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Effect of polymer nanofibers thermoelasticity on deformable fluid-saturated porous membrane

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ABSTRACT

We describe a novel thermo-responsive fiber mat showing controlled release of liquids upon heating. The fiber mat was composed of electrospun thermoplastic polyurethane (TPU) nanofibers, with liquid-filled inter-fiber spaces (pores). On heating above 60 °C, nanofibers underwent substantial contraction. This solid deformation was attributed to the heat-induced relaxation of a non-equilibrium stretched state of the polymer fibers formed during the electrospinning process [Alhazov et al., 2013]. Fiber mat contraction drove expulsion of a glycerol/water solution stored in the pores of the mat, as evidenced by microscopic observations. The liquid flow in the deformable porous medium was analyzed, by means of confocal microscopy, which demonstrated liquid drainage from the mat as a function of temperature. UV-spectrophotometry revealed that 80% of a dyed liquid was expelled from the mat upon heating to 90 °C from room temperature. Finally, the potential of the thermoelastic fiber mats as reliable time-temperature indicator (TTI) was demonstrated with a simple model device in which the fiber mat was designed to release a liquid dye as an indication of the time-temperature history.

1. Introduction

The applicability of thermoresponsive polymer materials in design of smart textiles [1], deployable structures [2], drug delivery [3–6], smart implants [7], and tissue engineering [8] is attracting increased interest. Examples of such materials include shape memory polymers [9], hydrogels [10] and liquid crystal elastomers [11]. Under heat stimulation, these materials exhibit significant changes in deformation state [12], optical properties [13], wettability [14] or water vapor permeability [15]. In the present study, we report the fabrication of thermoplastic polyurethane (TPU) thermoresponsive non-woven fiber mats for the encapsulation and subsequent release of a liquid via a thermally-triggered contraction mechanism.

We recently described TPU non-woven fiber mats produced by electrospinning, which exhibited massive (>40%) contraction upon heating [16]. This phenomenon was attributed to the heat-induced relaxation of a non-equilibrium stretched state of the polymer fibers formed during the electrospinning process [17–20] and destruction of hard segment clusters [16]. We hypothesize that simultaneous longitudinal contraction and radial expansion of the fibers are likely to induce fiber mat pore closure upon heating. We propose to exploit these mechanisms to use the pores of TPU mats as liquid reservoirs, which can later expel their content upon heat stimulation (Fig. 1).

The functional liquid-releasing fiber mats were fabricated by simultaneously electrospraying the liquid and electrospinning the fibers on a grounded rotating wheel. Upon direct-contact heating, the liquid initially entrapped between the polymer fibers drained out from the mat controllably due to the contraction of the fibers network. This work first describes an experimental investigation of the three-dimensional contraction process of the dry fiber mats, i.e., in the absence of encapsulated liquid. Preparation of wet fiber mats and the liquid encapsulation methods are also discussed, as well as in-situ microscopic evidence of the thermally-induced release mechanism. Finally, the potential of the fiber mats in time-temperature indicator (TTI) applications will be demonstrated.

2. Materials and methods

2.1. Materials

Krystalflex PE-399 was purchased from Huntsman. This TPU is a block copolymer composed of a poly(tetramethylene ether) glycol

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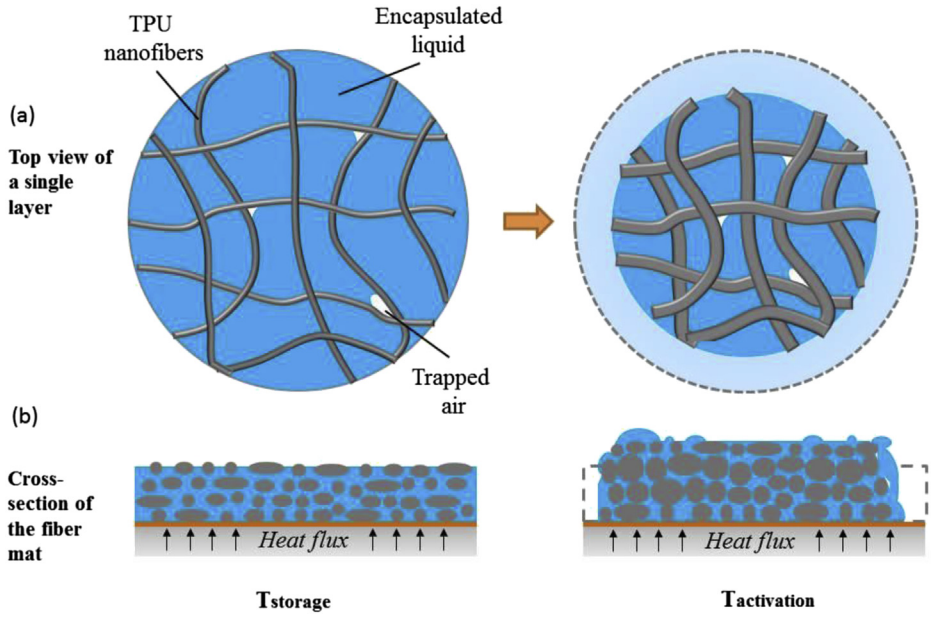

