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Photoluminescence study of the surface modified and MEH-PPV coated cotton fibers

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ABSTRACT

In this paper, we report a study on the photoluminescence properties of pure cotton fibers from chemically surface and morphology modified and coated with MEH-PPV polymer samples by dip-coating method. The treated and coated fibers surfaces were characterized using scanning electron microscopy (SEM), luminescence and FT-IR spectroscopy. The SEM photos showed that cotton fiber surface was covered by a layer of MEH-PPV with the thickness around 1 μm. The effects on the crystalline structure and photoluminescence (PL) were studied as a function of the alkali modification conditions. It was found that the blue light intensity of the mercerized and bleached specimen is approximately two orders higher than the scoured one. The performance of fibers with MEH-PPV polymer as a coating component was investigated and an excellent white-light emission which consists of blue-, green-, and red-light-emitting bands was demonstrated.

1. Introduction

Cellulosic fibers (CF) constitute an interesting alternative to the inorganic counterparts used as reinforcing agents in the preparation of composite materials because of their good mechanical properties, low cost, ubiquitous availability in a variety of forms and recyclability [1]. Its molecular structure has an ultrafine network composed of ribbon-like microfibrils whose three-dimensional network endows CF unique properties including high tensile strength and high specific surface area. Therefore, the interest in using cellulose fibers as reinforcing elements in composite materials based on polymeric matrices is constantly growing, mainly because of the many advantages associated with this renewable material [2]. Chemical modification of cotton has been extensively studied for the past years in order to improve its wrinkle resistance, shrinkage resistance and dimensional stability. Many properties can be altered by modifying the surfaces of fibers, including surface hydrophilicity (or hydrophobicity), biocompatibility, electrical conductivity, antibacterial and antistatic properties [3,4]. Available surface modification technologies for cellulosic fibers include physical, chemical, mechanical and biological methods [2–4].

Surface grafting and coating process is a rather useful technology and has various advantages, because it is easy and controllable to graft polymer chains onto fiber surfaces without changing the bulk properties of the materials. Thus permanent grafting of different chemicals results in specific performances and new properties for these fabrics [5]. Coating the surface of fibers by nano-TiO_2/nano-ZnO particles and conductive polymers is one approach for the production of highly active surfaces to have UV-blocking, antimicrobial properties and enhancing of conductive properties. Recently, Mao et al. [6] grew nano ZnO crystallites on cotton fabrics to achieve excellent UV-blocking property. Li et al. [7] reported to treat cotton fabric with nano ZnO to have antibacterial activity. The morphology of ZnO nanoparticles prepared by Xin's group was dump-bell shaped [8,9]. Other functions can be added to cotton fabric by nano ZnO treatment. Li et al. [10] reported that coating Zn/ZnO nanoparticles on cotton fabric could emit 82% more infrared than untreated cotton fabric.

Conductive polymer-coated textiles are part of a family of recently developed composite materials with potential applications in many fields. Some coatings have been advantageously used to form surfaces with a light responsive adhesion for emission layers and photovoltaic cells. The most commonly used conductive polymers are poly(para-phenylenevinylene) (PPV), polyaniline (PANI), polythiophene (PTH) and their derivatives [11]. Yanumet et al. [12] investigated the effect of polypyrrole, polyaniline and polythiophene to increase the electrical conductivity of the cotton

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fabrics. They found that after polymerization the conductive polymer was successfully carried out on the fiber surface and both the surface and volume conductivities of the fabric improved after the treatment. A recent and excellent study by Krebs et al. [13] demonstrated strategies of the incorporation of polymer photovoltaics into cotton textiles and garments for potential use in "intelligent clothing".

It is well known that PPV, PTH and its derivatives are among the most promising organic materials for exploitation in novel efficient optical and electro-optical devices; this is exemplified by the large number of studies devoted to the use of these polymers as emission layers in light emitting diodes [14,15] and photovoltaic cells [16,17]. However, polymer-based organic photovoltaic is presently limited in their power efficiency due to a number of device and material parameters that have yet to be optimized. One of the first such limitations is that the band gap of the conjugated polymers needs to be tuned in order to absorb a larger portion of the solar spectrum and increase the photocurrent. Various approaches are being investigated for addressing color tuning. Two of these include synthesis of copolymers and incorporation of "luminescent dopants", such as phosphorescent metal complexes, luminescent inorganic quantum dots and fluorescent organic dyes [18]. Unfortunately, this approach is somewhat costly in the fabrication process. An alternative is to use electro-optical responsive systems based on coatings, which offer a promising low-cost technique and a commercially very interesting one, since they require a relatively small amount of the expensive polymer to provide a significant effect. Nevertheless, developing new polymer materials that enable the creation of architecturally simple structures with equivalent functionality remains challenging. It is therefore interesting to investigate the optical properties of PPV derivatives coated cotton fiber composite materials.

