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Multiple Percolation in Conducting Polymer Blends

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Recently, several polymer blends were reported[1,2] to conduct at a much lower volume fraction of the conducting polymer than expected theoretically[3] for a random binary mixture of conducting and insulating hard spheres. Namely, the critical volume fraction Φ_c of the conducting polymer reported was far below 0.16, a classical percolation estimate.[3] Such a low content of a conducting polymer is desirable for applications since an excessive amount may affect other properties of the material such as mechanical strength or color. Suzuki et al.[4] gave an explanation for the low Φ_c in ternary blends reported by Fizazi et al.,[1] in terms of the adsorption of the rodlike conducting polymer onto the surface of the preexisting insulating gel. No explanation has been given to date for the anomalously high conductivity exponent observed experimentally.[1,2] In this paper we introduce a method to control the percolation in conducting polymer blends with a desired low content of the conducting polymer, which is due to phase separation. We also present an explanation of the low conductivity threshold and the high conductivity critical exponent in terms of a new concept of multiple percolation.

It has been shown[5] that the miscibility may be achieved in a conducting polymer blend which then exhibits the lower critical phase-separation temperature (LCST); that is, it phase separates when heated above the binodal curve (see Figure 1). The blend is made of the conducting polymer (CP) and the matrix polymer (MP) which are miscible in a limited composition range. The phase diagram on Figure 1 is a schematic presentation of a phase behavior achieved in a solid solution of the conducting polythiophene with substituted alkyl chains (poly(3-alkylthiophene) in a matrix poly(ethylene-*co*-vinyl acetate). The effect of the alkyl chains substituted into polythiophene is that of achieved flexibility and also miscibility with other polymers, as described in detail by Ho et al.[5]

While the starting composition A on Figure 1 contains less than 0.16 volume fraction of CP and, therefore, is not conducting, the composition B resulting after phase separation contains more than 0.16 volume fraction of CP (within the CP-rich phase B) and, thus, must be conducting. An additional requirement for conduction of the whole blend, however, exists: the phase B itself must also be connected. The continuous (connected) paths of phase B in the blend may be created in this procedure via either spinodal decomposition or nucleation. The choice of a phase-separation mechanism in the experiment is controlled by a heating regime as shown recently by Margolina et al.:[6] a fast heating regime results in spinodal decomposition, while a slow one leads to nucleation.

The next goal, once a continuous conducting phase B is achieved, is to lock in such a composition. This can be achieved via cooling the blend accompanied by order formation, e.g., crystallization, before the coarse-graining occurs as described by Lee et al.[7] While such a competition of phase separation and crystallization is itself a rich and complex process, it appears that the resulting structure of the blend preserves the desired connectivity and conductivity properties. A morphology with a connected phase structure presented in Figure 2 is taken from a phase-separated system of poly(3-octylthiophene) and ethylene-*co*-vinyl acetate.[5] Once there exists such a connected phase, the conductivity of the blend appears[5] at CP volume fractions of about 0.03. This CP content is, once again, much lower than $\Phi_c = 0.16$, the classical requirement of the percolation theory.[3]

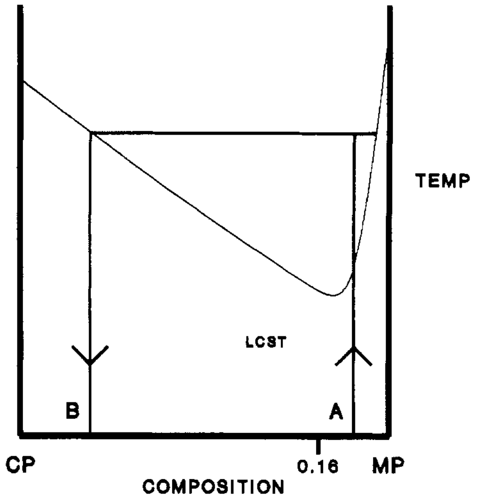

Figure 1. Schematic phase diagram with a lower critical temperature presented to illustrate double percolation. While the composition A is not conducting, the composition B conducts as the CP content is higher than 0.16 in phase B.

We will now present a theoretical explanation of the low CP content required for a conductivity threshold in such binary blends. Our argument is quite general for a new class of conducting blends which require CP connectivity in addition to a bulk connectivity of the whole sample. As the connectivity requirement for such blends is percolation within percolation, we suggest naming this new concept multiple percolation, since it is theoretically feasible to visualize a hierarchy of such connected paths within connected paths, only the last of which is conducting. Of course, the class of binary blends described above corresponds to only two levels in such a hierarchy and, thus, to double percolation.

