Directed Assembly of Nanoparticles at High Loadings in Ordered Polymer Systems

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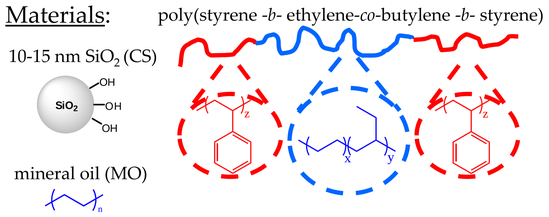
Introduction

Polymer nanocomposites have a wide range of attractive characteristics, ranging from significantly improved mechanical properties to functional properties resulting from the combination of nanoparticles and microphase separated polymer morphologies. In nearly all the work to date, researchers have focused their efforts on creating dispersions of very low volume fractions of the filler. Recent studies have focused on creating very exact dispersions of nanoparticles. This approach is challenging because of fundamental intermolecular forces that drive nanoparticles to aggregate, the expense of specialty additives, specific chemistries tailored for a single systems, thin film sample geometries, and fabrication methods requiring many steps. All of these parameters represent significant challenges to process scale-up and materials development.

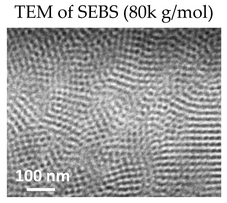
In this program, we are studying routes toward the fabrication of bulk polymer nanocomposites in which nanoparticle additives are allowed to flocculate by design. Such agglomerates will offer a mixture of properties, retaining some of the unique characteristics of NP additives, while offering some properties akin to those provided by traditional, microscopic filler particles. Our goal is the fabrication of a material in which dispersed NPs have been condensed into an agglomerate, in a microscopic morphology templated by a microphase separated polymer.

Experimental Procedure

Materials: poly(styrene -*b*- ethylene-*co*-butylene -*b*- styrene)



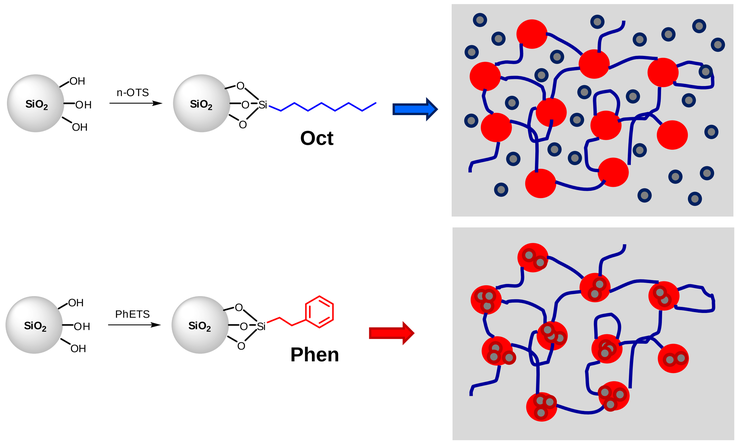
TEM of SEBS (80k g/mol)



Processing: Bulk mixtures compounded with increasing content of functionalized CS (1, 5, 10 vol %) and/or MO (0 – 80 vol %) using a twin screw extruder. $T_{extr.}$ = 110 – 180 °C per MO content. All samples were annealed at 130 °C for 48 h.

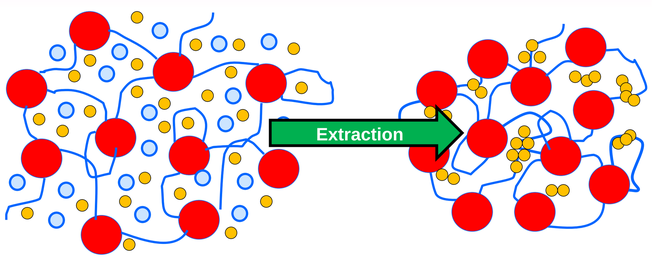
Approach I: Thermodynamics

- Non-specific / non-associating interactions
- Strongly miscible / immiscible polymer / ligand combinations
- Skew polymer composition to accommodate NP in desired morphology

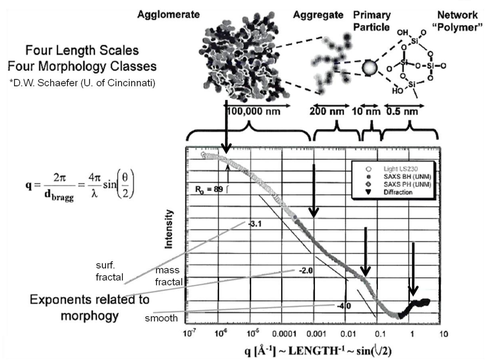


Approach II: Solvent Extraction

- Mid-block selective diluent swells polymer during processing
- Compound NP into swollen polymer followed by solvent extraction
- Possible hierarchical order with solvent directed artificially high loadings



