Alignment of Carbon Nanotubes in Polyimide Under Electric and Magnetic Fields

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ABSTRACT: Usually alignment of carbon nanotubes (CNT) in polymer composites can be induced by a single electrical or magnetic field. Here we report a comparison between the results of simultaneous application of both fields to the polyimide composite and a single field. Alignment of CNT in polyimide was performed under a 2 Tesla magnetic field and various electric fields (150, 300, 450, and 600 V/cm). Polarized Raman spectroscopy was used for assessing the degree of alignment of the nanotubes in the composites and many details of the alignment were examined. The results indicated that at the same electric field strength, incorporation of a magnetic field in a given direction will enhance the level of alignment as compared with only using an electric or magnetic field alone. The best alignment condition was for the CNT samples under parallel magnetic and electric fields. Optical microscopy observations also indicated that nanotube alignment appeared at the highest field strength and decreased when the field strength decreased. A possible mechanism for field alignment is presented. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3470–3475, 2012

Key words: alignment; carbon nanotubes; polyimide; electric field; magnetic field

INTRODUCTION

Polyimides (PI) are polymers known for their stability at high temperature, high glass transition temperature, flexibility, excellent thermal stability, favorable dielectric properties, and excellent chemical resistance. These are the properties for which polyimides have widely found applications in the composite and microelectronics industries. Therefore, a polyimide-based composite is of particular interest.[1–7] The discovery of carbon nanotubes (CNT) opens the door to enhance the properties of polymer composites by adding them to the matrix of materials for structural and multifunctional applications. Unique properties of CNT such as extremely high strength, high thermal conductivity, high electrical conductivity, high aspect ratio, and low density, offer crucial advantages over other nano-fillers. Therefore, CNT-based composites have attracted great interest due to an increasing technological demand for multifunctional materials with improved mechanical, electrical, and optical performance. In addition, these materials must be capable of forming complex shapes, and patterns and be easily manufactured at low cost. CNT are highly anisotropic in nature due to their high aspect ratio. To take advantage of their anisotropic structure, it is important to have aligned CNT in the polymer matrix, improving its properties in the direction of the alignment. By aligning CNT in the polymer matrix, the strength, stiffness, electrical, and thermal properties of the composite can be better controlled as compared with randomly oriented CNT in a polymer matrix. Numerous alignment techniques have been employed to produce this effect.[8–10] Carbon nanotubes are highly susceptible to electric and magnetic fields, which can align materials in response to their applied fields. Because of their susceptibility, it should be possible to place single-wall carbon nanotubes (SWNT) in a magnetic field and align them in a common orientation parallel to the direction of the applied filed. However, studies on the combined effects of electric and magnetic field induced alignment of CNT in polymer matrix have not yet been conducted.

In this work, the alignment of CNT/PI nanocomposites was achieved by simultaneous application of DC electric and magnetic fields. Sodium dodecyl sulfate (SDS), an ionic surfactant, in presence of ultrasonication was also used for assisting the homogeneous dispersion of SWNT into the polyimide matrix.

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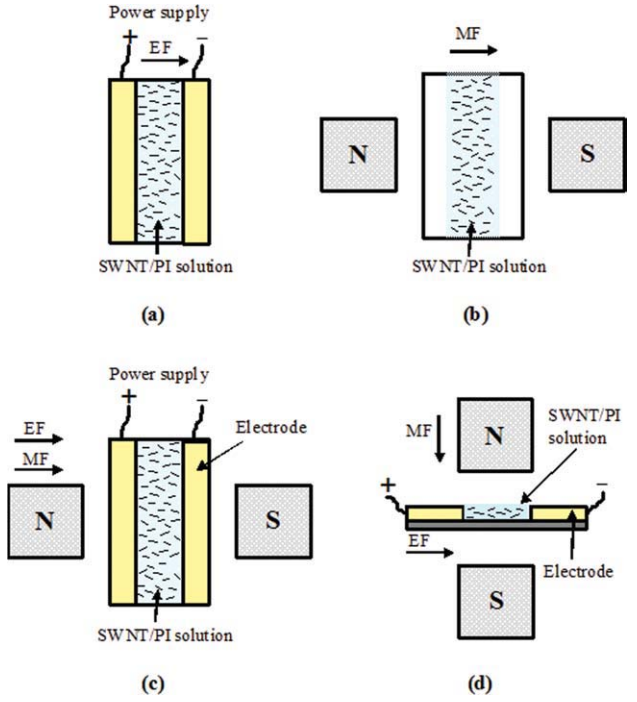

