

# ON THE NANO-FILLER PERCOLATION NETWORK IN POLYMER NANOCOMPOSITES

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## ABSTRACT

With addition of very low loading of high-aspect-ratio nano-fillers in polymers, the physical properties of polymer nanocomposites can be greatly improved. In the paper, the role of nano-filler percolation networks in polymers is discussed. The main focus is on the estimation of two key parameters: percolation threshold and critical exponent, where the former is an optimal volume fraction of nano-fillers and the latter reflects the variation of physical properties such as permeability, flammability and conductivity near the percolation threshold.

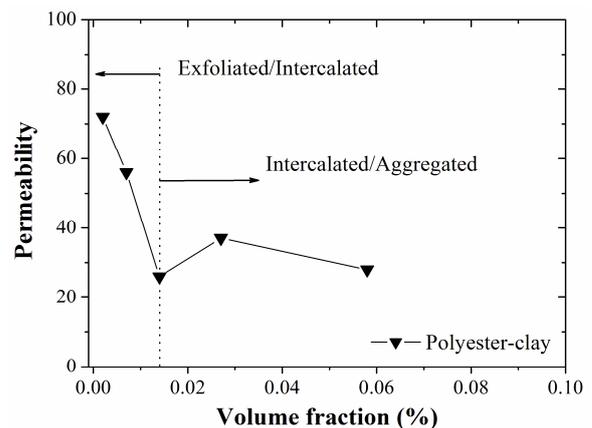
## 1 INTRODUCTION

In contrast to polymer composites reinforced with micro-sized particles or fibres, polymer nanocomposites have attracted a great deal of interest and research over the past decade [1]. With addition of very low loading of nano-fillers such as layered silicate or carbon nanotubes (CNTs) in polymeric matrix, the great improvement of physical and mechanical properties of polymers can be achieved. For example, a remarkable decrease in the gas/liquid permeability was observed at less than 5 wt.% clay in a range of polymer matrices (e.g., polyester, polyimide and poly-caprolactone) [2,3]. It is commonly believed that the improvement of barrier properties is mainly due to the high aspect ratios of exfoliated silicate platelets (~10–1000) or large interfacial areas between platelets and matrices. Similarly, owing to both high aspect ratios and unique properties of CNTs, the electrical and thermal conductivities rise sharply with addition of 0.1 vol.% or less nanotubes in polymers [4,5]. Extensive experiments and simulations have shown that the improving extent upon performance depends on the geometrical features of nano-fillers and their spatial distributions such as dispersion and alignment in polymers. There is still, however, not a good understanding on the influence of these factors on their physical properties and the development of polymer nanocomposites is largely empirical.

From the practical point of view, it is worth noting that the increase of filler contents will induce a tendency of aggregation as well as the high cost of expensive nano-fillers like CNTs. In most cases, it is expected that an infinite connective network or path will be filled by nano-fillers throughout polymer matrix, which can be described based on percolation theory [6]. In this paper, the role of nano-filler percolation networks in enhancing physical and mechanical properties of polymer nanocomposites is investigated. The focus is mainly on the estimation of two key parameters (i.e., percolation threshold and critical exponent) and their relationships with the geometrical structure of nano-fillers. In particular, we will highlight several open problems and challenges in developing polymer nanocomposites with tailored properties.

## 2 PERCOLATION AND NANO-FILLER NETWORK

The term *percolation* refers to the onset of a sharp transition or an infinite cluster at which long-range connectivity suddenly appears. In terms of percolation theory [6], the probability  $P$  of an infinite cluster near the percolation threshold obeys a power law and can be described as,  $P \sim (\phi - \phi_c)^\beta$ , in which  $\phi$  is the volume fraction of fillers,  $\phi_c$  is the percolation threshold, and  $\beta$  is the connectivity exponent. Similarly, the physical properties like electrical conductivity  $\sigma$  in the system increases monotonically and follows a universal power law,  $\sigma \sim (\phi - \phi_c)^t$ , where  $t$  is the critical exponent and  $|\phi - \phi_c| \ll 1$ . Here, the percolation threshold  $\phi_c$  is dependent on geometrical details of the system, but the exponents are only related to dimensions ( $\beta = 0.4$  and  $t = 2$  in a three-dimensional system).



