

# Effect of Fillers and Crosslinking Type on Degradation Phenomena of Ethylene Propylene Rubber Due to Electrical Ageing

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*Abstract:* - Ethylene-propylene rubber (EPR) degradation mechanism due to electrical ageing was studied in this research. Some parameters influencing the ageing properties such as fillers, air relative humidity (RH) and crosslinking type of EPR were investigated. Such specimens were subjected to partial discharge (PD) under surface discharge. The results showed the effect of cross-linked type and filler amount on ageing properties depended on the RH of air. At low RH=20~30%, the discharge activities of all EPR specimens tended to increase largely with the ageing time and there was no significance different between sulphur-type and DCP-type of EPR specimen. FT-IR absorbance of CH bond of EPR specimens was found to decrease significantly after ageing test with decreasing the amount of fillers, indicating scission of CH bond during ageing test.

*Key-Words:* - Ethylene-propylene rubber, partial discharge, cumulative charge, sulphur-type, DCP-type, FT-IR

## 1 Introduction

Ethylene-propylene rubber (EPR)-insulated cable and its accessories are widely used in medium and high voltage distribution, showing good electrical, thermal, mechanical and environmental behaviours. In some cases, insulation failure of EPR cables due to partial discharge (PD) particularly in the accessories may cause a black-out of the whole system [1-3]. However, the reports on EPR degradation used as cable insulation are still a few and EPR degradation mechanisms are not clear yet. From this view point, we performed experimental works to investigate the degradation phenomena of EPR.

Effect of fillers availability represented by testing two kind of samples (EPR with fillers and without ones), and effect of air relative humidity (RH) of EPR were reported in our previous research [4]. In this study, effect of crosslinking method of EPR structure, namely sulphur type (S type) and dicumyl peroxide type (DCP type), under surface discharges was investigated. In practice, the two kinds of these EPR are widely used as cable

insulation and its accessories. However, recently there is tendency in Japan to replace sulphur type of EPR with DCP one. Fourier transform infra-red (FT-IR) spectroscopy and three dimension scanning electron microscopy (3D-SEM) are employed to analyze the aged specimens.

## 2 Experimental setup

Fig. 1 depicts experimental setup for a surface discharge test; using electrode system recommended by IEC (b) method (IEC 60343). The electrode system consisted of a rod (6 mm of diameter, and 1 mm of curvature radius) and a plane electrode. The tested sample with size 50×50×2 mm was placed between the electrodes. Type of EPR samples and their relative permittivity ( $\epsilon_r$ ) were shown in Table 1. The manufacturer has determined a standard of filler amount indicated by index (1), so that S-1 means the sulphur type of EPR sample containing standard of filler amount, S-0 containing no fillers, S-0.5 containing half of filler

amount related to standard one, S-2 containing twice the filler amount related to standard, and so on.

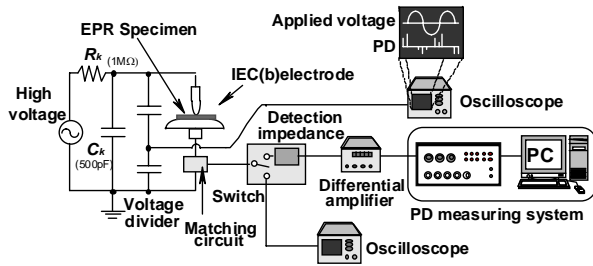


Fig.1 Experimental setup for surface discharge test

Table 1 Type of EPR specimen

Sample	Fillers Amount*	Relative Permittivity
S-0	0	3.75
S-0.5	0.5	4.00
S-1	1	4.26
S-2	2	4.40
D-0	0	3.84
D-1	1	4.15

\* (1) as a standard of filler amount  
S, D = S type and DCP type of EPR specimen

We measured phase-resolved PD ( $\phi$ - $q$ - $n$ ) pattern with a computer aided PD measuring system [5]. An impedance matching circuit with an ultra-wide frequency response was adopted to measure phase-dependence of PD current pulse waveform and to prevent reflection and distortion of PD current pulses. 1 set data of detected PD were obtained during 300 cycles of ac voltage. The phase angle of  $360^\circ$  at one cycle of the applied ac voltage with a frequency of 60 Hz was divided into 12 sections in order to investigate the phase-dependence of PD current pulses, which is known as the so-called phase-angle gate control technique [6].

