

News



The Society of Plastics Engineers

ENGINEERING PROPERTIES
& STRUCTURE DIVISION

July 2012

Chairperson's Report



Dear EPSDIV Members,

A year has passed really quickly and it is time for another newsletter. I recall having a good time networking with colleagues at ANTEC 2011 in Boston. I am pleased to take over the chairmanship for EPSDIV from Frank Cangelosi, who laid a strong foundation for my succession, during ANTEC/NPE 2012 in Orlando. I'm grateful for the many tips that he provided to help me in this new role.

It was a great year of achievements for EPSDIV. SPE fellowships were conferred on Drs. Brian Grady and Hoang Pham, with our heartfelt congratulations! We also witnessed many awards and award recipients including the best paper award and the John O'Toole award at our

Division reception in Orlando. The best paper awards for this ANTEC 2012 will be given to Daniel Schmidt and Luyi Sun, for their papers on "Mechanical Properties of Cycloaliphatic Terephthalate Co-polyester Clay Nanocomposites" and "Preparation of Intercalated Organic/Inorganic Hybrids via In-Situ Synthesis", respectively. Congratulations to them both. We also thank the judges who helped us select these papers. The Division also received the Pinnacle Silver Award again this year. The Technical Program for ANTEC 2012 was a great success, due to both TPCs, Drs. Sedat Gunes and Brian Grady who did a fantastic job. Sponsorship for ANTEC came in strongly with 12 companies sponsoring our program this year. We welcome new board members, Dr. Duane Simonson from the U S Naval Research Laboratory in Washington DC, and Dr. Sreekumar Pisharath, from the Energetics Institute at Nanyang Technological University, Singapore, and thank them for their willingness to serve and contribute to our plastics community.

CONGRATULATIONS!

Congratulations are extended to John Trent who is now the Chair-Elect for the Division in addition to capably continuing to serve as our newsletter editor. Sreekumar Pisharath is assisting with local organization and speaker coordination for ANTEC Mumbai on December 6-7, 2012 which will be held at the Renaissance Mumbai Convention Centre in India.

Continued on Page 3

SAVE THE DATE !



ANTEC® 2013

April 22-24 | Cincinnati, Ohio USA
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ANTEC 2013 TPC Report



Milan Ivošević and Theresa Hermel-Davidock

1.0 Focus Areas for EPSDIV ANTEC 2013

SPE's Engineering Properties and Structure Division will continue to strengthen our core focus areas such as structure – processing – property relationships, testing and characterization as well as green technologies. In addition, we are also striving to expand and introduce new opportunities during the ANTEC 2013 in Cincinnati, Ohio.

The following are proposed new and expanded focus areas:

- Polymers in Medical Device, Pharmaceutical and Life Science Applications
- Functional coatings and polymer surface modification
- Computer Aided Engineering – modeling structure, process and properties
- Polymers in Military and Defense applications

Our core focus and strength remains as follows:

- Structure – Processing – Property Relationships
- Testing and Characterization (Mechanical/Chemical/Thermal)
- New Polyolefins and Polymers: Copolymers, Blends, Composites
- Polymer nanotechnology and nanocomposites
- Green technologies and sustainable source polymers
- Renewable energy, energy generation and storage
- Structure and properties modification by additive technology

2.0 Expanding Presence in New Areas via Forums

Currently the main focus of TPC's activities is to explore ways of possibly expanding our presence in new areas using the forums. The main effort is to have at least one and hopefully two out of the following three proposed forums:

FORUM 1: Polymers in Medical Device and Pharmaceutical Apps.

(Different from general medical and health applications such as implants etc. Large industries - leveraging TPC's professional fields)

FORUM 2: Modeling polymer structure, properties and processing.

(Refreshing focus in this ever evolving field)

FORUM 3: Functional coatings and polymer surface modification.

