UV-Polymerizable Systems Containing Single-Walled Carbon Nanotubes

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ABSTRACT

Studies were conducted to investigate the effects of single-walled carbon nanotubes (SWNTs) on the rheological, thermal, and thermomechanical properties of UV-polymerizable formulations. The effect of SWNT concentration on the relative reactivity of the systems was also investigated. The acrylate-functional formulations contained an aliphatic acrylated urethane oligomer, three monomers: isobornyl acrylate, 1, 6-hexanediol diacrylate, trimethylolpropane triacrylate, and a photoinitiator, 1-hydroxy-cyclohexylphenyl ketone. Initially, a method was developed and optimized for dispersing the SWNTs in the monomer/oligomer mixture. Then, formulations containing concentrations of SWNTs ranging from 0.00 pph (control) to 0.20 pph were prepared by this method. Visible/Near Infrared (Vis/NIR) spectroscopy experiments indicated that the SWNTs were well dispersed in the liquid matrix, and subsequent rheological studies indicated the presence of dipole-induced dipole interactions among the nanotubes and the monomer/oligomer liquid matrix. These liquid dispersions were evaluated for their relative reactivity using differential photocalorimetry (DPC) methodology. UV-polymerized films of these formulations were also evaluated for thermal and thermomechanical properties using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) techniques, respectively. Results indicate that UV-polymerizable SWNT-containing dispersions can be prepared using relatively simple dispersion methods that do not involve the use of surfactants, solvents, or functionalized SWNTs.

INTRODUCTION

Background

Scientists have been investigating many possible applications of carbon nanotubes (CNTs) since their discovery in 1991. In fact, Kumar reported that as of December 2003, around 7500 research papers on CNTs had been reported. CNTs are nanostructures of graphitic carbon sheets rolled-up into cylinders. The two main types of CNTs are single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). These cylindrical carbon structures have very different chemical, electrical, and mechanical properties from those of diamond or graphite, and thus, they have been the focus of much research directed toward their potential applications as additives in a variety of different end-uses. Due to their demonstrated potential for significantly improving the mechanical, thermomechanical, and electrical properties of the polymer matrices in which they are dispersed, it seemed logical to ask what property enhancements might be realized in ultraviolet (UV)-polymerizable systems based on acrylate-functional materials. Thus, we embarked on a research program designed to determine if such property enhancements could be obtained.
While there are reports of work to develop UV-polymerizable systems containing CNTs, such work seems relatively limited. A review article concerning “Polymer/Carbon Nanotube Composites” was published in December 2004 by a group from the University of Alberta.\(^3\) Though that article cited 253 references only two of those reported the use of UV-polymerization processes.

In the first of those two references, Wagner et al. reported that they dispersed 0.1 wt % SWNTs in an acrylated urethane oligomer using ultrasonication for four hours.\(^8\) Subsequently, they dissolved a photoinitiator in the matrix and spread the composition onto a glass slide. Using a doctor blade to orient the nanotubes predominantly in one direction, they formed 150 \(\mu m\) thick films and then rapidly polymerized the composite material using UV irradiation to minimize the relaxation of the SWNTs back to a random orientation. Wagner’s purpose for preparing these dispersions was not to improve tensile, electrical, or thermal properties of the urethane acrylate. Rather, it was to use the SWNTs as a novel “probe” in Raman spectroscopy experiments designed to measure the strain in the polymer when it was placed under uniaxial tension. This group later applied this technique to two-dimensional strain mapping activities for fiber-polymer composites.\(^9\)

A second paper referenced by the University of Alberta group was by Xie et al. That paper described the development of UV-polymerizable CNTs for what they referred to as “microelectromechanical system applications”.\(^10\) This Pennsylvania State University group first functionalized MWNTs with carboxylic acid and alcohol groups using methods similar to those reported by Hiura et al.\(^11\) Then they reacted these functional groups with toluene diisocyanate (TDI) to make the MWNTs isocyanate-functional. Finally, they reacted the pendant isocyanate groups in a 1:1 mole ratio with hydroxyethyl methacrylate (HEMA) to produce acrylated urethane-functional MWNTs that were UV-polymerizable. Blended with 1 wt % of a photoinitiator, this product was reportedly quite high in viscosity, as would be expected from a highly functional and polar oligomeric material. Nevertheless, the Penn State group made castings of this material without further dilution with acrylate-functional monomers.

