News

The Society of Plastics Engineers

ENGINEERING PROPERTIES
& STRUCTURE DIVISION

August 2011

Chairperson's Report

Another (EPSDIV) Year Begins…

Dear EPSDIV Members,

It is an honor to once again serve as the chairman of our Division. The last time I took on this responsibility it was 1990 (at least that's according to the plaque on the wall, which I think MUST be a misprint!) Things have certainly changed in these twenty plus years. Of course, one of the biggest changes is how we communicate with each other, both in our professional and personal lives. It seems that we can be connected to the world without ever turning away from our computer screens. Call me old fashioned, but I do miss some of the personal interaction that was much more common back in 1990. Some of this change of course has migrated into how we involve ourselves in professional activities such as our membership in SPE. Certainly much is now efficiently accomplished without that personal interaction, yet I am also struck by how much the core mission of SPE and EPSDIV remains unchanged, and how important it is to stay active in professional societies like this. At our core, we remain a Division focused on the development and dissemination of plastics technical information and for EPSDIV that means our priority remains strong technical programming. I hope you will see some evidence of this priority by reading through the pages of this newsletter.

Looking ahead, my goals for the Division are simple: to continue to lead in technical programming related to the engineering properties and structure of plastics, and to accelerate our support of plastics education initiatives.

Fortunately, we are well positioned to achieve our goals with a group of dedicated professionals which comprise our Board of Directors and Technical Program Committee. I want to especially thank our outgoing Chairman, Pierre Moulinie, for his outstanding leadership during 2010-2011. I also wish to congratulate and welcome our new board members who won election (or in some cases re-election) in the spring, namely Paul Rothweiler, Rajen Patel, and Murali Rajagopalan.

(Continued on Page 2)

ANTEC 2012

NPE2012

Orange County Convention Center (OCCC) in Orlando, FL,

INSIDE THIS ISSUE

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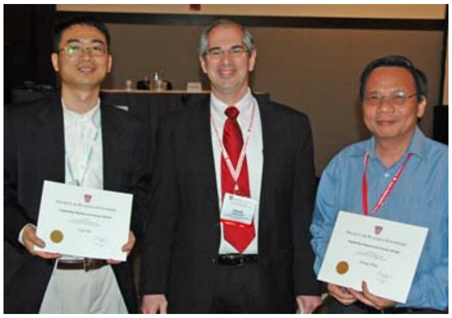
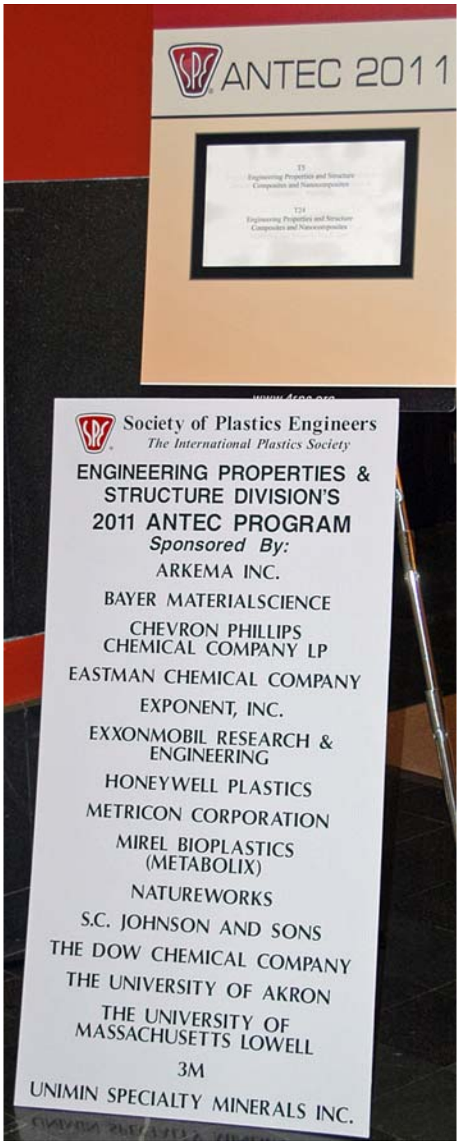
Thanks to the efforts of our 2011 TPC leaders, Luyi Sun and Hoang Pham, as well as our many members who contributed papers, our technical program at ANTEC in Boston was a major success. We were able to offer a robust program of 14 sessions, including global participation and 14 keynote speakers.



