Characterization of Chemically modified Nanodiamond Reinforced Natural Rubber Nanocomposite

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Abstract

Nanodiamond (ND) reinforced natural Rubber (NR) nanocomposites were prepared and the structures and the properties of the nanocomposites were investigated. We prepared three kinds of chemically modified ND in order to obtain the strong interaction between ND and NR. ND was modified with COOH (ND-COOH), Octadecylamine (ODA) (ND-ODA) and sulfide (ND-S). It was revealed that the tensile strength increased by 142%, 142%, 125% and 117% with 5 wt% of ND, ND-COOH, ND-ODA and ND-S, respectively, compared with that of the NR. The toughness increased by over 150% for all the nanocomposites by the incorporation of 5 wt% ND. Generally, elongation at break of polymers tend to decrease by the incorporation of the rigid filler such as nanocarbons. On the other hand, the elongation at break was maintained for the ND reinforced nanocomposites. This suggests that ND inhibits the elongation crystallization of NR.

1. Introduction

Natural Rubber (NR) has often been used as a practical product in various fields since the invention of sulfur cross-links by C. Goodyear in 1829 [1]. NR materials are blended with various fillers for the purpose of imparting functions such as improvement of mechanical properties, improvement of processability and electric conductivity. General fillers like carbon black and silica have been used in rubber composite materials to improve hardness, stiffness, strength and abrasion resistance of rubber composites materials. However, recently, the performance required for rubber materials has diversified, and limitations have been seen with carbon black. The filler content of carbon black NR composites tend to be high to obtain the desired physical properties. Therefore, the weight of the final products increased. In addition, there was a problem that the coloring of the products was impossible due to blackening. Furthermore, the brittleness due to agglomeration of carbon black has often occurred. As a result, it is difficult to provide the expected functions to the conventional NR composites [2-8].

Diamond is a material having very excellent characteristics such as high modulus of elasticity (about 10^3 GPa) and high thermal conductivity (about 2 kW/m・K) among natural solid substances. However, because of its low processability, diamonds of large size were only used industrially. Nanodiamond (ND) is a particle with the size of less than 10 nm with diamond crystal in its core. Therefore, ND shows excellent physical properties derived from diamond. On its surface, ND possesses oxygen containing functional groups such as OH, COOH, CO and COC. These groups can be a site of various chemical modifications of ND [9, 10]. In this study, we conducted the chemical modification of ND and prepared NR/ND nanocomposites. The structures and properties of the NR/ND nanocomposites were investigated.

2. Experimental method

2.1. Chemical modification of ND

2.1.1. Preparation of Oxidized ND (ND-COOH)

ND was added in a mixture of concentrated H_2SO_4 and HNO_3 (9:1(v/v)) and stirred at 75 °C for 3 days. Subsequently, the mixture was heated in 0.1 M NaOH aqueous solution at 90° C for 2 h, and then in 0.1 M HCl aqueous solution at 90℃ for 2 h. The resulted carboxylated/oxidized nanodiamond were extensively rinsed with deionized water. Purified ND-COOH was used in subsequent studies.

2.1.2. Preparation of octadecylamine (ODA) modified ND (ND-ODA)

ND - COOH was mixed with $SOCl_2$ and N, N-dimethylformamide (DMF). Heat reflux is performed at 70 ℃ for 24 hours. After removing the solution, it was washed with tetrahydrofuran (THF). The resultant was dried at room temperature and added to ODA. The mixture was mixed and heated and agitated at 90 to 100 ℃ for 4 days. After cooling, rinsed with methanol accompanied with ultrasonication. Soxhlet extraction was carried out with hot methanol to further remove ODA for 10 times with fresh methanol [11,12]. Purified ND-ODA was used in subsequent studies.

