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Short Communication

Percolation in ternary composites: threshold position and critical behaviour

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Résumé. — Nous présentons la conductivité de composites ternaires (fibres de carbone, sphères de carbone, polymère). Une transition métal - isolant est observée au dessus d'une concentration critique en particules conductrices. Près du seuil nous observons une dépendance en loi de puissance de la conductivité. Ces deux résultats sont analysés dans le cadre de la théorie de la percolation. En particulier nous discutons l'influence de la proportion fibres-sphères sur le seuil de percolation et sur l'exposant critique observé à l'aide d'arguments géométriques simples.

Abstract. — The conductivity of ternary composites (carbon fibers, carbon spheres and polymer) is presented. A transition from an insulating to a conducting regime is observed above a critical volume fraction of conducting particles. Near the threshold a power law dependence of the conductivity is found. Both results are analysed in the frame of the percolation theory. In particular the influence of the relative amount of fibers and spheres on the percolation threshold and on the critical exponent is discussed and quantitatively explained using simple geometrical arguments.

Introduction.

Carbon - polymer composites have been shown to be good model materials to study percolative conduction. Conducting particles with various geometries have been introduced in a polymer matrix to obtain an insulator - conductor transition. In particular spherical carbon particles or carbon fibers have been used [1, 2]. The study of these binary systems has shown that the percolation threshold is strongly dependent on the shape of the conducting particles. For the carbon spheres the critical volume fraction $\phi_c \approx 17\%$ is found to be in agreement with the classical result for monodisperse particles. It is much larger than the corresponding values (of the order of one percent) for fibers. In this case, it is found both theoretically and experimentally that the critical concentration goes like $\phi_c \sim (d/l)^2$ when $d \ll l$ where d and l are the diameter and length of the fiber respectively [2]. Close to the threshold, a power law dependence is found with a critical exponent t . When the conducting particles are spheres the observed exponent is $t = 1.6-2.0$ in agreement with the theoretical value found numerically, i.e. 1.9 [3]. This number is the universal

value expected close to the critical point, i.e. within the critical region where the fluctuations are important. The fact that it is observed with spheres indicates a quite large critical region in this case. On the contrary, the exponent found for the fibers is larger, i.e. $t \approx 3$. Two alternative explanations have been proposed for this result. On the one hand it has been suggested that the critical region is very small. In this case the observed exponent has the mean field value $t = 3$ [4]. On the other hand, an anomalous critical behaviour due to the peculiar structure of the system of interconnected fibers has also been anticipated [5].

We present in this report new results obtained with ternary systems (carbon spheres, carbon fibers and polymer) where the influence of the relative amount of fibers and spheres is studied. In particular the effect on the percolation threshold and on the conductivity exponent is evidenced. The evolution of the threshold is discussed with simple geometrical arguments. In the same way, the width of the critical domain is estimated to explain the observed critical exponent.

Experimental.

The composite is made of an insulating matrix in which conducting particles are introduced. Two kinds of particles were used, namely carbon fibers and carbon spheres. Carbon fibers are high modulus HMS from Courtaulds with a conductivity of $10^2 \Omega^{-1}\text{cm}^{-1}$. Their diameter and length are $8 \mu\text{m}$ and 1mm , respectively. Carbon spheres (type E from Versar M.C.) have a mean diameter of $20 \mu\text{m}$. The polymer matrix is an epoxy resin (Araltite F, hardener HY 905 and accelerator DY 061 from Ciba Geigy) which has a conductivity lower than $10^{-15} \Omega^{-1}\text{cm}^{-1}$.

To improve the dispersion and orientation of the particles in the matrix a new way of preparation has been designed. In a first step the constituents of the matrix are mixed. The particles are then introduced and spread into the sample. Ultrasonic agitation is used to disperse the particles randomly and cancel out the preferential orientations which may result from the previous mixing. The second step consists in a polymerisation (24 hours at 65°C) which freezes the composite in the obtained state.

Microscopic observations of thin slices of the samples are then performed to check the efficiency of the method. In most cases, no sedimentation is detected and the composite appears to be homogeneous and isotropic. These good quality composites are kept for conductivity measurements.

The DC conductivity was measured on small parallelepipedic samples using either an ohmmeter (when $R > 10^6 \Omega$) or an electrometer (when $R < 10^6 \Omega$).

