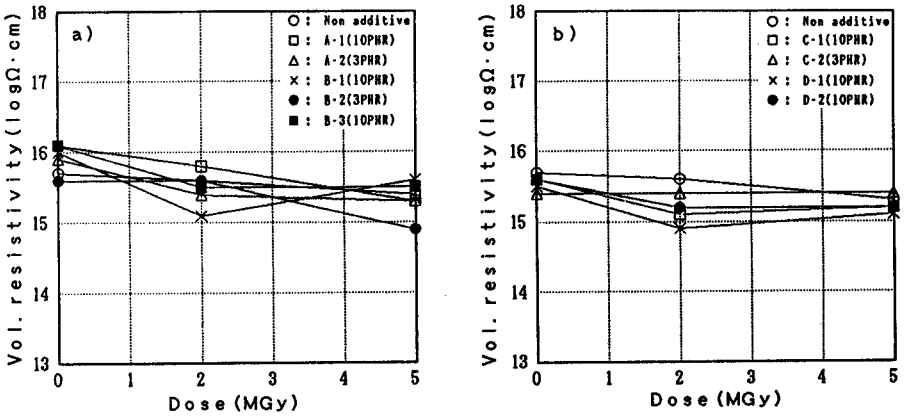


Fig.3 Dose-volume resistivity (for selection of additives).

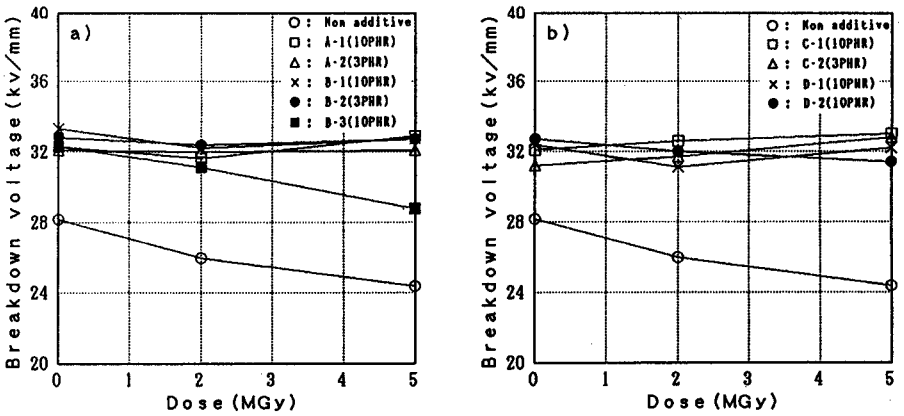
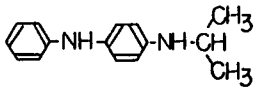


Fig.4 Dose-breakdown voltage (for selection of additives).

3. 2 Increasing of the amount of additive

Some additives with the radiation-resistance improving effect were selected from additives listed in Table 1. By increasing their amount, similar experiments as described above were carried out. Additionally, two types of new antioxidants were selected from some age resistors having a chemical structure similar to B-2, because even small amount of them was found to reduce the deterioration by γ-ray irradiation (Table 2). However, the cross linking agents for B-2 and the newly added antioxidants were replaced because the use of increased amount of antioxidants interfered with their cross-linking reactions.

Table 2 Classification of additive

Classification	Sym.	Chemical names	Structural formula
Antioxidants	B-4	Mixture of diaryl-p-phenylendiamine	
	B-5	1-phenylamino-4-isopropyl-amino benzene	

Figures 5 a) and b) show the relationship between irradiation dose and tensile strength. Though the addition of aromatic oil tended to reduce the tensile strength of EP rubber, the same tendency in tensile strength with increasing irradiation dose was not found in the case of the other specimens.

Figures 6 a) and b) show the relationship between irradiation dose and elongation. For the three kinds of additives shown in a), improvement of the radiation-resistance was found by increasing the amount.

