Acrylate-Functional Urethane- and Polyester-Based Formulations Containing Multi-Walled Carbon Nanotubes

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ABSTRACT

Single-walled and multi-walled carbon nanotubes (SWNTs and MWNTs) were dispersed in UV-polymerizable formulations containing an acrylated aliphatic urethane oligomer, an acrylated polyester oligomer, or combinations of both, along with several acrylate-functional monomers. An improved, relatively simple dispersion technique that involved simultaneous stirring and sonication was developed and optimized. This method was then utilized to disperse a set amount of the carbon nanotubes (CNTs) in the monomer mixture. Subsequently, the oligomer(s) were added and stirring and sonication were continued until visually uniform liquid mixtures were obtained. These liquid formulations were evaluated for their rheological characteristics under low shear conditions and UV-Visible spectra were obtained in an attempt to evaluate their relative degree of dispersion. These liquid dispersions were then drawn down into thin films and polymerized using a 600 W/in UV lamp system. The "cured" polymer films were subjected to dynamic mechanical analysis (DMA) to determine the effects of the CNTs on the thermo-mechanical properties of the polymers. They were also evaluated for their thermal decomposition properties using thermal gravimetric analysis (TGA). Results indicate that the polyester- and urethane-based systems are different in properties, as would be expected, and that the CNTs tend to impart higher viscosities, higher glass transition temperatures (Tg), and other differences in the properties of the polymers.

INTRODUCTION

Background

CNTs have been the focus of research since their discovery in 1991[1] because of their unique mechanical, chemical, and electrical properties. In previous research projects in this laboratory, single-walled CNTs (SWNTs) were successfully dispersed in acrylate-functional, urethane-based UV-polymerizable formulations at low concentrations. For example, Vien Lam et al.[2] dispersed SWNTs into these systems by sonicating the formulation after each addition of a new component. That work demonstrated that SWNTs can be dispersed in UV-polymerizable formulations when the concentration of SWNT is less than 0.20 pph. However, they also reported difficulties in dispersing SWNTs into formulations containing SWNTs in excess of 0.20 pph. Presumably, at higher concentrations, the SWNTs tended to agglomerate due to their high polarizability and surface area, resulting in large London force interactions[3] (often known as "Van der Waals attractions"). In order to obtain improvements in thermal, mechanical, and electrical properties of polymers that contain CNTs, it is essential to generate uniform polymer-CNT dispersions. In other words, the polymer-CNT system, at the molecular level, must be homogenous, with exfoliation or de-bundling of the CNTs throughout the polymer matrix. In the literature, much research has been devoted to achieving uniform dispersions with the aim of exfoliating the CNTs and thus reducing their tendency to agglomerate. Use of solvent[4], surfactants[5], and chemical functionalization of the nanotubes has been reported. In addition, electric and magnetic field forces[6] have been used to align the nanotubes in polymer matrices to maximize the effectiveness of dispersion throughout the polymer matrix.

Objectives

A first and central objective, which spans all CNT work in this laboratory to date, is to improve the technique for dispersing SWNTs and MWNTs in UV-polymerizable acrylate-functional formulations and, in particular, at concentrations above 0.20 pph.

A second objective is to assess differences between SWNTs and MWNTs, both for the effectiveness of the dispersion process and for the thermal and mechanical properties of the resulting UV-polymerized CNT-containing composites.

A final objective is to compare the effects of a urethane-based oligomer system vs. a polyester-based oligomer both for the ease of dispersion and for the thermal and mechanical properties of the resulting UV-polymerized CNT-containing films.

Purpose

The purpose of this paper is to report on findings related to the preparation and characterization of CNT dispersions in UV-polymerizable systems based on an acrylated aliphatic urethane oligomer and/or an acrylated polyester oligomer.

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.

Ebecryl-657, a polyester-based acrylated oligomer, was provided by Cytec Surface Specialities, Smyrna, GA.

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

Darocur-1173 (2-hydroxy-2-methyl-1-phenyl-1-propanone) and *Irgacure-184 (1-hydroxycyclohexylphenyl ketone)* photoinitiators were provided by Ciba Specialty Chemicals Corporation, Hawthorne, NY.

SWNTs were purchased from Carbon Nanotechnologies, Inc., Houston, TX and *MWNTs* were purchased from Sigma-Aldrich, Inc. St. Louis, MO.

Equipment

A Fischer Scientific *Solid State/Ultrasonic FS-14 Sonicator* was used to aid dispersion of SWNTs and MWNTs in the liquid formulations.

A *Brookfield Model DV-III Ultra Programmable Digital Rheometer* was provided by Brookfield Engineering, Inc., Middleboro, MA, to measure the viscosity of the liquid formulations. The

temperature of the formulations was controlled to within $0.1^{o}C$ using a with *TC500 Temperature Control* bath.

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

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

A *Model 2980 Dynamic Mechanical Analyzer (DMA)* from <u>TA Instruments</u> was used to measure thermo-mechanical properties of the polymer films.

A *Model Netzsch STA 409 CD (TGA/DSC/Quadrupole MS)* was used to measure various thermal properties of the polymer films. (NSF Grant Award # 0521636)

Formulation Compositions

Table 1 gives the compositions for SWNT-containing formulations while **Table 2** gives the compositions for MWNT-based formulations.

Dispersion Techniques

The correct mass of each monomer (see **Table 1**) was mixed in an 8-oz brown jar. This mixture was then sonicated for 60 minutes at $45^{o}C$ ($\pm 1.0^{o}C$) in a temperature-controlled water bath to insure absolute uniformity in composition.

Next, the total mass of CNTs (see **Table 1**) was divided into three equal portions. The first portion of CNT was added to the mixture of monomers followed by 45 minutes of sonication and stirring at $45^{o}C$ ($\pm 1.0^{o}C$) in a temperature-controlled water bath. The second portion of CNT was then added to the monomer-CNT mixture followed by a further 45 minutes of sonication and stirring at $45^{o}C$ ($\pm 1.0^{o}C$). This was repeated a third time for the remaining portion of CNT. This process brought the total sonication and stirring time to 135 minutes. At this point, the desired amount of oligomer (see **Table 1**) was added to the formulation followed by 120 minutes of sonication and stirring in a $45^{o}C$ ($\pm 1.0^{o}C$) water bath. Finally, the desired mass of photoinitiator was added to the formulation followed by a final 60 minutes of sonication and stirring at $45^{o}C$ ($\pm 1.0^{o}C$). This brought the overall sonication and stirring time for the formulating process to 315 minutes. The control formulations in this study were subjected to the same sonication time, stirring time, and temperature-control as the CNT-containing formulations.

