Improvement in characteristics of natural rubber nanocomposite by surface modification of multi-walled carbon nanotubes

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Abstract

We aim to develop high-level applications of NR through the innovative use of multi-walled carbon nanotubes (MWCNTs) to improve reinforcing performance and thermal resistance. In this study, we examined the structures and characteristics of composite materials in which NR was the matrix and MWCNTs were the fillers. We studied the properties of composites containing surface-activated MWCNTs with three different diameters. The results show that the reinforcing performance improves as MWCNT diameter decreases, while thermal resistance improves as we decrease the heat-treatment temperature. The latter occurs because adherence between MWCNTs and NR becomes stronger at lower heat-treatment temperatures. We also found that for practical applications, we need to control active sites on MWCNTs to balance adhesion against thermal resistance.

1. Introduction

Carbon nanotubes (CNTs) continue to attract attention as leading materials in nanotechnology, and methods for mass production and development of applications for CNTs are being actively pursued. At present, catalytic chemical vapor deposition (CCVD) is increasingly being used for mass production of single-layer, double-layer, and multilayer CNTs[1-3]. CCVD is especially effective for producing high-purity CNTs; in particular,

several companies are producing about 1,000 tons of multilayer CNTs each year. Also, according to long-term forecasts, they are planning to boost production. In recent years, developmental studies have been underway to exploit the excellent mechanical, electrical, and thermal properties of CNTs. Attempts to create composite filler materials started in 1990, and there are many research reports, but there are few successful examples of practical use. It is not easy to improve properties and create new functionalities. For example, homogeneous dispersions of CNTs are difficult to achieve, and we have difficulty in controlling nanospace properties and adhesion to the matrix material, because extremely long and thin (nanometer size) CNTs form aggregates that intertwine complicatedly with each other[4,5]. However, since 2004, composite materials of aluminum[6-8], rubber[9-16], resin[17-19], and ceramics[20] have been successively developed; homogeneous dispersions have been achieved and interface phases and 3D structures have been controlled using mixing-and-kneading method, which exploits singular properties of rubber elastic bodies. Rubber seal materials with a thermal resistance of 85 °C, twice improved pressure resistance, and three times greater endurance are now being used for exploration and production in oil fields all around the world[11]. Moreover, rubber parts with innovatively improved endurance are being used in automotive applications[12] with significant results. We have previously proposed a three-dimensional structured model, cellulation model, to achieve a strong nano-continuous 3D structure, which is a cell-like structure in which CNTs surround the matrix; this structure has allowed us to improve various major properties[11,12].

Apart from the specifics of CNT system, the most important technical component for a filler-based composite is wetting between the filler and matrix. Wetting controls dispersion of the filler into the matrix material, as well as various characteristics of the composite. Also, the diameters of the CNT as filler are presumed to influence the mechanical properties of the nanocomposite[11,16]. In this paper, we report the successful development of high-stiffness rubber materials, and we examine the influence of the composite, which uses natural rubber (NR) as the matrix material and multi-walled carbon nanotubes (MWCNTs) as the filler, on surface properties of MWCNTs.

2. Experimental

2.1 Matrix and filler materials

For the composite, the matrix material was a NR (CV-60) and the filler was one of three graphitized MWCNTs: MWCNT-1 with an average diameter of 156 nm, MWCNT-2 with an average diameter of 87 nm, or MWCNT-3 with an average diameter of 50 nm (Fig.1). Their lengths were approximately 10 μm . MWCNTs fabricated by CCVD contain crystals full of defects, which develop into a graphite structure after heat treatment at approximately 2,800 °C (depending on temperature). After the fabrication of MWCNTs, heat treatment was performed for graphitization in an argon atmosphere for an hour at 2,800 °C. To investigate the influence of surface conditions of MWCNTs on properties of the composite, the heat-treatment temperature was varied after fabrication of MWCNTs (87 nm in diameter). The heat-treatment temperature was 2,200 °C for MWCNT-2a, 1,800 °C for MWCNT-2b, and 1,200 °C for MWCNT-2c. Since MWCNTs contain defects, such as kinks and branches, MWCNT-2 (heat-treated at 2,800 °C) was crushed to reduce defects, increase surface irregularities, and oxidize the surface; the resulting material is referred to as MWCNT-2H. For comparison, we used HAF carbon black (HAF-CB), which is known to be a highly reinforcing filler material.