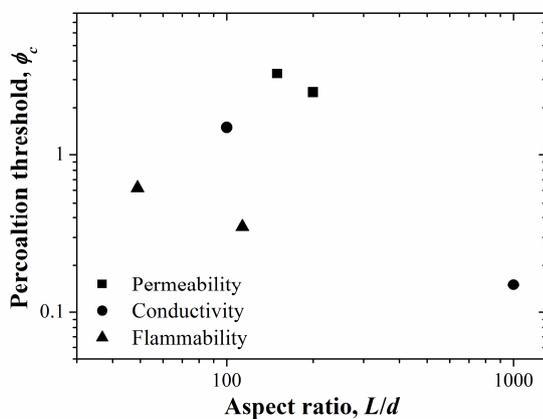
**Figure 1.** The relationship between oxygen permeability and volume fraction of clays (adapted from [3]).

Intuitively, the barrier phenomena such as permeability and flammability in polymer-clay nanocomposites and the electrical and thermal conductivities in nanotube composites are similar to that in classical percolation. However, the percolation process in a system containing highly anisotropic fillers such as exfoliated silicate and CNTs is much more complicated. As shown in Fig. 1,

the permeability in polyester-clay nanocomposites systematically decreases with increase of clay contents and follows an unexpected sudden drop and then up shift at a clay content of 1.4 vol% (2.5 wt%) [3]. There was a simple explanation that the sudden drop and subsequent increase of permeability at higher filler contents may be caused by the lack of exfoliation (the decrease of aspect ratio  $L/d$  with  $L$  and  $d$  being the length and thickness of platelets) or the aggregation of silicate platelets. It is obvious that, at the critical clay content, the correlation length of barrier clusters formed by exfoliated silicate platelets approaches infinity. Thus, such a phenomenon in the permeability in polymer-clay nanocomposites or the conductivity and flammability in nanotube composites can be considered as a typical aspect ratio-controlled percolation [7], but their percolation thresholds and critical exponents depend on the structures of nano-fillers such as clay and CNTs.

## 2.1 Percolation Thresholds

As shown in Fig. 2, the critical clay contents decrease as the increase of aspect ratios. But, this does not mean that the optimal reinforcement on physical properties such as permeability, conductivity and flammability of polymer nanocomposites can be achieved using a lower content of nano-fillers with a larger aspect ratio. To obtain the optimal performance of nano-fillers in polymer matrix, the interaction between fillers and polymer matrix as well as other properties such strength of nano-fillers has to be considered.



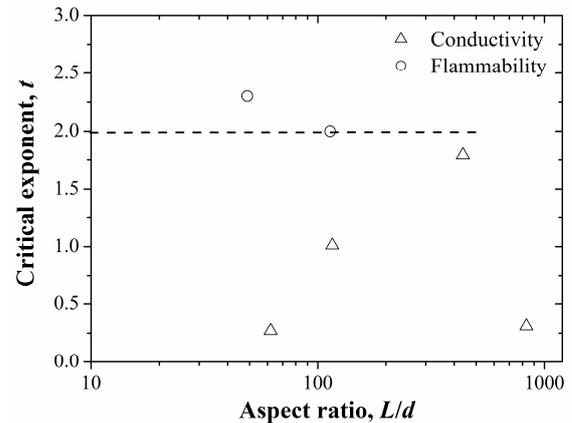
**Figure 2.** The percolation thresholds (wt.%) of clay or CNTs versus their aspect ratios (data from [2-4,8]).

Theoretically, the minimum nano-filler content can be estimated by using the concept of renormalization [9,10]. The results obtained from these models, as discussed below, may serve as a guide for the fabrication of polymer nanocomposites.

## 2.2 Critical Exponents

The concentration of nano-fillers in most polymer nanocomposites is usually a little higher than the critical or percolation threshold in order to gain the functions to be needed. Thus, the change of their physical properties near the percolation threshold is very important, which

can be described by the critical exponent of a power law. The results from theoretical and computational studies have shown that the critical exponents decrease as the increase of aspect ratios of CNTs; however, there seems not a clear trend between exponent and aspect ratio [11-13], as seen in Fig. 3. Here, it is worth noting that, for aggregates with the long-order interaction in an anisotropic system, the effective volume fraction of CNTs might be a better parameter instead of aspect ratio.