Preparation of Polymer-Composite Films

A Fusion UV Systems 600 W/in electrodeless "H-Bulb" was used to polymerize each thin film. To produce films of uniform thickness, the desired formulation was applied across a glass plate with an adjustable thickness drawdown bar. The coated glass plate was then passed under a moving conveyor which was pre-set to the appropriate total UV energy density (UV dose) and peak irradiance. The polymer films were subsequently removed from the glass and characterized.

Table 1
SWNT Formulation Compositions

Formulation	IBOA wt%	HDODA wt%	TMPTA wt%	Urethane Oligomer wt%	Photoinitiator pph	SWNT pph
1	11.67	11.67	11.67	65.0	2.00	0.00
2	11.67	11.67	11.67	65.0	2.00	0.35
3	11.67	11.67	11.67	65.0	2.00	0.50
4	11.67	11.67	11.67	65.0	2.00	0.75
5	11.67	11.67	11.67	65.0	2.00	1.00

Table 2
MWNT Formulation Compositions

Formulation	IBOA wt%	HDODA wt%	TMPTA wt%	Oligomer wt%	MWNT pph	Photoinitiator pph
1	11.67	11.67	11.67	65% Urethane	0.0	3.0
2	11.67	11.67	11.67	65% Urethane	0.2	3.0
3	11.67	11.67	11.67	65% Polyester	0.0	3.0
4	11.67	11.67	11.67	65% Polyester	0.2	3.0
5	11.67	11.67	11.67	32.5% Urethane + 32.5% Polyester	0.0	3.0
6	11.67	11.67	11.67	32.5% Urethane + 32.5% Polyester	0.2	3.0

Characterization

Criteria for Measuring Effective Dispersion

To assess the degree of dispersion of UV-polymerizable-SWNT liquid formulations and to demonstrate the relative effectiveness of the new dispersion technique, ultraviolet-visible

spectroscopy (UV-Vis) was conducted. The presence of Van Hove singularities in the UV-Vis spectra has been proposed by Bergin et al.[7] as a way to quantify SWNT exfoliation in a liquid system. Specifically, Bergin's group performed a series of experiments wherein they dispersed SWNTs in an amide solvent at increasing concentrations of SWNT using a high powered sonicating tip. After a given time of exposure to the sonic tip, they scanned the UV-Visible region of the electromagnetic spectrum to locate Van Hove singularities in the SWNT-amide solvent mixture. Using this technique, they demonstrated that at lower concentrations of SWNT, Van Hove peaks in the UV-VIS become sharper, which, according to their interpretation, signifies exfoliation or de-bundling of the SWNTs in the amide solvent.

Based on Bergin's rationale, UV-polymerizable acrylated SWNT dispersions reported in this paper were analyzed by UV-VIS spectroscopy to locate characteristic Van Hove singularities in the UV-Visible region of the electromagnetic spectrum. To this end, it was hoped to classify the liquid-CNT dispersions as "well-dispersed" or "poorly dispersed". Previous work in this laboratory conducted by Lam et al. demonstrated that these characteristic Van Hove singularities are present in the UV-Vis region of the electromagnetic spectrum using SWNT-dispersed urethane-based acrylate-functionalized systems. This current investigation was initiated to determine whether or not these Van Hove singularities extend to SWNT-dispersed formulations at higher concentrations and also to MWNT-dispersed formulations.

Viscosity Measurements

The viscosities of the liquid formulations listed in **Table 1** were measured by a Brookfield DV-III digital "*Ultra*Rheometer". All viscosity measurements were performed at 25°C ($\pm$ 0.1°C). To assess the rheological characteristics of the liquid formulations in **Table 1**, a range of step-speed programs were programmed into the rheometer. These programs measured viscosity of the liquid formulation as a function of shear rate (0 to 15 rpm) at discrete 1-minute time intervals. To measure the viscosity of a formulation, the formulation was poured into a cylindrical temperature-controlled small-sample adaptor and left there until the temperature had equilibrated to 25°C. Once the temperature of the formulation had equilibrated, the rheometer spindle number 25 was fully immersed in the sample and the desired program performed.

UV-Visible Spectroscopy

To measure the UV-Vis of a CNT-dispersed liquid formulation, the dispersion was smeared between two quartz microscope plates. The control formulation was also smeared between two quartz plates (no CNTs) and was used as the control. The desired CNT-dispersed formulation was then scanned from 1000 nm to 380 nm.

Dynamic Mechanical Analysis (DMA)

Polymer composite samples were cut to precise dimensions using a digital micro-caliper. These dimensions were known and factored into the instruments data analysis program. Each sample underwent oscillatory strain at a frequency of 1 Hz while heating from -50°C to 200°C at 5°C per minute. The storage and loss moduli were recorded as a function of temperature and their ratio was calculated by the instrument to determine the tan δ for the sample. The peak of the alpha-transition in the tan δ curve was taken to represent the glass transition temperature (Tg) for each sample.

Thermal Analysis—TGA/DSC/MS

Thermal properties of the polymer composites were analyzed using thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), and quadrupole mass spectrometry (MS). The *Netzsch STA 409 CD* instrumentation performed these analyses, TGA, DSC, and MS, simultaneously. To attain TGA/DSC/MS data, a sample of the desired film was cut into pieces weighing approx. 10 mg in total and loaded into a specialized crucible for use in the Netzsch instrument. Next, the crucible was placed onto a temperature probe on the Netzsch instrument alongside an empty reference crucible. The sample was then heated from 25°C to 600°C at a constant rate of 10°C per minute in the presence of helium gas. This technique measured mass loss as a function of temperature, energy transfer as a function of temperature, and relative abundance of gaseous ions emitted from the sample as a function of temperature.