In addition to the work done by the two previously mentioned groups, Prof. Richard Wool et al. of the University of Delaware have reported making stable dispersions of impure MWNTs and carbon “soot” in acrylated epoxidized soy oil (AESO) blended with styrene monomer.\(^12\) In addition to being free-radically polymerizable, the AESO appears to function as a surface active agent (surfactant) in these systems. This paper referenced similar work involving these same acrylate-functional materials wherein SWNTs were dispersed using sonication methods.\(^13\) Prof. Wool’s paper describes a thermal polymerization process for the composite materials using \textit{tert}-butyl peroxybenzoate as the initiator. While UV-polymerization is not mentioned specifically in the paper, Prof. Wool later indicated in a personal conversation that these systems can be polymerized photochemically.\(^14\) Prof. Wool’s paper indicates that while a good dispersion was obtained, the expected improvements in polymer properties were not realized, due apparently to agglomeration of the soot and MWNTs during polymerization.

**Objective**

This brief review of the literature indicated that there is still a need for research that involves the use of SWNTs in more conventional UV-polymerizable systems; research that would determine whether or not the SWNTs can significantly enhance thermal, thermomechanical, and electrical properties without adversely affecting photoreactivity. Thus, a project was initiated to investigate the effects of SWNTs on the relative reactivity and the rheological, thermal, and thermomechanical properties of UV-
polymerizable, acrylate-functional systems. Electrical properties were not investigated in this study. The purpose of this paper is to report the results of that investigation.

**EXPERIMENTAL**

**Materials**

The following raw materials were provided without charge by their respective suppliers and were used without further purification:

*ALU-350*, a polyether-based acrylated aliphatic urethane oligomer, was provided by Echo Resins and Laboratory, Versailles, MO.

*Isobornyl acrylate (IBOA), 1, 6-hexanediol diacrylate (HDODA), and trimethylolpropane triacrylate (TMPTA)* were provided by Cytec Surface Specialties, Smyrna, GA.

*Irgacure® 184*, a Norrish I cleavage-type photoinitiator, 1-hydroxycyclohexylphenyl ketone, was provided by Ciba Specialty Chemicals Corporation, Hawthorne, NY.

*Single-Walled Carbon Nanotubes* were supplied by Carbon Nanotechnologies, Inc., Houston, TX.

**Equipment**

A Fischer Scientific *Solid State/Ultrasonic FS-14 Sonicator* was used to aid dispersion of the SWNTs in the acrylate-functional monomers.

A Brookfield *Model DV-111 Programmable Rheometer* with *TC500 Temperature Control Bath* was used to measure the viscosity of the formulations.

A *Model F600 UV curing unit, with a 600 W/in H-Bulb and Model DRS 120 movable web*, provided by Fusion UV Systems, Inc., was used to prepare polymer films containing SWNTs.

An Electronic Instrumentation and Technology (EIT) *UV PowerMap™* was used to determine the UV-A total energy density and peak irradiance values utilized in the polymerization process.

A *Model Q100 Differential Scanning Calorimeter (DSC) w/photocalorimeter accessory (PCA)* from TA Instruments was used to determine the relative reactivity of the formulations. Both the reference and sample light guides contained 10 % neutral density filters.

The same *Model Q100 DSC* unit from TA Instruments was used to determine the glass transition temperature, Tg, and other thermal properties of the polymer films.

