Detecting Liquid to Liquid-Liquid Transitions in Solvent + Polymer + Nanoparticles Mixtures Using Rheology

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Background Information

❖ **Rheology** refers to the flow of matter. This is used when determining the viscosity of substances under applied shear [1]. Rheology is paramount for characterizing non-Newtonian fluids.

❖ Most solutions containing polymers and solvents are **non-Newtonian**[2]. This means that their apparent viscosity changes with shear rate (Figure 1).

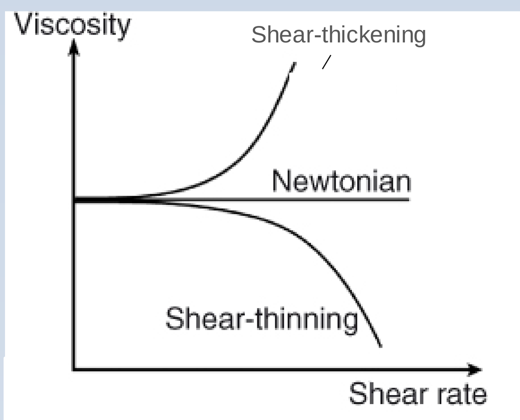

Figure 1. Newtonian vs. Non-Newtonian behaviour [3]

❖ Understanding the rheology of polymer solutions is essential in many fields including: polymer processing, waste water treatments, oil recovery, fluid mechanics, etc. [4].

❖ In this work, step changes in the rheological responses of polymer solutions are used to detect transitions from 2-phases to 1-phase as temperature is changed.

Objectives

❖ Investigate the rheological behaviors of mixtures of polymer (Polystyrene) + nanocolloid (Cyclohexane / Toluene + Silica Nanoparticles) in 1-phase and 2-phase regions.

❖ Determine whether rheological response is a suitable method for detecting transitions from 2-phase to 1-phase behavior for Nanoparticle + Polymer + Solvent mixtures.

Materials and Equipment

- ❖ Solvents
  - Cyclohexane
  - Toluene
- ❖ Nanoparticles
  - Fumed silica nanoparticles (7 nm average diameter)
- ❖ Polymer
  - Polystyrene (MW 237 kg/mol)
- ❖ Equipment
  - Rheometer Anton Paar 301 (Figure 2 & 3) with a Double Gap Cup (DG 23.04) configuration

Figure 2. Rheometer Anton Paar 301

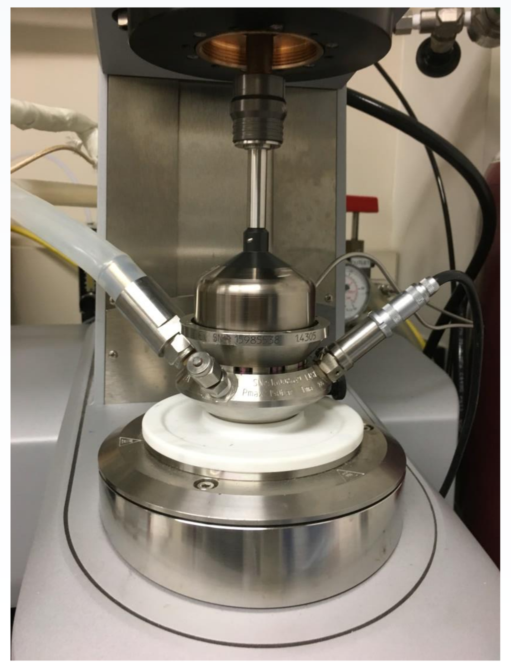

Figure 3. Pressure cell head

Methodology

❖ Mixtures were prepared using an ultrasonic bath. The samples were loaded into the rheometer and shear rates between 200-500 s^{-1} were applied to ensure accurate measurements (Figure 4).