RESULTS AND DISCUSSION

Dispersion of SWNTs in a Urethane-Based Formulation at High Concentrations

The dispersion method in this work resulted in black, opaque, "ink-like" dispersions that visually appeared to be homogenous. **Figure 1** shows UV-Vis spectra for a series of urethane-based formulations containing 0.20, 0.35, 0.50, 0.75, and 1.00 pph SWNT, along with a control formulation containing zero SWNT. As expected, characteristic Van Hove singularities at the three wavelengths marked on the spectra are present. The control UV-Vis spectrum did not produce Van Hove singularities, demonstrating that these singularities are intrinsic to the SWNT system rather than a function of the oligomer, monomer, or photoinitiator in the formulations.
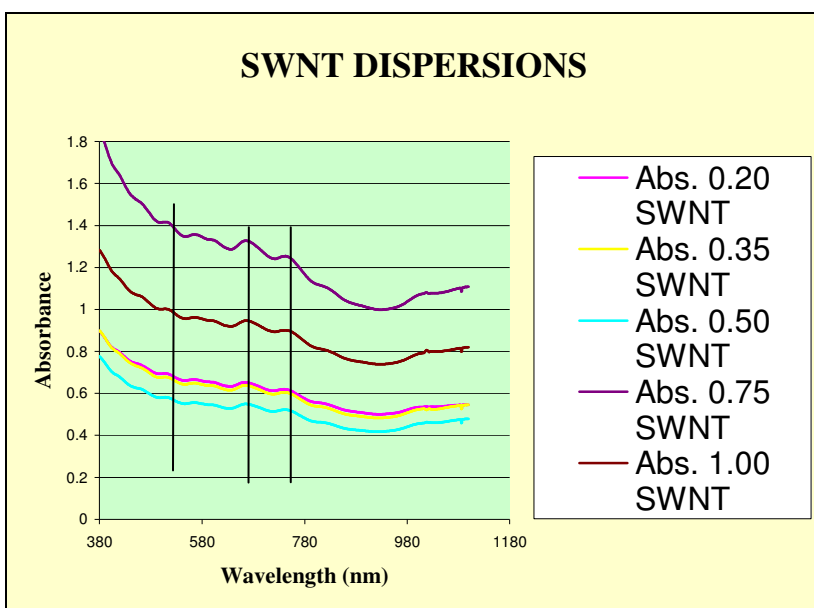

**Fig 1: Van Hove Singularities for higher concentration
SWNT formulations in Table 1**

In **Figure** 1 the respective curves are not directly in order of concentration. This is most likely due to small differences in the film thickness of the samples in accordance with Beer's Law. Nevertheless, these data so demonstrate that the dispersion technique developed and employed in this investigation did improve the degree of dispersion at levels of SWNT greater than 0.20 pph. The previous method used by Lam et al. was not effective at exfoliation above 0.20 pph SWNTs.

Dispersion of MWNTs in Urethane- and Polyester-Based Formulations at 0.20 pph

The MWNT formulations shown in **Table 2** were observed visually to be as well-dispersed as the SWNT formulations prepared in **Table 1**. Furthermore, the MWNT formulations have excellent shelf-life stability with respect to phase separation. In an attempt to verify the MWNT exfoliation in these formulations, UV-Vis spectra were recorded. However, they did not reveal the expected Van Hove Singularities. This may be due to the fact that MWNTs are inherently more hetero-geneous than SWNTs and for a given mass of material, will have significantly less surface area. This latter fact should make it easier to exfoliate the MWNTs but the more heterogeneous nanotubes may make the measurement of small UV-Vis absorption differences, such as those represented by distinct Van Hove Singularities more difficult to detect. Other data discussed hereinafter indicate that reasonable dispersion (exfoliation) was likely attained with the MWNTs.

Viscosity - Polyester vs. Urethane

A different way to obtain evidence for effective nanotube dispersion is to make rheological measurements of the control formulations and those containing MWNTs. It can be assumed that if the viscosity increases significantly with an addition of MWNTs, they are reasonably well dispersed and are interacting with the polar acrylate-functional materials by dipole-induced dipole interactions. **Figures 2, 3,** and **4** show formulation viscosity as a function of shear rate for formulations containing 100% urethane, 50/50 urethane/polyester, and 100% polyester oligomers. In each instance, the addition of 0.20 pph MWNT increases the viscosity of the formulation regardless of whether the oligomer is urethane- or polyester- based. At all shear rates examined in **Figures 2, 3**, and **4** the viscosity of the MWNT formulation is higher than its respective control formulation. However, addition of MWNTs to the formulation containing 100% polyester (**Figure 3**) increases the viscosity to a greater extent- in percentage terms - than addition of MWNTs to the formulation containing the urethane oligomer (**Figure 2**). At a shear rate of 2 revolutions per minute (rpm), for example, the increase in viscosity between the control urethane formulation and the urethane with 0.2 pph MWNTs is 1900 centipoise (cps) or about 17 %, whereas the increase seen with the polyester formulations is only 960 cps, but this is about 100 % of the initial control formulation's viscosity, perhaps indicating a much stronger interaction of the polyester-based system with the MWNTs than for the urethane-based system.

Since viscosity, by definition, is a measure of a substance's resistance to flow, an observed increase in viscosity due to addition of MWNTs to a fluid-state oligomer/monomer mixture demonstrates that interactions occur at the molecular level to reduce the overall molecular freedom of the oligomer/monomer mixture. However, although viscosity measurements provide clues about the MWNT and monomer/oligomer interactions that might be responsible for these observed increases in viscosity, a detailed picture would require other experimental information. It should be noted that the urethane oligomers neat viscosity is significantly higher than that of the polyester-based oligomer.

Figure 4 gives the data for the 50/50 oligomer blend systems. These systems, not surprisingly, are higher in viscosity than those with the polyester alone, but not as high as those with the urethane alone. The fact that the neat urethane oligomer is higher in viscosity than the polyester is the main reason for these differences. Another thing to note about **Figure 4** is that the 2 rpm increase in viscosity with addition of MWNTs is actually about 136%! This may indicate a
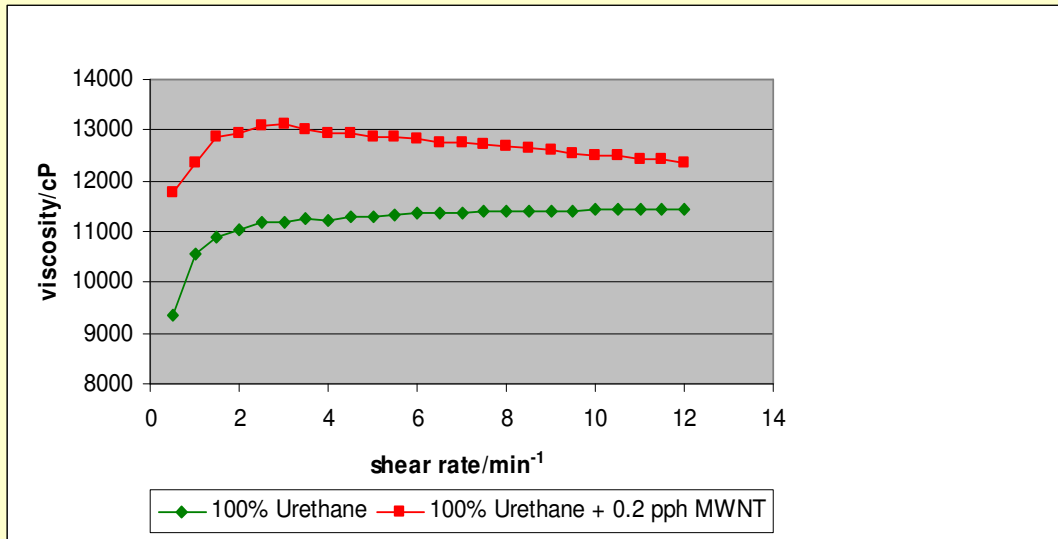
**Fig 2: Viscosity vs. shear rate for 100% urethane
control and 100% urethane with 0.2 pph MWNT**

