Supporting Information

Controlled Structure Evolution of Graphene Networks in Polymer Composites

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Supporting Information on polystyrene and carbon black composites

Composites of polystyrene (PS) with conducting carbon black (CB) were tested under shear, as a control sample to compare with the behaviour observed from the graphene nanoplate (GNP) composite. Figure S1a displays the impedance, phase angle, viscosity and shear stress data of a composite with 5 vol. % CB. For the first ten seconds of the test the initial impedance of the composite in the melt is recorded, and then 1.8 s^{-1} shear is applied. As soon as the shear is applied the impedance of the composite increases by two orders of magnitude, evidencing a disruption of the conducting CB network. The composite is sheared for five minutes, during which period the impedance remains fairly constant. The composite itself displays a slight shear thinning behaviour over time. Following cessation of the shear it can be seen that the shear stress of the polymer decays and the impedance of the composite reduces gradually over time. Throughout the test the phase angle of the impedance remains almost constant, and never increases above a value of 0.3 degrees. This indicates that throughout the test the composite can be modelled as a resistive network. It is interesting to look more closely at the response of the composite immediately following cessation of the shear. Figure S1b shows how both the impedance and shear stress decay as a function of time following cessation of the shear. Initially the first response can be seen in the stress decay. After ~40 s the stress has decayed by two orders of magnitude. This stress response is followed by a decay in the impedance over time. It suggests that once the polymer stress has decayed, the CB can then relax and re-establish the percolated network present prior to the shearing process. The impedance decreases back to the same order of magnitude as that prior to the shear, although complete recovery is not observed in the timescale monitored (~3000 s).
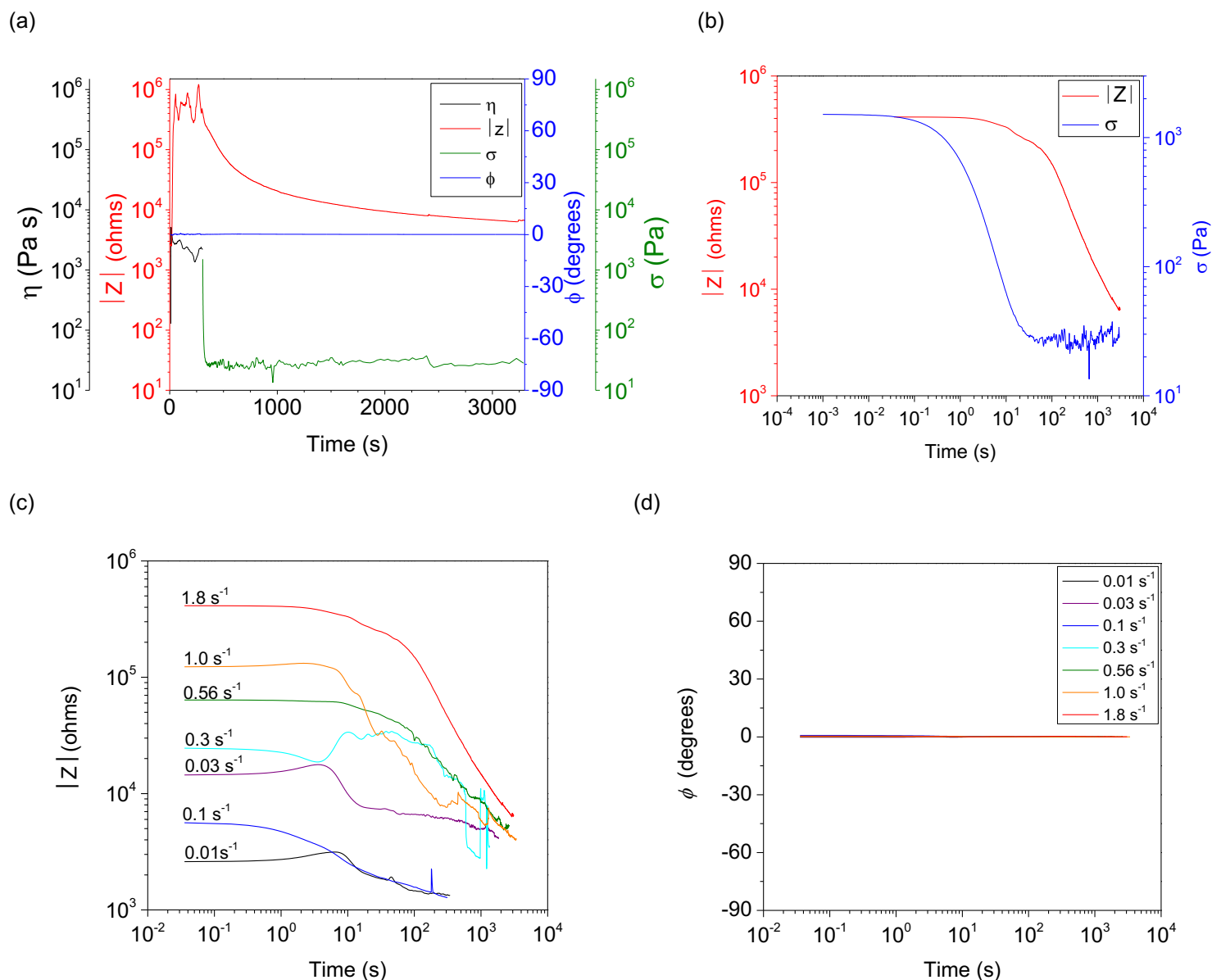
(a)

