

PREPARATION AND MECHANICAL PROPERTIES OF RUBBER COMPOSITES FILLED WITH CARBON NANOHORNS

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Abstract

NBR (acrylonitrile butadiene rubber) composites filled with single-wall carbon nanohorns (SWNHs, or simply NHs), hole-opened NHs (h-NHs) and carbon black (CB) were prepared, and their mechanical properties were comparatively investigated. The NBR composites filled with NHs and h-NHs showed tensile strength much greater than those for CB-filled composites at the same filler contents, while h-NHs performed better than NHs. At 5 and 20 phr (parts per hundred parts of rubber), respectively, the tensile stresses at break of the NBR composites filled with h-NHs were about 1.8 and 1.4 times larger than that filled with CBs, and the strains at break for h-NHs were 1.2 and 1.4 times larger than that for CBs. Hardness and swelling tests indicated that the composite with h-NHs is the hardest and that the composite with h-NHs has more dense networks than that with CBs. The present results indicate that NHs and h-NHs have reinforcement effects much superior to CB for NBR rubber matrix.

Introduction

Carbon black (CB) is generally used as a filler of rubber matrix due to its reinforcement effect, affinity to matrix and ready dispersion in matrix. It is a form of amorphous carbon that has a high specific surface area and its particle size is of about 10-100 nm, being one of the first nanocarbons to find common use. Some nanocarbons may show specific effects as a secondary filler to the rubber matrix, but the reinforcement effects of carbon black as a primary filler hardly seem to be surpassed by other materials. NHs are tubes made of single-graphene sheets whose diameters are of the nm order (Iijima, S., 1999). NHs differ from single-wall carbon nanotubes (SWNTs) in having long cone-shaped tips with cone angles of about 20 degrees and large tube-diameters of about 2-4 nm, and they form spherical aggregates with diameters of 80-100nm. The graphene sheets of SWNHs are not as perfect as those of SWNTs; i.e. they have many defects such as pentagons and heptagons in the hexagonal networks. These irregular tubule-structures cause the exotic performance characteristic of NHs. For example, holes can be made not only at the tips but also in the sidewalls of NHs through local combustion, and the diameters can be controlled by choosing appropriate combustion temperatures between 300 and 600°C in an oxygen gas atmosphere. The choice of hole diameter ranges from less than 1 to 3 nm. Those morphological as well as physicochemical properties characteristic to NHs may be suitable for the reinforcement of the rubber matrix. In this work, we prepared NBR composites filled with CB, NHs and hole-opened NHs (h-NHs), and their mechanical properties were investigated comparatively.

Experimental

NHs were produced by CO₂ laser ablation of a graphite target under Ar at 760 Torr. Two types of h-NHs were used; one was h-NH which was prepared by heat-treating NHs from room temperature up to 550°C in air with a ramp rate of 1°C/min. followed by natural cooling (Fan, J., 2006), and the other was h-NH which was oxidized in aqueous H₂O₂ (Zhang, M., 2007). The former is denoted as h-NH-O₂, and the latter as h-NH-H₂O₂. CB, NHs, h-NH-O₂ and h-NH-H₂O₂ were added to NBR (JSR N240S). The preparation of the nanocomposites was carried out by the solvent casting method using chloroform. The contents of the fillers ranged from 1 to 30 phr. Several standard additives were mixed and the samples were hot-pressed. The mechanical properties were examined via tensile, hardness, and dynamic viscoelasticity tests.

Results and Discussion

Figures 1, 2(a) and 2(b) show the results of the tensile tests for CB-, NH-, and h-NH-filled NBRs. The contents (in phr) of the fillers are indicated at the end of the sample names. The ratios of the stresses and the strains at break of the NH- and h-NH-filled rubbers to those of the CB-filled rubbers are summarized in Table 1. The NH samples, except for NH-1, show enhanced stresses at break but little effects on strain. The h-NH samples show not only enhanced stresses but also larger strains. The effects of h-NH-O₂ and h-NH-H₂O₂ cannot be compared at present, as samples with the same contents of h-NH-

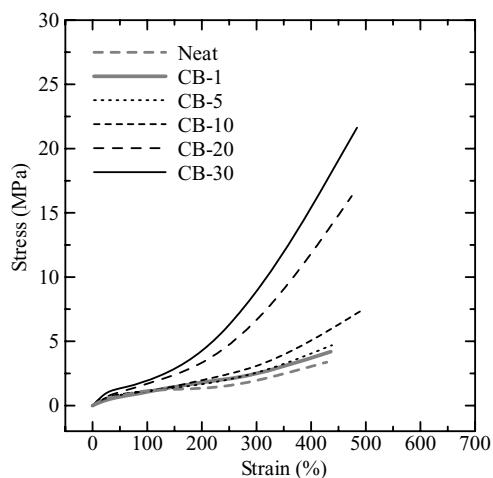


Figure 1. Stress-strain curves of the rubbers filled with CB at filler contents of 1 - 30 phr.