synergism between the urethane and the polyester with respect to interactions with MWNTs. But this idea has not yet been independently investigated experimentally.
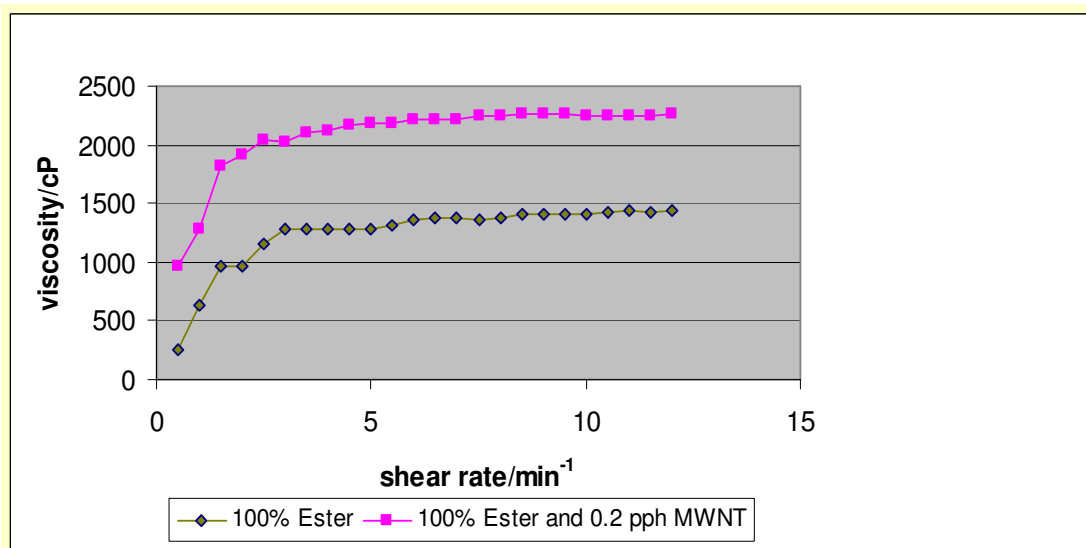

**Fig. 3: Viscosity as a function of shear rate for 100% polyester control
and 100% polyester with 0.2 pph MWNT**

In **Figures 2, 3,** and **4**, the shear rates were at or below 12 rpm. Even at this very low shear rate, it is clear that for two of the MWNT systems, the material was sheer thickening initially and then the viscosity began to decrease with shear rate ("shear thinning"). However, neither the neat oligomers nor the polyester-based composite material indicated shear thinning behavior up to 12 rpm. For the polyester composite formulation, the interaction of the MWNTs with the nanotubes seems to have been stronger (less shear sensitive) than for the systems containing the urethane oligomer.
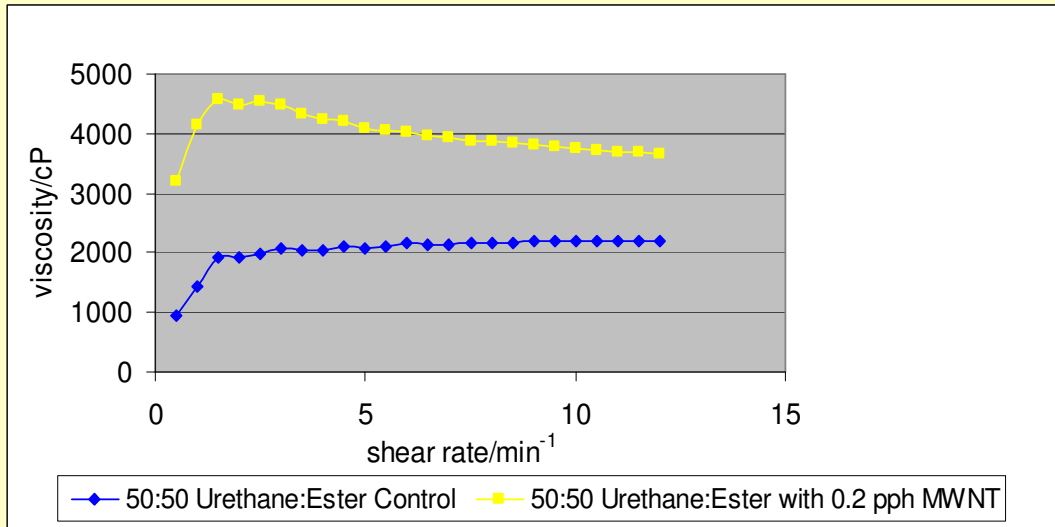
**Fig 4: Viscosity as a function of shear rate for 50/50 Urethane/polyester
and 50/50 Urethane/polyester with 0.2 pph MWNT**

