COLLABORATIVE: PROCESSING OF SELF-ASSEMBLED BOTTOM-UP POLYMER NANOCOMPOSITE MATERIALS

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Abstract

This award supports collaborative work by research teams from Case Western Reserve University (CWRU) and the University of Akron (UA) on fundamentals of nanocomposite formation by a "*bottom-up*" self-assembly approach from dispersions of polyhedral oligomeric silsesquioxane (POSS) molecules in several thermoplastic polymers. These nanocomposite materials will have the processing ease of unfilled polymers and will be suitable for manufacturing of articles with micro- and nano-scale features by high-speed injection molding, fiber spinning, and thermoforming. The fundamentals developed in this work will offer superior alternatives to most "top-down" polymer nanocomposites, where orders of magnitude increase in viscosity over that of the host polymers is a norm and achieving nanoscale dispersion is a challenge. The degree of nanofiller/polymer and nanofiller/nanofiller interactions will be governed by the choice of polymer systems and POSS grades. A continuous single screw chaotic mixing device with peak shear rate in the range 50-100s^{-1} will render POSS nanoparticles **oriented** in the form of spheres of ~50 nm dia, long fibrils with ~5 nm dia, and/or lamellas of ~5 nm thickness. The hierarchical structures and the nanoparticle morphology and orientation will be correlated with mechanical and thermal properties.

The research program brings together research teams with complementary expertise from CWRU and the UA and provides common platform to collaborate freely and seamlessly. Undergraduate researchers from CWRU, UA, and from the currently NSF-funded summer REU programs at these schools will participate in the proposed research. Every effort will be made to ensure that a diverse mixture of American students, including female and underrepresented minority students are included at each educational level of the team.

Presentations and publications:

(1) Processing of self-assembled Bottom-up polymer nanocomposite materials. Presented at CMMI Grantees Conference, University of Tennessee, Knoxville, January 7-10, 2008.

(2) Lee, B.J., Jana, S.C., Reinforcement of polyolefins by bottom-up self-assembly of POSS nanoparticles. Presented at Americas Regional Meeting, Polymer Processing Society, Charleston, SC, October 26-29, 2008.

(3) B.J. Lee, Jana, S.C. 2008 Strengthening of polyolefins by bottom-up self-assembly of POSS nanoparticles. SPE ANTEC 66, 177-180.

(4) B.J. Lee, S. Roy, Jana, S.C. 2009 POSS/PP nanocomposites: Characterization and properties. SPE ANTEC 67, 126-130.

Results to date:

(1) It was found that DBS aided the dispersion of POSS molecules during mixing with PP at temperatures higher than 180°C. Both bu-MPOSS and ph-TPOSS were dispersed in PP in the presence of DBS. In the case of ph-POSS, nanometer size particles were formed at an optimum ratio of DBS and ph-TPOSS. The dispersion was microscopic in the case of bu-MPOSS or when ph-TPOSS was dispersed in PP without DBS. The performance in fiber spinning greatly depended on the scale of dispersion of POSS. Composite with 10 wt% ph-TPOSS and 0.7 wt% DBS showed highest draw down ratio and hence the smallest fiber diameter.

(2) It was found that 0.5 wt% of ph-TPOSS was enough to prevent 3-D fibril formation of DBS at 0.5 and 0.7 wt% concentration. In this case, instead of gel-type 3-D networks, DBS formed straight or twisted fibrils of length ~100 µm. At higher concentration of ph-TPOSS, e.g., 15 or 20 wt%, fibrillation of DBS was still subdued, but hydrogen bonding among excess ph-TPOSS molecules by led to self-assembly and formation of microscopic ph-POSS particles. The study found that an optimum ratio of DBS to ph-TPOSS exists to achieve nanoscale dispersion; excess ph-TPOSS only leads to formation of microscopic ph-TPOSS particles.

(3) The materials obtained from shear-cell experiments at Caltech were analyzed for the level of birefringence and the thickness of skin layer as function of wall shear stress and the ratios of ph-TPOSS to DBS. It was found that skin morphology depended strongly on the concentration of DBS – the orientation of DBS fibrils under shear led to orientation of adjacent PP chains. These chains in turn could not relax easily due to the presence of well dispersed nanometer size ph-TPOSS particles. Accordingly, the skin layer thickness increased as well as the value of birefringence during crystallization increased with DBS concentration for a given amount of ph-TPOSS.

(4) It was found that ph-TPOSS molecules underwent substantial condensation reactions when heated above 210°C for a period of 5 minutes. It was also found that hydroxyl groups of DBS reacted with the silanol groups of ph-TPOSS molecules when heated at 240°C or above. Note, however, that such reactions did not occur in materials prepared at 190°C and, therefore, did not cause any deterioration of properties in the composites.

(5) The films of PP, 10 wt% ph-TPOSS, and 0.3 wt% DBS produced by film blowing process exhibited much higher tensile modulus and tensile strength in machine direction than PP. As in fiber spinning, the relaxation of chains oriented along the machine direction due to extensional was hindered in presence of well-dispersed nanoscale ph-POSS particles.

(6) ph-TPOSS particles rendered thermal stability to PP composites. For example, the temperature at 5 % weight loss increased by 7°C with 10 wt% ph-TPOSS and by 25°C with 30 wt% ph-TPOSS. The temperature at maximum rate of weight loss, however, did not change.