

TAILORED SURFACE REACTIVITY OF CARBON NANOTUBES FOR POLYMERIC COMPOSITE APPLICATIONS

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INTRODUCTION

Shape memory polymers (SMPs) are functional polymers, which find applications in a broad range of temperature sensing elements and biological micro-electro-mechanical systems (MEMS). These polymers are capable of fixing a transient shape and recovering to their original shape after a series of thermo-mechanical treatments [Kim 1996]. These materials are generally thermoplastic segmented polyurethanes with soft segments, usually formed from a polyether macroglycol, and with hard segments formed by diisocyanate with a low molecular mass diol. The reinforcement of SMPs using nanofillers represents a novel approach of enhancing the performance of these materials. The incorporation of these fillers into SMPs can produce performance enhancements (particularly elastic modulus) at small nanoparticle loadings (~1-2 wt %). An optimal performance of nanofiller-polymer nanocomposites requires uniform dispersion of filler in polymers and good interfacial adhesion. The addition of nanofillers like carbon nanotubes (CNT) and cellulose nanofibers (CNF) allows for the production of stiffer materials with deformation capacity comparable to that of the unfilled polymer and enhanced recovery force.

During the first year of this proposal we prepared modified carbon nanotubes and cellulose nanofibers. They were dispersed in a segmented polyurethane formulation in order to obtain composite films by casting and to produce composite fibers by extrusion. The shape memory behavior and thermal and mechanical properties of the films and fibers were evaluated.

RESULTS AND DISCUSSION

The following lists the main accomplishments generated during the development of the proposed work:

1) Nanofillers preparation.

The nanofillers, multiwall carbon nanotubes (CNT) and cellulose nanofibers (CNF), were surface modified. The nanostructures were analyzed using standard and advanced techniques such as polarized light microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM).

2) Preparation and thermal characterization of nanoreinforced/PU films

Samples of an unreinforced commercial polyurethane matrix (Huntsman) along with samples containing 1 and 2wt% nanofillers were prepared. After the addition of the

nanofiller to the polyurethane solution, a speedmixer (DAC 150) was used to aid in dispersion.

Thermal characterization of the samples was performed and the melting temperatures and enthalpies of the hard and soft domains were calculated.

3) **Rheological characterization**

Rheological experiments were used to investigate the percolation composition of the reinforced polyurethane matrix. Samples with more than 1 wt% CNF and 2wt% CNT exhibit solid-like viscoelastic behavior.

4) **Mechanical Properties**

Tensile tests of the samples with and without reinforcement were performed. The Young's modulus (E), the yield stress (σ_y), and the elongation at break (ϵ_b) for the samples were calculated. The addition of 1 wt% cellulose nanocrystals produced a 70% increase in the Young's modulus over the neat system. This improvement can be attributed to the polar groups in the filler walls that are capable of interacting with the PU matrix. The strength also increased with filler content, reaching a maximum value of 2.00 ± 0.76 MPa at 0.5 wt% cellulose crystals. Similar to cellulose, the addition of 1 wt% CNT-MDI produced a 51% increase in the Young's modulus over the neat system. The strength increased dramatically over that of the neat system with the increase of nanofillers, reaching a maximum value of 6.58 ± 0.53 MPa at 1 wt% CNT-MDI. All the nanocomposite strengths are higher than that of the unreinforced PU. So, it can be estimated that the nanofiller acts as a reinforcing material with good fiber-matrix interface.

5) **Shape memory behavior**

The shape memory characteristics for the reinforced samples were investigated. Shape fixity and recovery ratio were calculated.

For the CNTs samples, the recovery ratio decreased with increasing number of cycles, while the fixity increased (or remained largely unaffected) for both, composites and neat PU. On the other hand, the fixity and recovery ratios did not vary significantly, at least in the range of nanocellulose loadings studied.

PUBLICATIONS AND PRESENTATIONS

“Tailored Shape Memory Polyurethane Reinforced with Microcrystalline Cellulose Nanofibers”, Maria L. Auad, Mirna A. Mosiewicki, Tara Richardson, Mirta I. Aranguren, Norma E. Marcovich, accepted to be published in *Journal of Applied Polymer Science*, 2009.

“Segmented Shape Memory Polyurethanes”, Tara Richardson, Maria L. Auad, Mirna Mosiewicki, Mirta I. Aranguren, Norma E. Marcovich. 237th ACS National Meeting, Salt Lake City, Utah, United States, March 22-26, 2009.