

Synthesis, Characterization, and Testing of Polyurethane Nanocomposites

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Abstract

The dispersion of nanoscale reinforcements has been shown to raise the strength and stiffness of polymers [1]. In this project, polyurethane (PU) was reinforced with nanometer-sized clay platelets to make nanocomposites through the layer by layer (LBL) assembly process. Samples with 0, 12, 20 and 45 wt% clay were synthesized. Thermal characterization of these samples was done using a differential scanning calorimeter (DSC). Scanning electron microscopy (SEM) was used to measure the thickness, and thermo-gravimetric analysis (TGA) was used to determine the clay content in nanocomposites. Tensile tests at a constant strain rate were performed on a series of nanocomposite samples with an in-house built tensiometer. The nanocomposites were observed to exhibit enhanced mechanical stiffness, yield strength and toughness at various weight fractions of clay.

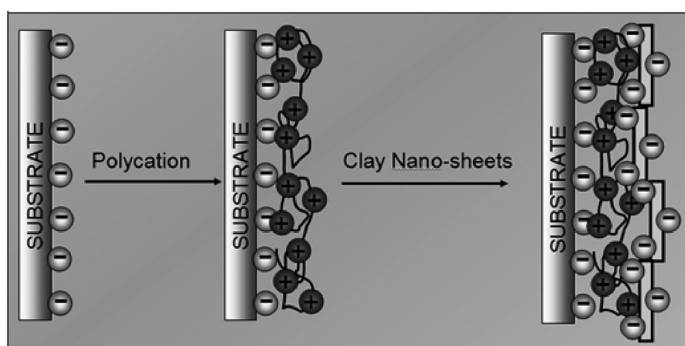


Figure 1: Adhesion of oppositely charged layers.

Synthesis (Layer by Layer Assembly)

The nanocomposites were synthesized by an emerging method of nanotechnology, the LBL assembly process. LBL is based on sequential deposition of nanometer-thick layers of oppositely charged components to build a multilayered structure. In this preparation, a glass substrate was alternately immersed into solutions of clay nanoparticles and cationic polyurethane, forming a new layer with each immersion through absorption. The oppositely charged layers adhered to each other resulting in homogeneously multilayered thin films on both sides of the glass substrate (Figure 1). These films were then separated from the substrate with a hydrogen fluoride solution. Finally, the films were treated with isopropanol alcohol.

Characterization

Clay content in each sample was determined with a Perkin-Elmer TGA. A small amount of sample (0.1-0.3 mg) was placed in a weighing pan of the instrument's ultra-sensitive balance and the sample was heated from 50°C to 1000°C at a heating rate of 10°C/min while being purged with air at 20 ml/min. The weight change of each sample was recorded as a function of temperature and the results were compared to pure clay. Given that the inorganic clay has much greater decomposition temperature than the organic polymer, the content of the clay inside the samples was estimated from the comparison of curves. Thermal characterization of the films was accomplished using a Perkin-Elmer DSC machine. A small amount of the sample (3-7 mg) was encapsulated in an aluminum pan and was heat treated from 30°C to 400°C at

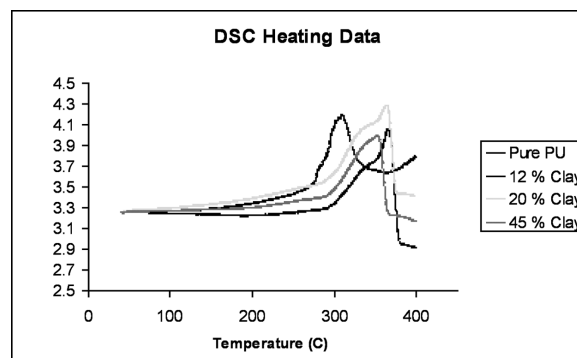


Figure 2: Thermal characterization data via DSC.