Results.

Before studying ternary composites, the corresponding binary systems have been prepared to be used as reference materials. Figure 1a shows the conductivity of fiber composites as a function of the volume fraction of fibers. As expected a transition towards a conducting state is observed. In the present case we find a critical concentration $\phi_c = (0.95 \pm 0.05)\%$. The corresponding critical exponent can be estimated from a log-log plot of σ as a function of $(\phi - \phi_c)$. A typical plot is given in figure 1b with $\phi_c = 0.98\%$ and gives $t = 3.1$. Changing slightly ϕ_c does not affect noticeably this exponent which stays around 3. Both results are in agreement with previous studies on fiber composites [2, 5]. A conductivity threshold is also observed with the spheres. In this case we obtain $\phi_c = (31 \pm 1)\%$. Too few samples were prepared to enable a determination of t . The obtained

value for ϕ_c is significantly higher than those previously reported [1]. However it is well known that the position of the threshold is sensitive to many microscopic parameters. In particular the polydispersity of the spheres may explain this difference.

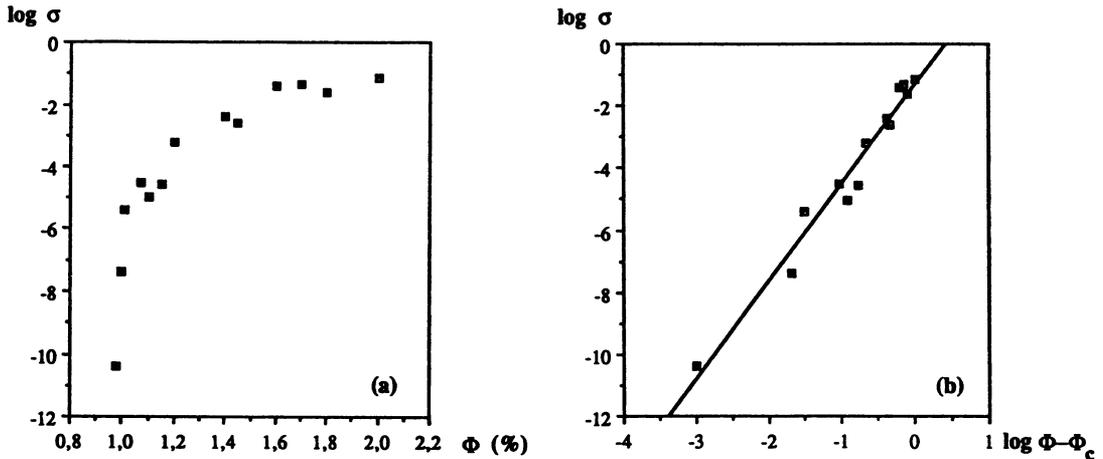


Fig. 1. — (a) Log of the conductivity σ of the binary fiber composites as a function of the volume fraction ϕ of conducting particles. (b) Log-log plot of σ against $(\phi - \phi_c)$ with $\phi_c = 0.98\%$. The solid line is the best linear fit. The slope gives the critical exponent $t = 3.1$.