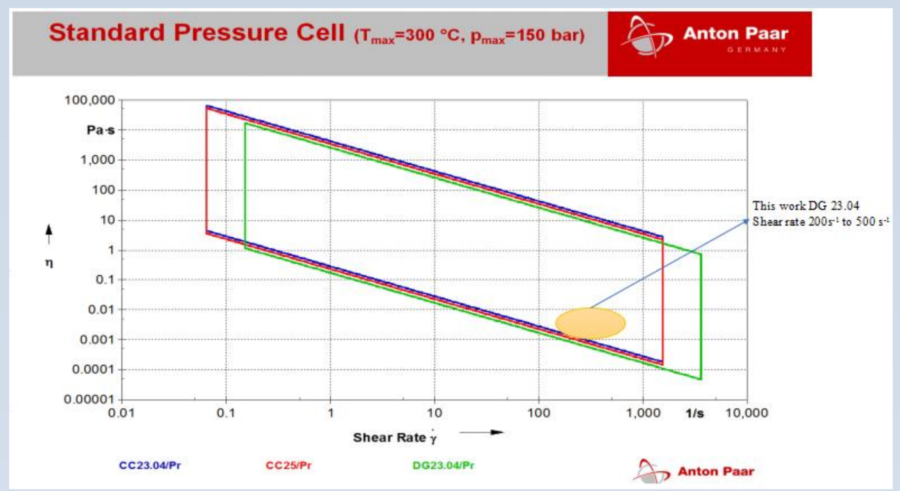

Figure 4. Anton Paar 301- 3 different geometries and recommended shear rates.

❖ In order to pin point liquid-liquid to liquid phase transitions (cloud points) for polystyrene + cyclohexane mixtures, measurements were performed using small temperature increments.

❖ Silica Nano-Particles were added into the polymer solutions to identify changes in the rheological behaviour of the mixtures.

Results

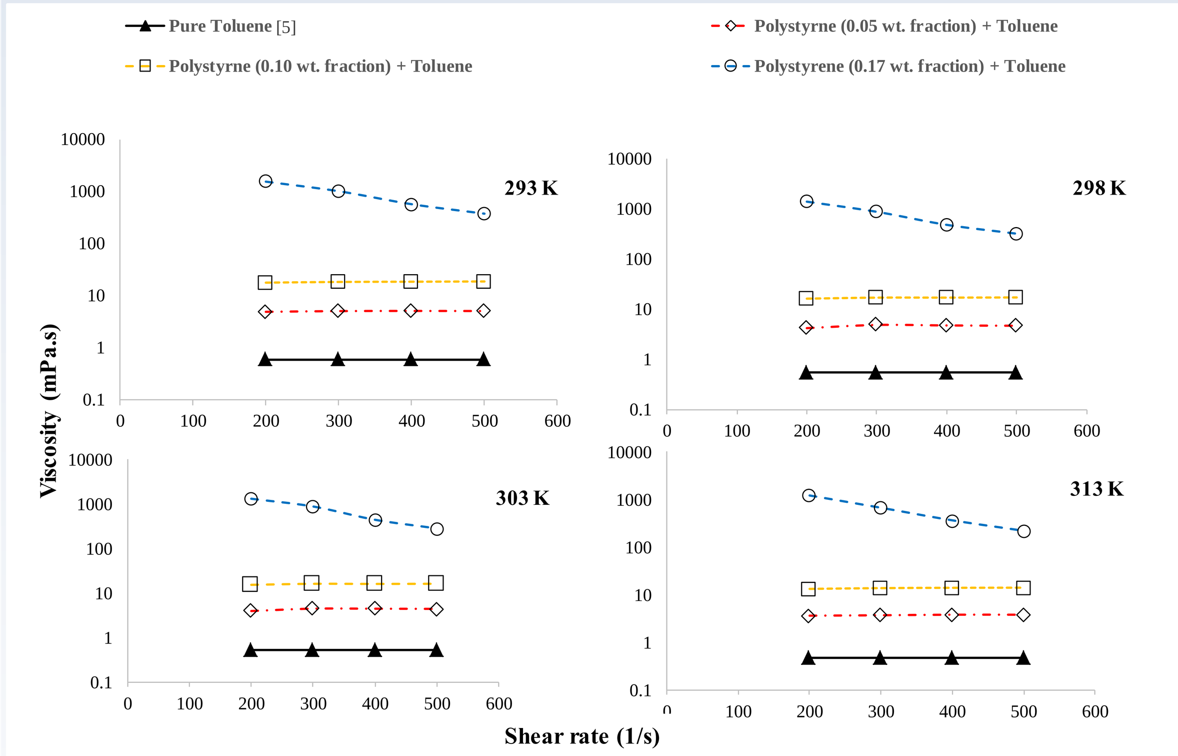

Figure 5. Rheological responses of toluene + polystyrene mixtures at different temperatures and shear rates.

