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Conjugated polymer nano-ellipsoids assembled with octanoic acid and their polyurethane nanocomposites with simultaneous thermal storage and antibacterial activity

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ABSTRACT

We prepared conjugated polymer nano-ellipsoids (CPNs) via emulsification of chloroform phase using the octanoic acid (OA) in dimethyl formamide (DMF), followed by the removal of chloroform by heating. The resulting CPN DMF solutions were thoroughly mixed with polyurethane (PU) DMF solutions to form composite films upon solvent removal, with uniformly distributed CPNs due to hydrogen bonds between PU matrix and the CPNs. Superior photothermal and antibacterial properties of the PU:CPN composite films were observed, presenting the usefulness of CPNs as an efficient light harvester and thermal storage material, and the OA as an antibacterial material for multifunctional fiber applications.

Introduction

Functional fibers with thermal storage and antibacterial properties have received considerable attention for use in future fiber technologies. For example, heat loss from the human body can be reduced by enhancing thermal insulation through trapped air in hollow fibers [1,2] or through reflecting radiation heat upon the application of metal coatings on fibers used in clothing [3]. Further, far-infrared ceramic nanoparticles, such as zirconium carbide nanoparticles, embedded in fibers effectively absorb 95% of the solar energy impinging on their surface and convert the energy to heat with a thermal emissivity above 90% or reflect the heat generated by the human body, thereby demonstrating efficient thermal storage capacity [4–8]. In addition, phase-change materials embedded in fibers can emit thermal energy upon phase change with decreasing temperature, thus providing warmth [9]. On the other hand, bacteria or fungi can proliferate in fibers, deteriorating the properties of the fibers and generating unpleasant odor. To hinder the aging of fibers by bacteria or fungi, inorganic antimicrobial materials such as silver, copper and zinc and zeolites have been added into, coated onto, or composited with fiber materials [10,11]. These inorganic antimicrobial materials diffuse through the cell membranes of bacteria or fungi as metal ions (Ag^+, Zn^{2+}, Cu^{2+}) and are adsorbed on the thiol groups of Cysteine in cellular enzymes, thereby decreasing the enzyme activity and ultimately killing the cells. Furthermore, active oxygen radicals that can destroy the molecular structures of bacteria can be generated by catalytic reactions of the metals. Moreover, the high specific surface area of porous zeolites allows for enhanced adsorption of bacteria, and consequently, effective removal of bacteria.

This letter presents the fabrication of multifunctional nanocomposites that have both thermal storage and antimicrobial properties, which have rarely been reported. Recently, conjugated polymer nanoparticles (CPNs) have been highlighted as promising photothermal, photoacoustic, and photocatalytic materials [12–17]. As organic semiconductors, conjugated polymers with low bandgaps can absorb a broad range of solar light, including visible and near infrared light, as widely demonstrated for polymeric photovoltaic devices. When dispersed in aqueous media as nanoparticles, they can effectively absorb energy and emit heat. Furthermore, CPNs can induce an increase in medium temperature upon static laser irradiation to kill cancer cells [12–14], or generate acoustic waves upon pulsed laser irradiation followed by the fluctuation of local densities [15,16], which should be useful for both photothermal therapy and photoacoustic imaging. As an

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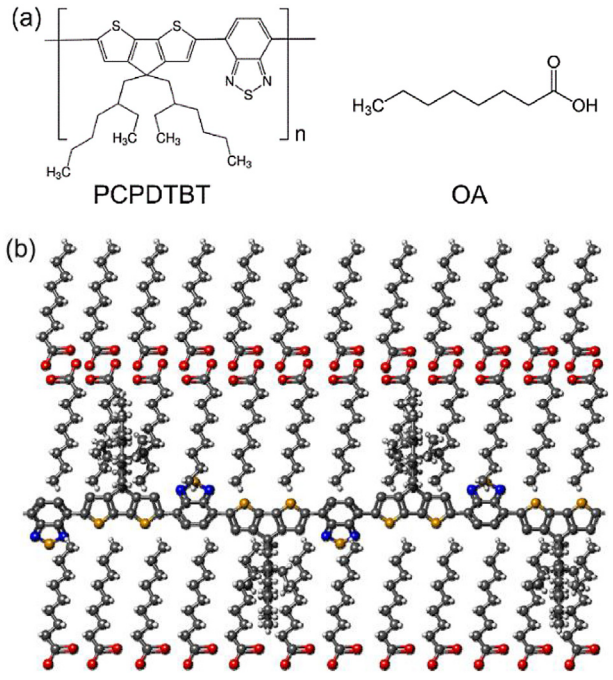
excellent light harvester, CPNs can absorb a vast quantity of solar energy and transfer this energy for photocatalytic reactions as recently reviewed [17,18]. Thus, CPNs may contribute to thermal storage by absorbing solar energy and emitting heat when they are composited with fiber materials. As for the antimicrobial material properties, we noticed the antimicrobial activity of fatty acids. For instance, saturated or unsaturated fatty acids with a carboxyl group (−COOH) at one end, such as scleropyric acid (natural C18 fatty acid), 2-hexadecynoic acid, and linoleic acid (18:2), showed antiplasmodial, antibacterial, and antifungal activities, respectively [19]. Although the origin of the antimicrobial activity of fatty acids is still unclear, a general, widely accepted mechanism is that fatty acids physically disturb the microbial cellular membrane structure which results in increased fluidity and disorganization of the membrane followed by leaking of intracellular components and finally disintegration of the cells [20]. It was also suggested, using *Escherichia coli* (*E. coli*) as reference organism, that the increased penetration of ionic species across the disordered cell membranes might cause the lowering of the cytoplasmic pH and disruption of the redox balance, thereby inhibiting proliferation of the organism [21].