2.1.3. Preparation of sulfide modified ND (ND-S)

ND-COOH was mixed with pure water and ultrasonicated. An aqueous solution of sodium thiosulfate was mixed with the suspension. Cetyltrimethylammonium bromide (CTAB) was added, and 5 wt% HCl aqueous solution was slowly added dropwisely with stirring. The reaction was continued for further 3 hours. The precipitate was filtered and washed several times with pure water and acetone to remove impurities. After filtration, the precipitate was vacuum dried for 24 hours and then heat treated at 200 ° C [13, 14]. Purified ND-S was used in subsequent studies.

2.2. Preparation of NR/ND nanocomposites

ND was added to NR emulsion and stirred and ultrasonicated. The mixed suspension was cast into a petri dish and dried at room temperature. The dried NR/ND sheet was vulcanized at 100 ° C for 90 minutes to obtain NR/ND nanocomposites. The ND content was controlled as 1, 3 and 5 wt% against NR.

2.3 Characterization

The NR/ND nanocompsites was observed using a scanning electron microscope (SEM) (JEOL, JSM-6510LA) at an accelerating voltage of 15 kV. Au was deposited on the sample surface prior to observation. Fourier transform infrared spectrum (FT-IR) of ND was recorded on a FT-IR spectrophotometer (JASCO, FT/IR-4200) using the KBr method. The resolution was 2 cm^{-1}. X-ray diffraction (XRD) was performed using an X-ray diffractiomerter) Rigaku, RINT2000). The X-ray beam was operated at 40 kV and 40 mA. The 2 θ scan date were collected at 0.02 ° intervals at a scanning speed of 1.0 °/min.

The equilibrium swelling experiment was performed to measure the crosslinking density (C_d) of the nanocomposites. The C_d was determined from the Flory−Rehner equation [15, 16]:

$$-[ln(1-\emptyset_r)+\chi\emptyset_r^2]=V_0 n\left(\emptyset_r^{1/3}-\emptyset_r/2\right) \quad (1)$$

where Φ_r is the volume fraction of the rubber in the swollen mass, V_0 is the molar volume of the toluene (106.2 cm^3), n is the number of active network chain segments per unit of volume (= C_d), and χ is the Flory−Huggins polymer solvent interaction term, which is 0.393 for toluene. The Φ_r was obtained according to Bala *et al* [17, 18].

$$\emptyset_r = \frac{m_2/\rho_2}{m_2/\rho_2 + (m_1 - m_2)\rho_1} \quad (2)$$

where m_1 and m_2 are the masses of swollen sample before and after dried, respectively. ρ_1 and ρ_2 are the densities of toluene (ρ_1 = 0.865 g/ cm3) and rubber, respectively.

The glass transition temperature (T_g) was measured using a differential scanning calorimeter (DSC) (Rigaku, Thermo plus EVO2 DSC8231), measured from -80 to 0 °C using liquid nitrogen.

The tensile properties of nanocomposites were measured at room temperature with AGS-X 1kN (Shimadzu Co.). Test pieces about 800 μm thick shaped with a cutter were subjected to tensile tests. A cross head speed of 200 mm/min according to JIS K6251-7. The toughness (K) was determined as the area surrounded by the stress (σ) - strain (ε) curve.

3. Results and Discussion

3.1. Characterization of Chemically modified ND

Figure 1 shows FT-IR spectrum of the ND, ND-COOH, ND-ODA and ND-S. Absorption bands around 1690-1740cm^{-1} (II) can be assigned to C = O stretching vibration of carboxyl group. These bands were observed for all samples. In addition, the peaks found in Ⅱ showed greater absorption in ND - COOH compared with ND. This is probably because the C = O bond increased due to the oxidation of ND. Amide bond (1550 cm^{-1} (Ⅰ)) and C-H bond (2800-3000 cm^{-1} (Ⅲ)) were observed in the spectrum of ND-ODA. Therefore, it was confirmed that ODA was successfully bonded on the surface of ND by amide bonding [12]. The C - S bond (1150 cm^{-1}) was observed in the spectrum of ND-S. Therefore, it was confirmed that S was successfully bonded on the surface of ND by C- S bond [13].