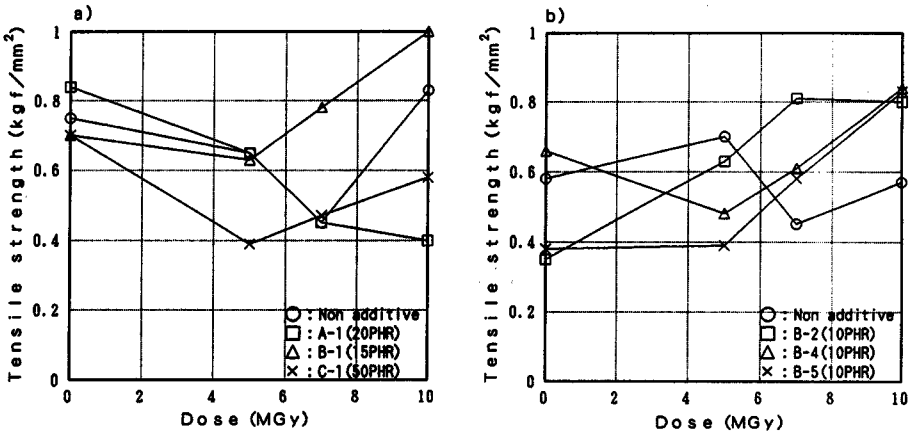


Fig. 5 Dose-tensile strength (for increasing of the amount of additives) .

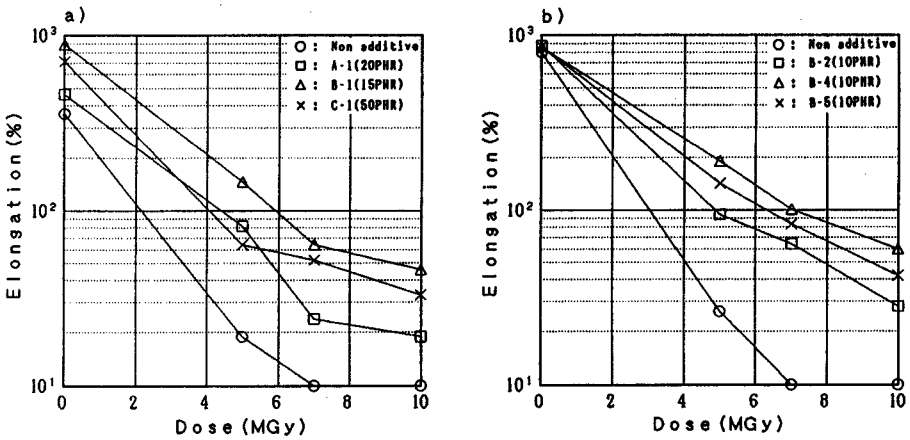


Fig.6 Dose-elongation (for increasing of the amount of additives).

With regard to the three kinds of antioxidants shown in b) , though their addition amount was only 4.5 wt% or lower than that of the others, large effects for improving radiation resistance were found. Among the specimens added with these antioxidants, both B-4 and B-5 are normally used for improving the ozone resistance of rubber material.[4] Therefore, this high effectiveness of these antioxidants can be considered due to the fact that they inhibit the oxidation deterioration of rubber material by ozone generated under γ-ray irradiation in air.[5] Increasing their addition amount is also expected to further enhance their effect for improving radiation resistance.

4. Conclusion

1. Lead-based stabilizers have no effect for improving radiation resistance.
2. Among aromatic oil, antioxidant and ultraviolet absorber, there are various differences in their effect for improving radiation resistance due to the difference in their chemical structure. In the case of additives having a large effect for improving radiation resistance, increasing of amount enhances their effectiveness further.
3. Among antioxidants, the effect of ozone-deterioration inhibitors is particulary large. This is considered to be caused by the fact that they inhibit the oxidation deterioration of rubber material by ozone generated under γ-ray irradiation.

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