Figure 5 shows the viscosity vs. shear rate profiles for the urethane-based formulations at higher shear rates (5 to 40 rpm). It can be seen that the nanotube composite formulation was quite shear thinning, decreasing about 10 % with shear rate. Interestingly, the control formulation continued to show moderate shear thickening up to 40 rpm.
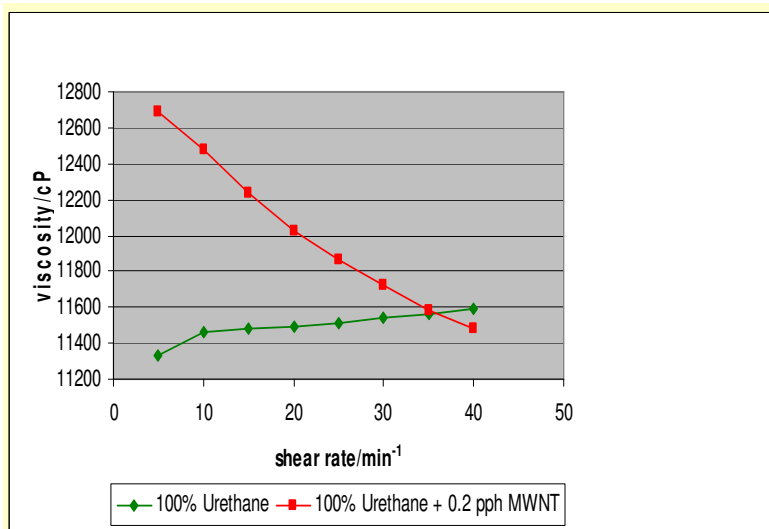

**Fig. 5: Viscosity as a function of shear rate for 100% Urethane
and 100% Urethane with 0.2 pph MWNT**

Shear thinning can be thought of as resulting from the breakdown of a network structure in the liquid mixture with increased shear force while shear thickening represents the build-up of a "tighter" network of interacting molecules with shear. This latter property indicates that more effective molecular alignments are achieved when shear forces are applied.

In contrast to the urethane/MWNT system's rheology, the polyester-based formulations both continued to resist shear thinning up to 40 rpm. **Figure 6** shows the rheological behavior of the composite liquid along with the control. Again, this indicates a relatively strong interaction between the MWNTs and the matrix materials. This is not surprising in light of the very polar nature of the acrylated polyester oligomer.
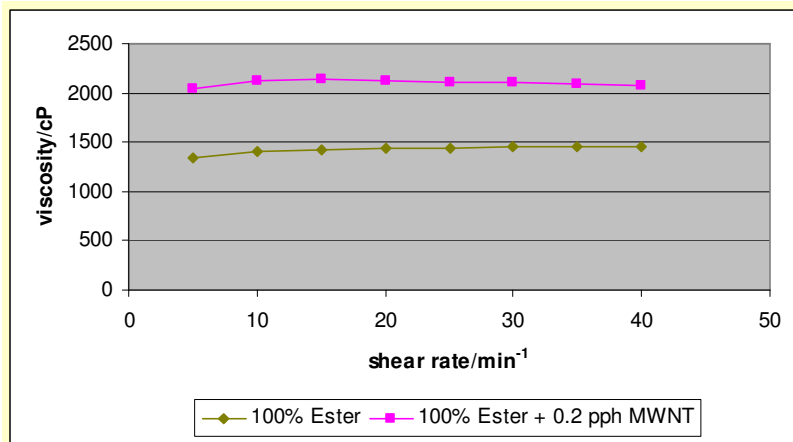

Fig 6: Viscosity as a function of shear rate for 100% polyester and 100% polyester with 0.2 pph MWNT

Thermomechanical Analysis of Polyurethane and Polyester MWNT Composites

DMA is a very powerful tool for characterizing polymers for a variety of thermal and thermomechancial properties. The experiment involves subjecting a polymer sample to a sinusoidal stress at a given frequency while ramping the temperature at a constant rate. From this experiment the visco-elastic nature of the polymer can be evaluated. That is, the "liquid-like" properties ("visco") and the "solid-like properties ("elastic") can independently be assessed. The elastic properties are represented by the storage modulus curve and the viscous properties are represented by the loss modulus curve. The storage modulus of a polymer gives its ability to absorb energy at different temperatures while the loss modulus reveals its ability to dissipate energy. The tan δ is the ratio of the loss to storage moduli at a given temperature and is useful in measuring the glass transition temperature (Tg) and the relative apparent homogeneity of the polymer film at the molecular scale.

In this paper, the tan δ characteristics of the various formulations were investigated. **Figure 7** shows the tan δ curves for the urethane control formulation and its corresponding MWNT composite. The composite material demonstrated a significant increase (~16.5%) in Tg (the peak of the tan δ curve) indicating a more tightly held network configuration than for the control. Thus the MWNTs restricted the segmental motions of the polymer/MWNT matrix.
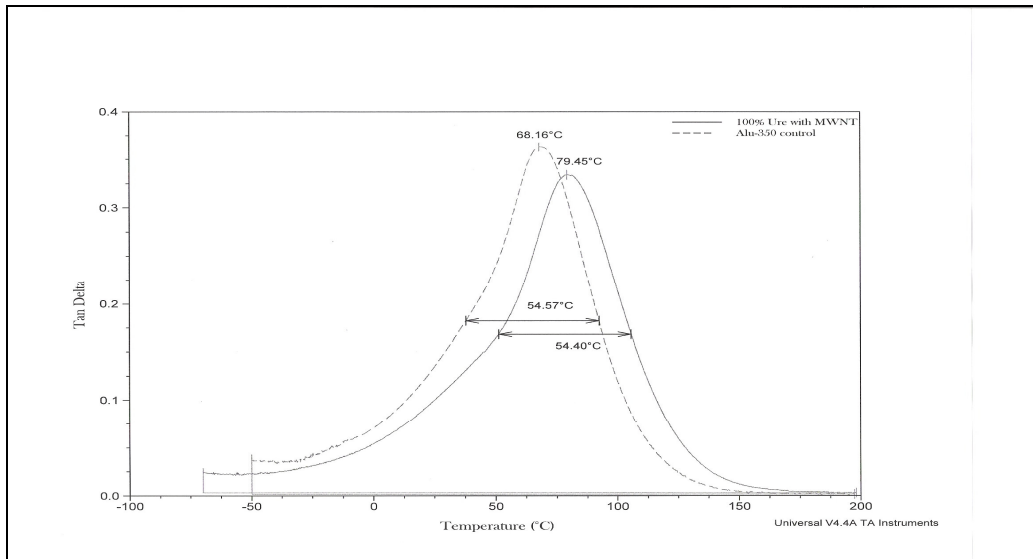
**Fig 7: Tan δ as a function of temperature for 100% urethane (----)
and 100% urethane with 0.2 pph MWNT(——)**

The half-height width of the tan δ peaks were also determined in this study. This parameter gives information about the relative homogeneity of a polymer film at the molecular scale. For example, a very heterogeneous (amorphous) polymer with few microgels or microcrystalline domains would have a very narrow tan δ curve, whereas a polymer with more microgels or microcrystalline domains would have a broader tan δ curve. In **Figure 7** the two systems appear to have the same degree of heterogeneity. This is a bit surprising since one might expect the addition of MWNTs to produce domains of significantly different morphologies and thus Tgs.