Figure 2 shows X-ray diffraction profiles of ND and ND-COOH, ND-ODA, ND-S and S. The diffraction peak assigned as 111 reflection of diamond structure were observed clearly for the ND particles at 2θ = 43.9 ° for all ND samples. This indicate that ND particles possess three-dimensional diamond structure even at a size of no more than 10 nm even if it was chemically modified. The diffraction peaks of sulfur can be indexed to crystalline orthorhombic sulfur (JCPDS no. 08-0247), indicating high purity of the as-synthesized sulfur. The diffraction peaks of sulfur were observed overlapped with those of ND around 2θ = 20 - 30 ° for ND-S. Therefore, it is considered that sulfur was successfully adsorbed to ND [13].

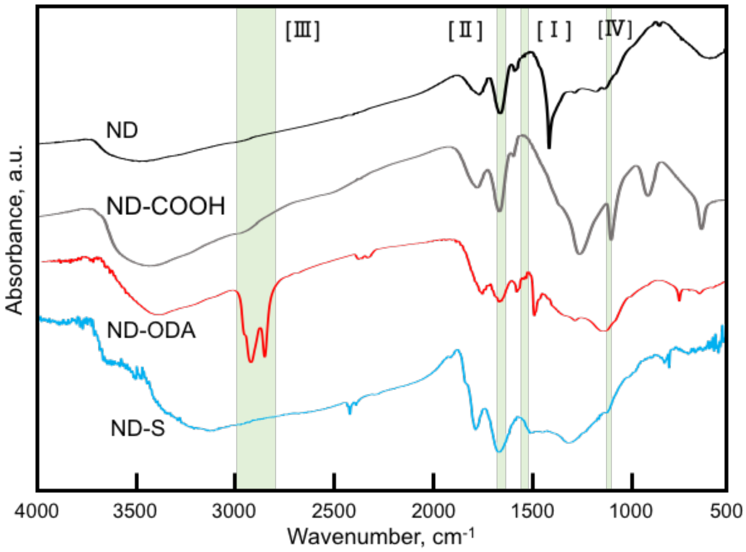

Figure 1. FTIR spectra of ND, ND-COOH and ND-ODA.

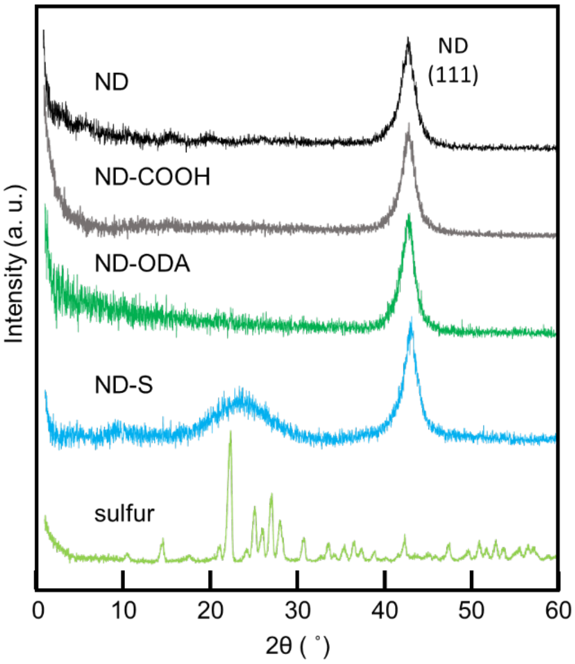

Figure 2. X-ray diffraction profiles of ND, ND-S and sulfur.

3.2. Structure of nanocomposites

Figure 3 shows the SEM images of the fracture surface of NR (A), NR/ND (B), NR/ND-COOH (C), NR/ND-ODA (D) and NR/ND-S (E) nanocomposites. The filler content of the nanocomposites was 5 wt%. Clusters of ND with the size about 200 nm was observed for the nanocomposites. It was revealed that the clusters were homogeneously dispersed in the nanocomposites.