Figure 1 Schematic of the alignment set up of (a) electric field (EF) and (b) magnetic field (MF) alone (Top view), electric field parallel and perpendicular to magnetic field, (c) (Top view) and (d) (Side view) respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

Single-wall carbon nanotubes (SWNT) were purchased from Nanostructured and Amorphous Materials, USA. According to the manufacturer's specifications, they were produced by a catalytic chemical vapor deposition (CVD) method and had a purity of 95 vol % CNT and 90 vol % SWNT. The majority SWNT had an average diameter and length of 1–2 nm, and 5–30 μm, respectively. The following monomers for polymer synthesis were purchased and used without further purification: 4,4′-(Hexafluoroiso-propylidene) diphthalic anhydride (6FDA, Aldrich, 97%), 4,4′-oxydianiline (ODA, Fluka, 98%) and *N*-methyl pyrrolidinone (NMP, Merck, 99.5%). The surfactant used for the dispersion of SWNT was sodium dodecyl sulfate (SDS, Aldrich, 99.5%).

Preparation of the aligned SWNT/PI nanocomposite films

In this process, 0.0203 g of SWNT were first dispersed in a nonaqueous solution (0.03045 g of SDS and 100 mL of NMP solvent) containing SDS as ionic surfactant, in presence of ultrasonication (40 kHz) for 1 h to exfoliate the SWNT bundle into individual tubes. The exfoliated SWNT suspension was introduced as electrically conductive filler in the polyimide matrix synthesized with ODA and 6FDA precursor. The homogeneous SWNT/PI solution was cast onto dried glass plate electrodes. DC electric and magnetic fields were separately and simultaneously applied to induce the formation of an aligned structure, followed by evaporation and thermal imidization to produce the aligned SWNT/PI nanocomposite films. The experimental setup is shown in Figure 1 and the summary of experimental samples is given in Table I.

Characterization

Carbon nanotube identification and degree of alignment in the SWNT/PI nanocomposite films were assessed using FT-Raman spectroscopy with a laser in the near infrared region (usually at 1064 nm). The development of the CNT alignment in the composites was investigated by optical microscopy. The aligned films were observed under the magnification range of 0.67x-4.5x, and a common camera was also used for taking a photographs. TEM image of raw

TABLE I
Summary of Composites Sample for Experiment

Sample	CNT content (wt %)	Electric field (Volt)	Magnetic field (Tesla)	Electrode spacing (cm)	Thickness of electrode (kÅ)	External field applied time (min)
Random	0.5	–	–	–	–	–
2T	0.5	–	2	–	–	7
150 V	0.5	150	–	1	300	7
300 V	0.5	300	–	1	300	7
450 V	0.5	450	–	1	300	7
600 V	0.5	600	–	1	300	7
150 V+2T[a]	0.5	150	2	1	300	7
300 V+2T[a]	0.5	300	2	1	300	7
450 V+2T[a]	0.5	450	2	1	300	7
600 V+2T[a]	0.5	600	2	1	300	7

[a] Two alignment system (EF//MF and EF $\perp$ MF).

