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Postprint version. "This is a preprint of an article published in *Journal of Polymer Science Part B: Polymer Physics*, Volume 41, Issue 24, 15 December 2003, pages 3333-3338."
Publisher URL: http://dx.doi.org/10.1002/polb.10701

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single-walled carbon nanotube, SWNT, PMMA, thermoplastic, composites, alignment, nanocomposite, electrical conductivity, thermal stability

**Comments**
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# A Coagulation Method to Prepare Single-Walled Carbon Nanotube/PMMA Composites and Their Modulus, Electrical Conductivity, and Thermal Stability

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## Abstract

A coagulation method that provides better dispersion of SWNT in the polymer matrix has been used to produce single-walled carbon nanotube (SWNT)/poly(methyl methacrylate) (PMMA) composites. Optical microscopy and SEM show improved dispersion of SWNT in the PMMA matrix, which is a key factor in composite performance. Aligned and unaligned composites were made with purified SWNT with different SWNT loadings, from 0.1 to 7 wt%. Comprehensive testing shows improved elastic modulus, electrical conductivity, and thermal stability with addition of SWNT. The electrical conductivity of a 2 wt% SWNT composite decreases significantly (>$10^5$), when the SWNT is aligned and this result is discussed in terms of percolation.

## Keywords

SWNT; PMMA; Composites; Alignment; Electrical conductivity; Thermal stability.

# 1. Introduction

Carbon nanotubes have shown exceptional stiffness and strength and remarkable thermal and electrical properties, which makes them ideal candidates for the development of multifunctional material systems. Previous research has shown the fabrication and characterization of carbon nanotube/polymer composites.[2-9] For example, Haggenmueller et al.[7] used solvent casting followed by melt mixing to produce single-walled carbon nanotube (SWNT)/poly(methyl methacrylate) (PMMA) composite fibers with enhanced elastic modulus and electrical conductivity. Barraza et al.[8] made SWNT/polystyrene (PS) composite films with high electrical conductivity by using a miniemulsion polymerization method. Kashiwagi et al.[9] reported that multi-walled carbon nanotube (MWNT)/poly(propylene) (PP) composites made by a shear mixing method showed a significant increase in decomposition temperature due to the presence of the nanotubes.

However, although remarkable properties of single carbon nanotubes have been reported, nanotube composites have not yet demonstrated their theoretical potential. One of the biggest challenges is to obtain a uniform dispersion of nanotubes in a polymer matrix because carbon nanotubes tend to bundle together even after attempts are made to disperse them.

In this paper, a new and versatile fabrication method called coagulation will be presented; this method achieves better dispersion of SWNTs in the polymer matrix. SWNTs were used in this work because they have better properties when compared to MWNTs. The resulting composites exhibit larger elastic modulus, higher electrical conductivity, and increased thermal stability relative to pure PMMA.

# 2. Experimental Methods

The matrix polymer in this paper is PMMA (MW: 100,000 g/mol, supplied by Polysciences). PMMA was chosen as a matrix for its good spinning qualities and solubility in dimethylformamide (DMF). SWNTs for the PMMA composites were synthesized by a high-pressure carbon monoxide method (HiPco) (Rice University)[10] and were purified by the method described in Zhou et al.[11] The metal residue in the SWNTs after purification is less than 8 wt%. The wet purified nanotubes were then dispersed in DMF, followed by a filtration step to get rid of the residual water. The nanotube-PMMA composites are denoted as x% pSWNT/PMMA, where x% refers to the weight fraction of SWNTs in the composite and pSWNT refers to the purified SWNT.

The coagulation method was used to produce the pSWNT/PMMA composites. pSWNTs were added to DMF to give a concentration of 0.25 mg(pSWNT)/ml(DMF). A sonication bath (260 Watts/45 kHz) was used for 24 hours to disperse the pSWNTs in DMF. Based on the desired weight fraction of pSWNT in the final composite, an appropriate quantity of PMMA was dissolved into the pSWNT and DMF mixture. The suspension was then dripped into a large amount of distilled water ($V_{DMF}$:$V_{water}$=1:5) in a blender. The PMMA precipitated immediately due to its insolubility in the DMF/water mixture. The precipitating PMMA chains entrapped the pSWNTs and prevented pSWNTs from bundling again. After filtration and drying under vacuum at 120ºC for 24 hours, the raw pSWNT/PMMA composites were obtained.

