Ambient reactive extrusion-additive manufacturing of thermoplastic polyurethanes

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Additive manufacturing (AM) has been utilized for multiple decades now and has proved innovative and transformative to the present world; however, not all desired materials can be manufactured using traditional methods of AM. Ambient reactive extrusion (ARE) is a rising alternative method of AM that was developed at the Oak Ridge National Lab. Using this method, the final material polymerizes during and after deposition onto the print bed. This eliminates the issue with traditional AM: mechanical anisotropy. Engineering of the polymer is necessary, especially when using thermoplastic polyurethanes (TPUs). Altering the hard block (HB) to soft block (SB) ratio of TPUs affects the chemorheological properties, but the effect of HB:SB ratio variation on ARE printability is unexplored. Herein, four TPUs of varying HB:SB ratios were synthesized utilizing 4,4'-methylenebis (cyclohexyl isocyanate), 1,4-butanediol, and polytetramethylene ether glycol. The chemorheological properties of the TPU were analyzed via rheology, in conjunction with real-time Fourier transform infrared spectroscopy (RT-FTIR) to observe polymerization. The thermal stability of each polymer was determined through thermal gravitational analysis (TGA), where the effect of altering the HB:SB ratio on degradation was observed. For each TPU, the degree of conversion (DOC) was determined at the time where the storage (G') and loss modulus (G") crossed; this provided a baseline of TPU chemorheological properties for ARE printing. It was determined that increasing the HB content decreased G'/G" crossover time, but the effect on DOC requires further evaluation. Future efforts will identify the balance between crossover time and DOC to determine the proper chemorheological properties that dictate successful ARE printing.