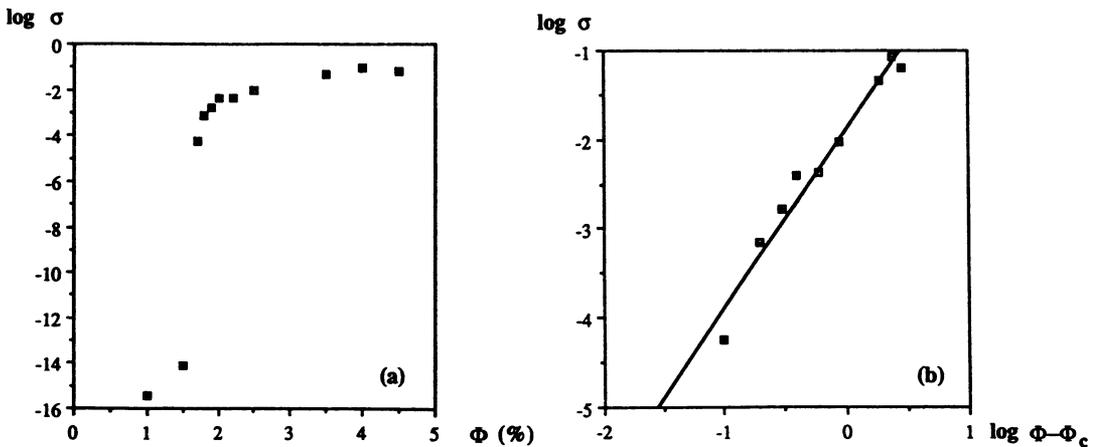


Fig. 2. — (a) Log of the conductivity σ of the ternary fibers-spheres composites as a function of the total volume fraction ϕ for $p = 0.5$ ($\phi_f = \phi_s$). (b) Log-log plot of σ against $(\phi - \phi_c)$ with $\phi_c = 1.6\%$. The solid line is the best linear fit. The slope gives the critical exponent $t = 2.0$.

Two ternary composites have been prepared with $p = \phi_s/\phi = 0.5$ and 0.8 (ϕ_s and ϕ are the volume fraction of spheres and the total volume fraction in conducting particles, respectively). Figure 2a gives the conductivity as a function of ϕ for $p = 0.5$, the obtained critical concentration is $\phi_c = (1.6 \pm 0.1)\%$. It corresponds to a fiber concentration close to the critical value determined for pure fiber composite. Figure 2b gives the Log-log plot to show the critical exponent t . We find $t \approx 2$, i.e. the value usually obtained with pure sphere composites [1]. Another series of samples with $p = 0.8$ has been prepared to estimate the position of the percolation threshold. In that case, we obtain $\phi_c(3.9 \pm 0.5)\%$ which confirms the low value of the critical concentration in the previous sample (Fig. 3a). We also report the log-log plot of the results to show their reasonable agreement with an exponent equal to 2 (Fig. 3b).

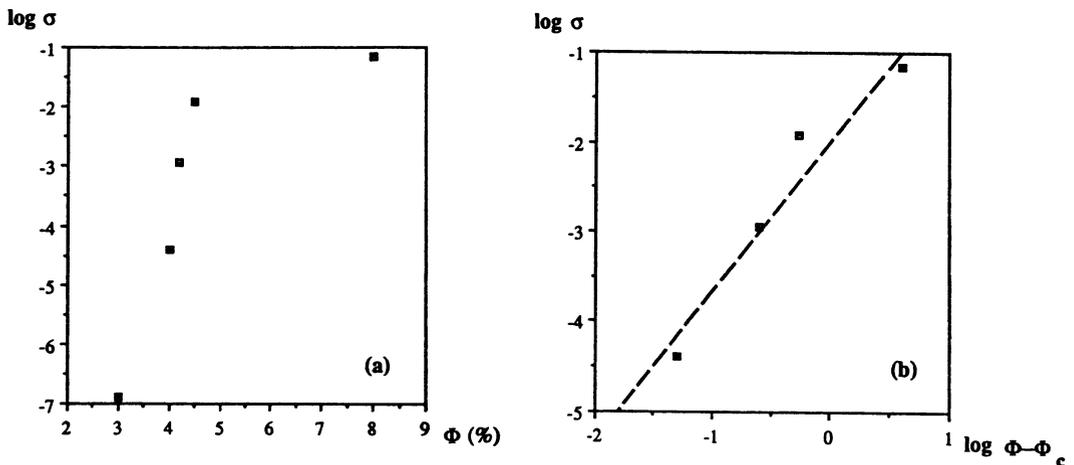


Fig. 3. — (a) Log of the conductivity σ of the ternary fibers-spheres composites as a function of the total volume fraction ϕ for $p = 0.8$ ($\phi_f = 0.25\phi_s$). (b) Log-log plot of σ against $(\phi - \phi_c)$ with $\phi_c = 3.9\%$. The dashed line has a slope equal to 2.

Discussion.

The striking results obtained with these ternary composites can be summarized as follows:

- the evolution of ϕ_c with p is strongly non linear and this critical concentration remains close to the value obtained for the fiber composite in a large domain of values of p ,
- at the same time the critical exponent $t \approx 2$ found for $p = 0.5$ and 0.8 is similar to the one reported for binary composites with spheres.

Both results are discussed in the following.

