

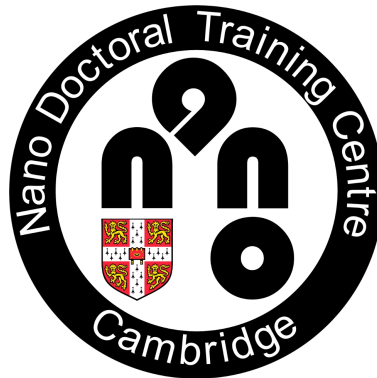
# Dielectric inks for Printable Electronics

Luka Skoric

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PIs: Tawfique Hasan, Yan Yan Shery Huang

Daily supervisors: Leonard Ng, Xiaoxi Zhu



Declaration: “This report is substantially my own work and conforms to the University of Cambridge’s guidelines on plagiarism. Where reference has been made to other research or work done by me in collaboration with others, this is clearly acknowledged in the text, bibliography and acknowledgements.”

## Abstract

Different polymers were investigated for their potential in dielectric inks for printable electronics in roll-to-roll processes. The investigation was limited on seven polymers commonly used in industry. The dielectric ink based on PU was previously developed by the group's PhD student Leonard Ng [1]. The ink was used as a benchmark for other polymers and its properties were further tested. Inks were formulated and deposited onto ITO coated PET with the Mayer bar method. The inks rheology was measured with a plate-to-plate rheometer and the surface topography of the coated samples was observed with profilometry and electron microscopy. Furthermore, the Au/Pd top electrode was sputter coated onto the samples to measure the dielectric properties of the inks. It was shown that out of the tested polymers, only PU and PVP40 inks could both deposit uniform films and exhibit suitable dielectric properties to be applied as inks in R2R processes.

## 1 Introduction

Industrial roll-to-roll (R2R) printing technologies are capable of reproducing high quality prints at high speeds ( $>200$  m/s) and at a very low cost [2]. The Hybrid Nanomaterials Engineering (HNE) group is actively working on investigating the potential of newly developed 2d materials such as graphene and hexagonal boron nitride (*h*-BN) as an ingredient in inks. The aim is to use the existing print technologies to exploit the unique properties of single-layered materials in a scalable and cost efficient way. The primary application of these methods is likely to be in flexible electronics.

This project investigates the properties of different dielectric inks and their potential for the use in R2R printing. To be considered useful for printing processes, the inks need to have shear-thinning properties while also having a high dielectric constant,  $\epsilon_r$ . We are aiming to have dielectric layers of  $\epsilon_r$  greater than 2. In comparison, the dielectric constant of *h*-BN film is 2-4 [3].

Seven commonly used and easily accessible polymers were chosen as binders in possible dielectric inks. Firstly, rheology of resulting inks was characterised with a plate-to-plate rheometer. The inks which were able to form good films were then deposited onto the indium tin oxide (ITO) coated PET. ITO is a transparent, flexible conductor and PET a polymer substrate. The top electrode was sputter-coated and the dielectric properties of resulting layers were measured in an impedance analyser to calculate  $\epsilon_r$ .

One of the aims of HNE group is to incorporate the novel nanomaterials such as carbon nanotubes, graphene and *h*-BN into inks in order to use their properties in large scale printable electronics. An alternating current electroluminescent device (ACEL) was chosen as a demonstrator for the performance of produced inks as it requires both good conductive and dielectric inks to achieve high luminescence.

Flexible ACEL devices were previously made using graphene by Wang *et al.* [4]. The schematic of their device is shown in Figure 1. While this device was shown to be an effective ACEL device, there are a number of problems preventing the device from being scalable. Firstly, the device requires 4 layers of CVD grown graphene deposited via a dry transfer method. This produces high-quality single layered graphene, but the process is not easily scalable and

the transfer is labour-intensive. Secondly, the overall cost of the materials used in the device is prohibitively high. The silver paste used as the back electrode costs £1500/kg. Furthermore, the barium titanate ( $\text{BaTiO}_3$ ) is a great dielectric with the dielectric constant as high as 2450 at room temperature [5], but can cost as high as £1500/kg [1]. The device also requires baking at  $110^\circ\text{C}$  for half an hour to optimise the cure of each deposited layer. This translates to the device being expensive and the production difficult to scale.

