Carbon Nanotube Polymer Composites

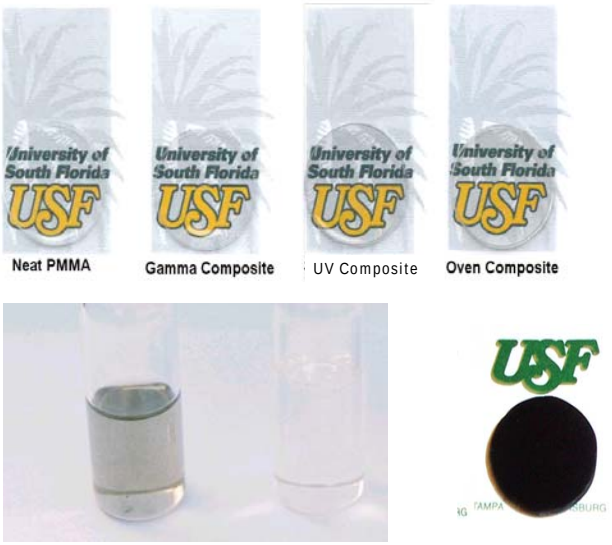

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Figure1

While there are limitless applications for these materials, we are interested in radiation shielding and radiation resistant materials for use in the space industry. Initially, we focused on optically transparent single wall nanotoube (SWNT) polymer composites (2-5). Three different *in situ* polymerization/sonication methods, heat, light and gamma radiation, were used to produce poly (methyl methacrylate) (PMMA) nanotube composites. When these composites are dissolved in methylene chloride and immediately cast into films, they exhibit a high degree of transparency (fig. 1). All of the composites in fig. 1 contain 0.26 wt% carbon nanotubes. The dark sample on the bottom right was made by melt blending 0.26% carbon nanotubes with the PMMA in a Banbury mixer. This illustrates the dramatic effect of dispersion quality on transparency. The dispersion in a typical sonicated sample is depicted in the SEM image shown in fig. 2. The intimacy of the nanotube-polymer interactions are evidenced by the appearance of a dielectrically active gamma transition associated with methyl group rotation in the polymer. This transition is normally inactive when neat polymer is probed by dielectric analysis.

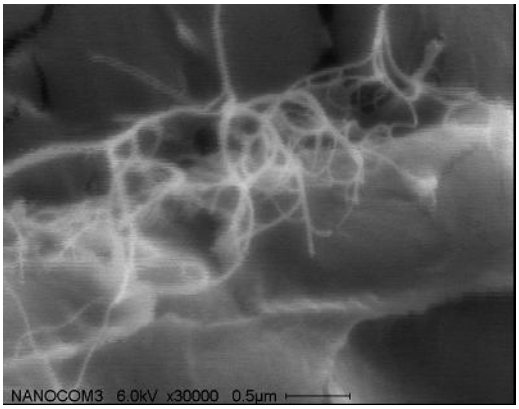

Figure2

We have observed this phenomenon in PMMA composites made with single wall nanotubes (SWNTs) (3), unpurified nanotube soot (6) and multiwall nanotubes (MWNTs) (7). The gamma transition region in a nanotube soot composite is shown in a plot of dielectric loss versus temperature in fig. 3. Although we are the first researchers that we are aware of to use nanotubes to "wake up" of the dielectric gamma transition in PMMA, Zhao et al (8) reported using nanotubes to observe secondary transitions via Raman spectroscopy.

