

## **Gamma Radiation Effects on the Glass Transition Temperature and Mechanical Properties of PMMA/soot nanocomposites**

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### **Summary**

Poly(methyl methacrylate) (PMMA) was produced via free radical polymerization. Polymer samples were sonicated and melt compounded to form 1%, 0.5%, and 0.25% PMMA/soot samples. Soot containing unpurified carbon nanotubes was provided by NASA Ames Research Center. The composites were compression molded and exposed to ionizing radiation in air from a Cesium-137 source. The PMMA/soot samples were characterized before and after exposure to radiation. Differential Scanning Calorimetry (DSC) was used to determine glass transition temperatures. Mechanical properties of composites were characterized via Dynamic Mechanical Analysis (DMA) and microhardness measurements. The glass transition temperatures from this study, when compared to similar studies conducted by Harmon et. al on purified single-wall and multi-wall carbon nanotube composites indicate that soot composites possess lower radiation resistance.

### **Introduction**

Radiation resistance of polymeric materials attracts significant interest of scientists due to the numerous applications of polymers when radiation exposure is a concern. Radiation resistance of polymers depends on the extent of molecular changes due to the irradiation. Poly (methyl methacrylate) (PMMA) composites are commonly used to determine the effects of various additives on polymer radiation stability. The behavior of this polymer under radiation has been extensively studied [1-6]. PMMA is known to undergo main chain scission when exposed to ionizing radiation; a decrease in polymer glass transition temperature as well as the evolution of products including monomer, carbon dioxide, carbon monoxide, methane, propane or hydrogen serve as indicators of polymer degradation [7-9].

Previous studies indicate that addition of aromatic groups to the polymer, either within the structure as a part of the composite increases radiation resistance [10,11].

The use of carbon nanotubes as additives in polymer matrices, including PMMA has been extensively studied [12-16]. Studies by Harmon et. al. [13,14] have shown that the addition of single-walled (SWNT) or multi-walled (MWNT) carbon nanotubes can increase radiation resistance of corresponding polymer/nanotube composite materials.

Both types of carbon nanotubes have unpurified components known as soot. Soot is composed of carbon nanotubes, metal catalyst, fullerenes and other amorphous carbons. This paper explores the use of the less pure, but considerably less expensive soot as a radiation hardening component in polymer/nanotube composites.

## Experimental

### *Polymer and nanocomposite preparation*

*PMMA.* Methyl methacrylate monomer was purchased from Aldrich and deinhibited using a packed column to remove the monomethyl ether hydroquinone (MEHQ) inhibitor. 0.2% of the initiator 2,2'-azobis (2,4-dimethylpentane nitrile) (Vazo 52) was added to the monomer. The mixture was then deaerated by bubbling dry nitrogen gas for one minute. Mixtures were placed in sample vials and heated in the oven for 26 hours at a temperature of 60°C. When polymerization was complete, polymer samples were dissolved in methylene chloride to make a 10% w/w solution. PMMA was then precipitated in methanol and dried in a vacuum oven for 4 days at 125°C. Dry polymer was dissolved in DMF and used for PMMA/soot composite preparation.

*PMMA/soot.* 1% of soot was sonicated in DMF for two hours. The sonicated soot was then added to the sonicated polymer solution (DMF). The PMMA/soot/DMF mixture was sonicated for an additional two hours. After sonication, the mixture was precipitated out in methanol. The resulting material was placed in a vacuum oven for 5 days at 145°C. Dry 1% PMMA/soot composite samples were mixed in a C. W. Brabender Plasticorder® with a banbury mixer attachment for 5 minutes at 210°C. In order to make composites with lower concentrations (0.25%, 0.5%) of soot, the dried 1% PMMA/soot composites were mixed with neat PMMA polymer in a C. W. Brabender Plasticorder® for 5 minutes at 210°C. Samples were then molded in a carver press for 5 minutes at a pressure of 5000 pounds and a temperature of 135°C. Compression molded samples (excluding the controls) were  $\gamma$ -irradiated in air at room temperature via a  $^{137}\text{Cs}$  source. The dose rate was constant at 985 rad/min for a total dose of 6 Mrad.

### *Sample Characterization*

The glass transition temperatures ( $T_g$ ) of the polymer samples were obtained on a TA Instruments 2920 Differential Scanning Calorimeter (DSC). A sample amount between 2–10 mg was obtained from the compression molded disc. The samples were heated to 145°C at a rate of 10°C per minute to insure that all samples had the same thermal history. Then the sample was cooled with liquid nitrogen to room temperature and reheated to 145°C. The  $T_g$  values were taken from the second heat as the inflection point of the curve [17].

