Physics Letters A 378 (2014) 2985–2988

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Effect of cylindrical filler aggregation on the electrical conductivity of composites

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ARTICLE INFO

Article history:
Received 20 February 2014
Received in revised form 6 August 2014
Accepted 12 August 2014
Available online 15 August 2014
Communicated by R. Wu

Keywords:
Nanocomposites
Polymer matrix composites
Electrical properties

ABSTRACT

This work reports on the effect of carbon nanotube aggregation on the electrical conductivity and other network properties of polymer/carbon nanotube composites by modeling the carbon nanotubes as hard-core cylinders. It is shown that the conductivity decreases for increasing filler aggregation, and that this effect is more significant for higher cylinder volume fractions. It is also demonstrated, for volume fractions at which the giant component is present, that increasing the fraction of cylinders within clusters leads to a break of the giant component and the formation of a set of finite clusters. The decrease of the giant component with the increase of the fraction of cylinders within the cluster can be related to a decrease of the spanning probability due to a decrease of the number of cylinders between the clusters. Finally, it is demonstrated that the effect of aggregation can be understood by employing the network theory.

1. Introduction

The addition of high aspect ratio conductive fillers to a polymer is known to enhance the polymer matrix electrical conductivity even for small amounts of reinforcement. One the main problems in using a polymer reinforced with high aspect ratio fillers is in controlling the dispersion of the fillers in the matrix [1]. Dispersing high aspect ratio fillers like carbon nanotubes or carbon nanofibers reveals to be demanding and the formation of clusters of aggregates reinforcement is generally observed [2,3]. These clusters strongly influence the composite electrical and dielectric response as experimentally reported in [1–3]. Most notably, few theoretical studies have addressed the problem of cluster formation and its influence on the electrical properties of the composite. Ounaies et al. [4] studied the electrical properties of single wall carbon nanotubes as a reinforcement of a polyimide matrix. Using several types of rods, and clusters of closely packed parallel cylinders that can overlap, the percolation threshold of the composite was studied. It was concluded that increasing aggregation, the number of fibers in the bundle, the percolation threshold increases. Grujicic et al. [5] also studied the effect of aggregation on the percolation threshold, using three, seven and nineteen cylinder bundles arranged in a closely packed order. It was also reported that increasing the number of cylinders in the bundles leads to a increase of the percolation threshold. The increase of the percolation threshold with increasing rod number in [4] and [5] is explained by the increase of an effective diameter that increases with the number of rods in the cluster. Another perspective for the study of the cluster formation was given in [6] by studying the effect of carbon nanotube (CNT) aspect ratio, electrical conductivity, shape and CNT aggregation on the composite electrical properties. "Soft" cylinders were used to simulate a 3D composite with CNT inclusions. The study of the agglomeration effect was performed be distributing the cylinders between four Gaussians evenly distributed in a cube. It was also defined a strength parameter, δ, that indicates the intensity of the aggregation. It was found that the electrical conductivity decreases with increasing δ and the percolation threshold decreases with increasing δ until a threshold after which the aggregates have no influence on the percolation threshold of the nanocomposite. Bao et al. [7] studied the effect of CNT aggregation on the composite conductivity, using penetrable cylinders and periodic conditions. The authors used several types of cluster distributions on the domain to conclude that the variation of the electrical conductivity with aggregation is very small. In this work, the effect of CNT, hardcore cylinders and aggregation statistical properties on the electrical conductivity and other network properties is analyzed. Contrary to the aggregation of penetrable cylinders with periodic conditions, as in [7], it is shown that the conductivity decreases with increasing

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http://dx.doi.org/10.1016/j.physleta.2014.08.011
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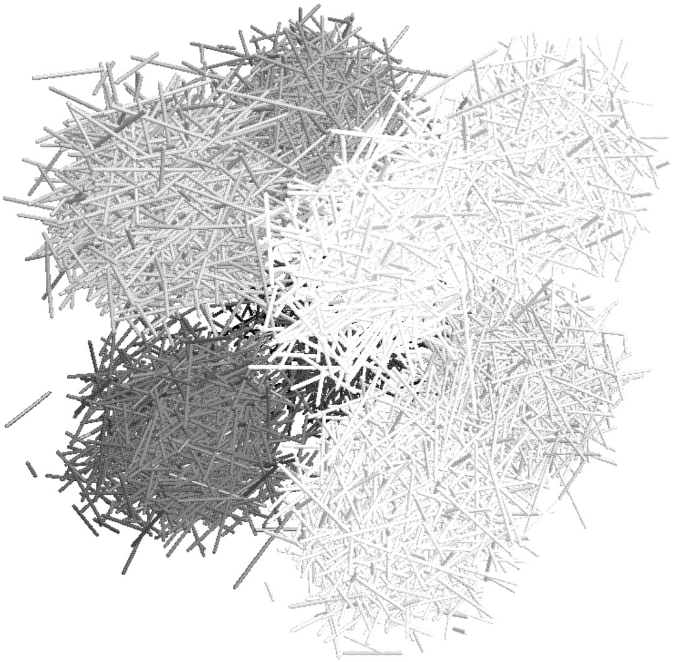

Fig. 1. Representation of the cylinder distribution in the eight clusters, for a material were all the cylinders belong to the clusters.

fraction of cylinders in the clusters as observed by Hu et al. [6] for penetrable cylinders and periodic conditions. With the objective of clarifying the effect of the aggregation on the composite conductivity, other network properties such as network diameter, size of the giant cluster, size of finite cluster and spanning probability are calculated that elucidate the origin of the conductivity decrease with increasing hardcore cylinder aggregates.