In this study, we prepare CPNs using octanoic acid (OA) as a surfactant in a polar medium via an emulsion process, fabricate composite films of CPNs and polyurethane (PU), and present both thermal storage and antimicrobial properties of the composites. Besides the antimicrobial activity of octanoic acid [21–23], it can be used as a surfactant to prepare nanoparticles of a non-polar hydrophobic conjugated polymer, poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-b;3,4-b′]-dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), dispersed in a polar medium of *N*,*N*-dimethyl formamide (DMF) because its octyl chain can be closely associated with ethylhexyl side chains of PCPDTBT due to the comparable chain length (Scheme 1), which is demonstrated in the literature regarding optoelectronic devices [24] and biomedical applications [12]. Furthermore, CPNs contain carboxylic acid groups on their surfaces due to emulsification in polar media and can form hydrogen bonds with a representative fiber material, PU, thereby guaranteeing excellent compatibility and uniform distribution of the CPN fillers in the PU matrix. As a model system, we prepared CPNs and PU composite films and characterized their light absorption, heat generation, and antimicrobial properties. The novelty of our study is that the composite films can simultaneously show both of the photothermal [25] and antimicrobial effects [26] while maintaining their mechanical property due to a homogeneous distribution of filler nanoparticles in the matrix. For example, a representative antimicrobial material, silver nanoparticles (Ag NPs) can present both photothermal and antimicrobial properties. However, Ag NPs need to be closely assembled with each other in a matrix to enhance the photothermal effect by surface plasmon resonance which should deteriorate the mechanical properties of resulting composites.



Scheme 1. (a) Chemical structures of PCPDTBT and octanoic acid (OA), and (b) schematic illustration of a molecular assembly between PCPDTBT and OA.

Experimental

Materials

PCPDTBT (MW = 34 kDa, PDI = 2.1, MW on a repeat unit basis = 534.845 g/mol, One Materials, Inc., Quebec, Canada), OA (MW = 144.21 g/mol, Sigma–Aldrich), PU (Estane® S TPU, Lubrizol Co., USA), and organic solvents (Sigma–Aldrich) were used as received.

Preparation of nano-ellipsoids, composite films and fibers

0.22 mL of OA solution (74 mg OA dissolved in 10 mL chloroform) was added to 20 mL of DMF under continuous stirring at 1500 rpm. After 15 min of stirring, 5 mL of PCPDTBT solution (1 mg PCPDTBT dissolved in 10 mL chloroform) was drop-wisely added and stirred for 1 h. The molar mixing ratio of PCPDTBT on a repeat unit basis to OA was 1:12 (0.94 μM PCPDTBT:11.29 μM OA). The solution was further ultrasonicated for 5 min and heated at 80 °C for 3 h under stirring at 1500 rpm to completely evaporate chloroform. To prepare PU:CPN composite films, PU was dissolved in DMF at 15 wt% and CPNs solutions in DMF were added to the PU solution under stirring at 1500 rpm. Mixture solutions of three different weight percentages (0.0, 0.25, 0.5, and 1.0 wt%) of CPNs to PU were prepared and poured into petri dishes, followed by drying in vacuum at 25 °C for two days. As a reference sample, silver nanoparticles (Ag NPs) were synthesized by adding an aqueous solution of silver trifluoroacetate into DMF. Then, the resulting solution was heated at 100 °C for 5 min to reduce the silver ions using DMF as both solvent and reducing agent. A detailed procedure can be found elsewhere [27]. Control samples of PU films composited with 1 wt% of OA and PCPDTBT were prepared by mixing the PU DMF solution (15 wt%, 0.4 g) with OA and PCPDTBT dissolved in DMF and chloroform, respectively, followed by drying onto petri dishes. The thicknesses of all prepared films were 120 μm as measured by a vernier calipers. Fibers of PU composited with 1 wt% CPNs were prepared by a conventional solution spinning process. The DMF solution of PU and CPNs was extruded through a syringe needle directly into a poor solvent, methanol, thereby precipitating the composite fibers. The resulting fibers were dried at room temperature in vacuum for overnight.

Characterization

UV–vis absorption spectra of the PCPDTBT nanoparticles were obtained with an ultraviolet–visible (UV–vis) spectrometer (V-670, JASCO, Japan). Morphological observations of the nanostructures were conducted on a field-emission scanning electron microscope (FE-SEM, SIGMA, Carl Zeiss, Germany) and a high resolution transmission electron microscope (HR-TEM, JEM3010, JEOL, Japan). Structural analysis using 2D grazing incidence X-ray diffraction (2D GIXD) was carried out at a synchrotron facility (6D

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