The basic interest of the Bluemel group is to immobilize homogeneous catalysts on solid supports in order to improve their lifetime and make them easily separable from reaction mixtures. Using phosphine linkers with ethoxysilane groups, we demonstrate, e.g. that Ni and Rh catalysts remain active and selective after immobilization and can be recycled many times. (Coord. Chem. Rev. 252 (2008) 2410). Figure 1 shows an immobilized Cu complex, one component of the Sonogashira Pd(0)/Cu(I) catalyst system. A new generation of rigid linkers, which prevents catalyst deactivation by dimerization and its contact with the support surface, will prolong the lifetime of heterogenized catalysts even further (J. Am. Chem. Soc. 130 (2008) 3771).

A powerful analytical method like solid-state NMR of the dry materials (CP/MAS) is very important in this field. Recently, we developed a new technique for measuring suspensions (HRMAS). Figure 1 shows that the mobilizing effect of the solvent leads to extremely narrow lines. The improved resolution allows even 2D spectra to be recorded (here: NOESY below). This new method has also successfully been employed for studying swollen polymers and even interactions of substrates with polymer coated silica particles as the stationary phase in chromatography.

Figure 1. $^{31}$P NOESY HRMAS (left), $^{31}$P CP/MAS (top right), and $^{31}$P HRMAS (bottom right) spectra of the shown immobilized Cu complex (J. Am. Chem. Soc. 128 (2006) 8394).
With support from the National Science Foundation, Texas A&M University chemist Donald J. Darensbourg has pioneered the use of well-defined metal catalysts for converting the non-toxic, inexpensive gas carbon dioxide (CO$_2$) and three-membered cyclic ethers (epoxides) to thermoplastics.\textsuperscript{1} This represents an environmentally benign route to these materials and provides a viable use for the greenhouse gas CO$_2$. As indicated in the graphics, this reaction yields cyclic carbonates in addition to polymers. Studies at understanding the factors governing the selectivity of this reaction have recently been elaborated.\textsuperscript{2} Notice that the plastic products are capable of being readily decomposed by biological means, i.e., they are biodegradable. Some current uses of polycarbonates include the automotive industry, the medical and healthcare industry, and many consumer goods.

Current research efforts in this program are aimed at improving the activity and selectivity of these metal catalysts for the production of polycarbonates from both epoxides and four-membered cyclic ethers(oxetanes).\textsuperscript{3,4} Notice that the polymers produced from oxetanes and CO$_2$ when coupled with polyesters provide biodegradable thermoplastic elastomers which have various applications in biomedical areas such as surgical sutures, drug delivery devices, and body or dental implants. Relative to this latter subject, research at Texas A&M University is being directed at developing catalysts derived from biocompatible metals, specifically calcium and zinc, for producing these materials from trimethylene carbonate and lactides which are obtained from corn.\textsuperscript{5}

B-Staged Epoxy/SWCNT Nanocomposite Thin Films for Composites Reinforcement

Graham L. Warren

A new strategy for placing epoxy nanocomposites with high content of SWCNT at the location of interest via the preparation of partially cured (B-staged) epoxy/SWCNT thin films has been developed. Specifically, B-staged thin films are to be utilized as interlayers for enhancing conductivity and inter-laminar strength and toughness of the laminated VARTM composites.

B-staged epoxy/single-walled carbon nanotube (SWCNT) nanocomposite thin films at 50% of cure have been prepared for improving conductivity and mechanical performance of laminated composites. The SWCNTs were functionalized by oxidation and subsequent grafting using polyamidoamine generation 0 dendrimers. The epoxy nanocomposites containing SWCNTs were successfully cast into thin films by manipulating the degree of cure and viscosity of epoxy. High degree of dispersion of SWCNTs in epoxy thin films has been achieved. The Raman microscopy investigation indicates that the degree of dispersion is dramatically increased as the SWCNTs are oxidized and functionalized by PAMAM G0 dendrimers. Tensile testing was performed to evaluate the effect of the SWCNT treatment on the mechanical properties of the epoxy nanocomposites. The key tensile properties are listed in Table 1.

