

# Influence of Residual Peroxide on the Degradation of Peroxide-Crosslinked Ethylene–Propylene–Diene Rubber

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**ABSTRACT:** The influence of residual peroxide on the degradation of ethylene–propylene–diene rubber (EPDM) and detection methods for undercrosslinking were investigated. The undercrosslinking of peroxide-crosslinked EPDM could be detected by the measurement of the heat generated by the crosslinking reaction due to residual crosslinking agent with differential scanning calorimetry, not by the determination of its amount, the reaction of which was found to correlate with the amounts of remaining dicumyl peroxide (DCP) and triallyl isocyanurate. As to the DCP-crosslinked EPDM in the undercrosslinking state, softening degradation occurred more remarkably

than hardening degradation, whereas the crosslinking agent remained in the rubber. By surface analysis of the aged DCP-crosslinked EPDM with Fourier transform infrared spectroscopy, we discovered that the oxidative degradation of the undercrosslinked EPDM occurred faster than in the EPDM without crosslinking agent remaining. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2578–2586, 2008

**Key words:** degradation; differential scanning calorimetry (DSC); FTIR

## INTRODUCTION

Peroxide crosslinking is applied to saturated uncrosslinked rubbers, such as ethylene–propylene–diene rubber (EPDM). Peroxide crosslinking has a tendency to often fall into forming a state of undercrosslinking because its crosslinking reaction is slower than that of sulfur vulcanization. When undercrosslinking is generated in the rubber because of the factors of crosslinking temperature and time, a part of the peroxide remains in the undercrosslinked rubber. In such cases, it is a concern that peroxide is so highly active that residual peroxide induces polymer degradation that exerts adverse effects on the quality of rubber products. When the undercrosslinking has taken place in peroxide-crosslinked rubber, troubles are usually not observed in short-time use. In cases of long-time use, such as several years, however, various troubles arise because of the degradation of rubber induced by residual dicumyl peroxide (DCP).

The physical properties of peroxide-crosslinked rubbers before heat aging were reviewed,<sup>1</sup> but the influence of residual peroxide were not investigated. The effects of additives such as antioxidants on the heat aging of peroxide-crosslinked EPDM were shown.<sup>2</sup> Then, it was shown that the concentration

of peroxide influences photodegradation.<sup>3</sup> However, the influence of residual peroxide on degradation was not clear.

In general, when the thermal conductivity of uncrosslinked rubber is lower, compared to other materials, the uncrosslinked rubber is prone to yield the state of undercrosslinking when crosslinked. In particular, in thick molded rubber products, the state of crosslinking in its center and that on its surface tends to come to be uneven. Such a state generates the inhomogeneous physical properties of crosslinked rubber, and the product is inclined to break because of stress concentration induced during use. To ascertain the cause of troubles yielded in peroxide-crosslinked rubber products, one needs to investigate whether crosslinking has been properly achieved during their production. Residual peroxide in crosslinked rubber decreases every moment, which makes it difficult to estimate the crosslinking density in early stages.

In this research, we examined a detection method of unreacted residual DCP and the influence of the amount of unreacted residual DCP on the degradation of peroxide-crosslinked rubber.

## EXPERIMENTAL

### Samples

Table I presents the recipe of the DCP-crosslinked EPDM produced for this experiment. The DCP-cross-

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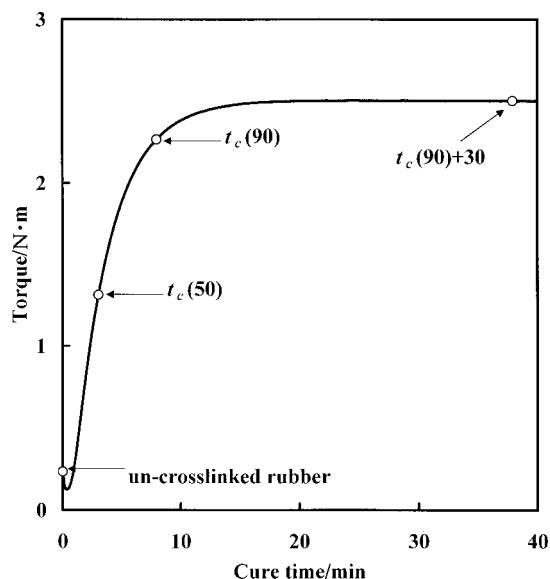
**TABLE I**  
Compound Recipe

Ingredient	Amount (phr)
EPDM (EP33)	100
Carbon black (HAF)	40
ZnO	5
Stearic acid	1
DCP <sup>a</sup>	6.75
TAIC	3

<sup>a</sup> Purity = 40%.