Figure 8 shows the same information for the 50/50 oligomer-based formulation and its corresponding MWNT composite. In this case, the two Tgs are identical but the relative heterogeneities are different with the composite film being more heterogeneous. Likewise,
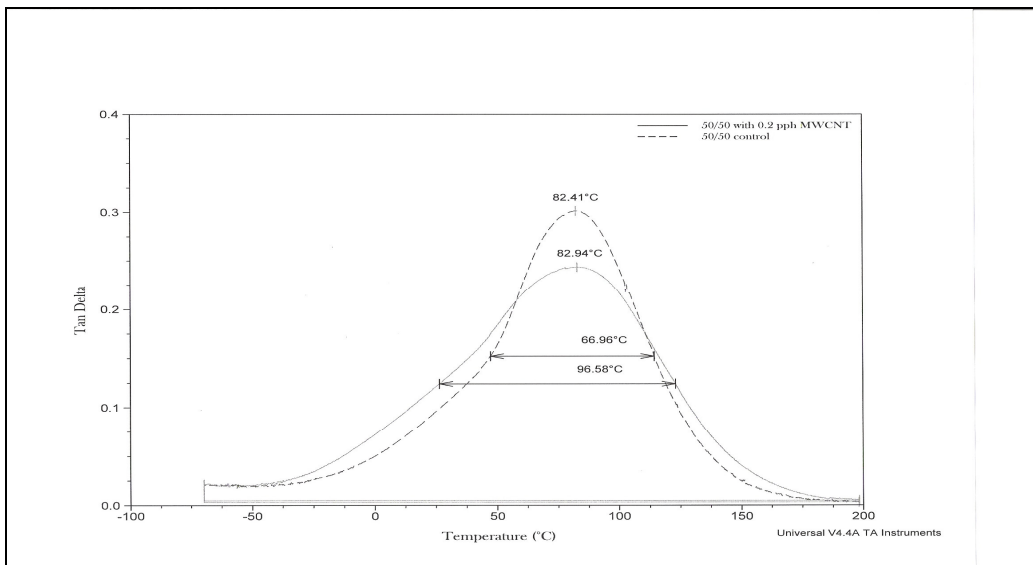

**Fig 8: Tan δ as a function of temperature for 50/50 urethane/polyester (----)
and 50/50 urethane/polyester with 0.2 pph MWNT (——)**

Figure 9 gives the tan δ properties for the polyester-based systems. These data show the fact that the polyester oligomer is quite polydisperse - it has a range of different molecular masses and/or molecular structures. This is revealed in the tan δ curve for the control formulation which shows something similar to a bimodal distribution; a pattern partially repeated in the composite material.
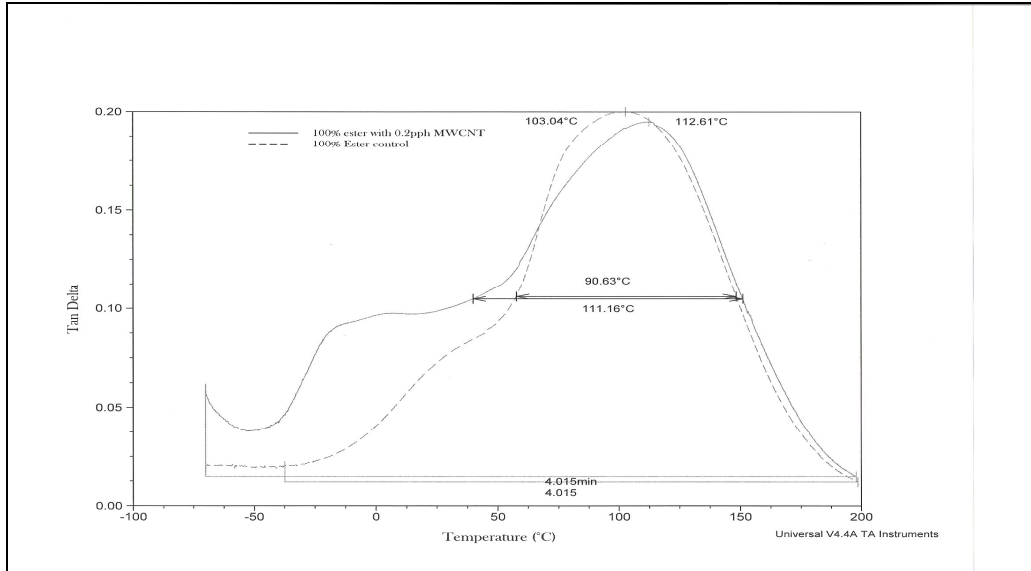

Fig 9: Tan δ as a function of temperature for 100% polyester (----)
and 100% polyester with 0.2 pph MWNT (—)

However, the MWNTs appear to improve the homogeneity fairly significantly as indicated by the reduction in the low temperature portion of the tan δ. This may indicate that the MWNTs provide an unexpected benefit in the polyester system by reducing the amount of microgel formation that is known to occur in the early stages of acrylate polymerizations[10, 11].
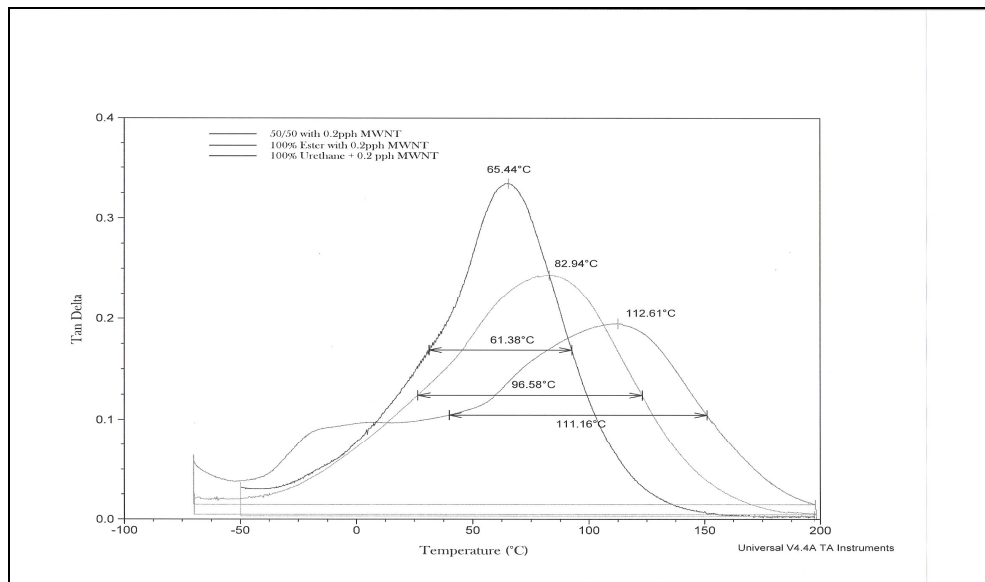

