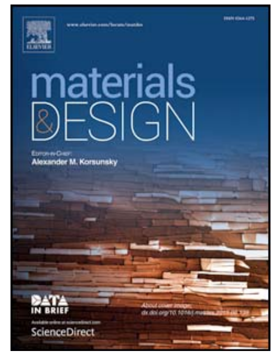
Accepted Manuscript



Operando observation of the Taylor cone during electrospinning by multiple synchrotron X-ray techniques

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PII: S0264-1275(16)31160-1
DOI: doi: 10.1016/j.matdes.2016.08.097
Reference: JMADE 2250

To appear in:

Please cite this article as: Tan Sui, Siqi Ying, Kirill Titov, Igor P. Dolbnya, Jin-Chong Tan, Alexander M. Korsunsky, *Operando* observation of the Taylor cone during electrospinning by multiple synchrotron X-ray techniques, (2016), doi: 10.1016/j.matdes.2016.08.097

Operando observation of the Taylor cone during electrospinning by multiple synchrotron X-ray techniques

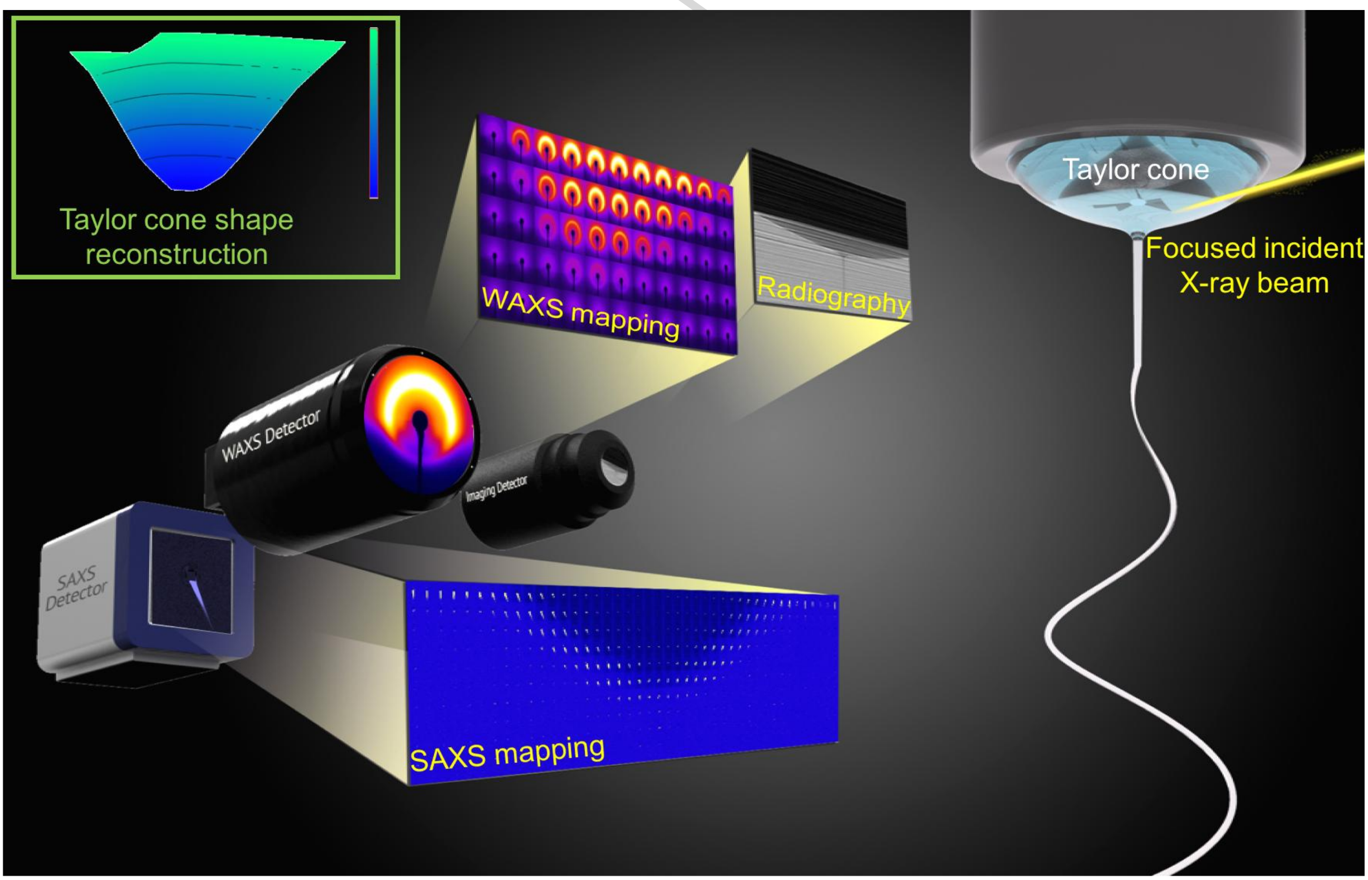
Tan Sui [a], Siqi Ying [a], Kirill Titov [b], Igor P. Dolbnya [c], Jin-Chong Tan [b], Alexander M. Korsunsky [a]