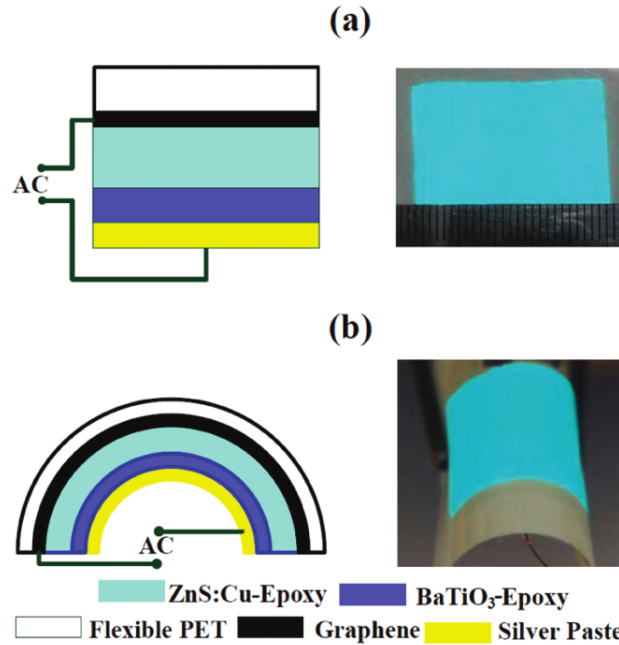


Figure 1: Schematic structure and photographs of the ACEL device fabricated by Wang *et al.* (a) before and (b) after bending. Adapted from [4]

The long term aim of this project is to produce a high luminescent ACEL device which can be printed with cheap, easily accessible inks using R2R processes. The HNE group's developed a different device schematic shown in Figure 2a. The conductive ink containing liquid-exfoliated graphene, carbon nanotubes and amorphous carbon was formulated by the group's PhD student Leonard Ng. The ink's sheet resistance was shown to be as low as  $50 \Omega/\square$  at  $25 \mu\text{m}$  while the cost was substantially lower than that of the silver paste ( $<£100/\text{kg}$  compared to  $>£1000/\text{kg}$ ) [1]. For the phosphorous layer, DuPont's luxprint series (product numbers ZEP152, ZCP274 and ZGO208) of electroluminescent paste were chosen as three different colours for the device. The inks were successfully incorporated in an ACEL device together with polyurethane ink as a dielectric (Figure 2b).

However, the efficiency and the brightness of the device needs to be improved. This greatly depends on the thickness and the dielectric properties of the polymer coating. The task of my project was to test the properties of polyurethane as a dielectric and investigate the possible alternatives to further improve on the characteristics of the device.

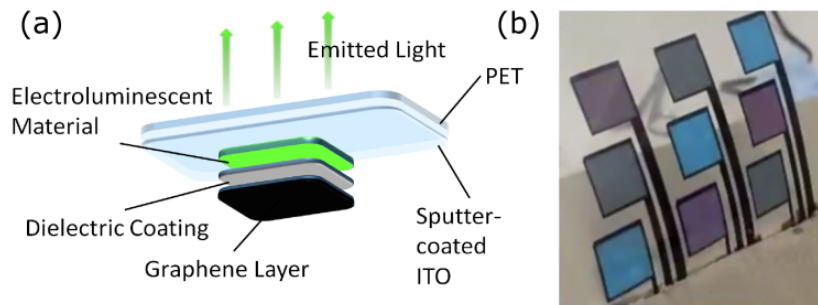


Figure 2: (a) Schematic of an ACEL device, (b) illuminated EL device Adapted from [1]

An important parameter in the ink's design is its response to shear strain and stress over time. This is studied by rheology and determines the behaviour of inks in printing processes, their ability to spread along the printing rolls, transfer between them, and finally, deposit and form structures on the substrate. Successful performance thus requires viscous inks which get thinner under high shear produced by the R2R processes.

