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Terahertz properties of bacterial cellulose films and its composite with conducting polymer PEDOT/PSS

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ABSTRACT

Terahertz response of free standing films of bacterial cellulose and its composites with conducting polymer complex PEDOT/PSS has been studied by terahertz time domain spectroscopy. Spectra of refractive index, extinction coefficient and complex dielectric permittivity are obtained in spectral range of 0.3–2.8 THz for both types of cellulose films. Considerable increase in the imaginary part of dielectric permittivity of bacterial cellulose films modified with a conductive polymer complex PEDOT/PSS as compared to that of pristine bacterial cellulose film was found out.

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1. Introduction

Development of biocompatible micro- and nanoelectronic devices will be the basis of medicine and bioengineering in the near future. In this connection, an intensive research in the field of functional organic polymeric materials and electrically active composites is of importance [1]. There is a practical interest in new composite materials based on biopolymers modified with organic or inorganic components, which are considered as inexpensive and promising materials for bioelectronics [2]. Moreover, such composites can be applied as components of “electronic paper” and flexible displays [3], as well as biocompatible and biodegradable flexible OLEDs, where the biopolymer membrane works as a substrate [4]. On the other hand applications of cellulose-based materials in medicine as effective non-drying nano-cellulose membranes, artificial blood vessels, materials for tissue reconstruction, coating stents attract a lot of attention recently [5–7]. New direction in this area is the study of hybrid nanosystems, including bio-cellulose as well as conducting polymers and (or) metals nanoclusters for creating antitumor, antiviral, immune stimulating drugs, wound dressings, artificial cartilages, bone precursor, membranes, flexible organic electronic devices, etc. In this regard, an interesting and promising material is the bacterial cellulose (BC), and the BC modified with conductive polymers and polymer complexes [8]. Prospects of practical applications of new composite materials described above generated a need of the investigation of their electrical and optical properties over a wide spectral range.

During the last two decades a powerful diagnostic technology based on coherent terahertz (THz) spectroscopy or THz time-domain spectroscopy (THz–TDS) is rapidly developing [9]. The THz–TDS method is based on generation and detection of coherent THz radiation using femtosecond laser pulses and on the analysis of the results of interaction of the THz radiation with an object. Basic issues of materials diagnostic and determination of materials optical constants with using THz–TDS were considered in several publications [10–13]. Currently the THz diagnostic methods have a number of promising applications in the pharmaceutics and medicine [14,15]. An important property of the THz–TDS technique is the ability to carry out the contactless

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study of conductivity including its frequency dependence in a variety of inorganic and organic materials [16–19]. There are several THz studies of electrical and optical properties of cellulose in different forms have been reported until now (see Refs. [20–22]). However the results of investigation of electrical and optical properties in the THz spectral region of BC and its derivatives such as BC composites with conducting polymers are not available till now.

In this paper, we report on the results of investigation of electrical and optical properties of the BC films and its composites with conductive polymer PEDOT/PSS by the THz–TDS method. Spectra of refractive index, extinction coefficient and the real and imaginary parts of the dielectric permittivity have been determined for both types of BC films in the spectral range of 0.3–2.8 THz. A significant increase in the imaginary part of dielectric permittivity of BC films modified with a conductive polymer complex PEDOT/PSS as compared to that of pristine BC films was found out.

2. Objects and Methods

Samples of the nano-gel bacterial cellulose films were obtained in a similar manner to that described in our previous publications (see Refs. [23,24]). Modification of the BC samples was carried out in an aqueous solution (~1.3 wt.%) of the polymer – thermochromic conductive polymer complex based on thiophene derivatives - poly (3,4-ethylenedioxythiophene)-poly(4-styrenesulphonate) (PEDOT/PSS) [25]. The chemical structures of BC [26] and conductive polymer complex PEDOT/PSS [25] are shown in Fig. 1a and b. PEDOT/PSS has a band gap, E_g ~1.6 eV, the conductivity at 300 K ~1 S/cm and pH ~2.0 at 20° C [27]. The conductive polymer complex PEDOT/PSS to modify the BC film was purchased in Sigma–Aldrich and used without further treatment. Original BC and BC modified with PEDOT/PSS (BC:PEDOT/PSS) films were dried at a temperature of ~100 C. The thickness of the dried free standing films of BC and BC:PEDOT/PSS was ~60 μm, still maintain their elasticity. The average roughness of the BC and BC:PEDOT/PSS films was ~25.4 nm and ~22.7 nm; the root mean square was ~32.3 nm and ~28.4 nm respectively [24]. The weight proportion of PEDOT/PSS in the BC:PEDOT/PSS composites was about ~10% (volume fraction of ~12%). We have investigated the transmission of THz radiation through BC and BC:PEDOT/PSS films in the spectral range 0.3–2.8 THz. The measurements were carried out using the THz–TDS apparatus, described elsewhere [28,29]. The spectral range of 0.3–2.8 THz is determined by components of the THz–TDS set-up [28,29], which provided sufficiently reliable determination of materials optical characteristics in this spectral range. The measurements were done with 0.1 THz spectral resolution at room temperature in open air with humidity of 56%.