(b)

(c)

(d)

Figure S1: Composites of polystyrene + 5vol% CB under shear: (a) Impedance $|Z|$, phase angle Φ, viscosity η and shear stress σ as a function of time during shear. The sample was sheared from the time-points 10 s to 310 s at a rate of 1.8 s^{-1}, where $|Z|$, Φ and η are recorded. Following shear $|Z|$, Φ and σ is recorded. (b) Post shear relaxation of σ and $|Z|$. (c) Relaxation of $|Z|$ immediately following cessation of shear. The effect of the preceding shear rate is shown across the range of 0.01-1.8 s^{-1}. (d) Independence of Φ following cessation of shear across the range of 0.01-1.8 s^{-1}.

The effect of shear rate on the impedance and phase angle of the 5 vol. % CB composite is shown in

Figures S1c and S1d. The initial time point of the impedance (Figure S1c) shows the impedance

immediately following cessation of the shear. The lowest impedance, ~2600 ohms, is seen for the

lowest shear rate studied (0.01 s^{-1}). At every shear rate the impedance relaxes after shearing stops.

The impedance then relaxes to ~1300 ohms after 300 s. The impedance of the composite during

shearing increases with the preceding shear rate, while at each rate the impedance is able to reduce under annealing to <10,000 ohms within one hour. Figure S1d shows that the phase angle of the composite remains constant at ~0 at each shear rate.

The behavior of the CB composite contrasts with that of the GNP composites (main text), which show a more complex range of changes in impedance and phase angle during shear and annealing.