Fluids can be divided into three types depending on how they behave under increasing shear rate (Figure 3a). Firstly, there are Newtonian fluids whose shear stress to shear rate ratio (*i.e.* viscosity) is constant. These include most of our everyday fluids such as water, oil and milk. Secondly, shear-thickening fluids increase in viscosity as the shear rate is increased. A common example is corn starch in water. Conversely, the shear-thinning (thixotropic) fluids have their viscosity decreased under increasing shear rates. Many emulsions, suspensions and dispersions display thixotropic characteristics.

Rheology can be measured with a plate-to-plate rheometer. The schematic of the device is shown in Figure 3b. A small sample of the ink is loaded between the top and the base plate. The torque required to rotate the top plate is measured which allows for the calculation of viscosity.

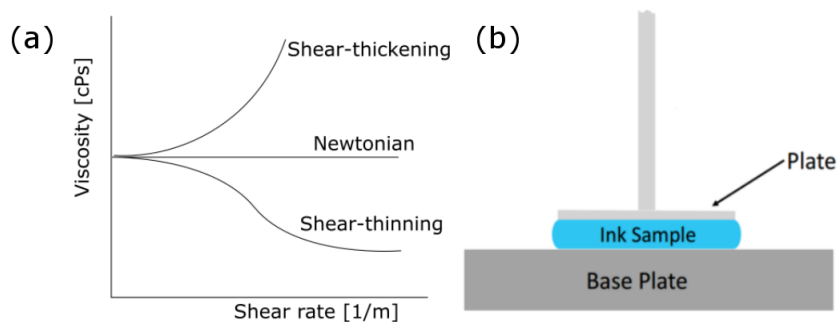


Figure 3: (a) Behaviour of viscosity for different types of fluids; (b) Plate to plate rheometer schematic. Adapted from [1]

## 2 Formulation of dielectric inks

### 2.1 Preparation and optimisation

The polymers and the list of solvents which were used for this experiment are shown in Table 1. I tested seven polymers including two molecular weights of Polyvinylpyrrolidone: PVP40 (Mw  $\sim$ 40,000) and PVP10 (Mw  $\sim$ 10,000) for their potential to make dielectric inks. For the purposes of this experiment, the polymers were acquired from Sigma-Aldrich with the product codes listed in the Table 1. These were compared with the PU ink previously formulated by Leonard Ng [1].

The formula for the optimal loading of polymers was found using the bracketing strategy. In the bracketing strategy, a sample experiment with a loading  $x$  is created and characterised. The loading is then halved or increased by 50% depending on whether or not the target was overshoot until convergence to the optimal ink is achieved [1].

The formulated inks need to have a high enough polymer content (usually higher than 10%) while maintaining a low enough viscosity and shear thinning behaviour to form pinhole-free films. Moreover, we want the dielectric constant of the resulting films to be as high as possible.

Polymer	Product code	Solvents used
Polyvinylpyrrolidone (PVP)	PVP40	Terpineol
	PVP10	
Polyvinylalcohol (PVA)	341584	Water
Polyvinylidene fluoride (PVDF)	182702	DMF, NMP, MEK
Polyethylene (PE)	427772	MEK, Xylene, Acetone
Polyurethane (PU)	SM Mani	Terpineol
Ethyl cellulose (EC)	200646	Terpineol

Table 1: polymers chosen for the experiment, together with their grade and solvents used [6]

### 2.2 Coating deposition method

K-bar (also known as Mayer bar) method was used to deposit inks onto substrates. A K-bar is a wired steel bar which is dragged along a substrate to deposit a uniform ink coating. The wires create crevices in the ink which spreads out during the drying process making a uniform layer. The schematic of the procedure can be seen in Figure 4.

