Transparent Poly(methyl methacrylate)/Single-Walled Carbon Nanotube (PMMA/SWNT) Composite Films with Increased Dielectric Constants**

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Poly(methyl methacrylate)/single-walled carbon nanotube (PMMA/SWNT) composites were prepared via in situ polymerization induced either by heat, ultraviolet (UV) light, or ionizing (gamma) radiation. The composites dissolved in methylene chloride and then cast into films exhibited enhanced transparency as compared with the melt-blended composite material. UV/visible spectroscopy was used to quantitatively analyze the transparency of the composites. The dielectric constant ($\varepsilon'$) was measured via dielectric analysis (DEA) and correlated to the refractive-index values using Maxwell's relationship. The dielectric constant increased in the composite samples as compared with the neat PMMA samples prepared by the same methods. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) provided images of the polymer–nanotube composites and single-walled CNTs, respectively.

1. Introduction

Polymer nanocomposites are a novel and fast-growing class of materials with nanosized filler domains finely dispersed in a polymer matrix.\[^{1-11}\] Polymer nanocomposites have improved thermal, mechanical, and dielectric properties as compared to conventional polymer composites due to the stronger interactions between polymer and filler phases.

Carbon nanotube-based polymer composites have become a focal point of nanocomposite research since the discovery of single-walled carbon nanotubes (SWNT) by Iijima.\[^{12}\] Carbon nanotubes (CNTs) exhibit a high aspect ratio, mechanical strength, high moduli, and novel electrical properties. Many different applications of CNTs have recently been developed, including their use in nanoscale transistors\[^{13-16}\] and chemical sensors.\[^{17}\] Polymer–nanotube composites allow us to take advantage of the extraordinary properties of CNTs on the macroscopic scale.\[^{11-13}\]

One of the important goals in nanocomposite fabrication is to enhance electrical properties, while at the same time limiting loss in transparency. However, advances in processing transparent CNT–polymer composites have been hindered because of the difficulties in achieving efficient dispersion. Various methods are currently used to optimize dispersion, including solution mixing of polymer and CNTs,\[^{1}\] a combination of sonication and melt processing,\[^{2}\] melt blending\[^{1}\] and in-situ polymerization in the presence of nanotubes.\[^{4-9}\]

CNTs can be chemically modified to improve their dispersion in polymers. Experimental results indicate that certain free-radical initiators open $\pi$-bonds in CNTs. When present during the addition polymerization of methyl methacrylate, CNTs have been shown to participate in the polymerization process.\[^{2}\] Such structural modifications in CNTs have the potential to alter and enhance transparency in composites.

This study focuses specifically on the fabrication and dielectric properties of transparent films utilizing a poly(methyl methacrylate) matrix and non-functionalized CNTs. Three methods were employed to initiate free-radical polymerization: initiation with thermal energy, UV light, and ionizing gamma radiation. The major difference between these three methods is the form of energy supplied for the initiation step, while propagation, transfer, and termination are virtually identical processes.\[^{18}\] In the cases of thermal- or UV-light-induced polymerization, the initiator decomposes through homolytic bond breaking. High-energy radiation ($\gamma$-rays, X-rays, and energy-rich particle rays) can initiate polymerization by the Compton effect,\[^{18,19}\] by the direct interaction between an extracted electron and the atom, or by direct homolytic bond breakage.\[^{18}\]
The effects of different fabrication techniques on the transparency and dielectric properties of SWNT–PMMA nanocomposites was studied in detail. For clarity, samples initiated via UV light will be referred to as UV-light initiated polymer samples; samples initiated via heat will be referred to as thermally initiated or heat initiated polymer samples; and samples initiated via ionizing (gamma) radiation will be referred to as gamma-radiation initiated polymer samples.

2. Results and Discussion

Number-average ($M_n$) and weight-average ($M_w$) molecular weights, as well as polydispersity indices (PDIs, $M_w/M_n$), were determined for the neat PMMA samples polymerized by all three initiation methods. The thermally initiated polymerized sample exhibited the highest $M_n$ of $3.0 \times 10^6$ g mol$^{-1}$ with a PDI of 4.4. The weight-average molecular weights of the UV-light-initiated and gamma-radiation-initiated polymerized samples were $2.9 \times 10^5$ and $5.4 \times 10^5$ g mol$^{-1}$ with PDIs of 1.8 and 1.9, respectively. The high molecular weight of the thermally initiated polymer sample is due to the Trommsdorff, or gel, effect, which is typical of the thermal polymerization of bulk methyl methacrylate [20-21]. The molecular weight study shows that the initiator, 2-hydroxy-2-methylpropionophenone, can be applied successfully for all three polymerization techniques. Average molecular weights and polydispersity indices of composite materials were not measured due to possible interactions between the CNTs and column-packing material.