Supporting Information on temperature effect on GNP composite processing

To see whether a change in temperature could be used to shift the timescales over which the various relaxation processes we observe in the GNP composites occur, we also tested the composite at a temperature of 180 °C. Figure S2 compares the relaxation of the composite following shear at a rate of 0.1 s^{-1} at temperatures of 200 °C and 180 °C. We observe a number of interesting changes when the processing temperature is lowered to 180 °C. The impedance reduces to a minimum at ~15 s. This behaviour is not observed at 200 °C and suggests that the decrease in temperature has reduced the minimum shear rate required to achieve alignment (see main text). Following this the impedance increases to a maximum after ~1000 s. The maximum in impedance at 200 °C is observed after ~130 s. Zhao et al., found that increasing polymer molecular weight slowed graphene aggregation rates, by increasing the matrix viscosity.[1] Our work shows that temperature provides an additional means of controlling GNP diffusion and the timescales over which the various GNP agglomeration processes (see main text) occur, without recourse to the use of new matrix materials as seen in Zhao's work.
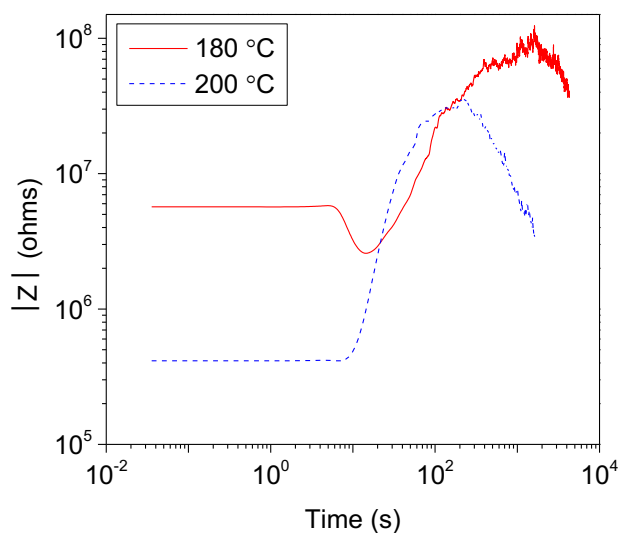

Figure S2: Impedance, │Z│, of polystyrene + 5 vol. % GNPs following cessation of shear at a rate of 0.1 s^{-1}, at 200 and 180 °C

Supporting Information on zero shear viscosity

The polystyrene zero shear viscosity was found to be ~18000 Pa s. This was then used to estimate the required shear rate for exfoliation of the GNPs in the composite (~0.04 s^{-1}) and also a rotational diffusion of the GNPs $\Theta=1.1\times10^{-8}$ s^{-1}.
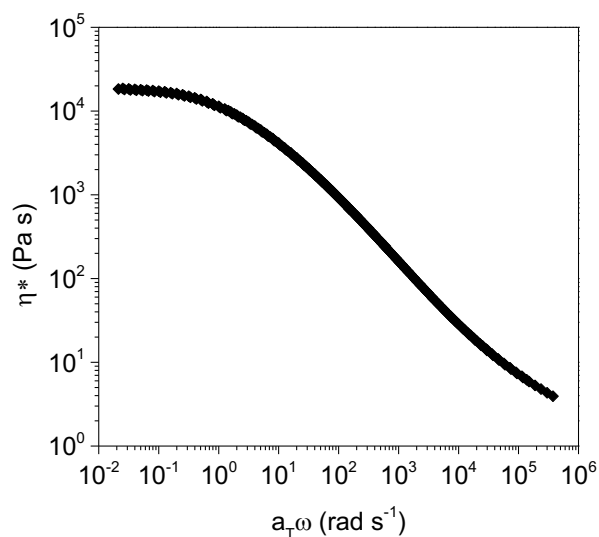

