A Colloidal Model to describe the Effects of Mixing Time on Filler Dispersion in Industrial Nanocomposites

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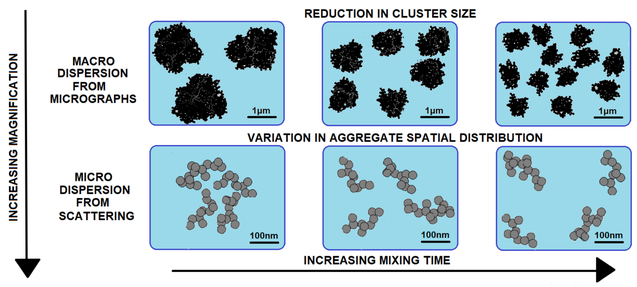
Abstract

- Properties of industrially relevant nanocomposites depend on the degree of filler dispersion under high-shear mixing.
- Conventionally, dispersion is quantified through an index based on the reduction in micron-scale agglomerate size observed in micrographs and bulk electrical conductivity measurements.
- An alternate nano-scale dispersion technique based on x-ray scattering has been proposed.[1]
- The impact of mixing time on dispersion is investigated taking advantage of the van der Waals equation to describe excluded volume and interaction energy in the dispersion.[2]
- An analogy is made between the thermally driven true colloidal dispersions and kinetically accumulated strain in nanocomposites.

Overview



Methods

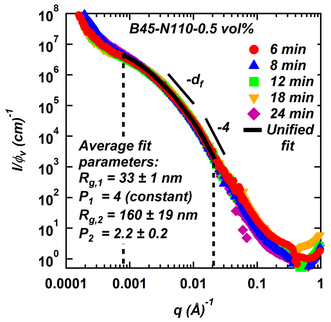
- Commercial PBD (*Mooney Viscosity* – 38, 45, 54 M.U.) and SBR (*Mooney Viscosity* – 50, 62, 80 M.U) milled with 6PPD (antioxidant) and varying amount of carbon black reinforcing filler (Vulcan 8 and Vulcan 3) for 6, 8, 12, 18 and 24 mins at 130 °C and 60 rpm.
- Scattering from ~1.2 mm (thk.) flat samples measured at Advanced Photon Source, Argonne National Laboratory using the ultra-small-angle X-ray scattering (USAXS) facility located at the 9 ID beam line, station C.
- Micrographs obtained through TEM in STEM mode from ~80 nm thin sections cryo-cooled below T_g of the nanocomposites

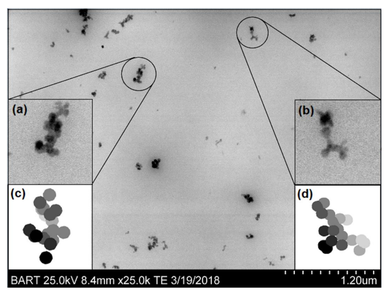
Results

Ultra-small angle X-ray scattering

- Structural parameters under dilute filler conditions are computed from the Unified fit.[3,4]

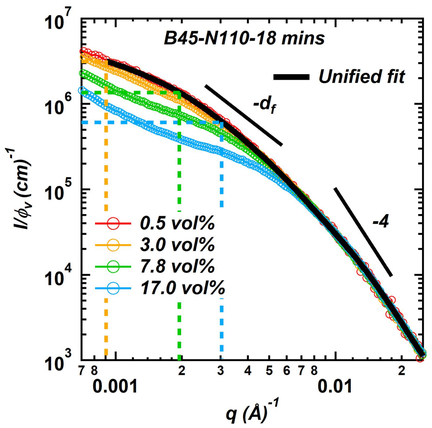
$$I_0(q) = \sum_0^3 \left\{ G_i \exp\left(\frac{-q^2 R_{g,i}^2}{3}\right) + \exp\left(\frac{-q^2 R_{g,i+1}^2}{3}\right) B_i (q_i^*)^{-P_i} \right\} \qquad q_i^* = \frac{q}{\left(\mathrm{erf}\left\{\frac{kqR_{g,i}}{\sqrt{6}}\right\}\right)^3}$$





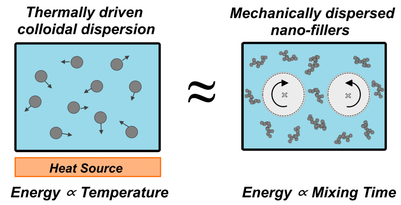
- Under semi-dilute filler conditions, structural features are screened, and the extent of screening is approximated by RPA.[5,6]

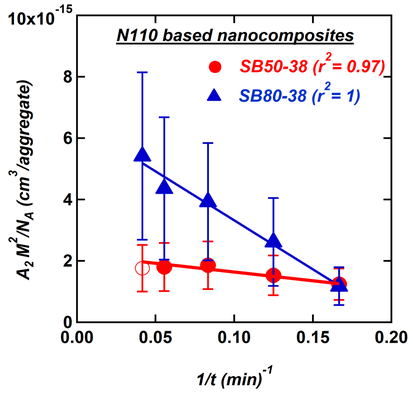
$$\left\{\frac{I(q,\phi_f)}{\phi_f}\right\}^{-1} = \left\{\frac{I(q,\phi_{f,0})}{\phi_{f,0}}\right\}^{-1} + \nu\phi_f$$



Kinetic van der Waals model

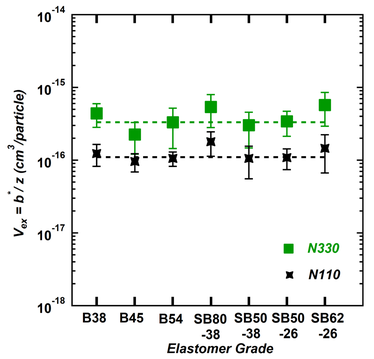
$$A_2 = \frac{\nu\langle\Delta\rho^2\rangle}{2N_A\rho_f^2}^6 \qquad A_2(t) = \frac{N_A}{M^2}\left(b^* - \frac{a^*}{t}\right)^2$$

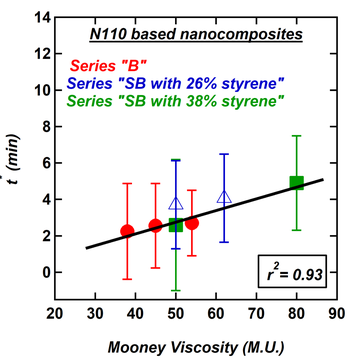




Conclusion

- The excluded volume depends only on the filler type and seems insensitive to bound rubber.
- The interaction energy is strongly dependent on viscosity and polymer chemistry.
- The wetting time for nano-scale incorporation of elastomer into filler can be predicted.





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Acknowledgements

This work was supported by the National Science Foundation through grants CMMI-1635865 and CMMI-1636036. This research used resources of the Advanced Photon Source under Contract No. DE-AC02-06CH11357. Data were collected at the X-ray Science Division at the Advanced Photon Source, Argonne National Laboratory. The authors are extremely grateful to Jan Ilavsky and Ivan Kuzmenko for their unwavering support during the course of the scattering experiments at beamline 9 ID-C.

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