Transparent films were produced from a methylene chloride solution of the composite, as depicted in Figure 1. The UV–vis spectra provide quantitative information concerning the transparency of the film, the presence of the CNTs, and the uniformity of dispersion. Figure 2 shows that the UV–vis spectra of all three composites exhibited a transmittance of 50% and higher at or above 300 nm. The percent transmittances at 300 nm, 400 nm, and 500 nm are tabulated in Table 1. In contrast, the melt-blended sample had a 0% transmittance.

Transparent polymer/CNT composites can be achieved if films are prepared immediately after dissolution. Figure 3 shows the evolution of the UV/vis spectra of the PMMA/SWNT/CH$_2$Cl$_2$ solution over time. After dissolution, the solution had an observable light-gray tint with no noticeable CNTs. However, over time the CNTs agglomerated, with a resulting decrease in transmittance. Thus, evaporation of the solvent before re-agglomeration resulted in transparent films. Similarly, if the agglomerated solutions are agitated, the particulates break apart and the solutions can be cast into clear films. The kinetics of agglomeration, and the size of the agglomerates, are being further investigated via optical microscopy.

The studies of PMMA–SWNT nanocomposites were further complemented by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images of the solvent-evaporated films (Fig. 4A–C) indicate the presence of nanotubes.
in the polymer matrix, regardless of the polymerization method employed. This verifies that dissolution of the composites in methylene chloride does not remove CNTs from the polymer matrix. A TEM image of the CNTs used in this study is shown in Figure 5.

Dielectric analysis (DEA) provides permittivity ($\varepsilon'$), loss factor ($\varepsilon''$), and $\tan \delta$ data from $-150^\circ$C–$200^\circ$C and $1–1 \times 10^7$ Hz. Two clear relaxations in PMMA, the $\alpha$ and $\beta$ relaxations, are evident in Figure 6A. The $\alpha$ relaxation is the segmental motion of the polymer main chain, whereas the $\beta$ relaxation relates to the hindered rotation of the ester side group attached to the main chain. PMMA also has an $\alpha \beta$ relaxation which is the result of main-chain slippage at high temperatures and high frequencies merged with the dominant $\beta$ relaxation.[22] The high-temperature peaks observed in Figure 6A,B correspond to the $\alpha$ transition, which has nearly merged with the $\beta$ transition. The extent of merging and the intensity of the peak are somewhat masked by contributions from conductivity, which are present in the loss-factor spectrum at temperatures near and above the glass-transition region. The activation energies for the $\beta$ relaxation, obtained via Arrhenius plots, are listed in Table 2. The activation energies are similar to the activation energies previously cited in literature for PMMA and PMMA–CNT composites.[22–26] It is clear that side-group rotation of the heat-, UV-light-, and gamma-radiation-initiated polymer samples is not hindered by the addition of the CNTs at these low concentrations.

Figure 6 illustrates the loss factor of the neat PMMA for each polymerization method (Fig. 6A) and the composite

![Figure 5. TEM image of the single-walled CNTs used in this study.](image)

![Figure 6. DEA loss factor of A) neat PMMA and B) PMMA-SWNT composites, polymerized via initiation with UV-light, thermal, and gamma-irradiation, at 60 Hz.](image)

**Table 2. Activation energies of the $\beta$ transition of composites analyzed by DEA (1–30 Hz).**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Neat [kcal mol$^{-1}$]</th>
<th>Composite [kcal mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>Gamma</td>
<td>16</td>
<td>19</td>
</tr>
<tr>
<td>Thermal</td>
<td>17</td>
<td>16</td>
</tr>
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</table>
samples (Fig. 6B). It is interesting to note the difference in peak intensity between the UV-light- and gamma-radiation-initiated neat samples and their composite counterparts in the β relaxation region of PMMA. This provides evidence that the CNTs provide additional dipoles to the polymer matrix. The loss factor for the thermally initiated composite, however, is less than that of the neat sample.

The γ relaxation in PMMA results from the rotation of the methyl groups attached to either the main chain or to the ester side group, and is not usually detected using dielectric analysis due to the nonpolar nature of the methyl group. Such transitions are typically characterized using mechanical analysis. However, a weak relaxation is present in the gamma-radiation-initiated (Fig. 7A) and thermally initiated composites (Fig. 7B), ranging from −130 to −30°C. This peak is difficult to ascertain in the UV-light-initiated composites. It is possible that this relaxation is a result of the interaction of polymer with CNTs. The apparent γ relaxation has also been seen in PMMA–multi-walled nanotube composites before irradiation. It has been suggested that CNTs can be used to identify or detect polymer relaxations. This may be due to the changes in chemical structure induced by the method of polymerization. This phenomenon is being further investigated.