In our previous work, the ageing test was performed in open and closed-air test; in order to investigate the RH effect, voltage application was set at 1.2 times, 1.5 of PDIV, 5 kVrms, and 6 kVrms for 12 hours of ageing test [4].

In this study, ageing test was performed in a steel chamber ( $\phi = 410\text{mm}$ ,  $t = 550\text{ mm}$ ) and higher voltage application,  $V_a$  was employed to investigate the more severe effect of high field, namely 10 kVrms and applied for a certain hours. Relative humidity of air inside the chamber was kept in range,  $RH = 20\text{-}30\%$ .

### 3 Experimental Results

#### 3.1 PD Characteristics of EPR

Fig. 2 shows partial discharge inception voltage (PDIV) plot of EPR samples for RH below 30%. It can be seen that PDIV of all samples varies from 3.20 ~ 4.55 kV. It was found that PDIV relatively decreased when fillers amount increase or by increasing the relative permittivity.

Fig. 3 shows microscopic photograph of the degraded surface of S Type EPR sample after 1h ageing. A center circle indicates the area onto which a rod electrode was attached and the area was not degraded. A degraded area is radiated out from the center circle. It is shown that the degraded surface due to PD of EPR without fillers (S-0) is more clearly seen on the surface indicating deteriorated trace around the rod electrode tip (Fig. 3(a)) compared with EPR with fillers (S-1) specimen in Fig. 3(b).

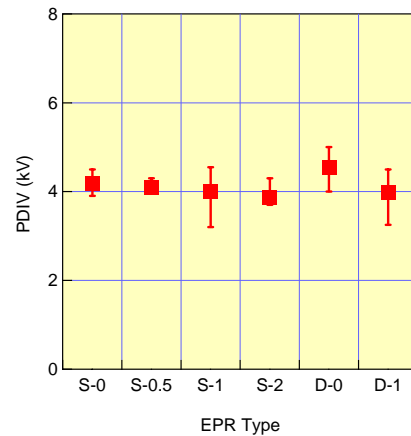
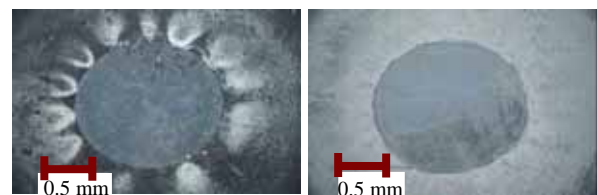


Fig. 2 PDIV of EPR samples (RH < 30%)



(a) EPR without fillers (S-0) (b) EPR with fillers (S-1)

Fig. 3 Microscopic photograph of degraded surface of EPR after 1h ageing, applied voltage is 1.2 times of PDIV

Figs. 4 and 5 show typical examples of ageing time dependence of phase resolved PD ( $\phi$ - $q$ - $n$ ) characteristics for S-1(#2) and D-1(#1) at applied voltage  $V_a = 10\text{ kVrms}$ , and  $RH = 22\%$ , respectively. It is shown that PD activities of both specimens relatively constant in amount of charge and pulse number during ageing time with maximum PD

charge about 24,000 pC. It can be seen from these figures that PD occurred in the phase angle region between the zero-cross and the peak of voltage application (0~90° for positive PD charges, and 180~270° for negative PD charges). These patterns are similar with those of XLPE/EPR interface of XLPE power cable caused by void defect [7].

