Reinforcement and Antioxidation Effects of Fullerenol-Containing Natural Rubber

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ABSTRACT: Natural rubber (NR) containing fullerenol, C60-OH, was prepared by two methods; one by mixing C60-OH aqueous solution to NR latex followed by coagulation (wet method) and the other by mixing C60-OH powder with solid rubber by an open roll mixer (dry method). C60-OH mixed by wet method was homogeneously dispersed in the rubber, while one mixed by dry method was particles in the size up to 70 μm. The former exhibited large reinforcing and antiaging effect than the latter. The large antiaging effect was explained by the finding that C60-OH had large radical scavenging ability and gel forming ability during heat treatment. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3625–3631, 2010

Key words: antioxidants; fullerenes; nanocomposites; reinforcement; rubber

INTRODUCTION

Fullerene (C60) consisting of 12 five-membered rings and 20 six-membered rings has high chemical reactivity because of the low energy level of lowest unoccupied molecular orbital. High reactivity of fullerene enables to provide oxidized or hydroxylated derivatives.[1–3] Fullerene derivatives are expected as a reinforcing agents (fillers) and radical scavengers of polymers. However, it sometimes becomes difficult to finely disperse them in polymers, because they tend to agglomerate because of their strong molecular interaction due to van der Waals force or hydrogen bonding. It has been reported that heat resistance is increased by mixing fullerene in poly (methyl methacrylate), polystyrene, or polydimethylsiloxane.[4–6] Fullerene-containing natural rubber (NR) is found to have superior antiaging properties.[7–9]

There is a report on the composites consisting of hydroxyl fullerene (C60-OH) and polymer.[10,11] Most of them investigate about C60-OH, the pharmacological activity.[12–14]

However, antiaging properties of C60-OH containing polymers are not reported. In this report, we prepared C60-OH-containing NR by two mixing methods and the reinforcing and antiaging properties were investigated. Antiaging mechanism was also discussed.

EXPERIMENTAL

Materials

High ammonia NR latex (HA NR latex) produced in Malaysia was used. C60 (purity of 99.5%) and C60-(OH)10 from Aldrich and Frontier Carbon, respectively, were obtained commercially. N-isopropyl-N′-phenyl-p-phenylenediamine (IPPD) and 2,6-di-tert-butyl-4-methylphenol (BHT) by Ouch Shinko were used. All the materials were used without further purification.

Preparation of samples

C60-OH solution was prepared by adding 1 g of C60-OH power and 25 mL of 1% NaOH aqueous solution and by stirring the mixture for 30 min. No insoluble materials were detected by stereomicroscopic observation. Precipitate was obtained by mixing this solution and 152.9 g of HA NR latex (solid content of 65.4%) followed by shaking at room temperature. The C60-OH/NR wet masterbatch was obtained by washing the precipitate and drying it at room temperature under reduced pressure.

For comparison, three samples containing 1 g of C60-OH, IPPD, or BHT and 100 g of rubber were prepared using the open roll and a sample containing no additive. Sulfur, vulcanization accelerator, and other vulcanization aids were added to the rubber composites by using an open roll mixer. Formulation for vulcanization was shown in Table I. Vulcanized sheets with 1-mm thickness were obtained by heating the sheet at 150°C for 10 min in the hot press.

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TABLE I
Compound Formulations

Sample Name	C60-OH Wet	C60-OH Dry	IPPD	BHT	Pure gum
NR	–	100	100	100	100
C60-OH/NR wet masterbatch	101	–	–	–	–
C60-OH (powder)	–	1.0	–	–	–
Zinc oxide	6	6	6	6	6
Stearic acid	1	1	1	1	1
Sulfur	3.5	3.5	3.5	3.5	3.5
TBBS	0.7	0.7	0.7	0.7	0.7
IPPD	–	–	1.0	–	–
BHT	–	–	–	1.0	–
Cure	150°C × 10 min	150°C × 10 min	150°C × 10 min	150°C × 10 min	150°C × 10 min

TBBS, N-tert-butyl-benzothiazole sulfonamide.
IPPD: N-isopropyl-N′-phenyl-p-phenylenediamine.
BHT: 2,6-di-tert-butyl-4-methylphenol.