HAF, high abrasion furnace.

linked rubber (EPDM) was prepared by the following procedure. EP33 (52% ethylene and 8.1% 5-ethylidene-2-norborene), made by JSR Corp. (Tokyo, Japan), was taken up as EPDM and was kneaded with an internal mixer to mix it with the compounding ingredients except DCP and triallyl isocyanurate (TAIC); it was then mixed together with DCP and TAIC with a 6-in. open-roll mill to make an uncrosslinked rubber compound. The uncrosslinked rubber compound was pressed with a vulcanizing press at a crosslinking temperature of 170°C to make DCP-crosslinked rubber sheets 2 mm thick. When the crosslinked rubber sheets were made, the crosslinking times were set at 50% cure time [ $t_c(50)$ ], 90% cure time [ $t_c(90)$ ], and at an additional 30 min after the 90% cure time [ $t_c(90) + 30$ ], according to the crosslinking curve given in Figure 1. In this way noted previously, the DCP-crosslinked EPDM sheets, with three grades of the crosslinking state from undercrosslinking to overcrosslinking, were made as rubber samples to be examined. Specimens made of the rubber samples were measured for their mechanical properties, such as tensile strength ( $T_B$ ) and



**Figure 1** Cure curve and prepared DCP-crosslinked EPDMs.

**TABLE II**  
Mechanical Properties of the Crosslinked EPDMs

	Sample		
	$t_c(50)$	$t_c(90)$	$t_c(90) + 30$
Hardness	54	64	68
$T_B$ (MPa)	16.1	11.6	12.3
$E_B$ (%)	440	170	150
$M_{100}$ (MPa)	1.56	4.01	5.53
$M_{200}$ (MPa)	3.52	—	—
$M_{300}$ (MPa)	7.28	—	—

$M_{100}$ , tensile modulus at 100% elongation;  $M_{200}$ , tensile modulus at 200% elongation;  $M_{300}$ , tensile modulus at 300% elongation.

hardness at room temperature, and their measurement results are shown in Table II.

### Heat aging

The specimens were heat aged at 50°C over 10, 20, and 40 days in a heat-aging tester on a system with unrestricted air convection (hereinafter, this system is referred to as the open system) to examine the influence of residual DCP on the degradation of the specimens. Moreover, additional specimens were heat aged at the same temperature and time with the heat aging tester on a system where they were kept in 20-L stainless steel airtight containers to restrict air convection and to limit the decrease of residual DCP decomposition products by evaporation during heat aging (hereinafter, this system is referred to as the closed system) to weigh the influence of residual DCP on the degradation of the specimens heat aged in the closed system against those of the specimens aged in the open system.

### Analysis

Each of the specimens was measured for its hardness with a hardness tester MD-1, made by Kobunshi Keiki Co., Ltd. (Kyoto, Japan), and  $T_B$  was measured according to JIS K 6251. Residual DCP amounts in each specimen were determined with high-performance liquid chromatography (HPLC; LC-2000 Plus series, Jasco Corp., Tokyo, Japan) with columns (L-column, ODS (octadecylsilylating silica gel) 5  $\mu$ m, length = 250 mm, inner diameter = 4.6 mm; Chemicals Evaluation and Research Institute, Tokyo, Japan). We determined the residual TAIC amount of each specimen with gas chromatography-mass spectrometry (GC/MS; 6890/5973N, Agilent Technologies Corp., Santa Clara, CA), with a DB-5 column (length = 30 m, inner diameter = 0.25 mm, membrane thickness = 0.25  $\mu$ m, made by Agilent Technologies Corp.), applying the selective ion monitoring method with a mass to charge ratio of 249. The content of acetophenone and cumyl alcohol (Fig. 2),<sup>4</sup>

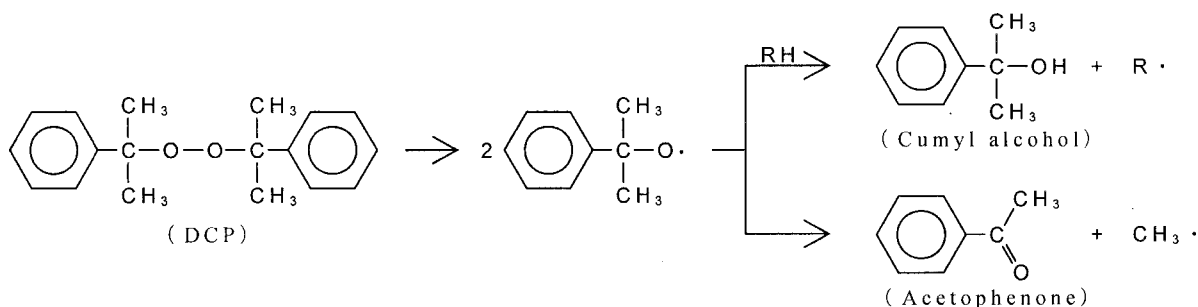


Figure 2 Cleavage reaction and decomposition products of DCP.

which are decomposition products of DCP, were determined with GC/MS as relative detected amounts. In cases where the GC/MS method was applied for determination, however, the residual DCP was thermally decomposed at the inlet, and it generated acetophenone and cumyl alcohol; the absolute amount of the decomposition products of DCP, therefore, could not be determined. *n*-Butylbenzene (5 ppm) was set as an internal standard substance, and then, the relative detected amounts of acetophenone and cumyl alcohol, including the decomposition products derived from the residual DCP, were determined to extrapolate the state of crosslinking. Heat generated by the crosslinking reaction because of residual crosslinking agents in the specimens (HRC) was measured at a heating rate of 10°C/min with differential scanning calorimetry (DSC; DSC-30, Mettler Toledo, Inc., Switzerland). To investigate the crosslinking density of the specimens, we examined them by swelling tests with cyclohexane as the solvent at 30°C, and we calculated the apparent total concentration of network chains with a revised Flory–Rehner equation for evaluation, applying the values of equilibrium degree of swelling at the immersion time of 72 h in the previous tests. Also, we evaluated the degree of oxidative degradation of the specimens aged with heat with a Fourier transform infrared microspectrophotometer (FTS-6000, UMA-500, Digilab, Inc., Canton, MA), applying a micro-attenuated total reflection method.