(Attracting more participants from the large field of organic coatings)

3.0 Keynote Speaker Focus Topics

The following are the main focus topics for EPSDIV ANTEC 2013 keynote speakers:

- Green technologies and sustainable polymers
- Polymers and energy
- Polymer modeling
- Medical and pharmaceutical applications
- Polymer testing and characterization
- New commercial polymers and compounds

4.0 Call for Papers

Submission deadline for papers is October 23, 2012 at 5:00 p.m. EST

- Both Abstract and Paper submission in ANTEC format, are required by above deadline

April 22-24 | Cincinnati, Ohio USA
Duke Energy Convention Center

Financial Report

from July 1, 2011 to June 22, 2012



Chairperson's Report Continued from Page 1

Our new TPCs, Milan Ivosevic and Theresa Hermel-Davidock, are actively organizing the technical sessions for ANTEC 2013 to be held in Cincinnati, Ohio. Additional topics on medical devices, modeling and functional coatings are being explored. We look forward to another great program ahead! Until next time, I wish everyone a great summer in 2012!

Shing-Chung "Josh" Wong

BALANCE as of July 1, 2011 **\$ 37,944.56**
(cash, checking, savings, investments)

INCOME	ACTUAL
Interest	\$ 505.71
SPE Rebate	1,741.76
ANTEC Sponsorships	6,631.10

TOTAL INCOME	\$ 8,878.57
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EXPENSES	
Newsletter Production	1,584.00
Awards	2,834.00
ANTEC	2,436.75
ANTEC TPC	3,500.00
Councilor Travel	3,539.76

TOTAL EXPENSES	\$ 13,894.51
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CASH FLOW	\$ 5,015.94
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ENDING BALANCE as of June 22, 2012	\$ 32,928.62
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*Submitted by Emmett Crawford, EPSDIV
Treasurer 2012-2013*



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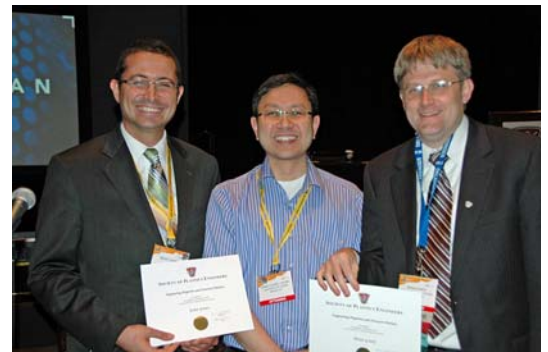
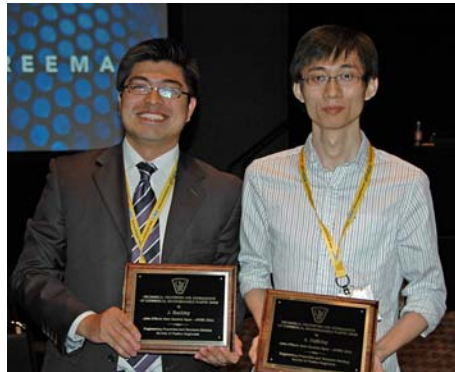
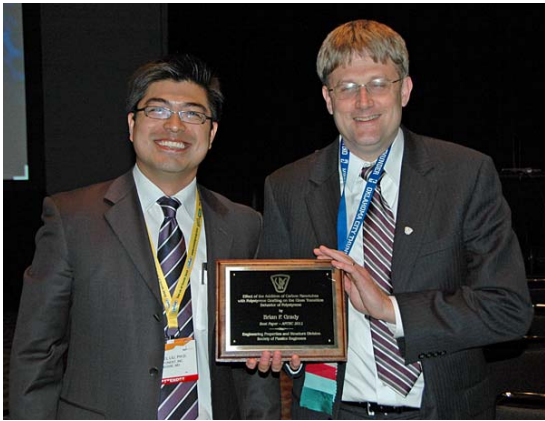
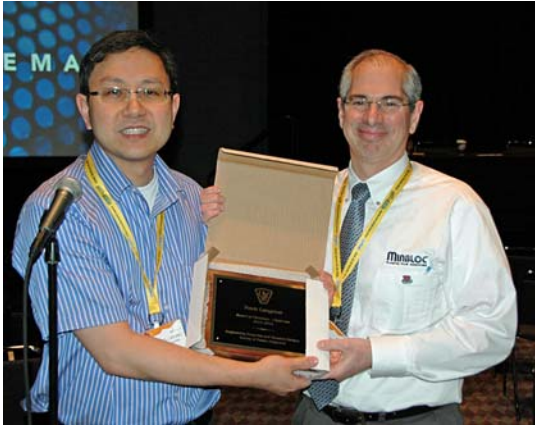
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“Thank You!” to all our Sponsors who supported EPSDIV Technical Programs during ANTEC 2012 in Orlando, FL.