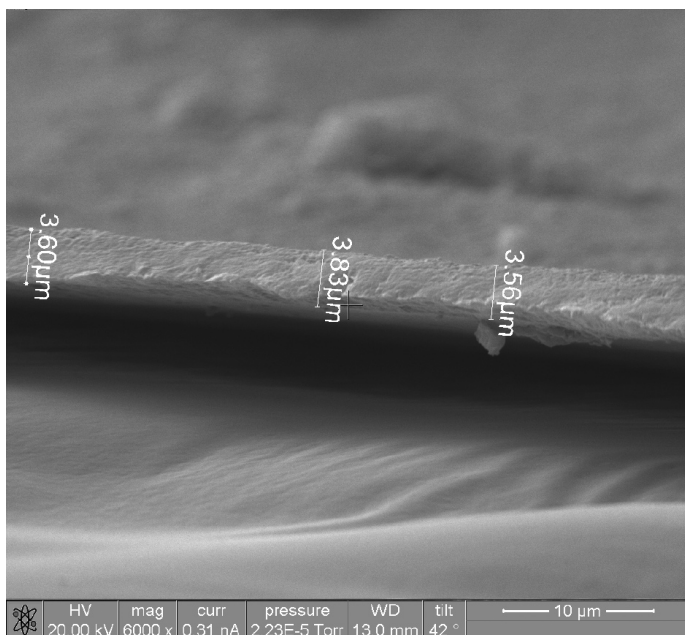


Figure 3: SEM of the 45% clay nanocomposite sample thickness.

10°C/min. The heat flow (W/g) was recorded as a function of sample temperature in order to analyze the results (Figure 3). The thickness of the nanocomposite film samples was measured via SEM to obtain the cross sectional area for stress calculations (Figure 3). The nanocomposites were gold sputtered prior to observation via SEM due to the nonconductive nature of the specimens.

Testing Methodology

Tensile testing was performed using an in-house designed tensiometer composed of a digital video camera focused on an inverted microscope (see [2] for details). Ultraspheres with a diameter of 25 μm were arranged on the specimen surface. The axial servomotors were controlled using LabVIEW software, which also synchronized data acquisition from the load element with image acquisition from the digital camera. The samples were loaded at a constant true strain rate of 0.005/s until the sample failed and LabVIEW recorded the corresponding force values and images. The load values were converted to stress and the strain was calculated using Metamorph software by tracking the distance between two ultraspheres. Nominal stress vs. nominal strain graphs were formed, the initial slope of which determined the modulus.

Results

A transition from ductile to brittle behavior was observed as the clay content increased. The addition of clay to the matrix of PU polymer increased the modulus and the yield strength significantly (Figure 4). When clay was dispersed into the PU with only 12% content, the modulus increased by 11 times and the yield strength increased by 7 times. The ultimate strain of the nanocomposite

with 12% clay content was measured to be about 1/7 of the pure PU strain. The DSC data showed that the peaks of the nanocomposites were all shifted about 50°C. The area under the curves of the DSC data decreased with the clay content increase (Figure 2B).

Conclusions and Future Work

A number of mechanical properties can be controlled with the change of clay content in the nanocomposite. As clay content increases: strength and modulus increases, while the strain (ductility) decreases. The decrease of the area under the DSC data curve also showed that the polymer becomes constrained by the clay particles. We also found that treating samples with isopropanol increased ductility of the nanocomposites. More samples should be synthesized and tested with 0% to 20% clay content to find the toughest nanocomposite of this family. Altering the polymer used in the nanocomposites could be another project. Finally, when the toughest nanocomposite is found, further characterization could be done by performing fracture tests and high strain rate tests.

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References

- [1] Podsiadlo, P., Kaushik, A.K., Arruda, E.M., Waas, A.M., Shim, B.S., Xu, J., Nandivada, H., Pumplin, B.G., Lahann, J., Ramamoorthy, A. and Kotov, N.A., "Ultrastrong and Stiff Polymer Nanocomposites," to appear in Science.
- [2] Calve, S., Mechanical and Morphological Characterization of Self-Assembling Tendons and Myotendinous Junctions *In Vitro*," PhD Thesis, University of Michigan, 2006.

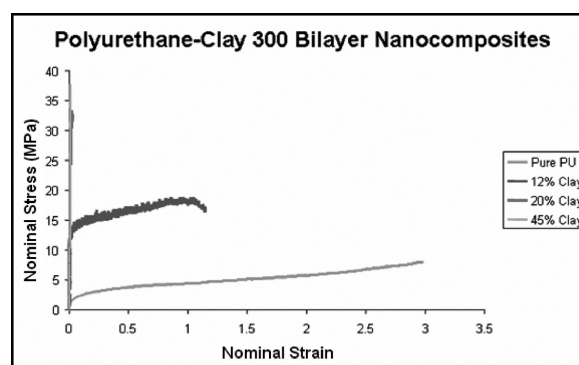


Figure 4: Nominal stress vs. nominal strain data for all nanocomposite samples tested.