Structural Studies of Polymeric Thin Film by Neutron and X-ray reflectometry

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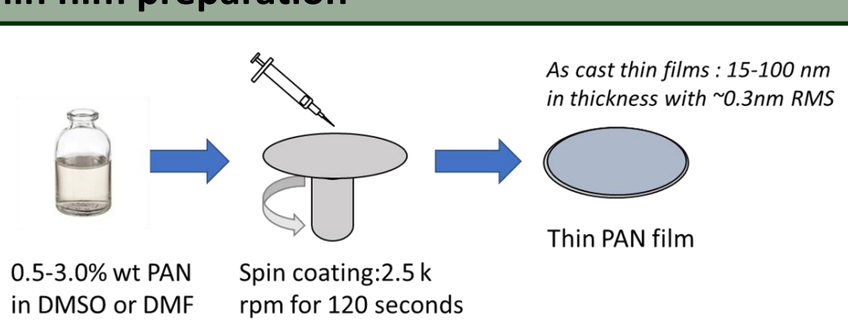
1. Introduction

- Polymeric thin films below a certain thickness range often exhibit physical properties that differ substantially from intrinsic bulk behaviour. This is due, in part, to the increasing influence of entropic effects (confinement and chain "packing") and interfacial interactions as the film thickness decreases.
- Polyacrylonitrile (C_3H_3N, PAN) is a popular and functional, applicative organic polymer and PAN thin films have a wide range of applications as gel polymer electrolytes, organic thin-film transistors to gate dielectric and piezoelectric materials.
- Neutron and x-ray reflectometry (NR and XRR) are powerful non-invasive techniques to determine the detailed structure (such as layer thickness, scattering length density, interlayer roughness) of buried layered interfaces with nanometre precision.

2. Aim

The aim of this project is to understand the impacts of the film thickness and thermal treatment on the chemical or physical structure of the PAN thin films. Thill will contribute to the rational design of PAN based thin films for their technological applications.