A *Model 2980 Dynamic Mechanical Analyzer (DMA)* from TA Instruments was used to determine the thermomechanical properties of the polymer films.
Procedures

Preparation of the Formulations

A control formulation without SWNTs was prepared using 65 wt % of the acrylated aliphatic urethane oligomer, 35 wt % of an equal mass mixture of IBOA, HDODA, and TMPTA monomers, and 2 pph 1-hydroxycyclohexylphenyl ketone photoinitiator. Methods used to prepare this formulation were reported previously.\textsuperscript{15} The SWNTs were then dispersed in this base formulation in concentrations ranging from 0.01 pph to 0.20 pph of the total mass of oligomer and monomer.

The dispersion technique used in this experiment involved grinding the SWNTs using a mortar and pestle, followed by incorporating them into an equal mass mixture of the three acrylate-functional monomers. An 8.17-g sample of each monomer (IBOA, HDODA, and TMPTA, respectively) was placed in a 4-oz brown glass jar. Next, about one-third of the desired mass of SWNTs was added to the monomer mixture (Table 1). The jar was capped and inverted several times by hand to facilitate the mixing. This mixture was then exposed to ultrasonication for 1 hour at 45.0°C. Another one-third of the sample of SWNTs was then added to the previous mixture and the same sonication process was used. Finally this process was repeated a third time to disperse the remaining one-third of the sample of SWNTs. The relatively low viscosity of the monomer mixture facilitated the dispersion process. Following a total of 3 hours sonication at 45.0°C, the SWNTs appeared visually to be very well dispersed.

Following dispersion of the SWNTs in the monomer mixture, 45.5 g of the acrylated urethane oligomer was added to the dispersion. This mixture was then sonicated for an additional 3 hours at 45.0°C, resulting in a visually uniform dispersion. Finally, a 1.4-g sample of photoinitiator was added and the mixture was sonicated for yet another 3 hours, bringing the total ultrasonication time to 9 hours. This resulted in black, opaque dispersions that visually appeared to have excellent shelf-life stability with respect to settling. Their relative opacity was proportional to the concentration of SWNTs. This is evident in the strips of UV-polymerized film shown in the photo in Figure 1.

Table 1: Composition of SWNT Dispersions

<table>
<thead>
<tr>
<th>Formulation</th>
<th>wt % IBOA</th>
<th>wt % HDODA</th>
<th>wt % TMPTA</th>
<th>wt% ALU-350</th>
<th>Irgacure-184 (pph)</th>
<th>SWNTs (pph)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>11.67</td>
<td>11.67</td>
<td>11.67</td>
<td>65</td>
<td>2</td>
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<td>11.67</td>
<td>11.67</td>
<td>65</td>
<td>2</td>
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</tr>
<tr>
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<td>11.67</td>
<td>11.67</td>
<td>11.67</td>
<td>65</td>
<td>2</td>
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<td>65</td>
<td>2</td>
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</tr>
<tr>
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<td>11.67</td>
<td>11.67</td>
<td>65</td>
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</tr>
<tr>
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</tr>
<tr>
<td>7</td>
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<td>11.67</td>
<td>11.67</td>
<td>65</td>
<td>2</td>
<td>0.20</td>
</tr>
</tbody>
</table>

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Viscosity Measurement

Samples of each of the SWNT dispersions were placed in a cylindrical sample holder which was subsequently placed within the small sample adapter of a Brookfield Digital Rheometer. The constant temperature bath was connected to the small sample adapter and equilibrated to 25.0 ± 0.1°C. A #25
A cylindrical spindle was used for the viscosity measurements and care was exercised to insure that no air bubbles were trapped beneath the spindle. The viscosity of each sample was measured at low shear rates ranging from 1 to about 125 rpm to determine whether or not the dispersions had Newtonian flow characteristics.