Mechanical data were collected on a TA Instruments 2980 Dynamic Mechanical Analyzer (DMA). The instrument mode was set to measure a tension film using frequencies ranging from 1 to 100 Hz with an amplitude of 5 microns at a temperature range from -150°C to 190°C. The average sample size was 19x6x2mm.

The Vickers hardness number (HV) for each sample was determined with a Leica VMHT MOT with a Vickers indenter. The values were taken from the average of four indents. A horizontal and a vertical reading was taken on each indent. A load of 500g and a dwell time of 20s was used.

The morphologies of the fractured surfaces of the composites with soot in PMMA matrix were observed using a Hitachi S800 scanning electron microscope. The fracture surfaces were coated with 15 nm thin films of evaporated gold/palladium alloy. The applied voltage depended on magnification.

## Results and Discussion

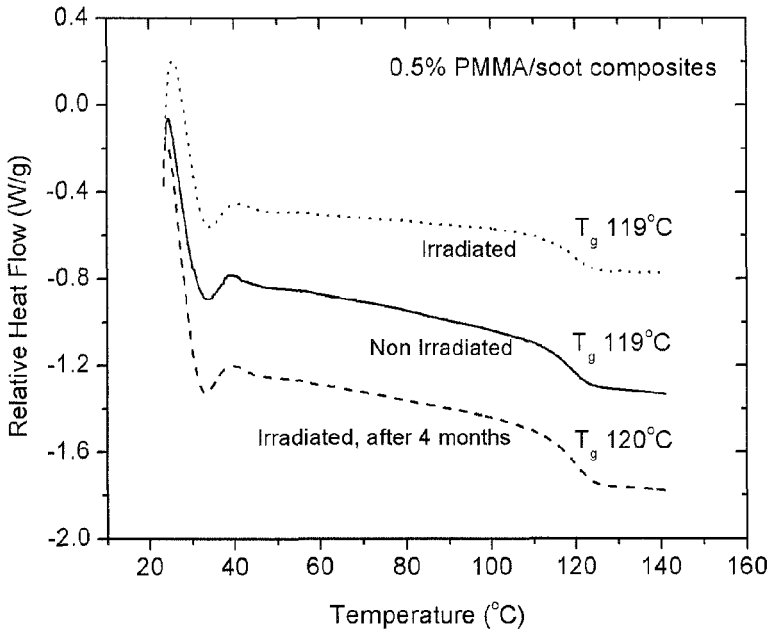
Glass transition temperatures of PMMA-based composites were measured before, immediately after and four months after exposure to gamma radiation. Four month aging was necessary to compensate for the unstable radiolysis products and free radicals reacting within sample over time. The  $T_g$  for the neat PMMA was 124°C. As the concentration of the soot increased the glass transition temperatures decreased slightly (as compared to the neat) before radiation exposure as shown in Table 1. This indicates that impurities in the soot have a plasticizing effect. This trend does not agree to studies on the glass transition temperature of SWNTs [13,14] and MWNTs [18] in PMMA. In these studies, the glass transition temperatures increased as the concentration of the carbon nanotubes increased.

**Table 1.** Glass transition temperatures (°C) of pure PMMA and PMMA/soot composites before irradiation, immediately after irradiation and four months after irradiation.

Sample	$T_g$ before irradiation (°C)	$T_g$ immediately after exposure to 6Mrads (°C)	$T_g$ 4 months after exposure to 6Mrads (°C)
Neat PMMA	124	114	115
0.25% PMMA/soot	122	116	120
0.5% PMMA/soot	119	119	120
1% PMMA/soot	122	114	118

After irradiation the glass transition temperatures decreased for all samples except the 0.5% PMMA/soot composite. The extent of decrease was greatest for the neat PMMA. The DSC plots for the 0.5% soot/PMMA composites before, after, and 4 months after radiation exposure are represented in Figure 1.

It is significant to note that the glass transition temperature of the soot composites appeared to recover after 4 months of post irradiation aging at room temperature. This phenomenon was not observed in the neat PMMA samples. While it is not possible at this time to assign a direct molecular mechanism for this recovery, it is tempting to speculate on possible reasons for the increase in the glass transition temperatures of the composites. Since free radicals persist in irradiated samples for periods of months [10,11], the soot may undergo reactions with the free radicals forming tighter matrix structures. Additionally, low molecular weight radiolysis products responsible for the decrease in  $T_g$  may migrate to the surface of the soot material and return the matrix to its original, un-plasticized state. We believe that soot particles can agglomerate at higher concentrations resulting in a smaller soot surface area, less efficient radiation absorption and less efficient incorporation of low molecular weight radiolysis products. This explains higher radiation resistance of 0.5% composite as compared to the 1% composite.

