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Chemical and Temperature Effects on Diffusion in a Model Polymer/Nanoparticle Composite<sup>1</sup> DUSTIN JANES, U.S. Food and Drug Administration, CHRISTOPHER DURNING, Columbia University — Polymers and inks used in medical devices may be strengthened with nanoparticle fillers, so an understanding of how they may affect the release of residuals and additives via diffusion will help modernize biocompatibility testing. Transport of small molecules in polymers with increasing volume fraction of impermeable nanoparticles is often poorly predicted by the simple Maxwell model for heterogeneous media. In this presentation we will examine two diffusant classes, only one of which possesses hydrogen bonding interactions with the nanoparticle surface. Since similar reductions in mutual diffusion coefficients were observed in both cases we attribute the enhancement of the "blocking effect" in nanocomposites to a reduction in polymer mobility in the interfacial volume near the nanoparticle. The temperature and penetrant concentration dependence of the diffusion coefficients were examined in the context of a Vrentas-Duda free volume model that includes a thermally activated prefactor. While data obtained for rubbery poly(methyl acrylate) clearly obeys the expected Arrhenius scaling with  $E_A = 11 \text{ kJ/mol}$ , results for films containing d = 14 nmspherical silica nanoparticles do not, providing more evidence that polymer free volume is perturbed in unexpected ways even for conceptually simple systems.

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