In order to perform comprehensive testing, three types of composite samples were prepared: fibers, aligned and unaligned composites. The composite fibers were made by melt spinning with a single spinner hole (diameter Do = 500 μm). The extruded

composite fiber was air-cooled and drawn under tension by a windup spool. The diameter of the composite fibers varied from 30 μm to 50 μm, as determined by a micrometer and optical microscopy. A heat gun was used to weld the composite fibers together while still on the windup spool. These welded fibers were then cut to size and stacked into a channel die. The channel die was then placed onto a hot press (1000 lbs, 160 ˚C for ~3 minutes) to produce an aligned composite with dimensions of 2mm×2mm×10mm. The unaligned composite was made by hot pressing in the same channel die using the raw pSWNT/PMMA composites. The hot press was also used to prepare the composite films of ~30 μm thickness, which were observed in an optical microscope to study the dispersion of pSWNT. Scanning electron microscopy (SEM) was also used to investigate fracture surfaces of the composites.

X-ray fiber diagrams were used to characterize the alignment of pSWNT within the polymer matrix. In principle, both wide angle and small angle x-ray scatterings should reveal texture.[12] But since the nanotube loading in our composite sample is relatively low (0.1~7%) and HiPco material generally has poor crystallinity, the intensity was dominated by the scattering from the polymer matrix in the wide angle region ($0.3<Q<2.0$). In the small angle region ($0.01<Q<0.1$), the amorphous polymer matrix has no large-scale features, thus the scattering intensity is mainly from the form factor scattering of nanotubes and nanotube bundles. The small angle x-ray scattering (SAXS) unambiguously reveals texture on which we focused. Measurements were performed in transmission on Penn's multiple-angle x-ray scattering (MAXS) apparatus equipped with a 2-D wire detector. From the 2D data sets, we integrated along the radial Q direction (e.g. $0.02<Q<0.05$) and plotted the intensity vs. azimuthal angle. These data were then

fitted by a simple Lorentzian function whose full width at half-maximum (FWHM) quantitatively describes the degree of nanotube alignment in the composite.

The mechanical testing for the elastic modulus of the composite fibers was performed in tension on an Instron 4206 with a 0.5 N load cell. The fibers were fixed on a testing tab with a gauge length of 25.4 mm and tested at room temperature with a deformation rate of 1mm/min. For both the unaligned and aligned composites, the electrical conductivities greater than $10^{-8}$ S/cm were measured by a four-probe method at room temperature, while smaller conductivities were measured by a two-probe method at room temperature. The electrical conductivity of the aligned sample was measured along the fiber direction; that is along the nanotube orientation. Thermal gravimetric analyses (TGA) were performed using a TA Instruments SDT 2960 at 5ºC/min from 25ºC to 800ºC in air and ~2.0 $mm^3$ samples cut from the unaligned composites.

# 3. Results and Discussion

Figure 1a is an optical micrograph of the 1% pSWNT/PMMA composite thin film made by the coagulation method. It shows that there are no obvious agglomerations of the SWNTs, indicating that the nanotubes are uniformly distributed within the polymer matrix at the micrometer scale. Based on the SEM image of the 7% pSWNT/PMMA fracture surface shown in Figure 1b, the diameters of the nanotube bundles are ~20 nm and they are uniformly distributed at the sub-micron scale. In our coagulation method the polymer chains entrap the surrounding nanotube bundles as the composite precipitates in the DMF/water system, as the conformation of the polymer chains changes from a

relatively expanded state in DMF to a collapsed state in DMF/water mixture. Figure 1c is taken from Haggenmueller et al,[7] which shows an optical micrograph of a 1% pSWNT/PMMA composite thin film made by solvent casting followed by melt mixing. Comparing Figure 1a and 1c, it can be seen that in Figure 1c there are numerous agglomerates with dimensions of ~10 μm. These images indicate that the coagulation method provides better dispersion of pSWNTs in the polymer matrix. The coagulation method appears to prevent the rebundling of nanotubes after sonication and the dispersion is comparable to that in the solvent. In contrast, the nanotubes apparently rebundle during the solvent evaporation in our previous solvent casting method.

