Large optical anisotropy in deformed rubber composites with conductive fillers revealed by terahertz polarization spectroscopy

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1. Introduction

Terahertz time-domain spectroscopy (THz-TDS) is a emerging and powerful technique for investigating polymeric materials, because terahertz wave can penetrate visibly opaque polymers and the intermolecular vibration mode of polymers exists in the terahertz frequency range. Recently, a polarization sensitive (PS) THz-TDS technique has been developed and improved[1–4]. The PS THz-TDS enables us to reveal the anisotropic optical responses due to the orientation of the molecular chains and the conductive additives[5,6]. In particular, we discovered that rubber materials with conductive carbon black (CB) fillers shows strong anisotropy in the dielectric responses due to the orientation distribution of the CB aggregates, and their anisotropy is strongly modulated by the mechanical stretching[6]. In this paper, we revealed the anisotropic dielectric responses in the deformed rubber-filler composites using the effective medium approximation (EMA)[7]. Our theoretical analysis based on the EMA indicates that the large optical anisotropy in deformed rubbers is strongly linked to the internal filler network.

2. General Instructions

Materials and Method

We used a styrene butadiene rubber (SBR) with various CB concentrations as a sample in this study. From the direct and alternating current conductivity measurements, we found that the SBR sample with dense CB fillers shows the percolation conductivity, where the CB fillers form the percolative network inside the host rubbers. We investigated draw-ratio (DR), which is a ratio of the final to initial length of the samples, dependence of the anisotropy in the complex dielectric functions in the SBR samples by means of the PS THz-TDS. Our PS THz-TDS system consists of a commercially available THz-TDS system (T-ray 5000, Advanced Photonix. Inc.) and a mechanically rotating polarizer[5]. Here, we focused on the difference in the optical anisotropy between the unstretched and stretched SBR samples.

Results and Discussion

In the unstretched samples, the optical anisotropy was not observed. This means that the CB fillers are almost randomly oriented. On the other hand, the stretched samples show the large optical anisotropy with a degree of birefringence of 0.2–0.4, which is quite larger than that of rubbers observed in the visible frequency region ($\sim 10^{-3}$). To further understand the DR-dependent spectral shape of the dielectric functions and conductivity, we fitted the experimental data of the unstretched and stretched samples by the EMA. From the fitting, it is found that the optical responses in the SBR without the percolation conductivity are well described by the EMA, whereas those in the SBR with the percolation conductivity are not well described by the EMA. We concluded that this difference between the SBR with and without the percolation conductivity would be resulted from the difference in the internal filler network. The details in the theoretical analysis will be discussed in the presentation.

3. Conclusions

We investigated that the anisotropic optical responses in the SBR with various CB concentrations based on the PS THz-TDS and the theoretical analysis based on the EMA. It is found that the anisotropic optical responses in the deformed rubbers are governed by the internal CB filler network. Our technique for easily measuring the anisotropic optical responses is applicable for the wide variety of materials.

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