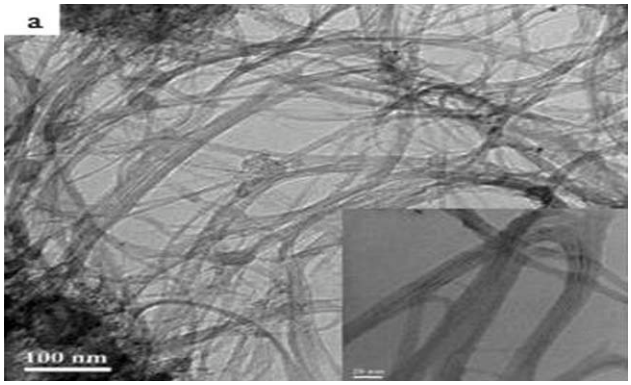

Figure 2 Typical TEM micrographs of SWNT.

SWNT was taken from Transmission electron microscopy (TEM, JEM-2010 JEOL, Japan) and SEM picture was taken from Scanning Electron Microscope (SEM, Hitachi model *S*-3400*N*, Japan). The films for SEM analysis were coated with gold particles by ion sputtering device to provide electrical contact to the specimen.

RESULTS AND DISCUSSION

TEM images of SWNT

Figure 2 shows TEM images for the SWNT. These images provide evidence that most of the as-synthesized CNT were curled and entangled into bundled structures with an average diameter larger than 20 nm due to their high aspect ratios and strong Van der Waals interactions. Carbonaceous impurities that typically include amorphous carbon, metal catalysts, and graphite particles could also be observed. However, the tendency of CNTs to agglomerate and entangle leads to many defect sites in the composites and limits the efficiency of CNT property transfer to the polymer matrix.

Raman spectroscopy of the SWNT/PI nanocomposite films

Raman spectroscopy was employed to confirm the presence of carbon nanotubes in the composites. The Raman spectrum of the composite containing 0.5 wt % SWNT, illustrated in Figure 3, shows characteristic peaks at around 179 and 1590 cm^{-1}, which correspond to the diameter dependent radial breathing mode (RBM) and the tangential G band of the SWNT, respectively. The RBM mode is the real signature of the presence of carbon nanotubes in a sample, since it is not present in graphite. The neat polyimide film gave rise to a featureless spectrum in the composite due to the exceptionally good scattering characteristics of SWNT. Also, it might be that the SWNT overwhelm the Raman spectrum, resulting in a composite spectrum with features was rather similar to that of raw carbon nanotubes.

Alignment of carbon nanotubes in nanocomposite films

The structural development and assessment of the degree of alignment of aligned carbon nanotubes in polyimide under the influence of magnetic and electric fields were studied using optical imaging and Polarizer Raman spectroscopy. Polarizer Raman spectroscopy is an important tool when attempting to characterize or assess the degree of alignment of carbon nanotubes in a polymer matrix. SWNT nanocomposites show resonance-enhanced Raman scattering effects when utilizing a visible or near infrared laser as the excitation source; other pure polymers do not display such a resonance effect. The tangential peak (G-peak, $\sim$ 1590 cm^{-1}) of the SWNT in the Raman spectra was very sensitive to the polarizer, and was attributed to the elongation of the carbon–carbon bonds along the longitudinal axis of the nanotubes. Raman intensity reached a maximum when the polarizer was parallel to the nanotubes axis (0°) and decreased as the angle of the polarizer increased from 0° to 90°. The reduction of Raman intensity from 0° to 90° indicates that SWNT were induced to align in the polyimide. Figure 4 shows a series of SWNT aligned by orienting the EF parallel to the MF (EF//MF), as a function of external field strength. Increasing the DC electric field strength resulted in an increase of the G-peak spacing. The G-peak spacing range was extended when the field strength increased from 150 to 600 V/cm. These results demonstrated that the best aligned structure of the SWNT occurred when higher field strengths were applied. Optical images also confirmed that the best alignment network occurred when the field strength was increased.