The nanotube purification process also affects the dispersion of the nanotubes in the composites. At the end of our purification of SWNT, deionized water was used to wash the nanotubes. Because pSWNTs have a better dispersion in DMF than in water, the remaining water has to be eliminated from pSWNTs. After drying pSWNTs under vacuum at room temperature, we find these completely dried nanotubes exhibit poor dispersion in DMF. Consequently, the resulting composite exhibits inhomogeneous pSWNT distribution via optical microscopy, Figure 2. The numerous black spots in Figure 2 are nanotube agglomerates that could not be separated by sonication in DMF after the pSWNT was completely dried. As a result, drying after purification leads to bad dispersion in the final composites. Thus, we exchange the water with DMF in the pSWNT and proceed with the coagulation method, as described in the Experimental Methods section.

The coagulation method can be used not only to produce nanotube polymer composites, but also to produce other nano-particle polymer composites. This method can

even be applied to a continuous operation in large-scale production. Furthermore, it is applicable to a wide range of thermoplastics given an appropriate combination of solvents.

SAXS provides a measure of the alignment of pSWNT in the composite, which makes it possible to study the influence of the alignment of the nanotubes on the properties of the composites. Figure 3 shows fairly good alignment with a FWHM of ~18º for the 1% pSWNT/PMMA aligned composite. It can also be seen that the FWHM increases with increasing pSWNT loading, which is consistent with the polarized Raman spectra results for the pSWNT/PMMA composite fibers, as reported in Haggenmueller et al.[13] As the pSWNT loading increases, the ability to align the small nanotube bundles decreases due to steric constraints imposed by these high aspect ratio objects. Figure 3 also shows that the FWHM of the 2% unaligned composite was ~160º confirming a nearly random orientation of pSWNTs in the polymer matrix.

The elastic modulus increases with pSWNT loading in the composite fibers as shown in Figure 4. For example, the average elastic modulus of the 2% composite fiber is ~6.3 GPa, which is ~90% higher than that of the pure PMMA fibers. While Haggenmueller et al.[7] have previously reported an increase in moduli with nanotube loading in pSWNT/PMMA composite fibers, our observed increase is more pronounced. For example, a similar elastic moduli was measured for a 2% and 8% pSWNT/PMMA composite fiber prepared by the coagulation and the solvent casting with melt mixing method, respectively. The improved mechanical properties are probably caused by the improved dispersion of the nanotubes within PMMA. The apparently improved dispersion also correlates to the higher viscosity of these composites, which prevents melt

fiber spinning composites with more than 2% pSWNT. Note that Haggenmueller et al.[7] were able to melt spin fiber composites with up to 8% pSWNT.

Relative to PMMA, the electrical conductivity of the 2% unaligned composite increases by 11 orders of magnitude, up to ~$10^{-4}$ S/cm, Figure 5. The electrical conductivity remains approximately constant for the composites with the higher nanotube loading and exhibits a percolation threshold of ~1%. The composition dependence of the electrical conductivity implies that a nanotube network spans the composite at nanotube loadings higher than this threshold. Consequently, adding more nanotubes does not significantly alter the electrical conductivity.

Several other groups have also reported an increase in the electrical conductivity for the SWNT/polymer composites. For example, Barraza et al.[8] reported an increase in electrical conductivity of the SWNT/polystyrene composite from $10^{-16}$ S*cm$^{-1}$ with a 4% nanotube loading to $10^{-6}$ S*cm$^{-1}$ with a 8.5% nanotube loading, corresponding to a threshold of ~6%. Benoit et al.[14] reported a threshold of 0.33% in electrical conductivity for the SWNT/PMMA composite film ~10 μm thick. Nanotubes confined to a film might be able to form a network at lower nanotube loading, because the nanotubes may not be isotropic. Figure 5 demonstrates the influence of nanotube alignment by comparing the electrical conductivity of the aligned (~$10^{-10}$ S/cm) and unaligned (~$10^{-4}$ S/cm) 2% pSWNT/PMMA composites. This indicates that alignment of nanotubes in the composite worsens electrical conductivity and will also shift the percolation threshold. The reason for the decrease in electrical conductivity is that there are fewer contacts between the nanotubes when they are aligned, thus aligned composites require more nanotubes to

reach the percolation threshold. Nanotube orientation, dispersion and length will also influence electrical conductivity threshold.

