Impact of carbon black aggregates on the optical properties of black rubber samples in the terahertz frequency range

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Abstract

We report on the optical responses of black rubber samples in the terahertz regime as a function of the carbon black (CB) concentration. We prepared samples with different CB concentrations and investigated their absorbance, birefringence, and the angle of the slow optic axis in the terahertz frequency range. A monotonic increase of the terahertz absorbance is observed with increasing CB concentration, which indicates that the density of the CB aggregates inside the black rubber plays a crucial role for controlling the absorbance. In addition, a systematic increase of the birefringence is observed with increasing draw ratio, while the spatial fluctuation of the angle of the slow optic axis systematically decreases. This simultaneous behavior indicates that the mechanical stretching of the black rubber sample induces an alignment of the CB aggregates along the stretching direction. These results provide the fundamentals to understand the correlation between the terahertz response and the condition of the CB aggregates inside the samples. The thorough understanding of this correlation is important for future applications. Copyright © 2019 VBRI Press.

Keywords: Carbon black, black rubber, terahertz polarization spectroscopy.

Introduction

Rubber products are widely used in our daily life. For example, tires, seismic dampers, and seals are made of rubbers. Consequently, the non-destructive inspection of rubber products is an important technique for the industrial sector because aging of rubber may induce cracks in the products. For this purpose, the digital image correlation technique is commonly employed to inspect the surface strain of rubber products [**1**]. However, because most cracks and defects appear inside the material, it is important to probe not only surface strain but also the internal strain.

The photoelastic method has been widely used to investigate the internal stress and strain distribution of materials in a contactless manner [**2**]. This method probes the polarization of light transmitted through or reflected from the material to evaluate its birefringence. Because the degree of birefringence is proportional to the difference between the two principal stresses in the material, this method can probe the spatial distribution of the thickness-averaged stress and strain in the sample. In order to probe the internal stress and strain distribution of a rubber product with the photoelastic technique, it has to be optically transparent. However, most rubber products are usually visibly opaque. In particular, the optical transmittance of black rubber containing carbon black (CB) fillers is almost zero over wide spectral ranges from visible to mid-infrared [**3**] due to the conductive nature of the CB fillers.

Recently, we have reported that the abovementioned black rubbers with CB fillers are partially transparent in the terahertz frequency range, and thus the terahertz polarization spectroscopy (or also termed terahertz photoelastic measurement) is a very powerful technique for investigating their internal strain [**3**]. By using the polarization-sensitive terahertz spectroscopy, it is possible to extract the internal triaxial strain information from the black rubber samples [**4**] as well as the anisotropic percolation conductivity of samples with high CB concentration [**5**]. However, a systematic study on the CB concentration dependence of absorbance and birefringence of the black rubber samples is still lacking. Such a study will shed light on the impact of the CB fillers that form aggregate in the rubbers on the optical properties of the black rubber samples.

In this letter, we prepared a series of black rubber samples with different CB concentrations. For each sample, we determined the absorbance, birefringence, and the angle of the slow optic axis in the unstretched and stretched conditions using the terahertz polarization spectroscopy. We found a clear correlation between these quantities and the CB density as well as the alignment of the CB aggregates inside the black rubber samples. This systematic study includeing a quantitative data set will be useful for the design of future terahertz photoelastic measurements to examine the internal strain in black rubber products.

Experimental

Materials

We prepared black rubber samples with different CB concentrations using the following procedure. First, the weights of both ingredients, liquid urethane rubber (VytaFlex® series, smooth-on) and carbon black (CAS No. 1333-86-4, Sigma-Aldrich), were determined and then the constituents were filled into a single disposable cup. This cup was set in a planetary centrifugal mixer (AR-100, THINKY MIXER) to mix, disperse, and degas the ingredients for three minutes. After that, the solution was sandwiched between two metal plates and pressed to form a thin film. Both plates were fixed by screw bolts to control the thickness of the thin film during the drying process (about 2 mm). After drying of the sample for more than one day, the rubber film was post-cured at 60 °C for eight hours. For the optical measurements, the sample was cut into a rectangular specimen with dimensions of 20 mm × 50 mm.

