Study of the electrical conductivity in fiber composites

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ABSTRACT
Three-dimensional simulations have been conducted to predict the percolation threshold in fiber composite materials. It has been shown that the expansion of the sample's size increases the sharpness of distributions curves of the percolation threshold. Decreasing the percolation threshold with longer fiber is also verified. A method is proposed to evaluate the electrical resistance of fibrous composites. Assuming meandering paths, the calculation is based on detecting conductive pathways through the insulating matrix. The percolation is detected by the height of the conducting cluster instead of its number at the two electrodes. The electrical resistivities and the conduction thresholds of the carbon fiber reinforced polycarbonate composites have been characterized. The simulation results are in good agreement with an experimental study result found in the literature.

Keywords: Fibers, Polymer-matrix, Composites, Electrical resistance, Simulation

1. INTRODUCTION

The composite materials are commonly used in a wide variety of industrial applications such as pressure-sensing elements, resistors, transducers, thermistors, piezoresistors, chemical sensors and as packaging materials for substrates in electronic applications. An important topic, closely linked to the basic fundamental physical properties of those materials [1], is the investigation of their heat and electrical transport phenomena.

The electrical conductivity of random mixtures of conductors and insulators (as for example, conducting particles in a polymer matrix) has been successfully interpreted using the percolation theory (based on the observation of a dramatic increase of the effective conductivity for a certain filler concentration called the percolation threshold [2–9]). The classical percolation applies to this class of solids under the following definite conditions: the particles must be spherical in shape, monodispersed and have an isotropic conductivity [10]. The interest about the percolative properties of random assemblies of elongated elements characterized by large aspect ratios (the ratio of the length to the transversal size) is aroused by the large development of fibrous composite materials.

Although the percolation theory has received the greatest attention as a predictor of the electrical conductivity of composites versus the filler content, other non-percolation models (such as thermodynamic models, geometrical and structure-oriented models) have also been proposed [11, 12]. From the engineer's point of view, the structure-oriented models are the most promising ones in this group. They are based on microstructural data such as fiber's orientation, length and packing arrangement. Either the conductivity of the matrix or the filler is predicted by most of these theories, however the percolation threshold is not taken into account [13].

The present work deals with a quantitative estimation of the electrical fiber composite resistance by studying the connectivity of the fibers. Our approach uses the percolation and structure-oriented modeling concepts, to perform a simulation of a 3-D random dispersion of elongated elements with various aspect ratios and to predict the percolation threshold for the formation of continuous particles chains. All of our computations are based on the spatial configuration of the generated samples. The simulation is used to evaluate the electrical resistance of polymer/carbon fiber composites by updating the connectivity of the resistor network formed by the conducting clusters assumed to be meandering through the matrix and to compare the obtained theoretical results with the existing experimental ones.

2. DESCRIPTION OF THE METHOD

The composite samples studied have a cubic shape with n sized edges called sample's size. They are divided into n^3 elementary cubes. The conductive fillers are fibers of length L, occupying a volume fraction p of the global composite's volume (Figure 1). For each fiber, a position (expressed by coordinates x, y and z of an elementary cube, and an orientation (1, 2, or 3 in one of the three possible directions X, Y or Z) are attributed.

The method is based on the following assumptions:

- Each conducting fiber is represented by a group of L adjacent cubes (in order to control the fiber's length) lined up along one of the principal axes of the lattice.
- The sample is considered to percolate if it is spanned by a conducting path in a given direction chosen to calculate the resistance and if the cluster's height corresponds to the size of the sample (instead of finding the same cluster's number at the two electrodes as usually done).
- The conduction occurs between two different fibers when they touch along a non-zero surface.
- The electrical resistivity ρ_i of the polymer matrix is not considered in the resistivity of the composite when the probability of percolation exceeds 50%.

2.1. SAMPLE GENERATION

The samples are generated following the steps listed bellow:

- For each sample, the fibers are introduced randomly starting with an empty lattice. The center (x, y, z) for the conductive filler is first generated as three random numbers and tested whether these coordinates are already attributed to another fiber.