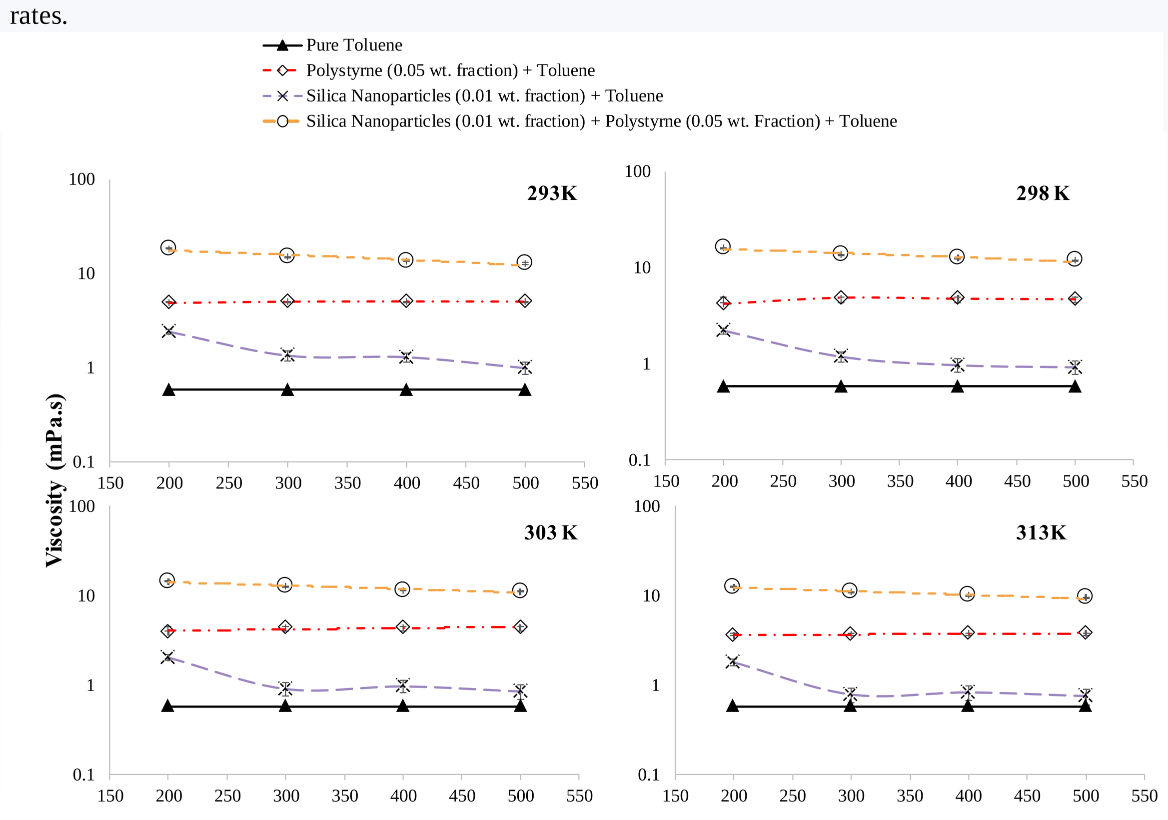

Figure 6. Rheological responses of adding Silica Nanoparticles to the mixture of Polystyrene (0.05 wt. fraction) + Toluene.