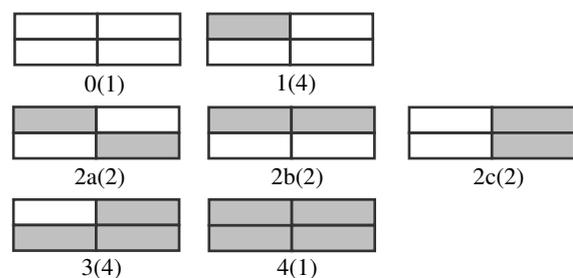


**Figure 3.** The critical exponent versus aspect ratio of CNTs, where  $t = 2$  in a three-dimensional percolation with  $L/d = 1$  (data from [8,13]).

There are few experimental results on the critical exponents of flammability in nanotube composites [8] and seem still no reports on the permeability in polymer-clay nanocomposites.

## 3 ESTIMATION OF CRITICAL INDICES

According to the renormalization group theory, a simple model (see Fig. 4) can be used to highlight the difference between various types of physical phenomena in polymer nanocomposites. The basic hypothesis is that the probability a cell acts as a given role is the same at all scales and the essential step is the construction of a renormalization transformation,  $p' = R(p)$ , between original probability  $p$  and renormalized one  $p'$  when the degree of coarse-graining is changed [9,10].



**Figure 4.** Illustration of a renormalization group model, in which there are 7 different topological configurations labelled 0, 1, 2a, ..., 4 with their multiplicities in parentheses. The elements filled with silicate platelets or CNTs are marked in gray colour [14,15].

### 3.1 Permeability and Flammability

Based on the theory of suspension rheology and the spatial distribution of nano-fillers, a simple relationship between the critical volume fraction  $\phi_c$  and the threshold probability  $p_c$  can be obtained as,  $\phi_c = C(L/d)^{-1}p_c$ , where  $C$  is a constant that is dependent on the spatial distribution of nano-fillers such as orientation [14-17]. Because permeation is mainly along a pressure direction (say from top to bottom), configurations 2a, 2b, 3 and 4 in Fig. 4 behave as barrier cells, and the renormalization  $R(p)$  can be expressed as,  $p' = p^4 + 4p^3(1-p) + 4p^2(1-p)^2$ . The critical probability,  $p_c = 0.38$ , can be obtained by solving the iterative equation,  $p' = p_c = R(p_c)$ . The more comprehensive analysis can be done by a three-dimensional renormalization model [16]. Such a model can be also applied to the study of flammability of nanotube composites and in all these configurations shown in Fig. 4, configurations 2b, 2c, 3 and 4 behave as barrier cells. Here, we think configuration 2b rather than 2a as a barrier cell because, as discovered in experiments, the structure affects the char by increasing both its barrier properties and reinforcing its structure [18,19]. In other words, the factor of strength should be considered in modelling the flammability of polymer nanocomposites.

### 3.2 Conductivity

Similarly, the model in Fig. 4 can be extended to the study of the conductivity of CNT-reinforced composites. In a general case, configurations 3 and 4 behave as conductive cells and the renormalization  $R(p)$  can be expressed as,  $p' = p^4 + 4p^3(1-p)$ , and the critical probability,  $p_c = 0.768$ . In combination with the analysis on the spatial distribution of CNTs in a cell, we have,  $\phi_c = 0.6(L/d)^{-1}$ , which is well consistent with that obtained by much more complicated theoretical calculations [11]. It is worth noting that, however, the difference between electrical and thermal conductivities is due to their different sensitivities and there is also a thermal percolation in nanotube composites [20]. The distinction between these two transport behaviours can be easily explained by percolation theory: the thermal resistance is fully determined by a percolation cluster of CNTs but the electrical resistance is governed by the backbone of a percolation cluster [15].

## 4 CONCLUSIONS

The mechanical and physical properties such as permeability, flammability and conductivity in polymer nanocomposites can be described by an aspect-ratio controlled percolation. The results have shown that both the critical volume fraction and exponent are closely related to the geometrical features of nano-fillers such as aspect ratio and dimension. Using a two-dimensional renormalization model, the critical volume fractions of nano-fillers such as clay and CNTs can be well estimated, which are inversely proportional to their aspect ratios. The difference between these phenomena is dependent on the details of percolation networks. But,

the estimation of critical exponents near the percolation threshold is still a big challenge in experimental and theoretical studies.

### Acknowledgements

This work was supported by the Curtin Research Fellowship and the Australian Research Council.

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