Mixed Matrix Materials comprised of inorganic nanoparticle (NP) filler and organic polymer have been extensively researched for their enhanced mechanical properties compared to the pure polymer for their ability to slow chain aging, though typically have reduced gas transport capabilities. We report here a new polymer/NP composite construct using NPs grafted with polymer chains. Mixed matrix systems incorporating grafted NPs (GNPs) show anomalous and exciting transport and mechanical characteristics.

CO_2 and CH_4 gas permeation measurements interestingly show that permeability is elevated by up to 10 times that of the pure polymer, and varies strongly with the graft molecular weight and areal density of grafted chains. Experimental measurements and computer simulations of the GNPs show that the free volume accessible for gas transport in these materials is elevated compared to the pure polymer and is strongly correlated with the observed permeability increases. This free volume increase can be reliably and repeatedly controlled by altering the grafted polymer properties, creating a new design platform for tunable membrane materials. The design of optimal GNPs is also intrinsically linked to the relative sizes of the NP core and polymer brush properties. Additionally, the presence of the NPs serves to mechanically strengthen the grafted polymer as well as strongly suppress deleterious physical aging of the chains.

The grafting chemistry can be extended to incorporate existing high performance rubbery and glassy polymers to create superior membrane constructs. Other more advanced architectures, such as the addition of a matrix polymer, substantially alter the CO_2/CH_4 permselectivity in the resulting material both by introducing new NP structures and potential heterogenous diffusion. Evidently the enhanced gas transport changes in these GNPs offer a novel platform for the rational design of both rubbery and glassy membranes with tunable free volume and permeability/selectivity exceeding the current best for many applications.

