

Supplementary Information

“ Network formation in graphene oxide composites with surface grafted poly-N-isopropylamide chains in aqueous solution characterized by rheological experiments ”

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GO & RGO preparation

Graphene oxides (GOs) were prepared by a modified Hummer's method.¹ Graphite flakes were added to a round-bottom flask containing 120 ml of H₂SO₄ under stirring for 1 h. KMnO₄ aqueous solution was titrated to the mixture at an interval of 20 ml. The mixture was maintained at 40°C for 5 h and then 150 ml of deionized water was added to the mixture. Additionally, H₂O₂ solution was added to the mixture during 30 min and then maintained for 24 h. After exfoliated GOs were separated by centrifuge, the GOs were put into the dialysis tube to neutralize. Finally, the GOs was dried by freeze-drying equipment.

The procedure of preparing typical RGO sheets is described as follows. In a typical procedure, GO (100 mg) was loaded in a 250-mL round-bottom flask and water (100 mL) was then added, yielding an inhomogeneous yellow-brown dispersion. This dispersion was sonicated until it became clear with no visible particulate matter. Hydrazine hydrate (1.00 mL, 32.1 mmol) was then added and the solution heated in an oil bath at 100°C under a water-cooled condenser for 24 h over which the reduced GO gradually precipitated out as a black solid. This product was isolated by filtration over a medium fritted glass funnel, washed copiously with water and methanol, and dried on the funnel under a continuous air flow through the solid product cake.

TEM

The morphological structure of GO produced by a modified Hummer's method was examined by TEM.

