



Surface free energy analysis of electrospun fibers based on Rayleigh-Plateau/Weber instabilities



Urszula Stachewicz^{a,b,c,*}, J. Frits Dijkstra^d, Chaïma Soudani^b, Lewis B. Tunnicliffe^b, James J.C. Busfield^b, Asa H. Barber^{a,b,e}

^a Nanoforce Technology Ltd., Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

^b School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

^c AGH University of Science and Technology, International Centre of Electron Microscopy for Materials Science and Faculty of Metals Engineering and Industrial Computer Science, Al. A. Mickiewicza 30, 30-059 Kraków, Poland

^d University of Twente, Faculty Science and Technology, Physics of Fluids, Drienerlolaan 5, 7522NB Enschede, The Netherlands

^e School of Engineering, University of Portsmouth, Portsmouth PO1 3DJ, United Kingdom

ARTICLE INFO

Keywords:

Surface free energy
Rayleigh-Plateau/Weber instabilities
Fibers
Rubber
Electrospinning
Fluids

ABSTRACT

Electrospinning is an increasingly common technique used to produce fibers with a range of diameters. These electrospun fibers are used extensively in applications that exploit the material's high surface area to volume ratio, thus requiring detailed knowledge of the surface properties of the fibers. The surface free energy of individual free standing electrospun styrene-butadiene rubber (SBR) fibers was determined here from the time-dependent break-up of long fibers driven initially by Rayleigh-Plateau/Weber instabilities. Individual free standing electrospun rubber fibers were observed to change from a cylindrical fibrous geometry to semi-spherical droplets during a time period of several days when above the glass transition temperature of the polymer. A wave-like transition from fiber to droplet was attributed to a surface tension driven break-up process occurring over a time strongly influenced by the rubber's viscosity. The surface free energy for an electrospun rubber fiber was found using a Weber approach for the free standing fibers and Diez et al theory for dynamic fluid instability of fluid ridges. Both methods lead to similar values of fiber surface free energy and were confirmed from bulk measurements exploiting Owens-Wend theory. The approach presented here is powerful as the surface free energy, indicative of the physical and chemical behavior of the fiber surface, can be determined for any fiber diameter provided the geometric break-up of the fiber is observed.

1. Introduction

Electrospun polymer fibers are used extensively for applications where their large ratio of surface area and volume is of critical importance, such as for filtration [1], tissue engineering [2,3], energy [4] and in composites [5,6]. Electrospun fibers have benefits over many other fibrous materials due to their relatively large surface area to volume ratio, especially when fiber diameters approach nanoscale dimensions. The physical and chemical properties of the fiber surface, in addition to geometric considerations such as orientation of fibers in a network, define electrospun fiber performance [7–10]. Recent work has highlighted how the physical properties of electrospun polymer fiber surfaces, quantified by the surface free energy, differ from bulk polymer behavior [11] using a

* Corresponding author at: AGH University of Science and Technology, International Centre of Electron Microscopy for Materials Science and Faculty of Metals Engineering and Industrial Computer Science, Al. A. Mickiewicza 30, 30-059 Kraków, Poland.

E-mail address: ustachew@agh.edu.pl (U. Stachewicz).

<http://dx.doi.org/10.1016/j.eurpolymj.2017.04.017>

Received 17 January 2017; Received in revised form 31 March 2017; Accepted 13 April 2017

Available online 18 April 2017

0014-3057/ © 2017 Elsevier Ltd. All rights reserved.

modified Wilhelmy balance approach applied to individual fibers [12]. While this work is powerful in measuring electrospun fiber surface free energy, a number of complex nano-manipulation steps are required prior to testing [13]. This paper seeks to define a method of measuring the surface free energy of electrospun polymer fibers by using surface energy driven polymer flow generally described by Rayleigh-Plateau/Weber instability [14–16]. Rayleigh-Plateau/Weber instabilities are notable in the electrospinning process when a polymer solution in the form of a jet is drawn under the action of an electric field [17]. During electrospinning, the typically rapid solvent evaporation, which reduces polymer chain mobility until solid polymer is collected, competes against the surface energy driven instability and break-up into droplets [18]. Similar instabilities were observed recently when annealing nanowires at 400–600 °C [19] as well as during ink-jet printing [20] and electrospraying processes for aerosols of liquid and solid particles [21–26]. For fibrous geometries, the surface of the cylindrical shape is always initially perturbed if material is able to flow. This flow is related to ability of rubber to change the shape spontaneously. This perturbation is manifest of the formation of initial crests and troughs of specific wavelength in fiber topography. This change in the topography of fiber initiates the break-up process. The fiber curvature drives material to flow from the troughs to the crests, amplifying the wave amplitude, and this arises when the polymer molecules have sufficient mobility.