Also responsible for this achievement were the many companies and universities who participated in EPSDIV's ANTEC Sponsorship Program. The funds generated from this program helped us tremendously to put this all together.

Next on the calendar, EPSDIV members (and particularly Brian Grady) are working hard to bring success to Eurotech, which will be held on November 14-15 in Barcelona, Spain. EPSDIV members are helping with technical programming as well as paper submissions and reviews for this event.



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Looking beyond to 2012, our co-TPC Chairs Sedat Gunes and Brian Grady are hard at work preparing our next ANTEC program in Orlando. Areas of focus will include such hot topics as polymer nanocomposites and renewably sourced polymers.

Orange County Convention Center

EUROTEC™ 2011
November 14-15, 2011
Barcelona, Spain

Please keep in mind that paper submission deadlines are early this year due to the co-location of ANTEC with NPE. The due date is October 19 – so start working on those papers!

Regarding support of plastics education, this year EPSDIV commemorated a significant milestone – the twenty fifth anniversary of the John O'Toole Award. It has been sponsored since its inception by Honeywell Plastics (formerly Allied Chemical). This award is open to all undergraduate students (not just EPSDIV members) who deliver podium presentations at ANTEC. In addition to a financial award and plaque for the winner, EPSDIV is now sponsoring SPE student memberships for all award finalists.

Let me close by stating that our successes and future initiatives would not be possible without the hard work and dedication of both our board members and our membership. I am extremely lucky to be supported by a talented and capable board of directors. Nevertheless, a truly vibrant society requires the involvement of all its members and our future success depends on your ideas and contributions. So I urge all EPSDIV members to get involved in our activities - if you see anything in this newsletter that sparks your interest, by all means let us hear from you!

Until next time, I wish everyone a happy and productive summer!

- Frank Cangelosi

Engineering Properties and Structures Division / SPE Memo

TO: **All SPE Student Chapter Advisors**
DATE: August 18, 2011
SUBJECT: **O'Toole Outstanding Undergraduate ANTEC Paper**

Since the 1980s EPSDIV has sponsored the John O'Toole Memorial Award for Outstanding Undergraduate Student Paper presented at ANTEC. This globally-recognized award is generously funded by The Honeywell Corporation in memory of its outstanding Allied Chemical employee, John O'Toole.

Through the years this award has been presented to undergraduates who have delivered podium presentations on a myriad of topics, including alloys & blends, thermoplastics composites, innovative packaging materials, and modified elastomers.

EPSDIV invites undergraduates to submit papers for presentation at ANTEC 2012 in Orlando. A committee of EPSDIV members will review these papers and the finalists will be incorporated into the ANTEC podium presentation schedule. **Each finalist will also be offered an EPSDIV-sponsored SPE Student Membership.**

To be considered for the O'Toole Award, undergraduate students should simply follow the rules and observe the deadlines for all ANTEC papers. Additionally, at the same time, a separate copy of your paper should be mailed directly to Daniel Liu for EPSDIV panel review. The author(s) undergraduate advisor's contact information **must** be included.

If you have any questions, please contact Daniel Liu, Ph.D. at: Exponent, 17000 Science Drive, Suite 200, Bowie, MD 20715 (Office: 301-291-2504) or e-mail (djliu@exponent.com).

We look forward to your students participating in our EPSDIV awards competition.

Steve Driscoll
Secretary, EPSDIV

ANTEC 2011 Student Luncheon

…

Matthew Bernasconi receiving John O'Toole Best Student Paper Award from Daniel Liu

ANTEC 2012 Technical Progran Committee Report

I. Sedat Gunes and Brian Grady

The EPSDIV technical program for ANTEC 2012 is shaping up rapidly with excitement. Most of our Keynote speakers and contributors in our memorial sessions promptly and graciously accepted our invitations. We are still working with a couple more contributors to resolve their scheduling conflicts and finalize the program. In accordance with our strategic technical plan which was discussed at the planning meeting in ANTEC 2011, we aimed to have contributors from different technical backgrounds and countries in addition to the US and Canada. Below is the list of our confirmed Keynote speakers.

