Terahertz complex conductivity of nanofibrillar cellulose-PEDOT:PSS composite films

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Abstract We investigate the terahertz transmission through flexible composite films that contain nanofibrillar cellulose (NFC) and different blending percentages of the conductive polymer poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS). The real part of terahertz complex conductivity is found to decrease with decreasing frequency for each NFC composite film and to approach a finite positive value dependent on the PEDOT:PSS blending percentage in the limit of zero frequency. Both the real and imaginary parts of complex conductivity spectra can be fitted simultaneously with an extended Drude model that describes a partially localized nature of carriers. Our spectral analysis indicates that carriers in the NFC composite become denser and also less localized as the PEDOT:PSS blending percentage is increased.

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Graphical abstract

Nanofibrillar cellulose composite films with different PEDOT:PSS blending percentages

Complex conductivity spectra indicating a partially localized nature of carriers

Keywords Nanofibrillar cellulose - Conducting polymers - Composite films - Terahertz spectroscopy - Charge transport

1 Introduction

Nanofibrillar cellulose (NFC) is a promising material owing to its useful properties such as optical transparency, high aspect ratio, mechanical flexibility and strength, small surface roughness, and environmental sustainability (Eichhorn et al. 2010; Klemm et al. 2011; Isogai et al. 2011; Moon et al. 2011; Dufresne 2013). Recently, NFC has been intensively functionalized for organic optoelectronics applications by coating NFC surfaces with conductive materials (Hu et al. 2013; Huang et al. 2013; Penttilä et al. 2013; Wang et al. 2014; Jung et al. 2015; Valtakari et al. 2015) or incorporating them into NFC matrices (van den Berg et al. 2007; Nyström et al. 2010; Müller et al. 2011; Torvinen et al. 2012; Koga et al. 2013; Salajkova et al. 2013; Aleshin et al. 2015; Khan et al. 2015) to provide dc conductivity (Tobjörk and Österbacka 2011; Nyholm et al. 2011). These types of conductive NFC structures have been successfully applied to flexible solar cells (Hu et al. 2013; Nogi et al. 2015), transistors (Huang et al. 2013; Fujisaki et al. 2014), sensors (Koga et al. 2013), and microwave integrated circuits (Jung et al. 2015).

Terahertz (THz) time-domain spectroscopy is a powerful tool for investigating carrier dynamics in semiconductors and biomolecules at frequencies (typically 0.1–10 THz) that characterize the intermixing between electronics and photonics (Ferguson and Zhang 2002; Lloyd-Hughes and Jeon 2012). So far, only a few reports have been published on the THz response of cellulose-based nanomaterials (Andrianov et al. 2015; Carnio et al. 2016; Elfwing et al. 2018), including a conductive composite of bacterial cellulose and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Andrianov et al. 2015). Nevertheless, it is not well understood how the optoelectronic nature of carriers induced by conductive materials can be controlled in NFC composites.

In this paper, we report an observation of the THz transmission through flexible composite films that contained NFC and systematically varied blending percentages of the conductive polymer PEDOT:PSS. The real parts of THz complex
conductivity $\tilde{\sigma}(\omega)$ were found to decrease toward finite positive values (dependent on the PEDOT:PSS blending percentages) with decreasing frequency $\omega/2\pi$, indicating a partially localized nature of carriers in the NFC composite. The real and imaginary parts of $\tilde{\sigma}(\omega)$ were reproduced simultaneously by an extended Drude model with three adjustable parameters. We have shown that carriers in the NFC composite become denser and also less localized as the PEDOT:PSS blending percentage is increased up to 50%.

2 Materials and methods

The samples in our experiment were free-standing NFC composite films with different PEDOT:PSS blending percentages, as listed in Table 1. We prepared composite dispersions in water, blending a PEDOT:PSS dispersion (Clevios PH 500, Heraeus Holding, Germany) in six different dry weight percentages (0–50%) with a hardwood NFC dispersion at a solids content of 2.5% (Bleached Eucalyptus Kraft Pulp, Votorantim Cellulose e Papel, Brazil) received from South China University of Technology. We fabricated the samples by casting the composite dispersions on polystyrene Petri dishes (with a diameter of 8.5 cm) in a controlled atmosphere (temperature: 23°C, relative humidity: 50%) and by lifting the dry films off the dishes. The samples had thicknesses of $d = 19–27 \mu m$ (see Table 1) in the parts used for THz transmission measurements.

