Supplemental Information

Ionic-Liquid-Based Polyurethane Dispersions for Stabilizing Graphene in Water

Harshit Gupta[§] and John Texter[*]

Coatings Research Institute, School of Engineering, Eastern Michigan University, Ypsilanti, MI 48197, USA
[§]Present Address: Axalta Coating Systems, Global Innovation Center, 1050 Constitution Avenue, Philadelphia, PA 19112, USA

The vibratory stirrer we used is illustrated in Fig. SI-1. When a 15 mL to 40 mL vial is pressed into one of the recessed areas illustrated in the upper rubber platform, the off-centric motor-drive produces a circular vibratory shaking that produces a swirling vortex in suspensions and solutions subjected to mixing.

Figure SI-1. Fisher Scientific vibrator stirrer used for low-shear mixing applications in this study.

The ultrasonic bath (Branson) used for low power sonication is shown in Figure SI-2. It is used by filling the top pan volume to a given height with DI water, placing a beaker in this pan, with the sample vial supported in this beaker. The beaker is partially filled with water to a level just above that in the sample vial. The front view of Figure SI-2(a) illustrates on-off and start functions. The top view of Figure SI-2(b) illustrates an insert that can be used to support objects placed in the top pan. The main ultrasonic crystal is located in the center of this upper pan, just subsurface. When turned on, the start button initiates continuous ultrasonication that runs for about 15 min. Its automatic nature can be used to meter lengthy doses.

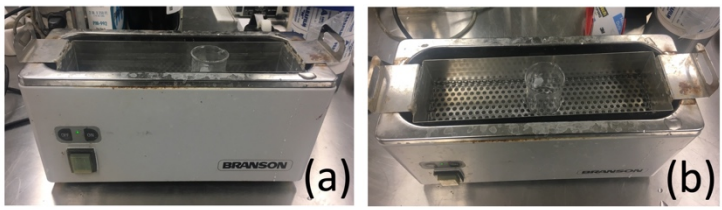

Figure SI-2. Front (a) and upper (b) views of Branson ultrasonic cleaning bath. Function and operation are discussed in text above.

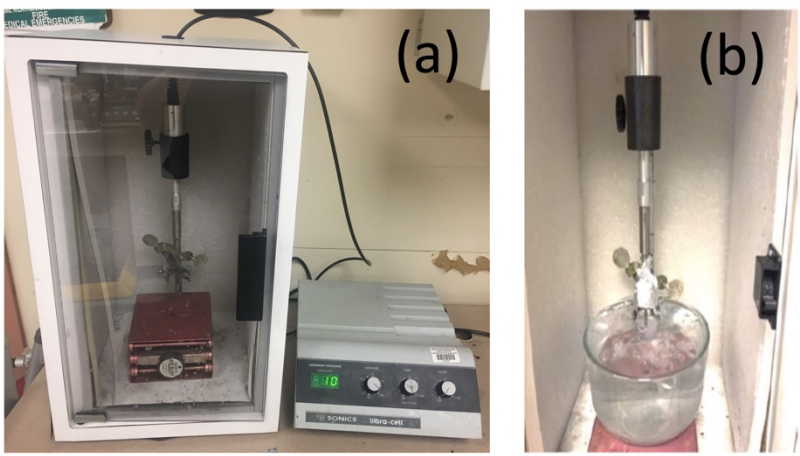

Figure SI-3. (a) Sonics Vibra Cell, Model VC 30 controller, converter, and sound-attenuating sample chamber and (b) sound-attenuating chamber illustrated with sample vial suspended in ice water bath.

The strong sonication system comprising a Sonics Vibra-Cell model VC-30 controller, converter, attached microtip ultrasonic horn (about 4 mm in tip diameter), and sound-attenuating sample chamber is illustrated in Figure SI-3. Also illustrated is a sample vial suspended in an ice-water bath with microtip inserted in sample dispersion. This bath prevents excessive heating during ultrasonic treatment. The LED green display on the controller front panel illustrated in Figure SI-3 displays power output to sample in watts. This quantity depends on acoustic coupling between the converted, microtip, and sample multiphase fluid. The quantity of 10 W displayed in this photo is coupled to air. Output powers of 14-20 W typically can be obtained in preparing 1% by weight graphene dispersions in water. The experiments in this study typically generated about 16 W of output power to the sample dispersions.