[a] MBLEM, Department of Engineering Science, University of Oxford, Parks Road, Oxford, OX1 3PJ, United Kingdom
[b] MMC, Department of Engineering Science, University of Oxford, Parks Road, Oxford, OX1 3PJ, United Kingdom
[c] Beamline 16, Diamond Light Source, Harwell Oxford Campus, Didcot, OX11 0DE, United Kingdom

Keywords:
Electrospinning
Taylor cone
SAXS
WAXS
Radiography

a b s t r a c t

Electrospinning has introduced a powerful means of fabricating polymer nanofibres into the broader realm of nanotechnology and polymer science. It has attracted considerable attention due to its outstanding versatility and numerous applications, such as the incorporation of nanoparticles within the fibres. The Taylor cone formed at the tip of the syringe that delivers the solution (or melt) plays an important role in controlling the structure, and thus the mechanical and functional properties of the fibres produced. Characterising the dynamic processes that occur within the cone is a challenging experimental task. In this study, *operando* synchrotron X-ray techniques were used to observe the Taylor cone formed during electrospinning. The combination of imaging with spatially resolved mapping by small angle and wide angle X-ray scattering provides a wealth of information about the cone exterior shape, surface orientation and inner morphology. This express note illustrates the rich body of data that can be collected using multi-modal X-ray imaging and scattering setup. From the observed patterns it is possible to extract information concerning particle density and flow patterns that persist within the Taylor cone.



Polymer science is a rapidly advancing interdisciplinary field that brings together various research techniques and communities in physical sciences, materials, engineering, manufacturing, energy and healthcare technology. This diversity has manifested itself in the explosive growth in polymer research and applications making use of the flexible characteristics, competitive cost and versatile capabilities for highly tailored fabrication of materials and structures, such as electrospun nanofibres [1] and nanocomposites [2], elastomeric thermoplastic polyurethanes (TPUs) [3], polymer opal (PO) films [4] and shape memory polymers [5].

Electrospinning continues to attract extensive interest in polymer science as a versatile method for the fabrication of nanofibres that may be varied in terms of dimensions, materials, architectures and functionalities. Due to its inherent adaptability this method finds extensive applications ranging from tissue engineering [6] to electronics industry [7] and energy storage [8]. Although electrospinning is a robust manufacturing route, several challenges remain in terms of understanding and controlling the resultant structural features that must be overcome to meet the ever evolving new technological requirements. Understanding the structure and behaviour of the Taylor cone that forms as a polymer solution is ejected and drawn from the tip of a nozzle under the action of electric field is essential for enabling control over the properties of electrospun mats that are determined by their structural features, such as the fibre diameter and the degree of alignment, but also the internal arrangement of polymer molecular chains within the fibres at the nano-scale [1]. *Operando* exploration of the Taylor cone is a challenging experimental task, due to the dynamic nature of the problem and the high spatial and temporal resolution required.

The pioneering work by Greenfeld et al. [9] employed fast phase contrast X-ray imaging of electrospinning jets. By observing the movement of entrained nanoparticles, the authors obtained information about the velocity magnitude and distribution within the flow. However, the use of particles as ‘markers’ does not reveal the conformation of polymer molecules or the evolution of their orientation during their journey through the cone. In contrast, X-ray scattering techniques possess sensitivity to the overall statistical properties of the flow, such as density and orientation.

