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A PERCOLATION MODEL FOR CARBON NANOTUBE-POLYMER COMPOSITES USING THE MANDELBROT-GIVEN CURVE

© 2011 **M. Monajjemi[1], H. Baheri[2]*, F. Mollaamin[3]**

[1]*Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran*
[2]*Ph.D. student, Science and Research Branch, Islamic Azad University, Tehran, Iran*
[3]*Department of Chemistry, Qom Branch, Islamic Azad University, Qom, Iran*

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A model is introduced for the conductivity of carbon-nanotube polymer composites based upon percolation theory and fractals. These types of polymer composites have been developed in the recent years, and experimental data on their percolation threshold is available. We constructed a fractal space with the aim of the generalized Mandelbrot-Given curve and used the experimental critical exponent of conductivity to calculate the parameters of such a curve. Finally, the moments of the current distribution function are estimated, and the effect of the critical exponent on this function is investigated.

K e y w o r d s: percolation theory, fractal, Mandelbrot-Given curve, carbon nanotube composites.

1. INTRODUCTION

Carbon nanotubes (CNTs) [1] have unique properties that make them attractive systems for fundamental scientific studies and a wide range of applications [2—4]. Carbon nanotubes are excellent electrical conductors [5] with current densities of up to 10^{11} A·m^{-2}, and have very high thermal conductivities [6]. Many of these properties can be best exploited by incorporating the nanotubes into some form of matrix. The preparation of nanotubes containing composite materials is now a rapidly growing subject [7, 8]. Multiple applications are expected for nanocomposite materials and therefore many research works are currently devoted to their incorporation into a metal, ceramic or, more commonly, polymer matrix. The composites are generally prepared by mixing the desired quantity of single- or multi-walled carbon nanotubes (SWCNT or MWCNT) with the matrix, which is either dissolved or in suspension in a liquid medium, before further treatments. One of the most important properties of nanocomposite materials is conductivity, and many researches work on electrical percolation of carbon nanotubes in polymer composites [9]. *Percolation threshold* was experimentally measured for many types of carbon nanotubes and polymer matrices. In this paper, we introduce a model based on percolation theory in fractal space for predicting electrical behavior of carbon nanotube-polymer composites (CNTCs).

Percolation processes were first developed by Flory (1941) and Stockmayer (1943) to describe how small branching molecules react and form very large macromolecules [10]. In 1957, Broadbent and Hammersley introduced percolation theory as a stochastic way for modeling the flow of fluid or gas through a porous medium with small channels that may or may not let fluid or gas pass [11]. The terms fluid and medium were viewed as totally general: a fluid can be liquid, vapor, heat flux, electric current, infection, a solar system, and so on. The medium can be the pore space of a rock, an array of trees, or the universe. We can define percolation theory as a general mathematical theory of connec-

* E-mail: h.baheri@gmail.com

tivity and transport in geometrically complex systems [12]. The remarkable thing is that many results can often be represented in a small number of simple algebraic relationships.

Percolation theory is classified into two types: *site percolation* and *bond percolation*. In the first type, we have an infinite lattice of sites that may be occupied with the probability p or unoccupied with the probability 1-p. In the other type, an infinite lattice of bonds exists, and each bond may be closed with the probability p and open with 1-p. A set of sites (or bonds) connected to each other makes a cluster, and in a lattice, one can find clusters different in shape and size (lattice animals). It is clear that if p increases, the mean cluster size grows, and in a particular probability we envisage an infinite spanning cluster that connected two sides of the lattice (percolation done). This particular probability is the phase transition threshold of a system and it was introduced as the *percolation threshold* p_c. This quantity relates only on the geometry of the lattice, and it was calculated for many lattices (some by exact calculations and others by computer simulation) [10, 13].

It is very important that we attend to the difference between the diffusion process and the percolation process. In the first case, fluid particles decide where to go in the medium, but in the second case, the topology of the medium dictates the paths of particles. The topological properties of percolation networks are characterized by several quantities, and the effective conductivity $g(p)$ is affected by these quantities. The value of each percolation quantity for any p depends on the microscopic details of the system, but near the percolation threshold most of these quantities obey scaling laws that are largely insensitive to the network structure. For the effective conductivity near p_c we have the following scaling law:

$$g(p) \propto (p - p_c)^{\mu}. \tag{1}$$

The exponent μ is one of the transport exponents in percolating systems, and it is almost universal. It means that μ has no relation to the microscopic details of the system and depends only on the dimensionality of the system.