The rubber samples were heat aging treated at 70°C for 96 h using gear oven (Toyo Seiki Seisaku-Sho).

Measurements

Vulcanization curves were recorded by FDR:VR-3110 rheometer (Ueshima Seisakusho). Hardness was measured using MD-1 hardness meter (Kobunsh Keiki). Stress-strain curves were measured using Tesometer 10 tensil tester (Alfa Technology). The fracture surface was observed by a JSM-6510 scanning electron microscope (SEM: JEOL) and the elemental analysis was conducted by a JED-2300 energy dispersive X-ray spectroscopy (JEOL) attached to the SEM. Infrared absorption spectra were recorded by a FTS 6000 FT-IR spectrometer (Bio-Rad) equipped with a UMA 500 optical microscope (Bio-Rad) and with attenuated total reflection method using a germanium prism. Thermal decomposition was observed by TG-DTA 320U thermogravimeter (SII Nanotechnology) under the nitrogen atmosphere at the heating rate of 10°C/min.

Radical scavenging ability of C60 and C60-OH was determined by the concentration of residual 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical, which was measured by a JES-FA200 electron spin resonance spectrometer (JEOL) at 100 kHz. Measurements were done in ethanol or toluene solution for C60-OH or C60, respectively, at 23°C. The concentration of DPPH was determined from the relative intensity of DPPH (the central signal of five signals) to the standard material of manganese (Mn^{2+}).

Gel content was determined from the insoluble fraction of a sample in the 320 mesh stainless steel cage, which was soaked in toluene at 23°C for 24 h. The unvulcanized sample was used after heat treatment at 100°C for 24 h.

RESULTS AND DISCUSSION

Mechanical properties (reinforcing effect)

NR composites containing C60-OH were prepared by two methods. One was wet process of mixing C60-OH aqueous solution with natural latex (wet process) and the other was mechanical mixing of C60-OH powder with solid rubber using an open roll mixer (dry process). The vulcanized sample prepared by the former method is named as C60-OH Wet and the other C60-OH Dry. For comparison, samples containing IPPD and BHT were prepared together with sample without any additives (Pure Gum). The samples were vulcanized with a normal formulation shown in Table I.

Minimum torque (M_L), maximum torque (M_H), vulcanization induction time (t_{10}), 50% vulcanization time (t_{50}), and 90% vulcanization time (t_{90}) were determined from vulcanization curves. Table II shows these data for C60-OH Wet, C60-OH Dry, and Pure Gum. C60-OH Wet showed higher M_L and M_H values than Pure Gum, while C60-OH Dry almost the same M_L and M_H values. Both C60-OH containing samples exhibited almost the same t_{10} and t_{90} values as those of Pure Gum, which indicates that C60-OH negligibly affected vulcanization reaction.

Figure 1 shows stress-strain curves and Table III lists the hardness and the mechanical properties of the samples. C60-OH Wet had more than 20% higher modulus and tensile strength than Pure Gum and hardness of C60-OH Wet was 8% higher than that of Pure Gum. On the other hand, C60-OH Dry showed almost the same mechanical strength and hardness as Pure Gum. Therefore, it is concluded that C60-OH mixed with wet process had reinforcing effect, while one mixed with dry process had negligible reinforcing effect.

TABLE II
Effect of Mixing Method in the fullerenol Composite on the Vulcanization Curve

Sample	M_L (N m)	M_H (N m)	t_{10} (min)	t_{50} (min)	t_{90} (min)
C60-OH Wet	0.05	0.86	2.9	4.1	7.1
C60-OH Dry	0.03	0.76	2.9	3.9	6.6
Pure gum	0.03	0.77	2.7	3.8	6.5