Images from EPSDIV Annual Meeting at ANTEC 2012/NPE2012





The Dizziness of Freedom

As I recently sat in an outdoor Orlando pub with my frosty pint, skyscraper burger, and ocean of French fries, I contemplated how different my dining landscape would look in only a few minutes – based on my personal preference. Scenario one is a barren wasteland (an empty, ketchup smeared plate, foam lined mug, crumpled napkin) that leaves me satisfied and full from experiencing all my options. Scenario two has me leaving with a neatly arranged “to go” box with roughly half of my meal available for a later time. Still satisfied, I’m also positioned for an evening run while mentally solving the world’s problems. Alternatively, scenario three holds a bevy of emptied pints, and a grocery sized bag housing my entire untouched meal, recognizing my thirst while at the pub prior to squirreling away to catch some solitude of thought while watching a big game on television. Each of the scenarios had appeal. And the freedom to choose my own option made the pub “work” for me. Likewise, we want SPE to appeal to members and potential members because it presents options that fit their preferences.

We spent a lot of time discussing potential new choices within SPE during the council meetings at ANTEC. These discussions center around making SPE “work” better for all members AND for those who are not members yet. What we are finding is that this means we need to be a more flexible, dynamic organization, and we must be effective at communicating to a broader professional community. How will the SPE landscape look in the near future? Keep your eye out!

- Look for your SPE in large media news publications (Time, Newsweek, Popular Science etc.) where we showcase the global innovations of our industries and members.
- Look for SPE in small travelling Mini-Tec’s, which could be half or full day programs with no formal paper requirements.
- Look for SPE booths at other (non-SPE related) conferences and expos.
- And for our own conferences look for ANTEC Mumbai (December 2012) and Eurotec 2013 (Lyon, France) to build on the momentum generated at Eurotec 2011 (Barcelona) where over 200 papers were presented.

Why? Because as we work to appeal and meet the needs of a broader audience, we will need to offer a more flexible membership,

better communication, and easier access to both information and expertise. These will be tailored to Young Professional Members, Senior Members, and everyone in between. We are even evaluating a model where Student Members can obtain full membership in a group of societies (SPE included) for one small fee. Of course the success of all of this will depend on me and you. We need your innovation stories to be told to the world, your latest findings to be discussed at the regional Mini-Tec’s, and your interpersonal skills to advocate for SPE at a local conference or expo. So unlike Kierkegaard who said, “Anxiety is the dizziness of freedom,” I am saying, “Excitement is the anticipation of freedom in SPE.” I am excited that we will have greater ability to choose and greater opportunities to actively participate in SPE. I suppose it could be dizzying to think of the possible landscapes. SPE is moving toward a tasty new menu that will allow our organization to be exactly what each of us prefers in a professional society. So what landscape will you select or create? I would be happy to take your order!

