



## Ph.D. DISSERTATION DEFENSE

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**Degree:** Doctor of Philosophy  
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**Title:** **Mechanical Properties of Polymer Nanocomposites with Topologically Constrained Chains**  
**Chairperson:** **Dr. Pinar Akcora**, Department of Chemical Engineering and Materials Science, Charles V. Schaefer, Jr. School of Engineering & Science  
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### ABSTRACT

Polymer entanglements play a critical role in influencing the viscoelastic properties of polymer nanocomposites. Factors such as crosslinking, chain adsorption onto nanoparticles, and chain architectures (such as linear and loop grafting) dictate the degree of entanglement within these composite materials. This thesis aims to explore the influence of entanglements on the viscoelastic properties of three systems with different topological constraints. In the first system, we synthesized entangled and unentangled composite networks to elucidate the impact of both entanglements and particle loadings on the reinforcement. The study demonstrated that the elastic moduli of crosslinked composite with entangled chains remained unaffected with particle loading, whereas both the elastic moduli and crosslinking degree were enhanced with increasing particle loading in unentangled crosslinked composite. In the crosslinked composite system with entanglements, the complete recovery of modulus was observed after large deformation and the unentangled composite network did not recover its initial moduli. This comparison between the two crosslinked composites implies that entangled networks can sustain large deformation, and nanoparticles do not disrupt the chain relaxations of the entangled network, even at high particle loadings. The second composite system comprises the poly(methyl acrylate) matrix with dispersed bare nanoparticles and plasticizer. It is expected that the plasticizer will impede the topological constraints of adsorbed chains on nanoparticles. However, the results indicated that the plasticizer does not alter the chain dilution scaling in the composites and it follows the same scaling law of the neat polymer. The plasticizer did not change the polymer adsorption or particle dispersion in attractive polymer composites. In the third system, polymer loop-grafted chains were engineered to explore intricate chain topologies and their effects. Looping the linear grafted chains influence the interfacial blending with the matrix chains and mechanical properties of polymer nanocomposites. The rheological behavior of the loop composite displayed a network-like behavior, arising from the threading of linear matrix and loop-grafted chains. These interpenetrated networks exhibit a low critical strain, sustain large deformation and can recover their initial elastic modulus unlike the linear-grafted and bare particle nanocomposites. Our results demonstrate the loop architectures exhibit good interfacial mixing, elasticity and modulus recovery to large deformation as needed in adhesive materials.