**Visible/Near Infrared Spectroscopy**

The relative degree of dispersion of the SWNTs in the liquid formulations was evaluated qualitatively using UV/Vis/NIR instrumentation in the laboratory of Prof. Ramanan Krishnamoorti in the Department of Chemical Engineering at the University of Houston. Figure 2 shows a typical Vis/NIR spectrum for the liquid SWNT dispersions. Scans were made only between 400 and 1400 nm because the shorter, more energetic UV wavelengths may have caused polymerization. The presence of “van Hove singularities” seen in Figure 2 indicate good dispersion – exfoliation – of the SWNTs.16, 17

**Preparation of Polymer Composite Films**

A Fusion UV Systems 600 W/in electrodeless “H-Bulb” was used to polymerize thin films of each SWNT dispersion. Liquid films were exposed to approximately 620 mJ/cm² of total UV energy and approximately 1450 mW/cm² peak irradiance. All films were tack-free on both the upper and lower surfaces, indicating good through-cure characteristics.

**Differential Photocalorimetry (DPC)**

Approximately 3.0 mg of each sample was placed in the sample cell of a TA Instruments Q100 DSC/DPC unit. The sample was equilibrated at 25.0°C for 30 seconds. Then the shutter covering the UV lamp was opened and remained open for 60 seconds. The UV irradiance used was approximately 60 mW/cm². Induction time, time to the peak maximum, peak maximum height, and the total thermal energy evolved were all measured for each sample.

**Dynamic Mechanical Analysis**

Polymer composite samples were cut to the approximate dimensions: 17.8 mm x 5.7 mm x 0.11 mm. Each sample’s dimensions were accurately known and factored into the instrument’s data analysis.
program. Each sample underwent an oscillatory strain at 1 Hz frequency while being heated from –100°C to +200°C at 5°C per minute. The resulting storage and loss moduli were recorded as a function of temperature. The peak of the alpha-transition in each curve was taken to represent the Tg for each sample.

RESULTS AND DISCUSSION

The previously cited papers and others revealed significant difficulties in getting adequate dispersion of CNTs in polymer matrices. In a “perfect world”, effectively dispersing the SWNTs would result in every individual nanotubes being fully separated – “exfoliated” - from the other nanotubes. However, to achieve this, one must overcome significant dispersion forces that bind the nanotubes to each other in “bundles” or “ropes”. As in the previously cited work, attempts to make stable dispersions of CNTs in organic media (including polymer matrixes) have normally involved the use of surfactants\textsuperscript{12,18}, chemical modification of CNT surfaces\textsuperscript{10}, or \textit{in situ} polymerization\textsuperscript{19} of the matrix, including UV-polymerization\textsuperscript{8,9}, and/or ultrasonication.

![Image](Visible/NIR Spectrum of 0.01 pph SWNT Dispersion showing van Hove Singularities)

The acrylate-functional oligomer and monomers are polar substances that should provide for significant dipole-induced dipole interactions with the highly polarizable but non-polar SWNTs. The question is how to disperse the SWNTs in these materials. It was considered a disadvantage to use a surfactant package to facilitate dispersion. Likewise, chemically modifying the SWNTs themselves was undesirable. Therefore, a decision was made to attempt the development of a dispersion technique that did not involve either of these approaches.

Various techniques were investigated, including an attempt to disperse the SWNTs in a mixture of both monomer and oligomer. This approach did produce visually uniform dispersions that appeared to have reasonable shelf stability, but viscosity measurements indicated little interaction among the acrylated materials and the SWNTs. The data indicated that the 0.20 pph SWNT sample had only marginally higher viscosity than that of the control formulation. This is quite unexpected for a system that has adequate exfoliation of the SWNT. The relatively high initial viscosity of the oligomer/monomer mixture most likely made it more difficult to get adequate dispersion, even with ultrasonication.
Ultimately, it was determined that dispersing the SWNTs in the low viscosity monomer mixture, followed by addition of the higher viscosity oligomer, was the best approach for making uniform dispersions. Figure 2 shows the Vis/NIR spectrum of a dispersion made by this “low viscosity” method. The “ripples” in that absorption spectrum indicate the van Hove singularities. As previously stated, these are expected if adequate exfoliation of the nanotubes occurs during dispersion in a liquid medium.16, 17 Thus, it appears that simple sonication of the SWNTs in the monomer mixture was effective at producing good dispersions.