3. PAN thin film preparation

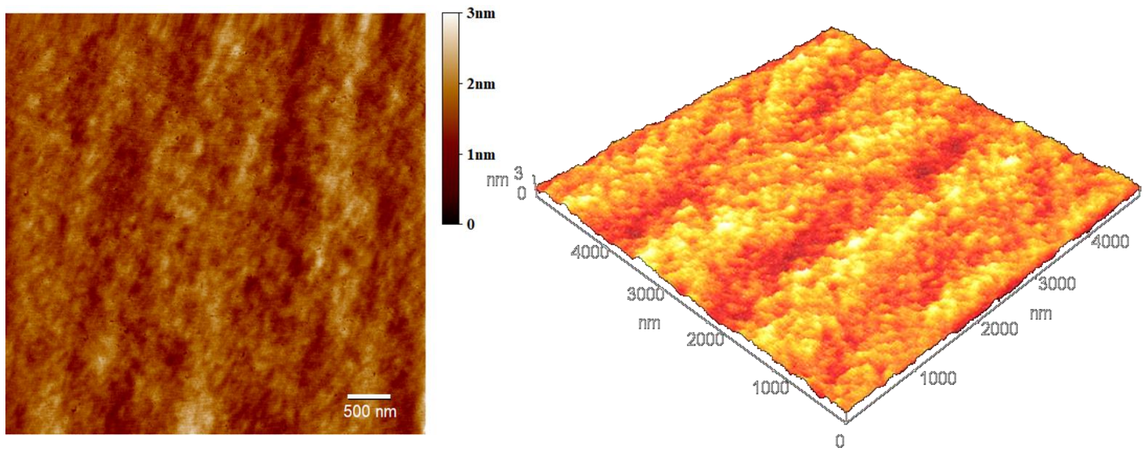


2 wt% PAN in DMSO
@1.75*1.75 cm²

3 wt% PAN in DMSO
@1.75*1.75 cm²

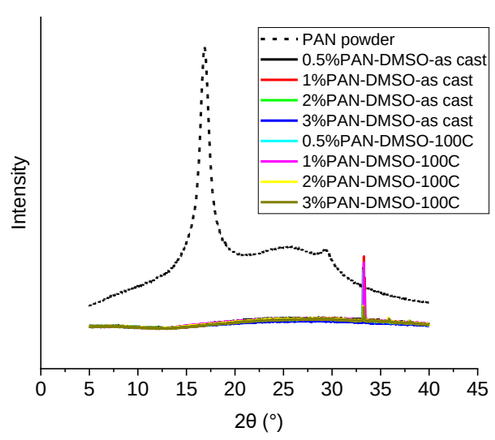
4. Characterisation and Results

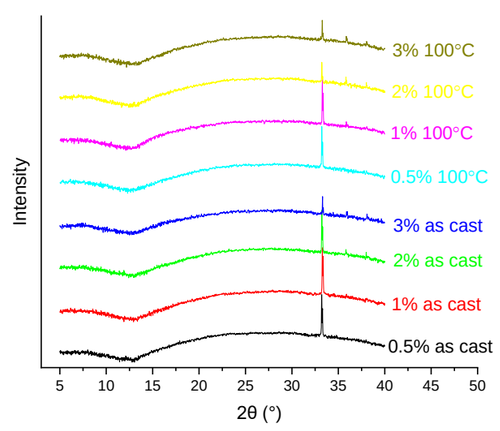
4.1 surface topography-AFM



- 2 wt% PAN as cast film, 5 x 5 μm², root mean square (RMS) roughness ~ 0.3 nm

4.2 Film crystallinity-XRD

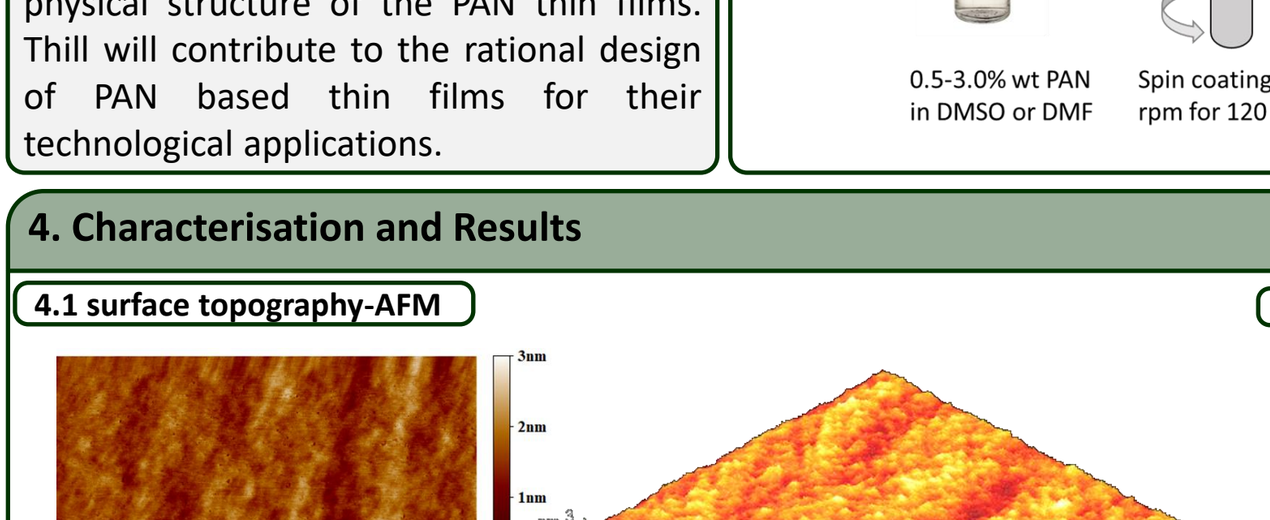




- PAN thin films prepared in this study were shown to possess relatively low crystallinity which seems to be PAN concentration-dependent.