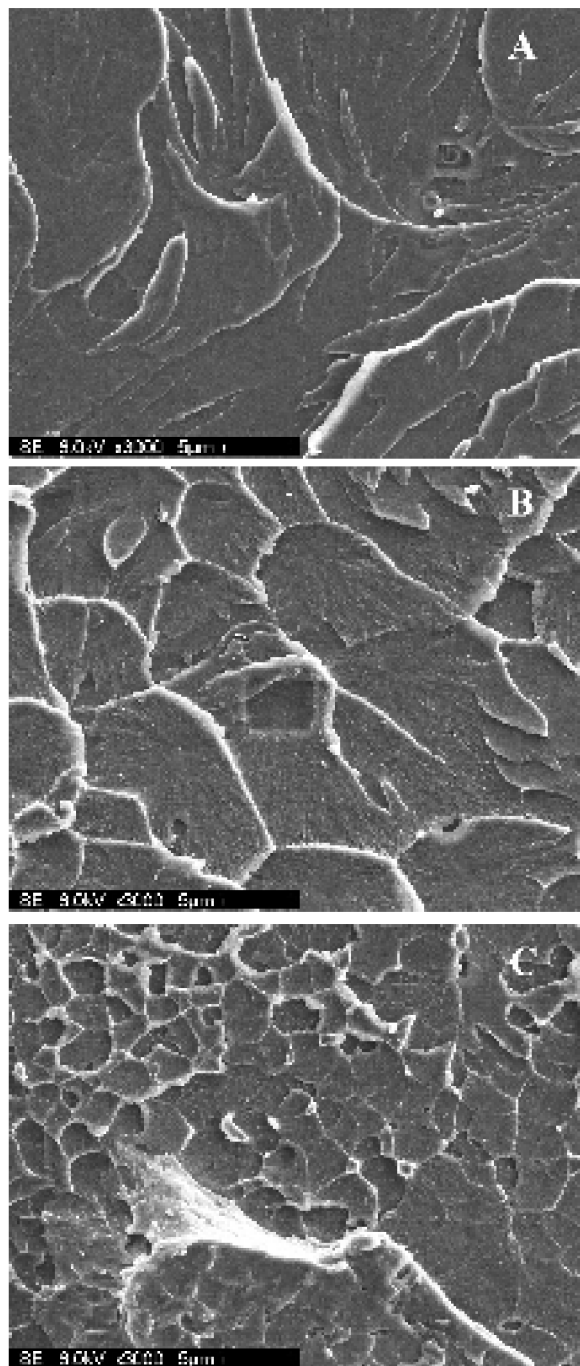


**Figure 1.** Glass Transition Temperatures of 0.5% soot/PMMA composites before, after, and 4 months after radiation exposure.

Figure 2 depicts SEM images of the fracture surfaces of neat PMMA, 0.5% and 1% composite samples before radiation exposure. All images were captured at the same resolution. There is a noticeable difference in the surface morphology between the neat and composite samples. As the soot concentration increases from 0% to 1% the size of the morphological features decreases indicating possible adhesion failure between the soot particles and the polymer matrix.

Microhardness measurements were conducted for all samples before and after the irradiation, shown in Table 2. The Vickers hardness numbers support the trends that have been previously stated in literature. After exposure to radiation, the neat PMMA behaves as expected with a decrease in hardness. The composite samples show an increase in hardness after radiation exposure, with the 0.5% PMMA/soot composite having the greatest potential for resistance to radiation.