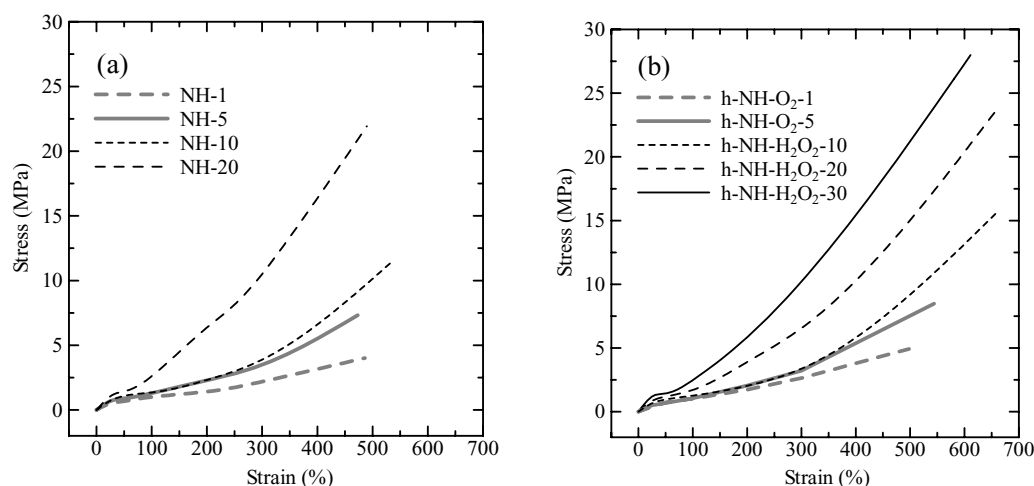


Figure 2. Stress-strain curves of the rubbers filled with NHs (a), and hole-opened NHs, h-NH-O₂ and h-NH-H₂O₂ (b).

O₂ and h-NH-H₂O₂ were not prepared yet. In general, NHs, especially h-NHs, show reinforcement effects superior to CB, but the effects seem to be greater at lower filler contents; at higher filler contents the effects of NHs may become similar to those of CB at the same filler contents. Figure 3 shows the specific gravity of the rubbers as a function of filler content. The CB and h-NH samples show the similar tendency; *i.e.* the specific gravity increases as the filler content increases. On the other hand, the specific gravity of the NH samples hardly increases. This is probably because that the hollow inner space of the NH samples without hole-opening treatment is not accessible from outside (Murata, K., 2005). The inner space of the h-NHs may accommodate or trap parts of the rubber matrix through the open windows, leading to the formation of the matrix network and resulting in the reinforcement of the rubber. Some additive or solvent molecules may also be incorporated. Figure 4 shows the hardness of the rubbers as a function of filler content. The NH samples seem to become harder than the CB and h-NH samples as the filler content increases, while the h-NH samples are slightly harder than the CB samples.

Table 1. Ratios of the stresses and the strains at break of NH- and h-NH-filled rubbers to those of CB-filled rubbers.

	1 phr		5 phr		10 phr		20 phr		30 phr	
	Stress	Strain	Stress	Strain	Stress	Strain	Stress	Strain	Stress	Strain
NH	0.95	1.11	1.56	1.07	1.54	0.89	1.34	1.03	–	–
h-NH-O ₂	1.18	1.14	1.80	1.24	–	–	–	–	–	–
h-NH-H ₂ O ₂	–	–	–	–	2.13	1.35	1.43	1.38	1.29	1.26

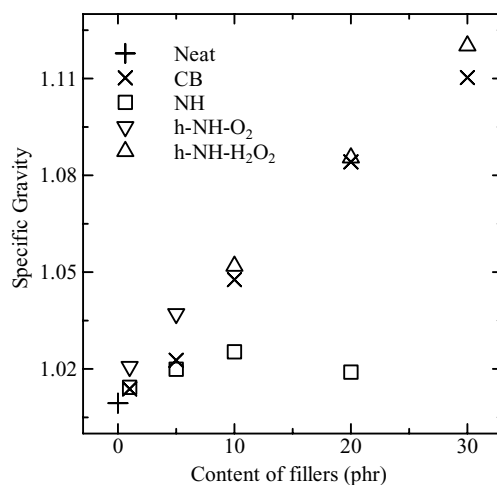


Figure 3. Specific gravity of the rubbers as a function of filler content.

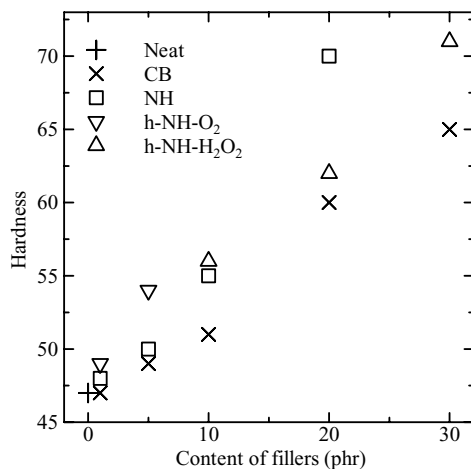


Figure 4. Hardness of the rubbers as a function of filler content.

Therefore rubbers filled with NHs without holes can possess advantages of being lighter (less dense), harder and stronger at the same time than ordinary rubbers.

Conclusions

The present data indicate that NHs, especially h-NHs, have reinforcement effects much superior to CB for NBR rubber matrix. The superiority of h-NHs over NHs may be attributable to the availability of the inner space of the nanohorns for engaging branches of rubber matrix polymers.

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