



# Polymer composites with lychee-like core covered by segregated conducting and flexible networks: unique morphology, high flexibility, stretchability and thermoelectric performance

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## ABSTRACT

Polymer nanocomposites show great potential as platforms for the development of organic synthetic devices and systems, while a rational structural design of the matrix and the precursors are still urgently needed to ensure the viable development of these composite materials. Here, we report the controlled preparation of the novel composites with lychee-like polymer core covered by carbon nanotube/polyurethane segregated conducting and flexible networks. The composites were fabricated using a simple aqueous coating strategy. The resultant self-supporting films showed outstanding flexibility and stretchability with the minimum bending radius of less than 1 mm and an elongation at break of 3.8%. In addition, the composite films exhibited excellent thermoelectric function with the electrical conductivity, Seebeck coefficient, and power factor of  $109.3 \pm 4.3 \text{ S cm}^{-1}$ ,  $24.0 \pm 0.2 \mu\text{V K}^{-1}$ , and  $6.28 \pm 0.52 \mu\text{W m}^{-1} \text{ K}^{-2}$ , respectively.

## 1. Introduction

Compared with the corresponding counterparts, polymer/inorganic composites can combine the advantages of organic and inorganic constituents. By judiciously morphological controlling and strong interfacial interaction, significantly enhanced mechanical properties and excellent functions such as optical, electrical conductive, thermal and thermoelectric performances can be achieved [1–6]. A common strategy is the surface coating with a 2D thin-layer film of highly conducting materials to improve the electrical conductivity of insulating polymer materials [7,8]. The recent-developed method of 3D conducting polymer-based matrices with well-distributed inner segregated conducting networks [9–11] display better mechanical durability and ability to retain their functions under mechanical deformation. Unfortunately, such research is scarce. A fluorinated polymer was broken into fragments by a jet-milling high-pressure homogenizer, and carbon nanotubes (CNTs) were subsequently uniformly dispersed in the polymer matrix along with an ionic liquid [9]. In addition, 3D-interconnected matrices such as polydimethylsiloxane sponges were modified with poly [2-(methacryloyloxy)ethyl-trimethylammoniumchloride], and consequently underwent electroless metal deposition [10]. An easier and

more versatile method was to prepare a solution of polymer particles and CNTs, so that a segregated CNT network could be formed during the drying process as the polymer particles forced the CNTs into the interstitial spaces [11]. Therefore, a rational structural design of the matrix and the precursors is still greatly desired to achieve complex morphology and excellent performances.

In recent years, polymer thermoelectric (TE) composites have received increasing attention [12–18]. Surface wrapping of CNTs or graphene by conducting polymer layers may be the most extensively studied technique [19–24]. Besides smooth coating layers, an unusual coating morphology such as coral-like structure has also been observed for poly (3,4-ethylenedioxy-ythiophene) (PEDOT)/single-walled CNT (SWCNT) TE composite [25]. In addition, conducting polymer nanostructure/carbon nanoparticle composites have been found to exhibit dramatically enhanced TE performance [26,27]. However, the research of insulating polymer/inorganic TE composites is very limited.

Herein, we report a novel morphology design and controlled preparation of a polymer-based matrix with both segregated conducting and flexible crosslinked networks. In the polymer-based matrix, polymer particles bearing many small bumps and crosslinkable

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hydroxyl groups on their surfaces (PPBH) were synthesized via emulsion polymerization. The bumps on the polymer particle surfaces provided larger surface areas, thus facilitating the crosslinking of these polymer particles. SWCNTs were wrapped around the polymer particles, forming the desired segregated conducting networks. A water-dispersible polyurethane with blocked terminal isocyanate groups (PUBI) was designed and used as a flexible component as well as a crosslinking agent. During the curing process, the isocyanate groups were liberated and underwent crosslinking with the hydroxyl groups on the PPBH surfaces, thus yielding a flexible crosslinked network. In addition, we investigated the mechanical property and the TE function of the flexible composite films. The strategy of construction of this novel polymer-based matrix provides a novel and versatile way to fabricate polymer composites with complex morphology, mechanical property and multi-functions.

## 2. Materials and methods

### 2.1. Materials

Polytetramethylene ether glycol (PTMEG, with an average molecular weight of 1000 g/mol) and polyethylene glycol monomethyl ether (PEGME, with an average equivalent weight of 1000 g/mol) were purchased from Perstorp Chemical Co., Ltd., and distilled under reduced pressure prior to use. 3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI), dibutyltin dilaurate, and acetone were purchased from Aldrich and were used as received. Styrene (S), divinylbenzene (DVB), 2-hydroxypropyl methacrylate (HPMA), methyl ethyl ketone oxime (MEKO), and 2,2'-azobis (2-methylpropionamide) dihydrochloride (V50) were supplied by Hersbit Chemical Co. Ltd., and were of analytical reagent (A.R.) grade. SWCNT suspensions (0.2 wt% in water, TUBALL type) with an average diameter of ~10 nm (Fig. S1) were obtained from OCSiAl Company and were used as received.