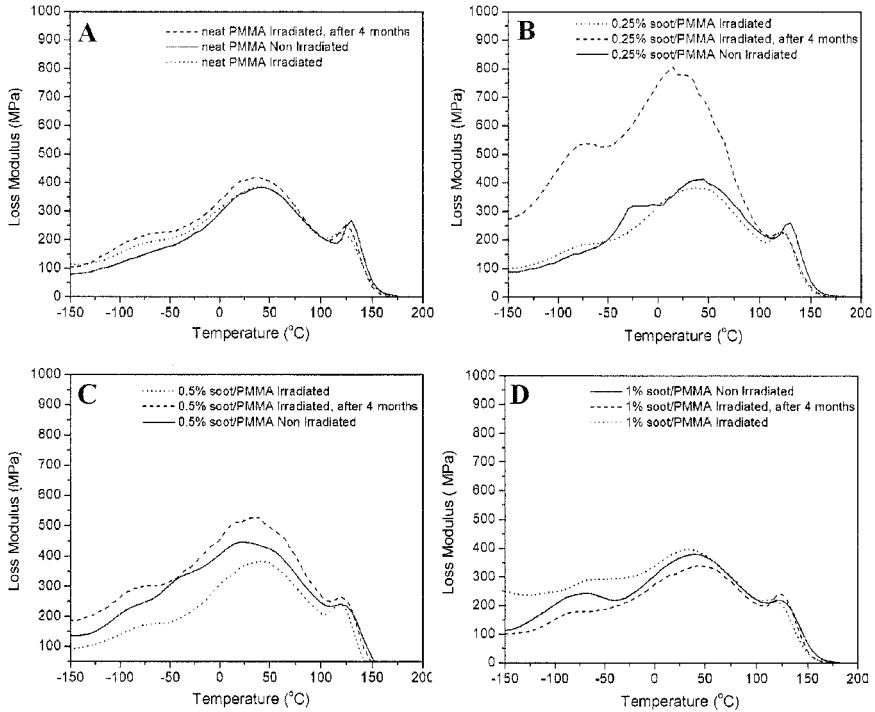
PMMA exhibits three clear transitions when characterized under Dynamic Mechanical Analysis (DMA):  $\alpha$ ,  $\beta$ ,  $\gamma$ . The  $\alpha$  corresponds to main chain molecular motion,  $\beta$  corresponds to the rotation of the ester side group, and  $\gamma$  corresponds to the rotation of the methyl side group [19]. Figure 3 plots loss modulus ( $E''$ ) of PMMA and PMMA/soot composites vs. temperature, noting the three typical transitions. The Loss Modulus ( $E''$ ) is an expression of the viscous properties associated with the polymer's ability to dissipate mechanical energy. The Loss Modulus values were recorded before, immediately after and 4 months after radiation exposure. The activation energies for  $\beta$  transitions, shown in Table 3, were determined from the  $E''$  spectra.



**Figure 2.** SEM images before radiation exposure of (a) neat PMMA, (b) 0.5% soot/PMMA, (c) 1% soot/PMMA.

**Table 2.** Vickers hardness numbers of neat PMMA and PMMA/soot samples before and after the irradiation.

	Control	Immediately after Irradiation
Neat	21.2 ± 0.43	20.2 ± 0.02
0.25%	20.3 ± 0.22	21.1 ± 0.08
0.50%	18.9 ± 0.19	24.1 ± 0.19
1%	21.1 ± 0.47	21.8 ± 0.49



**Figure 3.** Loss Modulus ( $E''$ ) of Neat PMMA at 30 Hz. (a) neat PMMA, (b) 0.25% soot/ PMMA composite, (c) 0.5% soot/PMMA composite, (d) 1% soot/PMMA composite.

**Table 3.** Activation energies kcal/mol (kJ/mol) for  $\beta$  transitions of neat PMMA and PMMA/soot composites.

Sample	Before irradiation kcal/mol (kJ/mol)	Immediately after exposure to 6 Mrads kcal/mol (kJ/mol)	4 months after exposure to 6 Mrads kcal/mol (kJ/mol)
Neat PMMA	16 (67)	17 (71)	14 (59)
0.25% PMMA/soot	18 (75)	16 (67)	24 (100)
0.5% PMMA/soot	15 (63)	16 (67)	15 (63)
1% PMMA/soot	17 (71)	20 (84)	14 (59)

These values were obtained by taking the inverse of the temperature at maximum peak height plotted against the natural log of the frequency. A linear relationship showing Arrhenius behavior was obtained for the  $\beta$  transition. The values of activation energies are similar for all the samples except for the 0.25% composite tested four months after exposure. The reason for the 0.25% composite deviation is not apparent at this time. These activation energy values reported in this paper are also consistent with the previously published data on PMMA  $\beta$  transitions [13,14,19].

## Conclusions

The PMMA/Soot samples were characterized before and after exposure to radiation. The data obtained via DSC and DMA analysis shows increased radiation resistance of 0.25% and 0.5% PMMA/soot composites as compared to pure PMMA. 1% PMMA/soot composite does not exhibit increased radiation hardness. The behavior of the 1% composite may be a result of strong agglomeration of soot particles.

A comparison of radiation resistance study of PMMA/soot composites with similar studies conducted on PMMA/SWNT and PMMA/MWNT composites [13,14,18] shows that the single-walled and multi-walled carbon nanotubes are more suitable fillers than the unpurified soot for mechanical radiation resistance.

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