The results show that the incorporation of P-SWCNT can improve the epoxy Young’s modulus and tensile strength by 3% and 23%, respectively. The limited improvement on tensile properties is believed to be due to the poor SWCNT dispersion in the epoxy matrix, as evidenced in Figure 1. Oxidation of SWCNTs leads to a much better dispersion effect and thus the mechanical properties of epoxy/O-SWCNT were further improved. The incorporation of F-SWCNTs leads to the best overall reinforcement effect in modulus and strength by 16% and 35%, respectively. The improvement on tensile properties is believed to be due to the surface modifiers effect on SWCNT dispersion in the epoxy matrix, as shown in Figure 2. The tensile properties of the nanocomposite samples show a good correlation with the level of dispersion of SWCNTs in the epoxy matrix.

The B-stage thin films with 50% cure give satisfactory properties for VARTM processing to help enhance mechanical properties of the laminated composites. The B-staged thin films can be seamlessly integrated into laminated composite systems upon heating, and can serve as interlayers for improving conductivity and mechanical strengths of laminated fiber composite systems.

Table 1: Mechanical properties of bulk epoxy/SWCNT nanocomposites (0.5 wt%).

<table>
<thead>
<tr>
<th>Property</th>
<th>Neat Epoxy</th>
<th>Epoxy/P-SWCNT</th>
<th>Epoxy/O-SWCNT</th>
<th>Epoxy/F-SWCNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>2.77±0.01</td>
<td>2.84±0.05</td>
<td>3.17±0.01</td>
<td>3.21±0.15</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>60.1±5.6</td>
<td>74.2±0.5</td>
<td>76.5±3.9</td>
<td>82.7±3.2</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>1.98±0.22</td>
<td>2.57±0.18</td>
<td>2.97±0.40</td>
<td>4.88±0.91</td>
</tr>
<tr>
<td>( K_{IC} ) (MPa m^{1/2})</td>
<td>0.78±0.01</td>
<td>0.76±0.03</td>
<td>0.83±0.05</td>
<td>0.93±0.04</td>
</tr>
</tbody>
</table>

Figure 1. Optical image of 60×60 μm² area on the surface of an epoxy/P-SWCNT (0.5 wt%) nanocomposite thin film (a); reference Raman spectra of P-SWCNT (orange color) and epoxy matrix (green color) (b) used for producing the Raman image in (c), brighter colors denote higher intensity; G-band intensity distribution, darker color corresponds to higher intensity (d).

Figure 2. TEM micrographs (b) (c) (d) are illustrated in (a). The sequence of toughening events are illustrated in (a).

Toughening of Epoxy Based on Self-Assembly of Nano-Sized Block Copolymer Micelles

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An amphiphilic PEP-PEO block copolymer (BCP) toughener was incorporated into a bisphenol-A based epoxy and self-assembled into well-dispersed spherical micelles with a size of about 15 nm (Figure 1). The nano-sized block copolymer at 5 wt% loading can significantly improve the fracture toughness of the cured epoxy without reduction in modulus at room temperature and with only a slight drop in \( T_g \) (Table 1). The toughening mechanisms were investigated by the double-notch four-point-bending (DN-4PB) technique. It was found that the BCP micelles could cavitate to induce matrix shear banding (Figure 2), which mainly accounted for the observed remarkable toughening effect. It is important to mention that the nano-cavitation phenomenon observed in the 15 nm BCP particles is the smallest rubber particle size experimentally shown to cavitate and to promote shear banding of a polymer matrix. The likely contributing factors for the remarkable toughening effect in modulus and strength by 16% and 35%, respectively. The improvement on tensile properties is believed to be due to the surface modifiers effect on SWCNT dispersion in the epoxy matrix.

Table 1: Mechanical properties of bulk epoxy/SWCNT nanocomposites (0.5 wt%).

<table>
<thead>
<tr>
<th>Property</th>
<th>Neat epoxy</th>
<th>BCP-epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg (°C)</td>
<td>115</td>
<td>110</td>
</tr>
<tr>
<td>Storage Modulus (Pa)</td>
<td>3.86±10^1</td>
<td>4.04±10^1</td>
</tr>
<tr>
<td>at low temp. (-100°C)</td>
<td>2.25±10^1</td>
<td>2.36±10^1</td>
</tr>
<tr>
<td>at room temp. (25°C)</td>
<td>1.41±10^1</td>
<td>1.01±10^1</td>
</tr>
<tr>
<td>at rubbery plateau</td>
<td>0.96±0.04</td>
<td>2.73±0.08</td>
</tr>
<tr>
<td>Fracture Toughness, ( K_{IC} ) (MPa m^{1/2})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Nano-structured morphology of BCP-toughened epoxy: (a) a TEM micrograph and (b) a schematic illustration.