## RESULTS AND DISCUSSION

### Consideration of the evaluation method of residual DCP amount

Evaluation of the DCP amount in specimens not heat aged and specimens heat aged in the open system

Heat generation caused by the crosslinking reaction of the residual crosslinking agent in DCP-crosslinked EPDM was determined with DSC as HRC. Figure 3 presents the HRC measurement result of DCP-uncrosslinked EPDM as an example. HRC was observed around 180°C during the first heating; how-

ever, it disappeared perfectly for the second heating. Moreover, its glass-transition temperature shifted to the higher temperature side by approximately 3°C, and an increase in its crosslinking density was recognized. This clearly revealed that the crosslinking reaction was generated by the residual DCP.

Also, the following measurements were also carried out on each of the specimens:

1. The residual DCP amount was indirectly measured by the determination of HRC with DSC.
2. The residual DCP amount was directly measured by the HPLC method.
3. The residual TAIC amount was determined by the GC/MS method.
4. The crosslinking density was acquired from the swelling test results.

Figure 4 exhibits the measurement results of measurements 1–4, together with crosslinking curves. As a result, the amounts of residual DCP and TAIC and also HRC reduced with increasing progress of crosslinking (increasing crosslinking density). From these

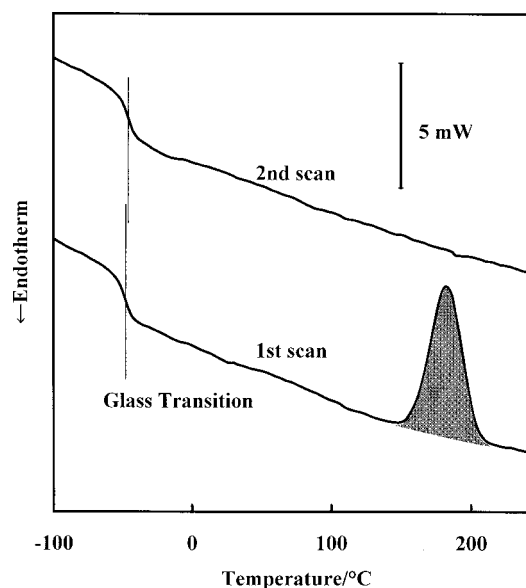
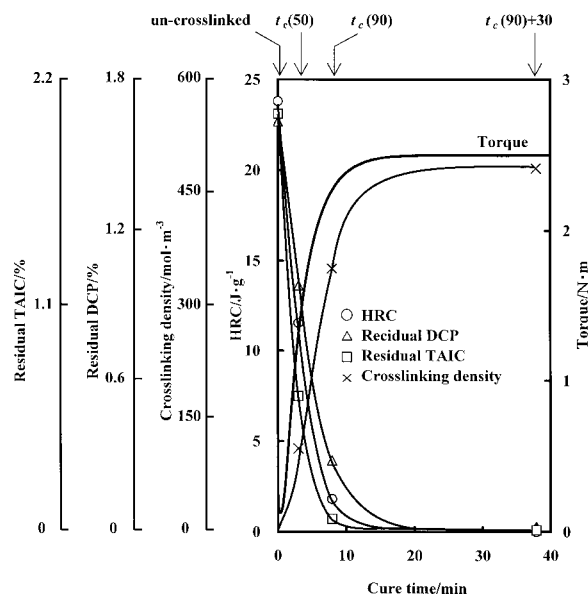


Figure 3 HRC of uncrosslinked EPDM.