The Rayleigh-Plateau/Weber wavelength is defined for the break-up process that proceeds at the highest rate. Such a break-up process can be avoided by using liquid phases with low mobility, as used when electrospinning high viscosity polymer solutions to produce nanofibers, or accelerated with a higher mobility phase. Rubber materials are an example of a polymer where cross-linking between the polymer chains is used to reduce their mobility. Conversely, a rubber material prepared without cross-linking will exhibit viscous characteristics and flow with time as the polymer macromolecular chains are able to move away from the troughs to initiate break-up. The observing rubber material above its glass transition temperature provides sufficient mobility for polymer chains to the break-up the fibrous geometry into droplets. The uncross-linked rubber behaves as a viscous fluid above its glass transition temperature and is therefore considered as such when developing methods to evaluate the surface free energy contribution to this process. As Rayleigh-Plateau/Weber instability is driven by surface free energy, observing the break-up of fibers of such non-cross-linked rubbery polymers can provide information on the surface free energy when the viscosity of the material is known. Previous work has shown how surface free energy values of fluid systems can be estimated from recording geometric changes [27]. Therefore, the surface free energy of fibers using Rayleigh-Plateau/Weber instability principles can be calculated by observing the break-up of electrospun rubber fibers driven by their surface free energy and by measuring the relaxation times involved in the process at room temperature. Efforts to describe the flow of a polymer were developed from initial perturbation of cylindrical geometries using Rayleigh-Plateau/Weber [15,16], through Diez et al. [28] and finally more established surface free energy method measured at equilibrium using the common contact angle measurement approach and interpretation using Owens-Wendt theory [29]. The Rayleigh-Plateau/Weber and Diez et al. theories are used to calculate the surface free energy from fiber break-up. The Rayleigh-Plateau/Weber mechanism is applied for the initially cylindrical shape of electrospun fibers. In this study a styrene-butadiene rubber (SBR) without cross-links, that acts as a viscoelastic polymer liquid was observed to attempt to understand the mechanism of expected break-up of the fibers into droplets at room temperature.

2. Materials and methods

2.1. Electrospinning of rubber fibers

Rubber nanofibers were prepared using electrospinning. We used styrene-butadiene rubber (SBR, Emulsion, Europrene 1502, Polimeri Europa, U.K.) with an average molecular weight (M_w) of 68,600 g·mol⁻¹ with error estimated to be in the range of 0.5%. Molecular weight was determined by gel permeation chromatography using an Agilent 1260 GPC by adding tetrahydrofuran/2% triethylamine eluent. However, to prepare polymer solution for electrospinning, the SBR without any cross-linkers was first dissolved in a mixture of tetrahydrofuran (THF, AnalaR NORMADUR, VWR BDH Prolabo, U.K.) and dimethylformamide (DMF, 99.8%, Sigma Aldrich, U.S.A.) (75/25% mass ratio) to produce a polymer concentration of 5 wt.% in solution. The SBR solution was electrospun from a pin electrode using commercially available equipment (Nanospider, Elmarco, Czech Republic). The rubber fibers were produced using free surface electrospinning approach, from the polymer solution volume deposited in the meniscus with a diameter approximately 1 cm in the vertical pin. A positive voltage of 26 kV was applied between the pin electrode situated 16 cm above a ground electrode. Experiments were performed at room temperature (21–22 °C) and a humidity of 30–36%. The collected fibers were dried after evaporation of most of the solvents during electrospinning [30,31]. Electrospun fibers were deposited on glass slides to be able to observe their break-up process over long time taking several days using an optical microscope. Other collecting methods for fibers, such as in frame to have fibers freely hanging, would not allow long break-up observations.

2.2. Optical microscopy observations

Electrospun SBR fibers were deposited onto glass slides to allow subsequent observation of the fiber geometry using optical microscopy (Olympus BX 60 with Digital Imaging, Japan), as shown in Fig. 1. The microscope light was used for short observation times of 5 s to avoid any heating of the rubber fibers from the light source. The electrospun SBR fibers are loosely distributed over the substrate surface after electrospinning and contact the substrate at a limited number of points, as during electrospinning the solvent evaporates and solid fibers are deposited [32,33]. In some cases fibers during electrospinning can be deposited wetted and having possibility to spread on the collecting substrate. This process is depending on the added salts to polymer solution, electrospinning conditions, surface wettability of collecting electrode and type of electrospinning, such as core-shell or blended electrospinning.

Download English Version:

<https://daneshyari.com/en/article/5159633>

Download Persian Version:

<https://daneshyari.com/article/5159633>

[Daneshyari.com](https://daneshyari.com)