Methods

The complex refractive index and the birefringence of the sample in the terahertz frequency range were measured by a home-made polarization-sensitive terahertz time-domain spectroscopy (THz-TDS) system. For the terahertz pulse generation and detection, we used a commercially available high-speed THz-TDS system (T-ray 5000, Advanced Photonics Inc.). The terahertz pulse emitted from the T-ray 5000 system was focused on the sample by an aspherical Teflon lens, and the pulse that was transmitted through the sample was collected by another aspherical Teflon lens, and then forwarded to the detector. We placed a waveplate in front of the sample to obtain an incident terahertz pulse at 0.3 THz that is almost circularly polarized. A rotating wire-grid polarizer in front of the detector was used for analyzing the polarization state of the terahertz pulse that passed through the sample. More details of our system are provided in Ref. [**3**].

By analyzing the difference between the polarization states of the terahertz pulses that are detected with and without sample, we can determine the birefringence Δn and the angle of the slow optic axis θ of the rubber sample under a certain stretching condition [**3**]. In the following, we briefly explain this method with an example. If the sample has no birefringence ($\Delta n = 0$), the polarization state after the sample is unchanged, that is, almost circularly polarized at 0.3 THz. This is also true for a measurement without any sample. In case of a sample with optical anisotropy ($\Delta n \neq 0$), the polarization state after the sample is more elliptical. When we determine the orientation of these polarization ellipses and their ellipticity angles, we can determine both Δn and θ at 0.3 THz. It should be noted that the uncertainty of the calculated θ is large if Δn is small.

After evaluation of Δn and θ , the quantitative values of the complex refractive index along the slow and fast optic axes can be determined with the following procedure. Firstly, we measured the four electric field traces of the detected terahertz pulses along the two optic axes whose directions are determined by the angle θ of the sample, with and without sample. Secondly, the Fourier transforms of the two electric field traces with and without sample were computed and the complex transmission spectrum was calculated by dividing the Fourier transformed data with sample by those without sample. The frequency dependence of the complex refractive index $\hat{N}(\omega) = n(\omega) + ik(\omega)$ (with ω being the angular frequency) is derived from the complex transmission spectra. The sample thickness was estimated by the total variation metric, which measures the smoothness of the complex refractive-index functions along the two optic axes and identifies the most appropriate pairing of thickness and $\hat{N}(\omega)$ [**6**]. The optical absorbance $\alpha(\omega)$ was calculated using the relation $\alpha \equiv 2k\omega/c$ where c is the speed of light. The data shown in this paper are values that are obtained from averaging over the range $\omega/(2\pi) = 0.2$–0.4 THz.

Results and discussion

CB concentration dependence of the absorbance and birefringence in the terahertz frequency range

Table 1 shows the absorbance α and the birefringence Δn of the unstretched black rubber samples for various CB concentrations. There is a finite absorbance even in the sample without CB fillers (0 wt%), indicating that the urethane rubber used in this study is not completely transparent for the terahertz pulse. The absorbance exhibits a strong increase with CB concentration, which clearly indicates that the absorbance of the black rubber samples in the terahertz frequency range is dominated by the absorption due to the CB fillers. In particular, for the sample with a CB concentration of 20 wt%, the absorbance is more than 1 mm^{-1}. This large absorption results in a very low transmittance of thicker samples (> 1 mm) with large CB densities. It has been suggested that the CB aggregates absorb terahertz light because of their inherent conductivity [**3,6**].

Table 1. Absorbance and birefringence of the black rubber samples with different CB concentrations.

CB concentration (wt%)	α (mm^{-1})	Δn
0	0.38	0.002
2	0.53	0.001
4	0.64	0.002
6	0.84	0.005
8	0.92	0.006
20	1.79	0.015

In contrast to the strong dependence of the absorbance on the CB concentration, the birefringence Δn has a less clear correlation with the CB concentration and the values are very small as shown in **Table 1**. We have previously reported that the birefringence of the black rubber samples in the terahertz frequency range originates from the orientation distribution of the anisotropically shaped CB aggregates inside the sample [**3**]. The small value of Δn in the present samples indicates that the CB aggregates are almost randomly oriented under the unstretched condition. This experimental fact can be explained with the sample preparation process. Since we simply sandwiched and pressed the liquid mixture of urethane rubber and CB fillers by two metal plates, the CB aggregates cannot be aligned in any particular direction, which is in contrast to the conventional fabrication process with a roller. As a result, even in the sample with a CB concentration of 20 wt%, the optical anisotropy is very small. The observed dependences of α and Δn on the CB density are almost insensitive to the sample thickness.