The argument is quite straightforward. Let us denote the critical volume fraction of CP in phase B required for conductivity as Φ_{CP} and the critical volume fraction of phase B in the blend required for B itself to be connected as Φ_B. Then the critical volume fraction of CP in the blend Φ_c is found as:

$$\Phi_c = \Phi_{CP}\Phi_B \tag{1}$$

Applied to our binary blends, we estimate both Φ_{CP} and Φ_B at about 0.16 for ideal hard spheres. Thus, our estimate for the CP content in double percolation is about 0.026, in good agreement with 0.03 measured[5] (see also Wang and Rubner[2]).

The argument can be readily generalized for multiple percolation. If there are *n* levels in the multiple percolation hierarchy, only the last of which is required to actually

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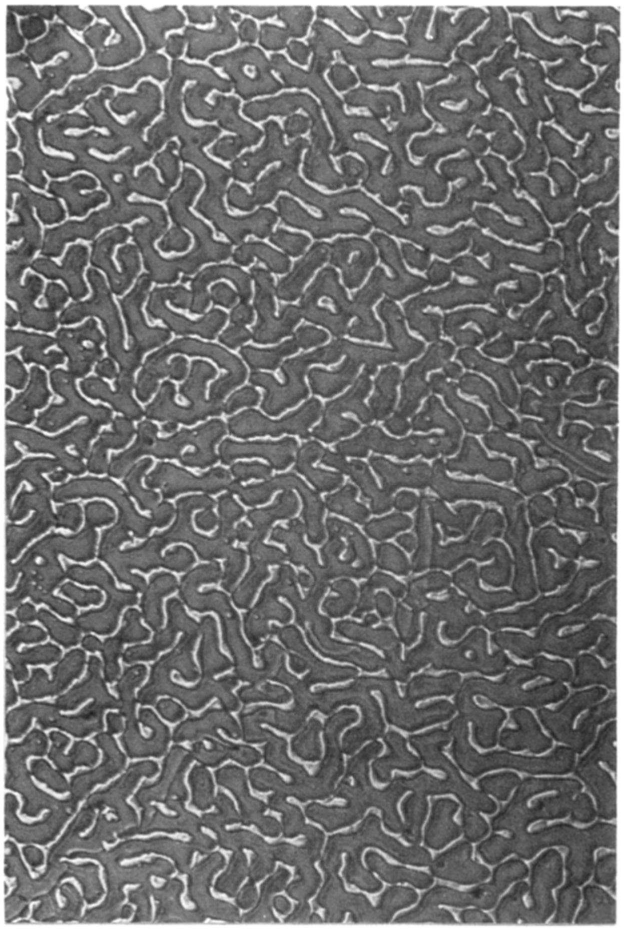

Figure 2. Optical micrograph (magnification ×240) of a poly(3-octylthiophene) and ethylene-*co*-vinyl acetate blend. The 70/30 composition has been selected to emphasize the presence of the connectivity achieved via phase separation during solvent evaporation. The connected dark phase is clearly visible.

conduct, we get

$$\Phi_c = \Phi_{CP}\Phi_B^{\ n-1} \qquad (2)$$

Thus, it is, at least theoretically, feasible to obtain the CP content in a conducting blend as low as desired via multiple percolation alone. The experiment may decide how far one can proceed along this way in reality. E.g., adding a third polymeric component, which is in our experiment a stabilizer,[8] to a binary blend described above would result in a ternary blend with a predicted CP content of 0.004.

We note that our estimate defines an upper boundary for the CP content since this approach is based on spherical particles. In reality, anisotropic shapes may appear in the morphology, the effect of which will make the required CP content even smaller as is well-known from percolation theory.[4] If anisotropic shapes appear on any level of the multiple percolation hierarchy, the appropriate numerical estimate of the percolation threshold needs to be substituted instead of spherical Φ_B or Φ_{CP} in eqs 1 and 2.

The quantitative results of the multiple percolation approach in eqs 1 and 2 are based on the notion of the statistical independence of multiple percolation hierarchy levels which leads to the simple product rule. We note that in our approach the percolation threshold is always well-defined, no matter how low, and in the ideal case is independent of the ratios of consecutive spatial scales in the percolation hierarchy, as long as these ratios are small enough. The latter is of utmost importance if multiple percolation is aimed to adequately describe the physical reality on all levels of its hierarchy and is to be applicable to any morphology. To justify this generality of our approach, we suggest the following reflection: let us imagine the highest level in multiple percolation hierarchy as a statistical, e.g., random, choice of cubes with side L_1 filling an original cube with side L. Then the connectivity threshold of the chosen cubes corresponds to the percolation threshold if $L_1/L \rightarrow 0$. The threshold is estimated for the conductivity of hard spheres on any type of lattice to be about 0.16.[3] However, for the cubes the critical volume fraction could be $6/\pi$ times more (or almost 2 times), i.e., about 0.3. This value corresponds to the estimate for continuum percolation of soft-core spheres (see, e.g., Margolina and Rosso[9]). Thus, for our purposes we may use something in between, e.g., 0.2. In any case, our threshold should be viewed as an estimate, which may depend on the heterogeneity of shapes and sizes for the building blocks of a connected phase. The main point, however, is valid, apart from numerical and geometrical considerations: the connectivity on the highest level of the percolation hierarchy is achieved as $L_1/L \rightarrow 0$, at a certain percolation threshold independent from L_1/L. Such a consideration corresponds to the connectivity of phase B in double percolation.