Fig 10: Tan delta as a function of temperature for all MWNT formulations
(from left to right: 100% urethane, 50/50 urethane/polyester, and 100% polyester)

Figure 10 shows an overlay of the tan δ for all three composite formulations. From left to right, the Tgs are increasing as are the half-height widths (relative heterogeneity). These three curves represent the urethane, 50/50, and polyester oligomer systems, respectively. Along with the lack of shear thinning characteristics, the Tg data indicate stronger interactions between the polyester oligomer and the MWNTs than for the urethane-containing systems.

Thermal Analysis of Polyurethane and Polyester MWNT Composites

Figures 11, 12, and **13** give the thermal decomposition behavior of the formulations investigated in this project. **Figure 11** shows the thermal gravimetric analysis (TGA) for the urethane control and composite. At just above 100°C, the control begins to lose some mass - mostly water - while the composite polymer film is more stable. However, both films begin substantial thermal decomposition around 290°C and by the time 450°C is reached, both films have lost substantial mass. This represents essentially complete decomposition of the polymer matrix. However, as seen with the composite in the TGA for the composite film, the weight loss ceases before
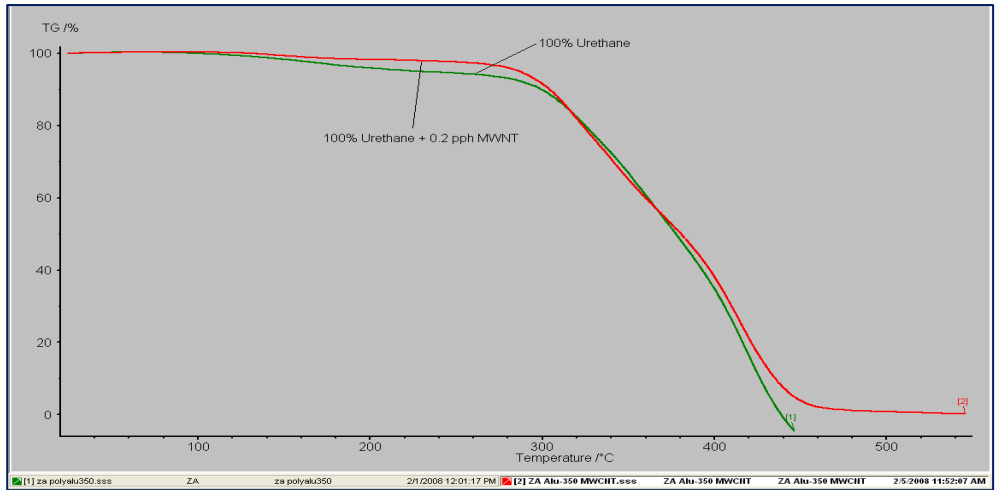

Figure 11: TGA curves for 100 % urethane (with and without 0.2 pph MWNT)

complete decomposition. What remains at that point are most likely CNTs. **Figure 12** shows similar data for the 50/50 oligomer blend systems. This time both the control and the composite seem to have higher thermal stability than the urethane-based system and decomposition occurs
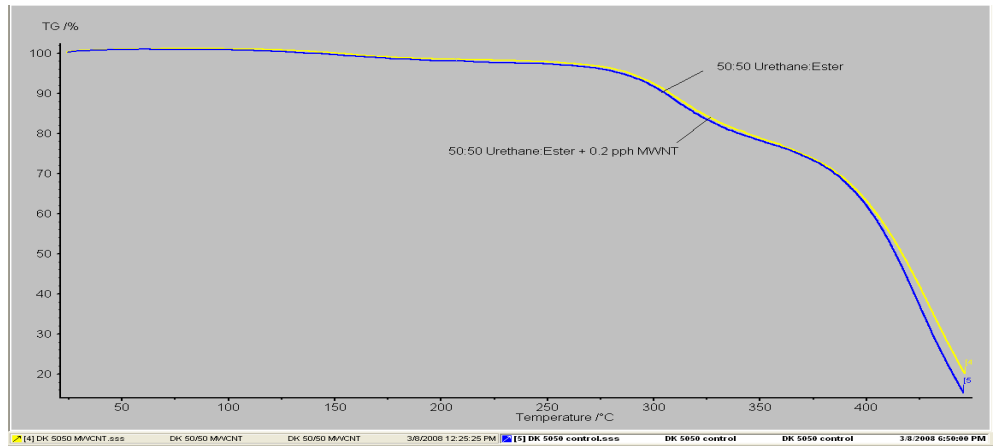

Fig 12: TGA curves for 50/50 urethane/polyester (with and without 0.2 pph MWNT)

in two stages. At the end of the scan, both the control and the composite had in excess of 15% of their mass remaining.