### 2.2. Preparation of PPBHs

In a typical trial, S (2.25 g, 30 wt%), V50 (0.0375 g), and 64.00 mL of distilled water were added into a flask and stirred at 80 °C for 1 h to obtain the initial emulsion. The mixture of S (1.50 g, 20 wt%), DVB (3.00 g, 40 wt%), and HPMA (0.75 g, 10 wt%) along with the V50 solution (0.0525 g) were simultaneously added dropwisely into the flask over a period of ~2 h. More V50 solution (0.01 g) was then added into the mixture and the reaction was allowed to continue for another 1 h at 80 °C. The reaction mixture was cooled to room temperature, and was subsequently filtered through a 50 mesh filter before it was collected at a > 96% yield. Any coagulum remaining on the walls of the vessel and agitator was collected on the 50 mesh filter, and this filter along with the residue was subsequently dried at 105 °C to determine the yield.

### 2.3. Preparation of PUBI

Calculated amounts of PTMEG (50.0 g, 0.0500 mol), PEGME (50.0 g, 0.0500 mol), and IPDI (33.3 g, 0.150 mol) were mixed into a flask. The reaction mixture was purged under a flow of nitrogen for 30 min at room temperature, and the flask was subsequently heated to 80 °C. Dibutyltin dilaurate (0.100 g, 0.158 mmol) was added into the above mixture and the reaction was allowed to continue at 80 °C for 3 h. The reactants were cooled down to 50 °C, and MEKO (9.58 g, 0.110 mol) was subsequently added into the above mixture, which was stirred for another 1 h to obtain the PUBI.

### 2.4. Preparation of PPBH/CNT/PUBI composites

PPBH (1.00 g, 10 wt%) was mixed with SWCNTs (5.00 g, 0.2 wt%) via ultrasonication. Subsequently, a desired amount of PUBI (5, 15 or 20 wt%) was added and dispersed into the above mixture. The mixture

was then drop-cast onto a polytetrafluoroethylene (Teflon) substrate and was cured at 160 °C for 1 h.

### 2.5. Characterization

<sup>1</sup>H NMR spectra of the PUBI was recorded using a Bruker Avance 500 spectrometer and acetone-*d*<sub>6</sub> as the solvent.

The morphologies were characterized via scanning electron microscopy (SEM). The SEM characterization was performed using a Hitachi S-530 scanning electron microscope and the samples were sputter-coated with palladium and gold.

Mechanical tensile property tests were conducted using an HZ-1007E testing instrument and the measurements were performed at 25 °C. The length, width and thickness of the band-shaped samples were 100 mm, 20 mm and 0.025 mm, respectively. And the tensile speed is 100 mm min<sup>-1</sup>. The quantitative measurements of the minimum radii were carried out by rolling the films on cylindrical objects. If the films could be successfully mounted on the objects, their radii were adopted as the bending radii.

The Seebeck coefficients for the composite films were measured using a commercialized Seebeck coefficient measuring system, Thin-Film Thermoelectric Parameter Test System (MRS-3RT, Wuhan Joule Yacht Science & Technology Co., Ltd). During the measurements, a quasi-steady-state mode was adopted. The electrical conductivities for the composite films were measured by Keithley 2000 multimeter (Keithley Instruments Inc., USA). At least five samples were measured, and the average value was used.

## 3. Results and discussion

The PPBHs were prepared via the post-addition method by allowing the monomer HPMA to participate during the particle growth stage of the seeded emulsion polymerization, thus yielding particles with denser crosslinkable hydroxyl groups on their surfaces (Fig. 1a) [28]. In addition, the particle inner crosslinker DVB was used to introduce bumps onto the particle surfaces to provide larger surface area thus more crosslinking groups, thus facilitating interparticle crosslinking [29]. To explore the influence of the DVB contents on the surface morphology of PPBH, various DVB concentrations (of 0, 5, 10, 20, 30, and 40 wt%) were used in the preparation of PPBHs. The SEM topography images of these PPBHs are shown in Fig. 1b–g. As the DVB concentration increased, the surface roughness of the particles increased obviously. However, it was found that a precipitate occurred rather than well-dispersed particles when the DVB content exceeded ~50 wt%.

The electrical conductivities of the polymer-based matrices of PPBH (40 wt% of DVB) and various SWCNT contents are shown in Fig. 2a. Due to the formation of the 3D interconnected segregated network of SWCNTs, the PPBH/SWCNT matrices revealed electrical conductive. Moreover, with increased SWCNT content, the electrical conductivity increased. When the SWCNT content was 35 wt%, the electrical conductivity reached  $117.9 \pm 6.8 \text{ S cm}^{-1}$ . Fig. 2b and c present the well-distributed PPBHs in the mixed matrix, and it was apparent that the SWCNTs were wrapped around the PPBHs, thus yielding the desired segregated conducting network.

The films of these polymer-based matrices comprising PPBHs and SWCNTs were very difficult to peel off from the substrate. In order to overcome the difficult and improve the film flexibility, the PUBI was introduced to the composites. The PUBI was designed to not only serve as a flexible component but also offer a strong connectivity among the PPBHs due to the crosslinking, and thus yielded a self-supporting film. The preparation of the PUBI is illustrated in Fig. 3a, and the structural characterization is provided in Fig. S2 in the Supporting Information. PTMEG was selected for its flexibility, while PEGME was incorporated into PUBI to provide water-solubility, thus allowing us to prepare the water-based precursor containing PPBHs, SWCNTs, and PUBI [30]. The isocyanate groups in the PUBI's structure were blocked using MEKO as a

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