We proceed now to the next, lower level in the multiple percolation hierarchy. Each of the cubes with side L_1, chosen before, undergoes a procedure, similar to the one above, of a statistical choice for the cubes with side L_2 filling it. The statistical characteristics of this choice and the shape and size heterogeneity of building blocks for a new connected phase may or may not be the same as on higher level, in correspondence with the mateials and processes used for preparation of the sample. However, again apart from the numerical estimate of the percolation threshold, the connectivity is still achieved for $L_2/L_1 \rightarrow 0$, the threshold being independent from L_2/L_1. This consideration corresponds to the connectivity of the CP polymer within phase B in double percolation. The sizes L_1 and L_2 correspond to the thicknesses of the connected path for phase B and of the CP threads, respectively.

Obviously, all the higher levels of the percolation hierarchy should be arranged slightly above their respective percolation thresholds, so that the next, lower level is always allowed, whereas the lowest, conducting level may be situated right at the threshold. Thus, once again the estimate of the multiple percolation threshold introduced in eq 2 represents only a rough estimate and reflects the notion of statistical independence of levels in multiple percolation. This means that in a rough approximation we view multiple percolation as an ideally self-similar fractal structure, in which each block on each scale is conducting, and the overall conductivity of the sample is ensured by small enough ratios of consecutive scales.

In the framework of this rough approximation we suggest an estimate of the conductivity exponent t for multiple percolation which we expect to be higher than that for classical percolation.[10] On each scale the conductivity σ is described by a scaling relation:[10]

$$\sigma = \sigma_0(\Phi - \Phi_B)^t \qquad (3)$$

where Φ and Φ_B stand for current and critical volume fractions, in a higher scale phase, of a phase corresponding to a current scale (e.g., volume fraction of phase B, corresponding to a first scale, in the bulk, for double percolation); t is a presumably universal conductivity exponent for each scale; σ_0 is a nonuniversal conductivity constant for each scale. Φ_B corresponds to our estimate of the critical volume fraction on each scale which may or may not be universal depending on the preparation mechanism. In what follows, we consider it the same for all scales for simplicity, as we did in eq 2. σ_0, a nonuniversal conductivity constant for each scale, may be further specified through its detailed structure on the next lower level as $\sigma_0 = \sigma_{0,\mathrm{low}}(\Phi_{\mathrm{low}} - \Phi_{\mathrm{B}})^t$, where the new conductivity constant and phase volume fraction describe the next lower scale. Continuing this process until the lowest level of multiple percolation hierarchy which must be conducting, we get for n levels

$$\sigma = \sigma_n(\Phi_n - \Phi_{\mathrm{CP}})^t(\Phi_{n-1} - \Phi_{\mathrm{B}})^t...(\Phi_1 - \Phi_{\mathrm{B}})^t \qquad (4)$$

where level n is the lowest, conducting level. For an optimal case when all volume fraction separations from critical are equal, we get the maximum for the effective conductivity exponent of the whole sample, estimated via fitting the data onto eq 3 in all reported experiments:[1,2] $t_{\mathrm{eff}} = nt$. Thus, the maximum effective exponent for double percolation would be $2t$ which is about $t_{\mathrm{eff}} = 4$ in three dimensions.[10] Of course, the apparent effective exponent t_{eff} may be much smaller, but it is predicted for double percolation to be definitely larger than the classical estimate $t = 2$ alone. This prediction corresponds well to experimental findings of Wang and Rubner:[2] $t_{\mathrm{eff}} = 3.2$.

Moreover, such a detailed structure for the conductivity in multiple percolation leads to a nontrivial dependence of the conductivity on the CP concentration in the bulk. Namely, while in classical percolation the conductivity is defined by the CP concentration in the bulk, as in eq 3, in multiple percolation this is not true anymore. An easy exercise in algebra shows that, for small differences on each scale between the phase volume fraction and the critical one, the critical CP bulk volume fraction, Φ_c, is defined by the sum of these differences via eq 2, while the conductivity is defined by their product via eq 4. Thus, the conductivity depends on the preparation mechanism of the sample, rather than simply on its CP content.