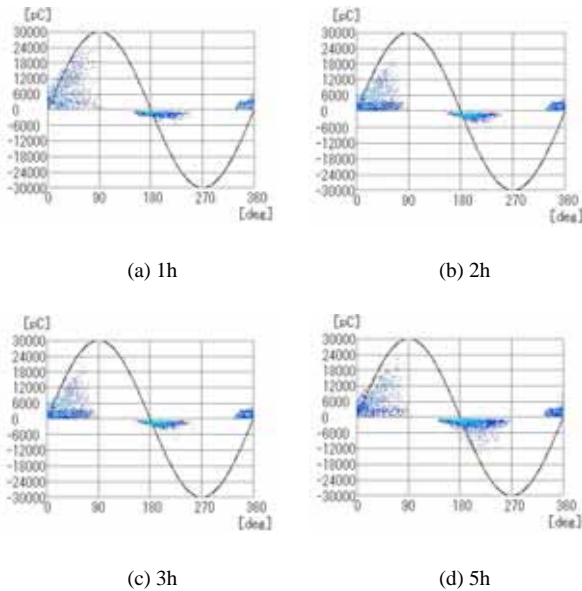


Fig. 4  $\phi$ - $q$ - $n$  patterns of S-1(#2) at 5h ageing,  $V_a = 10$  kVrms,  $T = 295\text{K}$  ( $22^\circ\text{C}$ ),  $\text{RH} = 22\%$

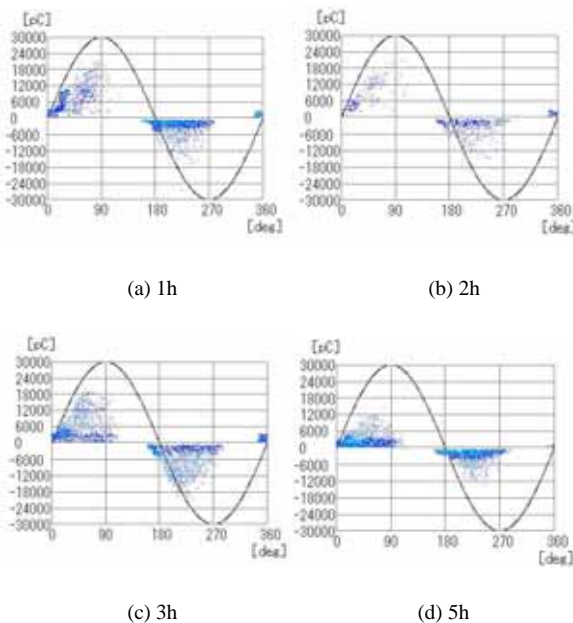


Fig. 5  $\phi$ - $q$ - $n$  patterns of D-1(#2) at 5h ageing,  $V_a = 10$  kVrms,  $T = 295\text{K}$  ( $22^\circ\text{C}$ ),  $\text{RH} = 22\%$

Figs. 6 shows graph of typical cumulative charge,  $Q_c$  when  $V_a = 10$  kVrms applied until  $Q_c = 26$  mC of two kinds of EPR samples (S-type and D-

type). As can be seen from the graphs, it is clear that cumulative charge,  $Q_c$  of both samples in relatively low RH tend to increase significantly with ageing time. The effect of higher RH (up to 60%) to cumulative charge graph of S type and D type was reported in [8].

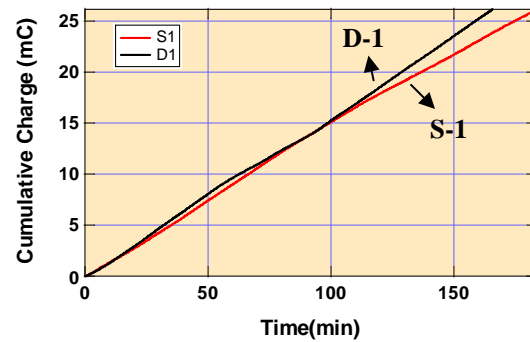


Fig. 6 Cumulative charge of S-type and D-type at  $\text{RH} = 19\text{-}21\%$ ,  $V_a = 10$  kVrms

### 3.2 Degradation Analysis of EPR

Figs. 7 and 8 show the typical spectra of S type and D type of EPR samples obtained from FT-IR spectroscopy for unaged,  $Q_c = 26$  mC,  $Q_c = 52$  mC, and  $Q_c = 104$  mC, respectively. The significant bands of peak spectra are summarized in Table 2. It is clear that peak spectra index no.1 and 2 (C-H) greatly decrease and peak spectra no.7 (C=O) and 8 (O-H) increases with increasing charges for all samples.