These studies are aimed at producing composites with enhanced optical and dielectric properties. Up until this time we have not explored the use of surfactants to enhance

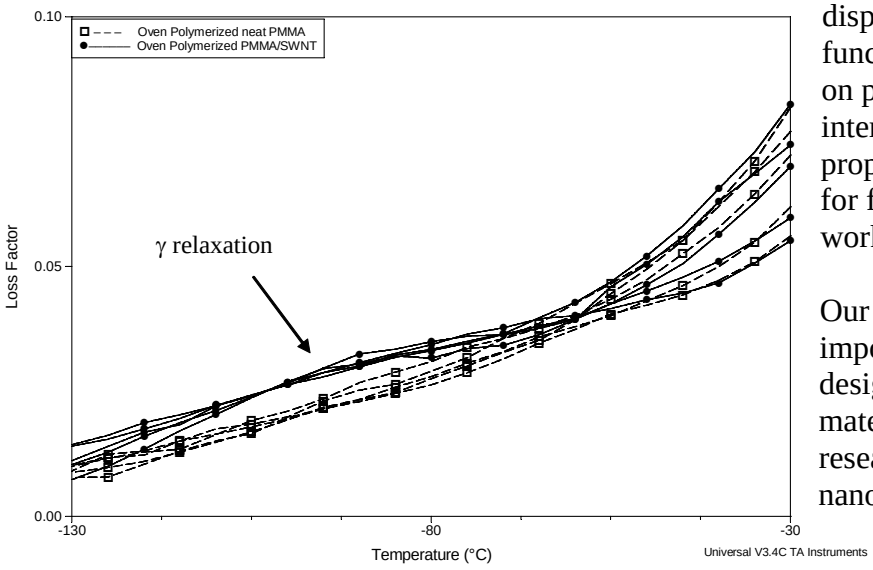

Figure3

dispersion, or the effect of functionalizing nanotubes on polymer-nanotube interactions and dielectric properties. This is a topic for future collaborative work.

Our group has made important advances in the design of radiation hard materials. The goal of this research is to use carbon nanotubes as gamma radiation sinks, dissipating energy and decreasing the frequency of radiolysis events. Single wall carbon nanotube (SWNT) (0.26 wt%) / poly(methyl methacrylate) (PMMA) composites were fabricated via sonication of the polymer with the nanotubes in solvent followed by vacuum annealing. Samples were exposed to ionizing radiation for a total dose of 5.9 Mrads.(9-11). Nanotubes increase the Vickers hardness number, the modulus and increase glass transition temperature (Tg) by 12 °C. Importantly, irradiation of the composites does not change these properties. This is in sharp contrast to degradation noted in PMMA controls. However, the real and imaginary parts of the complex permittivity determined by DEA, increase after irradiation. Hence, the dielectric properties are found to be more labile to radiation effects than mechanical properties. Multiwall nanotube (MWNT) (7) and nanotube soot (6) composites do not exhibit the radiation hardness noted in the SWNT composites.

Another area of nanotube research focuses on interaction of polymeric composite materials and highly energetic heavy atoms that are known to be part of Galactic Cosmic Radiation (GCR). Such radiation is encountered on Mars. A biological effectiveness (amount of damage) of the heavy ions consists of two major parts: a) energy transferred by a heavy particle along its trajectory, b) secondary radiation effects due to the nuclear interactions of incoming particles with shield material (12). Shield materials composed of atoms with small atomic mass (small number of inner shell electrons) have lower possibility of induced X-ray radiation as well as fewer neutrons to release during the nuclear interactions. Nanotubes and polymers consisting of only small atomic weight atoms (carbon, hydrogen) are considered to be promising materials for the production of GCR shields. Our group is in the process of developing new polymer nanocomposites that are designed to exhibit enhanced resistance to GCR. We are the first group to propose the use of poly(4-methyl-1-pentene) carbon nanotube composites for GCP protection (1) (fig. 4). The thermal and mechanical properties of PMP are superior to

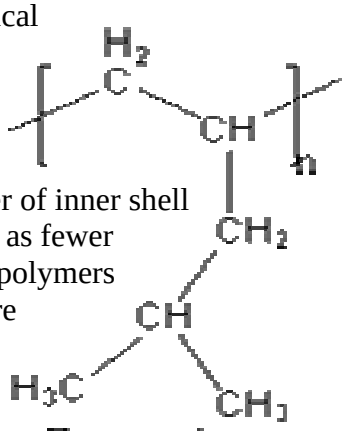

Figure4

those of the current baseline material, polyethylene(PE). In addition, PMP is transparent and can be used to process transparent nanocomposites at low concentrations. For non-optical applications higher concentrations of nanotubes will be used to produce ultra-strong materials.

