Colloidal Polymer Composites: Are Nano-Fillers Always Better for Improving Mechanical Properties?

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Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was carried out using a commercial instrument (Q1000, TA Instruments, New Castle, DE) to determine the polymer T_g before and after the addition of the coalescing aid (TexanolTM). Approximately 10 mg of a dried film sample was placed in an aluminum pan in nitrogen. The temperature was equilibrated at -30 °C before heating to 120 °C at a ramp rate of 10 °C/min. The temperature was then reduced to -30 °C at a cooling rate of 10 °C/min before re-heating to 120 °C at a ramp rate of 10 °C/min to complete the cycle.

Atomic Force Microscopy (AFM)

AFM images were obtained using an atomic force microscope (NTEGRA, NT-MDT) and analysed using NT-MDT Nova software. An NT-MDT Au-coated cantilever (nominal spring constant of 0.05 N/m) was used. Images were obtained over an area of 2.5 $\mu\text{m} \times 2.5 \mu\text{m}$.

Scanning Electron Microscopy (SEM)

SEM images of composites were obtained using a JEOL JSM-7100F electron microscope. Before imaging, samples were sputter coated with a 2 nm layer of Au. For cross-sectional imaging, films were submerged in liquid nitrogen until frozen then fractured using plastic tweezers. Images were obtained using an accelerating voltage of either 5 or 10 kV. Images of individual calcium carbonate particles were obtained when using an accelerating voltage of 5 kV. Samples were sputter-coated with 2 nm of Au prior to imaging.

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Dynamic Scanning Calorimetry (DSC)

DSC was used to obtain the T_g of P(St-BA-AA) before and after the addition of 10 wt.% TexanolTM plasticizer.

Figure S1. DSC thermograms for P(St-BA-AA) (top) and with P(St-BA-AA) with 10 wt.% TexanolTM plasticizer added before film casting (bottom). The results from the first heating are shown. The second heating found similar values (21.8 °C and 4.6 °C).

The DSC thermogram for P(St-BA-AA) shows a broad transition in the range from approximately 15°C to 28°C, with midpoint values of 21.6°C and 21.8°C, for heating and cooling, respectively. The thermogram for P(St-BA-AA) with 10 wt.% added plasticizer added shows a narrower transition ranging from approximately 0 °C to 10 °C. Mid-point T_g values of 5.5 °C and 4.6 °C were obtained from the first and second heating, respectively. This relatively small decrease in T_g value upon re-heating indicates that no significant amount of plasticizer was lost from the DSC pan.

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Stress-Strain and Failure Analysis

Figure S2 shows representative stress-strain curves of P(St-BA-AA)/calcium carbonate composites at $T = 13\text{ }^{\circ}\text{C}$, which is approximately $8\text{ }^{\circ}\text{C}$ below the T_g of P(St-BA-AA).

Figure S2. Representative stress-strain curves obtained at $T = 13\text{ }^{\circ}\text{C}$ for P(St-BA-AA)/calcium carbonate composites for increasing calcium carbonate volume fractions, ϕ_{CC} : 0.00 (orange), 0.10 (blue), 0.20 (green), 0.30 (red), and 0.35 (purple). Four different particle size ratios, α , are presented: (A) 0.4; (B) 4; (C) 17; and (D) 26.

The data shown in Figure S2 highlight a significant reduction in the average strain at failure for all samples, relative to the results at $30\text{ }^{\circ}\text{C}$, regardless of ϕ_{CC} and α . Figure S2 also shows that the stress at failure is significantly higher at $13\text{ }^{\circ}\text{C}$ than at $30\text{ }^{\circ}\text{C}$. The highest stress at failure is at 25 MPa when $\alpha = 4$ and $\phi_{CC} = 0.10$. With other size ratios and concentrations, most values fall in the range from 10 to 20 MPa.

Figure S3 shows the average strain at failure for P(St-BA-AA)/calcium carbonate composites at $T = 13\text{ }^{\circ}\text{C}$, which is obtained from the analysis of the data in Figure S2.

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Figure S3. Average strain at failure for P(St-BA-AA)/calcium carbonate composites at $T = 13\text{ }^{\circ}\text{C}$ as a function of ϕ_{CC} where $\alpha = 0.4$ (red triangles), $\alpha = 4$ (green diamonds), $\alpha = 17$ (orange squares), and $\alpha = 26$ (blue circles).

When $T = 13^{\circ}\text{C}$, the average strain at failure when $\phi_{CC} = 0$ is 33%, which is considerably lower than the value when $T = 30\text{ }^{\circ}\text{C}$ ($\sim 200\%$) or when $T = 13\text{ }^{\circ}\text{C}$ ($\sim 300\%$) when the sample has been plasticised. As ϕ_{CC} is increased, a sharp decrease in the average strain at failure is observed, and all samples experience failure below 15% strain when $\phi_{CC} = 0.1$. Thus, at $13\text{ }^{\circ}\text{C}$, brittle fracture occurs for all samples when $\phi_{CC} = 0.10$, whereas when $T = 30\text{ }^{\circ}\text{C}$ brittle failure does not occur until $\phi_{CC} = 0.24$ when $\alpha = 0.4$ and until $\phi_{CC} = 0.35$ when $\alpha \geq 4$. When $\alpha = 0.4$, the decrease in the average strain at failure, when $\phi_{CC} = 0.10$ and 0.20 , is greater than when $\alpha \geq 4$. This may be because, although all size ratios introduce the same *volume* of voids (points where fracture may begin), smaller particles introduce a greater number of individual voids. When $\phi_{CC} = 0.30$, all size ratios exhibit a similar average strain at failure of only about 3%.