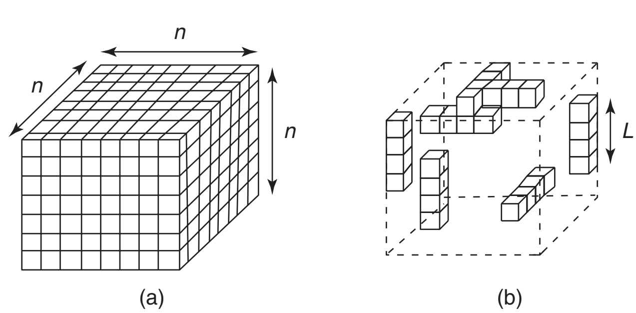


Figure 1 Sample generation: (a) Discretized matrix, (b) Fibers with length L = 4.

- An orientation is randomly chosen for the fiber.
- A new fiber is rejected if it would overlap a fiber already introduced.
- For each fiber introduced, a cluster's number is attributed to it.
- The fibers in contact are found and the smallest cluster's number of them is attributed to these fibres. Then, the cluster's lengths in the three directions are calculated and the corresponding electrical resistance is computed.
- A spanning cluster is found in one of the three directions by testing the cluster's length. If this occurs, the volume fraction kept at this stage is called percolation threshold p_c.

For each sample, the building process is stopped when the percolation occurs first; the corresponding density is then registered. The process repeats for *M* different distributions of fibers when determining percolation threshold distribution. For the electrical composite resistance prediction, the spatial distribution of the conductive fillers is generated by repeating the above described procedure until the pre-determined volume percentage is reached. At that point, the evaluation of the electrical composite resistance begins.

2.2. ELECTRICAL RESISTANCE COMPUTATION

When two conductive particles are in contact, there is a resistance associated with the constriction of the electrons flow through the contact area. This resistance, known as the constriction resistance R_{cr} at the contact interface, depends on the contact area and has been shown to be the Holm's resistance [14, 15] for a contact diameter larger than the mean free path of the electrons in the metal. Its expression is given by:

$$R_{cr} = \rho_f / d \tag{1}$$

where ρ_f is the intrinsic filler resistivity and *d* the diameter of the contact spot.

Assuming clean contacts (no thin insulating films surrounding the particles), the electrical contact resistance R_c can be assumed to be the constriction resistance R_{cr}. Then, the resistance of a fiber-to-fiber contact R_{ff} is the sum of the constriction resistance R_{cr} and the bulk resistance R_b of the fiber [14]:

$$R_{ff} = R_c + R_b = R_{cr} + R_b \tag{2}$$

$$R_b = \rho_f \times \mathrm{L/S} \tag{3}$$

where *L* and *S* are the fiber's length and cross section respectively, the shape of the fiber (characterized by the aspect ratio AR) being expressed in the simulation by a length *L* and a thickness equal to unity.

Knowing the resistivities of the two phases, the cluster resistance is calculated according to equations (1), (2) and (3). For the contacts between clusters, the same method is used with replacing the center of the fiber by the center of the cluster.

Searching conducting pathways in a given direction for a fixed fraction of the filler is based on computing the lengths of all the clusters in the considered direction. Each path is assumed to be a set of serial resistors representing the fibers in contact. So the total path resistance R_s is deduced by adding the bulk resistance R_b to the contact resistance R_c of the fibers in contact (R_{ff}) [14, 15]:

$$R_s = \Sigma\,(R_c + R_b) \tag{4}$$

Then, the effective resistance R_e of the sample is the equivalent resistance of these conducting pathways assumed to be in parallel:

$$1/R_e = \Sigma\, 1/R_s \tag{5}$$

Each resistance value is obtained by averaging M different networks.

For each volume fraction, when the probability of percolation do not exceed 50%, we consider that there is no continuous conducting path through the matrix and the electrical resistance of the composite is taken to be the electrical resistance of the matrix and is given by:

$$R_e = \rho_i / n \quad (6)$$

where ρ_i is the matrix resistivity and n the sample's size.

It most be noticed that the bulk resistance R_b in a considered direction will depend on the fiber's orientation. Following the X axe direction, the bulk electrical resistance for a fiber having a width and a thikness of unity will be, when oriented in the:

X axe direction,

$$R_{bx} = \rho_f \cdot L \quad (7)$$

Y axe direction,

$$R_{by} = \rho_f / L \quad (8)$$

Z axe direction,

$$R_{bz} = \rho_f / L \quad (9)$$

3. RESULTS AND DISCUSSION

The results provided by the algorithm are: the number of inclusions, the volume fraction of occupied cubes at percolation in each direction, the number of clusters, the number of the cluster responsible of the percolation and the effective electrical resistance of the sample.