**Figure 4** Amounts of residual DCP and TAIC and crosslinking density and HRC of the DCP-crosslinked EPDMs.

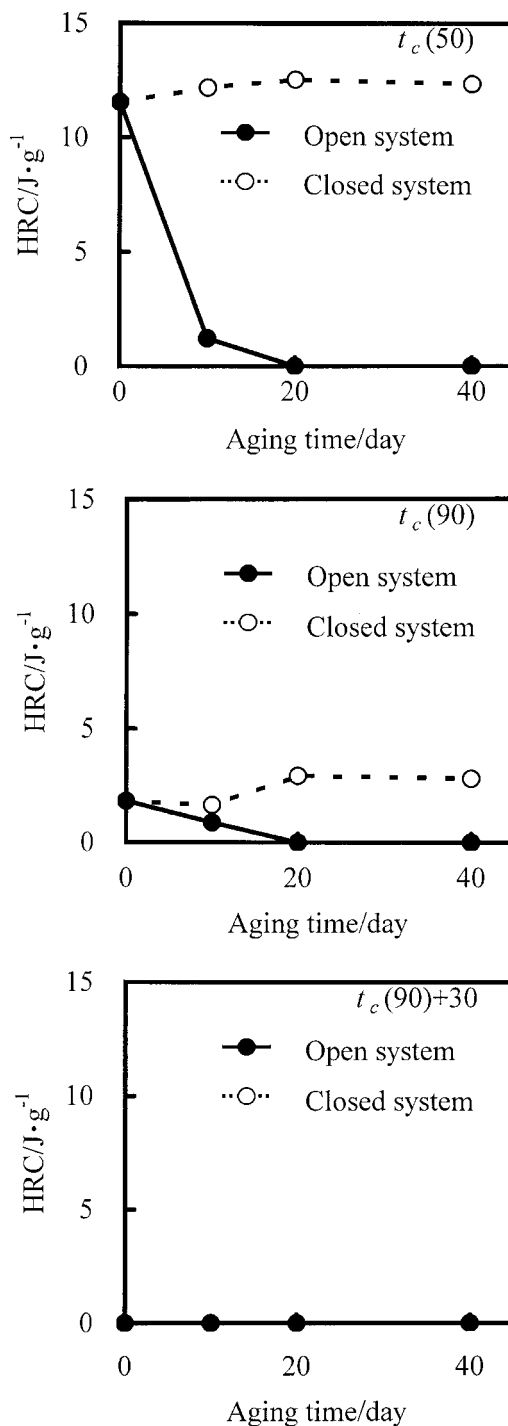
results, it was ensured that the amount of residual DCP was detectable by HRC as a relative detected amount. The measurement of HRC with DSC has advantages, such as easy and prompt application for use, compared with the HPLC and GC/MS methods, because it does not require pretreatment, such as solvent extraction. Thus, the measurement of HRC with DSC was an assessment technique for the amount of the residual crosslinking agent, which offered a highly convenient means for quality control.

When we considered that the initial cleavage temperature of DCP was 150°C, as observed in the DSC curves for uncrosslinked EPDM (Fig. 3), the specimens were heat aged at 50°C in the systems to prevent their crosslinking reactions from initiating. Subsequently, the following examinations were carried out to inspect the change in amount of the residual crosslinking agent with time:

5. HRC was determined with DSC.
6. Residual DCP amount was determined with the HPLC method.
7. Residual TAIC amount was determined with the GC/MS method.

The results of examinations 5–7 are given in Figures 5–7. When the specimens were heat aged with the heat-aging tester in the open system, their HRC, the amount of residual DCP, and that of residual TAIC decreased together with time via similar trends with each other. These results indicate that the state of crosslinking at an early stage could be adequately inferred by the measurement of HRC with DSC for molded rubber products used in the market. Furthermore, the values of HRC and resid-

ual DCP amount of each of the specimens measured before and after heat aging in the systems were plotted to investigate the relation of HRC to the residual DCP amount, as shown in Figure 8. As shown in Figure 8, a favorable positive correlation was obtained, but it deviated from a linear function. The reason for this was considered as follows: the coagent TAIC contributed to crosslinking together with DCP, and HRC observed with DSC was not the



**Figure 5** Change in HRC by aging test at 50°C.

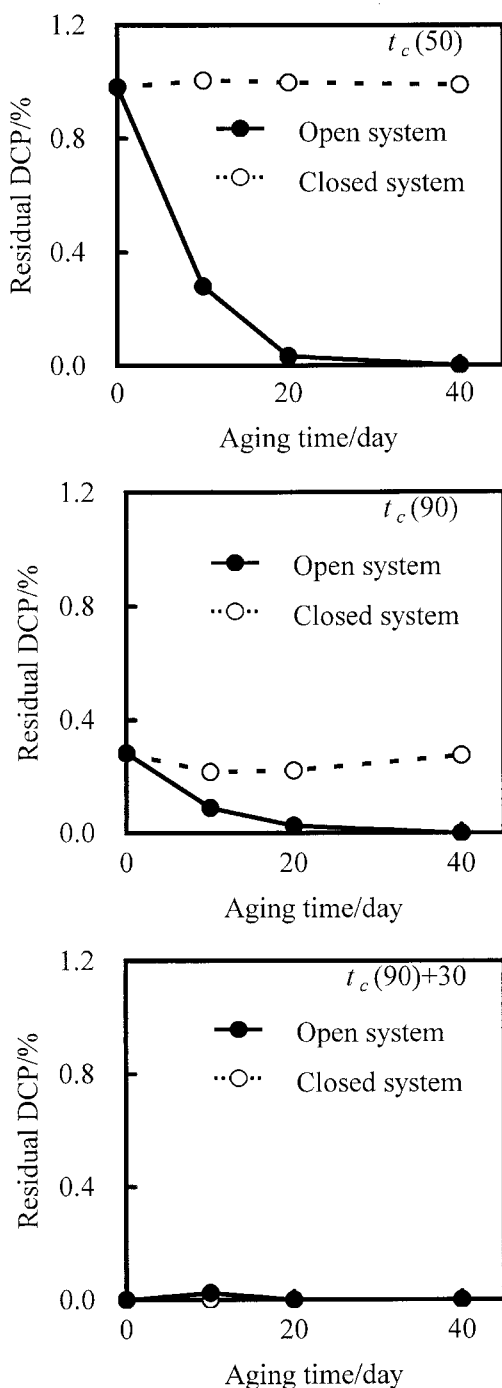


Figure 6 Change in residual DCP by aging test at 50°C.