2.2 Preparation of composite materials

NR of a predetermined quantity was wrapped around a 6-in open roll and kneaded for about 10 min with roll spacing of 1 mm, so that more free radicals were created as the molecular weight decreased. The rotation speed was 22 rpm and 20 rpm, and a shearing force was applied at a speed ratio of 1.1. Then, a predetermined quantity of MWCNTs was slowly added, and NR was brought out after the mixing was finished. The roll gap was then narrowed to 0.1 mm, and the mixture was milled five times to open MWCNT aggregates. To prevent any increase in roll temperature during mixing and kneading, a coolant was used to maintain the temperature at 15-20 °C. And then, after the roll spacing was returned to 1 mm, the kneaded mixture material was wrapped, the cross-linker (dicumyl peroxide) 2 phr was added, and the mixture was rolled into a sheet having a thickness of 1.1 mm. Finally, the sheet was press formed for 20 minutes at 165 °C, resulting in a 1 mm thick, cross-linked sample.

2.3 Measurements

We examined the following characteristics of MWCNTs: bulk density, specific surface area, and crystallinity (R-value in the Raman spectrum). Based on JIS K 1464, the bulk density was obtained from the volume; 1 g of MWCNT was placed in a measuring cylinder (500 ml), and the cylinder was patted on a plate until the volume stabilized. To examine the specific surface area, the adsorption isotherm was measured at 77 K using nitrogen as the adsorbate (ASAP2020, Micromeritics); the specific surface area was calculated using BET method. Using a Raman spectroscopic analyzer (Hololab 5000, Kaiser Optical Systems; 532 nm), the crystallinity of the sample was measured in the G band ($\sim 1590\text{ cm}^{-1}$), which is derived from graphite on the basis of vibrations in the hexagonal lattice structure of carbon, and the D band ($\sim 1350\text{ cm}^{-1}$), which indicates defects associated with carbon, such as amorphous carbon. The R-value to measure the crystallinity was calculated from the intensity ratio (I_D/I_G).

A tensile test of the composite material was based on JIS K 6251. After being smashed with a No. 3 dumbbell, the sample was pulled at a rate of 500 mm/min and the stress σ_{100} , tensile strength (at break) TB, and elongation (at break) EB were measured at 100% extension. Based on JIS K 6253, the hardness was measured using a type-A durometer. Using a dynamic viscoelasticity measuring apparatus (DMS6100, SII), the storage modulus E' and loss tangent $\tan\delta$ were measured in a nitrogen atmosphere at 1 Hz and a rate of temperature rise of $3\text{ }^\circ\text{C}/\text{min}$ from $-100\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$. To calculate the creep rate (ppm/h) in the steady creep state between 120 min and 900 min, the dimensional change of a sample was measured using TMA (TMA/SS6100, SII) under a load of 250 KPa at $120\text{ }^\circ\text{C}$.

The configuration of MWCNTs and the tensile fracture surface of the composite material were observed using a field emission-type scanning electron microscope (FE-SEM; JSM-7400F, JEOL).

3. Results and discussion

3.1 Configuration

Figure 2 shows the SEM images of the filler (MWCNT-2). The figure shows aggregates of fibrous materials whose straightness was relatively good, with fibers intertwined with each other. The diameter of 87 nm for MWCNT-2 was obtained from the average of 100 fiber diameters appearing in the magnified SEM image. Average diameters were also obtained for MWCNT-1

(156 nm in diameter) and MWCNT-3 (50 nm in diameter); these fibers also had good straightness. Also, Fig.3 shows the TEM images of (a) MWCNT-2b (HTT:1200°C) and (b) MWCNT-2 (HTT:2800°C), MWCNTs are changed to graphite structure by high temperature heat treatment.

Figure 4 shows SEM images of the tensile fracture surface of MWCNT-2/NR composite material. Sea-island structures, which characterize poor dispersion, do not appear in the fracture surface, indicating that the dispersion was homogeneous. The magnified SEM image in Fig.3(b) shows that the constituents of MWCNT-2 were separated individually; tubes were fibrillated to the smallest size and uniformly distributed. We believe this was caused by wetting MWCNTs, and mediated by free radicals created by the break of NR molecular chains during the mixing and kneading, as well as mixing and kneading by means of NR elasticity[6,9,11,12]. However, Fig.3(b) shows that adhesion between MWCNT-2 and NR was only partially good; this conclusion is supported by the long drawn out MWCNT-2 fibers and the presence of dropout cavities.

3.2 Tensile properties

Stiffness, an index that applies to rubber and elastomers, is one of the first properties considered when identifying possible applications. Stiffness is a resistance to deformation, but we also use other standards, such as hardness, stress (σ_{100}) for mild extension, and in some cases the storage modulus. Figure 5 shows hardness as a function of filler content for MWCNT/NR composite materials for each of the three thicknesses. For comparison, the figure also shows the hardness of HAF-CB/NR composite materials. Hardness, which increases with the amount of content in any filler system, increases most rapidly in MWCNTs and especially, in thinner MWCNTs. Note that, MWCNT-2, with an average diameter of 87 nm, and MWCNT-3, with an average diameter of 50 nm, behave similarly. Although we can increase hardness and enlarge the range of use by adding more filler, flexibility generally decreases as stiffness increases; this causes a paradoxical problem.