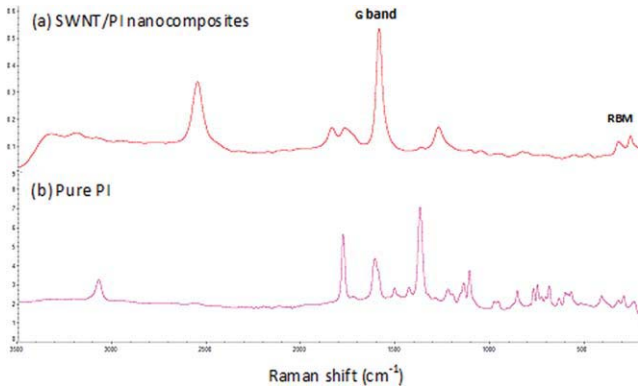

Figure 3 Raman spectra of (a) composite with 0.5 wt % SWNT loading and (b) pure polyimide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

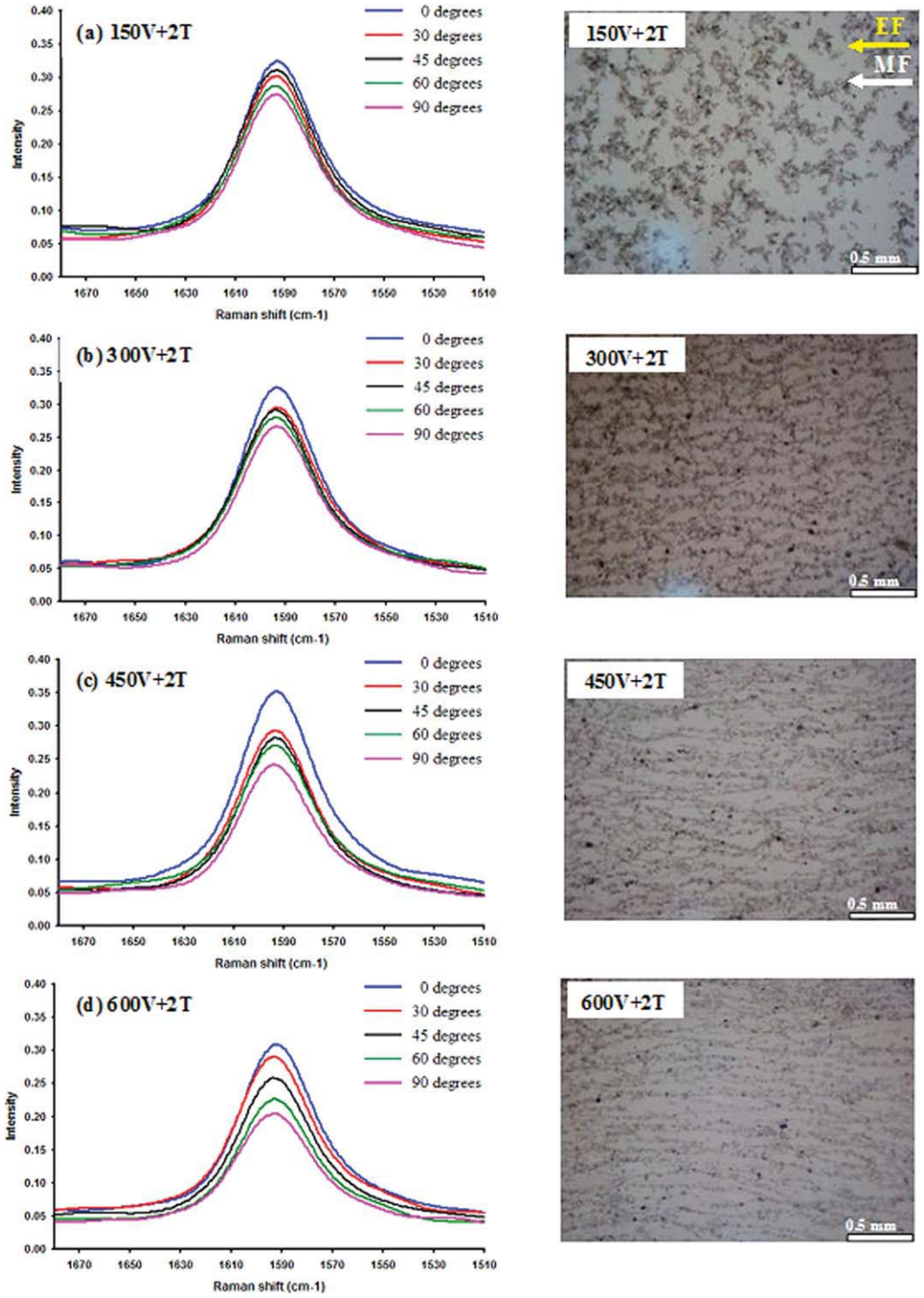

Figure 4 G-peak spectra and Optical micrographs of 0.5 wt % SWNT/PI nanocom- posite films with 7 min of applied 2 Tesla magnetic and various dc electric field in parallel direction (EF//MF). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Raman spectra of different field strengths can be used to compare the degrees of alignment of the SWNT. These spectra were obtained for SWNT/polyimide nanocomposites with different field strengths to observe the difference in the alignment of the SWNT in a polyimide matrix under various field strengths. The tangential peak of Raman intensity for the polarizer angles at 0° and 90° was represented by P0 and P90, respectively. The relative intensity ratio (P0/P90) was used for comparing the degree of alignment of SWNT in the composites under various conditions to observe the effect of field strength on the degree of alignment of nanotubes.

TABLE II
Raman Intensity of Oriented SWNT at Different Angle

Sample	Maximum intensity of G-peak		
	0° (P0)	90° (P90)	P0/P90
random	0.732	0.711	1.030
2T	0.416	0.389	1.069
150 V	0.265	0.228	1.162
300 V	0.274	0.220	1.245
450 V	0.296	0.217	1.364
600 V	0.298	0.209	1.426
^{A}150 V+2T	0.324	0.274	1.182