heat generated by the reaction of only DCP. To confirm this consideration, uncrosslinked EPDM without TAIC was made, and its HRC was measured. The HRC was 15.5 J/g and was less than that of uncrosslinked EPDM with TAIC (23.8 J/g; see Fig. 4 at cure time = 0 min). This result supports the aforementioned consideration. Because the relation of HRC to the residual DCP and TAIC amount indicated a proper positive correlation, as shown in Figure 9, we were assured that the residual crosslinking

agent could be easily detected with the measurement of HRC without the complex and time-consuming quantitative analysis of DCP and TAIC with the HPLC and GC/MS methods.

Evaluation of the DCP amount of specimens not heat aged and specimens heat aged in the closed system

Examining the specimens heat aged in the closed system and judging from the values of HRC and the variation of residual amounts of DCP and TAIC (see

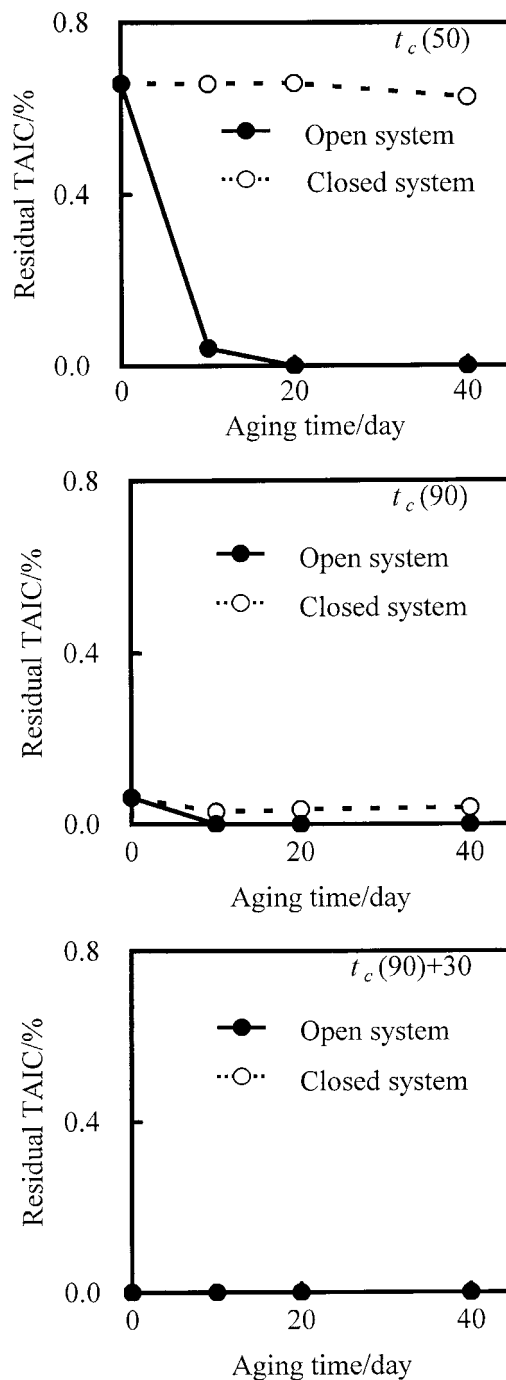
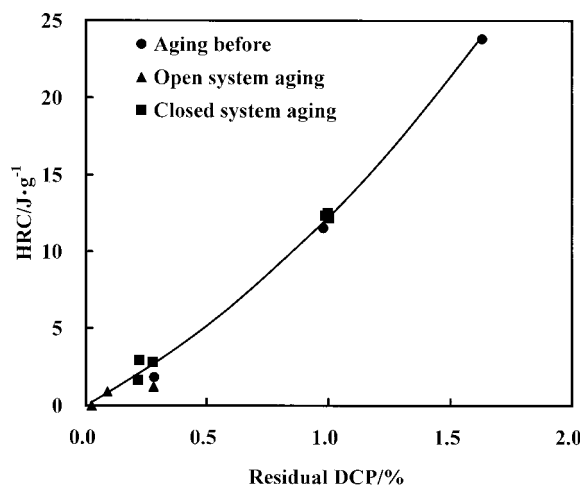


Figure 7 Change in residual TAIC by aging test at 50°C.