3.1. EFFECT OF THE FINITE SIZE OF THE SAMPLE AND THE FIBER'S LENGTH ON THE PERCOLATION THRESHOLD

The finite size and fiber asymetry effects are verified by varying the sample's size n from 20 to 120 and the fiber's length L from 2 to 10. The distributions of percolation thresholds, shown in Figure 2, are obtained by fixing the iteration number to 1000.

Each distribution has a Gaussian shape centred at an average value. This value decreases with increasing the sample's size n (Figure 2.a) and is of about 20 volume percent for $n = 70$. This behavior is reproducible for other fiber's lengths (Figure 2.b). The peaks of the distributions become sharper for large samples. Similar results have been noticed by Boissonnade et al. [16]. It is well-known that the percolation threshold depends strongly on the particle shape [17, 18]. A Monte-Carlo simulation made on fiber composites gives Gaussian shaped distributions of the percolation threshold for large sample's sizes, centered at 0.32 volume fraction for $L = 1$ [16]. This result is the characteristic percolation threshold of a square lattice containing spherical particles [18, 19]. A wide range of conductivity thresholds has been reported, depending upon the packing densities of the filler, the shape of the filler, the distribution of the filler's size, the aggregation effects and the filler particle size.

The numerical results shown in the curves of Figure 2.a indicate that the percolation volume fraction is very dependent on the sample's size. It begins to converge at $n = 60$ for $L = 4$ (the distribution's width decreases and the p_c values converge). To overcome this effect, large sample's sizes are used. Figure 2.b shows the stability of the percolation threshold with increasing n for $L = 20$.

Figure 3 shows the evolution of the percolation threshold versus the sample's size. p_c trends to a limit at $n = 80$ for $L = 4$.

In all the curves, one can note the decrease of the conduction threshold with increasing

(a)

(b)

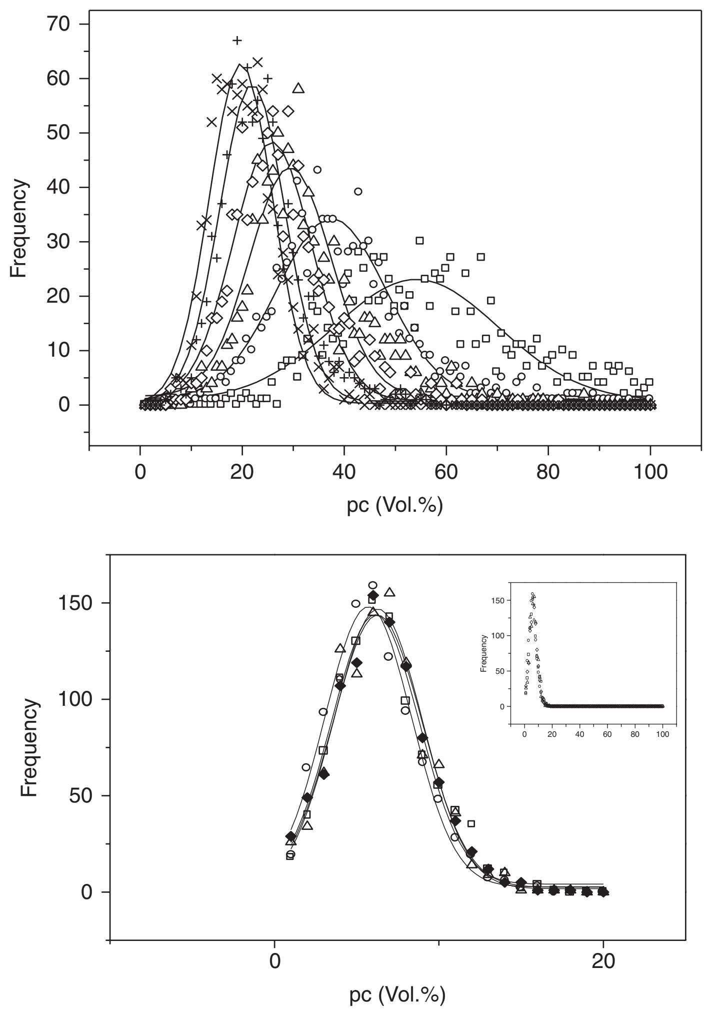


Figure 2 Distributions of percolation thresholds p_c for two fiber's lengths L and different sample's sizes n:
(a) □ $n = 20$, ○ $n = 30$, △ $n = 40$, ◇ $n = 50$, + $n = 60$, X $n = 70$, $L = 4$,
(b) □ $n = 90$, ○ $n = 100$, △ $n = 110$, ◇ $n = 120$, $L = 20$.