Rheology

Rheological measurements were also indicative of good dispersion for these systems. Figure 3 gives an overlay of viscosity vs. shear rate data for all of the SWNTs evaluated in this study. These data indicate that the viscosity increases significantly with increasing levels of SWNTs. This was not evident from the data generated for the “high viscosity” method.

It also appears in Figure 3 that there is a critical concentration of SWNTs below which the systems are “shear thickening” or “dilatent”. Both the control and the 0.01 pph sample are shear thickening up to about 15 to 20 rpm shear rates. Then they both appear to become relatively newtonian, at least in this low shear region. Ironically, the ultimate viscosity of the control sample is actually about 19% higher than that of the 0.01 pph sample. This is more evident in Figure 4 which shows a magnified plot for samples from 0.00 to 0.08 pph SWNTs. While the control and the 0.01 pph samples are clearly shear thickening, the 0.04 and 0.08 pph samples are “shear thinning” or “pseudoplastic” throughout the range of shear rates investigated. In fact, around 20 rpm their viscosities drop below that of the control and continued to decrease. The shear thinning properties of the three most concentrated dispersions (Figure 3) are even more pronounced.

The data displayed in Figures 3 and 4 seem to indicate that the SWNTs may be disrupting a relatively strong network formed through intermolecular attractive forces (including hydrogen-bonding) among
the monomers and the oligomer. Above 4 rpm shear rates, the resistance to flow of the 0.01 pph sample is actually lower than that of the control. Further, as previously mentioned, the 0.04 and 0.08 pph samples have lower viscosities than the control above 20 rpm shear rate, while the 0.12 and 0.16 pph samples decrease in viscosity to near that of the control at 25 and 90 rpm, respectively.

The shear thickening behavior of the control and the 0.01 pph SWNT sample indicates that when these mixtures are subjected to shear forces, realignment of component molecules occurs, resulting in more intimate contact among the molecules with increasing shear rates, up to a limiting viscosity above which their rheology becomes newtonian. The shear thinning behavior of the four higher concentration samples indicates a much higher resistance to flow in the absence of shear. However, this monomer/oligomer-SWNT network is relatively easily broken down as the shear rates increase. Perhaps this indicates that even though monomer/oligomer – SWNT interactions are strong enough to allow for good dispersion, the resulting network is easily disrupted by shear forces.

In addition to measuring the shear thickening and thinning properties with increasing shear rate, the time-dependent thixotropy was also investigated. This type of experiment involves measuring the viscosity at a constant shear rate over a period of time. Figure 5 shows the results of this experiment. The highest concentration dispersion (0.20 pph SWNT) was subjected to 60 minutes of continuous shear at 1.0 rpm shear rate. At first glance, these data seem to indicate that this material may be thixotropic. However, over the 60 minute time frame, the viscosity only decreased by about 3.5%, which is within the limits of reproducibility for the viscometer. This is in contrast to the shear thinning observed for this system where the viscosity dropped by around 75-80 % from 1.0 rpm to 125.0 rpm shear rate. Thus, this system does not appear to be thixotropic. While thixotropy was not measured for the other dispersions, it is assumed that it would be most noticeable for the highest concentration sample.

Differential Photocalorimetry (DPC)

SWNTs are quite absorbent in the UV and visible regions of the electromagnetic spectrum. So naturally it was assumed that there might be difficulty in getting the systems to polymerize with UV irradiation. However, there was really no difficulty encountered in producing polymer films under typical
Thixotropy of 0.20 pph SWNT Dispersion @ 1.0 rpm

Figure 5
Thixotropic Behavior of 0.20 pph SWNT Dispersion

commercial curing conditions. Figure 1 is a photograph of several “cured” polymer films that range from the control on the left to 0.12 pph SWNT on the right. It is evident that as the concentration of SWNTs increases, the opacity increases indicating the increasing absorbance of visible light. The same could be expected for UV energy. Nevertheless, these films are tack free and seem to be adequately through-cured. Thus, from a practical standpoint, there seems to be little or no difficulty in polymerizing acrylate-functional systems containing SWNTs.