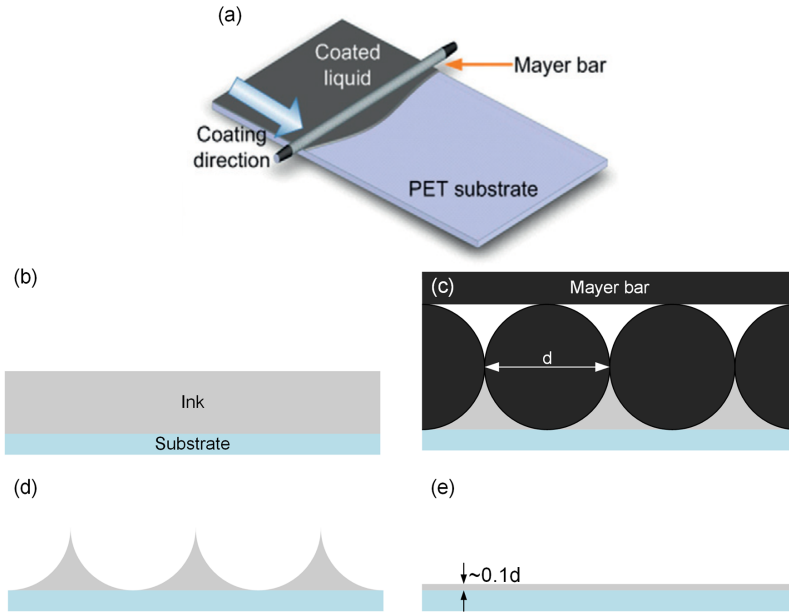


Figure 4: Mayer bar coating a substrate: (a) Schematic of Mayer bar coating, (b) Ink on a substrate, (c) Ink-Mayer bar interaction, (d) ink immediately after the coating, (e) during the drying process the ink spreads to form a uniform layer with thickness proportional to the radius of the Mayer bar wire  
Adapted from [7]

Prior to deposition, the inks were degassed to remove any residual air bubbles which might lead to defects in the deposited layer. To ensure the constant speed and pressure during layer deposition, an automated K bar coater was employed.

The wet film layer thickness is proportional to the radius of the wire,  $r$ , and is usually about  $0.1d$ . K bar coaters are made of stainless steel and have different numbers denoting the thickness of the coating they deposit (Table 2). In our experiments, a thick, pinhole free layer was required to test the dielectric properties. Therefore, K5 was used making the wet layer of deposited ink about  $50 \mu m$  thick. The substrates are left to dry for a day producing solid layers of  $\sim 10 \mu m$  in thickness.

Bar No.	Colour Code	Wet Film Thickness ( $\mu m$ )
1	Yellow	4
2	Red	12
3	Green	24
5	Horn	50

Table 2: Different thicknesses deposited by the corresponding Mayer bars [1]

### 3 Results and discussions

#### 3.1 Formulated inks

Due to its resistivity to solvents, PE was not able to produce inks. I attempted dissolving it in Xylene, MEK and acetone with no substantial success. Moreover, PVDF and PVA were not able to produce uniform films using the K bar method due to the inks being too viscous, even at low polymer concentrations.

I formulated successful inks with PVP10, PVP40 and EC binders. Terpeneol was found to dissolve all of them in the concentration as high as 50% weight loading. Furthermore, the inks were diluted to get the appropriate rheology with butyl cellosolve (BC). BC is a common solvent for the inks and chosen due to its low surface tension of  $27.4 \cdot 10^{-5}$  N/cm and its slow evaporation rate of 0.079/hour at 25°C (where water is 1/hour) [8].