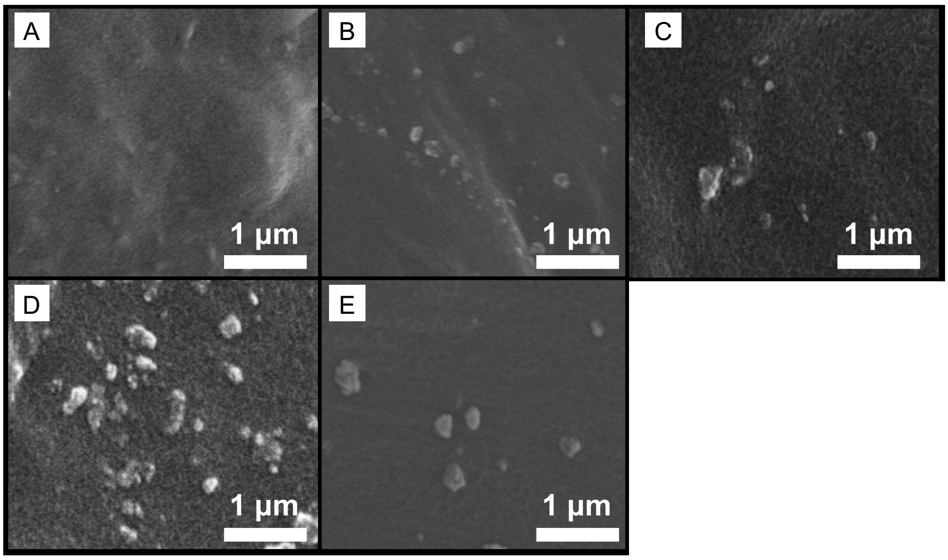

Figure 3. SEM images of NR (A), NR/ND (B), NR/ND-COOH (C), NR/ND-ODA (D) and NR/ND-S (E) nanocomposites (5 wt%).

Table 1 shows C_d of NR, NR/ND, NR/ND-COOH, NR/ND-ODA and NR/ND-S nanocomposites. The C_d of the nanocomposites was slightly increased by the incorporation of ND or chemically modified NDs. Since C_d was measured by the equilibrium swelling experiment, it was shown that the rigid structure of ND effectively suppressed the swelling of NR in the nanocomposites. It was revealed that the C_d of the chemically modified NDs reinforced nanocomposites were higher than that of unmodified ND nanocomposites, showing that the interaction between NR and ND was increased by the chemical modification. As for NR/ND-ODA nanocomposites, it seemed that the long side chains of ODA entangled NR molecular chains, serving as a crosslinking in the nanocomposites. On the other hand, S of ND-S acted as a cross-linking agent in the nanocomposites, therefore, the C_d of the NR/ND-S nanocomposites increased.

Table 1. Crosslink density (C_d) of NR and NR / ND nanocomposites

Matrix	NR												
Filler		ND			ND - COOH			ND - ODA			ND - S		
Filler content (wt%)	0	1	3	5	1	3	5	1	3	5	1	3	5
C_d (10^{-4} mol/cm^3)	1.20	1.08	1.30	1.23	1.67	1.39	1.33	1.23	1.67	1.69	1.42	1.55	1.54

3.3. Properties of nanocomposites

3.3.1. Thermal Properties

Figure 4 shows DSC curve of NR/ND, NR/ND-COOH, NR/ND-ODA and NR/ND-S nanocomposites. The glass transition temperature (T_g) of the nanocomposites was almost the same as that of NR. Similar results were reported for other nanocarbons reinforced NR nanocomposites [21].

