

The influence of coiled nanostructure on the enhancement of dielectric constants and electromagnetic shielding efficiency in polymer composites

S. Park¹, P.R. Bandaru¹, A.M. Rao²

¹Department of Mechanical & Aerospace Engineering,
University of California, San Diego

²Department of Physics, Clemson University, Clemson, SC

Introduction

Polymer composites containing conducting fillers have been extensively investigated for various applications such as electromagnetic interference (EMI) shielding[1], electronic packaging[2], radar absorption[3], and high charge storage capacitors[4]. However, presently used composites require high filler to polymer loading ratios which deteriorates the overall mechanical properties, through destruction of intrinsic matrix morphology. A possible way to ameliorate the above problems, through using low filler volume fractions, incorporates carbon nanotubes (CNTs) in composites. A concomitant large aspect ratio and tunable electrical conductivity would enable electrical percolation to be achieved at very small CNT volume fractions[5], with large shielding efficiencies being obtained. However, economic costs and clustering of the CNTs within the polymer matrix are issues that have to be overcome prior to large scale application. In this paper, we tackle the clustering problem by considering the synthesis of well dispersed functionalized CNT composites.

Additionally, a change in structure and morphology, at the nanoscale, could have a profound influence on macroscopic characteristics, through the paradigm of “function follows shape”[6]. For example, in the case of carbon based nanostructures, nonlinear and coiled carbon nanotubes (CCNTs)[7]/ nanowires (CNWs) have been proposed. We then suggest yet another application, that the incorporation of coiled structures could be used to enhance the intrinsic electromagnetic properties, e.g., the dielectric constants and the EMI shielding, of polymer matrices.

Experimental

In this paper, we report on the effects due to uniformly dispersed CCNTs incorporated into a Reactive Ethylene Terpolymer (RET: Elvaloy 4170) polymer matrix. The RET structure is constituted from[8] (1) polyethylene, (2) a polar methyl-methacrylate group, and (3) epoxide functional groups. While (1) and (2) contribute to the mechanical characteristics (elastomeric properties) and corrosion resistance underlying the utility of RET as a hot-melt adhesive and coating, the epoxy group has high reactivity[9] and facilitates effective anchoring with the CNTs. For comparison, we also embedded linear CNTs, i.e., both single walled (SWCNTs) and multi-walled (MWCNTs) and a mixture of linear and coiled CNT varieties. While a range of volume fractions were tested, we report here on the results of a particular volume fraction, i.e., ~ 0.9 %. Such a volume

fraction is intermediate within the range of percolation thresholds, estimated from excluded volume percolation theory of 0.1 vol% to 2 vol% - depending on whether the extended or the coiled length of the helical nanostructure was considered. Uniform dispersion without nanotube agglomeration was facilitated through localized chemical reactions between the –COOH functional groups on CNTs with epoxy groups on the RET. The CNTs were then dispersed in toluene with sonication for 20 minutes. The CNT dispersion was added to the RET (also mixed with toluene) and then the mixture was stirred, poured into glass dishes and evacuated in vacuum. A hot press was used to fabricate composites of desired thickness (~ 2 mm). More details been reported elsewhere[8].

The EMI shielding efficiency (SE) of the CNT-RET nanocomposites was then determined, in the microwave frequency (f) range (8.2-12.4 GHz: X-band) through the use of a vector network analyzer (VNA: Agilent 5242A PNA-X). The R (reflection), A (absorption), and the T (transmission) components were then obtained through the measurement of the S -parameters (S_{ij}) using the VNA, where $T = |S_{21}|^2$, $R = |S_{11}|^2$, and $A = 1 - |S_{11}|^2 - |S_{21}|^2$. The total effective shielding effectiveness, SE(Tot), of the composite was considered as: $SE(Tot) = SE(R) + SE(A)$, where $SE(R) = -10 \log(1-R)$ and $SE(A) = -10 \log[\frac{T}{1-R}]$. The determination of

S_{11} and S_{21} also enables the calculation of the relative complex permittivity ($\epsilon = \epsilon' + j \epsilon''$) and permeability ($\mu = \mu' + j \mu''$), along with the reflection and transmission coefficients. Concomitantly, the dc conductivity (σ_{DC}) was measured on the through four-point electrical measurements.

Results and Discussion

SEM micrographs of the composite fracture surfaces do indicate a uniform dispersion of the CNTs, e.g., as seen in Figure 1, due to our synthesis procedures.

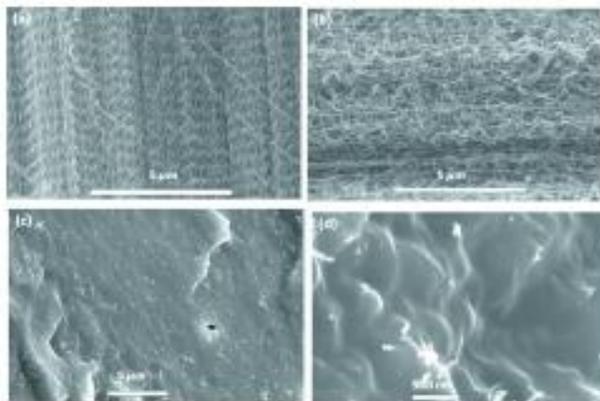


Fig. 1 SEM micrographs of (a) aligned coiled CNTs with nearly identical diameter and pitch, (b) a mixture of linear and coiled CNTs, (c) uniformly dispersed coiled CNTs, and (d) a higher resolution image of (c)

It was observed that the both ϵ' and ϵ'' of the CCNTs is larger, by approximately a factor of two, compared to SWCNTs- Figure 2 (a). In the figure is also shown the corresponding variation for a mixture of linear and coiled CNTs (with an approximately 1:1 distribution) – as in Figure 1(b), which is seen to be intermediate to the CCNTs and SWCNTs. The increased ϵ' in the coiled CNTs over linear CNTs (SWCNTs/MWCNTs) is explained on the basis of enhanced capacitive coupling between alternate windings/segments of the coil in the former - see Figure 2(b) inset, which effectively increases ϵ' . The relatively weak f dependence of ϵ'' could be indicative of the composition used in the present study.