Fig. 1. Schematic presentation of the release of liquid from a thermoresponsive fiber mat upon contact heating, (a) top and, (b) cross-section views.

(PTMG)-type soft block and an aliphatic diisocyanate. Analytical-grade dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Frutarom Ltd., Israel. Glycerol was purchased from Biolab Ltd., Israel. Tinopal CBS-x was purchased from BASF, Germany. Congo Red was purchased from Merck Millipore KGaA, Germany. Using Gel permeation Chromatography (GPC), a molecular weight of Mn ~ 50 [kDa] was obtained for the TPU.

2.2. Electrospinning

TPU pellets were dissolved in a mixture of DMF and THF (7:3 (w/w)) to obtain a 12 wt% TPU solution. The solution was electrospun with a voltage of 12 kV and a feed rate of 1 mL/h, using a standard electrospinning setup comprised of a spinneret (needle 23G) located at a distance of 12 cm above a grounded collector wheel [21], which was found sufficiently slow to avoid fiber alignment.

2.3. Electrospraying

A liquid fluorescent dye made from a 1 or 10 g/L dispersion of Tinopal in a mixture of glycerol and water (5:1 (w/w)), was sonicated and subsequently encapsulated within the TPU mat pores by electrospraying the liquid with a second spinneret, located on the side of the rotating wheel, during the collection of the nanofibers, with a voltage of 12 kV, a feed rate of 0.1 mL/h and at a distance of 8 cm.

2.4. SEM

Samples were sputtered with a thin film of gold. SEM images of the nanofiber mesh surface were obtained using FEI E-SEM Quanta 200 at 20 kV. The images were recorded using SE2 detectors at a sample–detector distance of 5 mm.

2.5. Contraction measurement

10 × 10 mm^2 fiber mat samples with a thickness of 0.09–0.12 mm were immersed in glass vials containing a buffer solution of glycerol/water (5:1 (w/w)) and a magnetic stirrer. The immersed mats were heated to 40, 50, 60, 70, 80, and 90 °C in a water bath, under stirring, at a rate of 2 °C/min and maintained in isothermal conditions for 15 min. The three dimensional engineering strains were computed using a caliper. All experiments were run in triplicates.

2.6. Confocal fluorescent microscopy

Fiber mats filled with UV fluorescent dye were observed under an LSM 510 META confocal microscope (Zeiss, Germany), via a 25× immersion objective in the 2-photon mode. A drop of a glycerol-Tinopal solution was used as a liquid lens between the mats surface and the objective. The laser wavelength was set to 720 um in order to excite the dye at 360 um, close to the peak of absorption of the dye, and detection was performed at 450 nm, at the emission peak. Samples with dimensions of 5000 × 5000 × 100 μm^3 were attached to a planar heater using double-sided tape. A scan area of 440 × 440 μm^2 was selected in the center of the specimen. Direct-contact heating of the samples was controlled by applying an electrical current to the heater and the temperature was measured with a K-type thermocouple. Z stacks were acquired every 1 μm, later used for 3D reconstruction. The laser power was increased linearly, from 0.2 to 1.5 W, from the fiber mat surface ($z = 0$) to 140 μm below the surface, in order to compensate for the loss of detected signal through the thickness. The temperature was raised by steps, at a heating rate of about 10 °C/min, and maintained for 10 min for equilibration and image acquisition.

2.7. Image analysis

Image analysis was performed using Imaris 7.4 (Bitplane AG, Switzerland). The raw 3D images were first segmented using the following parameters: smoothing: 0.2 μm; local contrast: 2 μm; threshold: 1000–3065; seedpoint (region growing): 3 μm, quality filter: >200; volume detection threshold: 1 voxel. Using the Vantage module, the detected liquid pockets were counted and statistical measurements were performed in terms of dimensions, spatial distribution (center of mass) and volume. The 3D distribution of pockets was characterized using the median (M) and interquartile range (IQR), also called the middle fifty, being equal to the difference between the upper and lower quartiles. Due to the