Small extraneous particles with brownish-red color were detected on the fractured surface of the elongated sample by the naked observation. The particles were observed by SEM equipped with energy dispersive X-ray analyzer (EDX). Figure 2 shows the SEM image and distribution state of carbon and oxygen atoms. C60-OH Wet sample had no larger particle than 10 μm and showed more uniform distribution of carbon and oxygen atoms. These results indicate that by the wet processing method C60-OH were finely dispersed in the rubber matrix. On the other hand, many large particles in the size of 15–70 μm were observed in the C60-OH Dry sample. The large particles had higher carbon and oxygen concentration indicating that they were C60-OH. C60-OH powder particle before mixing was about 70 μm in size. Therefore, it is concluded that C60-OH was not finely dispersed in the polymer by dry method, indicating that the mechanical shear force in not strong enough to disaggregate C60-OH particles. The negligible reinforcing effect of dry mixed sample can be explained by the strong aggregation of C60-OH molecules because of the hydrogen bonding and van der Waals force.

Several researchers reported that C60 can be finely dispersed in polymers, such as polystyrene, poly (methyl methacrylate), and NR, by dry mixing.[4–6] In our experiment, it was found that C60-OH aggregate could not be broken by mechanical mixing. The difference can be explained by the strong hydrogen bonding of C60-OH molecules. Furthermore, NR is nonpolar material and has weak interaction with the polar compound of C60-OH.
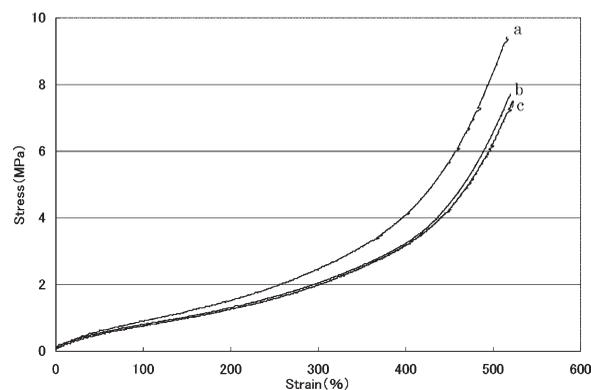
Figure 1 Comparison of stress-strain curve difference in fullerenol composite. a: C60-OH Wet; b: C60-OH Dry; c: Pure gum.

Antioxidant effect (antiaging effect)

The rubber samples were heat aging treated at 70°C for 96 h. The differences of mechanical properties before and after the heat treatment are shown in the lower part of Table III. The difference of tensile strength and elongation at break are shown as the percentage of change, while that of hardness as the absolute value. Pure Gum showed decrease in the hardness, indicating softening degradation, which is typical degradation of NR. On the other hand, samples containing C60-OH showed slight increase of hardness. The hardness increase of the latter samples can be explained by the presence of the reactive double bond and phenolic hydroxyl groups in C60-OH, which reacted with radical species generated during the heat treatment and provided new crosslink. The new crosslink was confirmed by the production of gel portion by the heat treatment of unvulcanized C60-OH sample prepared by Wet method as described in section 3.3.

Pure Gum exhibited slight increase of tensile strength and large decrease of elongation by heat treatment. C60-OH Wet showed large increase of tensile strength and small decrease in elongation, which may be caused by the generation of new crosslink during heat treatment. On the other hand, C60-OH