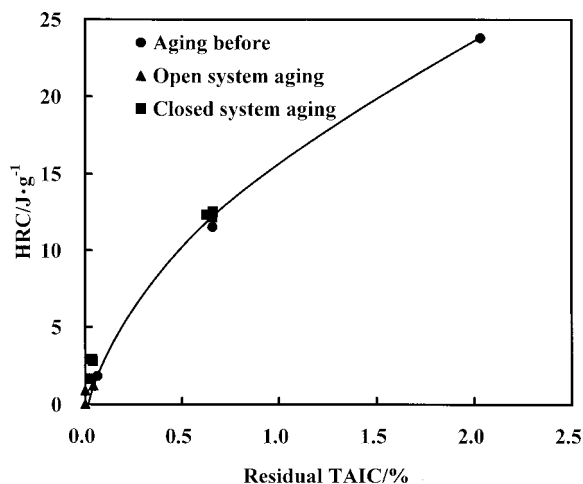


**Figure 8** Relationship between the amount of residual DCP and HRC.

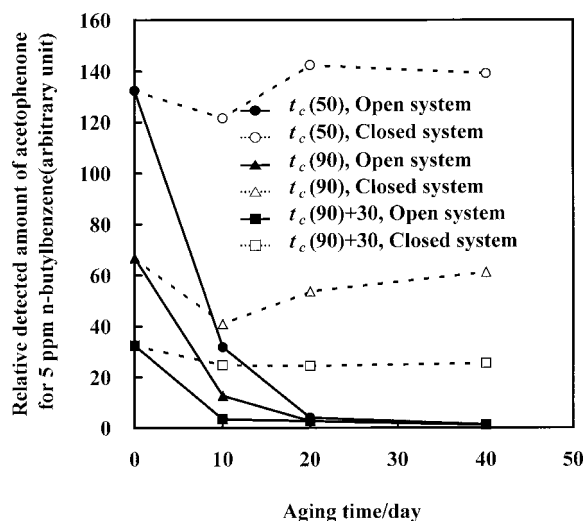
Figs. 5–7), we concluded that there was little admissible decrease in residual crosslinking agent. Therefore, the decreasing behavior of the residual crosslinking agent of molded rubber products being used in the marketplace strongly depends on the environmental conditions used for such products and, in particular, on air convection.

#### Extrapolating method of crosslinking density of molded rubber products at an early stage by means of the detection of the thermal decomposition products of DCP

It is predicted that DCP generates acetophenone and cumyl alcohol via thermal decomposition<sup>4</sup> and that their traces remain within molded DCP-crosslinked rubber products. In fact, the characteristic odor of acetophenone constantly develops when molded rubber products have been piled up anywhere. So sheet-

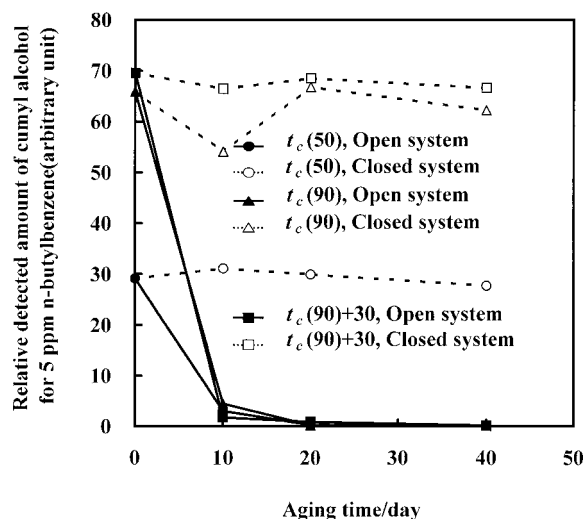


**Figure 9** Relationship between the amount of residual TAIC and HRC.



**Figure 10** Change in the relative detected amount of acetophenone by aging test at 50°C.

like specimens 2 mm thick made within a range from undercrosslinking to overcrosslinking were heat aged at 50°C in the systems, and the relative detected amounts of acetophenone and cumyl alcohol contained within the sheetlike specimens were measured with the GC/MS method. The variation in the relative detected amount depending on heat aging at 50°C are given in Figure 10 and 11. In the case of the undercrosslinking [at  $t_c(50)$ ], much acetophenone and a little cumyl alcohol were detected in the specimen that was not heat aged (aging time = 0 day). On the other hand, in the case of overcrosslinking [at  $t_c(90) + 30$ ], a little acetophenone and much cumyl alcohol were detected in the specimen that was not heat aged (aging time = 0 day). Judging from the previous results, we believe that the detected amount



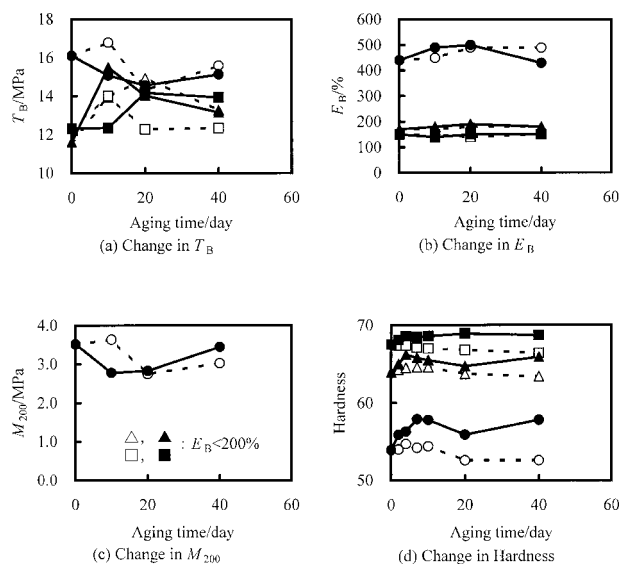
**Figure 11** Change in the relative detected amount of cumyl alcohol by aging test at 50°C.