I. Effect of CS on Morphology (USAXS)

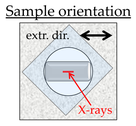


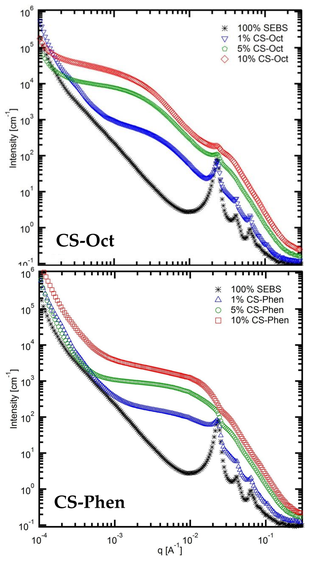
$$q = \frac{2\pi}{d_{bragg}} = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

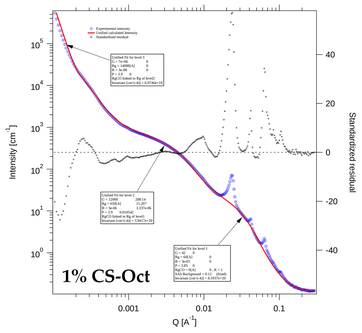
Unified Fit: multilevel Guinier + Porod

$$I(q) = \sum_i A_i e^{\left(\frac{-q^2 R_{gi}^2}{3}\right)} + B_i \left[\frac{erf\left(\frac{qR_{gi}}{\sqrt{6}}\right)^3}{q}\right]^{P_i}$$

Sample orientation





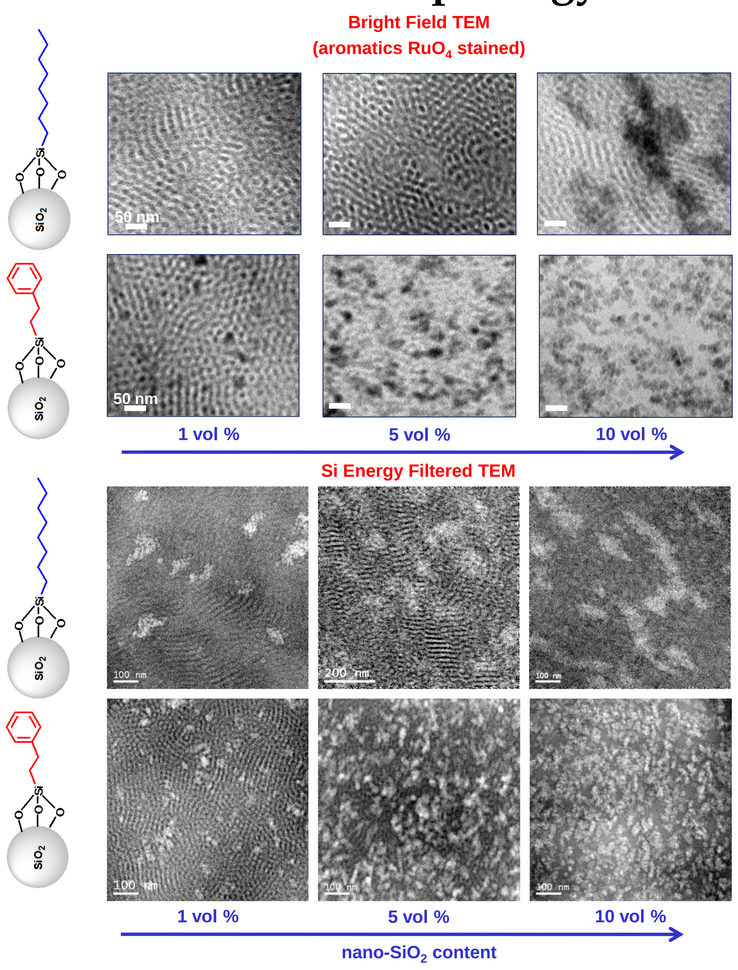


- BCP characteristic peaks and primary particle scattering from CS overlap at high *q*.
- Guinier knee at low *q* indicates larger aggregates of CS-Oct than CS-Phen in SEBS.
- Orthogonal scans detected anisotropy in BCP morphology but little effect on aggregates.