TABLE III
Mechanical Property

Sample Name	C60-OH Wet	C60-OH Dry	IPPD	BHT	Pure gum
Dispersion of fullerol	good	poor	–	–	–
Hardness/MD-1	40	36	37	35	37
Tensile strength (MPa)	9.43	7.72	8.36	9.13	7.11
Elongation at break (%)	520	530	560	550	520
100 % Modulus (MPa)	0.90	0.77	0.72	0.72	0.73
300 % Modulus (MPa)	2.43	1.92	1.87	1.84	1.88
After aging test					
Change in Hardness	+1	+2	+2	±0	−1
Change in Tensile strength Ac (%)	+39	−7	+30	−18	+2
Change in Elongation at break Ac (%)	−4	−15	−11	−15	−15
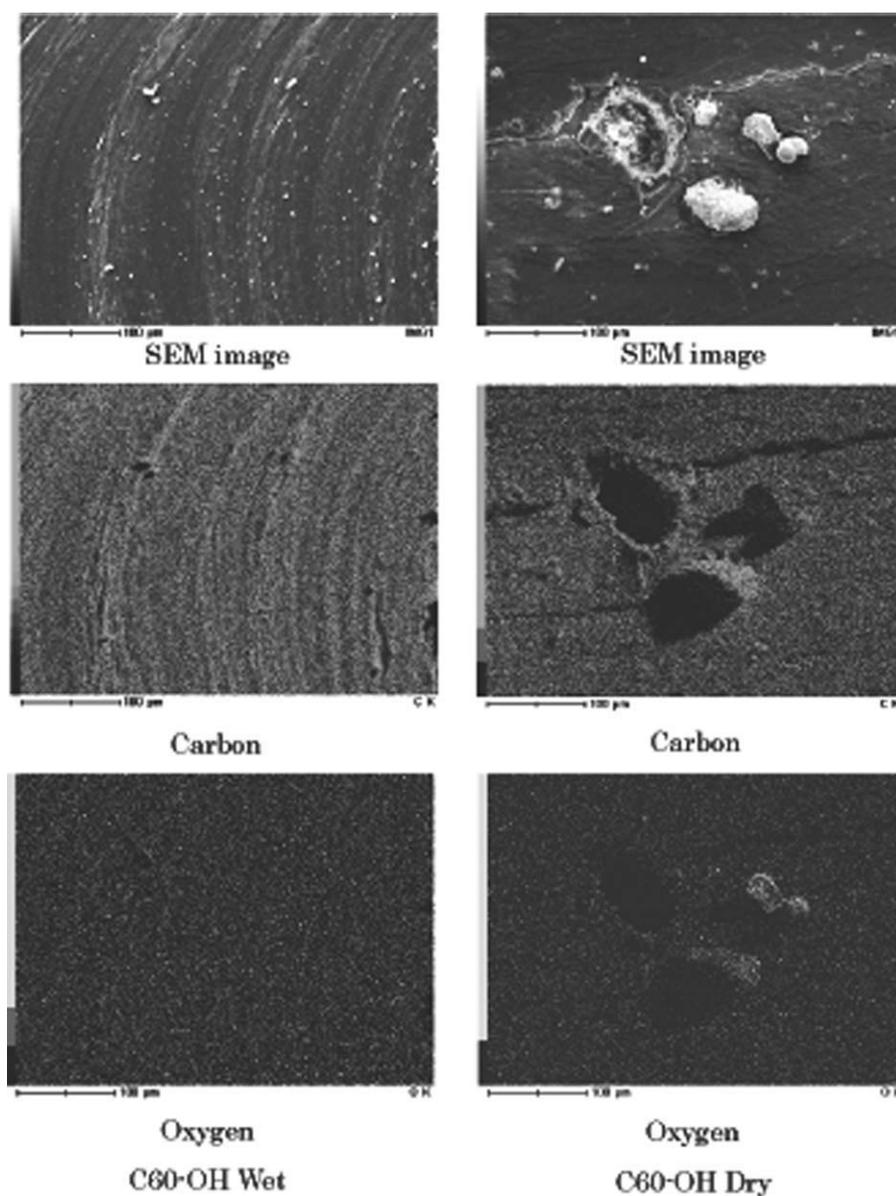
Figure 2 SEM-EDX images of fracture in the rubber compounds prepared by wet process and dry process.

Dry showed opposite change in the tensile strength and elongation after heat treatment. Thus, it is clear that distribution state of C60-OH played an important role in the antiaging effect, and homogeneous distribution of C60-OH is necessary for the superior antiaging effect. Amine-type antioxidant of IPPD showed similar mechanical property change as C60-OH Wet, while phenol-type antioxidant of BHT exhibited similar change as C60-OH Dry.

Figure 3 shows IR-spectra of Pure Gum before and after heat treatment.