Fig. 9 shows peak absorbance of CHsv (index = 1; wavenumber =  $2920\text{ cm}^{-1}$ ) of each EPR samples. It can be seen that the peak spectra decrease as charge increases. It is also seen that the more filler amounts, the less decrease of the peak spectra for all samples.

Furthermore, in order to quantify the degradation of EPR samples with regard to fillers amount and their crosslinking type, it is defined the peak absorbance ratio,  $R_a$  of EPR spectra as :

$$R_a = \frac{\text{Peak absorbance of aged specimen}}{\text{Peak absorbance of unaged specimens}} \quad (1)$$

Fig. 10 and 11 show histogram of peak absorbance ratio,  $R_a$  of aged sample to that of unaged sample for all EPR samples obtained from FT-IR results as shown in eq. (1).

It is shown that absorbance peak ratio  $R_a$  of CH stretching vibration spectra (wavenumber =  $2920\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$ ) of all specimens decreases as  $Q_c$  increases.

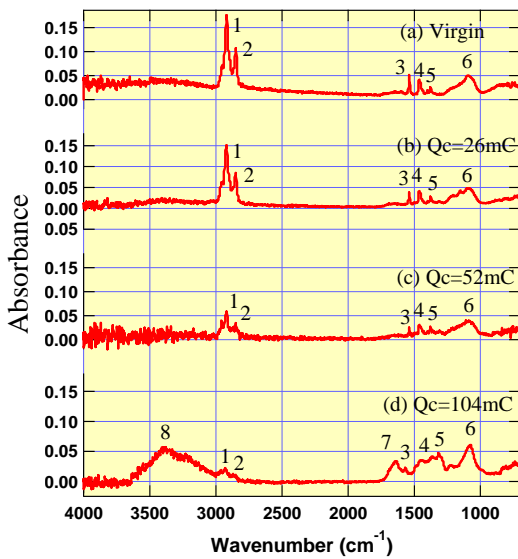
It can be seen that the decreasing peak spectra of

DCP type samples are less than those of S type. While, the specimens with higher filler amount have higher peak absorbance ratio compared with specimen with less or without ones. The lowest value observed in S-0 (sample without fillers) for S type samples, the ratio decrease becomes less than 10% when Qc increased up to 52 mC. The similar results were also observed in DCP type samples. The lowest value in D-0 is about 60% at Qc=56 mC. These results revealed that scission bond (CH) is more likely to occur in S type samples.

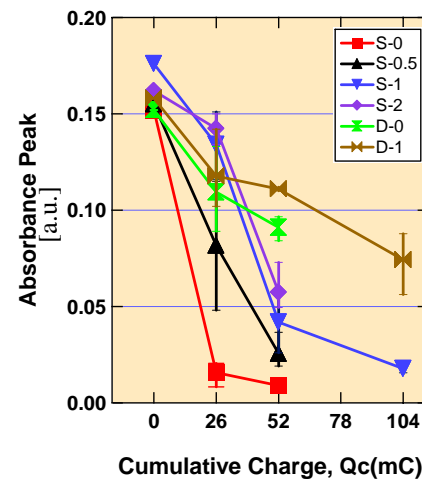
**Table 2.** Significant band and functional group of EPR

Index	Wavenumber(cm <sup>-1</sup> )	Functional Group
1	2920	C-H sv-asymmetric
2	2850	C-H sv-symmetric
3	1540	C=C sv
4	1460	CH <sub>3</sub> dv-asymmetric
5	1380	CH <sub>3</sub> angular deformation
6	1090	Si-O-Si sv
7	1640	C=O sv
8	3700-3200	OH