Table 1 PEDOT:PSS blending percentages and film thicknesses of NFC composite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Film thickness ($\mu m$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% blended</td>
<td>19</td>
</tr>
<tr>
<td>1% blended</td>
<td>23</td>
</tr>
<tr>
<td>2% blended</td>
<td>22</td>
</tr>
<tr>
<td>10% blended</td>
<td>21</td>
</tr>
<tr>
<td>25% blended</td>
<td>27</td>
</tr>
<tr>
<td>50% blended</td>
<td>26</td>
</tr>
</tbody>
</table>
strong absorption particularly at 1.7 THz and gives rise to spectral distortion. We obtained the complex conductivity spectra \( \tilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega) \) of the 1–50% blended samples, where the real part \( \sigma_1(\omega) \) and the minus imaginary part \(-\sigma_2(\omega)\) describe the conductive and dielectric properties of carriers at frequency \( \omega/2\pi \), respectively.

3 Results and discussion

The temporal waveforms of THz electric fields transmitted through the samples are shown in Fig. 2, together with that passing through the sample space for reference. We found two pronounced features, on which the current extent of thickness variation (see Table 1) had minor effects qualitatively, in these THz waveforms. First, the THz signals appeared with systematic shifts in time, indicating that the velocity \( c/n \) of the THz waves (\( c \): vacuum light velocity, \( n \): refractive index) inside the NFC composite decreased significantly as the PEDOT:PSS blending percentage was increased. Second, the amplitude decreased substantially with the PEDOT:PSS blending percentage, suggesting an increase in the absorption coefficient \( \alpha \) of the NFC composite.

Performing the Fourier transformation of the observed THz waveforms, we obtained the complex transmission coefficient spectra \( \tilde{t}(\omega) \) of the samples. The
complex refractive index spectra $\tilde{n}(\omega) = n(\omega) + i\kappa(\omega)$, whose imaginary parts are

the extinction coefficient spectra associated with the absorption coefficient spectra

via $\alpha(\omega) = 2\omega\kappa(\omega)/c$, are linked to $\tilde{l}(\omega)$ as given by (Unuma et al. 2010, 2013b)

$$\tilde{l} = \frac{4\tilde{n}}{(\tilde{n} + 1)^2} e^{i\omega(\tilde{n} - 1)d/c} \sum_l \frac{(-1)^l}{(\tilde{n} + 1)^2} e^{i\omega 2\tilde{n}d/c},$$

(1)

where $l (= 0, 1, 2, \cdots)$ is the integer numbering a pair of internal reflections on the

back and front surfaces of the NFC composite. The inclusion of multiple reflections

with $0 \leq l \leq 5$ in Eq. (1) was sufficient to find the proper numerical solution for $\tilde{n}$

at each $\omega$ because the THz waves were significantly damped by absorption during

the multiple reflections. The complex conductivity spectra $\tilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$

for carriers induced by PEDOT:PSS are expressed as $\sigma_1 = 2\omega\epsilon_0\kappa$ and $\sigma_2 =

\omega\epsilon_0(\kappa^2 - n^2 + \varepsilon_{\infty})$, with $\epsilon_0$ being the vacuum permittivity and $\varepsilon_{\infty}$ being the high-

c-frequency background dielectric constant (Unuma et al. 2010, 2013b). The pristine

NFC, i.e., 0% blended sample, exhibited almost constant refractive indices of 1.8–

1.9 and sufficiently small extinction coefficients at frequencies of up to $\sim 3$ THz,

suggesting that $\varepsilon_{\infty}$ can be set to 3.3 for a crude approximation. Thus, we were

able to determine $\tilde{\sigma}(\omega)$ for carriers in the NFC composite.