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Figure S4. Bar chart showing average K values for non-plasticised samples with $T = 30^\circ\text{C}$ (blue shades) and $T = 13^\circ\text{C}$ (red shades) and plasticised samples with $T = 13^\circ\text{C}$ (green shades). Lighter shaded bars (on the left side) show data for $\alpha < 1$. Darker shaded bars (on the right) show data for $\alpha > 1$.

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DMA Data

Figure S5. (A) Storage modulus and (B) loss modulus for P(St-BA-AA)/calcium carbonate composites as a function of temperature where $\phi_{CC} = 0.2$ and for four particle size ratios: $\alpha = 0.4$ (red), $\alpha = 4$ (green), $\alpha = 17$ (orange), $\alpha = 26$ (blue). Data for P(St-BA-AA) without any calcium carbonate ($\phi_{CC} = 0.00$) are shown for comparison (grey).

Figure S6. (A) Storage modulus and (B) loss modulus for P(St-BA-AA)/calcium carbonate composites with 10 wt.% plasticizer as a function of temperature where $\phi_{CC} = 0.20$ and for four particle size ratios: $\alpha = 0.4$ (red), $\alpha = 4$ (green), $\alpha = 17$ (orange), $\alpha = 26$ (blue). Data for P(St-BA-AA) without any calcium carbonate ($\phi_{CC} = 0.00$) are shown for comparison (grey).

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Figure S7. (A) Storage modulus and (B) loss modulus for P(St-BA-AA)/calcium carbonate composites with 10 wt.% plasticizer as a function of temperature where $\phi_{CC} = 0.35$ and for four particle size ratios: $\alpha = 0.4$ (red), $\alpha = 4$ (green), $\alpha = 17$ (orange), $\alpha = 26$ (blue). Data for P(St-BA-AA) without any calcium carbonate ($\phi_{CC} = 0.00$) are shown for comparison (grey).

Examining the loss moduli in Figures S5 and S6, it is apparent that the peak, which occurs at the polymer's T_g , varies slightly in its position along the x-axis (temperature); this is not the case in Figure S4 (without any added plasticizer). This variability occurs only in samples containing the plasticizer; therefore, it is a strong indication that some plasticizer is lost from the sample after the films have been cast. It is most likely that some plasticizer is evaporated when heating under the IR lamp, as it is a volatile substance.

Creep Data

Figure S8. Creep results for P(St-BA-AA)/calcium carbonate composites, obtained at $T = 30$ °C, where (A) $\alpha = 26$ and (B) $\alpha = 0.4$. The experiments studied four different volume fractions of calcium carbonate: $\phi_{CC} = 0.00$ (grey); $\phi_{CC} = 0.10$ (green); $\phi_{CC} = 0.20$ (orange); and $\phi_{CC} = 0.30$ (red).

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For both size ratios, it is clear that as ϕ_{CC} is increased, the amount of strain is lower and the rate of strain becomes slower. It is also apparent that there is less strain and a slower strain rate when $\alpha = 0.4$ compared to when $\alpha = 26$ for a particular value of ϕ_{CC} .

Figure S9. Creep results for P(St-BA-AA)/calcium carbonate composites, obtained at $T = 13$ °C, when (A) $\alpha = 26$ and (B) $\alpha = 0.4$. $\phi_{CC} = 0.00$ (grey), $\phi_{CC} = 0.10$ (green), $\phi_{CC} = 0.20$ (orange), and $\phi_{CC} = 0.30$ (red).

For non-plasticised samples, at $T = 13$ °C (below the T_g of P(St-BA-AA)), very slow strain is exhibited in Figure S8, even when $\phi_{CC} = 0.0$, because the polymer is glassy below its T_g . As ϕ_{CC} is incrementally increased, the strain slows further. Comparing Figure S8A and Figure S8B, there appears to be little effect of particle size ratio. The total strain is very low for each.

Figure S10. Creep results for P(St-BA-AA)/calcium carbonate composites with 10 wt.% plasticizer, obtained at $T = 13$ °C, where (A) $\alpha = 26$ and (B) $\alpha = 0.4$. $\phi_{CC} = 0.00$ (grey), $\phi_{CC} = 0.10$ (green), $\phi_{CC} = 0.20$ (orange), and $\phi_{CC} = 0.30$ (red).

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The creep behavior of plasticized samples at $T = 13\text{ }^{\circ}\text{C}$, shown in Figure S9, is remarkably similar to that of non-plasticised samples at $T = 30\text{ }^{\circ}\text{C}$ (in the rubbery state). Again, incremental increases in ϕ_{CC} result in a slowing of the strain rate for both size ratios. Importantly, an increase in ϕ_{CC} results in a slower strain rate and lower amount of strain when $\alpha = 0.4$ compared to when $\alpha = 26$.

Creep Enhancement

Figure S11. Enhancement factor of the viscoelastic components of the Burger's model, E_K (left column) and η_K (right column), for P(St-BA-AA)/calcium carbonate composites as a function of ϕ_{CC} for non-plasticised samples at $T = 30\text{ }^{\circ}\text{C}$ (top row) and plasticised samples at $T = 13\text{ }^{\circ}\text{C}$ (bottom row). Data are presented for two different size ratios: $\alpha = 0.4$ (red) and $\alpha = 26$ (blue).

Both of the viscoelastic parameters, obtained from fitting the Burger's model to the creep data, are presented in Figure S10. They are presented as enhancement factors, which are found by dividing by the value obtained from the polymer without any calcium carbonate addition. Both parameters increase with increasing ϕ_{CC} , which are consistent with the enhancements for the Hookean elastic and Newtonian viscous components, and are presented in the main text. For instance, significant enhancement for both parameters is exhibited at $\phi_{CC} = 0.2$ when $\alpha = 0.4$, while the sample in which $\alpha = 26$ shows very little enhancement. The main text presents the structural arguments as to why this difference between the size ratios occurs.