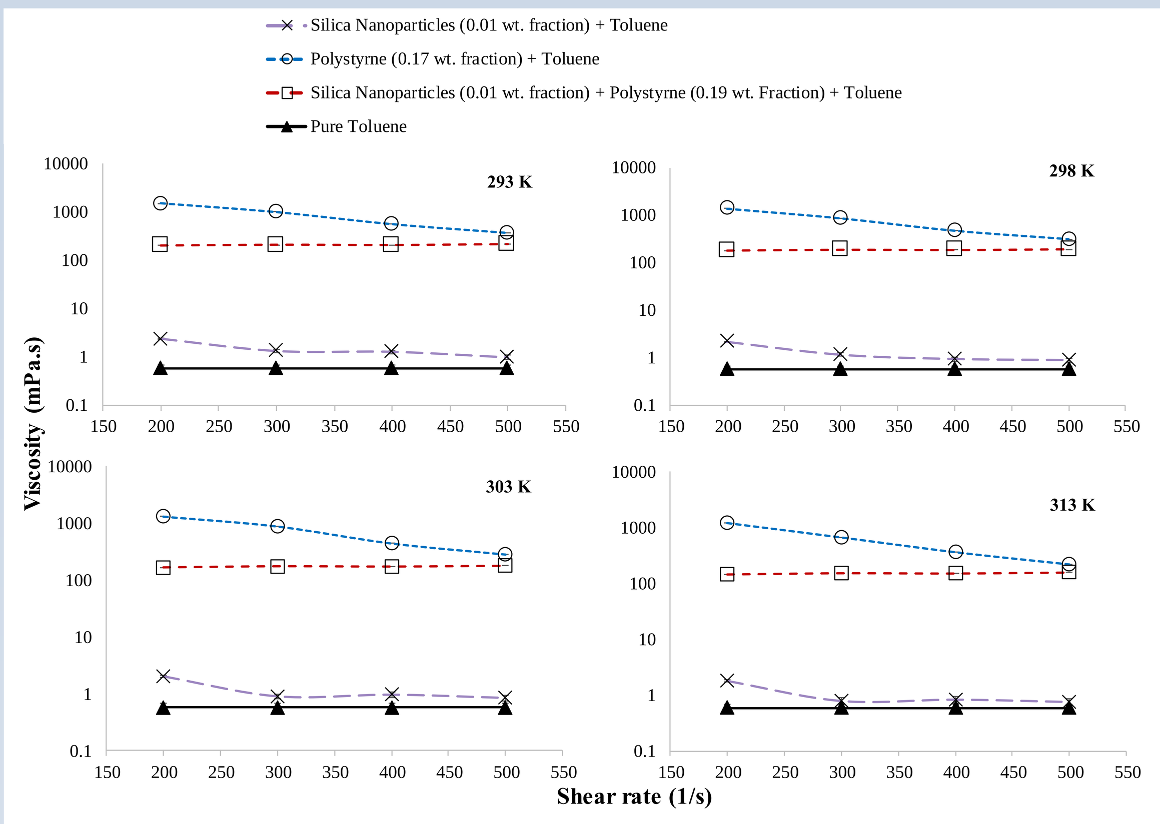

Figure 7. Rheological responses of adding Silica Nanoparticles in Polystyrene (0.19 wt. fraction) + Toluene mixture.

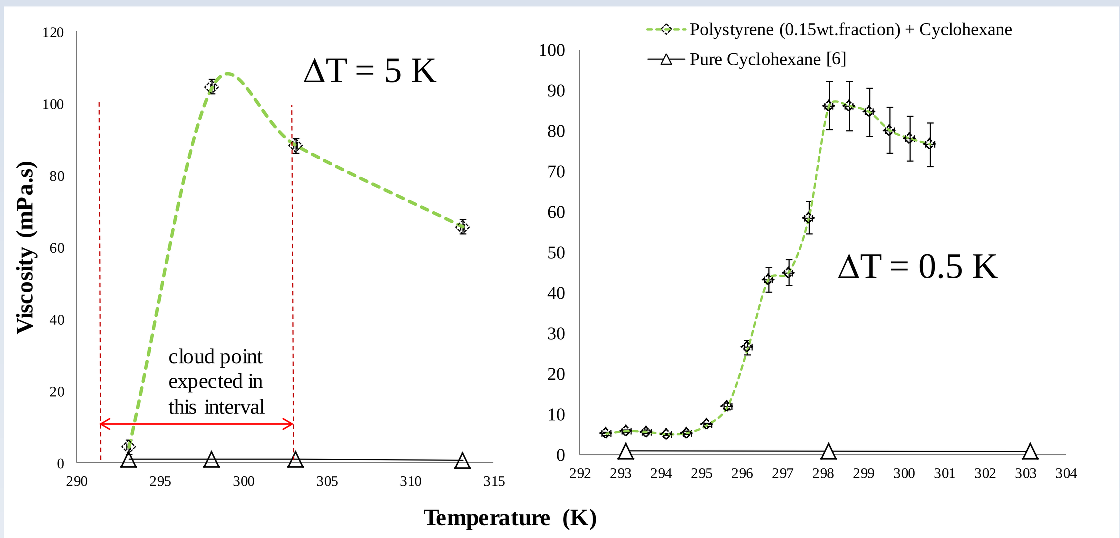

Figure 8. Rheological responses of cyclohexane + polystyrene (0.10 wt. fraction) mixture.