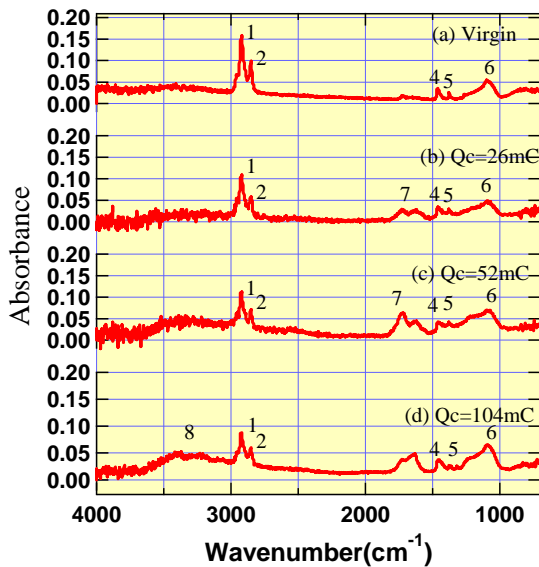
sv=stretching vibration, dv=deforming vibration



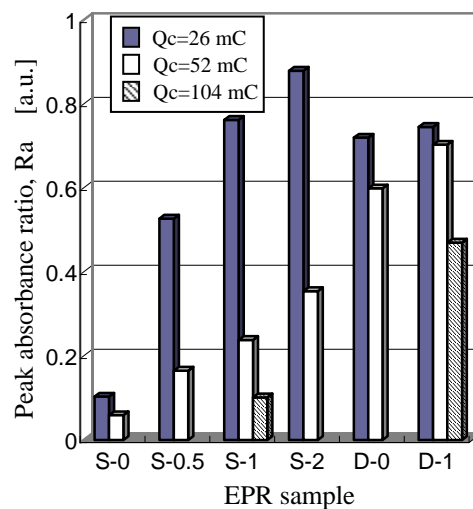
**Fig. 7** Typical spectra of S-1 sample



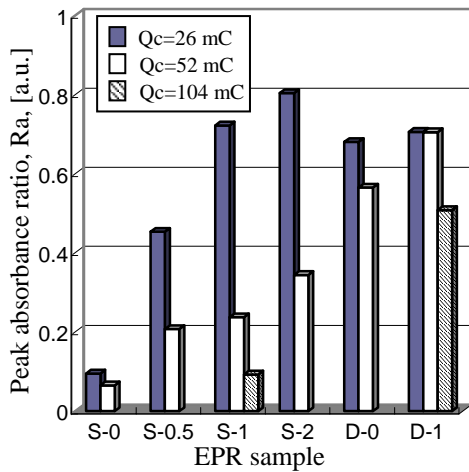
**Fig. 9** Absorbance of CH sv (2920 cm<sup>-1</sup>) of aged EPR specimen



**Fig. 8** Typical spectra of D-1 specimen

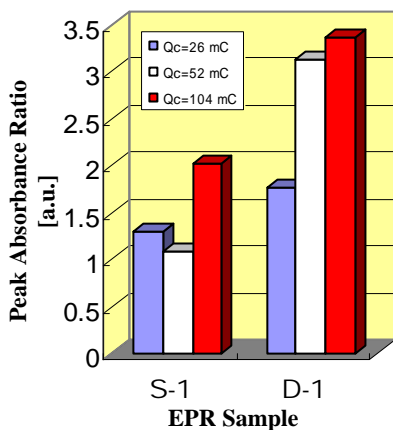


**Fig. 10** Peak absorbance ratio of CHsv spectra (2920 cm<sup>-1</sup>) of EPR specimen



**Fig. 11** Peak absorbance ratio of CHsv spectra ( $2850\text{ cm}^{-1}$ ) of EPR specimen

Fig. 12 shows histogram of peak absorbance ratio, Ra of aged sample at C=O bond obtained from FT-IR results. As can be seen from the figure, the peak absorbance ratio of D-1 increases at higher rate compared with those of S-1 as PD charge Qc increases. At Qc up to 104 mC, the ratio become more than 3 times as much as the origin one. This revealed that oxidation process more likely to occur in DCP type samples.



