indicate good repeatability of the freeze/thaw cycle, compatibility with high-density polyethylene, thermal stability, and flashpoints exceeding 100 °C. Based on the individual components, the phase change fluids are expected to have low acute toxicity.

There are several types of phase change materials (PCMs) that can be considered for the preservation of biological samples at a temperature of about –68 ºC. These include hydrated salts in water, non-hydrated or weakly hydrated salts in water, non-electrolyte aqueous solutions, and pure, non-aqueous fluids. However, none of these options resulted in a –80 °C freezing point stable PCM during the freeze/thaw cycling. Therefore, a non-aqueous mixture was formulated yielding a pseudo melting point plateau, adequate stability over numerous thermal cycles, and suitable latent heats. The product is a non-aqueous base fluid with a somewhat tailored freezing point, and latent heats on the order of 100 J/mL for the –85 °C PCM.

The fluid developed is an organic solution with adequate resistance to biological growth, compatible with HDPE (high density polyethylene) plastic, and is characterized by a negative freezing expansion ratio. The negative expansion ratio during freezing will allow for the ICEPAC modules to be completely filled with PCM material as compared to previously used fluids requiring a 20-mL air bubble (within a 120-mL capsule). This translates to a 20-percent increase in cooling capacity for a given latent heat. Furthermore, the specific gravity of the PCM is on the order of 0.92 g/mL, making it lighter than an aqueous-based solution per ICEPAC capsule.

This work was done by J. Michael Cutbirth of Mainstream Engineering Corp. for Johnson Space Center. Further information is contained in a TSP (see page 1). MSC-24460-1

Soft-Bake Purification of SWCNTs Produced by Pulsed Laser Vaporization

A more efficient, cost-effective, environmentally friendly method purifies high-quality c arbon nanotubes.

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The "soft-bake" method is a simple and reliable initial purification step first proposed by researchers at Rice University for single-walled carbon nanotubes (SWCNT) produced by high-pressure carbon monoxide disproportionation (HiPco). Soft-baking consists of annealing as-produced (raw) SWCNT, at low temperatures in humid air, in order to degrade the heavy graphitic shells that surround metal particle impurities. Once these shells are cracked open by the expansion and slow oxidation of the metal particles, the metal impurities can be digested through treatment with hydrochloric acid.

The soft-baking of SWCNT produced by pulsed-laser vaporization (PLV) is not straightforward, because the larger average SWCNT diameters (≈1.4 nm) and heavier graphitic shells surrounding metal particles call for increased temperatures during soft-bake. A part of the technology development focused on optimizing the temperature so that effective cracking of the graphitic shells is balanced with maintaining a reasonable yield, which was a critical aspect of this study. Once the ideal temperature was determined, a number of samples of raw SWCNT were purified using the soft-bake method.

An important benefit to this process is the reduced time and effort required for soft-bake versus the standard purification route for SWCNT. The total time spent purifying samples by soft-bake is one week per batch, which equates to a factor of three reduction in the time required for purification as compared to the standard acid purification method. Reduction of the number of steps also appears to be an important factor in improving reproducibility of yield and purity of SWCNT, as small deviations are likely to get amplified over the course of a complicated multi-step purification process.

The full JSC characterization protocol consisting of UV-Vis-NIR absorption, Raman spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) was applied to all samples. In addition, the nanotube content as the percentage out of total carbon was calculated from UV-Vis-NIR absorption, using a procedure similar to that proposed in earlier research. The nanotube percentage relative to the total sample weight was calculated from the absorption data, taking into account the metal content. These measurements were used to quantify various aspects of the "quality" of the material in terms of: metal content (TGA residue weight percentage), oxidation temperature (the temperature of the most significant peak in the first derivative of the TGA), stability of DMF dispersion by optical absorption, nanotube content (weight percentage of total from UV-Vis-NIR absorption and TGA), the frequency of the Raman G-band peak, and the ratio between the D-band and G-band intensities. All measurements (except dispersion stability) were repeated three times to determine variability of the purification route through statistical methods. Standard deviations of the experimental results are considered important parameters to quantify the homogeneity of nanotube samples.

The data indicate that the major properties, such as metal content, nanotube content, oxidation temperature, and extent of defects as determined by Raman, are similar or superior for the soft-baked samples when compared to the standard acid-purified samples. TGA and Raman data suggest that there is more metal removed, less oxidative damage, less protonation, and less derivatization incurred from the acid treatment in soft-baked samples. The stability and reproducibility of DMF dispersions is also superior, suggesting that soft-baking leads to greater homogeneity in materials than standard acid purification routes.

The observed improvement in efficiency translates directly into greater yield and quality of nanotubes, reduced cost and processing time, and the use of lesser amounts of organic solvents and concentrated acids, making the process safer and more environmentally friendly. This approach, as well as the development of a quality control, may be useful in the industrial scale-up of production and purification of carbon nanotubes.

This work was done by Leonard Yowell of Johnson Space Center, and Pavel Nikolaev, Olga Gorelik, Rama Kumar Allada, Edward Sosa, and Sivaram Arepalli of ERC, Inc. Further information is contained in a TSP (see page 1). MSC-24379-1