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Butadiene as Exfoliation Medium (fully supported by PRF grant) Clay/polymer systems are ideal model materials to study exfoliation. Exfoliation can be achieved through mild thermal annealing in the presence of a low-molecular-weight, hydroxyl-terminated “telechelic” polybutadiene (tPB) matrix. However, the specific role of the hydroxyl groups, their placement, and polymer mobility in the intercalation/exfoliation process still remains unclear. In this study, these matrix parameters were evaluated by replacing the tPB with randomly functionalized polybutadienes (rPBs) of increasing hydroxyl group densities. The rPB was synthesized by covalently grafting mercaptoethanol to the PB backbone, and its ability to exfoliate organically modified montmorillonite clay was evaluated. While some functional groups are required to exfoliate the clay, it was found that exfoliation proceeds successfully regardless of the number of hydroxyl groups or their location on the PB backbone. Instead, it was found that polymer mobility played a key role in the extent of exfoliation. As the grafting concentration was increased, the rPB molecular mobility decreased because of its higher glass transition temperature (T_g). A detailed analysis of their linear viscoelastic properties was able to decouple the two phenomena, change in mobility and effectiveness of polymer–clay interaction. Nanocomposites using highly grafted polymers showed a decrease in their connectivity because of reduced exfoliation of the clay. This was overcome by introducing a highly grafted and highly mobile rPB with a low T_g (low vinyl content), which successfully exfoliated the clay. The combined results suggest that intercalation can be achieved through favorable polymer–clay interactions, whereas exfoliation can proceed beyond intercalation only when there is enough polymer mobility. Published as Tanna VA, Enokida JS, Coughlin EB, Winter HH* (2019) functionalized polybutadiene for clay/polymer nanocomposite fabrication. *Macromolecules* 52(16): 6135-6141.

2D Zeolites (partially supported by PRF grant) Polybutadiene-zeolite interactions were used to exfoliate a variety of 2DZ precursors, modified with structuring agent (OSDA), and to test the resulting polymer/zeolite composite rheologically. It was found that the presence of aluminum in the framework and the nature of the OSDA in the interlayer spacing play important roles in the preparation of the exfoliation process. We report the disassembly of an ITQ-1 layered precursor, a pure silica analogue of our previously studied precursor MCM-22 (S. Sabnis et al., *Chem Commun* 2017, 53:7011–14). ITQ-1 zeolites were suspended in commercially available liquid polybutadiene at room using low shear forces. The objective was to find processing conditions which minimize the damage to the lateral size of the ITQ-1 nanosheets. ITQ-1 nanosheets with a high aspect ratio were obtained. They formed a stable suspension in an organic solvent. The results will be reported in a follow-up publication, which is practically ready for submission.

Ionomer Polymer Matrix (partially supported by PRF grant) Ionomers are ideal matrix materials for charged 2D chips. We studied the role of counterion sterics on the structure and dynamics of a low glass transition temperature, amorphous poly(isoprene-*ran*-styrenesulfonate) copolymer was investigated using a series of symmetric, tetraalkylammonium counterions with methyl (TMA), ethyl (TEA), propyl (TPA), and butyl (TBA) pendent groups in addition to a sodium (Na) control. The T_α relaxation of the copolymers revealed a rigid isoprene fraction, associated with the ion clusters, and a mobile isoprene matrix fraction. Copolymers with larger counterions exhibited an increase in the dynamic moduli at high frequency and a decrease in the dynamic moduli at lower frequencies in addition to possessing faster molecular dynamics. These two observations are attributed to an increased incorporation of ionic groups into the isoprene matrix and a screening of the dipole-dipole interactions. Reference: JS Enokida et al., *Macromolecules* 2019, under review