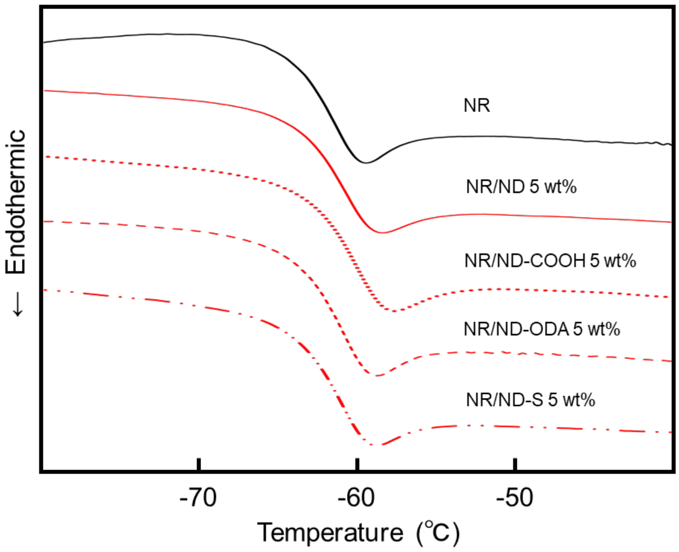

Figure 4. DSC curve of NR and NR / ND nanocomposites.

3.3.2. Mechanical Properties

Figure 5 shows the stress-strain curves of NR/ND, NR/ND-COOH, NR/ND-ODA and NR/ND-S nanocomposites. Table 2 shows the elongation at break (ε_{max}), tensile strength (σ_{max}), Young's modulus at strain 500% (E_{500}) and toughness (K) obtained from stress-strain curves. The σ_{max}, E_{500} and K were improved for all nanocomposites. The σ_{max} was largely increased by the incorporation of small amount of ND or chemically modified ND. Compared with σ_{max} of NR, it was increased by 92% for 1 wt% ND nanocomposite and by 67% for 1 wt% ND-COOH, ND-ODA and ND-S nanocomposites. It was revealed that the E_{500} increased by 50%, 57%, 61% and 70% with 5 wt% of ND, ND-COOH, ND-ODA and ND-S, respectively. The increase in the mechanical properties can be explained by the formation of a firm nano-matrix structure [22]. It was assumed that the ND particles disperse in NR and form a mixed network of hard and soft parts in the nanocomposites and the hard parts effectively reinforced the overall materials. In addition, it was also attributed to the increase in the C_d by the incorporation of NDs as shown above [20, 22, 23]. Since the chemically modified ND reinforced nanocomposites showed higher E_{500} than that of unmodified ND reinforced nanocomposites, it was suggested that the interactions between NR and ND was increased by the chemical modification of ND.

In general, nanocomposites reinforced by rigid filler such as nanocarbons shows increase in σ_{max} and E, while σ_{max} drastically decrease. As a result, K tend to decrease for the nanocomposites. On the other hand, ε_{max} increased for the nanocomposites prepared in this study. Therefore, K largely increased for the nanocomposites. It was revealed that the K increased by over 150% for all the nanocomposites with 5 wt% NDs.