3. Results and discussion

Inset to Fig. 2 shows characteristic waveforms of THz radiation transmitted through free space and through films of BC modified

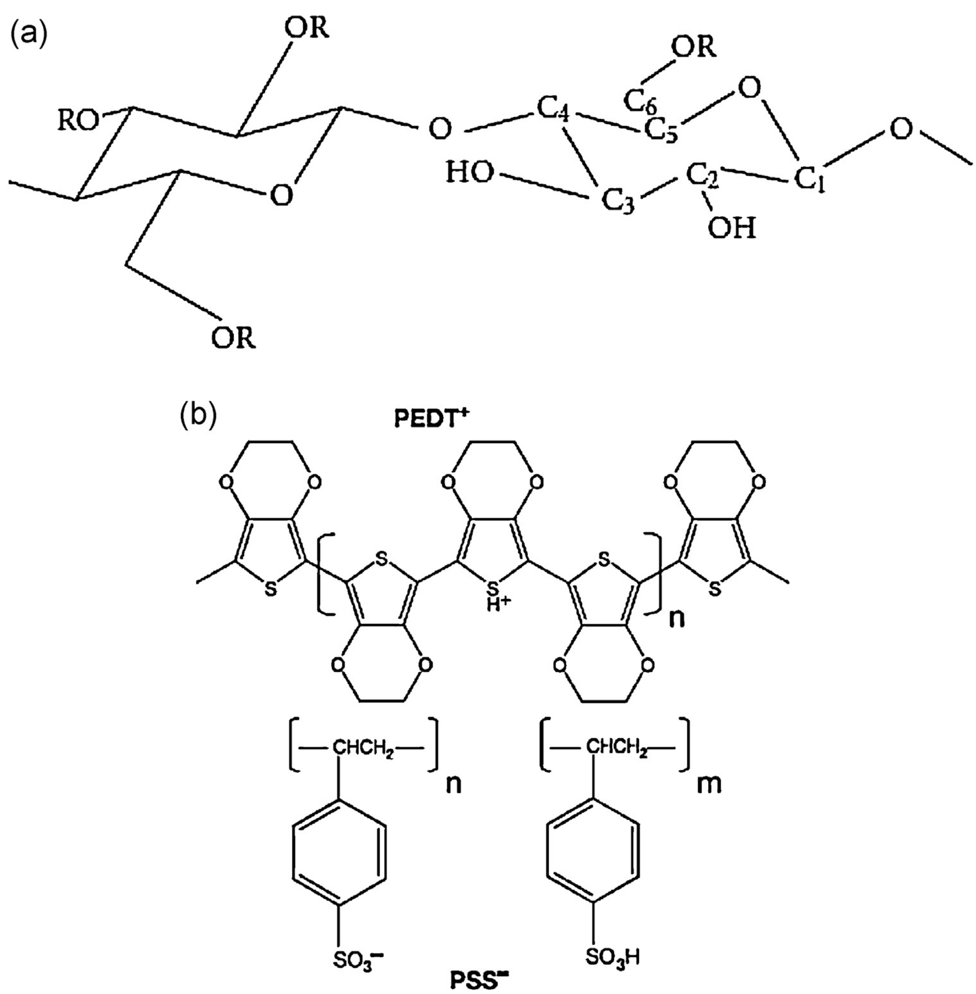

Fig. 1. Chemical structure of BC (a) and a conductive polymer complex PEDOT/PSS (b).

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