

# Thiol-ene modification of electrospun polybutadiene fibers crosslinked by UV irradiation



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## ARTICLE INFO

### Article history:

Received 13 July 2014

Received in revised form

1 September 2014

Accepted 2 September 2014

Available online 16 September 2014

### Keywords:

Electrospinning

Thiol-ene reaction

Crosslink

## ABSTRACT

Electrospun polybutadiene (BR) was crosslinked *in situ* during the spinning process to obtain stable fibers. Crosslinking was induced by addition of photoinitiator to the electrospun BR solution. Due to the very low glass transition temperature ( $T_g$ ) of BR (below  $-80$  °C) it is necessary to crosslink the fibers thereby improving the mechanical properties and creating stable fibers by preventing fibers from melting together. In order to prevent the polymer fibers from melting onto the grounded collector, a solution of sodium chloride in methanol was used to collect the fibers thereby letting the fibers float and increase the irradiation time of the UV curing during the electrospinning process. Subsequent surface modification via thiol-ene click chemistry on remaining C=C bonds was successfully employed with mercaptoethanol or thioglycolic acid, leading to superhydrophilic fiber mats.

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## 1. Introduction

Electrospinning is a very useful technique for the production of polymer fibers, which are produced by an electrostatically driven jet of a polymer solution, with diameters down to the nanometer scale [1]. These polymer nanofibers have attracted much interest for their varieties of applications, such as templates for preparation of functional nanotubes [2], membranes [3], biomedical applications [1] and scaffolds for tissue engineering [4]. The diameter of electrospun fibers can be influenced by the induced electric field, the applied voltage, the tip-to-collector distance, the conductivity of the polymer solution, the diameter of the nozzle, and the flow rate of the syringe pump [5]. The formation of stable fibers is further influenced by the concentration of the polymer solution, the molar mass of polymer, and the choice of solvent.

Polymers having a glass transition temperature ( $T_g$ ) higher than room temperature, readily form stable fibers via the electrospinning process; however, rubbery polymers, such as butadiene rubber (BR), natural rubber (NR), or styrene-butadiene rubber (SBR) do not readily form stable fibers due to the effects of their low  $T_g$ , typically below 0 °C. For rubbery polymers, the jet of polymer solution can be formed regularly, but the fiber morphology is

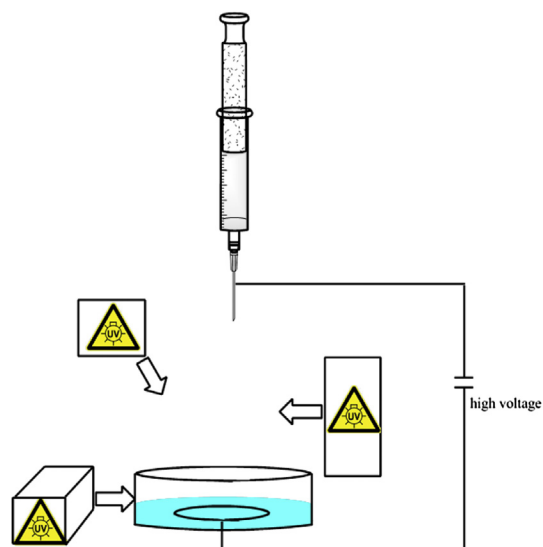
immediately compromised upon contact with the collector or other fibers. Previous work shows that single fibers of BR can retain fiber morphology upon *in situ* crosslinking during the electrospinning process since the crosslinked BR fibers had a higher  $T_g$  than the raw BR [6].

Crosslinking polymer fibers with a low  $T_g$  requires a highly efficient, low temperature curing process. Therefore a curing system, which is initiated by the irradiation of UV light, is most promising to build crosslinks within the fiber while leaving sufficient reactive double bonds on the surface of the fiber. The reactive surface of the fiber can be then utilized for post-polymerization modification such as the thiol-ene click (TEC) reaction [7]. TEC chemistry is a highly efficient tool used for the polymerization and modification of polymers. The modification has been applied to various polymers, including polybutadiene [8,9]. TEC chemistry has been shown as an efficient way to modify surfaces via UV curing in order to receive a superhydrophobic surface [10].

Post-polymerization functionalization represents a versatile tool for the preparation of tailor-made functionalized polymers starting from a single precursor. Consequently, the combination of post-polymerization modification and electrospinning allows the fabrication of fibers with adjustable properties due to the required application [11].

Within the present study, we attempt to produce the crosslinked BR fibers via electrospinning and UV curing, followed by a post-modification of the fibers via TEC chemistry.

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**Fig. 1.** Electrospinning apparatus with *in situ* UV irradiation. Process was performed into a 1% sodium chloride solution in methanol.