Draw ratio dependence of the terahertz birefringence

In the following we discuss the birefringence of the black rubber samples under stretched conditions. We defined the draw ratio (DR) of the sample as the ratio between the length of the sample under stretched condition and that under unstretched condition. **Fig. 1** shows the birefringence Δn measured at the center of the sample for different CB concentrations and different DRs. Except for the sample without CB fillers, it is found that Δn dramatically increases as the DR increases. This DR dependence of the birefringence indicates that the CB aggregates tend to align along the stretching direction as the DR increases. In addition, Δn shows a strong dependence on the CB concentration under stretched conditions (for instance, DR = 2). This strong CB concentration dependence of Δn is different from that under the unstretched condition shown in **Table 1**.

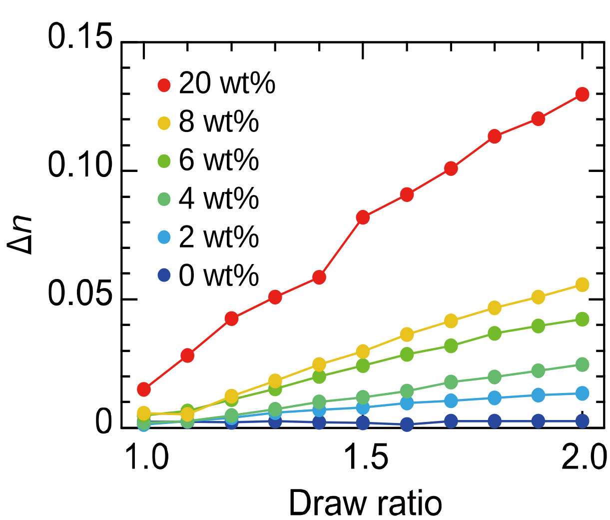

Fig. 1. DR dependence of the birefringence at the center of the sample for different CB concentrations.

For engineering purposes, the birefringence Δn with its strong dependence on the DR constitutes a good indicator to estimate the internal strain of the black rubber samples. Indeed, we have demonstrated that the polarization-sensitive THz-TDS can be used to estimate the triaxial internal strain of visibly opaque black rubbers [**4**]. A more sensitive detection of the strain may be achieved by using black rubber samples with higher CB concentrations, because the value of Δn is significantly larger at the same DR condition and thus also the signal intensity is larger.

Spatial mapping of the birefringence and the angle of the slow optic axis

Next, we investigate the spatial variation of the birefringence, Δn, and the angle of the slow optic axis with respect to *x*-axis as shown in **Fig. 2**, θ, for the unstretched and stretched black rubber sample with the highest CB concentration in this work (20 wt%). **Figs. 2 a** and **b** show the spatial distributions of Δn and θ for DR=1, respectively. Δn is small in the entire region of the sample, which indicates that there is a small spatial distribution in the anisotropic orientation of the CB aggregates inside the unstretched black rubber sample. From **Fig. 2 b**, we find that the angle of the slow optic axis has a random distribution, which indicates that the orientation angle of the anisotropic CB aggregates is almost random in the unstretched sample.

Figs. 2 c and **d** show the spatial distributions of Δn and θ for DR=2, respectively. In stark contrast to the spatial distributions obtained under DR=1, the Δn in **Fig. 2 c** is large, and the spatial variation of θ in **Fig. 2 d** is very small and its average value is about -0.2 rad. This is the consequence of the mechanical stretching which aligns the CB aggregates along the stretching direction, which is almost parallel to *x*-axis. The observed small spatial inhomogeneity of θ may be due to slightly different mounting conditions at the right and left edges of the sample that induce slightly non-uniform orientation directions of the CB aggregates.