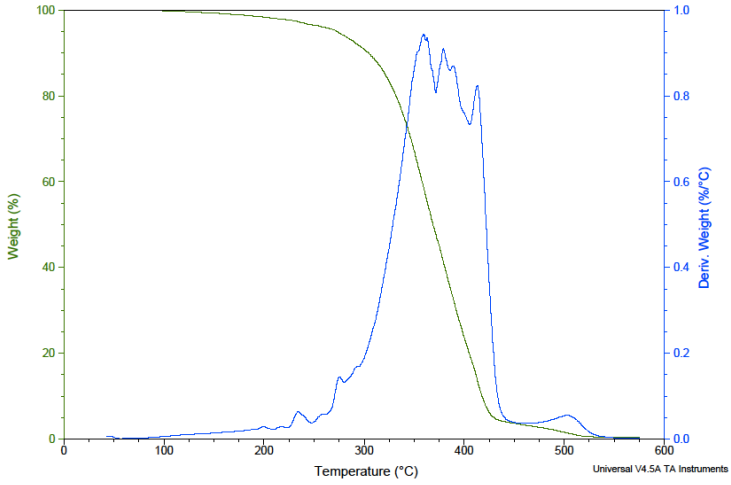

Figure SI-4. TGA data for PU resin from room temperature to about 580 C. Temperature was increased linearly at 10 °C/min.

TGA data for our PPO/Gly PU resin after removing all solvent by heating in vacuo for two hours in a vacuum oven are illustrated in Figure SI-4. The green line denotes relative sample weight as a function of temperature while heated at a rate of 10 °C/min. The lack of weight loss below 100 °C indicates solvent removal in the vacuum oven was effective. Samples were suspended in a Pt pan, but an expendable DSC pan was placed in this Pt pan, and sample was placed in this DSC pan, in order to minimize producing ash in the Pt pan. Scans were terminated at about 580 °C in order to avoid melting the aluminium DSC pans.

DSC scans of our PU resin sample after solvent removal are illustrated in Figure SI-5. Heating and cooling rates of 10 °C/min were used. This sample was initially heated (not illustrated) from room temperature to an upper hold temperature of about 120 °C, and held for 5 min. It was then cooled to about -85 °C and held there for about 5 min. Then it was heated to the upper hold temperature, 120 °C, and allowed to cool to room temperature. Second and third segment scans, cooling and heating, respectively, are illustrated in Figure SI-5. A clear glass transition in heat flow is illustrated in the cooling curve (lower) over the -8 °C to -20 °C interval, and some catalyst freezing is shown in the small exothermic transition over -39 °C to – 50 °C. This transition is discussed at length in Gupta's thesis. In the heating curve (upper), the glass transition is clearly evident over the -15 °C to 0 °C interval.

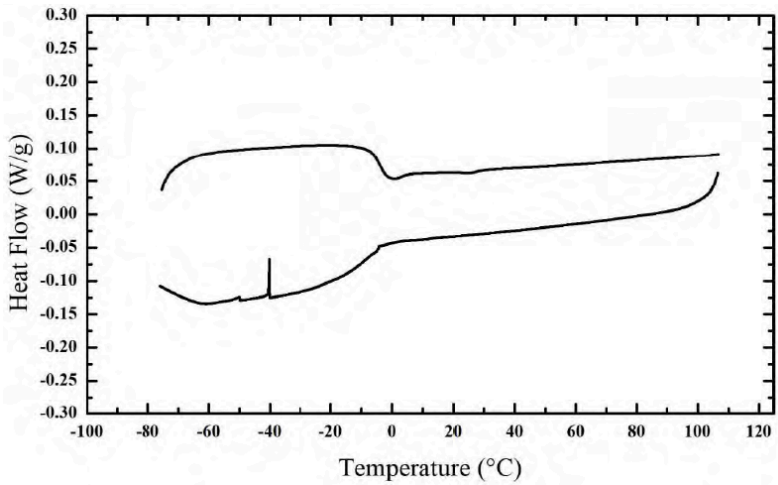

Figure SI-5. DSC of PU resin at a scan rate of 10 °C/min. Sample was degassed in a vacuum oven for two hours at 100 °C prior to measuring DSC. Reproduced with permission from H. Gupta, MS Thesis, Eastern Michigan University (2019), https://commons.emich.edu/theses/964; accessed 13 June 2019.