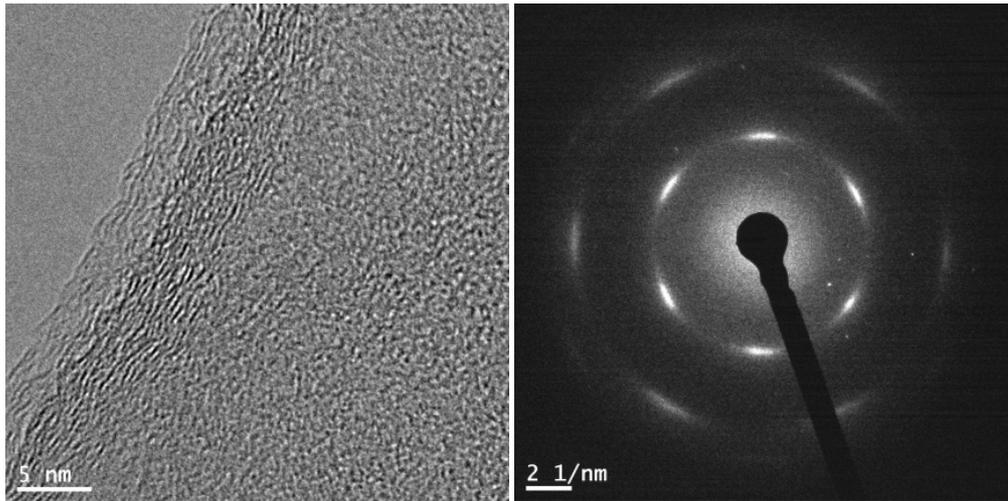


Figure S11: TEM images of GO

FTIR

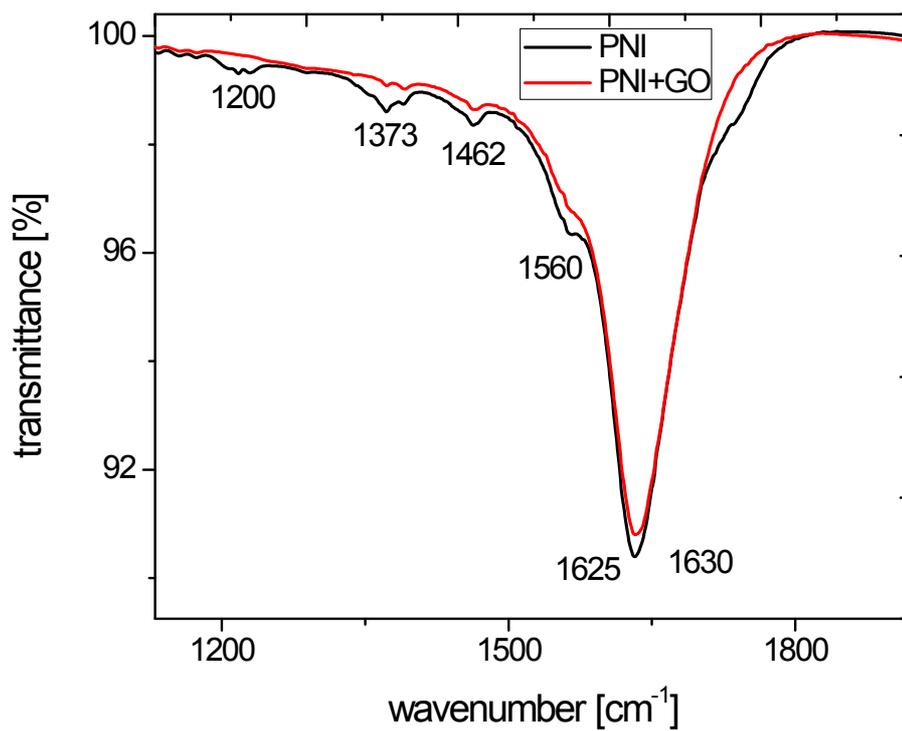


Figure S12: FTIR of PNIPAM and PNIPAM-GO blend in solution state

As it discussed in the manuscript, the rheological data suggests that the supramolecular interaction basal GO-plane forms a weak network structure with PNI, which can be easily destructured by high shear and takes some time to rebuild. FTIR spectroscopy analysis was performed in the solution state, to examine the bonding between functional groups of polymer and GO. The prominent FTIR bands of PNIPAM solution are the amide I band (1625 cm^{-1}), the amide II band (1560 cm^{-1}), the deformation bands due to the isopropyl groups

(1462 cm^{-1} , 1393 cm^{-1} , and 1373 cm^{-1}), the amide III band 1200 cm^{-1} , and C–H bending vibration band (1136 cm^{-1}). After mixing polymer with nanoparticles, amide I shifts slightly to higher wavenumbers (1625 cm^{-1} →1630 cm^{-1}). This characteristic shift of amide I band towards more higher wavenumber clearly reflects the formation of hydrogen bonding between functional groups of polymer molecules and GO sheets.² Moreover, the intensity of the amide II and III band groups decreases after mixing with GO, which might be due to the destruction of hydrogen bonds between amide group of polymer and water molecules by GO.

Temperature dependency

Figure SI3 shows a typical example of the temperature dependence of PNIPAM with GO in both heating and cooling rate (T_{up} and T_{down} , respectively). The LCST at around 33.5°C can be easily seen, with significant increases of $G'(T)$ and $G''(T)$. Above 40°C, the shrinkage of the polymer part of the sample leads to partial detachment from the geometry and thus, the lower modulus is an unavoidable artefact. The transition temperature determined for this material closely corresponds to the LCST temperature of pure PNIPAM which is 32.9°C.³⁶ Table 1 shows a summary of the LCST temperatures determined in the same way as shown in Figure 1. It is obvious that the low amount of GO or RGO below 3 wt.% relative to the polymer content does not significantly influence the LCST temperature. For this reason, it can be concluded that the LCST, which is typical for all PNIPAM-based systems, does not influence the rheological properties determined at 25°C.

Table 1: LCST values of PNIPAM and PNIPAM-GO composites

Sample ID	Transition Temperature [°C]
PNIPAM	33.5
PNIPAM-GO3%	35
PNIPAM-RGO3%	35
PNIPAM-GO3%-blend	33.5