Figure 2. TEM micrographs of the BCP-epoxy DN-4PB fracture at different locations around the crack (a-e). The sequence of toughening events are illustrated in (a).

Continue on page 4
Jia (Daniel) Liu is currently a PhD candidate in Materials Science and Engineering. His research interests include development & structure-property relationship study of polymers/composites/nanocomposites, fracture & failure analysis, toughening mechanism study, etc. Mr. Liu is planning to graduate in December 2008. He is willing to be contacted for R&D related job opportunities at (979) 739-4624 or danieljliu@gmail.com.

Happy 81st Birthday, Dr. Clearfield!

Abraham Clearfield was born in Philadelphia, Pennsylvania, USA and received a B.A. and M.A. in chemistry from Temple University. He received his Ph.D. in 1954 from Rutgers University in inorganic chemistry and crystallography. Upon graduation he spent one year with the Army Quartermaster Corp. in Natick, Massachusetts working on problems related to supplies for the Army. In 1956, he joined the Titanium Alloy Manufacturing Division of the National Lead Company (now NL Industries) in Niagara Falls, New York. He conducted research on the applications of zirconium compounds in numerous commercial processes. He obtained a number of patents for processes he developed and improved the efficiency of the manufacturing processes.

In 1963, Dr. Clearfield joined the faculty of Ohio University in Athens, Ohio and was promoted to full professor in 1968. During his stay at Ohio University, Dr. Clearfield synthesized and determined the structures of a number of zirconium phosphates that became the focus of a world wide research effort that continues to this day. One of the forms of zirconium phosphate is used as a sorbent in portable artificial kidney machines and another is used to immobilize certain proteins and DNA for study of their chemical behavior.

In 1976 he joined the faculty at Texas A&M University and served as Chairman of the Inorganic Division, Associate Dean of the College of Science and Director of the Materials Science and Engineering Program. He has worked extensively on layered compounds, intercalation chemistry, inorganic ion exchangers including zeolites and metal phosphonate chemistry. Dr. Clearfield has received several awards for excellence in teaching and research. In 2007 he was promoted to the rank of Distinguished Professor, the highest university academic rank.

From the early days of his university career, Dr. Clearfield has fostered a global outlook on science. He has had longstanding collaborations with laboratories in Sweden, Yugoslavia, Italy, Australia, China, Poland, and Spain. Dr. Clearfield has published 530 papers in peer reviewed journals, edited three books and holds 15 patents. After spending more than forty five years with students in academia, Dr. Clearfield remains very active in both teaching and research.

PTC Visiting Scholar from Columbia

Howdy, my name is Mauricio Baez and I come from the Universidad Industrial de Santander (UIS) in Colombia. I am in my last year as an undergraduate in Chemical Engineering. I came here through a joint program between my University in Colombia and the Dept. of Chemical Engineering at Texas A&M University. I have been working in the PTC at Texas A&M University during my six months here on an interdisciplinary project between Dr Jayaraman’s Group in Chemical Engineering and Dr. Sue’s group in Mechanical Engineering.

I am very grateful to Dr. Jayaraman and Dr Sue for giving me the opportunity to experience research at a graduate level, and for allowing me to interact with people from other cultures and learn from them. After this experience, I am convinced that discipline, responsibility, and perseverance are qualities of every good professional.

The aim of my project is to evaluate the antimicrobial properties of ZnO QDs at low concentrations. They have been tested against Enterohaemorrhagic E. coli, an important human pathogen. Through different biological techniques, I have been able to determine the behavior of ZnO QDs as antibacterial agents, and to evaluate the effect of ZnO on the genetic expression of some genes involved in the important virulence factors of this pathogen. I am currently carrying out preliminary studies to evaluate ZnO ability to reduce established bacterial biofilm using microfluidic devices. Finally I would like to thank both professors’ lab members for their valuable collaboration and their teaching.