It is not easy to obtain any exact analytical results for cluster properties, and much of our knowledge comes from complex numerical calculations. In these cases, it is very useful to invent a simple mathematical model on which we can make analytical calculations. It was clear that the geometry of infinite cluster at p_c was fractal [14]. Benoit Mandelbrot introduced fractal geometry as a unifying description of natural phenomena that are not uniform, but still obey simple power laws of the form

$$M \propto L^D. \tag{2}$$

D is the non-integer dimension and L is the linear size of the system. Fractal dimensions describe a subset of cluster sites (or bonds) necessary for calculating different cluster properties. The formal mathematical definition of a fractal was given by Benoit Mandelbrot. It says that a fractal is a set for which the Hausdorff Besicovich dimension strictly exceeds the topological dimension [14]. However, this is a very abstract definition. Generally, we can define a fractal as a rough or fragmented geometric shape that can be subdivided into parts, each of which is (at least approximately) a reduced-size copy of the whole. Fractals are generally self-similar and scale-independent.

MODEL

A calculation of the critical exponent in equation (1) shows that there is no distinction between different types of two-dimensional lattices, such as square, triangular or honeycomb lattice. The result remains in force for d-dimensional lattices. In addition, bond and site percolation have the same exponent. All evidences suggest that the critical exponent depends only on the dimensionality of the lattice, and they are *universal* [10]. Critical exponents were exactly calculated for the Bethe lattice, in which each site is connected to z closest neighbors in a way that no closed loops are possible. In such a lattice, we have $p_c = (z - 1)^{-1}$ and $\mu = 3$. The value of the critical exponent obtained from the Bethe lattice is the limiting case when the dimensionality of the system approaches to infinity. The accurate studies show that the Bethe lattice critical exponent value is exact at $d \geq 6$, but in less dimensions it is identified with an expansion factor (ε) as follows:

$$\mu = 3 - (5\varepsilon / 21). \tag{3}$$

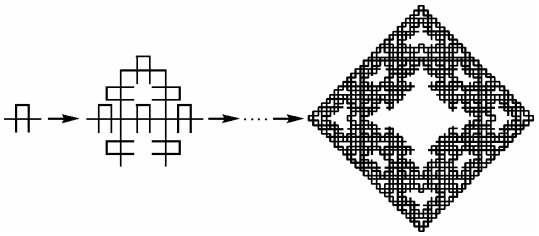

Fig. 1. Mandelbrot-Given curve generation for $b = 3$

On the other hand, if we suppose that the geometry of the infinite cluster at p_c is fractal (so the subsets of this cluster are fractal), then it is possible to determine the fractal dimension of such a cluster (and its subsets) in terms of ε

$$D = 4 - (10\varepsilon / 21), \tag{4}$$

$$D_B = 2 + (\varepsilon / 21), \tag{5}$$

$$D_{\min} = 2 - (\varepsilon / 6), \tag{6}$$

$$D_{\max} = 2 - (\varepsilon / 42). \tag{7}$$

In the above-mentioned equations, D, D_B, $D_{\min}$, and $D_{\max}$ are the fractal dimensions of the infinite cluster, backbone, minimum path (chemical distance), and maximum self-avoiding path respectively. The backbone is a set of clusters connected to each other by single bonds, and it connects the opposite edges of the system. It means that there is practically only one chain of bonds in the infinite cluster, which connects two sides. One can find the shortest way in the backbone, it is the minimum path. Also, the longest way in the backbone is called the maximum self-avoiding path.

With a close look at relation (3) between the critical exponent and the expansion factor, and relations (4 to 7) between the fractal dimensions and the expansion factor, we expect a direct relation between the fractal dimensions and the critical exponents as follows:

$$D = 2\mu - 2, \tag{8}$$

$$D_B = (13 - \mu) / 5, \tag{9}$$

$$D_{\min} = (7\mu - 1) / 10, \tag{10}$$

$$D_{\max} = (\mu + 17) / 10. \tag{11}$$

Now we can construct a fractal space and expand our system in this environment. Mandelbrot and Given proposed the recursive construction (Fig. 1). The construction begins with a straight segment of unit length replaced by eight segments at each iteration [15].

The length scale changes by a factor b called the generalized rescale factor. The generalized Mandelbrot-Given curve (GMGC) has L_1 singly connected bonds, $L_2 + L_3$ bonds in the blob (with $L_2 \le L_3$), and L_4 dangling bonds, and they are related to fractal dimensions

$$D = \log(L_1 + L_2 + L_3 + L_4)/\log b, \tag{12}$$

$$D_B = \log(L_1 + L_2 + L_3)/\log b, \tag{13}$$

$$D_{\min} = \log(L_1 + L_2)/\log b, \tag{14}$$

$$D_{\max} = \log(L_1 + L_3)/\log b. \tag{15}$$

A simple calculation shows the fractal dimensions ability to explain the GMGC parameters (L_1 to L_4)