We have almost finalized the technical programs of our memorial sessions as well. Our first session will be in memory of Dr. Kyonsuku Min, Professor of Polymer Engineering at The University of Akron, Akron, OH, USA, who unfortunately passed away in April 2010. The following colleagues of Professor Min kindly agreed to contribute to the memorial session:

1. **Professor Robert Weiss,** The University of Akron, USA
2. **Professor Sadhan Jana,** The University of Akron, USA
3. **Professor Avraam Isayev,** The University of Akron, USA
4. **Professor Yusuf Menceloglu,** Sabanci University, TURKEY
5. **Professor Ica Manas-Zloczower,** Case Western Reserve University, USA
6. **Dr. Baris Yalcin,** 3M Energy & Advanced Materials Division, USA

(Continued on Page 6)

EPSDIV 2012 Keynote Speakers

1. **Dr. Haris Doumanidis,** Nanomanufacturing Program Director, US National Science Foundation, USA
2. **Dr. Amit Naskar,** Staff Scientist, Polymer Matrix Composites Group, US Oak Ridge National Laboratory, USA
3. **Professor Evan Mitsoulis,** School of Mining and Metallurgical Engineering, National Technical University of Athens, GREECE
4. **Dr. Tommie Kelley,** Advanced Research Specialist, 3M Display & Graphics Film Laboratory, USA
5. **Professor Abdellah Ajji,** Department of Chemical Engineering, École Polytechnique de Montréal, CANADA
6. **Professor Yusuf Menceloglu,** Department of Materials Science & Engineering, Sabanci University, TURKEY
7. **Professor Maria Auad,** Department of Polymer & Fiber Engineering, Auburn University, USA
8. **Professor Guillermo Jimenez,** Laboratorio de Polímeros, Universidad Nacional, COSTA RICA
9. **Dr. John Wagner,** Editor-in-Chief of *Journal of Plastic Film & Sheeting*, USA

Call for Papers

ANTEC® 2012

Engineering Properties & Structure Division (EPSDIV)

April 2-4, 2012
Orange County Convention Center
Orlando, Florida, USA

Paper Submission Deadline:
October 19, 2011

For detailed Information:
www.antec.ws

Research areas of interest:

Polymer Nanocomposites
Chemical/Mechanical/Thermal Characterization
New Polyolefins & Polymers
Energy & Renewable Energy
Renewable Sourced Polymers
Modeling of Engineering Properties

Financial Report
from July 1, 2010 to June 30, 2011

BALANCE as of July 1, 2010	**$ 36175.23**
(cash, checking, savings, investments)	
INCOME	**ACTUAL**
Interest	$ 980.54
SPE Rebate	1091.61
ANTEC Sponsorships	4973.00
New Member Drive	75.00
TOTAL INCOME	$ 7120.15
EXPENSES	
Education	93.00
Newsletter Production	1584.00
ANTEC TPC	2083.84
Awards	506.00
Teleconferences	102.64
Councilor Travel	981.49
TOTAL EXPENSES	$ 5350.97
CASH FLOW	$ 1769.18
ENDING BALANCE as of June 30, 2011	**$ 37944.41**

- Submitted by Emmett Crawford, EPSDIV
Treasurer 2011-2012

(Continued from Page 4)

Our second session will be in memory of Dr. Jim Harrington, founding editor and long time editor-in-chief of *Journal of Plastic Film & Sheeting*, who unfortunately passed away in February 2010. The following colleagues of Dr. Harrington kindly agreed to contribute to the memorial session:

1. **Dr. John Wagner,** Editor-in-Chief of *Journal of Plastic Film & Sheeting*, USA (Keynote speaker)
2. **Professor Abdellah Ajji**, École Polytechnique de Montréal, CANADA
3. **Professor Miko Cakmak**, University of Akron, USA
4. **Professor Douglas Hirt**, Clemson University, USA
5. **Professor Evan Mitsoulis,** National Technical University of Athens, GREECE
6. **Professor HJ Sue**, Texas A&M University, USA

Starting with our next newsletter, we will be presenting brief highlights about our Keynote speakers and the invited speakers in our memorial sessions.

