Smart materials by Inkjet

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Abstract

There is growing interest in voxelated matter as it allows to build up tailored made surface functionalization and innovative new gradient materials. Inkjet-based printing is the only method that can create voxelated materials with high precision, digital and extremely versatile through high controlled formation of small pico-liter droplets [1, 2]. In this case the droplet will be the smallest material unit called voxel. The spatially controlled deposition allows to functionalize surfaces, build materials gradients, and combine different materials to generate printed surfaces with new features. In this way, the preparation of surfaces and coatings with a tailored functionalization and performance on demand becomes possible.

Through the vehicle of inks with different softness grades which are doped with mechanochromic additive, we have developed a multi-material inkjet platform, which allows to create gradient materials with new performance. The additive has helped to characterize this new kind of materials on one hand and on the other hand it will be the start of creating new smart materials with gradient properties by inkjet. The first drop casting tests of these two inks has proven the mechanochromism by the measurement of the ratio between the intensity of the monomer and the excimer under UV light. The intensity in the mixing zone was measured at different strain. Finally, it was proven that the hardness in the mixing zone could be defined.

Materials and Methods

Commercially available polyurethanes (PUs) with different hardnesses were dissolved in a solvent to formulate an inkjet ink. A mechanochromic additive developed by the Adolphe Merkle Institute [3, 4], which changes its fluorescence absorption and color in response to mechanical forces (elongation) was added to the ink (Figure 1). This additive is a marker and has no impact on the properties of the PU. The additive was added to the inks at low concentration (0.2-1 wt%).

Figure 1: Images taken under UV illumination of an elastomeric polyurethane/tOPV blend film containing 0.2 wt% tOPV subjected to uniaxial tensile deformation at the indicated strains

First challenge was to find a suitable solvent both for the additive and for the printhead. Compatibility tests with the RC1535 printhead were performed as described by the printhead manufacturer. Rheological properties of these inks were analyzed with a piezo axial vibrator rheometer (Tri-PAV) at high-frequency from 100 Hz to 10'000 Hz at room temperature to find suitable formulations for inkjet printing.

A standard inkjet printing platform for research was adapted to print two different PU inks at the same time with two printheads. After dropwatching and waveform optimization, two inks were selected: ink A composed of 20 mg/ml of soft35A12P PU from BASF (hardness Shore 35A) and ink B composed of 15 mg/ml of irogranA80P from Huntsman (hardness Shore 80A). Both inks were dissolved in dioxane.

Best drying conditions to obtain a good mechanochromic response without altering it had to be fixed. It was found that rest of solvent after drying didn't give any mechanochromic response. High temperatures deteriorate the mechanochromic agent.

The selected inks containing the mechanochromic additive were deposit by inkjet at room temperature on a PU substrate fixed on a heating plate at 40°C (Figure 2).

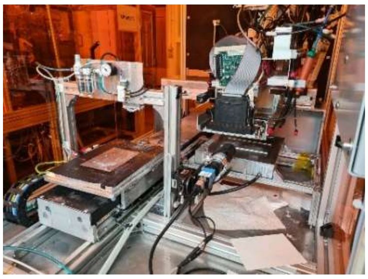


Figure 2: Inkjet printing plateform

Different printing patterns were tested, with different thicknesses (1 to 20 layers). Inkjet and dropcast samples were then dried overnight at 60°C in oven and analyzed by the Adolphe Merkle Institute. Spectroscopic analysis was performed using a microtensile tester and an optical fiber setup, as well as with a fluorescent confocal microscope (Zeiss LSM710) with a special tool developed to elongate the samples uniformly up to 100 %. The local monomer-to-excimer ratio (I_M/I_E) was measured at different elongation rates.

Results and Discussion

Drop casting deposition

First tests were performed by dropcasting of the two polymers with a pipet to show the mechanochromism. The local monomer-to-excimer ration (I_M/I_E) was measured for each polymer at different elongation rates (Figure 3). This spectroscopic analysis shows clearly the mechanochromism of the different PU inks. Harder PU exhibit higher I_M/I_E values than softer PU. We have also shown the mechanochromism with fluorescent confocal microscope analysis (Figures 4, 5 and 6). Thanks to the mechanochromic additive and the measurement of its intensity, the hardness of the blend material can be measured.

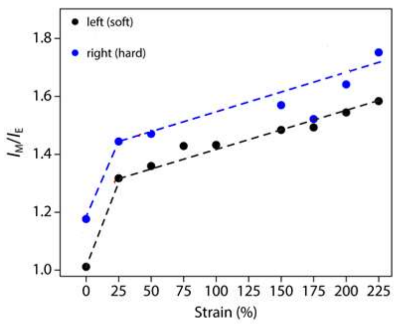
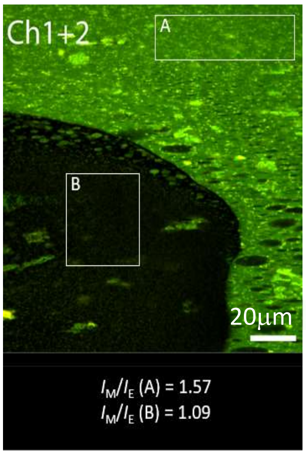