Embedding the nanotubes into the polymer matrix also improves thermal stability of the polymer as shown in Figure 6. PMMA and the 0.5% pSWNT/PMMA unaligned composite begin to lose weight at the same temperature, but the temperature at the maximum mass loss rate is 372°C for the composite, which is ~61°C higher than for PMMA. Furthermore, the maximum mass loss rate is only ~7.8%/min for the 0.5% composite, as compared to 14.5%/min for PMMA. Similar results were found for the other pSWNT/PMMA composites (0.1, 1, and 5%). The improved thermal stability of PMMA by the addition of pSWNT is consistent with recent results showing improved fire retardation.[15]

# 4. Conclusion

In summary, a coagulation method was designed and implemented to obtain improved dispersion of pSWNTs within a PMMA matrix, as seen in optical and SEM micrographs. Extensional flow during melt fiber spinning aligned the pSWNTs as measured by SAXS. These composites exhibited better improvement in the mechanical, electrical and thermal stability properties than our earlier pSWNT/PMMA composites. Alignment of the nanotubes in the polymer matrix greatly influences the electrical conductivity of the composites; aligned composite is 5 orders of magnitude lower in electrical conductivity than that of the unaligned composite with the same pSWNTs loading. A nanotube network formed in the composites limits the ability to melt spin fibers while increasing the electrical conductivity and thermal stability.

# Acknowledgements:

This research was supported by ONR grant N00014-00-1-0720 and DURINT grant N00014-01-1-0789. We thank R. Haggenmueller, W. Zhou, M. Hsu, J. Vavro, and C. Guthy for valuable discussions and assistance in the experiments. We are grateful to Rice University for providing HiPco SWNT.

# References


1. Iijima, S. Nature 1991, 354, 56.
2. Thostenson, E.T.; Ren, Z.; Chou, T.W. Comp. Sci. Technol. 2001, 61, 1899.
3. Thostenson, E.T.; Li, W.Z.; Wang, Z.D.; Ren, Z.F.; Chou, T.W.; J. Appl. Phys. 2002, 91, 6034.
4. Fisher, F.T.; Bradshaw, R.D.; Brinson, L.C. Appl. Phys. Lett. 2002, 80, 4647.
5. Jia, Z.; Wang, Z.; Xu, C.; Liang, J.; Wei, B.; Wu, D.; Zhu, S. Mater. Sci. Eng. A 1999, 271, 395.
6. Stéphan, C.; Nguyen, T.P.; de la Chapelle, L.; Lefrant, S.; Journet, C.; Bernier, P. Synth. Met. 2000, 108, 139.
7. Haggenmueller, R.; Commans, H.H.; Rinzler, A.G.; Fischer, J.E.; Winey, K.I. Chem. Phys. Lett. 2000, 330, 219.
8. Barraza, H.J.; Pompeo, F.; Orear, E.A.; Resasco, D.E. Nano Letters 2002, 2, 797.
9. Kashiwagi, T.; Grulke, E.; Hilding, J.; Harris, R.; Awad, W.; Douglas, J. Macromol. Rapid Commun. 2002, 23, 761.
10. Nikolaev, P.; Bronikowski, M.J.; Bradley, R.K.; Rohmund, F.R.; Colbert, D.T.; Smith, K.A.; Smalley, R.E. Chem. Phys. Lett. 1999, 313, 91.
11. Zhou, W.; Ooi, Y.H.; Russo, R.; Papanek, P.; Luzzi, D.E.; Fischer, J.E.; Bronikowski, M.J.; Willis, P.A.; Smalley, R.E. Chem. Phys. Lett. 2001, 350, 6.
12. Zhou, W.; Winey, K.I.; Fischer, J.E. Mater. Res. Soc. Symp. Proc.: Boston, MA, 2003, 740, I12.21.1.
13. Haggenmueller, R.; Zhou, W.; Fischer, J.E.; Winey, K.I. J. Nanosci. Nanotech. 2003, 3, 1.

