Strain-induced Crystallization and Mechanical Properties of Carbon Nanotubes Reinforced Natural Rubber

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ABSTRACT

Strain-induced crystallization of natural rubber containing various amounts of carbon nanotubes (CNTs) was studied by synchrotron X-ray scattering. X-ray scattering intensities from the oriented rubber are decomposed into three phases; isotropic amorphous (IA), oriented noncrystalline (ON), and crystalline (Cr) phase and their changes are monitored upon stretching. The CNTs in the rubber helps to orient the chains and strain-induced crystallization during the uniaxial stretching.

Keywords: rubber, CNTs, strain-induced crystallization, synchrotron X-ray scattering

1 INTRODUCTION

Natural rubber, the biopolymer possesses excellent elastomeric properties and has been mainly used as industrial material. Intensive studies have been carried out to improve the mechanical and physical properties like elastic property, abrasion resistance, a resilience of natural rubber. Carbon nanotubes (CNTs) have identified as an excellent reinforcing material to modify mechanical, thermal and other properties of polymers [1-3].

Recently, real time X-ray studies using synchrotron radiation have been carried out during in situ deformation of sulfur vulcanized natural rubber where structural development and stress-strain relationship were measured simultaneously [4,5]. It was demonstrated that the roles of both molecular orientation and strain-induced crystallization are critical for determining the final mechanical properties of rubber [6-9]. In this work, we studied the process of strain-induced crystallization in CNTs reinforced natural rubber by the in-situ X-ray scattering utilizing the synchrotron radiation source.

2 EXPERIMENTAL

2.1 Materials

Multi-layer CNTs with diameter of 5-20nm and ~10,000nm in length were used to reinforce the natural rubber. Natural rubber (CNT0) and carbon nanotubes reinforced natural rubber (CNT1, 3, 5) were prepared with the recipe shown in Table 1. The samples were vulcanized at 145℃ for 60min to form 2mm thick sheet. Sample size for in situ X-ray scattering and mechanical test was 20×5×2mm (L×W×T).

Sample name	CNT0	CNT1	CNT3	CNT5
Materials	PHR			
NR(SMR)	100.0	100.0	100.0	100.0
CNT	**0.0**	**1.0**	**3.0**	**5.0**
ZnO	1.0	1.0	1.0	1.0
A/ACID	2.0	2.0	2.0	2.0
A.O(PPD)	1.0	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5	1.5
TBBS	1.0	1.0	1.0	1.0
Sub total	106.5	107.5	109.5	111.5

Table 1: Recipe of materials

2.2 X-ray Scattering and Uni-axial Deformation.

In situ wide angle X-ray diffraction (WAXD) experiments were performed utilizing a synchrotron X-ray source (2.5GeV, 180mA) at the 4C2 X-ray beamline in Pohang Accelerator Laboratory (PAL). The wavelength and sample to detector distance were 1.38Å and 80mm, respectively. Mechanical test was performed using Shimadzu AG-5000G Intron. Uni-axial deformation was carried out at room temperature with a head speed of 5mm/min.

3 RESULTS AND DISCUSSION

X-ray scattering intensities from the oriented rubber can be decomposed into three phases; isotropic amorphous (IA), oriented noncrystalline (ON), and crystalline (Cr) phase. We investigated the change of these three phases during the uniaxial stretching. The results are shown in figure 1.

The plots in figure 1 indicate that the rubber containing CNTs exhibits faster chain orientation. The rubber without CNTs do not show any ON phases until the deformation reaches 300%, while that containing 5% CNTs begins to show chain orientation (ON phase) at 100% extension. It is also noted that the rubber containing CNTs shows early onset point of strain-induced crystallization and the amount of crystal phase (Cr) is higher with the rubber of higher CNTs content. It is interesting to observe that the ON value to initiate strain-induced crystallization is around 0.1 for all

samples examined in this study. We are not certain about the result where the 0.1 (fraction of ON phase) has the physical meaning.

Our results clearly demonstrate that the CNTs in the rubber play a key role to induce chain orientation and the strain-induced crystallization.

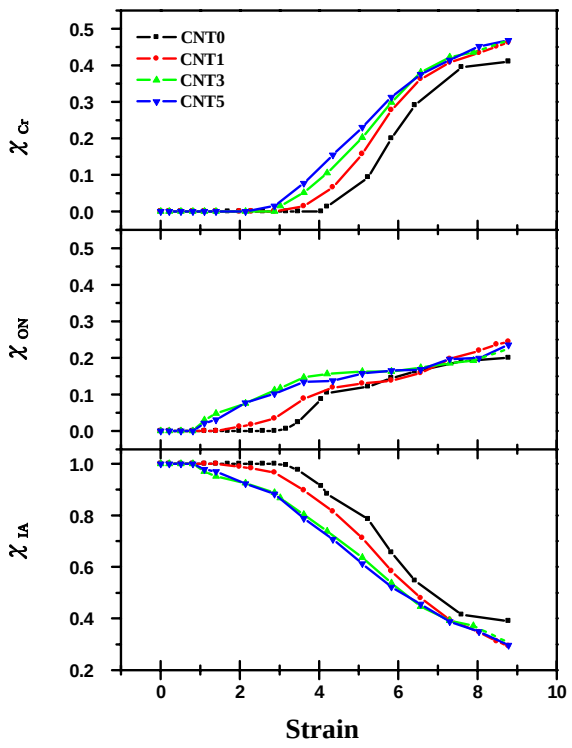

Figure 1: Change of three phases upon uniaxial stretching.

4 CONCLUSIONS

We studied the structural development of carbon nanotubes reinforced natural rubber upon stretching uni-axially by the in-situ X-ray scattering. We found that the rubber containing CNTs exhibits faster chain orientation and early onset point of strain-induced crystallization. The amount of crystal phase (Cr) is higher with the rubber of higher CNTs content. The existence of CNTs in the rubber apparently helps the chain orientation and the strain-induced crystallization upon stretching.

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