Figure 13 indicates that once again, the 100% polyester control is less thermally stable than the composite material. But the two-stage decomposition is evident here also. Thus, it appears that the MWNTs may impart some small amount of thermal stability to acrylate-based formulations but mixing the oligomers also seems to help in this regard (**Figure 12**).
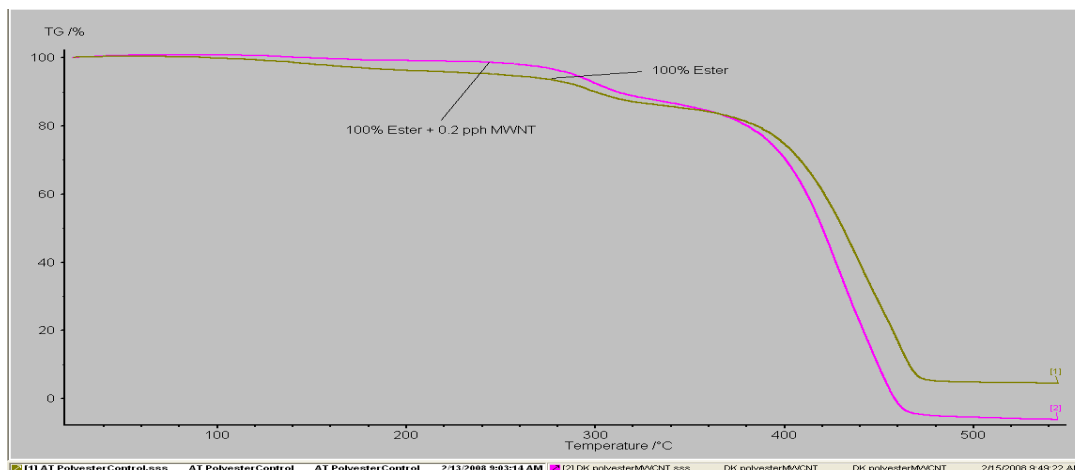

Figure 13: TGA curves for 100% (polyester with and without 0.2 pph MWNT)

A direct comparison of the TGA results for the three composite materials is given in **Figure 14** while **Figure 15** shows that the MWNTs themselves have good stability over the temperature range investigated.
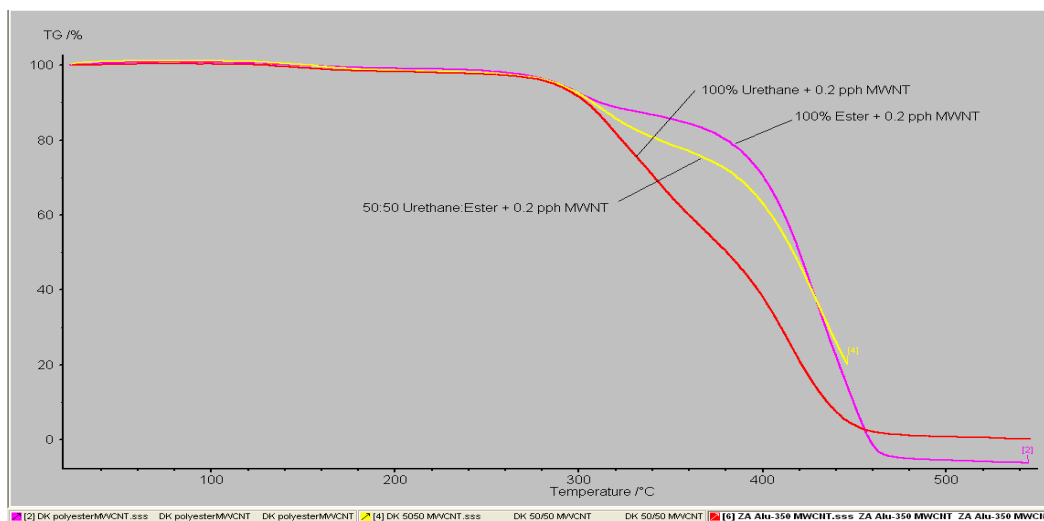

Figure 14: Overlay of 100% urethane with 0.2 pph MWNT, 50/50 urethane/polyester with 0.2 pph MWNT, and 100% polyester with 0.2 pph MWNT

Summary and Conclusions

UV-polymerizable acrylate-functional formulations containing SWNTs and MWNTs have been prepared using an updated dispersion process that involves neither surfactants nor conventional solvents. These liquid dispersions have been characterized by UV-Vis spectroscopy and by
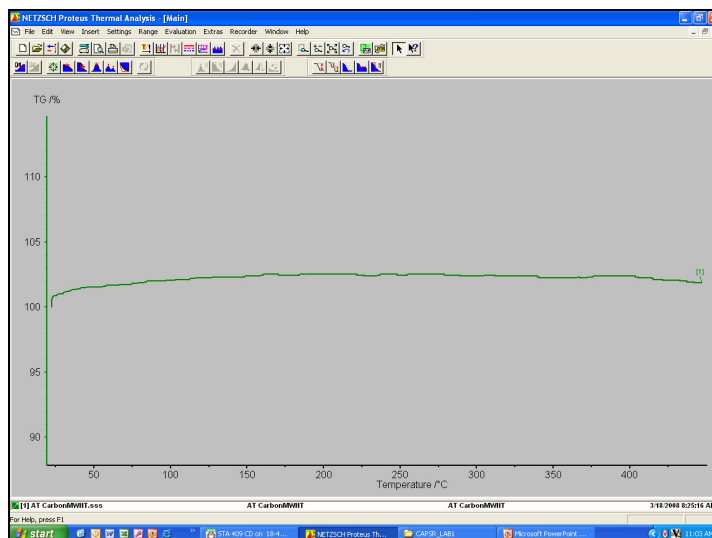
Fig. 15: TGA for MWNTs

measurement of their viscosities as a function of shear rate. Using UV, these liquids have been polymerized and crosslinked and the resulting polymer films have been characterized using DMA and TGA techniques.

The SWNT-containing formulations were prepared at higher concentrations than previously reported in this laboratory. This was accomplished through an improved dispersion technique and UV-Vis spectroscopy confirmed adequate exfoliation of the SWNTs was achieved by the presence of Van Hove Singularities.

MWNT-based formulations were very easy to prepare with the new dispersion process and had very good shelf-stability with respect to phase separation and settling. However, due to the more heterogeneous nature of the MWNTs, no distinct Van Hove Singularities were observed.

Previously reported work from this laboratory[2] involved only acrylated aliphatic urethane oligomer-based systems. In this project, polyester-based oligomers and blends of polyester and urethane were investigated. The polyester-based systems appeared to have stronger interactions with the MWNTs than did the urethane-containing formulations. This was revealed by the fact that the polyester liquid formulations did not exhibit shear thinning up to 40 rpms and the Tg of the polymer composites were higher. The MWNTs may also have reduced the amount of microgel formation in the polyester systems as indicated in the tan δ half-height width data.

This investigation, once again, demonstrates that CNTs can be easily dispersed in acrylate-functional, UV-polymerizable systems and can impart enhancements of certain properties of the polymers produced. More work is needed to determine the effects of the CNTs on electrical properties and mechanical properties of the polymers.

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