14. Benoit, J.M.; Corraze, B.; Lefrant, S.; Blau, W.; Bernier, P.; Chauvet, O. Synth. Met. 2001, 121, 215.

15. Kashiwagi, T.; Du, F.; Winey, K.I.; Harris, R.H.; Shields, J.R.; Douglas, J.F. Submitted to Macromol. Rapid Commun., 2003.

Figure captions

Figure 1: (a) Optical micrograph of a 1% pSWNT/PMMA composite thin film as fabricated by the coagulation method showing uniform SWNT distribution. (b) SEM of a 7% pSWNT/PMMA composite fiber fracture surface also prepared by the coagulation method showing good SWNT distribution. (c) For comparison, an optical micrograph of a 1% pSWNT/PMMA composite thin film fabricated by solvent casting from DMF and then melt mixing showing aggregation of pSWNT. (From Haggenmueller et al.[7])

Figure 2: Optical micrograph of a 1% pSWNT/PMMA composite thin film made by the coagulation method using dry pSWNT indicating considerable pSWNT agglomeration.

Figure 3: FWHM of the Lorentzian function fitted to the azimuthal distribution of the SAXS intensity from the pSWNT/PMMA composites, both unaligned composite (▲) and aligned composite (■), as a function of pSWNT loading.

Figure 4: Elastic tensile modulus of the pSWNT/PMMA composite fibers as a function of the pSWNT loading.

Figure 5: Electrical conductivity of the pSWNT/PMMA composites, both unaligned composite (▲) and aligned composite (■), as a function of the pSWNT loading.

Figure 6: TGA analyses of normalized weight loss and its rate by the initial sample weight at a heating rate of 5ºC/min in air: (solid) pure PMMA; (dash) 0.5% pSWNT/PMMA composite.