- Sedat Gunes & Brian Grady

ANTEC 2011 - EPSDIV
Best Paper Award

goes to

Brian P. Grady, University of Oklahoma, & **Abhijit Paul and Warren T. Ford**, Oklahoma State University

"Effect of the Addition of Carbon Nanotubes with Polystyrene Grafting on the Glass Transition Behavior of Polystyrene"

CONGRATULATION!

(This paper is presented on page 9

Are We Sustainable?

Less than a decade ago this question would have evoked a very different response from me than it does today. It would have prompted me to evaluate whether or not there were enough resources (financial, people, and even personal) to continue to *survive* as a business, professional society, club or any other type of organization that I may have been a part of. Less than a decade ago a “sustainable business” was simply one that would turn a profit year after year. The question, are we sustainable, might have forced the business to evaluate the reliability income streams, the potential to reduce costs, or potential for new revenue sources. Does any of this sound familiar? During the past decade we have discussed openly, as individuals, and as a society, the challenges that we have faced in ensuring the “sustainability” of SPE – based on this definition of the term. We asked these questions, and answered them with concrete strategies designed to propel our society into the next decade.

Today, however, “sustainability" has morphed its meaning into something very different – and evokes a very different response. It has become both an organizational buzzword and a personal commitment.

Sustainability now drives a triple bottom line: the economic, environmental and social impact of an organization. A company that wants to be sustainable today is not just a business that can survive year after year financially, but one that flourishes without compromising the environment or negatively affecting the global community.

Ten years ago… our response in SPE to the question, “Are we sustainable,” would have been parallel to the business’ questions, asking ourselves: do we have enough people paying dues to sustain the programs, and can we cut costs to sustain our programs? Today, rather than the “survivalist” mentality, our response now becomes, “Are we equipping our members to *be* more sustainable – using a new definition?” Today, sustainability has become a basis for disruptive innovation – thinking outside the historical box to reinvent the future. We engage our collective membership to create and become a part of a new “vision,” one that evaluates the entire life cycle of products, processes and inventions. We, as SPE, are uniquely positioned to connect products and technology with human progress. We are also positioned to help educate consumers to understand the inherent benefit-risk scenarios associated with technological solutions. Our responsibility has extended beyond the business decisions to personal and professional responsibility. Sustainability has taken on a multi-faceted personality and has become the “right way” to do business, going beyond a self-centered perspective to a global perspective.

SPE continues to evolve to provide members with that global perspective; it is your vehicle to put you in contact with sustainability expertise in government, NGO, academic, industrial, and professional organizations. As individuals we need to cultivate these relationships to help us to grow – to be sustainable. Together, as a society, we can design, promote, contribute to, and share in the global sustainability vision! We can be a very real part of important solutions that will change the shape and health of our society and the entire world. That is now how we answer the question, “Are we sustainable?”

- 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
Abhijit Paul and Warren T. Ford, Oklahoma State University, Stillwater, OK

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 x 10^3 g/mol, 1.5 x 10^4 g/mol, and 5.0 x 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.

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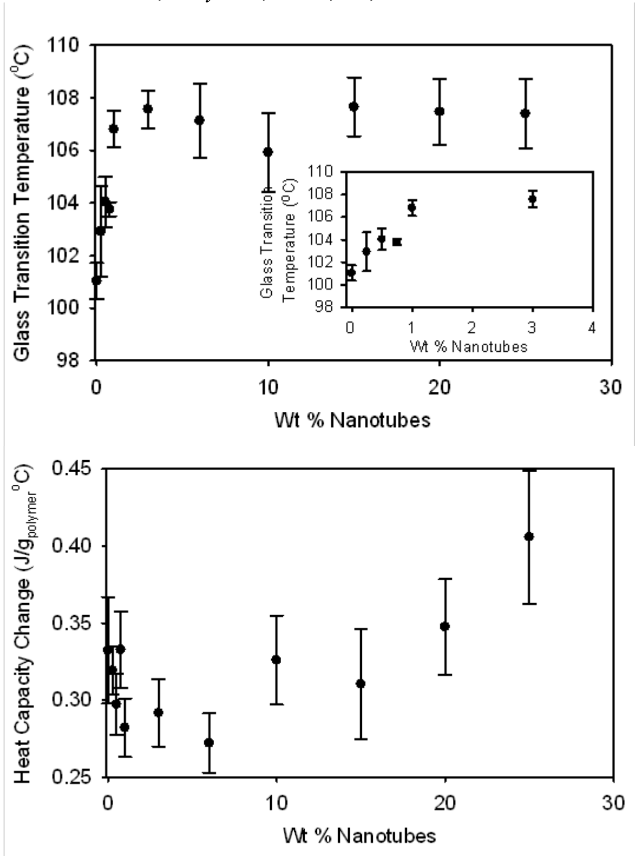