Two absorption peaks around 1740 and 3400 cm^{-1} arising from carbonyl and hydroxyl groups, respectively, were significantly increased. To quantitatively evaluate the change peak intensity ratios to the C—H bending peak at 1450 cm^{-1} (1740 cm^{-1}/1450

cm^{-1} and 3400 cm^{-1}/1450 cm^{-1}) were obtained as shown in Table IV. All the samples showed relative intensity increase (96 h–0 h) after heat treatment for both peaks. In Pure Gum, relative intensities of carbonyl and hydroxyl group increased from 0.027 to 0.068 (difference of 0.041) and from 0.081 to 0.159 (difference of 0.078), respectively. C60-OH Wet showed only 10 and 47% increases for C=O peak and OH peaks, respectively, compared with Pure Gum, while C60-OH Dry showed 46 and 76% increases. Here, again the dispersion state greatly affected the changes of carbonyl and hydroxyl peaks and finely dispersed sample showed smaller relative intensity increase after heat treatment. It is clear that finely dispersed C60-OH suppressed the oxidation.
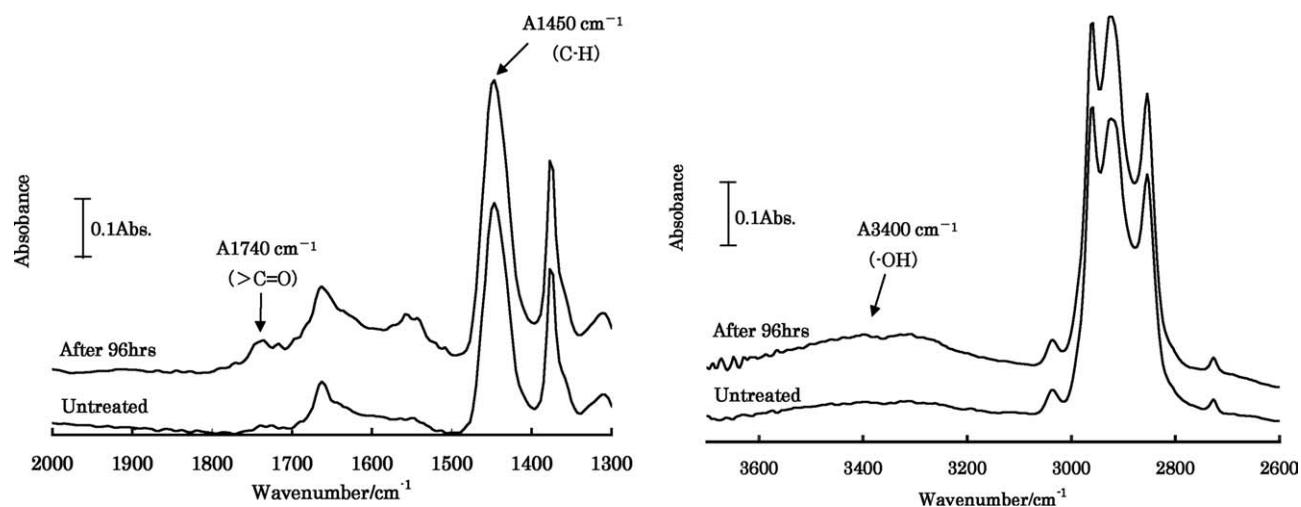
Figure 3 Change in IR-spectra for pure gum after aging test at 70°C.

Thermogravimetry was carried out for the five samples before and after the heat treatment. Thermogravimetric curves are shown in Figure 4. The temperature at which weight loss reached 10% was determined as the decomposition temperature. All the samples had almost the same decomposition temperature of 246–268°C before the heat treatment. Pure Gum showed the decomposition temperature decrease of 28°C after the heat treatment. The temperature decreases of C60-OH Wet, C60-OH Dry, BHT, and IPPD were 3, 26, 24, and −1°C, respectively. C60-OH Wet showed much smaller change, while C60-OH Dry showed almost the same change as Pure Gum, indicating that the former had higher antiaging effect, while the latter had only small effect. IPPD had almost the same effect as C60-OH Wet and BHT only small effect. All the results of mechanical properties, IR spectroscopy, and thermogravimetry showed that C60-OH Wet had good antiaging effect and that the dispersion state of C60-OH was very important for antiaging effect as well as reinforcing effect.