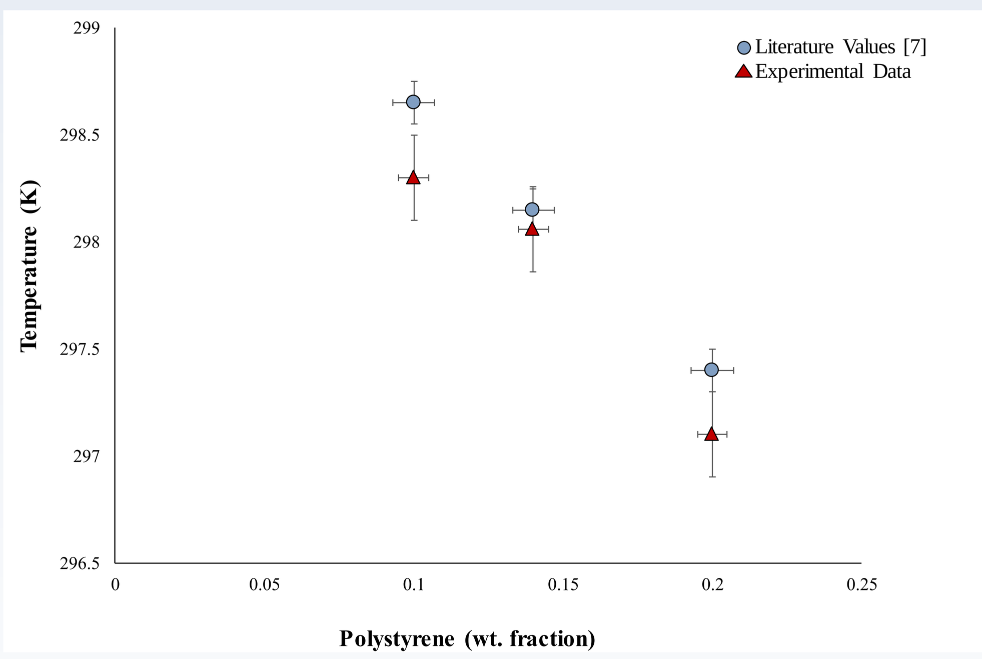

Figure 9. Cloud points for Cyclohexane + Polystyrene mixtures.

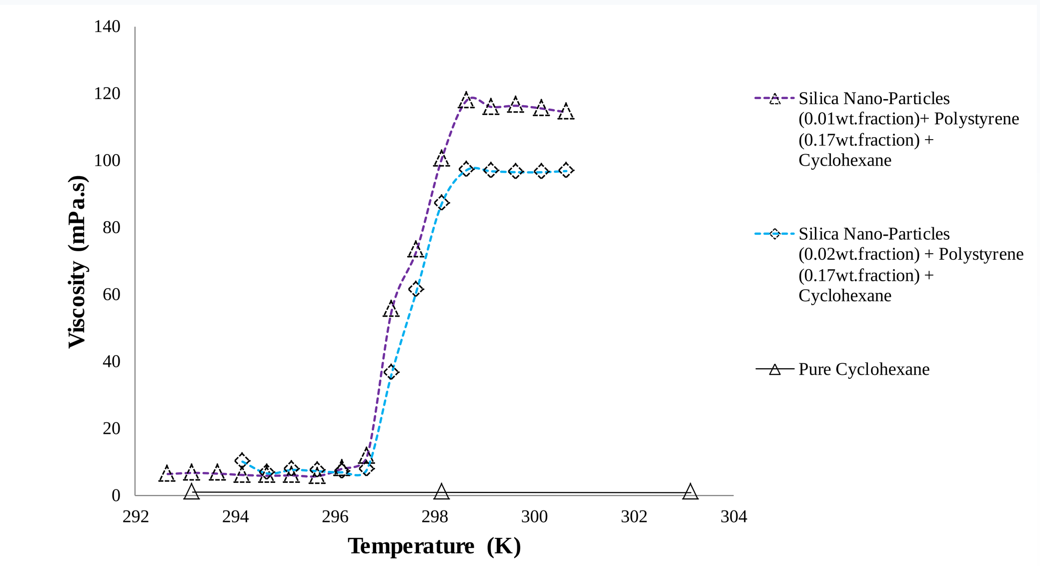

Figure 10. Rheological responses of silica nanoparticle + polystyrene + cyclohexane mixtures.

Summary of Findings

❖ Mixtures of polystyrene + toluene show Newtonian behavior at 5 and 10 wt.%, and showed shear thinning behavior at 17 wt. % polystyrene (Figure 5). Changes in the rheological behavior of these mixtures with temperature were not significant.

❖ The addition of silica nanoparticles to polystyrene + toluene mixtures did not show a significant change in viscosity at low polystyrene concentrations (Figure 6). However, at high polystyrene concentrations (19 wt. %), non-Newtonian behavior is observed (Figure 7).

❖ Polystyrene + cyclohexane mixtures show a step change in viscosity (Figure 8) at the transition from 1-phase (high temperature) to 2-phase (low temperature). This transition is also called the cloud point.

❖ The peak in viscosity value corresponds to the cloud point temperature (Figure 9). The response of the silica nanoparticle + polystyrene + cyclohexane mixtures is similar (Figure 10) and is interpreted similarly.

❖ With calibration to avoid misinterpreting secondary peaks below cloud points, this method has the potential to provide rapid and robust cloud point measurements.

References

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