$$L_1 = b^{D_{\max}} - b^{D_B} + b^{D_{\min}}, \tag{16}$$

$$L_2 = b^{D_B} - b^{D_{\max}}, \tag{17}$$

$$L_3 = b^{D_B} - b^{D_{\min}}, \tag{18}$$

$$L_4 = b^{D} - b^{D_B}. \tag{19}$$

In CNTC, we can propose a network of conductive particles that are distributed in a nonconductive medium, and also we can study the distribution of these particles with the aim of a distribution function. It is often convenient to calculate the moments of the distribution function. The distribution of current in a random network is *multifractal* and therefore

$$\frac{M_q(L)}{M_0(L)} = \sum_j \left(\frac{I_j}{I}\right)^{2q} = L^{\psi(q)}. \tag{20}$$

In the equation, $M_q(L)$, I_j, I, and $\psi(q)$ are the qth moment of the current distribution function, current through the j bond, total current, and the multifractal exponent respectively. The concept of *multifractality* implies that there is no linear relation between $\psi(q)$ and q.

If it is supposed that the network of CNTCs is a random network, which is a necessary assumption for applying the percolation theory, and this network has a structure of the GMGC type, we will be able to predict the moments of the current distribution function. Blumenfeld *et al*. (1986) found that the multifractal exponent for the current distribution in such a curve is given by

$$\psi(q) = \frac{\log[L_1 + (L_2 L_3^{2q} + L_3 L_2^{2q}) / (L_2 + L_3)^{2q}]}{\log b}. \tag{21}$$

Our model is based on calculating the GMGC parameters with respect to the fractal dimensions of an infinite cluster in a CNTC matrix (*eqs*. 16—19), and then it applies these parameters for predicting $\psi(q)$ (Eq. 21). In order to compute the fractal dimensions, the experimental results for the critical exponent are applied (Eqs. 8—11).

RESULTS AND DISCUSSION

There is one point about dangling bonds, and it is their role in limitation of the model. It is clear that the upper limit for our model is the Bethe lattice, in which we have infinite dimensions and $\mu = 3$. On the other hand, a calculation of dangling bonds in GMGC shows us the lower limit of 23/11 for the model

$$\frac{23}{11} \le \mu \le 3. \tag{22}$$

The experimental critical exponents for some composites in the above area are collected in Table 1 [16—24].

Table 1

Experimental data for p_c and μ

N	Matrix	Filler	Aspect ratio	p_c (vol. %)	μ	Ref.	N	Matrix	Filler	Aspect ratio	p_c (vol. %)	μ	Ref.
1	PANI	SWCNT	—	0.3	2.1	[19]	6	PAT	MWCNT	>200	12	2.6	[20]
2	PE	SWCNT	—	0.25	2.2	[22]	7	Epoxy	SWCNT	400	0.005	2.7	[16]
3	PMMA	MWCNT	—	0.2	2.3	[23]	8	PC	SWCNT	—	0.1	2.8	[21]
4	Epoxy	SWCNT	—	1	2.4	[18]	9	Epoxy	MWCNT	100	0.6	2.9	[17]
5	—	—	—	—	2.5	—	10	PU	MWCNT	>100	1	≈3	[24]

SWCNT = single wall carbon nanotube, MWCNT = multi wall carbon nanotube, PANI = polyaniline, PE = = polyethylene, PMMA = polymethyl methacrylate, PAT = polyhexadecyl thiophene, PC = polycarbonate, PU = = polyurethane.

Table 2

Moment exponents of the current distribution function

μ	$\Psi(0)$	$\Psi(1)$	$\Psi(2)$	$\Psi(3)$	$\Psi(4)$	μ	$\Psi(0)$	$\Psi(1)$	$\Psi(2)$	$\Psi(3)$	$\Psi(4)$
2.1	2.18	1.178618	0.79954	0.63821	0.557954	2.6	2.08	1.672996	1.593418	1.565137	1.551144
2.2	2.16	1.289696	1.008681	0.897399	0.843216	2.7	2.06	1.758525	1.705584	1.686891	1.677518
2.3	2.14	1.393425	1.184085	1.104932	1.066608	2.8	2.04	1.841249	1.809778	1.79869	1.793047
2.4	2.12	1.491206	1.33616	1.279285	1.251671	2.9	2.02	1.921616	1.907527	1.902557	1.899988
2.5	2.1	1.584115	1.471227	1.430622	1.410751	3	2	∞	∞	∞	∞