Antiaging mechanism of C60-OH

Aging is considered as the reaction with active oxygen or oxygen radical. Antiaging effect is often estimated by the scavenging ability of radical species. The stable radical of DPPH is often used for estimating antaging effect.[15] Radical scavenging ability of C60 and C60-OH was measured by the radical concentration decrease rate of DPPH. Figure 5 shows ESR spectral of DPPH after adding 0–10 μM of C60 or C60-OH to 0.1 μM of DPPH. In the case of C60, the ESR signal changed only a little although up to 100 times of C60 to DPPH was added. On the other hand, the signal significantly decreased as the increase of C60-OH added. At the addition of 10 μM of C60-OH, the signal almost disappeared. Thus, C60-OH reacted with DPPH radical much faster than C60. The higher reaction rate of C60-OH can be explained by the presence of phenolic OH group and/or shorter conjugation length of C60-OH. The fast reaction with radical may lead to the higher antiaging effect.[16–18]

TABLE IV
Absorbance Ratio of Functional Group by FT-IR Microscope

Sample Name		1740 cm^{-1}/1450 cm^{-1} (>C=O)	3400 cm^{-1}/1450 cm^{-1} (OH)
C60-OH Wet	0 h	0.040	0.120
	96 h (96 h–0 h)	0.044 (0.004)	0.156 (0.036)
C60-OH Dry	0 h	0.023	0.045
	96 h (96 h–0 h)	0.042 (0.019)	0.104 (0.059)
IPPD	0 h	0.021	0.083
	96 h (96 h–0 h)	0.040 (0.019)	0.100 (0.017)
BHT	0 h	0.040	0.060
	96 h (96 h–0 h)	0.042 (0.002)	0.146 (0.086)
Pure gum	0 h	0.027	0.081
	96 h (96 h–0 h)	0.068 (0.041)	0.159 (0.078)
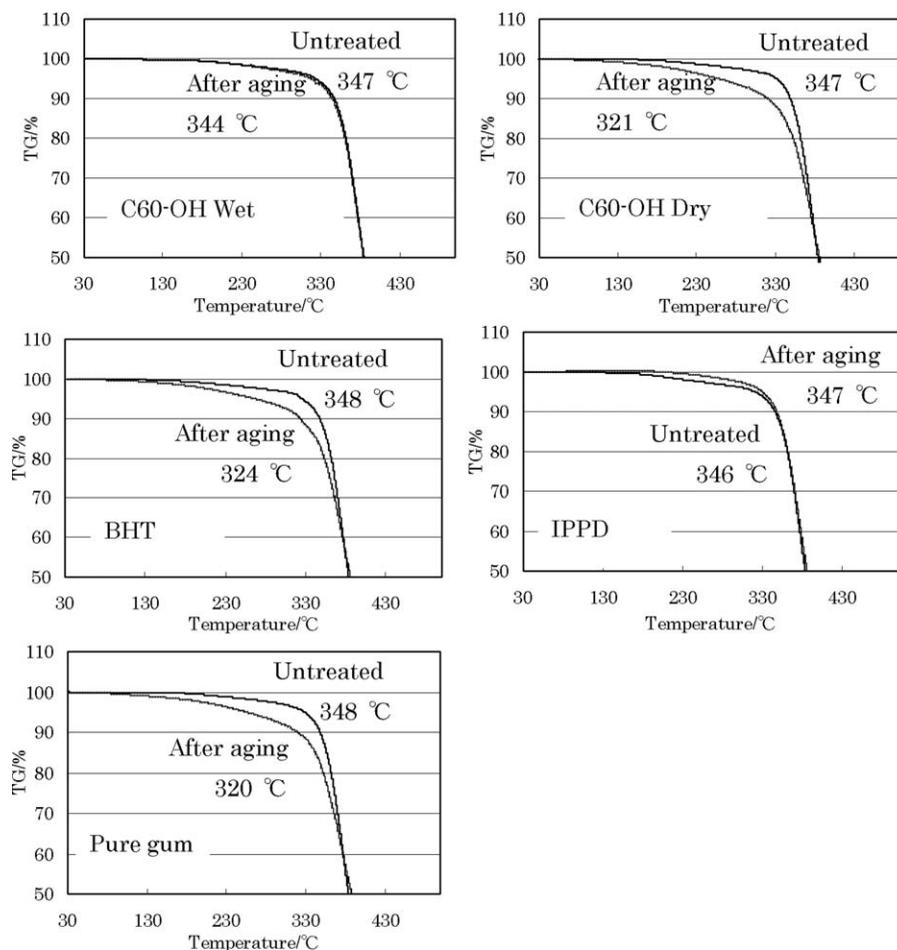
Figure 4 Change in thermogravimetry after aging test at 70°C.