Figure 1: T_g and heat capacity change for polystyrene filled with SWNTs that have been lightly treated with nitric acid to form carboxylates on the surface.

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

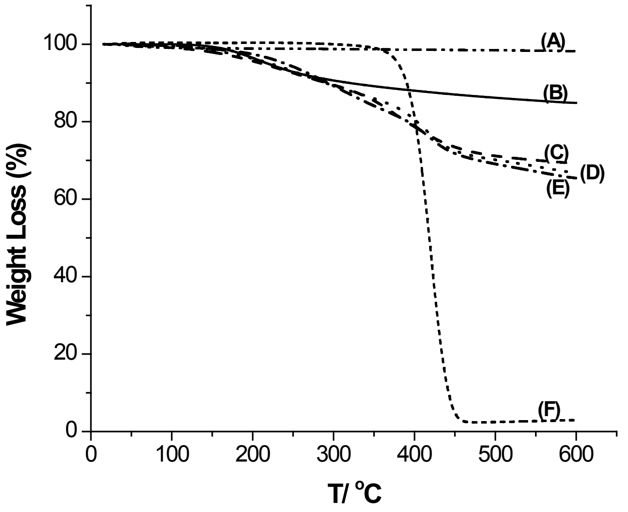


Figure 3: Thermogravimetric analysis of (A) pristine SWNT, (B) nitric acid treated SWNT-COOH, (C) SWNT-g-PS (M_n= 2274 g/mol), (D) SWNT-g-PS (M_n= 15000 g/mol), (E) SWNT-g-PS (M_n= 50000 g/mol), and (F) polystyrene (M_n= 50000 g/mol), under nitrogen at 5 °C/min.

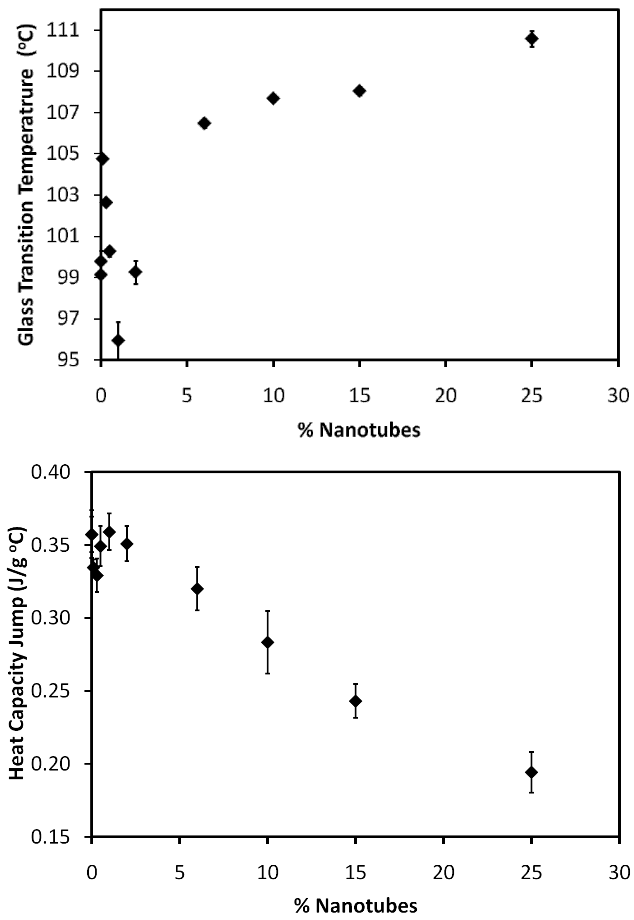
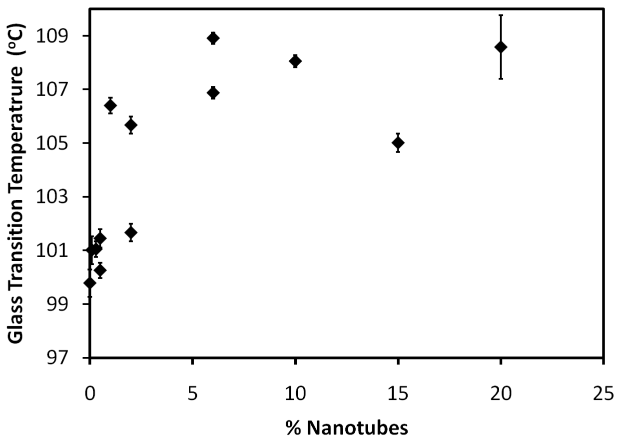