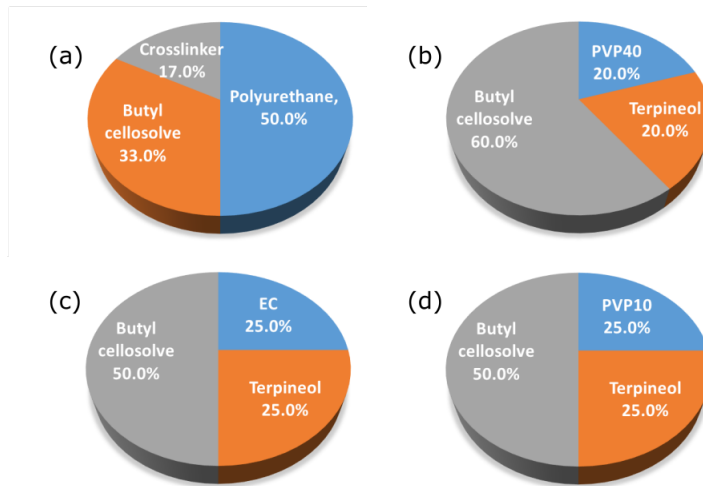


Figure 5: Formulated inks with different polymers as binders: (a) PU, (b) PVP40, (c) EC, (d) PVP10

The rheology of formulated inks was measured using the plate-to-plate capacitor over the large range of shear rates (Figure 6). I showed that my inks have the shear thinning behaviour and that their viscosity is between 10 cP and 1000 cP making them applicable in R2R printing. For reference, the viscosity of water is 0.9 cP at 25°C [9] and honey roughly 10,000 cP.

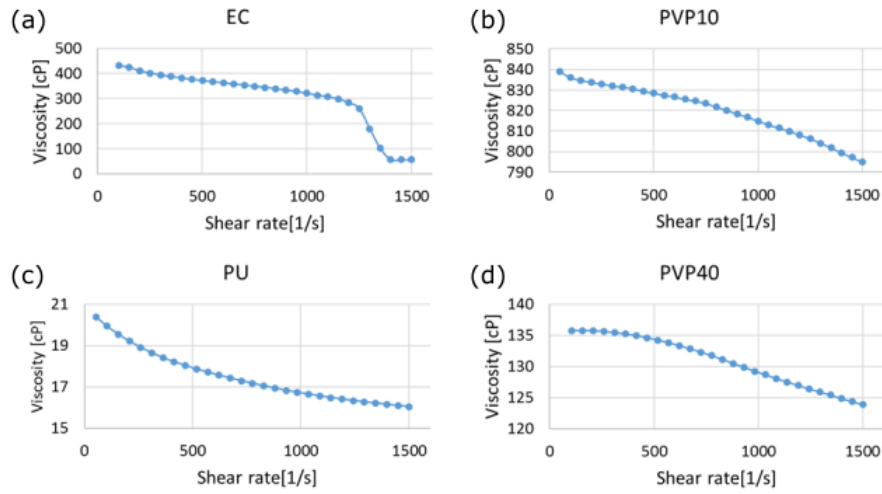


Figure 6: Rheology data for characterised binders: (a) EC, (b) PVP10, (c) PU, and (d) PVP40

### 3.2 SEM surface characterisation

The polymers deposited on ITO were characterised under SEM. I looked for defects in the polymer layer and at the interface between ITO and the polymer. Several surface defects can occur during the fabrication process which can lead to device failure (Figure 7).

If the agglomerates and aggregates of polymer particles were not completely broken down, it is possible to get undissolved polymer on the surface of the coating. This is preventable by using a dispersion machine capable of producing high pressures and shear forces such as the high speed dissolver. For my purposes common magnetic mixing has proven to be enough to disperse the polymers.

Fractures can appear on the deposited layer during the drying of the solvent due to polymer shrinkages. This can create regions which will have much higher electrical fields when the voltage is applied across the polymer reducing the dielectric characteristics. Moreover, they create areas prone to pinholes. Pinholes are the holes in the dielectric that can be caused by dust or imperfections during the deposition. These can lead to the breakdown of the device due to shorting.