Figure 6 shows the relationship between EB and (a) hardness, (b) σ_{100} and (c) stress-strain curve. In HAF-CB, EB decreases monotonically as the fraction of filler increases, resulting in degradation of flexibility. In contrast, for MWCNT-based composite materials, length

increases as hardness increases up to around 70; so, degradation in flexibility does not occur despite the increase in hardness. For hardness above 70, EB decreases, but the change is small compared to the CB system. Similar tendencies occur in Fig. 6(b) for the relationship between the stress σ_{100} measured at 100% extension and EB. Unlike the reinforcement provided by particles such as CB, the behavior of MWCNT composites probably occurs because the long and fine fibrous MWCNTs can deform more freely due to the increase in stiffness, despite the decrease in flexibility; Fig. 6 illustrates the merits of using MWCNTs for reinforcement. This behavior is an extremely advantageous feature in designing rubber products.

Now we examine the influence of the surfaces of MWCNTs. Cavities, due to the dropout of MWCNTs, appear in the tensile fracture surface, as shown in the SEM image in Fig. 4(b). This was most probably caused by insufficient wetting and adhesion between MWCNTs and NR matrix. Therefore, we tried two ways to reform the surface of MWCNTs. The first surface treatment was a heat treatment after fabrication of MWCNTs. The heat treatment was performed to remove impurities, such as catalysts, and to promote graphitization; however, MWCNTs have a tendency to assume a graphite structure (high crystallization) as the process temperature increases (see Raman R-value in Table 1 and TEM images in Fig.3). In MWCNTs processed at lower temperatures, there are many defects and functional groups on surfaces and inside, while in MWCNTs processed at higher temperatures, there are fewer defects, and the surface becomes extremely inert. Therefore, we examined the influence of surface activity by comparing results from heat treatments at temperatures of 2,200 °C (MWCNT-2a), 1,800 °C (MWCNT-2b), and 1,300 °C (MWCNT-2c).

For the second surface treatment, mechanical crushing was performed to decrease defects (such as branches) in MWCNTs (MWCNT-2H) and give irregularity to surfaces. The results are shown in Figs. 7 and 8. As seen in Fig. 7, MWCNT-2c system heat-treated at 1,200 °C shows a significant increase in tensile strength. In the relationship between σ_{100} and EB, as shown in Fig. 8, the elongation of the sample heat-treated at higher temperatures (more than 1,800 °C) shows a tendency to decrease, while MWCNT-3c heat-treated at 1,200 °C maintains elongations of over 100% under the very high stress of $\sigma_{100} = 20$ MPa.

Figure 9 shows SEM images of tensile fracture surfaces in (a) MWCNT-2a(HTT:2200°C), (b) MWCNT-2b(1800°C), and (c) MWCNT-2c(1200°C). It is found that compared with the

SEM image in Fig. 2(b), MWCNTs that have fallen out in Fig. 9 are shorter, and smaller numbers of fractures and dropout cavities corresponding to decreasing of heat treat temperature of MWCNTs(see arrows in Fig.9). In particular, in MWCNT-2c, MWCNT and NR adhere well with each other without cracks. We believe this strong adhesive strength will improve the tensile characteristics of the composite materials discussed earlier. In another surface treatment, the significant change expected for the crushed MWCNT-2H sample was not observed.

Table 1 shows the basic characteristics of MWCNT raw materials. The table shows that the specific surface area of MWCNT-2c is large and crystallinity is greatly degraded, as indicated by the R-value in the Raman spectrum. We believe the high tensile stress of MWCNT-2c system is due to low crystallization, increased specific surface area, and creation of active sites. This high tensile stress should be suited for applications that require pressure resistance; currently, the fluorine rubber seal material containing MWCNT-2c is being used as an O-ring material in oil exploration where the hitherto known technology is difficult to apply[11].

3.3 Temperature dependence

Figure 10 shows the temperature dependence of the (a) loss tangent $\tan\delta$ and (b) storage modulus E' obtained by measuring the dynamic viscoelasticity. Variations in the size of the glass transition region are not discussed here; details will be reported in a future publication. At temperatures below the glass transition region, E' of HAF-CB behaves similarly to NR without appreciable deviation, but MWCNT system shows higher values, and the rigid graphitized MWCNT-2 shows the greatest increment. At temperatures above room temperature, NR sample was cracked by a very small deformation and became difficult to measure at 200 °C. In contrast, the filler system remained measurable up to 300 °C even though E' slowly decreased; this behavior indicates improvement in short-term thermal resistance. In Fig. 10(b), E' , which begins to decrease from approximately 200 °C in HAF-CB and MWCNT-2c, is stable up to 300 °C in MWCNT-2 and MWCNT-2H. This suggests that the physical properties of HAF-CB and MWCNT-2c, which have high surface activity, become inferior to those of MWCNT-2 and -2H, which have inert surface characteristics. In Fig. 10(a), at temperatures above the glass transition region, very high values of $\tan\delta$ were maintained up to very high

temperatures in MWCNT-2 and -2H, while $\tan\delta$ remained low in MWCNT-2c, much like the behavior of the single-body NR sample. This behavior shows that $\tan\delta$ is high in a system with poor adhesion, while it is low in a system with excellent adhesive strength. Further details will be reported after the theoretical analysis and modeling are complete.