the sample's size indicating then an increase of the probability of percolation in larger samples. This phenomenon is called finite size effect and is due to a finite sample's size [16]: when n is finite, the percolation threshold decreases with increasing the sample's size. When the latter is large enough, the real value of p_c can be approached. The same behavior is observed for the used two fiber's lengths.

It is evident from the simulation results that a large box size requires a smaller fiber's volume fraction to percolate. The shape of the filler particle has been shown to alter the conductivity. For spherical particles, a smaller particle's size will lower the percolation threshold, while for particles with an aspect ratio AR (ratio L/D of the length L to the diameter D) greater than 1, larger AR and broader ranges of AR will lower the percolation threshold [20]. It is evident that conductive filler particles are more effective in contributing to the development of the electrical properties of the composite when they are used at high loading levels, but it was shown that an

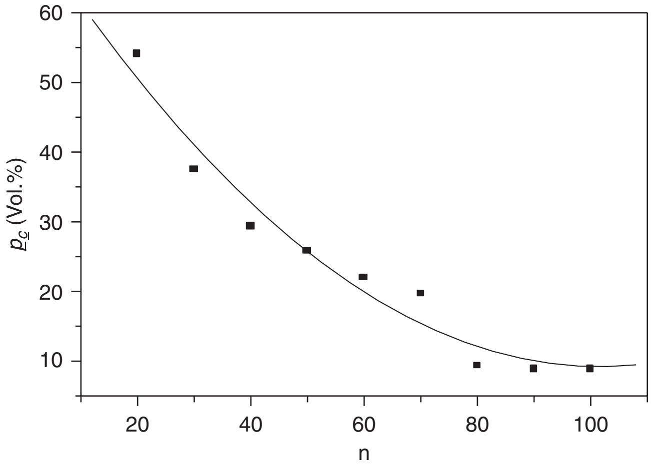


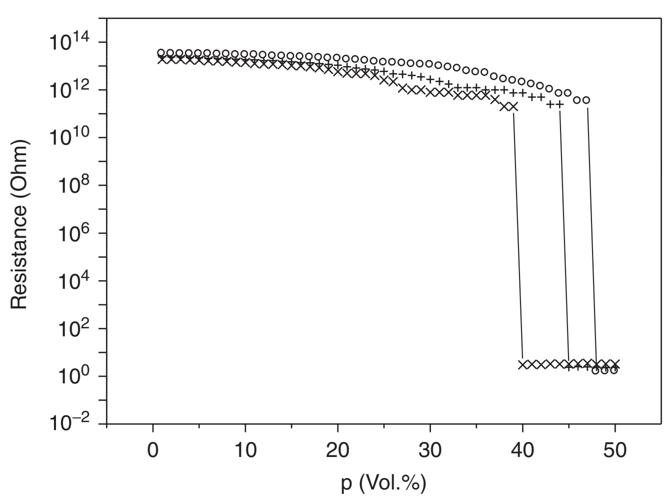
Figure 3 Evolution of the percolation threshold p_c versus the sample's size n for $L = 4$.

additional advantage is provided by asymmetric filler's particles in terms of the distance of separation. This verify results of percolation studies carried out with conductive particles in polymeric matrices which indicate that asymmetric fillers establish conducting networks within the polymer at lower volume fractions than the powders [21].