The extent of alignment of the dipoles in an electric field can be determined from the permittivity data, also referred to as the dielectric constant. The experimental data published for polymer/SWNT composites demonstrate an increase in permittivity for the composite samples compared with the neat samples. Permittivity data obtained in this study agrees with previously published results. Table 3 shows the relative permittivity (ε') at 100 Hz and 25°C. The UV-light-initiated polymer samples exhibit the largest increase in permittivity, followed by the heat- and the gamma-radiation-initiated polymer samples, respectively. The permittivity of the non-transparent melt-blended PMMA–SWNT composite with CNT loading identical to that of the film samples also increased as compared to the neat PMMA.

Table 3. Relative permittivities of samples at 100 Hz and 25°C, and the difference between the neat and composite sample permittivities (Δ).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Neat</th>
<th>Composite</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamma</td>
<td>3.71</td>
<td>4.56</td>
<td>0.85</td>
</tr>
<tr>
<td>UV</td>
<td>4.99</td>
<td>7.29</td>
<td>2.3</td>
</tr>
<tr>
<td>Thermal</td>
<td>3.74</td>
<td>4.75</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Both the electronic nature of the polymer and the effect of CNTs in the composites can be understood by correlating the dielectric constant values from DEA with the refractive index. According to van Kreveland, if the sample is a non-polar insulator, the dielectric constant (ε') for low frequencies can be expressed by Maxwell's equation ε' = n², where n is the refractive index. A large difference between the squared refractive index and the dielectric constant is a result of permanent dipoles and the semi-conductive character of the sample. Table 4 presents values of the dielectric constant (ε') and the squared refractive index (n²) for the neat samples and the composites. The difference between ε' and n² for the composites is greater than that observed in the neat samples. The largest difference is seen in the UV-light-initiated composite sample. The refractive index of PMMA is 1.49. PMMA has permanent dipoles in the ester side group, which explains the difference between ε' and n² in neat PMMA samples. The CNTs, which consist of one-third metallic character and two-thirds semi-conductive character, contribute to the conductive nature of the composites.

Table 4. Relationship between refractive-index values and the dielectric constants at 100 Hz and 25°C of neat PMMA and PMMA–SWNT composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RI (n)</th>
<th>ε'</th>
<th>n²</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV neat</td>
<td>1.4916</td>
<td>4.9857</td>
<td>2.2248</td>
</tr>
<tr>
<td>UV composite</td>
<td>1.4913</td>
<td>7.2933</td>
<td>2.2239</td>
</tr>
<tr>
<td>Gamma neat</td>
<td>1.4919</td>
<td>3.7113</td>
<td>2.2257</td>
</tr>
<tr>
<td>Gamma composite</td>
<td>1.4913</td>
<td>4.5639</td>
<td>2.2239</td>
</tr>
<tr>
<td>Thermal neat</td>
<td>1.4919</td>
<td>3.7368</td>
<td>2.2257</td>
</tr>
<tr>
<td>Thermal composite</td>
<td>1.4910</td>
<td>4.7517</td>
<td>2.2230</td>
</tr>
</tbody>
</table>
ites. The refractive indices of the composite samples are slightly lower than their neat counterparts. This demonstrates that while dielectric properties are significantly affected by the nanotubes, optical properties are less sensitive to the presence of nanotubes.

3. Conclusions

Three different in-situ-polymerization initiation methods were used to produce the composites: heat, UV light, and gamma radiation. We have shown that the method of polymerization has an effect on the optical and dielectric properties of the composites. However, using a modified sample preparation technique, comprising dispersion of the nanotubes through sonication, in-situ polymerization, and dissolution of the resulting polymer composite and casting of the film immediately after dissolution, a transparent composite film can be achieved with all three initiation methods. The polymer matrix for all of the produced nanocomposites interacts with dispersed CNTs, as demonstrated by the presence of γ transitions in the dielectric loss data and an increased dielectric constant. The fabrication of transparent polymer–nanotube composites may prove to be a useful tool in developing transparent composites with enhanced optical and electrical properties.

4. Experimental

Single-Walled Carbon Nanotube (SWNT) Preparation: Raw laser-ablation material provided by NASA Johnson Space Center was purified as described elsewhere [33]. The raw nanotubes were refluxed in 2.6 M nitric acid for approximately 160 h and then diluted with doubly distilled water. This solution was then centrifuged (4000 rpm), the solvent mixture decanted, and the sample again suspended in doubly distilled water. This step was repeated two more times in order to remove the acid from the nanotubes. Finally, the solution was filtered through a cellulose nitrate filter and dried at 60 °C in a vacuum oven to form a buckypaper.

