Stimuli-responsive supramolecular polymers with tunable toughness and stiffness for debonding-on-demand adhesives

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The quest to develop reversible debonding-on-demand adhesive technologies is motivated by economic and environmental considerations and is of interest in industries that range from transportation to consumer electronics.[1] In this context, supramolecular polymers (SPs) offer an interesting opportunity as the dynamic nature of the such assemblies renders materials that are susceptible to external stimulation.[2] Using appropriate triggers, such as heat or light, it is possible to temporarily disassemble supramolecular polymers into the constituting building blocks, and thereby drastically alter the material's mechanical properties, decreasing both modulus and viscosity.[3] However, the development of SPs that combine high toughness, high strength and high stiffness with low melt viscosities, and which are useful for adhesive formulations, remains challenging.

We here report the development of tunable SP networks based on trifunctional polypropylene oxide (PPO) cores with number-average molecular weights M_n of 440, 3000, and 5000 g/mol, which were end-functionalized with three quadruple hydrogen-bonding 2-ureido-4-pyrimidinone (UPy) groups. While the SP based on UPy_3PPO-440 formed a glassy material with a glass transition temperature (T_g) at 84 °C, the macromonomers UPy_3PPO-3000 and UPy_3PPO-5000 adopted phase segregated morphologies, with a crystalline phase formed by the UPy-dimers melting around 95 - 113 ºC and a rubbery phase with T_g = -60 ºC. We show that by blending the building blocks, it is possible to tune toughness and stiffness of the materials via the formation of microphase-segregated structures that feature a rubbery phase constituted by the higher-molecular weight building blocks, and a glassy phase formed by UPy_3PPO-440. Investigations of the (thermo-) mechanical properties by means of dynamical mechanical analysis and tensile testing demonstrate that compression-molded films exhibit storage moduli ranging from 14 – 550 MPa at 25 °C, tensile strength of 2.0 – 5.4 MPa and strain at break of 1.6 – 7.7 %. Adhesion properties were probed by shear experiments using thermally bonded stainless steel lap joints. Shearing strengths up to 5 MPa were obtained and no loss in adhesive properties was observed upon subsequent debonding/rebonding cycles. In combination with the low melt viscosity ($|\eta^*| < 100$ Pa·s, 130 °C) measured by rheological experiments, the new platform offers tunable mechanical performance, promising adhesive properties, and (de)bonding-on-demand features that may be useful for a wide range of industrial applications.

[1] Y. Lu, J. Broughton, P. Winfield, *Int. J. Adhes. Adhes.,* **2014,** *50*, 119–127.
[2] L. Yang, X. Tan, Z. Wang, X. Zhang, *Chemical Reviews*, **2015**, *115*, 7196-7239.
[3] K. M. Herbert, S. Schrettl, S. J. Rowan, C. Weder, *Macromolecules*, **2017**, *50*, 8845–8870.