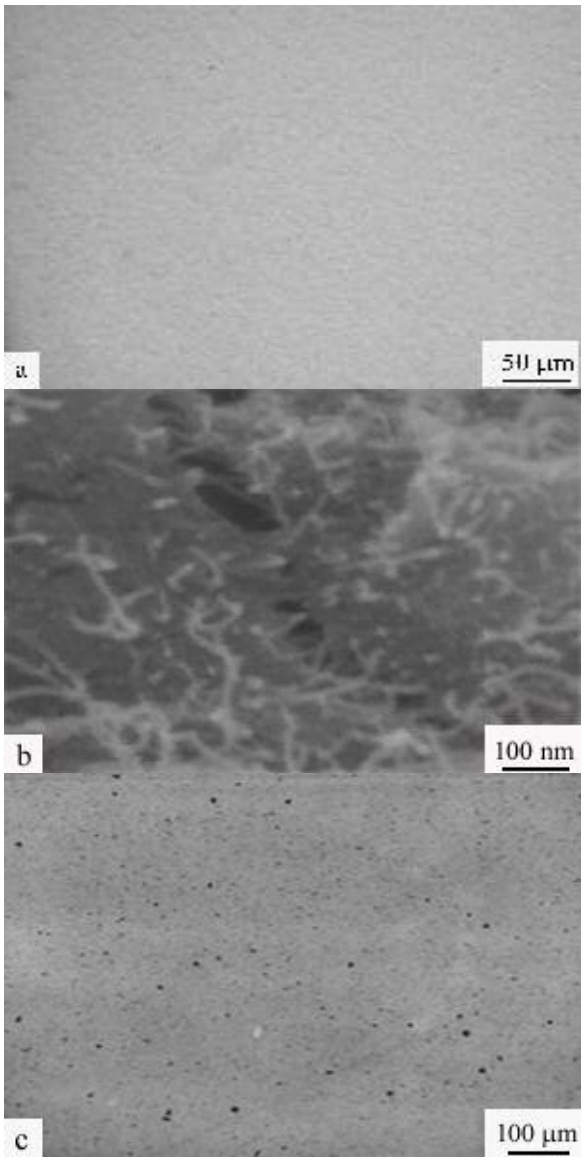


Figure 1

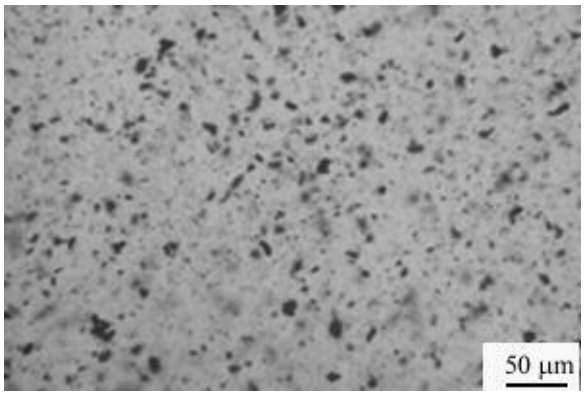


Figure 2

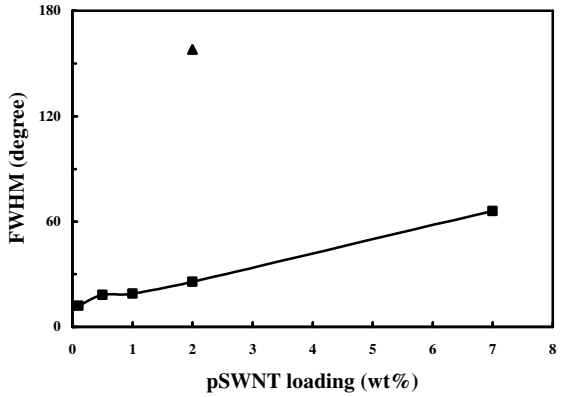


Figure 3

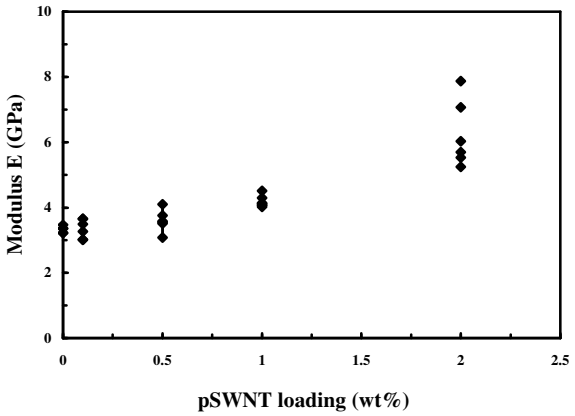


Figure 4

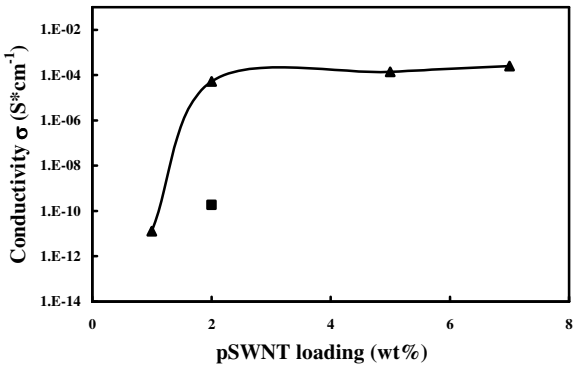
1.E-02
1.E-04
1.E-06
1.E-08
1.E-10
1.E-12
1.E-14
Conductivity σ (S*cm-1)
0
2
4
6
8
pSWNT loading (wt%)

Figure 5

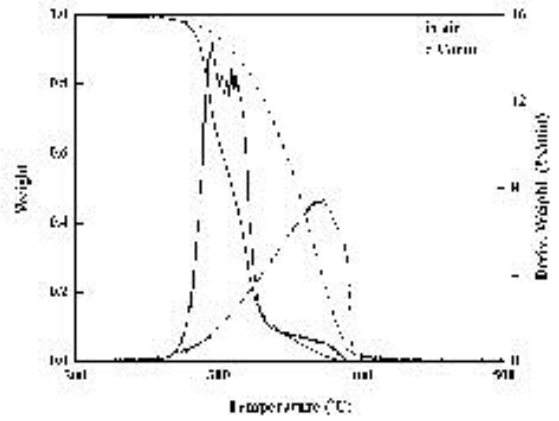

Figure 6