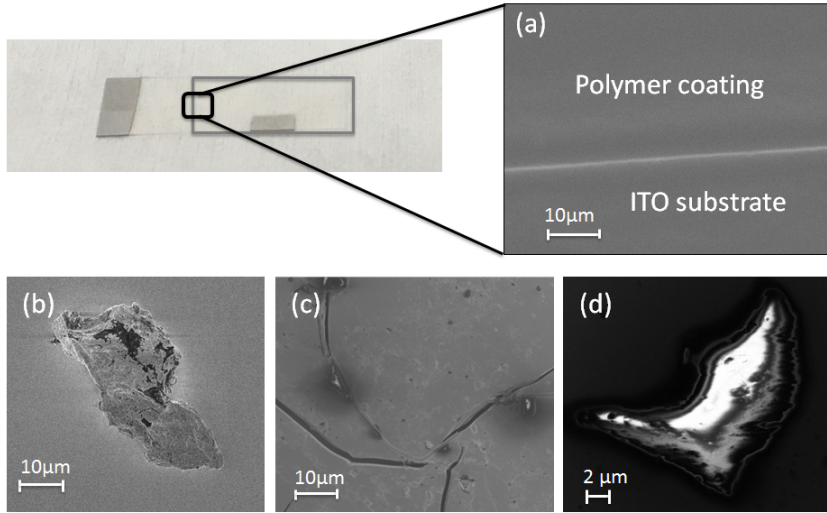


Figure 7: SEM pictures of the surface-polymer interface and defects in the polymer: (a) defect-free interface between the substrate and the coating, (b) undissolved polymer (PU), (c) cracks (in EC polymer), and (d) pinhole

### 3.3 Dielectric constant measurements

To measure the dielectric properties of the inks, the top electrode was sputter-coated with a gold-palladium alloy making ITO-dielectric-Au/Pd structure (Figure 8). When connected to an external circuit this creates a parallel-plate capacitor allowing for the dielectric constant ( $\epsilon_r$ ) measurements using the formula:

$$C = \epsilon_0 \epsilon_r \frac{A}{d} \quad (1)$$

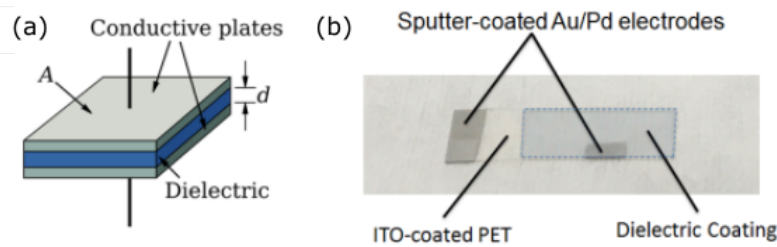


Figure 8: (a) Capacitor schematic, (b) picture of my sample

The measurements of the sides of the sputter coated electrodes with calipers allowed for calculation of the capacitor area. The area of the electrodes for our samples was: The deposited electrodes were measured to be: The thickness of the deposited dielectric layer was measured with profilometer. Due to the problems with the equipment and the scope of the project, the thickness of the layer for PVP40 and EC inks was not measured. However, in the thickness

calculations, I assumed that the thickness of both films is between  $10\ \mu\text{m}$  and  $14\ \mu\text{m}$  which corresponds to the predicted thickness acquired with the K5 bar and agrees with the measurements of PVP10 and PU layers ( $12.5 \pm 0.4\ \mu\text{m}$  and  $11.2 \pm 0.4\ \mu\text{m}$ ).

Finally, the capacitance of the structure was measured with the impedance analyser. The results for the dielectric constants can be found in Figure 9. It has been shown that EC and PVP10 have  $\epsilon_r < 1$  making them unsuitable for applications as dielectrics in electronic devices. PVP40 layer was shown to have the highest dielectric constant. A low frequency of 200Hz was chosen as a reference value as the polymer films exhibited a rapid decline in capacitance at higher frequencies. This effect has to be further investigated to determine how to improve on the high frequency performance of the dielectric layers.