Figure S3: Complex viscosity of polystyrene as a function of the oscillating frequency at 200 °C. The data was collected in the temperature range 200-140 °C at a strain of 1%, and shifted to a single reference temperature using the theory of Williams-Landel-Ferry[2] in the RepTate program.[3]
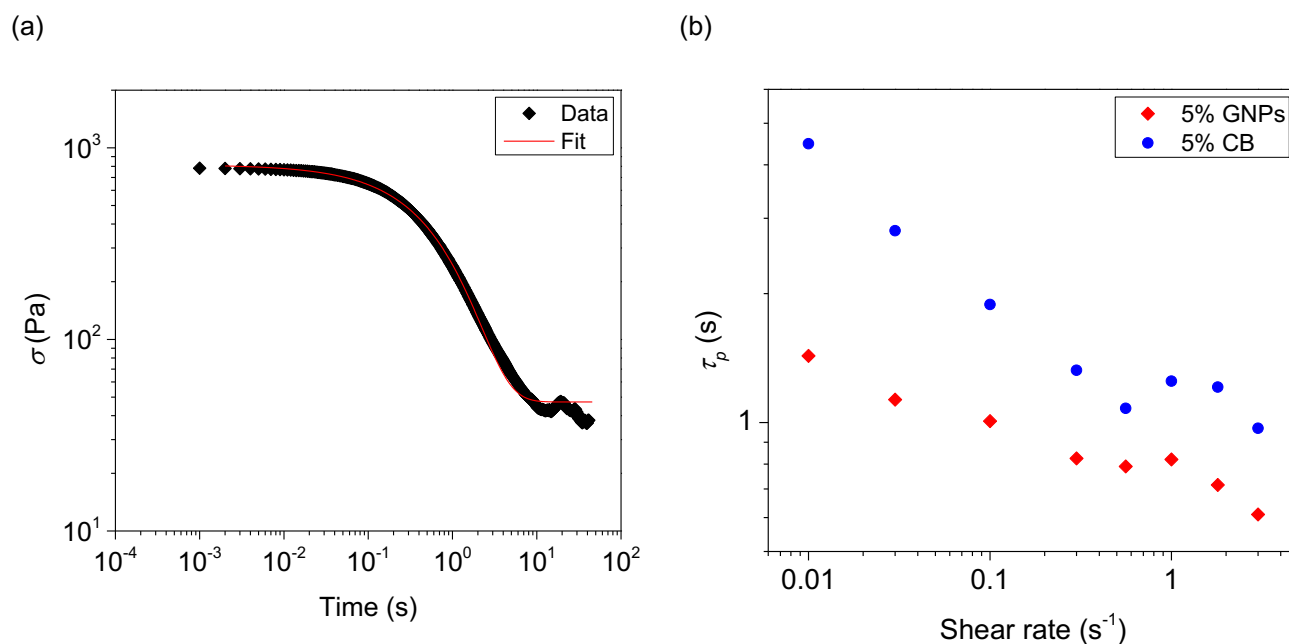
Supporting Information on polymer stress relaxation

(a)

(b)

Figure S4: (a) Stress relaxation of polystyrene + 5 vol. % GNPs following 3 s^{-1} shear at 200 °C, and fit using equation 1 (b) Polymer stress relaxation time, τ_P, for PS + 5% GNPs and PS + 5% CB by vol as a function of shear rate

Having monitored a number of structural changes by impedance and SAXS measurements, we now look at the stress relaxation of the polymer in the composites following cessation of shear. Figure S4a shows the stress relaxation of PS + 5 vol. % GNPs following a shear rate of 3 s^{-1}. The polymer relaxation time, τ_P, can be determined by fitting the data with a stretched exponential decay:

$$\sigma = \sigma_0 e^{\left(\frac{-t}{\tau_P}\right)^{\beta}} + C \tag{1}$$

where σ is the shear stress, σ_0 is the initial stress following shear, t is the time, C is the final plateau value of the stress and β is the stretching exponent. The relaxation time of the polymer is shown as a function of shear rate in Figure S4b. At a shear rate of 0.01 s^{-1} the CB composite has a relaxation time of 4.5 s, while the GNP composite has one of 1.4 s. The longer relaxation time for the CB composite is reflected in its order of magnitude lower impedance, showing a more effective network of filler

particles within the composite. τ_P reduces steadily for both the CB and GNP composites with increasing shear rate, as the filler network is broken and the polymer shear thins.