- Brian Landes

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EFFECT OF THE ADDITION OF CARBON NANOTUBES WITH POLYSTYRENE GRAFTING ON THE GLASS TRANSITION BEHAVIOR OF POLYSTYRENE

*Brian P. Grady, University of Oklahoma, Norman, OK
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Abstract

The effect of single-walled carbon nanotubes on the glass transition of polystyrene with and without polystyrene grafting has been quantified. Three different molecular weights, 2,800, 15,000 and 50,000 g/mol, of polystyrene were grafted to the nanotubes with the weight fractions of grafted chains approximately the same. Composites with 50 K grafted nanotubes were statistically identical in terms of the glass transition temperature and change in heat capacity. Composites with lower molecular weight grafted nanotubes did show significant differences vs. the composites with ungrafted nanotubes, especially in terms of the change in heat capacity.

Introduction

Fundamental studies of how a surface affects the chain dynamics of polymers have been a very fertile field of investigation. The influence of a solid interface on the glass transition (T_g) behavior of a polymer was first investigated by using thin films cast on flat surfaces.¹⁻⁴ More recently, polymers containing particles with significant surface area/volume ratios, i.e. nanofilled materials, have been used.⁵ In the latter case, geometric arguments indicate that the average distance between a polymer and a surface is in the tens of nanometer range depending on dispersion, filler loading etc.

The effect of a solid surface on polymer dynamics depends on the nature of the interaction between the polymer and the surface. In the case of a favorable interaction between a surface and polymer, three effects could be observed in a normal differential scanning calorimetry (DSC) heating scan of an amorphous polymer around the glass transition temperature: (1) an increase in T_g ; (2) a change in the temperature range over which the glass transition occurs; (3) a reduction in the heat capacity increase at the glass transition (ΔC_p). The latter represents the case where the dynamics have been altered for a fraction of the material to such an extent so as to cause a separation between regions of the polymer in a dynamic sense. This separation could cause a noticeable second glass transition at a higher temperature, or could cause no noticeable second glass transition due to the fact that the second T_g is above the polymer degradation temperature. A third possibility is that the glass transition is so broad that a normal jump in heat capacity is not distinguishable; the authors are not aware of any situations where this much broadening has occurred in nanocomposites.

A previous study by our group investigated the effect of the addition of nanotubes that had been lightly functionalized with carboxylate groups (primarily carboxylic acids) on the glass transition of polystyrene.⁶ The results of this study, critical to understanding the current study, are presented in Figure 1. T_g increased until reaching a constant value, while the heat capacity showed a decrease, followed by a plateau. At high nanotube concentrations, the heat capacity increased which was extremely unexpected and a unambiguous explanation for this behavior was not presented, although the best idea was that the nanotubes were relaxing as the polymer relaxed at high concentrations.

Experimental

Materials Styrene was purchased from Acros and purified by passing through basic alumina. Benzoyl peroxide, 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%), tetrahydrofuran (THF, laboratory grade), and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 98%) were purchased from Sigma-Aldrich and used as received. HiPco single-walled carbon nanotubes (SWNTs) were purchased from Carbon Nanotechnologies, Inc, Houston, Texas; Lot#: P0340.

Synthesis

SWNTs were treated with 8 M nitric acid for 2 h with sonication at 40°C to produce lightly carboxylated tubes; further details are given elsewhere.⁷ This procedure was the same used to produce the tubes used in the samples represented by Figure 1. The PS-TEMPO samples were synthesized as described elsewhere.^{8,9} Three different number average molecular weight end-functionalized polystyrene molecules were grafted to the nanotubes: 2.8×10^3 g/mol, 1.5×10^4 g/mol, and 5.0×10^4 g/mol. In all cases, the polydispersities were less than 1.4.