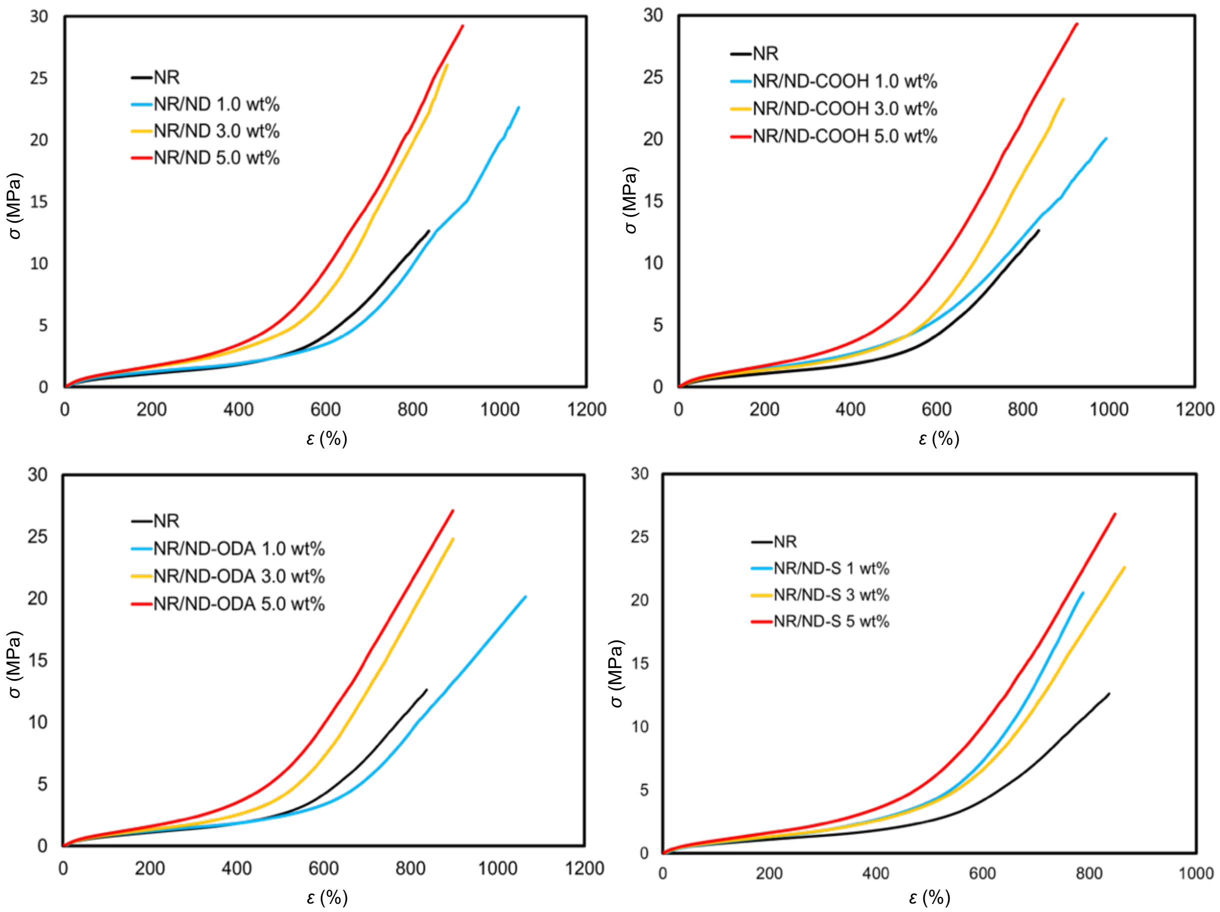

Figure 5. Stress-strain curves of NR and NR/ND nanocomposites.

Table 2. $\varepsilon_{\max}$, $\sigma_{\max}$, E_{500} and K of NR and NR/ND nanocomposites.

Material	$\varepsilon_{\max}$ (%)	$\sigma_{\max}$ (MPa)	E_{500} (MPa)	K (J/g)
NR	837	12	2.3	26
NR/ND 1 wt%	1043	23	2.4	45
NR/ND 3 wt%	882	26	3.1	55
NR/ND 5 wt%	915	29	3.5	65
NR/ND-COOH 1 wt%	993	20	3.2	55
NR/ND-COOH 3 wt%	894	23	3.2	47
NR/ND-COOH 5 wt%	926	29	3.6	76
NR/ND-ODA 1 wt%	1064	20	2.3	53
NR/ND-ODA 3 wt%	897	24	3.3	54
NR/ND-ODA 5 wt%	899	27	3.7	65
NR/ND-S 1 wt%	788	20	3.7	35
NR/ND-S 3 wt%	865	22	3.7	46
NR/ND-S 5 wt%	848	26	3.9	67

4. Conclusion

In this study, ND reinforced NR nanocomposites were prepared by using a simple casting method from aqueous medium. In order to achieve the strong interaction between NR and ND, we conducted the chemical modification of ND. It was revealed that ND particles were homogeneously dispersed in the nanocomposite as clusters with the size around 200 nm. The C_d was revealed to be increased by the incorporation of ND, especially by chemically modified NDs. It was suggested that the strong interaction was generated between NR and chemically modified NDs. The mechanical properties remarkably increased for the nanocomposites with a small amount of ND, showing that the unique properties of ND were successfully imparted to the nanocomposites. We achieved to develop a new light-weight NR nanocomposites with excellent physical properties which can be the potential material for various industries.

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