Improvement in thermal durability of fluorinated rubber by the addition of single-walled carbon nanotubes as a thermally stable radical scavenger

Seisuke Ata [a, b, *], Shigeki Tomonoh [a, b], Takeo Yamda [a, b], Kenji Hata [a, b]

[a] CNT-Application Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Central5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
[b] Technology Research Association for Single Wall Carbon Nanotubes (TASC), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

ABSTRACT

Rubber is an excellent material, but its usage has been limited due to its low heat-resistance. In a high-temperature environment, rubber decomposes due to the heat radicals generated by the bond cleavage reaction. In order to improve the heat-resistivity of rubber, it is necessary to stabilize the radicals. Therefore, carbon nanotubes (CNTs), which are known for their excellent radical scavenging ability, were added to fluorinated rubber. The upper limit of the temperature for continuous use was increased from approximately 200 to 340 °C with the addition of the small amount of CNTs. This technology would make it possible to easily improve the heat resistivity of rubber and would expand their use in a variety of applications that were previously limited due to the issues of heat-resistivity.

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1. Introduction

Rubber and thermoplastic elastomer (which are known by the generic name, elastomer) possess many exceptional characteristics such as, excellent mold-ability and high impact resistance, and they are also lightweight and inexpensive. Additionally, their excellent barrier properties against gas and liquids make the elastomers suitable for sealing materials (e.g., O-ring, gasket), tires, and medical equipment. On the other hand, elastomers are disadvantageous when exposed to heat [1,2], hot water, acid, alkali [3], and metal [4], because their properties deteriorate due to the breaking of the bonds of the molecular chain. Therefore, the applications of elastomers are limited and in particular, the vulnerability to heat has reduced their reliability.

Elastomers are comprised of one-dimensional polymer chains and cross-linking region, and this is the reason behind the softness and elasticity of elastomers. The polymer chains and the cross-linking sites of any polymer material, not limited to elastomers, are cleaved due to autoxidation caused by the thermal radicals when exposed to a certain temperature [5]. This reduces the elasticity of elastomers and results in the loss of the elastic recovery property, and they are no longer able to function at the required level as sealing materials. Therefore, for each type of elastomer, the "upper limit temperature for use T_{lim} (<thermal degradation temperature T_G)", i.e., the maximum temperature at which continuous, long-term use is possible, is defined. For example, the T_{lim} of natural rubber is 65 °C, hydrogenated NBR is 110 °C, fluorinated rubber (FKM) is approximately 200 °C, and perfluoroelastomer (FFKM), which has high heat resistivity, is approximately 300 °C. In order to improve heat-resistivity of polymers, it is necessary to stabilize the thermal radicals, which cause the decomposition of the molecular chains. Generally, radical scavengers with low molecular weight (e.g., 2-tert-Butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate) are added to improve the heat-resistivity of polymer. However, in the temperature range of 200–300 °C, radical scavengers when added to the typical organic matters tend to lower their functionality, and therefore, major improvement in the heat-resistivity has not been achieved up to the present.

Fullerene [6,7] is a material known to be stable against heat and maintains a high radical scavenging ability even in a high-temperature environment. As it is not easy to uniformly disperse fullerene into the polymer, a practical application using fullerene to improve the heat-resistivity has not been realized. On the other

hand, carbon nanotubes (CNTs) [8] which are also a type of nano-carbon material like fullerene, are easier to combine with polymers. In addition, it is becoming clearer theoretically and empirically, that their terminals and defects possess radical scavenging ability [9–13]. As the radical scavenging ability is related with curvature of carbon sheet, radical scavenging ability of CNT must be lower than it of fullerene, because the CNTs have larger diameter and 2-dimensional curvature. However, CNT have several superior points for making composite material compare with fullerenes. CNTs can be uniformly distributed in rubber and resins [14–16], and it is believed that CNTs will effectively express their radical scavenging ability within such materials. In addition to improving the heat-resistivity, it is expected that the compounding of CNTs will improve the mechanical properties such as the tear and the tensile strengths because of continuous CNT network in matrix.

Over the past few years, several studies have been made on efect of CNT for improving thermal resistivity of polymers. Noguchi et al. had reported the high heat resistivity and the mechanical strength of FKM composite materials using CNTs based on the reinforcing effect by cellulation, and the amount of CNTs used for the filling was very high, up to 15 vol% [17]. Duong et al. reported that FKM and CNTs (1 wt%, 5 wt%) composites were superior to FKM/carbon black composites in tensile strength and abrasion property [18]. Furthermore, Martinez and Watt et al. have brought to light the radical scavenging ability of the CNTs in composite materials, but their discussion is limited to the thermal decomposition temperature and the oxidation rate [19,20]. These reports were focused on effect of physical-reinforcement of CNT for improving thermal resistivity of polymers. Furthermore, they reports short time thermal resistivity (less than 30 min). If radical scavenging ability of carbon nanotubes improve thermal resistivity of polymers, it is possible to improve thermal resistivity for long-period which is important for application for structural materials. Radical scavenging ability of CNT may affected their length, diameter, wall-number, crystallinity etc.