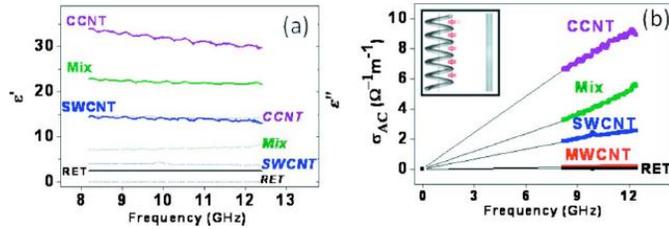


Fig. 2 The (a) ϵ' and ϵ'' of functionalized CCNT-RET composites are larger than those of composites constituted from linear CNTs (single- and multi-walled), (b) The ac conductivity, σ_{AC} , is also larger for the CCNTs and is ascribed to increased capacitive coupling between alternate windings.

The linear dispersion of the ac conductivity, σ_{AC} (computed through $\sigma_{AC} = \omega\epsilon_o\epsilon''$, where $\omega = 2\pi f$ with frequency is plotted next in Figure 2(b)). As could be expected from Figure 2(a), the CCNT based materials have a higher σ_{AC} compared to the linear CNT based composites. Concomitantly, we explain the enhanced σ_{AC} on a simple model based on the formation of parallel resistors and capacitors in the composite. In this model, the CNTs contribute to the electrical resistance while the polymer matrix serves as the capacitor dielectric and contributes to the AC conductance. The increased number of parallel resistors and capacitors in the CCNTs due to the coiled structure, compared to linear CNTs, decreases the overall resistance and capacitive impedance (X_c) of the composite due to the availability of several alternative electrical conduction paths.

Additionally, a higher EMI SE was observed for the CCNT composite- Figure 3(a), which shows a comparison of the frequency variation of the SE values of composites with similar σ_{DC} . Figure 3(b) illustrates the variation for the case of CNTs with similar diameters and length. Since we observe that the SE *decreases* with frequency- Figures 3 (a) and 3(b)-the shielding mechanism seems to be reflection dominated at 0.9 vol%. We could also explain the higher SE by invoking the aspect ratio of the constituent nanostructures by considering the total/extended length and intrinsic CNT diameter. For example, in the case of CCNTs the L_{ext} to d_{CNT} ratio (~ 2140) was on the average much larger than in the case of SWCNTs (~ 895) or MWCNTs (~400). It was previously determined[8] that nanocomposites constituted of the former indeed have a higher SE. A good agreement ($\pm 10\%$) of the

shielding efficiency for the composite composed of both linear and coiled CNTs, SE_c , was obtained through $SE_c = \sum_i SE_i \phi_i$, where SE_i refers to the shielding efficiency of the i^{th} constituent, i.e., $i =$ coiled CNT, linear CNT, etc.

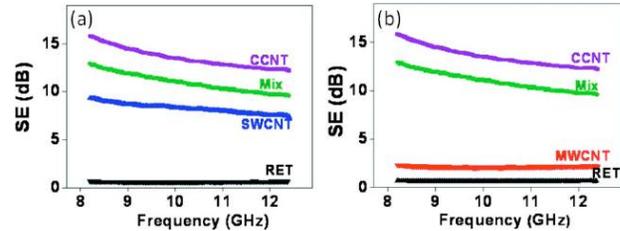


Fig. 3 The frequency variation of shielding efficiency (SE) of composites with fillers of (a) same σ_{AC} , and (b) similar diameter.

Conclusions

We conclude that the coiled CNT filler morphology and geometry can substantially influence the electromagnetic properties of polymer composites. It was noted that while the projected length and diameter could influence the dielectric permittivity due to depolarization effects, the total extended length and diameter could determine EMI shielding.

Acknowledgments We appreciate the support from the National Science Foundation (Grant ECS-06-43761)

References

- [1] Bigg D M and Stutz D E 1983 *Polymer Composites* **4** 40-6
- [2] Rashid E S A, Ariffin K, Akil H M and Kooi C C 2008 *Journal of Reinforced Plastics and Composites* **27** 1573-84
- [3] Liu Z, Bai G, Huang Y, Li F, Ma Y, Guo T, He X, Lin X, Gao H and Chen Y 2007 *Journal of Physical Chemistry C* **111** 13696-700
- [4] Hughes M 2004 *Dekker Encyclopedia of Nanoscience and Nanotechnology*, (London: Taylor & Francis) pp 447-59
- [5] Saib A, Bednarz L, Daussin R, Bailly C, Lou X, Thomassin J M, Pagnouille C, Detrembleur C, Jérôme R and Huynen I 2006 *IEEE Transactions on Microwave Theory and Techniques* **54** 2745-54
- [6] Bandaru P R and Rao A M 2007 *Journal of Materials (Special Issue on Nanomaterials for Electronic Applications)* **7** 33-8
- [7] Wang W, Yang K, Gaillard J, Bandaru P R and Rao A M 2008 *Advanced Materials* **20** 179-82
- [8] Park S-H, Thielemann P, Asbeck P and Bandaru P R 2009 *IEEE Transactions of Nanotechnology*
- [9] Tasis D, Tagmatarchis N, Bianco A and Prato M 2006 *Chemical Reviews* **106** 1105-35