EVOLUTION OF THE THRESHOLD IN TERNARY SYSTEMS. — As already mentioned, one important parameter which makes the difference between composites with spheres or fibers is the shape anisotropy of the conducting particle. A fiber is an anisotropic particle characterized by the ratio

l/d between its length and diameter. The role of this anisotropy has been discussed with geometrical arguments [2] that we summarize briefly. The volume of a fiber reads:

$$v = \frac{\pi}{4}d^2l$$

Similarly the number of particles per unit volume is (n has the dimension of l^{-3}):

$$n = \frac{4}{\pi}l^{-3}f\left(\frac{d}{l}\right)$$

where f is a function of d/l . The factor $4/\pi$ has been introduced for convenience.

The volume fraction is therefore:

$$\phi = nv = \left(\frac{d}{l}\right)^2 f\left(\frac{d}{l}\right)$$

This expression contains the asymptotic limit $d \ll l$. In this case $f(d/l) \rightarrow f(0)$ and $\phi = f(0)(d/l)^2$ i.e. ϕ is proportional to l^{-2} . However it can be used for any value of d/l . In particular we can consider that spherical particles correspond to the case $d = l$ and assume that both sphere and fiber composites can be described using the above relation with different values of d/l . This implies simple relations for any ternary mixture containing two kinds of particles with anisotropies $(d/l)_1$ and $(d/l)_2$. Both states can be obtained from a reference state of anisotropy $(d/l)_0$ through a geometrical transformation. If the volume fractions of each species are ϕ_1 and ϕ_2 , they are related to the corresponding concentrations in the reference state ϕ_{01} and ϕ_{02} by:

$$\phi_i = \left(\frac{d_i}{l_i}\right)^2 \left(\frac{l_0}{d_0}\right)^2 f\left(\frac{d_i}{l_i}\right) \left[f\left(\frac{d_0}{l_0}\right)\right]^{-1} \phi_{0i} = A_i \phi_{0i} \quad i = 1 \text{ or } 2$$

The total concentration in conducting particles reads:

$$\phi = \phi_1 + \phi_2 = A_1 \phi_{01} + A_2 \phi_{02} = A_2 \phi_0 + \left(1 - \frac{A_2}{A_1}\right) \phi_1$$

where $\phi_0 = \phi_{01} + \phi_{02}$.

Introducing p as: $\phi_1 = (1-p)\phi$, $\phi_2 = p\phi$ we finally obtain:

$$\phi = \frac{A_2 \phi_0}{p + \frac{A_2}{A_1}(1-p)}$$

This expression can be used to deduce the critical concentration of any ternary system as a function of p . If $\phi_c(0) = A_1 \phi_{c0}$ and $\phi_c(1) = A_2 \phi_{c0}$ are the critical concentration for the binary composites (respectively for $p = 0$ and $p = 1$) we obtain:

$$\phi_c(p) = \frac{\phi_c(1)}{p + \frac{\phi_c(1)}{\phi_c(1)}(1-p)}$$

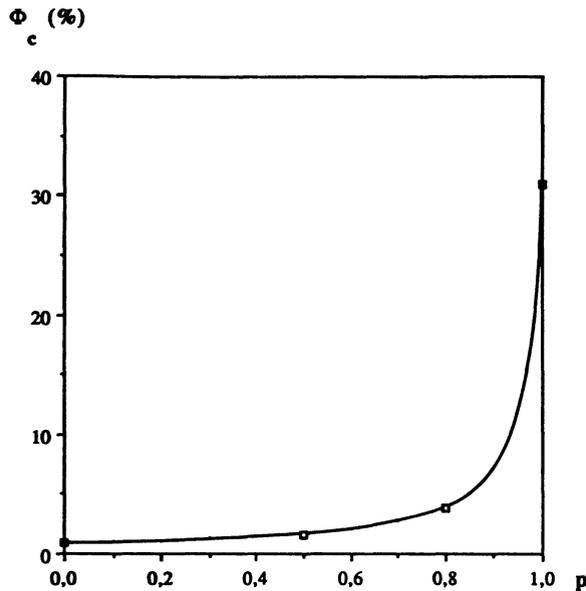


Fig. 4. — Critical volume fraction ϕ_c as a function of p . Continuous line: theoretical calculation. The experimental critical concentration for the binary systems ($p = 0$ and $p = 1$) are used as input parameters (full squares). Open squares: the experimental critical volume fraction for $p = 0.5$ and $p = 0.8$.