## 2. Experimental part

### 2.1. Materials

Two polybutadiene rubber (BR) samples were generously provided by STYRON. The sample BUNA cis 132 with a content of *cis*-1,4-butadiene of 95%, and PB 5800 with a 37% *cis*-1,4-butadiene and 12% 1,2-butadiene. Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), 2-mercaptoethanol and thioglycolic acid were purchased from Sigma–Aldrich and trimethylolpropane trimercaptoacetate (TMPMA) was generously provided from Bruno Bock Thiochemicals.

### 2.2. Instrumentation

Two UV lamps (365 nm, 8 W) and an additional OSRAM UVA 18 W Lamp were used. FT-IR measurements were recorded on a

Nicolet iS10 spectrometer from Thermo Scientific. Glass transition temperatures ( $T_g$ ) were measured by DSC (second heating curve) using the DSC1 Star<sup>e</sup> System from Mettler Toledo.

### 2.3. Electrospinning

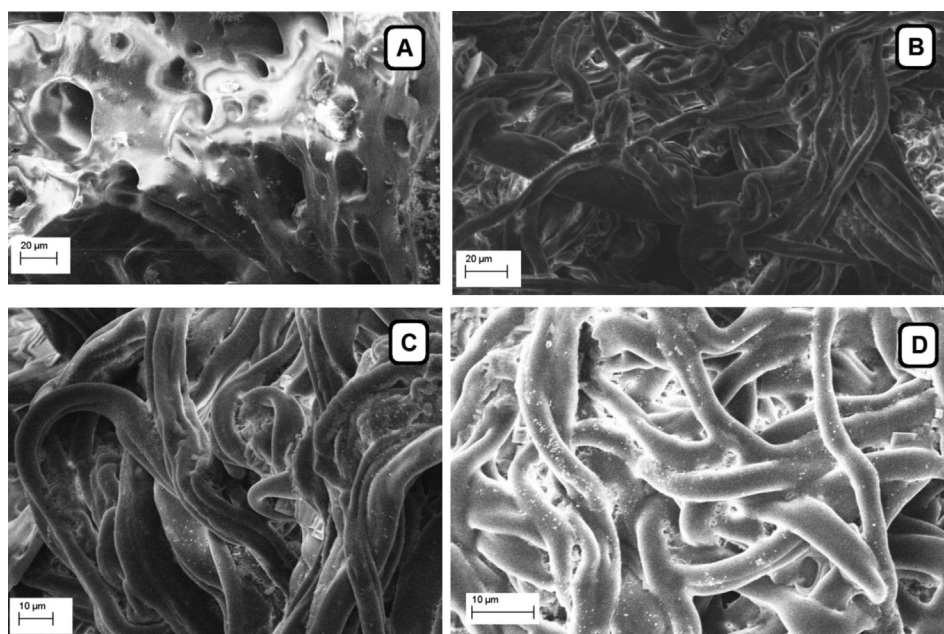
*In situ* irradiation of the electrospun fibers is made possible by immersing the grounding collector in a methanolic sodium chloride solution (1%). This type of apparatus also prevents the fibers from melting onto the surface of the grounded collector and losing their fiber-shaped structure by allowing the fibers to float within the solution (see Fig. 1).

Electrospinning was performed with 5 wt% solution of BR in THF/DMF (4:1).

In addition to the photoinitiator diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, 1 wt% of BR), various concentrations of crosslinker trimethylolpropane trimercaptoacetate (TMPMA) were used in the electrospun polymer solution. The applied mass fractions of TMPMA were 0 wt%, 1 wt%, 2 wt%, and 3 wt% of BR, respectively. Two different BR samples were investigated, varying in their content of *cis*-1,4-butadiene.

Polymer fibers were electrospun into a methanol solution containing 1% sodium chloride. Fig. 1 shows the electrospinning apparatus with UV lamp for curing. A syringe was used with a blunt metal needle (0.4 mm diameter) with a flow rate of 1 mL/h. The electrospun fibers were collected on the solvent layer, which remained 2 cm above the grounded collector immersed in the methanol solution. The total distance of the capillary tip and the counter electrode was 20 cm, and the applied voltage was 20 kV. The UV-lamps were placed directly on the side of the methanol bath, orthogonal to the polymer jet. The OSRAM UVA 18 W lamp was placed beside the tip to irradiate the methanol bath from the top. The fibers were irradiated in total from 1 to 2 h.

After the isolation of the BR fibers from the methanol bath, the fibers were washed with methanol to remove excess salts. The surface modification of the fibers was investigated by exposing the fibers in a 6.25 wt% solution of 2-mercaptoethanol or thioglycolic acid in methanol to UV irradiation for 48 h ( $\lambda = 365$  nm, 8 W).



**Fig. 2.** SEM images of electrospun BR fibers with 95% of *cis*-1,4-butadiene: Uncrosslinked fibers (A) without use of TMPMA, (B,C,D) Crosslinked fibers and fiber mats, spun with 3 wt% TMPMA.

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