Still, it is of interest to quantify the CNT effect on the rate of the photopolymerization reaction. To do this, DPC techniques were utilized. The induction time, time to the exotherm peak maximum, and the maximum height of the exotherm peak were all evaluated. The total amount of thermal energy evolved was also evaluated to get a qualitative idea of the relative degree of polymerization.

A typical DPC curve is shown in Figure 6. This graph shows the exotherm of the photopolymerization reaction as a function of time. The highest point in the curve, the “peak maximum”, corresponds to the fastest reaction rate. The time it takes to reach that peak is taken to represent the overall relative reaction rate. Longer “peak maximum times” imply slower reactions, of course. This technique also gives an indication of “induction time”. This is the time it takes for all the inhibitory factors such as oxygen, stabilizing inhibitors, etc. to be overcome after the lamp shutter is opened. In Figure 6, the peak maximum for this sample is about 242 mW or 242 mJ/s. This is the maximum rate of evolution of thermal energy during the polymerization. The peak maximum time is 1.42 s (the shutter was opened 30 s into the run), and the induction time is 0.40 s. The total amount of energy evolved during this polymerization was about 262 J/g over the 60-second time period that the shutter was open.

One would hypothesize that the peak maximum time and the induction time for the SWNT dispersions should increase with increasing SWNT concentration, while the peak maximum should decrease with increasing SWNT concentration. Also, since the SWNTs will absorb some of the UV energy, it might be expected that the total exotherm (the total energy evolved during the photopolymerization) would decrease due to a lower conversion of monomer to polymer. These hypotheses, in general, were found to be correct. Figure 7 gives an overlay of all the DPC curves for SWNT dispersions ranging from
0.00 pph for the control to 0.16 pph SWNT. This figure also includes data for two samples with concentrations of 0.005 and 0.0025 pph SWNT, respectively. A careful examination of these plots clearly reveals a decrease in the maximum rate of the reaction and an increase in the time it takes to reach that peak maximum as the concentration of SWNTs increases.

Figures 8, 9 and 10 show DPC data for dispersions ranging from 0.00 pph (control) to 0.16 pph SWNT. Each of the dependent variables discussed previously are plotted as a function of SWNT concentration. Figure 8 gives the effect of SWNT concentration on both the induction time and the peak maximum time. Not surprisingly, both were observed to increase with higher levels of SWNT. Since SWNTs absorb in the UV region of the electromagnetic spectrum, they absorb some of the energy needed by the photoinitiator. Further, the SWNTs can scatter the energy, causing “shadow” areas directly beneath the nanotubes. The induction time increased by about 100% from the control to the 0.16% sample, while
the peak maximum time increases about 160%. The total reaction time – the induction time plus the peak maximum time - actually increased around 300% going from 0.00 pph to 0.16 pph SWNT.

**Figure 9** shows a plot of the Maximum Rate vs. SWNT concentration up to 0.12 pph SWNT. As expected, the maximum rate of reaction decreased with increasing levels of SWNTs. **Figure 10**, though somewhat irregular, shows a substantial decrease in the total thermal energy evolved at SWNT levels above 0.04 pph. This indicates that the system experiences lower conversion of monomer/oligomer to polymer as the SWNT concentration increases.