^{A}300 V+2T	0.325	0.266	1.222
^{A}450 V+2T	0.351	0.241	1.456
^{A}600 V+2T	0.308	0.204	1.510
^{B}150 V+2T	0.324	0.304	1.066
^{B}300 V+2T	0.277	0.236	1.174
^{B}450 V+2T	0.313	0.241	1.299
^{B}600 V+2T	0.326	0.245	1.331

Superscript A and B is represented as EF//MF and $EF_{\perp}MF$ system, respectively.

Table II exhibits the P0/P90 relative ratio for all the samples. Theoretically, if the nanotubes were unaligned in the composites, then the P0/P90 value should be equal to 1. For an improved degree of alignment, the P0/P90 value should be far away from 1. From Table II, unaligned SWNT had a value P0/P90 equal to 1.030, which differed from the theoretical 1 by about 3%, an acceptably small error. At low external field strengths (2 Tesla or 150 V/cm), the relative ratios were 1.069 and 1.162, respectively. A slightly different relative ratio from the unaligned indicated that there was a very small degree of alignment in the composites. At higher applied DC electric field strengths (300, 450, and 600 V/cm) the value of P0/P90 increased from 1.245 to 1.426, indicating that the degree of alignment of SWNT under a DC electric field had a tendency to follow the order: 600 > 450 > 300 > 150 V/cm. A similar trend could also be found when simultaneously applying an electric and constant 2T magnetic field to the system: 600 V/cm + 2T > 450 V/cm + 2T > 300 V/cm + 2T > 150 V/cm + 2T.