SWNTs in a NMP dispersion were functionalized with TEMPO ended polystyrene by the method of Lou.¹⁰ A 150 mL round-bottomed flask was charged with 25 mg of SWNT-COOH and 50 mL of NMP. Nitrogen gas was bubbled through the solution for 30 min, followed by bath sonication at room temperature for 1 h, continuously purging with nitrogen. The polystyrene solution was prepared from 1.25 g of PS-TEMPO in 5 mL of NMP with stirring for 4 h. The PS solution was added with stirring to the SWNT dispersion. After 30 min of stirring the nitrogen gas flow was stopped, and the flask was

sealed and immersed for 24 h in an oil bath at 130°C. The resulting mixture of SWNT-g-PS and ungrafted polystyrene was diluted into 20-fold of THF and centrifuged for 30 min at 540 x g. The supernatant liquid was removed, and the sample was re-dispersed again in THF. The process was repeated 3 times until the supernatant liquid showed no precipitate in excess methanol. Afterwards the solution was filtered by using a vacuum glass filtration cell and 0.2 μm polytetrafluoroethylene membrane, washed with THF and re-dispersed in 25 mL of NMP solvent. The dispersion was bath sonicated for 15 min at room temperature followed by 24 hr stirring with magnetic stirrer. The SWNTs remained dispersed in NMP for at least 3 months, but were used for composite preparation right away. Figure 2 shows this process schematically. The grafting densities (weight of polymer/weight of tubes) were approximately equivalent in all cases at about 0.25. Thermogravimetric analysis (Figure 3) was used to determine the percentage of polymer grafted to the tubes.

Samples of SWNT-g-PS in 0.045 g/L dispersions in NMP described above were used for composite preparation. An industrial grade polystyrene having $M_n = 70,000$ and $M_w/M_n = 3.2$ was the matrix polymer. The dispersion of SWNT-g-PS in NMP was mixed with the matrix polystyrene in NMP and stirred for 1 h. The mixture was added dropwise to a ten-fold excess of distilled water with vigorous mechanical stirring. The composite was filtered, washed with water and methanol, and dried at 70°C overnight.

DSC Methods

Glass transition temperature (T_g) and heat capacity jump at the glass transition (ΔC_p) were measured using a 10°C/min temperature ramp after a 60°C/min cooling from a fully melted sample. Both the heat capacity jump and T_g were determined using the midpoint method. Calibration was performed using indium, tin and biphenyl for temperature, and sapphire for heat capacity and enthalpy.

Discussion

T_g change with added nanotubes is identical within experimental error as shown in Figure 4,5 and 6. Error bars on the plots represent error bars for the same sample measured multiple times; duplicate measurements (i.e. two points at the same nanotube concentration) represent the results for a sample that was remade. As noted in our previous paper,⁶ the largest error in these experiments is in the making of multiple samples, not in the measurement of a single sample. The behavior of all samples can be described as a steep increase in T_g at low concentrations of about 8°C/wt% nanotube, followed by a plateau region that starts at about 1% nanotube content and remains constant.

One important characteristic of this study is that the grafting densities were almost identical, at about 25 wt% polymer. In other words, the total number of polystyrene chains attached in the case of the 2800 molecular weight polystyrene was approximately 20 times higher than that of the 50,000 molecular weight sample. In the limit of infinite grafting molecular weight under these restrictions, the behavior should revert to that of the unmodified material. Clearly then, it is possible that at some finite molecular weight the behavior of the composites made with grafted-to nanotubes will match that of the unmodified composite. Our data suggests that grafted material with 50 K molecular weight is not significantly different than the ungrafted material. However, this statement is a bit misleading since the two highest nanotube concentrations, 20 and 25%, do not appear on the graph. These particular samples had a qualitative change in the DSC spectra, namely the glass transition region was much broader. We are unable to assign a cause to this behavior; although our belief is that something in the sample making procedure causes this behavior. The key clear issue with Figure 6 is that the introduction of nanotubes causes a reduction in the heat capacity, which is a result of polymer immobilization at the nanotube interface.