In this research, we prepared FKM composite with several types of CNTs and investigated their thermal resistivity by using dynamic mechanical analysis. We found that the single-wall carbon nano-tube (SWNT) with large surface (up to 1000 m^2/g) area showed highest effect for improving thermal resistivity of FKM, which bring down the reduction of the storage modulus of FKM from 80% to just 5% at 280 °C for 24 h. Additionally, we have verified that the FKM/CNT composites are usable even after heat treatment at 347 °C for 24 h, as there was no degradation in their elastic modulus values. Furthermore, the FKM/CNT composite materials prepared in the present study exhibited 1.5 to 2 times improvement in the various mechanical properties such as tear strength and tensile strength. The FKM/CNT composite materials could therefore be used as sealing materials where high thermal-resistivity is required such as, automobile industries, factory plants, and in the field of oil drilling etc.

2. Experimental

In this research, we have primarily used super-growth single-walled CNT (SG-SWNT) [8] which is synthetically created through the super-growth CVD method. The SG-SWNT is ~2 mm long and has a large specific surface area more than 800 g/m^2. In addition, we have used multi-walled CNTs, C-Nano (Flo tube 7000, Cnano Technology), Nanocyl (NC7000, Nanocyl SA), and single-walled CNT, HiPCO (purified grade, Nanointegris). The specific surface area, length, diameter and G/D ratio (ratio of intensity of G-band and D-band with Raman spectroscopy) of each CNT are listed in Table 1.

A typical method for the manufacture of rubber consists of the process of kneading the fillers and the rubber by twin rollers to disperse the filler evenly. However, in the cases where the flow direction and the shear direction of the rubber match, it is difficult to de-fibrate with the twin rollers. Therefore, after dispersing the CNT using a wet method [21], we mixed it into the rubber.

To make the de-fibration of the CNTs easier and to increase the affinity to rubber, the CNTs were placed in a vacuum oven at 200 °C for 24 h, which removed all the adsorbed water on the surface of the CNTs. Then, 1000 ml of MIBK (methyl isobutyl ketone) was added to 100 mg of the dried CNTs, and the SG-SWNT was processed at pressures of 100 and 120 MPa using a jet mill (HJP-17007R, Sugino Machine Co. LTD.,) to prepare the dispersion liquid [16,21]. The FKM [16] (Dai-El G-912, Daikin Co. LTD.,) was then added to the CNT/MIBK solution, and the resulting solution was stirred well using a mixer. Subsequently, the solution was heated to 80 °C using a hot plate and left for a day. After removing the bulk of the MIBK, we further reduced the remaining MIBK to 0.1 wt% by keeping the material in vacuum condition at 120 °C for 48 h to prepare a masterbatch. Next, we used the twin rollers in a setting where the shear force is less (rotation speed ratio of two rollers is less than 1.2, roller gap is more than 1 mm) and added a cross-linking agent (triallyl Isocyanurate, Tokyo Gosei) and a cross-linking initiator (2,5-dimethyl-2,5-di(t-butyl peroxy) hexane, NOF Corporation). After press molding (SDOP-1042-2H-AT, Dumbbell Co. LTD.) of this mixture at 170 °C for 10 min, followed by post curing at 180 °C for 4 h, we obtained 2 mm thick CNT-rubber sheets. The sequence of the procedure is shown in Fig. 1(a). The test pieces at the required sizes and samples for the various tests were prepared by punch cutting (Fig. 1(b)).

A dynamic mechanical analyzer DMA (strain 0.1%, 10 Hz, RSA3, TA instrument Co. Ltd.,) was used for measuring the heat resistivity of CNT/FKM composites. After isothermal holding of the test pieces at 200, 220, 250, 280, 350, and 370 °C for 24 h, the storage modulus was measured by DMA. The storage modulus G is related to the entanglement molecular weight, M_e of rubber according to the following equation.

$$M_e \equiv \frac{\rho RT}{G} \tag{1}$$

Here, ρ is the density of sample, R is the gas constant and T is the absolute temperature. In the case of polymers, since the molecular weight M is greater than M_e, the storage modulus is constant regardless of the molecular weight. However, when there is a cleavage in the crosslinking due to degradation, or if the length of the molecular chain is reduced, the average molecular weight M becomes smaller than M_e. In such cases, $M \leq M_e$ and the reduction in the molecular weight reduces the storage modulus of material. For this reason, the storage elastic modulus is an indicator of the thermal decomposition of polymer materials. The reduction in the storage elasticity occurs at a lower temperature than the thermal decomposition temperature. However, since decline in the storage elastic modulus implies that long term use of the rubber in that environment is impossible, we have chosen to use it as an index for the heat-resistivity. The maximum temperature at which the decreasing storage modulus for 24 h is less than 20% of its original value is defined as upper limit temperature for use T_{lim}. Furthermore, we considered that the when the ratio of the storage modulus after 24 h (E_{24}) and the initial storage modulus E_0 (E_{24}/E_0) is closer to 1, the rubber is more heat-resistant, and when the ratio is closer to 0, degradation has progressed. Test piece for DMA was cut out from the rubber composite sheet using a blanking machine to evaluate the storage modulus based on the ISO 37 standard by International Organization for Standardization.

The glass transition temperature (T_g) of the sample was tested