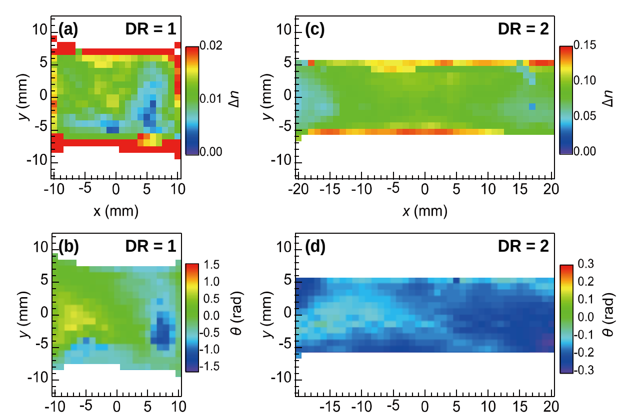

Fig. 2. (a) Spatial distribution of Δn and (b) θ for the sample with a CB concentration of 20 wt% and DR=1. (c) Distribution of Δn and (d) θ for DR=2. We only plot the experimental data that are located more than 3 mm off the sample edges, because the data around the edges may include experimental error due to scattering.

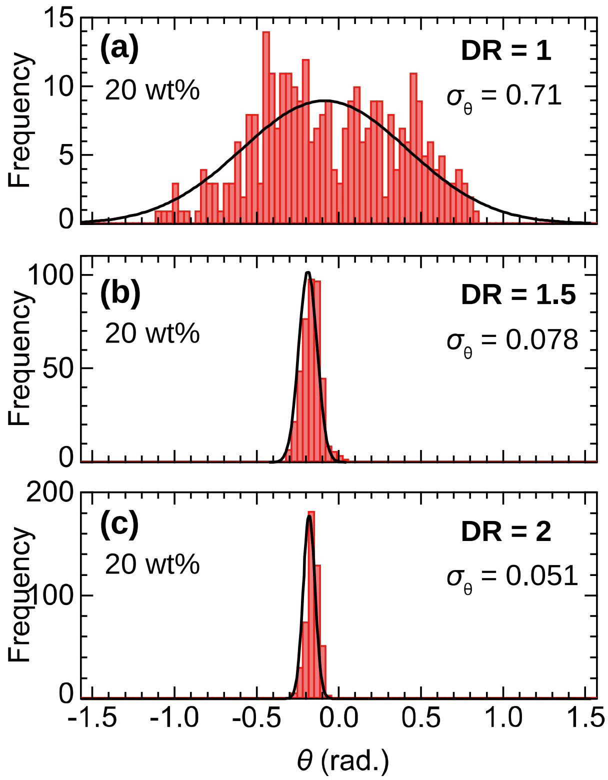

Fig. 3. (a) Histogram of the angles of the slow optic axes that were obtained at each point of the spatial-distribution image for the 20 wt% sample at DR = 1, (b) 1.5, and (c) 2. The standard deviation of θ, σ_θ, is also shown.

Finally, we investigate the statistical variation of the angles θ that were obtained at each pixel of the spatial map for a certain DR condition. In **Figs. 3 a–c**, we plot histograms that describe the occurrences of the angle θ for the samples with a CB concentration of 20 wt% under DR=1, 1.5, and 2, respectively. The standard deviation of θ (σ_θ) dramatically decreases and the peak value of occurrence increases as the DR increases. This result strongly supports our conclusion that the CB aggregates in all sample locations improve their alignment along the stretching direction ($\theta \approx -0.2$ radians) by stretching the sample and the angle of the slow optic axis becomes uniform in the entire sample.

Conclusion

In this Letter, we report a systematic study of the absorbance, birefringence, and angle of the slow optic axis of black rubber samples at terahertz frequencies as a function of the CB concentration. We found a linear relation between the absorbance and the CB concentration, which evidences that the absorption due to the CB fillers dominates the transmissivity of the sample in the terahertz frequency range. We also observed a linear relation between the birefringence and the DR of the sample in stretched black rubber samples, which is a result of the tendency of CB aggregates to align in the stretching direction as the DR increases. Finally, we showed that the spatial variation of the angle of the slow optic axis is very small for the stretched samples. With these quantitative experimental results, the role of the CB aggregates for the optical properties of black rubber samples at terahertz frequencies can be clarified and the results help to design terahertz polarization spectroscopy systems that investigate the internal strain condition of black rubber samples in actual applications.

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Author's contributions

Conceived the plan: SW; Performed the experiments: MF; Data analysis: MF, MO; Wrote the paper: SW. The authors have no competing financial interests.

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