Figure 3 shows the complex conductivity spectra $\tilde{\sigma}(\omega)$ of the 1–50% blended

samples. Both the real parts $\sigma_1$ (filled circles) and the imaginary parts $\sigma_2$ (open circles)

are larger for higher PEDOT:PSS blending percentages. Note that the values

of $\sigma_1$ observed for the 10%, 25%, and 50% blended samples are one or two orders of

magnitude larger than those reported previously for a PEDOT:PSS blended bacterial

cellulose film ($\sigma_1 \sim 1$ S/cm) (Andrianov et al. 2015). For each sample, $\sigma_1$

gradually decreased toward a finite positive value with decreasing frequency $\omega/2\pi$,

while the imaginary part $\sigma_2$ remained negative. These spectral features are similar

to those reported for doped poliythiophenes (including PEDOT:PSS) (Unuma et

al. 2010), meaning that carriers in the NFC composite have a partially localized

nature.

We performed a detailed spectral analysis of $\tilde{\sigma}(\omega)$ by adopting the Drude-Smith

model (Smith 2001), which has been widely used to describe the optoelectronic

response of partially localized carriers in nanoparticle composites (Turner et al.
Fig. 3 THz complex conductivity spectra $\tilde{\sigma}(\omega)$ of NFC composite samples, having larger values for higher PEDOT:PSS blending percentages. Fits of the Drude-Smith model to $\tilde{\sigma}(\omega)$ are shown by curves.

The fits to $\tilde{\sigma}(\omega)$ for the 1–50% blended samples are shown in Fig. 3 by curves, and the corresponding sets of fitting parameters $N$, $C$, and $\tau$ are shown in Fig. 4 by symbols. As seen in Fig. 3, the observed spectral features of $\sigma_1$ and $\sigma_2$ are reproduced simultaneously by the DS model for each sample. When the fit for the 50% blended sample is extrapolated to lower frequencies, it gives $\tilde{\sigma}_{DS}(0) = 47$ S/cm in reasonable agreement with the four-probe measurement of dc conductivity.
Fig. 4 Carrier density $N$ (circles), localization degree $C$ (squares), and relaxation time $\tau$ (triangles) plotted versus PEDOT:PSS blending percentage for NFC composite samples. The dashed line in (a) shows a linear regression.

Now, let us discuss a possible reason for this behavior of the three fitting parameters. Carrier density $N$ is expected to express the number of carriers in PEDOT:PSS divided by the total volume of the NFC composite. Hence, $N$ should increase in proportion to the PEDOT:PSS blending percentage. A linear regression (dashed line) indeed applies well to the data points for $N$ (circles) in Fig. 4(a). On the other hand, localization degree $C$ and relaxation time $\tau$ are expected to be governed by conduction paths (Unuma et al. 2010, 2013b, 2013a) in the NFC composite. The values of $C$ and $\tau$ for the 10–50% blended samples can be regarded as taking over the original nature of carriers inherent in PEDOT:PSS because similar values have also been observed for doped conjugated polymers themselves (Unuma et al. 2010, 2013b, 2013a). Conduction paths for much lower PEDOT:PSS blending percentages may well be rather separated from each other, e.g., owing to the coagulation or adsorption of PEDOT:PSS onto NFC fibrils, and can exhibit stronger localization of carriers ($C$ nearer to $-1$).
We measured the THz complex conductivity spectra $\tilde{\sigma}(\omega)$ of NFC composite films with different PEDOT:PSS blending percentages. The real parts of $\tilde{\sigma}(\omega)$ decreased toward finite positive values (dependent on the PEDOT:PSS blending percentages) with decreasing frequency $\omega/2\pi$, while the imaginary parts of $\tilde{\sigma}(\omega)$ remained negative. These spectral features indicate that carriers in the NFC composite have a partially localized nature. The real and imaginary parts of $\tilde{\sigma}(\omega)$ were fitted simultaneously with the Drude-Smith model. From the behavior of fitting parameters, we found that carriers in the NFC composite become denser and also less localized as the PEDOT:PSS blending percentage is increased up to 50%. Thus, we have provided an essential insight into how the optoelectronic nature of carriers in NFC composites can be controlled with conductive materials, demonstrating potential usefulness of NFC composites in the THz region.

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