

Influence of Molecular Ordering on Surface Free Energy of Polymer Nanofibres using Scanning Probe Microscopy

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ABSTRACT

Fibrous materials are used in a variety of applications due to their relatively high surface area to volume as well as anisotropic behavior. Electrospinning is a popular fabrication method which produces polymer nanofibres with a potentially high molecular alignment. In this work we examine the surface free energy of electrospun polyvinyl-alcohol nanofibres and its relation to molecular ordering using scanning probe microscopy adhesion measurements. Comparisons are made with bulk polymer material to show that a high degree of molecular orientation is present at least at the surface of the polymer nanofibre. As a result, the surface free energy of electrospun polymer nanofibres is greater than that of a bulk polymer. This effect indicates that the electrospinning process is effective at polymer alignment over a variety of experimental parameters.

INTRODUCTION

Polymer nanofibres have been attractive materials for a wide range of applications because of their large surface area to volume ratio and potentially improved mechanical performance due to high molecular alignment. Their potential applications include tissue engineering scaffolds [1], drug delivery media [2], filtration media [3], protecting clothes, and as reinforcement in nanocomposites [4]. It is well known that the properties and internal molecular structure of polymer solids are greatly affected by their processing conditions. Therefore, an understanding of the processing–structure–property relationship is essential for engineering polymer nanofibres to meet the demands of their applications. A number of processing techniques such as drawing [5], template synthesis [6], phase separation [7], self-assembly [8] and electrospinning [9, 10] have been used to prepare polymer nanofibres. Electrospinning is particularly important for mass production as the method is both simple and easy to scale-up for mass production.

Electrospinning uses a high voltage electrostatic field to charge the surface of a polymer solution droplet and thus induce the ejection of a liquid jet through a spinneret [11]. In a typical process, an electrical potential is applied between a droplet of a polymer solution, or melt, held at the end of a capillary tube and a grounded target [12]. When the applied voltage overcomes the surface tension of the droplet, a charged jet of polymer solution is ejected. The route of the charged jet is controlled by the electric field [13]. The jet exhibits bending instabilities caused by repulsive forces between the charges carried with the jet. The jet extends through spiraling loops; as the loops increase in diameter the jet grows longer and thinner until it solidifies and collected on the target [14, 15].

The surface of polymer fibres plays an important role in many applications. Composites require good adhesion between the fibre and surrounding matrix to allow efficient stress transfer

for mechanical reinforcement [16-18]. Other examples include filters, made of polymer fibres, are critically dependent on the interaction between the polymer surfaces and filtrate. Therefore, measurement of the surface properties of these polymer nanofibres is essential but challenging due to their small size. In this paper we present evidence to show how the surface free energy of the electrospun polymer nanofibres is different to bulk values using scanning probe microscope (SPM). This technique has been particularly useful in other nanofibre surface free energy measurements [19, 20] with little application to electrospun material. Previous studies using SPM have quantified the work done to separate the SPM probe from the surface of a sample. If the SPM tip-sample contact is known, the work of adhesion can be related to the surface free energy of the sample [21]. This work accurately describes the surface properties of electrospun polymer nanofibres and determines the surface properties of the nanofibres using SPM techniques.

EXPERIMENTAL DETAILS

Poly(vinyl alcohol) (PVA) with an average molecular weight of 98,000-143,000g.mol⁻¹ was selected as the polymer material for electrospinning. PVA solutions of various concentrations were prepared by dissolving the polymer in distilled water 80-90°C and gently stirred for 2-3 hours. Electrospinning was performed as previously described [9-15]. Briefly, prepared polymer solutions were fed into a 10ml syringe using a constant flow rate of 3 µl min⁻¹ controlled by a programmable syringe pump (Harvard PHD4400, Harvard Apparatus Ltd., UK). The syringe is connected to one end of a silicone capillary, with the other end connected to a stainless steel tubing needle. This tubing needle was connected to a high voltage power supply (Glassman Europe Ltd., Tadley, UK). A constant pressure was applied to the syringe tip due to the weight of solution so that a small stable drop of solution was suspended at the needle tip. The power supply was used to apply a voltage of 15 kV between the needle and a grounded collector plate 15cm below the needle. A charged polymer solution jet was ejected when applying high voltage and traveled under bending instability [13, 15, 22] towards the target. A significant amount of solvent evaporated during this process to leave ultrafine polymer fibres deposited on the grounded collector plate target. All the experiments were performed at room temperature.