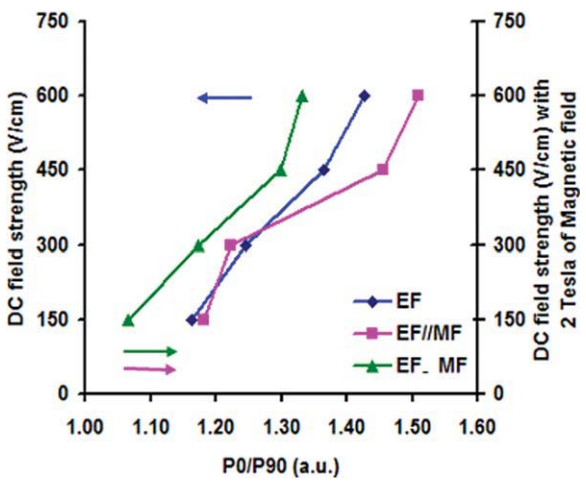

Figure 5 P0/P90 value of the aligned SWNT as function of the different aligned conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 shows the relationship between P0/P90 values for different alignment conditions, suggesting that the level of the aligned SWNT in the composite is in the order: EF//MF > EF > $EF_{\perp}MF$ (EF perpendicular to MF). A possible mechanism for understanding the alignment of nanotubes under the effect of electric and magnetic fields is as follows. Under the electric field alone, the SWNT were rotated, oriented, and moved toward the nearest electrode along the direction of the electric field due to torque force acting on each CNT. Coulombic attraction was generated among oppositely charged ends of different CNT and the electrophoretic force was induced by the presence of charged surfaces. As soon as these nanotubes were close enough to the electrode to allow charge transfer, the nanotubes discharged, and adsorbed onto the anode. The tips of the nanotubes connected to the electrode then became sources of very high field strength and the location for adsorption of further filler particles. As a result, this ramified a nanotube network of structures that stretched across the electrodes and provided conductive pathways throughout the sample as can be observed by optical microscopy. However, only torque is acted upon the nanotubes by the magnetic field. Therefore, the highest P0/P90 value was obtained with EF//MF. Consequently it is believed that the incorporation of the electric and magnetic forces in the supportive direction will be better enhance the level of alignment than when only using an electric or magnetic field alone. In the case of $EF_{\perp}MF$, the torque force on the CNT induced by the magnetic field could force the nanotubes to stand up normally to the substrate surface, as shown in Figure 6. At the same time, these nanotubes were caused to lay parallel to substrate surface by the electric field. Therefore, the alignment direction of nanotubes deteriorated under the strength of both

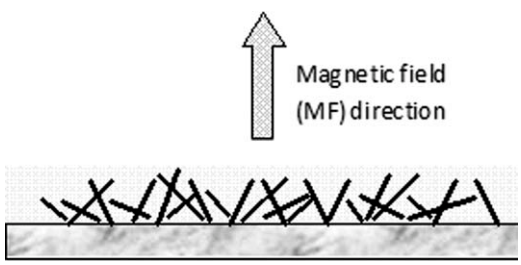

Figure 6 Schematic image of effect of magnetic field on CNT-film structure.

the electric and magnetic fields, which were not in the same direction, and finally decreased the degree of alignment of the nanotubes in the composite films.

CONCLUSIONS

Alignment of carbon nanotubes in polyimide was performed under the optimal condition for CNT/polyimide nanocomposites. A magnetic field of 2 Tesla and several electric field strengths (150, 300, 450, and 600 V/cm) were employed to induce the alignment of nanotubes in a polymer matrix. Raman spectroscopy was employed to confirm the presence of carbon nanotubes in the composites. The spectrum showed characteristic peaks which corresponded to the RBM mode, the real signature of the presence of carbon nanotubes in a sample, since it is not present in graphite. Optical microscopy observation indicated that an alignment could clearly be found by increasing the field strength to the highest strength and alignment decreased when the field strength was decreased. The incorporation of a magnetic field in a certain direction will enhance the level of alignment better than using an electric or magnetic field alone. The three elementary forces induced from electric and magnetic fields displayed an important role in improving the degree of alignment in the composites.

In this research, we assessed and verified the degree of alignment of carbon nanotubes in polyimide at various conditions of electric and magnetic fields. Incorporation of electric and magnetic field in the same direction could create the maximal degree of alignment due to torque, Coulombic, and electrophoretic forces of such external fields. A more complete result will be achieved after an investigation on the properties of the aligned films for useful information of future applications.

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