We report the first successful *operando* scattering acquisition of 2D scattering maps combined with radiographic imaging of the electrospinning process using synchrotron X-ray Test beamline B16 at Diamond Light Source. *Operando* collection of multi-modal scattering data was performed using simultaneous imaging (full field), SAXS and WAXS X-ray mapping using 2D detectors, as well as the sample environment for *in situ* electrospinning that included the sample positioning table, and the power and solution supply and control system. The collector plate was grounded, and the entire electrospinning system was positioned on a translation stage. This arrangement allowed flexible positioning of region of interest (ROI) with respect to the stationary focused synchrotron X-ray beam, and the placement of different detectors in the scattering beam for pattern collection. The beamline setup was optimised to allow the combination of good spatial resolution with efficient X-ray flux utilisation. Multilayer Monochromator (MLM) (Ru/B4C: 8 keV) was used to maximise the incident beam flux and the beam was focused down to 200×200 µm spot size using Compound Refractive Lenses (CRLs). The electrospinning system consisted of a high voltage (HV) supply connected to a delivery nozzle to which the solution of polyvinylpyrrolidone (PVP) in methanol loaded with ~2 wt% of yttria-stabilised zirconia nanoparticles was fed by a syringe pump through a flexible tube. Applied voltage of 15 kV and 4.5 mL/hr flow rate were supplied to the electrospinning system, and a steady-state electrospinning process was achieved. The steady state Taylor cone that was formed allowed long duration raster scan to be performed. The sCMOS “X-ray Eye” transmission imaging detector (Photonic Science Ltd., UK) was placed in the straight through (unfocused) beam to obtain radiographic images of the Taylor cone. This detector was then moved out of the beam, and 2D Small Angle X-ray Scattering (SAXS) detector (Pilatus 300K, Dectris, Baden, Switzerland) and 2D Wide Angle X-ray Scattering (WAXS) detector (Photonic Science Image Star 9000, Photonic Science Ltd., UK) were translated laterally into the beam. The CRL system was also introduced at this stage in order to focus the beam onto the sample. The beam was scanned across the ROI with the step size of 200 µm along both *x*- and *y*- directions, and 2D SAXS and WAXS patterns were collected.

A schematic diagram of the overall *operando* experimental set-up is provided in the Figure. It shows the radiographic image of the Taylor cone in a steady state, as well as amontage of polymer solution SAXS and WAXS raster scans covering the entire Taylor cone.

Strong small-angle scattering occurs at the polymer solution / air interface, with the scattering spikes following the *tangential* direction of the Taylor cone surface. The origin of this observation remains somewhat uncertain to the authors, but it is likely to be associated with the polymer solution within the cone being accelerated towards the jet “funnel”., This effect causes vortex fluid motion within the cone, which is dominated by a tangential velocity profile in the near-surface region [10]. It is worth noting that SAXS associated with the cone surface produces “spikes” directed along the surface *normal*, as seen at the cone periphery where the flow velocity is low.

The overall WAXS intensity of each pattern in the 2D map corresponds to the integral volume of the strongly scattering zirconia nanoparticles along the beam path [11]. With the help of appropriate calibration, this provides an alternative means (i.e. not based on the transmitted beam intensity) of reconstructing the shape of the Taylor cone without the need for sample rotation. The outcome is illustrated in the left top corner of the Figure.

The results reported here identify opportunities and challenges for further improvements in X-ray microscopy (full field and 2D mapping) of the Taylor cone during electrospinning. 2D SAXS/WAXS raster scans of the entire Taylor cone reveal the spatial distribution of scattering intensity and direction. This can be linked to the flow velocity field inside the Taylor cone and the electric field effects at the liquid jet surface. Insights obtained in this way will benefit the understanding of polymer structuring during electrospinning.

Acknowledgements

Funding for the MBLEM laboratory at Oxford received under EU FP7 project iSTRESS (604646) is acknowledged, along with the access to the facilities at the Research Complex at Harwell (RCaH), under the Centre for In situ Processing Studies (CIPS).

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