It is important to notice that the acquired results do not directly correspond to the dielectric constants of the polymer binders as the measured capacitance is influenced by any possible imperfections in the coating. However, the measurements give us information on how the inks behave electrically and how capacitance scales when thin layers are deposited onto substrates.

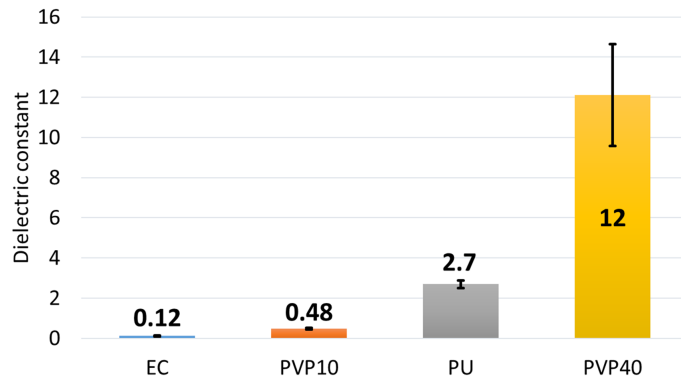


Figure 9: Dielectric constants of the analysed inks at 200Hz

## 4 Conclusions and further work

I have tested seven polymers for their potential as binders in dielectric inks for R2R processes. It was shown that PVA, PVDF and PE do not make film forming inks with commonly used solvents. While PVP10 and EC do form pinhole-free electrically isolating coatings on ITO substrates, the resulting films act as poor dielectrics. This is the result of both material properties and the structure of coated layers.

PU and PVP40 binders both satisfy the conditions for R2R printing and act as good dielectrics with the dielectric constant of  $2.7 \pm 0.2$  and  $12.1 \pm 2.5$  at 200Hz respectively. Due to its higher dielectric constant, it would be interesting to see how PVP40 ink performs in the ACEL device. Also, the behaviour at high frequencies has to be further investigated.

Moreover, the HNE group will attempt to further improve on the dielectric constant of their inks using 2d materials. *h*-BN is a good candidate due to its dielectric properties. It also has the ability to create pinhole-free het-

erostuctures for fabrication of dielectric capacitors using inkjet printing and spray-coating [10]. The next step in the group's work will be testing whether the incorporation of *h*-BN from liquid dispersions is able to improve the dielectric properties of the inks while maintaining the appropriate rheology for R2R printing.

## References

- [1] Leonard Ng Wei Tat. Roll-to-roll formulation of 2d material inks, 2016. First year report, University of Cambridge.
- [2] R. H. Leach and R. J. Pierce. *The Printing Ink Manual*. Springer, Netherlands, Dordrecht, 1993.
- [3] Ki Kang Kim *et al.*. Synthesis and characterization of hexagonal boron nitride film as a dielectric layer for graphene devices. *ACS Nano*, 6(10):8583–8590, 2012.
- [4] Ze gao Wang, Yuan fu Chen, Ping jian Li, Xin Hao, Jing bo Liu, Ran Huang, and Yan rong Li. Flexible graphene-based electroluminescent devices. *ACS Nano*, 2011.
- [5] Shepard Roberts. Dielectric constant of barium titanate at high temperatures. *Phys. Rev.*, 75(989), 1949.
- [6] James E. Mark, editor. *Polymer Data Handbook*. Oxford University Press, Inc, 1999.
- [7] R.C.T Howe. *Two-dimensional material inks for photonics and electronics*. PhD thesis, University of Cambridge, June 2016.
- [8] Dow Chemical Company. *Technical Data Sheet, Butyl cellosolve*.
- [9] Sokolov Kestin and Wakeham. Viscosity of liquid water in the range  $-8^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ . *J. Phys. Chem.*, 1978.
- [10] Adam G. Kelly *et al.*. All-printed capacitors from graphene-bn-graphene nanosheet heterostructures. *Appl. Phys. Lett.*, 2016.