Composites made with 15 K grafted material also qualitatively match the behavior of the unmodified material, although the dip was not as deep. Alternatively, Figure 5 possibly could be interpreted as no change in ΔC_p , i.e. no immobilization. The graph for the 2.8 K modified nanotubes (Figure 4) shows a very different behavior; a consistent decrease in the heat capacity. The low molecular weight grafted material should act as a plasticizer and hence lead to no change in the ΔC_p ; we are quite surprised about this behavior. One possible explanation is that the dispersion in the polymer is better due to the high grafting density. However we would have expected a more steady decrease in T_g as well, although the equivalence of the T_g change does not rule out dispersion being the cause of the different behavior. Alternatively, it could be some subtle interaction of the matrix polymer with the grafted polymer. Again, the 20% material is missing because of a qualitative change in the behavior, i.e. extreme T_g broadening.

Conclusions

The introduction of nanotubes into a polymer can cause a reduction of material that participates in the glass transition, which is caused by an immobilization of material at the interface. The qualitative and quantitative characteristics of this immobilization are affected by the grafting of the same polymer of different molecular weights on the nanotube surface.

References

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- ¹⁰ X. Lou, C. Detrembleur, V. Sciannamea, C. Pagnoulle and R. Jerome, *Polymer*, 2004, **45**, 6097.

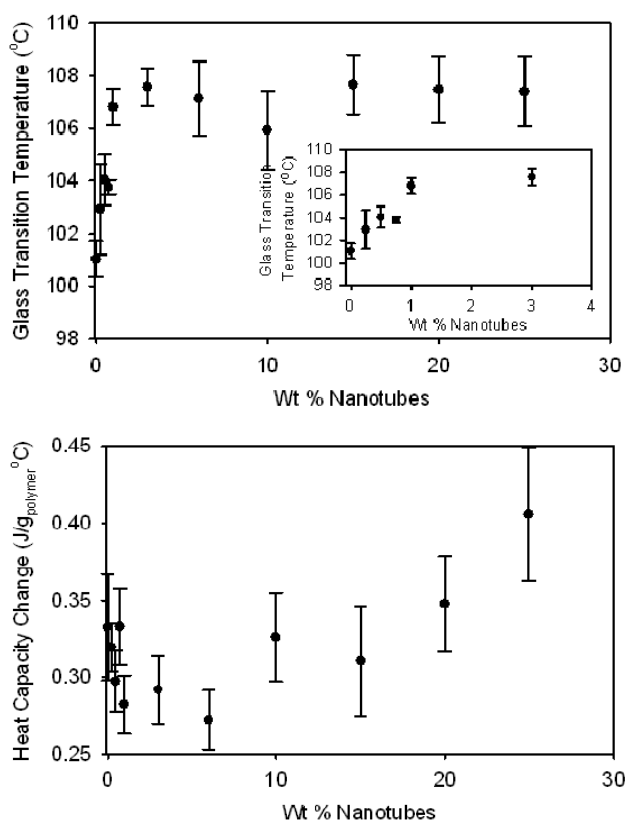


Figure 1: T_g and heat capacity change for polystyrene filled with SWNTs that have been lightly treated with nitric acid to form carboxylates on the surface.

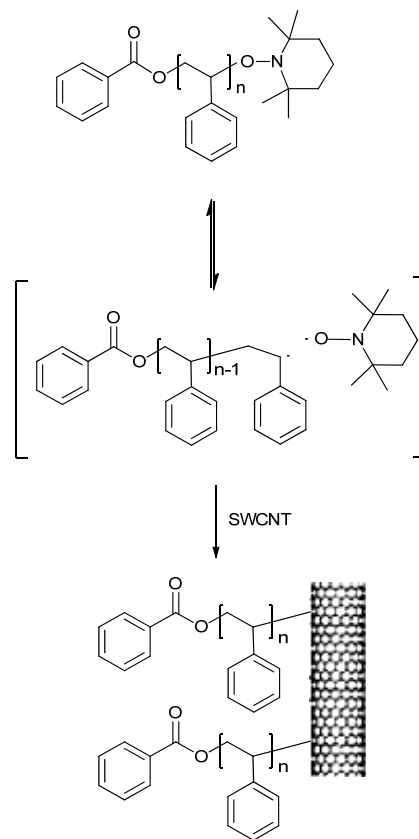


Figure 2: Schematic of grafting to process of polystyrene-TEMPO to nanotubes.