The gel content of the unvulcanized samples was determined after heat treatment. A sample without any additive contained no gel, while one containing C60 possessed small amount of gel. On the other hand, a sample containing C60-OH mixed by wet method had 4.0% of gel. Therefore, higher reactivity of C60-OH to the radical may facilitate the formation of crosslink by reacting with carbon and/or oxygen radicals in the rubber produced during the heat treatment. The only small amount of gel in C60 containing sample can be explained by slow reaction rate of C60 to radical. Cataldo studied reaction of C60 with NR and synthetic cis-1,4-polyisoprene.[7,8] He also found that C60 causes the cross linking of
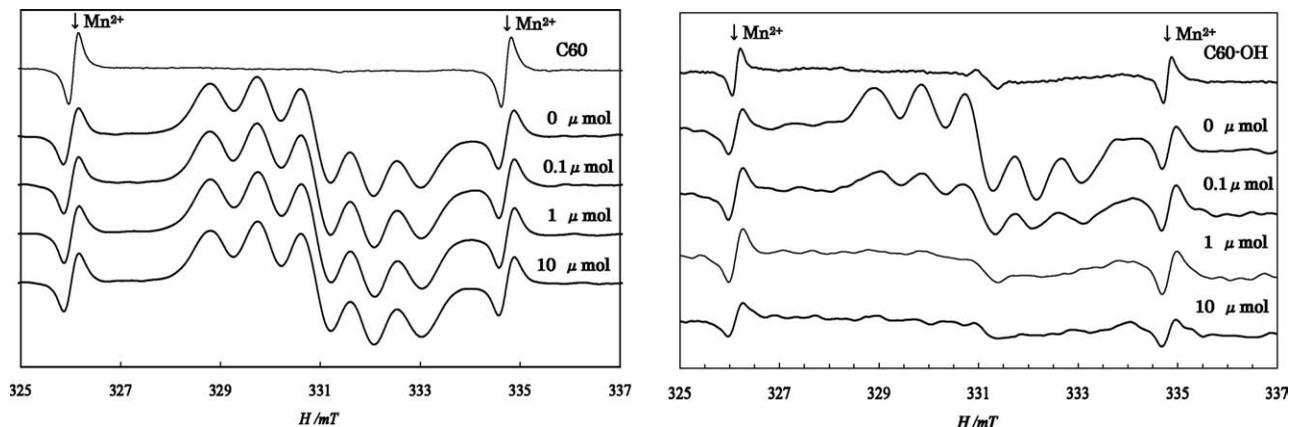
Figure 5 ESR spectra at 23°C of DPPH/C60-OH and DPPH/C60.

NR and cis-1,4-polyisoprene at 190°C under nitrogen.

Considering that C60-OH had the large amount of gel and rapid reaction rate to radical, C60-OH has larger antiaging effect than C60. It is reasonable to think that new crosslink was produced also in the vulcanized C60-OH Wet sample during the heat treatment. The formation of new crosslink may lead to the increase of hardness and mechanical strength leading to the higher antiaging effect.

CONCLUSIONS

A rubber composite having finely dispersed C60-OH was obtained by mixing C60-OH aqueous solution with NR latex (Wet method). The vulcanized sample of the composite (C60-OH Wet) exhibited higher modulus, tensile strength, and elongation, indicating that finely dispersed C60-OH had reinforcing effect. The sample showed smaller damage because of the heat treatment showing that C60-OH possessed antiaging effect. On the other hand, C60-OH mix with an open roll formed aggregates and had negligible reinforcing and antiaging effects.

It was found that C60-OH had radical scavenging ability and that an unvulacnized rubber composite containing finely dispersed C60-OH formed small amount of gel during the heat treatment. The antiaging effect of C60-OH was explained by these findings.

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