In particular we can apply this formula for a ternary composite with fibers and spheres. Using our experimental determination $\phi_c(0) = 0.95\%$ for fibers and $\phi_c(1) = 31\%$ for spheres we obtain the variation of the threshold given in figure 4. The experimental results obtained for $p = 0.5$ and $p = 0.8$ are also reported. They are in excellent agreement with the theoretical prediction.

It is interesting to mention that the theoretical evolution of $\phi_c(p)$ can be justified with a very simple argument. The above formula also reads:

$$\frac{1}{\phi_c(p)} = \frac{1-p}{\phi_c(0)} + \frac{p}{\phi_c(1)}$$

which simply means that the two conducting species act in parallel in the clusters. They are weighted by $(1-p)$ and p respectively. When $\phi_c(0) \ll \phi_c(1)$ the connectivity inside a cluster is dominated by the particles of larger anisotropy.

VALUE OF THE CRITICAL EXPONENT t . — We now discuss the observed critical behaviour for $p = 0.5$ and 0.8 . The interesting result is that the universal exponent ($t \approx 1.9$) is obtained although the threshold is very close to the one observed for pure fiber binary systems, i.e. when the connectivity between conducting particles inside a cluster is dominated by the fibers.

As we mentioned previously, two alternative explanations have been proposed to explain the critical behaviour of fiber composites. One of them is based on the peculiar structure of the system of interconnected fibers. Since we believe that connectivity is still dominated by the fibers in particular for $p = 0.5$, this explanation can be ruled out. Thus, the width of the critical region is more likely at the origin of the observed exponent. We give arguments which rationalize this point of view in the following.

Quite generally the width of the critical region is related to the size of the fluctuations. This problem has been discussed in detail by de Gennes for the vulcanization process which belongs to the same universality class as percolation [6]. In this case the size $\Delta\phi^*$ of the critical region is given by:

$$\frac{\Delta\phi^*}{\phi_c} \sim \left(\frac{\xi_0}{a}\right)^{-2}$$

where ξ_0 is the prefactor for the correlation function ξ :

$$\xi = \xi_0 \left(\frac{\phi - \phi_c}{\phi_c}\right)^{-\nu}$$

a is the microscopic length used as reference (i.e. the smallest characteristic length scale in the system).

The length ξ_0 can be estimated with geometrical arguments. Following reference [6] :

$$\xi_0^2 \sim \langle (R_i - R_j)^2 \rangle$$

where R_i and R_j are the centers of gravity of two neighbouring particles in a cluster. $\langle \rangle$ indicates an average over all possible configurations.

This simple expression allows the determination of ξ_0 for either binary or ternary composites.

In the case of binary systems with spheres this expression gives $\xi_0 \sim D$ (D is the diameter of a sphere). Since D is also the reference length a , we expect a large critical region as experimentally revealed by the exponent $t \approx 2$. On the other hand we expect $\xi_0 \sim 1$ and $a \sim d$ for fibers (the exact calculation of the average mentioned above gives $l^2/6$ in the limit $d/l = 0$) and therefore a very narrow critical region and a mean field exponent. A similar explanation is given in reference [6] to argue that long polymer chains have a mean field like behaviour. Thus this simple argument explains why $t = 3$ is found for the binary composites with fibers.

With similar arguments we can estimate ξ_0 for ternary systems. Since the average is taken over all pairs of neighbouring particles we now write:

$$\xi_0^2 \sim \xi_{ff}^2 p_{ff} + \xi_{fs}^2 p_{fs} + \xi_{ss}^2 p_{ss}$$

where ξ_{ff} , ξ_{fs} and ξ_{ss} are the averages $\langle (R_i - R_j)^2 \rangle$ for fiber-fiber, fiber-sphere and sphere-sphere couples respectively. The p_{ij} are the probabilities of finding these couples as nearest neighbours in a cluster.