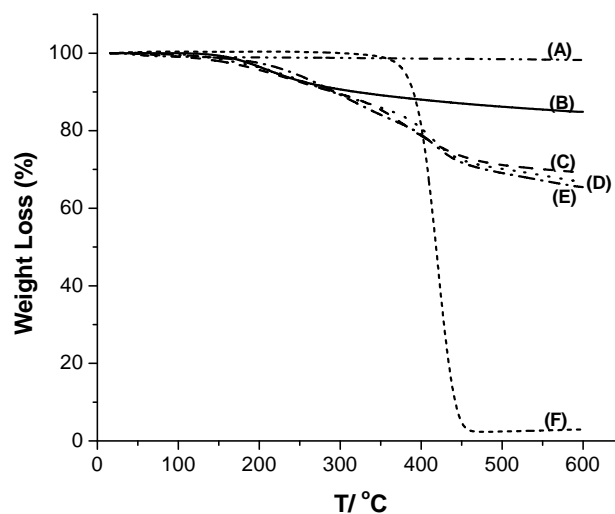


Figure 3: Thermogravimetric analysis of (A) pristine SWNT, (B) nitric acid treated SWNT-COOH, (C) SWNT-g-PS ($M_n = 2274$ g/mol), (D) SWNT-g-PS ($M_n = 15000$ g/mol), (E) SWNT-g-PS ($M_n = 50000$ g/mol), and (F) polystyrene ($M_n = 50000$ g/mol), under nitrogen at 5°C/min .

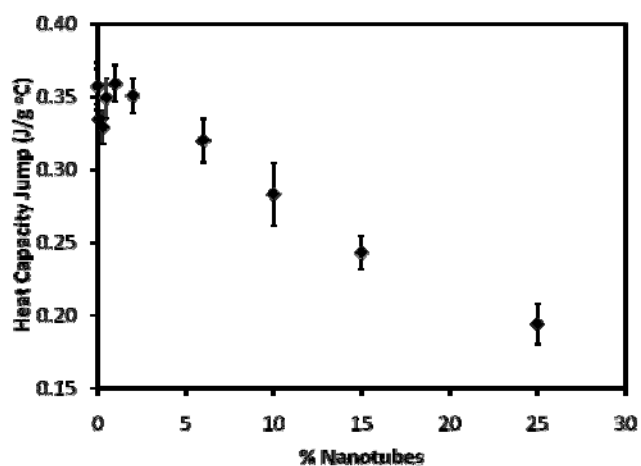
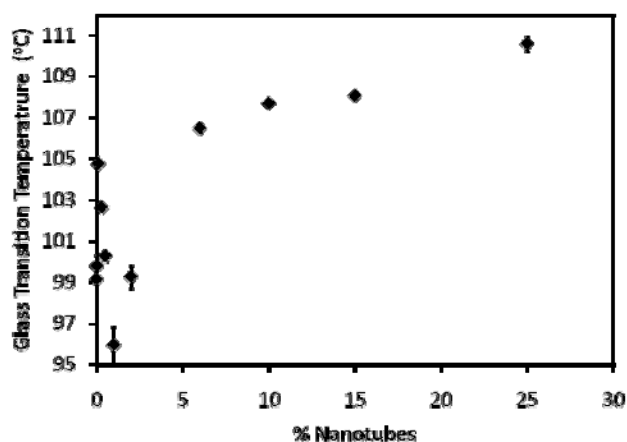


Figure 4: Tg and heat capacity change for polystyrene filled with SWNTs that have been grafted with 2.8 K MW polystyrene.