Creep tests were performed to examine long-term thermal resistance; the results are shown in Fig.11. When a large load of 250 KPa is applied at a high temperature of 120 °C, the sample deforms significantly in the initial stage up to 120 min, and then maintains a steady rate of deformation. Long-term thermal resistance is judged to be excellent if both the initial deformation and the steady creep rate between 120 and 900 min are small. The initial deformation (Fig.11(a)) decreased substantially as the fraction of filler increased, but in HAF-CB, good improvement did not occur even if filled to 20 wt%. Figure 11(a) shows that MWCNT-1, with a large diameter, behaved similarly to HAF-CB, while MWCNT-2 and MWCNT-3 had the lowest initial deformations and creep rates. For the single-body NR sample, we cannot show the behavior in the figure because creep failure occurred at about 450 min, but improvement due to use of filler was apparent. For MWCNT-2c system, Fig.11(a) shows that the initial deformation was very small, while Fig.11(b) shows that the creep rate was about the same as that for HAF-CB and an improvement parallel to that of MWCNT-2 did not occur. A tendency analogous to the lowering of short-term thermal resistance observed above 200 °C in Fig. 10(a), also occurs at 120 °C in the long-term behavior. In other words, thermal resistance decreases if we try to improve adhesive properties by improving surface activity. This suggests that the large number of active sites remaining after molding the sample may enhance degradation at higher temperatures and when exposed to oxygen. This means that if MWCNT-2c system is to be used in practical applications, residual active sites must be deactivated.

4. Conclusions

We have studied the structures and characteristics of composite materials containing uniformly dispersed MWCNTs; MWCNTs had three different diameters, and their surfaces were activated by heat treatment or crushing. When MWCNTs were used as fillers in the composite, reinforcement effects were greater for finer MWCNTs, and the surface reactivity of

MWCNTs was greatly improved by heat treatment after fabrication. The best adhesion of MWCNTs with NR was obtained by heat treatment at 1,200 °C. High-temperature characteristics and thermal resistance degraded as the surfaces of MWCNTs became more active; this causes a paradoxical problem between adhesion and thermal resistance. For practical use, active sites must be controlled to achieve a balance between thermal resistance and adhesive properties.

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Figure captions

Fig.1 SEM images of various multi-walled carbon nanotubes((a) MWCNT-1, (b) MWCNT-2, (c) MWCNT-3), average diameters of MWCNTs are 156nm(a), 87nm(b), 50nm(c), respectively.

Fig.2 SEM images of Multi-walled carbon nanotube raw materials(MWCNT-2) , (a)×100, (b)×10k, (c)×58k.

Fig.3 TEM images of Multi-walled carbon nanotube (MWCNT-2) , (a) MWCNT-2b (HTT:1200°C), (b) MWCNT-2 (HTT:2800°C).

Fig.4 SEM images of fracture surface of MWCNT-2(16wt%)/NR composites.

Fig.5 Relationship between MWCNT fraction and hardness for NR matrix composites.

Fig.6 Relationships between hardness and EB (a), σ_{100} and EB (b) for NR matrix composites and stress-strain curves.

Fig.7 Relationships between MWCNT fraction and tensile strength for NR matrix composites.

Fig.8 Effect of MWCNT surface on relationships between σ_{100} and EB (a) for NR matrix composites.

Fig.9 SEM images of fracture surface of MWCNT-2a(a), MWCNT-2b(b), MWCNT-2c(c) (16wt%)/NR composite.

Fig.10 Temperature dependences of E' (a) and $\tan\delta$ (b) for NR matrix composites.

Fig.11 Initial creep (a) and creep rate (b) in creep test of 250 KPa at 120 °C for NR matrix composites.

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Table 1 Basic properties of various MWCNTs.

Sample	HTT °C	Diameter nm	Bulk density g/cm ³	Surface area(BET) m ² /g	R value I _D /I _G ratio
MWCNT-1	3000	156	0.040	15	0.10
MWCNT-2	3000	87	0.020	20	0.11
MWCNT-2a	2200	87	0.020	22	0.45
MWCNT-2b	1800	87	0.020	31	1.27
MWCNT-2c	1300	87	0.013	35	1.29
MWCNT-2H	3000	87	0.030	22	0.22
MWCNT-3	3000	50	0.020	20	0.11