Supporting Information on composite preparation

Size exclusion chromatography was used to determine the polymer molecular weight. A Viscotek TDA 302 instrument was used with THF as the mobile phase flowing at 1 mL min^{-1}, and the molecular weight calibrated to a polystyrene standard. This gave M_w =273,000 g mol^{-1} and M_n = 113,000 g mol^{-1}
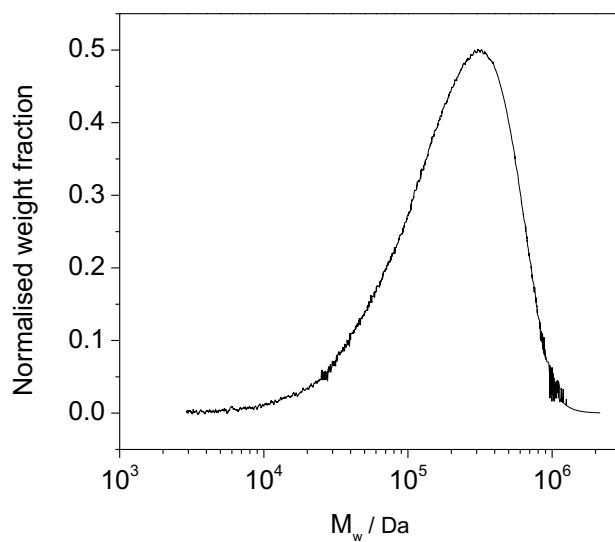
Figure S5: Size exclusion chromatography of polystyrene.

Supporting Information on GNP Percolation

Figure S6 (a) shows the change in the rheological storage modulus, *G'*, as a function of the GNP vol. %, recorded at 200 °C with an oscillating frequency of 0.025 s^{-1} and 1% strain. Monitoring the change in *G'* like this is a useful tool for determining the percolation threshold of the GNPs within the composite. It can be seen that *G'* increases steadily between 0-5 vol. % GNPs, before a more dramatic upturn between 5 and 7.5 vol. %. As the concentration is increased to 10 vol. % *G'* drops again, suggesting a drop in the dispersion quality of the GNPs at this higher concentration and a reduction in the effectiveness of the GNP network throughout the polymer. Such a change, and a consequent decrease in material properties, has previously been shown at high concentrations in other graphene polymer composite systems.[4–7] The upturn in *G'* between 5 and 7.5 vol. % shows that the percolation of the GNPs is around 5 vol. %. This is also shown by the impedance measurements in Figure S6 (b). Here the impedance of the as pressed samples (which were not given a pre-shear treatment following pressing) is measured at room temperature, as a function of the oscillating voltage frequency. The samples were measured by pressing 25 mm diameter discs of the polymer / composite as described in the materials and methods (main text) to a thickness of ~180 μm. The pressed discs were then sputter coated with gold to ensure good electrical contact with the electrodes. The impedance measurements were conducted using a Zurich Instruments HF2IS impedance spectrometer with an HF2TA transimpedance amplifier in the four wire mode. The measurements were run with parallel plate electrodes of 25 mm diameter. Oscillating voltages of 0.5 V and 0.1 V were used for the 0 and 5 vol. % GNP samples respectively. The gain of the amplifier was matched to the requirements of the sample being measured.
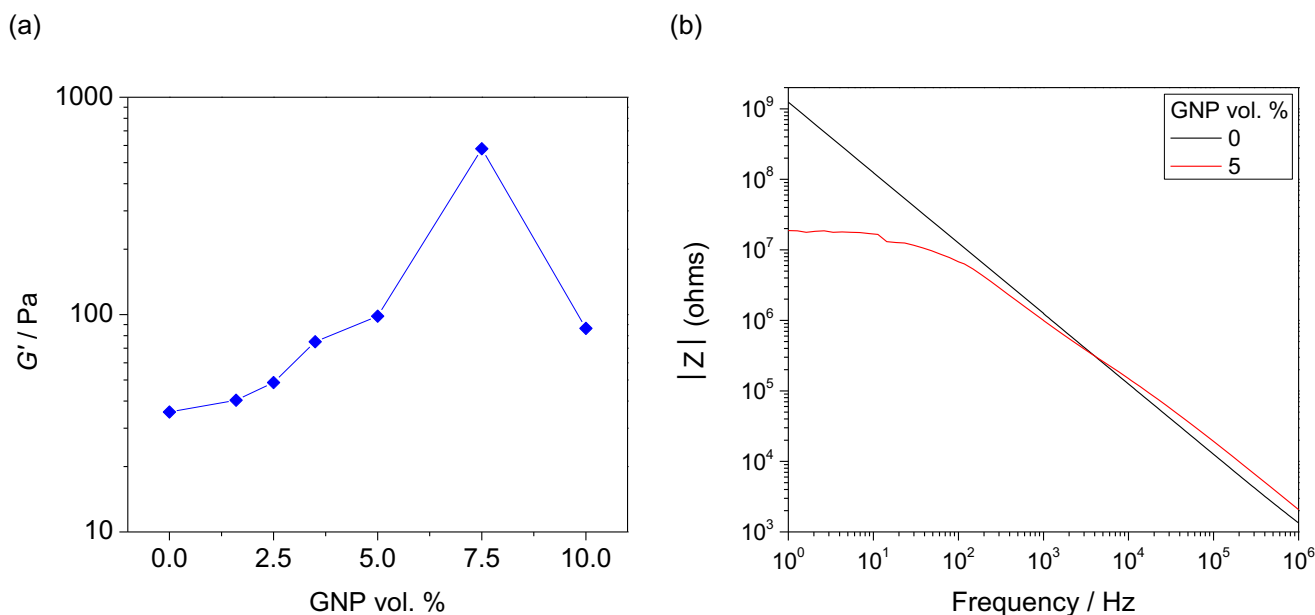
(a)

