Inkjet Printing of Functional Ionogels for Flexible and Transparent Conductive Electrode Materials

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Abstract

Printed electronics represent an emerging area of research that promises large markets due to the ability to bypass traditional expensive and inflexible silicon-based electronics to fabricate a variety of devices on flexible substrates using high-throughput printing approaches.

One of the major targets in printed electronics is reducing the overall process temperature. In roll-2-roll manufacturing common polymer foils are used that often have a relative low glass transition temperature (Tg), usually below 150 °C. In order to produce conductive features on these polymer foils the often used approach of printing inorganic nanoparticles and subsequent sintering by heating cannot be used, since high temperatures are necessary, although selective sintering techniques like microwave or plasma exposure can be used.

We present here a simple, practical approach to prepare ionic liquid gels that show conductivity in the semi-conductive region without the necessity of heating or sintering. Furthermore, these ionogel films are flexible and show optical transparency greater than 94% from near-UV to near-IR.

Introduction

Although drop-on-demand inkjet printers are widely used for graphical applications, it was only within the last decades that inkjet printing has developed into a mature patterning technique.[1] As a consequence, it has gained specific attention in scientific research because of its high precision and its additive nature: only the necessary amount of functional material is dispensed, and only at pre-determined locations[2]. Furthermore, the absence of physical contact between print head and substrate allows many potential applications, such as inkjet printing of labels onto rough curved surfaces, or surfaces that are sensitive to pressure. Inkjet printing is utilized to dose many different kinds of materials, such as conductive polymers and nanoparticles,[3,4] sol-gel materials,[5] cells,[6] structural polymers,[7] ceramics [8,9] and even molten metals.[10]

Inkjet printing, and in particular drop-on-demand inkjet printing, offers some unique attributes compared to lithography techniques, since it places material on demand and in a direct way without masks, which reduces the number of processing steps and the amount of material required, thereby also reducing time, space and waste consumption within production. Furthermore, inkjet printing can also be combined with roll-to-roll production.[11] Typical applications can be seen in the field of plastic electronic devices, which are microelectronic devices that are prepared on flexible polymer substrates, including radio frequency identification tags or electrodes for thin-film transistor circuits.[12]

Similarly, over the few last years, there has been a growing interest in the inkjet printing of conductive materials. One of the types of compounds that has been frequently used is poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS), due to its relatively low cost.[13] Although conductive polymers usually do not have a high conductivity, it may serve very well for low cost disposable electronic applications. Besides conductive polymers, inks that contain metals have been used to create microstructures on polymer substrates.[14,15] It has been shown that inkjet printing of conductive materials is a relatively cheap alternative for the fabrication of electronic devices when compared to other micro- and nanopatterning techniques,[16] such as photo-lithography[17] or laser patterning.[18]

Transparent conductive materials have a broad range of applications in solar cells, electronic light displays, and sensor devices, which will continuously increase with the next years. Some of the most commonly employed materials for these applications include derivatives of PEDOT:PSS and indium tin oxide (ITO). As flexible electronic devices become both more common and more diversely applied, materials are being sought out that will offer useful conductivity and transparency along with other specifications, including greater resistance to cracking, buckling, and delamination, as well as the possibility of processing under milder processing conditions, *i.e.* without the need for vacuum vapor depositions or high sintering/annealing temperatures.

Due to their unique and highly tunable properties, ionic liquid gels have become a popular topic of materials science in recent years.[19] The incorporation of ionic liquids into polymeric matrices allows for the development of materials which possess both the processability and mechanical properties of polymeric materials, but with added electronic functionalities. As a result, the variety of new materials and devices based on ionogel is expanding rapidly, including thin film transistors,[20] ultracapacitors and metal ion conductive membranes for batteries.[21,22]

Results and discussion

With drop-on-demand fabricated conductive ionogels as our goal, we set out some basic criteria to indentify appropriate candidates. The most common model for predicting the printability of a given ink for a given nozzle was developed by Fromm,[23] where the printability of a given system is determined by the ink density, the surface energy of the droplet, the viscosity of the in-flight droplet, and the diameter of the nozzle orifice.[24] In our experiences with printing highly-loaded customized functional inks, the most challenging criteria to be met is the viscosity, where inks with a high functional material loading tend to be highly viscous compared to the ranges commonly handled by micropipette systems (1 to 30 mPa.s). In terms of commonly available room temperature ionic liquids, the reported measured values for dynamic viscosity values under ambient lab conditions range from as low as 17 mPa.s for 1-ethyl-3-methylimindazolium dicyandiamide, to as high as 16,000 mPa.s for 1-methyl-3-octylimidazolium chloride. For highly concentrated solutions, the ionic liquids at the high end of the range do not seem to be applicable, and we therefore focused on ionic liquids of low viscosity.