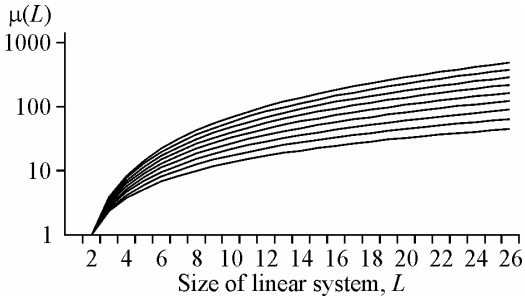

Fig. 2. Compare the effect of μ on the current distribution in CNTC

The exponent of the distribution function $\psi(q)$ was calculated for several moments (Table 2). It is seen that the exponent for the zeroth moment of the distribution function is equal to the backbone fractal dimension, as expected. With deliberation on $\psi(1)$, it will be clear that the model predict a logical relation between the average current and conductivity and it seems that the sensitivity of a system increases with μ. Also $\psi(2)$ is the noise exponent and it shows the fluctuation around the average current. $\psi(3)$ and $\psi(4)$ are exponents of the skewness and kurtosis of the distribution function. They are the ways to describe the shape of the distribution function: if the skewness is nonzero, the function skews to one side, and the kurtosis describes the flatness of the function.

The effect of μ on the first moment of distribution function is illustrated in Fig. 2.

With respect to the current distribution function, one can compute the potential energy of electrons in the CNTC matrix, since we can simulate the temperature effect on the conductivity. With such a simulation we will be able to propose CNTCs with semiconducting properties.

REFERENCES

1. *Iijima S.* // Nature. – 1991. – **354**. – P. 56.
2. *Heer W.A., Chatelain A., Ugarte D.* // Science. – 1995. – **270**. – P. 1179.
3. *Wang Q.H.* // Appl. Phys. Lett. – 1998. – **72**. – P. 2912.
4. *Rinzler A.G.* // Science. – 1995. – **269**. – P. 1550.
5. *Anazawa K., Shimotani K., Manabe C. et al.* // Appl. Phys. Lett. – 2002. – **81**. – P. 739 – 741.
6. *Kim P., Shi L., Majumdar A., McEuen P.L.* // Phys. Rev. Lett. – 2001. – **87**. – P. 215502.
7. *Thostenson E.T., Ren Z.F., Chou T.W.* // Comp. Sci. Technol. – 2001. – **61**. – P. 1899 – 1912.
8. *Lau T., Hui D.* // Composites. Part B. Engineering. – 2002. – **33**. – P. 263 – 277.
9. *Bauhofer W., Kovacs J.Z.* // Comp. Sci. Technol. – 2009. – **69**, N 10. – P. 1486 – 1498.
10. *Stauffer D., Aharony A.* Introduction to percolation theory. – Taylor & Francis, London, 1994.
11. *Broadbent S.R., Hammersley J.M.* // Percolation processes, I, II, Proc. Cambridge Philos. Soc. – 1957. – **53**. – P. 629 – 645.
12. *King P.R., Buldyrev S.V., Dokholyan N.V. et al.* Percolation Theory. http://www.lps.org.uk/dialogweb/current_articles/king_percolation_theory/precolation_th... 10/11/2002
13. *Muhammad Sahimi.* Application of Percolation Theory. – Taylor & Francis, 1994.
14. *Mandelbrot B.B.* The Fractal Geometry of Nature. – San Francisco: Freeman, 1982.
15. *Mandelbrot B.B., Given J.A.* // Phys. Rev. Lett. – 1984. – **52**. – P. 1853.
16. *Bryning M.B., Islam M.F., Kikkawa J.M., Yodh A.G.* // Adv. Mater. – 2005. – **17**, N 9. – P. 1186 – 91.
17. *Yuen S.M., Ma C.C.M., Wu H.H. et al.* // J. Appl. Polym. Sci. – 2007. – **103**, N 2. – P. 1272 – 8.
18. *Yu A.P., Itkis M.E., Bekyarova E., Haddon R.C.* // Appl. Phys. Lett. – 2006. – **89**, N 13. – P. 133102, 1 – 3.
19. *Blanchet G.B., Fincher C.R., Gao F.* // Appl. Phys. Lett. – 2003. – **82**, N 8. – P. 1290 – 2.
20. *Yoshino K., Kajii H., Araki H. et al.* // Full. Sci. Technol. – 1999. – **7**, N 4. – P. 695 – 711.
21. *Ramasubramaniam R., Chen J., Liu H.* // Appl. Phys. Lett. – 2003. – **83**, N 14. – P. 2928 – 30.
22. *Mierczynska A., Mayne-L'Hermite M., Boiteux G.* // J. Appl. Polym. Sci. – 2007. – **105**, N 1. – P. 158 – 68.
23. *Kim H.M., Choi M.S., Joo J. et al.* // Phys. Rev. B. – 2006. – **74**, N 5. – P. 54202, 1 – 7.
24. *Koerner H., Liu W.D., Alexander M. et al.* // Polymer. – 2005. – **46**, N 12. – P. 4405 – 20.