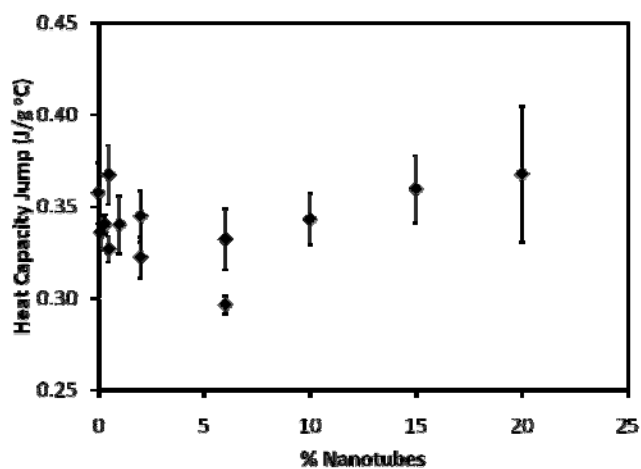
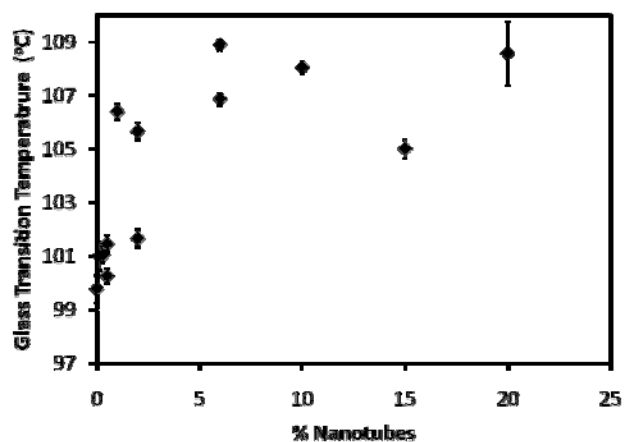


Figure 5: Tg and heat capacity change for polystyrene filled with SWNTs that have been grafted with 15 K MW polystyrene.

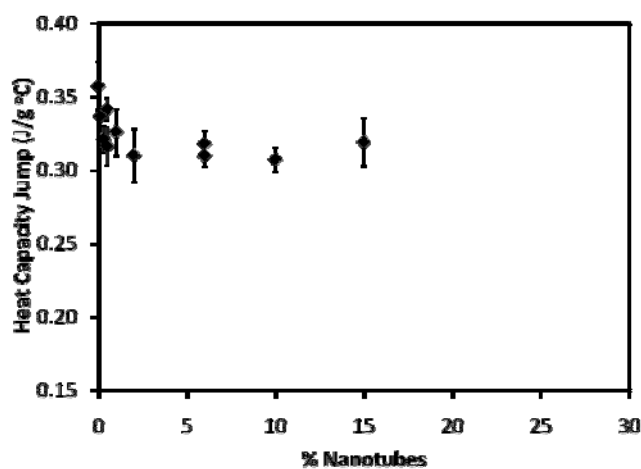
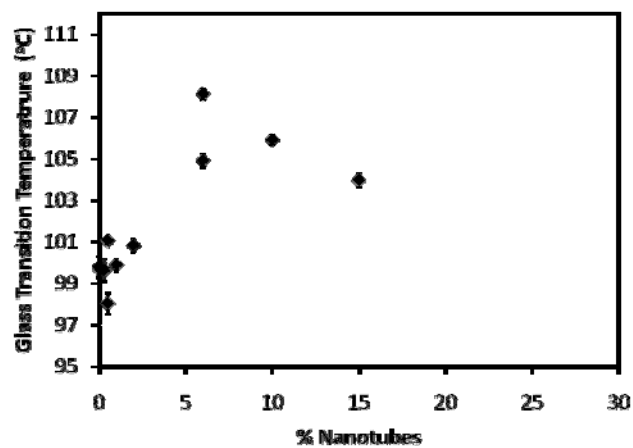


Figure 6: Tg and heat capacity change for polystyrene filled with SWNTs that have been grafted with 50 K MW polystyrene.