In this paper, the photoluminescence (PL) and FT-IR spectra at room temperatures were studied for a better understanding of the physical properties of surface modified and coated cotton fiber composite materials. The method of dip-coating process was applied to coat poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) on the different surface modified cotton fibers. Here we demonstrate that by appropriately controlling the fiber morphology of CF through chemical treatment, the PL intensity can be increased by two orders compared to the original material. The blue photoluminescence was observed for cotton fibers when excited with UV radiation. We have obtained MEH-PPV coated cotton fiber composite materials and observed white-light emission from this system, which consists of blue-, green- and red-light-emitting bands.

2. Experimental details

The various surface modified raw cotton fibbers were prepared by treatment with different aqueous NaOH solutions as described in [19]: (i) purifying and scouring treatments (2% NaOH; pH=11.5; t=90 min; T=95 °C; removal of non=cellulose compounds, the cellulose structure remains unchanged—cellulose I) (sample S1), (ii) mercerization (20% NaOH, pH=13, t=120 s, T=15 °C; the cellulose structure is changed—cellulose II) (S2). After each treatment the fibers were washed sequentially with distilled water and ethanol, thereafter air dried at 60 °C. In addition the mercerized fibers were bleached in a solution containing 7 g/l sodium silicate, 1.2 g/l sodium hydroxide, 1.8 g/l sodium carbonate and 9 g/l hydrogen peroxide for 60 min, at 85 °C. The bleached fibers were rinsed in hot water, neutralized in 2 g/l sulfuric acid for 10 min, and rinsed and air dried at 60 °C (S3).

For composite CF samples the 3 mg/ml chlorophorm solution of MEH-PPV (Aldrich) was coated using a dip-coating process. Each type of cotton samples (6 mg) was immersed in solutions of MEH-PPV in anhydrous chloroform and stirred at room temperature for 5 min and dried. The samples S1, S2 and S3 were manufactured on the quartz glass combined into ~10 mm-long parallel bundles. The pristine MEH-PPV was also prepared in the same way for comparison. Films were drop-cast on quartz glass substrates using 3 mg/mL solutions in chlorophorm. Before analysis, all samples were annealed for 30 min at 80 °C to remove any residual solvent and stabilize the film microstructures.

For studying its optical properties, absorption and photoluminescence (PL) methods have been applied. Infrared spectroscopy (ATR-FTIR, Shumadzu 8400S) was used to analyze the ground state vibrational mode. The morphologies of samples were investigated using a scanning electron microscope (SEM) (XL-30 PHILIPS). The absorption spectra were measured using Beckman DU-70 spectrophotometer and PL studies were carried out on a SPEX spectrometer equipped with a 0.75 m grating monochromator using a 50 mW cw He–Cd laser operating at the wavelength of 325 nm as the excitation source. The diameter of the focusing spot was about 300 μm. Neutral density filters were used to vary the excitation laser power. The resulting cotton fibers exhibit diameters in the range of 12–18 μm (samples S3–S1, respectively) and clockwise direction of helicity as we find by scanning electron microscopy. The coated surface and the uncoated surface of the specimen were tested, as we expected that the photoluminescence emission properties of the specimen would be different on the two surfaces.

3. Results and discussion

Fig. 1 shows the typical transmittance spectrum of CF and the steady-state photoluminescence spectra of the S1 and S2. The band gap energy of CF was evaluated to be about 3.36 eV from the transmittance spectrum. The intrinsic absorbance edge around 370 nm observed for samples S1 and S2 may be attributed to π–π^* transitions of C=C or to n–π^* transitions of C=O [20].

The corresponding PL spectra of the samples after incremental treatment with aqueous NaOH solution are much clear in contrast to the broad absorption features. The general features of the PL emission spectra and their dependence on the ordered crystalline structure of S1 and S2 are markedly different from the absorption spectra, suggesting that the origin of the blue emission is also different. The photoluminescence of the S1 sample covers the spectral range from 340 to 600 nm and peaks at 411 nm. However, its emission intensity is lower in comparison to the S2. A relatively narrow PL peak centered on 417 nm is observed for sample S2. It should be noted that other PL characteristics were found in [21],

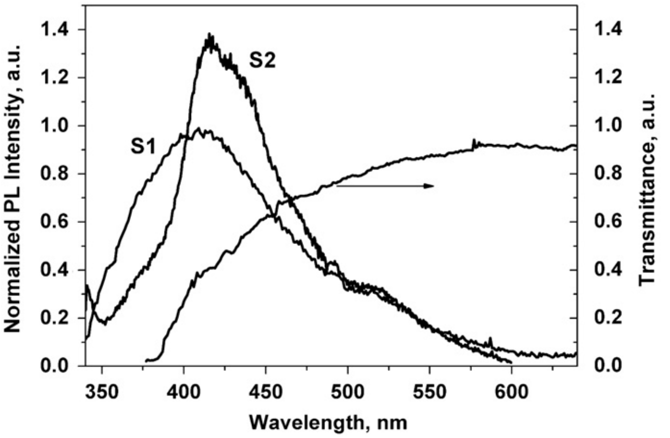

Fig. 1. The typical transmittance characteristics of CF and normalized to the intensity of S1 photoluminescence spectra of samples S1 and S2, respectively.