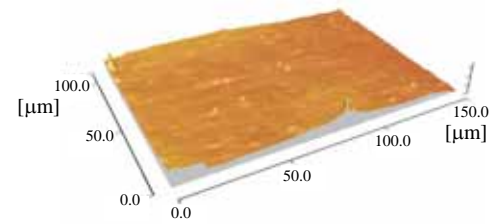
**Fig. 12** Peak absorbance ratio of C=O spectra ( $1640\text{ cm}^{-1}$ )

### 3.3 3D-SEM

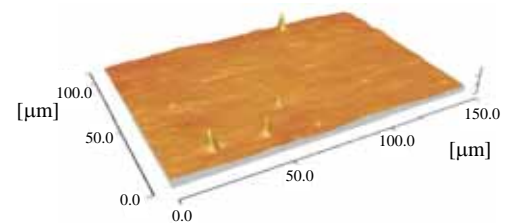
We also performed three-dimensional scanning electron microscopy (3D-SEM) of both kinds of EPR samples in order to investigate the surface degradation due to the electrical ageing.

Figs. 12 and 13 show the 3D-SEM of EPR

samples. No major change in surface erosion observed for S type sample after Va applied up to Qc = 21 mC, as shown in Fig. 12. On the other hand, it can be seen that more severe degradation of DCP type after Va applied up to Qc = 21 mC compared with unaged one, as shown in Fig. 13. The erosion surface clearly observed in this sample indicated that oxidation process much more rapidly occurred in DCP type of EPR sample under PD degradation.

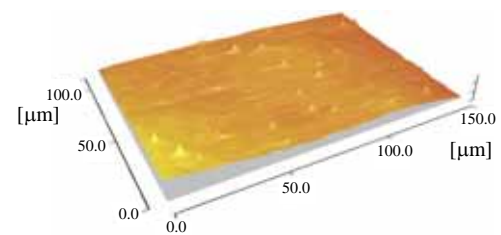


(a) unaged

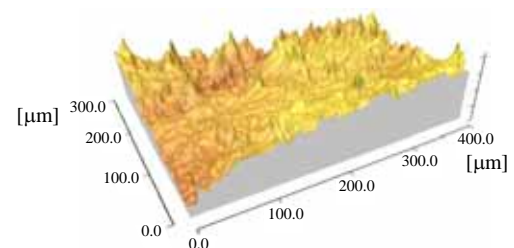


(b) Qc= 21 mC

**Fig. 13** 3D-SEM image of S-1specimen



(a) unaged



(b) Qc= 21 mC

**Fig. 14** 3D-SEM image of D-1specimen

Note that a big elevation profile of sample surface of aged DCP type due to PDs made technically quite difficult to get a good 3D-SEM image as shown in Fig. 13.

#### 4 Discussion

According to results mentioned above, the effect of fillers on EPR degradation can be considered as follows. The addition of clay (mainly consist of Al, Si, and Ti) as a filler led to formation of fine spherulites and improves the uniformity of the electric field within the specimen [9]. Consequently, the mean free path of electrons and the diffusion coefficient of charge carriers both decrease. This process illustrated schematically in Fig. 14.

As shown in Fig. 9, 10 and 11, the more filler amount the less decrease of CH bond.