Polymer–Nanotube Composite Synthesis: Methyl methacrylate (MMA) monomer was purchased from Aldrich and de-inhibited using a column to remove the monomethyl ether hydroquinone (MEHO) inhibitor. 0.26 wt.-% pure SWNTs were placed in 9.5 g of de-inhibited MMA. A loading of 0.26 wt.-% was used to compare with previously studied PMMA–SWNT composites with the same loading [23,24]. The mixture was sonicated for 30 min with a Branson Sonifier 450 until the nanotubes were finely dispersed in the monomer. The MMA–SWNT mixtures were then placed in borosilicate sample vials (Fisher Scientific). After sonication, 0.5 wt.-% of the initiator, 2-hydroxy-2-methylpropiophenone (Benacure 1173, Mayzo Corporation) was added to the MMA–SWNT mixture.

Three methods were utilized to initiate free-radical polymerization: thermal, ultraviolet (UV) light, and gamma-radiation initiation. The initiator undergoes α cleavage when exposed to UV light [34] which creates free radicals that initiate the polymerization process. Scheme 1 illustrates the cleavage of the initiator when exposed to UV light. Although commonly used as a photoinitiator, this material was successfully used for all three initiation methods.

Oxygen was removed from the reaction mixtures by bubbling dry nitrogen gas for 1 min. For thermally initiated polymerization, the MMA/SWNT mixture was heated in an oven at 70 °C for 16 h. For UV-light-initiated polymerization, a Spectroline UV light (Spectronics Corp., λ = 220–280 nm) was employed to expose the MMA/initiator mixture in the presence of SWNT to short-wave UV radiation for 5 h. In this study, the sample was placed 20 mm from the UV source. For gamma-radiation initiated polymerization, a cesium-137 gamma source was used to expose the MMA/SWNT mixture to ionizing radiation for 41 h at a dose rate of 985 rads min⁻¹ and a total dose of 2.42 Mrads. All samples were post-cured in the oven for 4 h at a temperature of 70 °C. Neat PMMA control samples were also prepared via each polymerization initiation method.

After the polymerizations, the composites resembled transparent polymers embedded with steel wool fibers, and the nanotubes were clearly visible. The neat and composite samples were then dissolved in methylene chloride to make a 5 wt.-% solution. The methylene chloride was first filtered through a 0.2 μm filter to ensure purity. After dissolution, the samples were much clearer than before; the “steel wool” disappeared upon dissolution.

Another PMMA–SWNT composite was prepared by adding CNTs to PMMA and melt blending via a previously described method [23,24]. After dissolution in methylene chloride, this composite sample exhibited visible agglomeration of CNTs resulting in non-transparent thin films. This sample was used as a transparency control and referred to as a melt-blended sample throughout this article.

Sample Characterization: Ultraviolet-visible spectra were recorded with a Hewlett–Packard 8452 A spectrophotometer. Polymer-composite films were prepared from composite/methylene chloride solutions by solvent evaporation. The samples were placed in a vacuum oven with a liquid nitrogen trap for a total of eight days at a temperature of 80 °C to remove any residual solvent. Spectra of the solvent-evaporated 0.127 mm thick films were scanned with air as the background. The spectra of PMMA–SWNT/CH₂Cl₂ solution were recorded in a quartz cuvette with 1 cm pathlength. Methylene chloride served as the reference blank.

Dielectric data were collected using a TA Instruments DEA 2970 dielectric analyzer equipped with parallel plate sensors. Samples for dielectric analysis were compression molded in a Carver press at 20.7 MPa and a temperature of 135 °C. Resulting samples had an inner diameter of 27 mm and thicknesses ranging from 0.4 to 1.7 mm. Then, compression molded samples were scanned in the temperature range between 200 and −150 °C with increments of −5 °C under a nitrogen purge. Scanning frequencies ranged from 1 Hz to 1.0 × 10⁴ Hz. A maximum force of 250 N was applied to all samples for the duration of scanning.

Gel permeation chromatography (GPC) was performed on a Perkin-Elmer series 200 Liquid Chromatograph with two PLgel 5 μm mixed columns in series. The chromatograph was calibrated with polymer standards. Solvent-evaporated films of the neat samples were analyzed. Each sample was dissolved in tetrahydrofuran and measured with a flow rate of 0.9 mLmin⁻¹. The chromatograph was equipped with a Perkin–Elmer series 200 Refractive Index Detector and a Perkin–Elmer 785A UV/vis Detector. Composite materials were not tested because interactions between the CNTs and column packing material are possible.

Solvent evaporated films with a thickness of 0.127 mm were measured on aIndex Instruments, CLR 12-70 contact-lens refractometer to obtain the refractive index values. The instrument sensitivity was ±0.005.

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