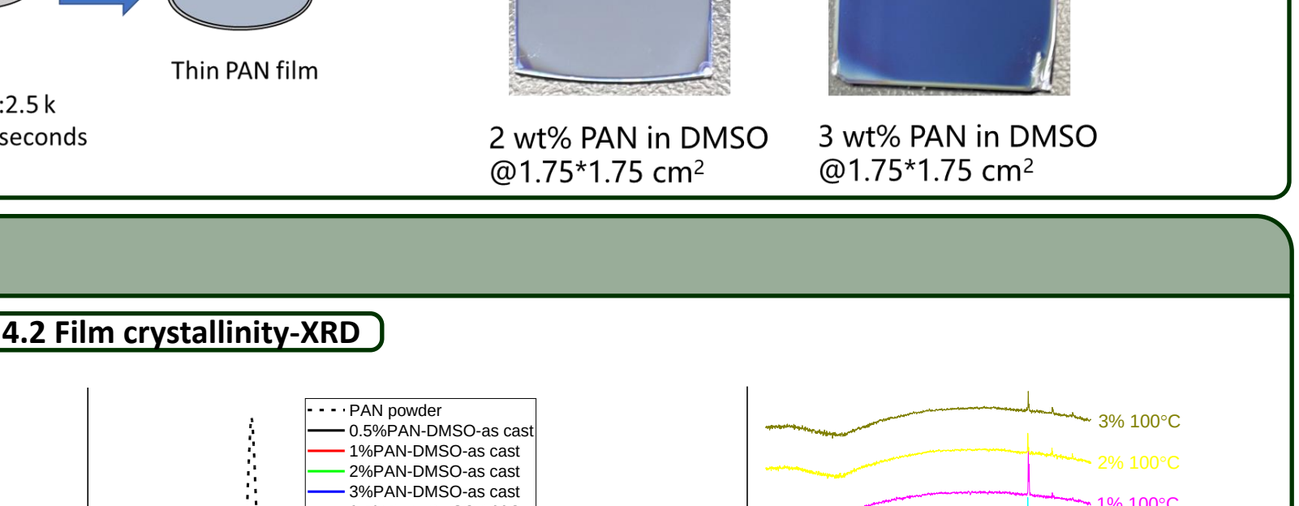
4.3 Film thickness and density-XRR and NR

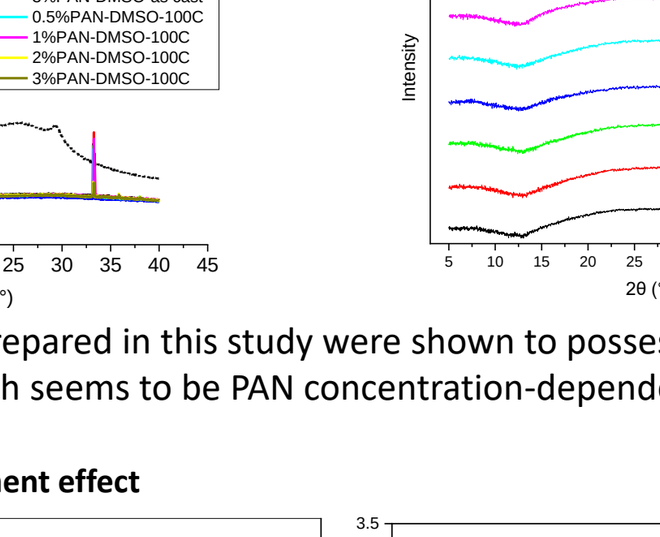
❑ **As cast thin films as a function of thickness**



- A three-layer model was applied to fit both XRR and NR data;
- A transition layer rich in hydrogen, a thick middle layer capped by a dense skin layer;
- H/D isotope effect on the structure of PAN thin films was observed when using deuterated solvent during spin-coating.

❑ **Post heat treatment effect**





- Thickness decrease was observed when heated to 100 °C but no discernible changes upon further heat treatment at 165 °C;
- Both the transition and middle layers were densified after thermal annealing as revealed by neutron SLD profiles;
- The structural of the transition layer is more complicated than expected which deserves further investigation in the near future.

5. Conclusion

- PAN thin films prepared from spin-coating display low crystallinity with surface roughness ~ 0.3 nm;
- The interfacial structural of the thin films can be divided into three regions: a heterogenous transition layer (1-2 nm) , a thick middle layer and a dense skin layer (~ 5 nm)
- The layer structure is greatly influenced by the concentration of PAN during the film preparation and post thermal treatment in addition to the H/D variations.

6. Acknowledgement

- Prof Tao Zhu and Prof Howard Wang for supervisions
- CSNS for beamline and the user characterisation lab
- SSLab for wet chemistry lab

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