Figure 3: Intensity measurement (I_M/I_E ratio) in function of the strain on both PU inks. Ink A (hard PU) with Shore 80A. Ink B (soft PU) with Shore 35A (dropcast deposition and spectroscopic analysis)



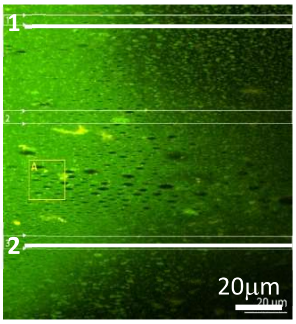


Figure 5: Confocal microscope image of a sample made by dropcasting ink A and ink B. Left side: ink A, right side: ink B

Figure 4: Confocal microscope image of a sample made by dropcasting ink A and ink B. 90% equibiaxial strain was applied to the sample before imaging

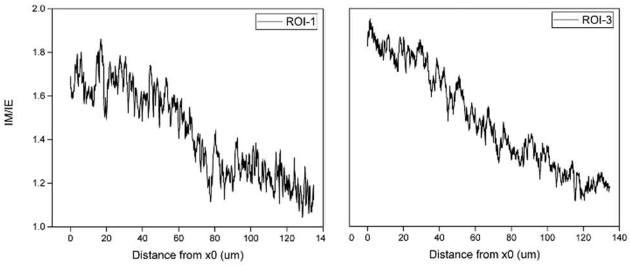


Figure 6: Intensity measurement (I_M/I_E ratio) in function of the distance along the two lines 1 (left graph) and line 2 (right graph) of Figure 4

Inkjet deposition

After having proven that the concept is working by dropcast deposition, the two PU inks were simultaneously deposit by inkjet with different patterns (Figure 7) and different thicknesses on the PU substrate heated at 40°C. Difficulties appeared due to the fact that the samples were not flat enough to be able to do a good focus (impossible to do big stitched pictures due to the loss of the focal plan), leading to difficulties to find an interface between the two PU at this very high zoom. Finally, the interface found (Figure 8) was not clear enough due to printing difficulties with lots of printing satellites and dewetting issues of the hard PU during the drying. It has been impossible to perform intensity measurement on these samples.

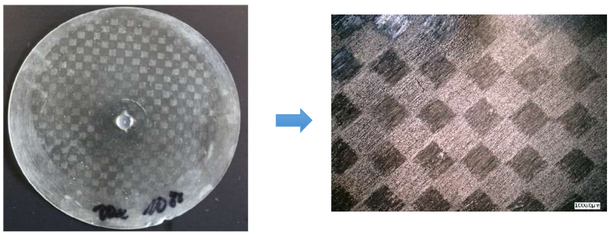


Figure 7: Inkjet printed chessboard pattern with ink A and ink B

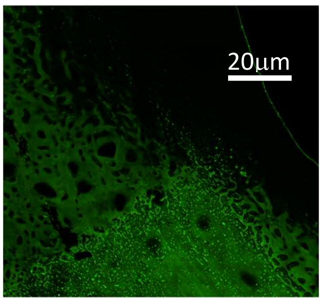


Figure 8: Fluorescent confocal microscope picture of inkjet printed inks composed of ink A (bottom right) and ink B (top left)

Conclusion

The mechanochromic additive was blended with two PUs with different hardnesses and dissolved in dioxane to create an ink that can be jetted by inkjet. The first drop casting tests by deposition of two drops of the two different inks close each other to have a mixing zone have proven the mechanochromism of the inks by the measurement of the ratio between the intensity of the monomer and the excimer under UV light. The intensity in the mixing zone was measured at different strain. Finally, it was proven that the hardness in the mixing zone could be defined. Unfortunately, difficulties appeared during the inkjet process leading the impossibility to perform these measurements after inkjet deposition due to printing inhomogeneity and issues such as ink splashing and satellite formation. Next step is to do simulations of the drop behavior and mixing to be able to predict the hardness and to be able to deposit the necessary quantities of each material to obtain the desired hardness to create materials with given hardness gradient with very high precision.

As summary, the present project is a first step to build up basic understanding on multimaterial droplet interaction for creating tailored made surfaces. It allowed us to build a dedicated inkjet printing platform, to formulate inkjet printable smart inks containing the mechanochromic additive, to prove the mechanochromism of the different polymers and to gain a deeper understanding of the requirements to achieve homogenous smart gradient material layers. Next step involves inkjet printing highly homogeneous gradient layers without substrate delamination. Once accomplished, we will analyze the collected data and results from the voxel inkjet printing process, as well as the characterization of the gradient material and surfaces, utilizing mechanochromism. These findings will enable us to further advance the process through numerical simulation and to consider other smart material like nanocomposites on demand (reactive systems) or stretchable conductive materials to be combined into new smart gradient materials.

References

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Author Biography

Muriel Mauron received her master in chemical and biological engineering from the EPFL in 2007. After six dynamic years of driving innovation in inkjet photo papers at Ilford in Marly, Switzerland, Muriel joined iPrint institute. Since 2014, she has been the main person to handle primarily all bio printing projects and inkjet-related chemicals, and additionally most recently rheological analysis for almost all the iPrint project.