of thermal decomposition products depends on the crosslinking time and the amount of residual DCP. The higher the temperature DCP is decomposed at, the more acetophenone is easily generated, whereas the lower the temperature DCP is decomposed at, the more cumyl alcohol is easily generated.<sup>4</sup> Therefore, the cause of the phenomenon described previously is considered as follows: In case of the specimens undercrosslinked at  $t_c(50)$  and containing much residual DCP, much acetophenone was yielded by the decomposition of residual DCP due to high temperature (280°C) at the inlet of GC/MS. In case of the specimens overcrosslinked at  $t_c(90) + 30$ , much cumyl alcohol was generated, whereas they were kept for a long time at a lower temperature for crosslinking (170°C) than the inlet temperature. Thus, much acetophenone was detected in the undercrosslinked specimens, and much cumyl alcohol was detected in the overcrosslinked specimens.

Also, when the specimens were heat aged in the open system, the amounts of these decomposition products decreased, but when the specimens were heat aged in the closed system, no remarkable increase or decrease of their amounts was recognized, and the variation behavior of their amounts was similar to that of the amount of residual crosslinking agent. It was, therefore, possible to extrapolate the crosslinking density of rubber products at an early stage by the investigation of the residual amounts of the decomposition products. This means that the differences in crosslinking density are compared among several rubbers that have used similar environmental conditions by the determination of the residual amounts of the decomposition products in the rubbers. Also, because the GC/MS method is capable of highly sensitive analysis, it becomes a particularly effective method for the extrapolation of the crosslinking density of such rubber products when the amount of residual crosslinking agent and its decomposition products are only present in trace quantities because of changes with time.

#### Influence of residual DCP on degradation (variation of mechanical properties)

To investigate the influence of residual DCP on degradation, the specimens were heat aged at 50°C in the systems, and their  $T_B$ , elongation at break ( $E_B$ ), and hardness change were inspected. The results are given in Figure 12.  $T_B$  and  $E_B$ , shown in Figure 12(a,b), of the specimens varied with different behavior at each of the specimens, and any dependence on the difference of the crosslinking density was not recognized. Figure 12(d) shows the behavior of hardness change depending on heat aging treatment. Typical hardening degradation, which often appears in EPDM, developed in the specimens cross-

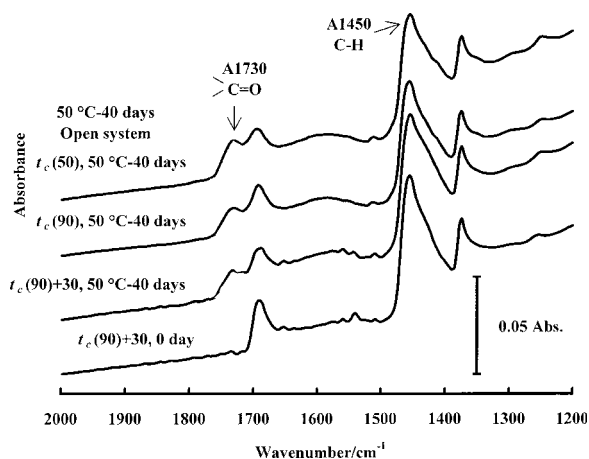


**Figure 12** Change in the mechanical properties by aging test at 50°C: (●)  $t_c(50)$  and open system, (○)  $t_c(50)$  and closed system, (▲)  $t_c(90)$  and open system, (△)  $t_c(90)$  and closed system, and (■)  $t_c(90) + 30$  and open system, and (□)  $t_c(90) + 30$  and closed system.

linked completely by overcrosslinking at  $t_c(90) + 30$  and then heat aged in the open system. On the other hand, the specimens crosslinked at  $t_c(50)$  and then heat aged in the open system showed behavior in which they softened once and then hardened after 20 days of heat-aging treatment. The specimens crosslinked at  $t_c(90)$  and then heat aged in the open system also presented a similar behavior trend. Also, for the specimens crosslinked at  $t_c(90)$  and then heat aged in the closed system, their hardness variation was close to that of the specimens heat aged in the open system. Moreover, as shown in Figure 12(c), the tensile modulus at 200% elongation of the specimens dropped once but then rose. For the specimens crosslinked at  $t_c(50)$  or  $t_c(90)$  and then heat aged in the open system, shown in Figures 5–7, the crosslinking agent remained in the specimens for about 20 days of heat-aging treatment. This remaining duration coincided with the duration of softening degradation. Because of these findings, we considered that the trend toward softening degradation was strong when the crosslinking agent DCP remained.