(b)

Figure S6: (a) Oscillatory rheometry, showing the storage modulus, *G'*, as a function of GNP vol. % at a frequency of 0.025 rad s^{-1} and a temperature of 200 °C; (b) Impedance, |Z| as a function of frequency at room temperature.

The impedance of the pure PS sample decreases linearly on the log-log plot with increasing frequency (Figure S6b). This is characteristic of a capacitive sample, where the capacitive impedance of the sample reduces with increasing frequency. This is as would be expected for a dielectric material. With the addition of GNPs the possibility to form a conducting network exists, which would dramatically change the impedance properties. Here it can be seen that at lower frequencies (< 20 Hz) the impedance plateaus to a maximum value of ~19 Mohms. This shows the onset of a conducting network at 5 vol. % GNPs, though it can be seen that the impedance is three orders of magnitude higher than that observed following pre-shear and shear processing at 0.01 s^{-1} (main text Figure 3). This highlights the effectiveness of low shear rates at developing the network structure of the composite.

Supporting information on impedance under shear

Figure S7a and S7b show the resistance, Z', and reactance, Z'', of the impedance during shear respectively. It can be seen that at shear rates where the impedance of the composite reduces (≤ 0.1 s^{-1}) both the resistance and reactance of the composite reduce. Their ratio, Z''/Z', tan ϕ (Figure S7c), also reduces as the network becomes more conducting under this low shear. At higher shear rates, where the impedance increases, both the resistance and reactance of the network increase. The reactance however increases by a greater amount, and this is shown by the increase in tan ϕ (Figure S7c) to the point where the resistance and reactance of the network are nearly equal at the highest rates. The changes in tan ϕ across the shear rate range studied reflect the structural changes of the GNPs within the composite, highlighting the importance of the processing to the composite properties.
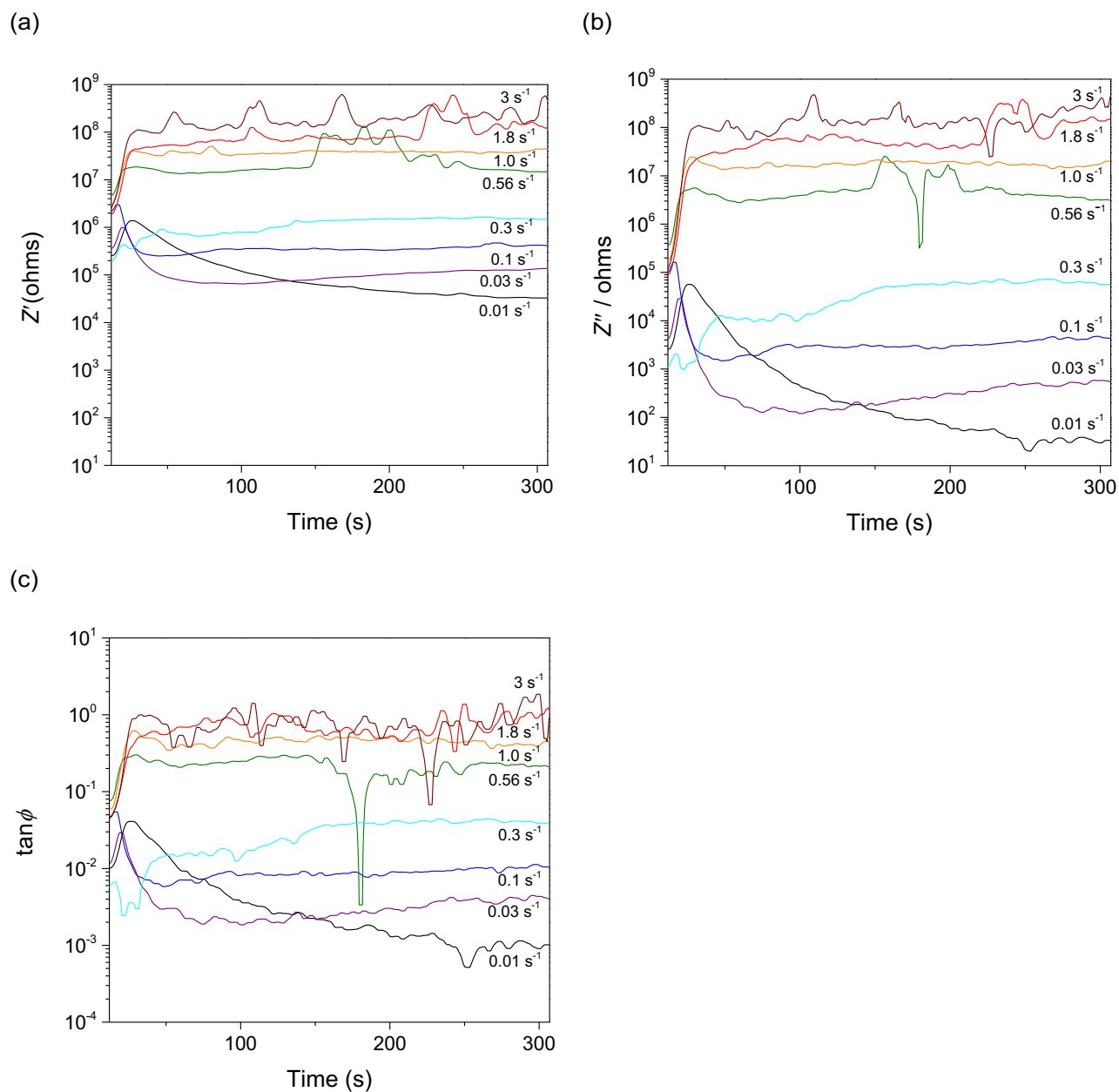
(a)

(b)

(c)

Figure S7: Impedance measurements of polystyrene + 5 vol. % GNPs during shear at rates of 0.01 – 3 s⁻¹: (a) Change in the resistance, *Z′*, (b) Change in the reactance, *Z″*, (c) Change in the ratio of Z″/Z′, tan *ϕ*.

Supplementary references

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