The morphology and dimensions of the collected electrospun nanofibres were investigated using SPM (NTEGRA Spectra, NT-MDT, Russia.). Surface property measurements were also carried out using the same SPM. Nanofibre samples covering an area of 1cm x 1cm on sapphire sheet were used for SPM studies. SPM tips (Nanosensors, Windsor Scientific Ltd, UK) with a spring constant of 0.1 Nm⁻¹ were used for semi-contact imaging and force measurements as discussed below.

DISCUSSION

A representative SPM topography image of the electrospun PVA nanofibres is shown in Figure 1. It can be seen that the diameter of the fibres is constant and the fibres themselves are continuous. The fibre diameter as measured from Figure 1 is 300±50nm. Electrospinning for short amounts of time produced more isolated nanofibres in which surface properties could be investigated as shown in Figure 1b.

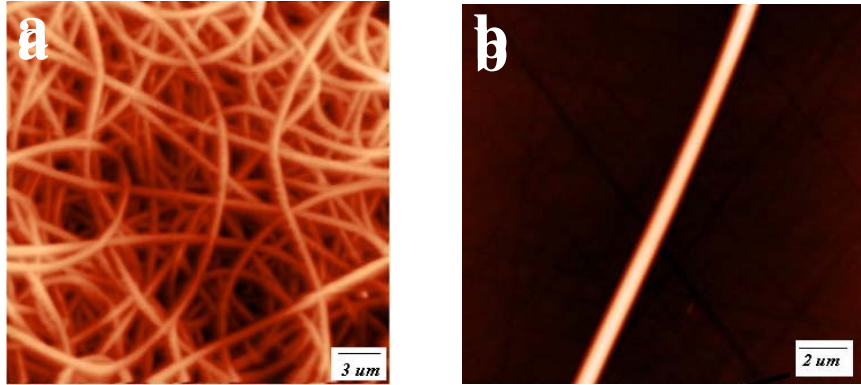


Figure 1. SPM semi-contact topography imaging shows a) how the nanofibres are of uniform diameter and continuous, b) electrospinning for short amounts of time gives a lower density of nanofibres on the substrate, allowing simple visualization of individual nanofibres.

Surface free energy determination using SPM

An isolated PVA nanofibre as shown in Figure 1b was selected to determine the contact adhesion force between a tip and a sample surface for the derivation of surface free energy. The SPM tip was moved into contact with the nanofibre's surface using the z-piezo of the SPM. Spatial drift between the sample and tip was minimal using the SPM's close loop system. Once in contact, the z-piezo was used to separate the tip from the sample's surface while monitoring the forcing acting on the tip using cantilever bending data. The cantilevers were calibrated using the thermal noise method [23]. A typical force-distance curve showing the tip pulling away from the sample surface is shown in Figure 2. This curve shows the contact point between the SPM tip and the nanofibre surface (1), the maximum adhesion force holding the tip at the sample surface (2) and the separation point (3).

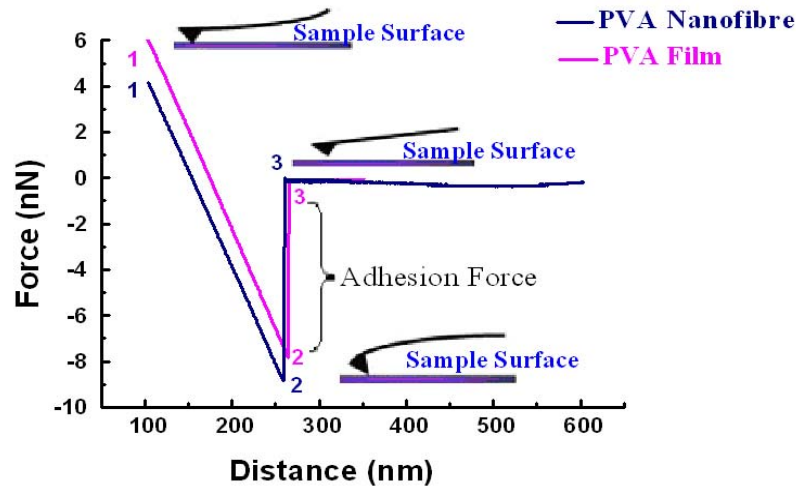


Figure 2. Force-distance curve for the separation of the SPM tip from the sample surface.