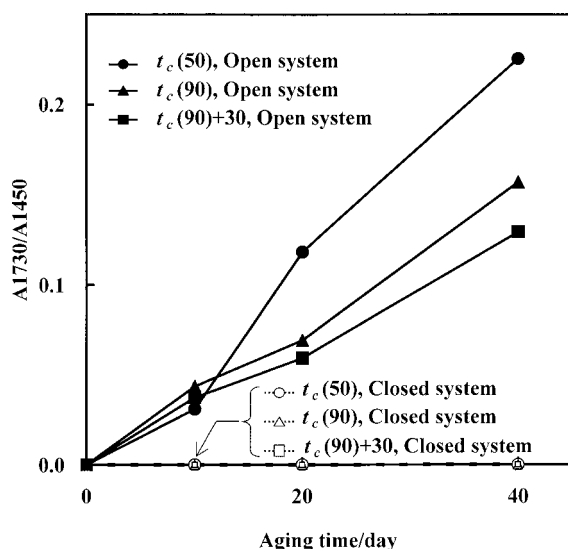
#### Influence of residual DCP on degradation (variation of chemical structure)

The specimens made of DCP-crosslinked EPDM were inspected with Fourier transform infrared spectroscopy and the micro-attenuated total reflection method to compare the degradation rates of their surfaces. As shown in the IR spectra presented in Figure 13, the absorption by carbonyl group at 1730  $\text{cm}^{-1}$ , which was not recognized in the speci-



**Figure 13** Change in the IR spectra for DCP-crosslinked EPDMs by aging test at 50°C for 40 days in an open system.

mens that were not heat aged, appeared in the specimens heat aged at 50°C for 40 days in the open system, which indicated that oxidative degradation was in progress on their surfaces. The degradation yielded in the specimens was determined by a ratio of peak area [absorbance at 1730 cm<sup>-1</sup> (A1730)/absorbance at 1450 cm<sup>-1</sup> (A1450)], with the absorption by C—H at 1450 cm<sup>-1</sup> set as a base peak to obtain the results given in Figure 14. On the other hand, oxidation was not observed in the case of the specimens crosslinked at  $t_c(50)$ ,  $t_c(90)$ , or  $t_c(90) + 30$  and then heat aged in the closed system. It is understandable that nonoxidation was due to an insufficient supply of oxygen to cause degradation on their surfaces. On the other hand, for the specimens crosslinked at  $t_c(50)$  and  $t_c(90)$  and then heat aged in the

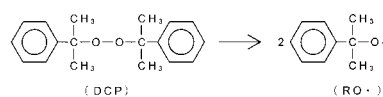


**Figure 14** Change in the degree of oxidative degradation by aging test at 50°C. The degree of oxidative degradation was evaluated by Fourier transform infrared-attenuated total reflection.

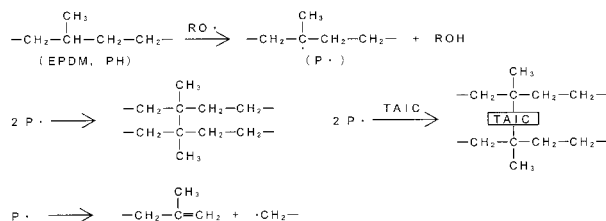
open system, the degradation development was quicker than that of the specimens made at  $t_c(90) + 30$  and then heat aged in the open system. In addition, there was a tendency for degradation to develop quickly, particularly the specimens heat aged for up to 20 days, over which period the crosslinking agent easily remained. As a result, we believe that radicals generated by DCP accelerated oxidative degradation.

Figure 15 presents, as an example, the assumed degradation mechanism of DCP-crosslinked EPDM caused by the residual DCP. The decomposition of the residual DCP can be considered to yield peroxy radicals, which react with the polymer to generate polymer radicals, and the polymer radical causes not only the crosslinking reaction but also the scission reaction of the main chains. It can be inferred that softening arises as a result of such reactions, and the oxidation reaction develops at the same time via a similar oxidation reaction reported already in the literature,<sup>5,6</sup> which shows the oxidation process of the ethylene-propylene copolymer.

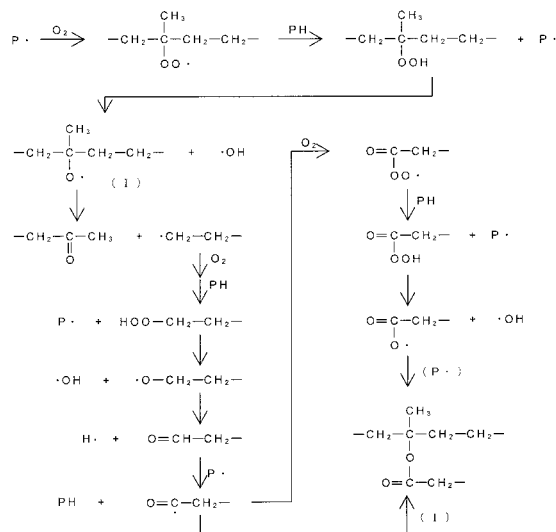
#### 1. Cleavage of DCP



#### 2. Crosslinking and scission of EPDM



#### 3. Oxidation of EPDM



**Figure 15** Estimated degradation mechanism of EPDM by DCP.



### CONCLUSIONS

1. Undercrosslinking can be quickly and easily evaluated by the measurement of HRC with DSC.
2. It was quantitatively clarified that residual peroxide of molded rubber products leads to polymer degradation by softening and accelerates oxidative degradation at the same time.
3. When DCP-crosslinked EPDM was heat aged in the closed system, which restricted the inflow of oxygen, oxidative degradation did not de-

velop, as the residual DCP did not react and continued to remain in the sample.

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