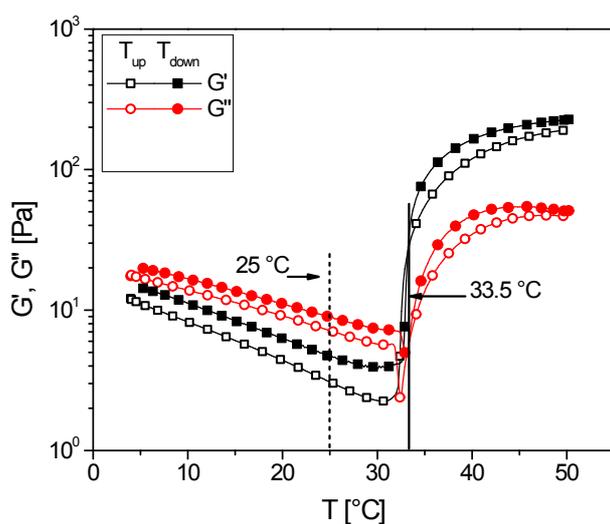
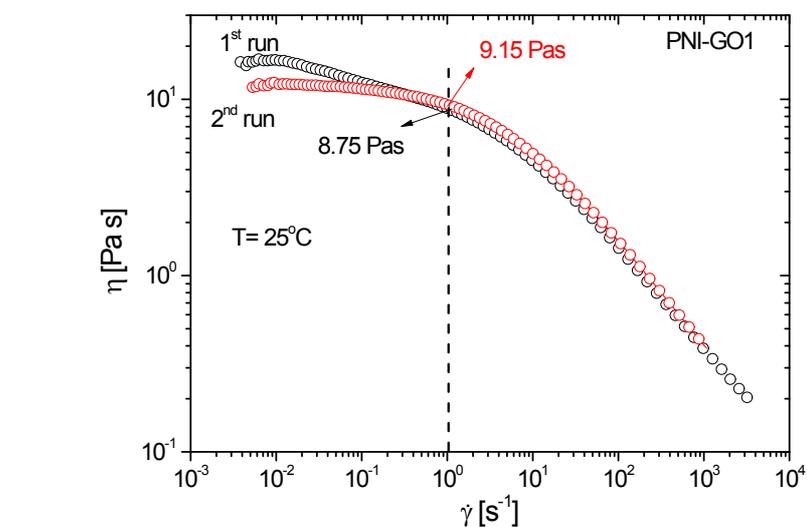
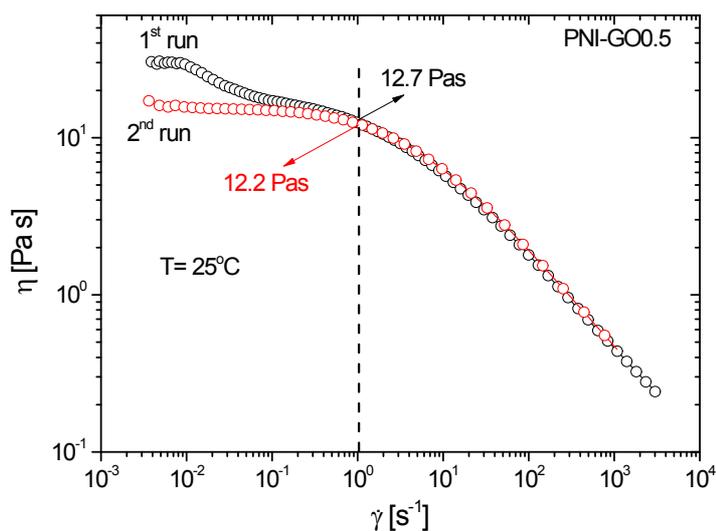


Figure SI3: Temperature dependence of the rheological properties of PNIPAM-GO3%-blend.

Viscosity Functions



a)



b)

Figure S14: Viscosity functions.

Reference

- 1 M. Hirata, T. Gotou, S. Horiuchi, M. Fujiwara, and M. Ohba, 'Thin-Film Particles of Graphite Oxide 1: High-Yield Synthesis and Flexibility of the Particles', *Carbon*, 42 (2004), 2929-37.
- 2 P. M. Reddy, M. Taha, P. Venkatesu, A. Kumar, and M. J. Lee, 'Destruction of Hydrogen Bonds of Poly(N-Isopropylacrylamide) Aqueous Solution by Trimethylamine N-Oxide', *Journal of Chemical Physics*, 136 (2012).