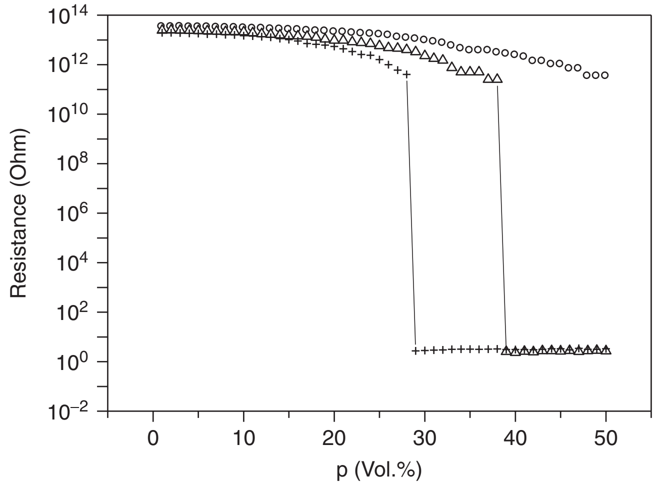
3.2. ELECTRICAL RESISTANCE ESTIMATION

Figures 4.a, b, c represent the evolution of the electrical resistance versus the volume fraction of a composite having a matrix resistivity ρ_i of about 10^{15} Ωm (for polycarbonate) and a filler resistivity ρ_f of about $1{,}67.10^{-3}$ Ωm for carbon fibers (these data have been reported in recent works on polymer composites [13, 20]). Each point of the curves is an average value calculated from 100 different sample's configurations. One can observe an abrupt decrease of the resistance with increasing the conductive volume fraction in the composite. From about 5.10^{13} Ω, the resistance decreases to few ohms at about 30 percent loading for 40 and 50 sample's sizes and

(a)



(b)



(c)

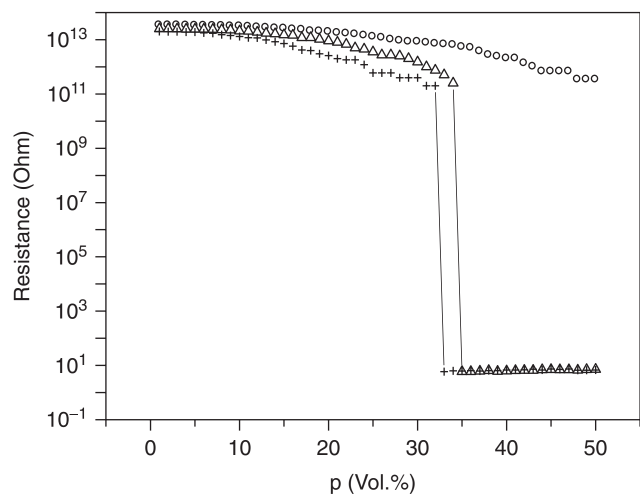


Figure 4 Variation of the electrical resistance of the composite versus the volume fraction for different sample's sizes and fiber's lengths
(a) $L = 2$: o $n = 30$, + $n = 40$, X $n = 50$
(b) $L = 4$, (c) $L = 8$: o $n = 30$, △ $n = 40$, + $n = 50$.

a fiber's length $L = 8$. This behavior is well known and was explained by Taipalus et al. [13] who argued that the particles are almost homogeneously distributed in the insulating matrix without any contacts between the adjacent filler's particles, at low filler loadings. The conductivity of these composites is comparable to that of the polymer matrix. However, with rising the filler's concentrations, the filler's particles begin to form clusters, in which the particles are in contact with each other. At a certain filler's concentration, the growing clusters reach a size which enables contacts between them; a continuous network structure of the conducting filler is formed. The network formation can be detected as a drastic decrease in the electrical resistivity. The abrupt decrease in the electrical resistivity occurs at a concentration called percolation threshold of the filler material. At loadings above the critical value, the resistivity reaches a plateau and does not increase significantly with a further addition of the filler [13].

We observe on Figure 4 the decrease of the percolation threshold with increasing the fiber's length: in the case $n = 40$, we notice that p_c drops from 45 vol.% for $L = 2$ to 40 vol.% for $L = 4$ and to 35 vol.% for $L = 8$.

Samples of size 30 (Figure 4.b and c) exhibit some delay in the resistance transition compared to the others. This is due to the increasing of the fiber length which renders filling the gaps between the fibers more difficult taking into account the fiber's orientation. In contrast, fibers of length $L = 2$ are short enough to fill the gaps and ensure conducting paths as shown in Figure 4.a where the electrical resistance reaches a steady state at about 47 volume percent.

