Instrumentation and Technique

15A/2003G239

Combined Measurement of SAXS and Dynamical Viscoelasticity on Filled Rubber

Yuya SHINOHARA*[1], Hiroyuki KISHIMOTO[2], Kentaro KAYASHIMA[1], and Yoshiyuki AMEMIYA[1]
[1]The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan
[2]SRI Research & Development ltd., Kobe, Hyogo, Japan

Introduction

It is widely known that the addition of filler such as carbon black and silica to an elastomer shows the reinforcement effect, which increases modulus of elasticity, tear strength, tensile strength, cracking resistance, and fatigue resistance [1]. The reinforcement effect has been extensively investigated since its discovery on 1904, although its mechanism has not been clarified yet. Filler composes hierarchical aggregate structure as shown in Fig.1. The aggregate structure of filler would be the origin of the reinforcement. Conventional methods such as TEM and light scattering are inappropriate for the study of filled rubber, because TEM is not suited to time-resolved measurement and light scattering is not applicable to opaque specimen. SAXS overcomes these difficulties and would become a major tool for the study of filler aggregate. By using ultra-SAXS, we showed that the aggregate structure of stretched rubber was anisotropic in micron-scale [2]. However, in order to understand the effect of aggregates on the reinforcement, we have to investigate the aggregate structure over a wide size-scale. We now investigate the effect of filler aggregate structure on the reinforcement, by using small-angle X-ray scattering (SAXS), In this study, we attempted to measure the SAXS and the viscoelasticity of filled rubber simultaneously.

Experimental

The sample used was Styrene-Butadiene rubber filled with various types of carbon black and silica particle. The thickness of sample was around 1 mm.

Experiments were performed at BL-15A. The schematic of the experiment setup is shown in Fig. 2. The X-ray wavelength was 1.50 A. An X-ray Image Intensifier (150 mmϕ) coupled X-ray CCD detector [3] was used as a detector. The sample-to-detector distance was around 2000 mm, which was calibrated with the scattering peak of silver behenate. We measured time-resolved SAXS simultaneously with dynamic viscoelasticity. The sample was set at the dynamic viscoelastic instrument, which enables X-rays to pass through the samples. The exposure and the strain of the sample were controlled with the stimulator installed at BL-15A. The sample temperature was controlled by the viscoelastic instrument at -30 °C, 0 °C, 20 °C, 70 °C. The cycle of elongation was 100 ms, and the SAXS was recorded every 10 ms. The maximum elongation ratio was 2, which was defined by the ratio of the elongation length to the initial length.

Results & Discussion

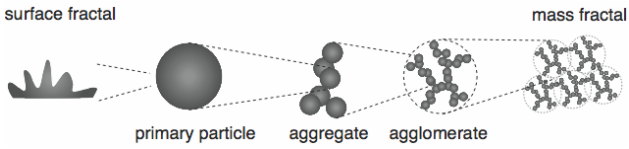

Fig.1: The hierarchical structure of filler in rubber. Primary particles compose *aggregate* and the aggregates compose *agglomerate*.

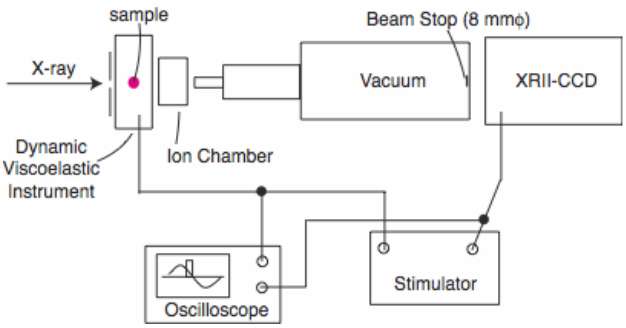

Fig. 2: Experimental setup. The sample was set at the dynamic viscoelastic instrument. SAXS was recorded with XRII-CCD. The exposure and the strain of samples were controlled with the stimulator.

We have successfully measured both SAXS and dynamic viscoelasticity simultaneously. The scattering intensity profile largely depends on the filler types, which would be a key for the understanding of the reinforcement. However, neither the change of intensity profile with the elongation nor the anisotropic scattering pattern, which were observed in ultra-SAXS, are not observed. These results show that the change of aggregate structure greatly depends on the size-scale.

References

[1] J. D. Ferry, "*Viscoelastic Properties of Polymers*", John Willy & Sons, New York, (1980).
[2] Y. Shinohara et al., SPring-8 User Exp. Report No. 13, (2004)
[3] Y. Amemiya et al., Rev. Sci. Instrum. 66, 2290, (1995)
* shinohara@x-ray.k.u-tokyo.ac.jp