In preliminary studies we produced SWNT/PMP composites at concentrations of 0.1-0.5% w%. Nanotubes increased the storage moduli over a wide temperature range. Stiffness is a desired property in many structural members that will be used on Mars. We have also produced transparent carbon nanotube PMP composites and have demonstrated excellent dispersion via SEM images. Furthermore, we have just started developing a Zeigler-Natta polymerization scheme for *in situ* synthesis of SWNT /PMP composites. NASA recently funded the enclosed proposal which describes this work in detail. The research is a joint effort between myself and S. Thibeault at NASA Langley. I am the proposal author.

References

1. "PMP/CNT Composites", J. P. Harmon and L. Clayton, USF Provisional Patent Application, 04A044PR.
2. "Transparent Polymer Nanotube Composites," J. P. Harmon, L. Clayton, P. Muisener, Utility Patent Application, 10/604,735.
3. "Transparent PMMA/SWNT Composites with Increased Dielectric Constants", L. Clayton, T. Gerasimov, M. Meyyappan and J. P. Harmon, Advanced Functional Materials, Vol. 15, No. 1, 101, (2005).
4. "Processing of Transparent Polymer Nanotube Composites via Heat, UV Radiation and Ionizing (Gamma) Radiation Using Ultrasonication and Solvent Dissolution", L. Clayton, R. Muisener, J. P. Harmon, A. Sikder, A. Kumar, A. Cassell, M. Cinke and M. Meyyappan, Materials Research Society Proceedings, Vol. 773, M 2.4, (2003).
5. "Transparent Polymer-Nanotube Composites Produced Via UV Radiation, Ionizing Radiation and Heat", L. M. Clayton, J. P. Harmon, M. Meyyappan, M. Cinke, A. Cassell, A. Kumar and A. K. Sikder, Materials Research Society Proceedings, Vol. 697, P9.7, (2002).
6. "Gamma Radiation Effects on the Glass Transition Temperature and Mechanical Properties of PMMA/SOOT Nanocomposites", L. Clayton, T. Gerasimov and J. P. Harmon, Polymer Bulletin, Vol. 52, 259-266, (2004).
7. "Probing Multi-walled Nanotube/PMMA Composites with Ionizing Radiation" Shelli R. Tatro, L. Clayton, Patricia A. O'Rourke Muisener, Apparao M. Rao, and J.P. Harmon. Polymer, Vol. 45, No. 6, (2004).
8. " Using Carbon Nanotubes to Detect Polymer Transitions", Q. Zhao, J. R. Wood, Journal of Polymer Science: Part B: Polymer Physics, Vol. 39, 1492, (2001).
9. "Effects of Gamma Radiation on Poly (methyl methacrylate)/ Single-wall Nanotube Composites," O'Rourke Muisener, P., Clayton, L., D'Angelo, J., and Harmon, J. P, Journal of Materials Research, Vol. 17, No. 10, 2507, (2002).
10. "Ionizing Radiation Effects on Interfaces in Carbon Nanotube-Polymer Composites," Julie P., Muisener, P. A. O., Clayton, L., D'Angelo, J., Sikder, A. K., Kumar, A., Meyyappan, M., and Cassell, A. M., Materials Research Society Proceedings, Vol. 697, P9.7, (2002).
11. "Ionizing Radiation Resistant Carbon Nanotube/Polymer Composites," J. P. Harmon, P. Muisener, L.Clayton and J. D'Angelo, Patent filed. USF Ref No: 01B090P.
12. Background information in NASA Research Announcement: NRA 03-OBPR-07, p. A-1.