When the total space volume of the sample is increased, the number of conducting paths between the external electrodes increases, resulting in an enhanced conductivity as well as a reduced percolation volume percentage [22]. This explains the decrease of p_c with increasing n, observed in all the cases (a, b and c).

Comparisons with experimental results obtained by Clingeman et al. [20] while investigating the conductivity in polycarbonate/milled PAN-based carbon fiber composites will be made assuming an AR of 20 ($L = 20$) since the authors used fibers with 7.3 microns diameter and 200 microns mean length. One unit mesh in our simulation corresponds to 10 μm. The resistivity of the polycarbonate and carbon fiber have been assumed to be of about 10^{15} and $1{,}67.10^{-3}$ Ωm respectively [13, 20].

The comparison is illustrated by the curves of Figure 5. It shows the efficiency of the method to predict the electrical conductivity level before and after percolation, and the percolation threshold itself. The difference in the curvature or inflexion is probably due to the dimensions of the samples (not fixed in the study of Clingerman et al. [20]), to the tunnelling resistance (neglected in our study) and to the filler-matrix interaction (surface energy of the two constituents) which was not considered. These factors will be the focus of the future investigations.

The method is only meant to offer a qualitative look at the factors affecting the electrical resistance and a quantitative comparison of two different filler or matrix materials with

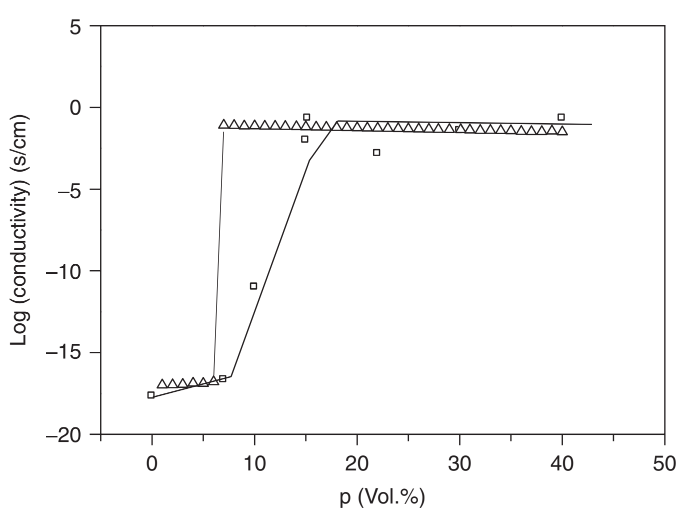


Figure 5 Variation of the electrical conductivity versus the volume fraction in polycarbonate/milled PAN-based carbon fiber composite, □ Experimental result, △ Simulation result ($n = 1{,}00$, $L = 20$).

regard to their intrinsic properties. It is shown that it is efficient to evaluate the electrical composites resistance versus the volume fraction of the fibers.

4. CONCLUSIONS

The study of the percolation in polymer fiber composites using a 3-D program is based on analyzing the connectivity of the fibers versus their volume fraction. It has allowed the determination of percolation threshold distributions for different sample's sizes and has verified the finite size effect on the percolation threshold. The procedure follows the approach of updating the matrix connectivity after addition of each inclusion and thus average threshold volume fractions were obtained for finite size boxes. For a sample's size of 70 and a fiber's length of 4 the threshold was estimated to be 20 percent.

A simulation method was presented to model the dependence of the electrical resistance as a function of the load and the particle's size for a carbon fiber-filled polymer. The evaluation of the electrical composite resistance was based on the notion that the composite is the result of a large number of resistors combined in series and parallel.

The evolution of the electrical resistance versus the filler volume fraction exhibited as predicted, a transition from an insulating to a conducting behavior for different sample's sizes and fiber's lengths. The finite size effect was also noticed on the curves, which suggested the usage of larger samples to avoid this effect in order to approach the real values of the percolation threshold and electrical resistance. Lower percolation thresholds were obtained with fibers of AR equal to 20.

Although simplifications were introduced in the model, such as all the fibers having the same size, it fits very well an experimental data and allows prediction of the electrical resistance curve for other particles' sizes. This method makes possible to us investigation of the effects of different parameters on the electrical properties of carbon fiber-filled polymers. Numerical simulation is shown to be a useful method to study the electrical properties of these materials.

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