

## Introduction

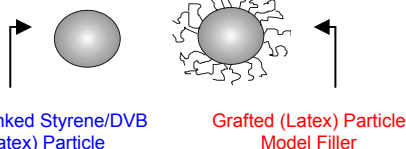
Commercial plastics, coatings, cements, and rubbers are often filled with solid particles to enhance their mechanical properties, or to reduce costs. The properties of these materials depend primarily on interactions between the matrix and filler particles.<sup>1</sup> Wolff et al.<sup>1</sup> indicated that while interparticle interactions are a dominant factor in some filled systems (e.g. silica-filled hydrocarbon-based rubbers), particle-matrix interactions may be more important in other cases (e.g. carbon black-filled rubbers). Although a lot of research has been carried out to investigate the effect of filler surface treatment on the rheological behavior of filled polymers, in general most studies have used industrial fillers such as silica, mica, calcium carbonate, and carbon black. These system form concentrated suspensions with poorly characterized interactions between the filler particles and the polymer matrix. In this research, we sought to elucidate the rheological implications of particle-matrix interactions in a polyisoprene rubber matrix filled with a low-density rubber-compatible model filler.

## Model Filler VS. Carbon Black

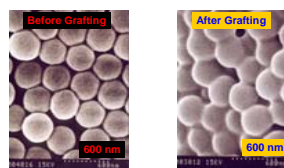
- Carbon black used as filler in the rubber industry
  - High-modulus solid particles
  - Storage modulus, abrasion resistance increased
  - High-density material (ca. 3.5 g/mL)
- Can a low-density filler be used instead?
  - High modulus required
  - Easy dispersion in rubber matrix
- Model rubber fillers
  - Control over size, particle rigidity, particle-rubber matrix interactions
  - Cross-linked latex particles grafted with polyisoprene chains used as model rubber fillers
  - Low-density material ( $\rho = 1 \text{ g/mL}$ )

## Model Filler

- Cross-linked styrene/DVB polymerization<sup>2</sup>
- Diameter ~400 nm, ~5.5% w/w divinylbenzene (DVB) content
- Functionalized by Friedel-Crafts acetylation<sup>3</sup>
- Grafted with linear polyisoprene chains<sup>3</sup> [ $M_w = 2 \times 10^3 \text{ g/mole}$  (2K),  $5 \times 10^3 \text{ g/mole}$  (5K) and  $3 \times 10^4 \text{ g/mole}$  (30K)]



## SEM Images



- Spherical particle morphology – Monodispersed with ~400 nm diameter before grafting
- Spherical particles “sticky” after grafting – Due to entanglement of the PIP chains on adjacent particles – No cross-linking of the PIP side chains
- Particles size increased to ~450 nm

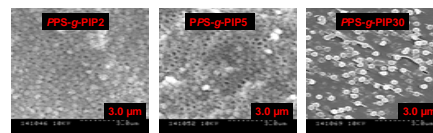
## Blending

Samples		PS Particles (g)	PIP250 Matrix (g)
<b>Blends Set-A</b>	PPS-g-PIP2	0.68	1.00
	Acetylation PPS-g-PIP5	0.71	1.00
	5% PPS-g-PIP30	0.72	1.00
<b>Blends Set-B</b>	PPS-g-PIP2	0.86	1.00
	Acetylation PPS-g-PIP5	0.85	1.00
	30% PPS-g-PIP30	0.94	1.00

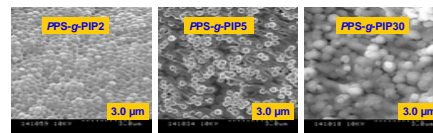
- Grafted particles :  $d = 450 \text{ nm}$ , PS volume fraction  $\phi = 0.35$

## Freeze Fracture Morphology of Blends by SEM

**Blends Set-A**  
[Acet. 5%]



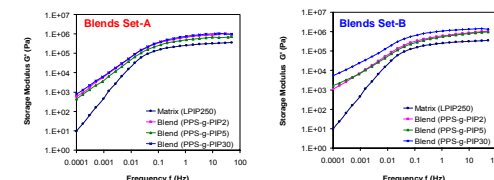
**Blends Set-B**  
[Acet. 30%]



- Particles uniformly dispersed within the matrix in all cases
- Set-A: No significant difference in size vs. isolated particles – no significant entanglement of side chains with the matrix
- Set-B: Particles with 30K side chains larger, presumably due to better entanglement of side chains with the matrix

## Rheology of the Blends

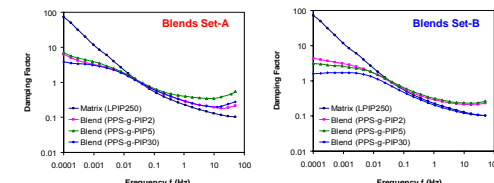
### Dependence of Storage Modulus ( $G'$ ) on Frequency ( $f$ )



Samples		Storage Modulus $G'$ (Pa) @ $f = 10 \text{ Hz}$	Increase (Fold)
<b>Matrix</b>	LPIP250	$3.2 \times 10^5$	—
<b>Blends Set-A</b>	PPS-g-PIP2	$8.5 \times 10^5$	2.7
	Acetylation PPS-g-PIP5	$6.2 \times 10^5$	2.0
	5% PPS-g-PIP30	$9.6 \times 10^5$	3.0
<b>Blends Set-B</b>	PPS-g-PIP2	$7.9 \times 10^5$	2.5
	Acetylation PPS-g-PIP5	$7.3 \times 10^5$	2.3
	30% PPS-g-PIP30	$1.2 \times 10^6$	3.7

- All blends exhibited increased storage modulus
- From the Guth-Smallwood equation  $G = G_0(1 + 2.5\phi + 14.1\phi^2)$ , 3.6 fold increase in  $G$  predicted for  $\phi = 0.35$
- Filler-matrix interactions better for 30% than 5% acetylation
- Filler matrix interactions decrease in the order  $30K > 5K \approx 2K$

### Dependence of Damping Factor ( $\tan \delta$ ) on Frequency ( $f$ )



- Significant decrease in damping factor for all blends
- Change most prominent for particles based on 30% acetylation
- Decreased damping, indicative of lower heat dissipation, is interesting for applications where heat generation is undesirable (e.g. tires)

## Related Publications

- Wolff, S.; Wang, M. *Rubber Chem. Technol.* **1992**, *65*, 329
- Ding, Z.Y.; Ma, S.; Kriz, D.; Aklonis, J.; Salovey, R. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1992**, *30*, 1189
- Li, J.; Gauthier, M. *Macromolecules* **2001**, *34*, 8198