In discussion, we compare our approach to that of Suzuki et al.[4] and offer our own explanation for very interesting experimental findings of Fizazi et al.[1] First, we note that the absence of the percolation threshold observed[1] may be suggesting that the percolation approach to this whole phenomenon is unnecessary. It is quite possible that the similar effect may be achieved via an adsorption of CP monolayer onto a preexisting connected structure, which might be constructed in the form of a tube rather than a ramified gel. Thus, here we are presented with two hypotheses: the existence of a preformed gel and the random rather than regular adsorption of CP on it.[4] In addition, the elongated shape of CP particles is essential to account for an anomalously low CP threshold.[4] If we explore the possibility of a regular adsorption with thickness d of pancakes with radius R, we introduce into the theory a free parameter d/R which may be arranged to be as small as desired. This automatically leads to a CP volume fraction as low as needed and may well alone explain the experimental findings. As opposed to this approach, multiple percolation is an explicit requirement for a new class of blends; the percolation threshold is well-defined and independent of spatial parameters.

We may continue exploring the possibility of a regular CP adsorption by suggesting the explanation for the effective conductivity exponent found by Fizazi et al.[1] to be $t_{\mathrm{eff}} = 2.6$. By simple analogy with eq 4 we may conclude that the preexisting gel requires one power t to percolate in three dimensions and, thus, contributes about $t_3 = 2$ to the effective conductivity exponent. The CP regular layer conductivity is simply proportional to its thickness d and, thus, to its volume fraction, contributing $t_1 = 1$ to the effective conductivity exponent. Altogether we get an estimate of $t_{\mathrm{eff}} = t_3 + t_1 = 3$, in rough agreement with the experimental 2.6. The alternative explanation, following the two hypotheses[1,4] yields the maximum $t_{\mathrm{eff}} = t_3 + t_2 = 2 + 1.3 = 3.3$, according to eq 4 with the contributions t_3 and t_2 from three- and two-dimensional conductivity exponents,[10] respectively. Thus, both regular and random CP adsorption give comparable estimates, the first being closer to the experiment.

In summary, we have introduced a new method of controling the low CP content in conducting blends. We have offered an explanation for the anomalously low percolation threshold and high effective conductivity exponent in terms of a new concept, called multiple percolation. Finally, we have made an attempt to explain away the experimental findings[1] and pointed out the differences between our approach and the original explanation of these findings.[4]

Note Added in Proof: After this paper had been submitted for publication, we came across the paper by Sumita et al.[11] in which an approach similar to ours is suggested to explain away a low CP content of carbon black filled polymer blends. Notably, the term coined for this approach is also double percolation. The experimental part of the paper constitutes, in our opinion, another interesting and useful example of multiple percolation, and the intent of the authors to apply the concepts of percolation is justified. However, the concept of percolation within percolation is arrived at qualitatively, and the quantitative analysis is not attempted. The anomalous conductivity is not discussed, even though it seems to be observed experimentally.

References and Notes

(1) Fizazi, A.; Moulton, J.; Pakbaz, K.; Rughooputh, S. D. D. V.; Smith, P.; Heeger, A. J. *Phys. Rev. Lett.* **1990**, *64*, 2180.

(2) Wang, Y.; Rubner, M. F. *Macromolecules* **1992**, *25*, 3284. Rabeony, M.; Sowa, J. M.; Berluche, E.; Ramakrishnan, S.; Peiffer, D. G. *Materials Research Society Extended Abstract* (*EA22*); Materials Research Society: Pittsburgh, PA, 1990. Inaba, N.; Sato, K.; Suzuki, S.; Hashimoto, T. *Macromolecules* **1989**, *19*, 1690.

(3) Scher, H.; Zallen, R. *J. Chem. Phys.* **1970**, *53*, 3759.

(4) Suzuki, Y. Y.; Heeger, A. J.; Pincus, P. *Macromolecules* **1990**, *23*, 4730.

(5) Ho, K. S.; Zheng, W. Y.; Mao, J.; Laakso, J.; Levon, K., submitted for pulication in *Macromolecules*. Ho, K. S.; Zheng, W. Y.; Mao, J.; Laakso, J.; Levon, K. *Synth. Met.* **1992** (in print)

(6) Margolina, A.; Izmailov, A. F.; Levon, K. *Phys. A* **1992**, *186*, 563.

(7) Lee, H. K.; Myerson, A. S.; Levon, K. *Macromolecules* **1992**, *25*, 4002.

(8) Levon, K., unpublished.

(9) Margolina, A.; Rosso, M. *J. Phys. A* **1992**, *25*, 3901.

(10) Stauffer, D. *Introduction to Percolation Theory*; Taylor & Francis: London and Philadelphia, PA, 1985.

(11) Sumita, M.; Sakata, K.; Hayakawa, Y.; Asai, S.; Miyasaka, K.; Tanemura, M. *Colloid Polym. Sci.* **1992**, *270*, 134.