*assume spherical aggregates & particles: $R_{gi}^2 = \frac{3}{5}R^2$

	CS content (vol %)	low q Porod exponent	low q R_g (Å)	**aggregate size d (nm)**	high q Porod exponent	high q R_g (Å)	**particle size d (nm)**
CS-Oct	1	3.57	650	**168**	3.89	60	**15**
	5	3.90	700	**181**	3.92	59	**15**
	10	3.90	800	**207**	3.63	53	**14**
CS-Phen	1	3.90	180	**46**	3.85	55	**14**
	5	3.85	200	**52**	3.87	53	**14**
	10	3.75	125	**32**	3.84	57	**15**

I. Effect of CS on Morphology (TEM)



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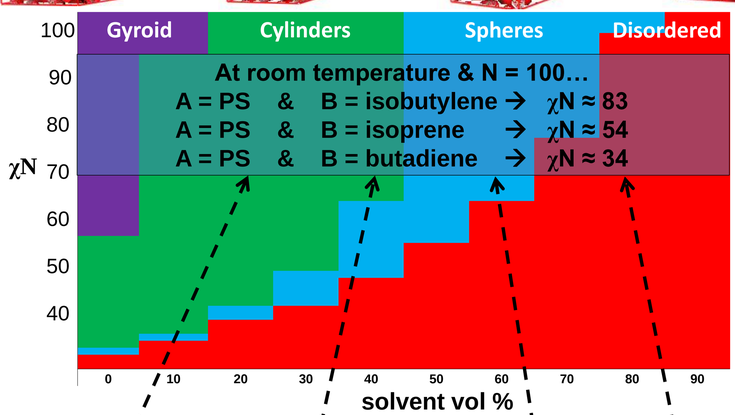
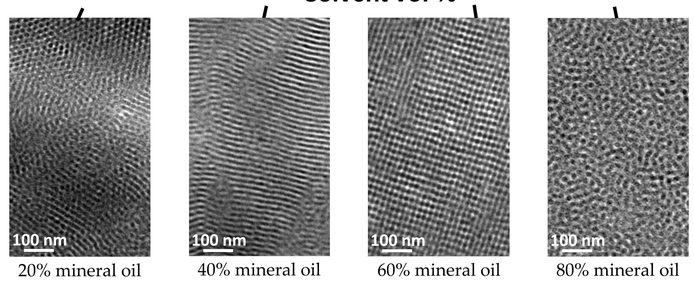
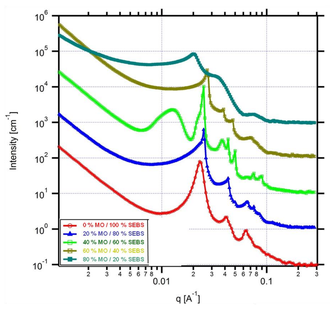
II. Effect of Mineral Oil on Morphology



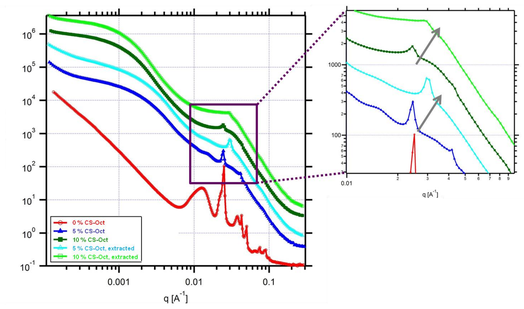


sample (MO/SEBS)	Mesoscale prediction	TEM observed	SAXS observed	lattice par. (nm)	q/q* Bragg maxima
0/100	gyroid	cylinders	cylinders	29.3	1, √3, √7, √9
20/80	cylinders	cylinders	cylinders	29.1	1, √3, √4, √7, √9, √12
40/60	cylinders	cylinders	cyl. & micellar?	29.1	1, √3, √4, √7, √9, √12, √16
60/40	spheres	spheres	BCC spheres	32.9	1, √2, √3, √8
80/20	disordered	micellar	micellar	---	---

USAXS of MO/SEBS Gels



Effect of Extraction on 40/60 MO/SEBS + CS-Oct)



Conclusions

- Surface miscibility based on ligand chemistry heavily impacts the extent of agglomeration and distribution of nano-SiO_2 in SEBS.
- Increased diluent fraction varies the gel morphology as confirmed by agreement between mesoscale modeling and TEM/USAXS.
- Diluent extraction decreases BCP domain spacing with negligible changes in the aggregation state due to minimal inclusion of the NP into the mid-block.

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