2. Material and methods

The microstructure for the isotropic materials was generated by a derivation of a sequential packing algorithm [8] in order to place randomly oriented cylinders in 3D space and using periodic boundary conditions, i.e., when part of a cylinder crosses the domain boundary it is cut and the segment that crosses the boundary is translated to the opposite domain boundary (i.e., symmetrically translated). The virtual composite is generated by assigning a percentage of the fillers to one of the eight clusters that are regularly located in an cube with every cluster positioned with a Gaussian centered at each octant as represented in Fig. 1.

After creating the virtual composite, the graph theory framework was used to study the composites, percolation threshold and conductivity. Within this framework, the cylinders are mapped to vertices and the edges to the minimum distance between the cylinders [9,10], which corresponds to the maximum electric field between the two fillers [9]. A maximum value for the minimum separation distance $\delta_{\max}$ is defined [9] and an undirected graph is constructed from the generated microstructure. The edges (junctions between cylinders) of the graph are assigned if the minimum separation distance is less than $\delta_{\max}$. The generated microstructure corresponds to a cube with a side of $L = 500$. The cube was filled with cylinders with an aspect ratio of 100 and $\delta_{\max} = 5$ and the generated volume fractions ranged from 10^{-3} to 5.0×10^{-3}, corresponding to a number of cylinders of $\approx 10^3$. It is stressed that by increasing the $\delta_{\max}$ value, the number of connected cylinders is increased, shifting the percolation threshold to lower values. For each data point (set of material parameters) of the results shown, $\approx 10^4$ different microstructures were simulated and all the respective graph properties were averaged. More precisely, using a breadth-first search algorithm [11] the size of the largest component, giant component S, was calculated by monitoring the size distribution, $P(s)$, of finite clusters, excluding the size of the largest cluster, to which a randomly node belongs, $P(s) = sn(s)/s_{av}$. The latter algorithm was also used to calculate the graph diameter. Here, s is the number of vertices, $n(s)$ is the cluster size distribution and s_{av} is the ratio of the number of vertices to the total number of clusters. By knowing $P(s)$, the size of the giant component can be calculated, $S = 1 - \sum_s P(s)$, as well as the mean size of a finite cluster to which a random vertex belongs, $\langle s \rangle = \sum_s sP(s)$. The conductivity is calculated by assigning to each edge a conductance given by $\exp(-ax_{ij})$ where a is a disorder constant, set to 1, and x_{ij} is the minimum distance between two fillers [10,12]. The latter expression is similar to the expression of hopping between nearest neighbours at room temperature with the decay of the wave function in the matrix set to the unit [13,14]. Another important question is the effect of the matrix in the composite conductivity. It was demonstrated [15] in an experimental work for carbon nanofiber/epoxy composites, that the matrix conductivity has an additive effect and will just shift up the overall composite conductivity.

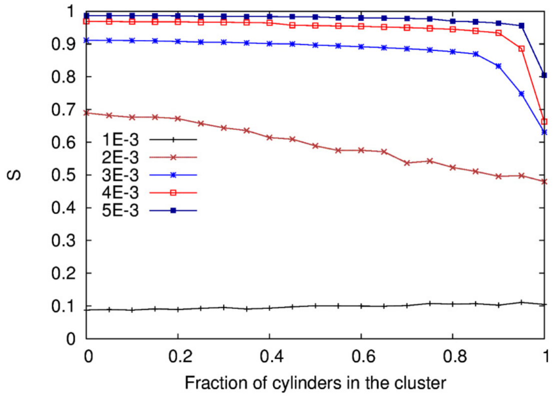

Fig. 2. Size of the giant component versus the fraction of cylinders in the clusters for several volume fractions.

3. Results and discussion

Fig. 2 shows the size of the giant component versus the fraction of cylinders in the clusters and it is observed that the size of the giant component increases with increasing volume fraction. It is also observed that when the giant component is formed, it decreases with increasing fraction of cylinders in the clusters. This decrease is more pronounced for the fraction of cylinders within the clusters larger than 0.8 except for the 2E-3 volume fraction in which a significant continuous decrease is observed.

The decrease of the giant component can be understood by a decrease on the number of cylinders available to connect the different aggregates being more pronounced when all the cylinders belong to the clusters. It is possible to observe in Fig. 3 that the spanning probability, the probability of the formation of a spanning cluster connecting two opposite sides, decreases when the fraction of cylinders in the clusters is higher. This decrease is more pronounced for the 2E-3 volume fraction.

The observed decrease of the spanning probability with the fraction of cylinders in the clusters in Fig. 3 is related to a decrease of the number of rods necessary to connect the voids between the clusters. This decrease is more pronounced for lower volume fractions due to the fact that there is an overall lower number of cylinders furthermore, for the lowest concentration of 1E-3, the spanning probability is near zero, showing again that there is a concentration threshold for the giant component for form, and which then enables spanning.