For thin fibers and small sphere ($l \gg d$ and D) one easily obtains:

$$\xi_{ff}^2 = l^2/6, \quad \xi_{fs}^2 = l^2/12, \quad \xi_{ss}^2 = D^2.$$

If the particles are spread randomly the probabilities p_{ij} are given by:

$$p_{ij} = \frac{n_i^2}{(n_i + n_j)^2}, \quad p_{ij} = \frac{2n_i n_j}{(n_i + n_j)^2} \quad \text{with } i \neq j$$

where n_i is the number of particles i ($i = f$ or s) per unit volume. Introducing p and ϕ we have:

$$n_s = p \frac{\phi}{v_s} \quad n_f = (1 - p) \frac{\phi}{v_f}$$

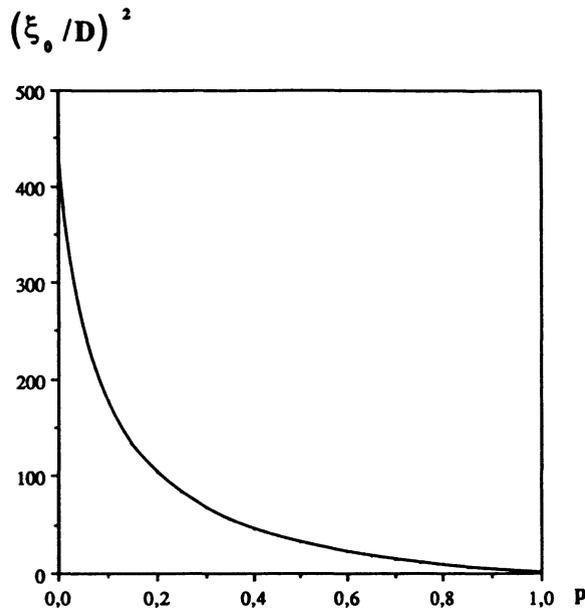


Fig. 5. — Theoretical variation of $(\xi_0/D)^2$ with p for the fibers-spheres ternary composites. ξ_0^2 is proportional to the inverse of the width of the critical region.

where v_s and v_f are the volumes of a sphere and a fiber respectively. With these expressions one easily obtains ξ_0^2 for a ternary composite as a function of p , $r = v_s/v_f$ and $\delta = D/l$:

$$\xi_0^2 \sim \frac{l^2 r^2(1-p)^2 + rp(1-p) + 6\delta^2 p^2}{6(p+r(1-p))^2}$$

Figure 5 gives a plot of $(\xi_0/D)^2$ as a function of p using the experimental dimensions $d = 8 \mu\text{m}$, $D = 20 \mu\text{m}$, $l = 1 \text{ mm}$. ξ_0^2 decreases strongly for small values of p .

Independently of details like numerical factors it is clear that ξ_0 should decrease as soon as p increases. Since $v_s \ll v_f$ we have $n_f \ll n_s$ as soon as p is not very small (because of the equality $\phi = nv$). Then the fiber-fiber couples only dominate for very small values of p . For larger p , the two other terms are the most important and lead to a smaller value of ξ_0 . As a consequence the critical region should increase quickly (as ξ_0^{-2}) as soon as a small amount of spheres is introduced in a binary fiber composite. With this respect the result $t \approx 2$ found for both ternary composites is consistent with our analysis.

Conclusion.

In summary, we have discussed the behaviour of ternary composites made of carbon fibers and spheres spread into an insulating matrix. Our findings can be summarized considering the series of samples with $p = 0.5$ ($\phi_s = \phi_f$). In this case we find a percolation threshold close to the one observed for the binary system of fibers but at the same time we measure the critical

exponent reported for spheres. We have shown that both properties can be understood with simple geometrical arguments:

- the position of the threshold reflects the connectivity inside the infinite cluster. For this property the particles of higher anisotropy are dominant. As a consequence, the relation between ϕ_c and p is highly non linear ($1/\phi_c$ is linear with p);
- the exponent t is related to the width of the critical region which in turns depends on the fluctuations inside the clusters. The pair correlation function is strongly influenced by the spheres in a large domain of p . Thus the critical region can be large enough for most of the ternary composites to observe the universal exponent $t = 1.9$.

Although our experimental results remain preliminary, there is clearly a good agreement between theory and experiment.

Further experimental studies are necessary to check the theoretical predictions in more detail. Among other things, the position of the percolation threshold of any ternary composite (made with two kinds of particles of different anisotropy) can be tested. Moreover with ternary systems of fibers and spheres a mean field - non mean field crossover is expected (presumably around $p \approx 0.1$) which should be evidenced by a crossover between $t \approx 3$ and $t \approx 1.9$. These two values being quite different, these ternary composites are certainly good systems for the study of this crossover.

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