The initial goal of this exercise was to investigate whether ionogels could be identified that would work as transparent conductive alternatives to PEDOT or ITO.[25] The resistivity of most of the ionogels tested in this work was in the range 10 to 1000 Ω·m. The lowest measured resistivity in the tested series was found with PEG-DMA:BMIM OTf ionogels films, with the local minimum found at 60 v/v-% ionic liquid loading, yielding a resistivity of approximately 12 Ω·m (see Figure 1).

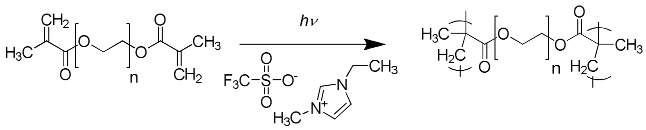

Figure 2. Schematic representation of the photopolymerization reaction of PEG-DMA in the presence of an ionic liquid.

Interestingly, the recorded value for the printed version of the same type of film were highly dependent on the addition of any cosolvents used to assist the processing steps. When DMSO was added to the formulation to lower the ink viscosity, the resistivity of the resulting cured film was 1,150 ± 439 Ω·m, while the resistivity of a similar film printed with the aid of ethanol was found to be 23.0 ± 2.2 Ω·m. This difference in resistivity may be due to the presence of unevaporated solvent lowering the number of percolating pathways. In terms of optical transparency, Figure 2 shows the transmittance of a 150 µm thick film of 60:40 PEG-DMA:BMIM OTf, which appear visually colorless and transparent, and offer transmittance for light above 94% in the range from near-UV to near infrared.

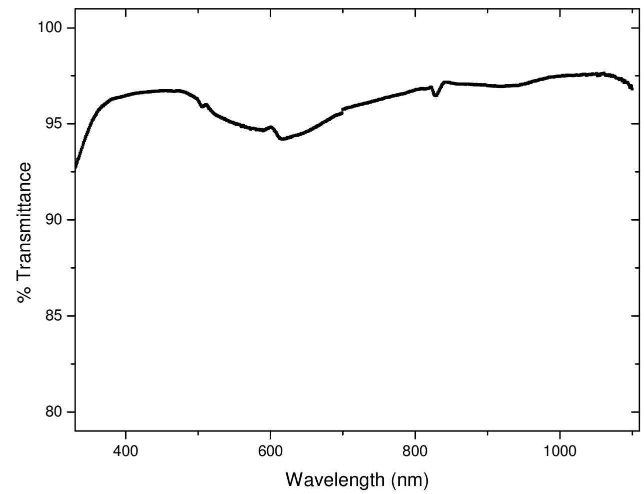

Figure 2. Transmittance spectrum of a printed ionogel film.

The resulting formulated inks yielded printed ionogels that were conductive without the need for thermal sintering. Even after a considerably aggressive folding treatment, the printed features retained their conductivity, see Figure 3.

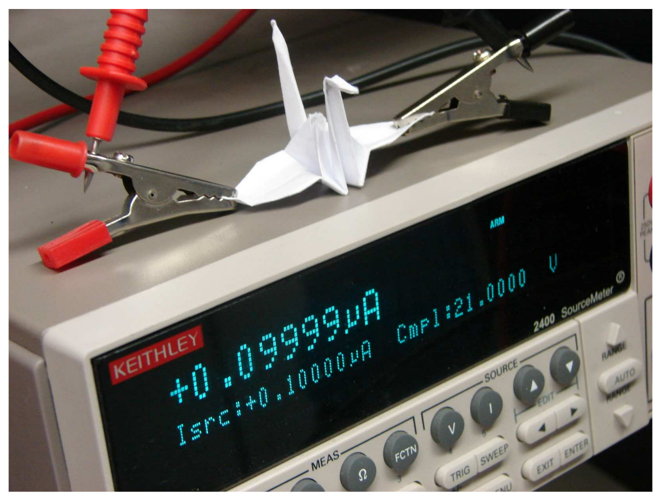

Figure 3. A sheet of paper with inkjet printed ionogel still demonstrates conductivity after being folded into an origami crane.

Conclusions

In conclusion, we have prepared colorless and highly transparent conductive films from ionogels by using PEG-DMA and an ionic liquid. Various ionic liquids have been studied, but 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIM OTf) was found to give the best combination of processability and low resistivity, with a measured value of approximately 12 Ω·m, while the obtained film remained colorless as well as transparent. The resulting ionogels may find applications as transparent, flexible conductors for flexible electronic applications.

Acknowledgements

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Author Biography

Jolke Perelaer obtained his masters in chemistry at the University of Utrecht in 2004. Under supervision of Prof. Ulrich S. Schubert (Eindhoven University of Technology, the Netherlands) he obtained in 2009 his PhD degree, which focused on inkjet printing and sintering of metal nanoparticles. He now is project leader of the inkjet group in the laboratory of Prof. Schubert at the Friedrich-Schiller-University Jena (Jena, Germany). The topics include printed electronics (photovoltaic, OLED, RFID), combinatorial materials screening and printed bio-materials.