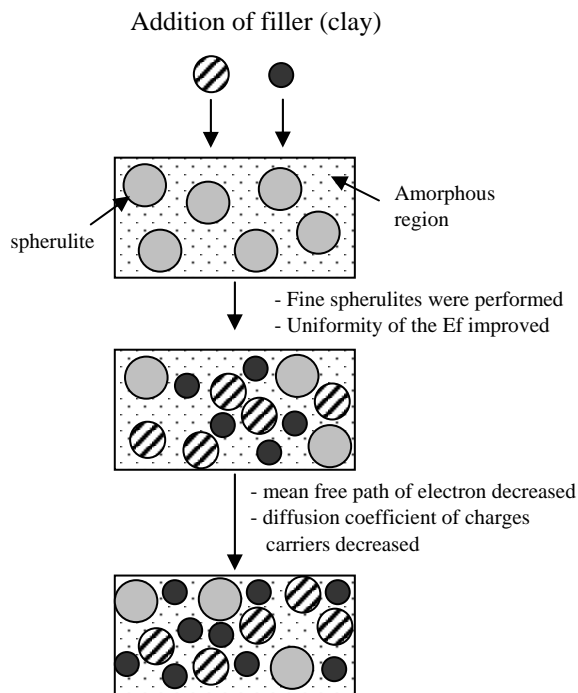


Fig 15. Schematic illustration of the filler effect

The effect of crosslinking type of EPR specimen to degradation level can be considered as follows. The chemical structure of S-type and D-type are shown in Fig. 16. The binding energy of C-S bond is 259 kJ/mol, which relatively lower than binding energy of C-C bond (348 kJ/mol) [10]. This is indicate that chemical structure of S-type specimen relatively easier to be broken if attacked by ion impact due to PD process compared with chemical structure of DCP type.

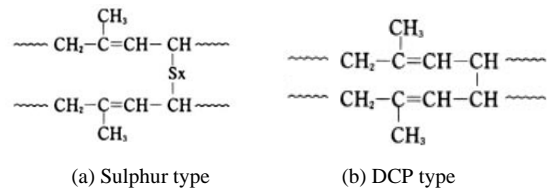
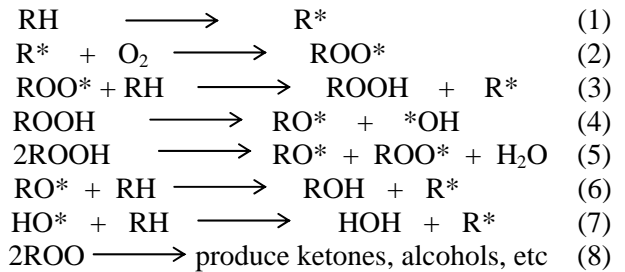


Fig 16. Chemical structure of EPR sample

Based on FT-IR results shown in Fig. 12 and 3D-SEM results in Fig. 13, the oxidation reaction is considered much more rapidly to occur in DCP type samples. Oxidation reactions generally involve a free radical chain reaction. Some of the main steps in this reaction are [11-15]:



The oxidation products such as ketones and some other or carboxylic acid in certain concentration might cause surface conductivity of samples increases. As consequence, when applied at constant voltage, the PD charges decreases [16]. So that, in long time ageing, the deposit of oxidation product on the surface might reduce the PD activities on it.

Moreover, it is observed that more oxidation occurred in DCP type sample while less decrease in CH bond compared with S type as shown in Figs 10, 11 and 12, respectively. These phenomena might be considered as follows. DCP type of EPR samples containing two oxygen atoms in their chemical compound. Decomposition of DCP caused by PDs produce free radical, which react to form acetophenone and methane. Acetophenone is known already as indicator of oxidation products [12, 17]. The experiments is performed in low RH (RH below 20%), make water vapor (H<sub>2</sub>O) surrounding the sample test is low. Therefore, the oxidation process seems difficult to occur in S type samples regarding to less availability of oxygen. Thus, the results exhibit that oxidation process much more likely to occur in DCP type than those of S type.

## 4 Conclusion

We have investigated the effects of the type of crosslinking structure and filler amount on EPR degradation mechanism. The results of PD characteristics showed that PD charge tended to increase with the ageing time for all specimens; S type and DCP type, with and without fillers in different slope under certain RH of air.

The results also showed the effect of cross-linked type and filler amount on ageing properties depended on the RH of air. At the RH=20~30%, the discharge activities of all EPR specimens tended to increase with the ageing time and that EPR with filler relatively had higher cumulative charge compared with specimens without ones.

FT-IR results revealed that the absorbance of CH bond of S type and DCP type of EPR specimens decreased due to PD process. The CH bond spectra decrease as the filler amount of aged EPR specimens decreased, indicating scission of CH bond during aging test.

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