Figure 4: Tg and heat capacity change for polystyrene filled with SWNTs that have been grafted with 2.8 K MW polystyrene.



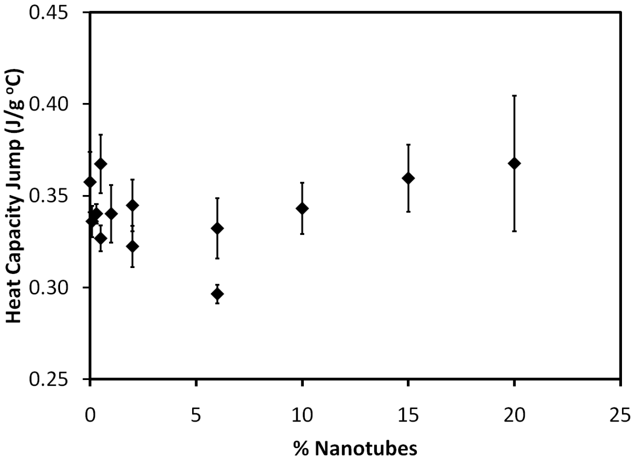


Figure 5: Tg and heat capacity change for polystyrene filled with SWNTs that have been grafted with 15 K MW polystyrene.

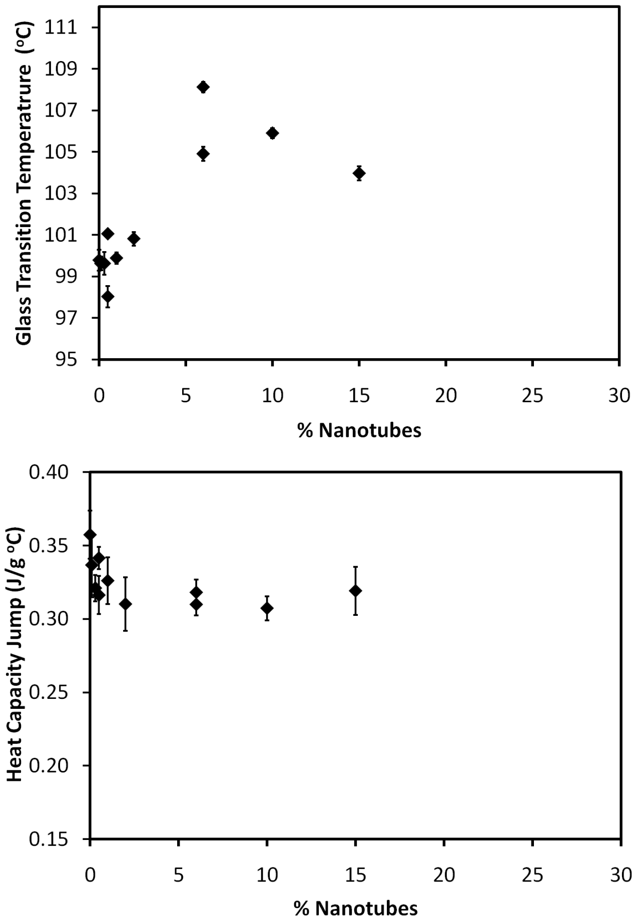


Figure 6: Tg and heat capacity change for polystyrene filled with SWNTs that have been grafted with 50 K MW polystyrene.