**Dynamic Mechanical Analysis (DMA)**

DMA was used to evaluate the thermomechanical properties of UV-polymerized films containing 0.00 to 0.16 pph of SWNTs. The frequency for each scan was 1 Hz and the temperature was ramped at 5°C per minute from – 100°C to 200°C. **Figure 11** shows a typical DMA scan depicting the storage and loss moduli as functions of temperature. Whether one takes the peak of the alpha-transition from the storage or loss modulus to be the Tg, the result is the same in this case: ~ 50°C. **Figure 12** shows an overlay of
all the DMA scans for samples from 0.00 to 0.16 pph SWNT. It is apparent from these graphs that the scans for all the samples coincide quite closely and that the Tg is not greatly affected by the addition of SWNT up to 0.16 pph concentration. However, in the so-called “rubbery plateau” of the storage modulus above the Tg, the SWNTs do appear to have had an effect on the polymer films. This rubbery plateau is the region above the Tg in the DMA scan where the storage modulus is no longer a function of temperature. For similar systems, the storage modulus in the rubbery region is proportional to the crosslink density. Data plotted in Figure 12 indicate, in general, an increase in the storage modulus in going from 0.00 to 0.16 pph SWNT. Although the 0.08 pph sample appears to be anomalous, it still appears that the effective crosslink density of UV-polymerizable system might be increasing with increasing levels of SWNTs. However, more studies are needed to verify or refute this hypothesis.

**Differential Scanning Calorimetry (DSC)**

Like DMA, DSC is a technique that, among other things, allows one to determine the Tg of a polymer film. The DSC results of this investigation indicated, as did the DMA results, that there was little or no effect of the SWNTs on the Tg of the polymer films, at least up to 0.12 pph SWNT. Above that level,
the Tgs determined by DSC appeared to move toward lower temperatures. Figure 13 shows a graph of the Tg of these films as a function of SWNT concentration. Each data point on this graph represents the average of two measurements, except for the 0.16 pph data point. The replicates for the control sample and the 0.12 pph SWNT sample ranged from 41°C to 54°C. For the other samples, the ranges were within ± 1°C. For the samples with 0.12 pph SWNT or less, the measured Tg values were fairly consistent with the Tgs determined using DMA methodology, i.e., ~ 50°C. However, for the 0.20 pph sample, there appeared to be a significant decrease to about 27°C. This result was reproduced within ± 1°C. If this result is valid, it indicates that a certain critical concentration of SWNTs is needed in order to observe a measurable effect on the Tg of the polymer. Above this critical concentration, the SWNTs either function as a plasticizer for the polymer, or else they inhibit the UV-polymerization sufficiently to reduce the percent conversion to a point where free monomer has a plasticizing effect. Further studies are needed at levels above 0.20 pph SWNT to determine whether or not the effect is continued to even lower Tgs. Also, studies are needed that will test which hypothesis best explains the lowering of the Tg.
SUMMARY AND CONCLUSIONS

Results of this investigation demonstrated that stable UV-polymerizable dispersions containing relatively low levels of SWNTs in an acrylate-functional monomer/oligomer matrix can be prepared without using either functionalized CNTs or surfactants. Ultrasonication of the CNTs in an equal-mass mixture of three monomers was found to be an acceptable dispersing method. Vis/NIR spectroscopy studies indicated that the degree of dispersion – exfoliation – of the SWNTs was significant. Rheological measurements indicated that the dispersions had non-newtonian flow characteristics in the low shear region from 1 to 125 rpm shear rates (Brookfield). Below 0.01 pph SWNT concentration, the systems (including the control) were slightly dilatant. Above this level, they were pseudoplastic. No appreciable thixotropy was observed. DPC studies indicated that the relative photoreactivity of these dispersions decreased with increasing SWNT concentration. This was reflected in longer induction and peak maximum times and in lower maximum rates of reaction, as expected. DMA and DSC experiments indicated that below about 0.16 pph SWNT, the SWNTs have little or no effect on the Tg of the polymer films. However, DSC studies do indicate that the Tg may be significantly reduced at the 0.20 pph level. The data generated for the rubbery plateau region of the storage modulus curves of the DMA may also indicate that the effective crosslink density of the polymers increases with increasing SWNT levels. Further studies are needed to corroborate these observations.

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