Contact mode cantilevers with a spring constant of 0.1Nm^{-1} were used so that there was minimal contact pressure between the tip and sample. Large contact pressures increase the tip-sample contact area and are avoided in this study. This was achieved by using a set point such that the cantilever bent back from the sample by less than 1nm upon contact.

The tip in contact with the sample surface is modeled according to a sphere in contact with a plane. This is reasonable as the tip radius of curvature is almost two orders of magnitude smaller than the nanofibre radius. Johnson-Kendal-Roberts theory [24] is used to correlate the maximum pull-off (adhesion) force F , shown at (2) in Figure 2, with work of adhesion W_A through the following analytical equation [25]:

$$F = \frac{3}{2} \pi R W_A \quad \text{Equation 1}$$

where R is the radius of the sphere (SPM tip radius of curvature). The work of adhesion can be calculated by using this equation:

$$W_A = 2(\gamma_1 \gamma_2)^{1/2} \quad \text{Equation 2}$$

where γ_1 and γ_2 are the dispersive components of the surface energy of the SPM tip and sample respectively. Combining last two equations it derives:

$$\gamma_2 = \left(\frac{F}{3 \pi R} \right)^2 \frac{1}{\gamma_1} \quad \text{Equation 3}$$

γ_1 was taken to be 42mJm^{-2} for the silicon tip [26, 27]. The surface free energy in this study refers to the dispersive component of the total surface free energy, which is mainly contributed from London forces. The adhesion between the SPM tip and sample measures the

sum of all the interaction, which may include electrostatic, capillary, and London forces. However, capillary forces have been removed by carrying out the experiments at very low humidity (<1% Relative Humidity) and electrostatic charges have been removed by heating up the sample up to 80 °C and by connecting the facility to a grounded electrode before all the force measurements. Finally it just leaves dispersive contribution as total surface free energy.

The SPM tip radius of curvature was found by performing force-distance curves on a clean silicon substrate with a known γ_1 of 42mJm⁻². Equation 3 was then used to calculate the tip radius of curvature R, which was about 20nm. As R can potentially get larger during extensive usage, such as prolonged imaging or after force-distance measurements, the tip radius was measured before and after every force-distance measurement.

Fifteen measurements were made for the PVA nanofibre and film respectively, with the same cantilever and experimental parameters. The adhesion force was taken from Figure 2 between points (2) and (3). The pull-off force for the PVA nanofibres has a typical average value of 8.8nN and a PVA film has an average value of 7.8 nN. Using Equation 3 and calibrated R values, the dispersive surface free energy of the PVA nanofibres were calculated as 40.6 ± 4mJm⁻². This is interesting as non-electrospun (bulk) PVA polymer film dispersive surface free energy was calculated as 25.5 ± 2mJm⁻² which is similar with a reported value of 25.1mJm⁻² [28]. The increase in surface free energy between electrospun PVA nanofibres and their bulk equivalents suggests that the two structures are quite different. Previous literature [29, 30] has suggested that electrospinning provides high molecular alignment when compared with polymer films. Consideration of the electrospinning process would support this; ejection of the polymer from the needle involves rapid stretching of an electrified jet and evaporation of the solvent. The polymer chains are expected to experience an extremely strong shear force during the electrospinning process. This shear force and rapid solidification could prevent polymer chains from relaxing back to their equilibrium conformations and resulting in better molecular orientation. From our measurements it is clear that the unique polymer morphology in electrospun polymer nanofibres influences and increases the surface free energy relative to bulk polymer.

CONCLUSIONS

The dispersive surface free energy of electrospun polymer nanofibres was measured using SPM. Force-distance curves show that the adhesion between the SPM tip and polymer surface is relatively large, with a calculated PVA nanofibre surface free energy of 40.6 ± 4mJm⁻². These values are much larger than bulk polymer, indicating that potentially unique polymer morphology in electrospun nanofibres can alter and increase the surface free energy of the fibres themselves.

ACKNOWLEDGMENTS

SWL wishes to thank the Department of Materials, Queen Mary University of London for the award of a research scholarship.

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