

# Polymer Nanocomposite Technology, Fundamentals of Barrier

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## Introduction

The term “nanocomposite” is widely employed to describe an extremely broad range of materials, where one of the components has a dimension in the sub-micron scale. A better –and far more restrictive– definition would require that a true nanocomposite should be a *fundamentally new material* (hybrid) in which the nanometer scale component or structure gives rise to *intrinsically new properties*, which are not present in the respective macroscopic composites or the pure components<sup>1</sup>. This latter definition necessitates that the nanostructure has dimensions smaller than a characteristic scale that underlies a physical property of the material. For example, for the electronic properties of a conductor or semi-conductor this scale would relate to the de Broglie wavelength of the electron (ranging from a few nanometers for a metal to hundreds of nanometers for a semiconductor), for the mechanical properties of a polymer it would relate to the size of the polymer coil or crystal (again ranging from a few nanometers to hundreds of nanometers), and for the thermodynamic properties of a polymer glass it would relate to the cooperativity length (a few nanometers).

Here we shall restrict our discussion even further, focussing on one subclass of polymer/inorganic nanocomposites, where the inorganic component is a high aspect-ratio nanoscale filler. Particular emphasis will be given to principles that apply to pseudo-two-dimensional layered inorganic fillers (such as 2:1 alumino-silicates<sup>2-8</sup>, from where most of our examples will be derived, and layered double hydroxides<sup>9</sup>). In these systems, concurrent improvements across multiple properties are typically achieved –with simultaneous enhancement of barrier, mechanical, thermal, and thermomechanical response– in addition to ‘new’ properties –such as improved flammability and biodegradability, or antimicrobial activity– compared to the unfilled polymer. Consequently, the resulting nanocomposite material is better described by the term “hybrid” (denoting the large scale changes in multiple material characters) rather than polymer “composite” (a term traditionally associated with an incremental improvement of one or two key properties<sup>10-12</sup>).

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## Theoretical Insights in Nanocomposites' Barrier

The permeability of small penetrant molecules through an organic matrix is determined by the solubility and diffusivity of the small molecule in this matrix, as well as by the mean square displacement (total traveled path length) divided by the sample thickness. In principle, the addition of a filler in the polymer matrix is expected to affect the solubility and diffusivity of a penetrant molecule, especially in the vicinity of the filler –*i.e.*, in the filler polymer interfacial region and at least one polymer  $R_g$  away from the filler surface. Also, it is expected that fillers will affect the path tortuosity (mean square displacement of penetrant versus film thickness) directly, when penetrants are forced to travel around impermeable fillers, and indirectly, when fillers induce polymer chain alignment or alignment and modification of polymer crystallites<sup>†</sup>.

Theoretical approaches on the barrier properties of nanocomposites, treat fillers as impermeable non-overlapping particles and assume no permeability changes in the polymer matrix<sup>14–17</sup>. Effectively, this means that the permeability of the composite will be smaller than the permeability of the matrix –unfilled polymer– by a factor equal to path tortuosity in the composite (simply assuming that the penetrant path does not cross any filler particles)<sup>‡</sup>. This path tortuosity was calculated by Nielsen<sup>14</sup> for completely aligned filler particles (all fillers have their larger surface parallel to the film surfaces, but there is no order in the filler center of mass), and its contribution to the composite permeability was derived to be:

$$\frac{P_{\text{comp}}}{P_{\text{poly}}} = \frac{1 - \phi}{1 + a\phi} \quad (1)$$

with  $a$  being the filler aspect ratio (for square fillers of length/width  $L$  and thickness  $W$ ,  $a=L/2W$ ) and  $\phi$  the volume fraction of the filler. Recently, Bharatdwaj modified<sup>17</sup> this equation to account for non-aligned fillers, by introducing an order parameter  $S$

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<sup>†</sup>The first mechanism, associated with chain alignment and the related diffusive anisotropy of small-molecule within aligned chains, bears a relatively weak effect on permeability<sup>13</sup>, whereas the second mechanism, associated with crystallite alignment and changes in the crystal morphologies, causes rather strong changes in permeability and is commonly employed in strain-hardened semicrystalline polymers for barrier applications.

<sup>‡</sup>This approach obviously ignores any filler-induced changes in the polymer crystal morphology, and thus is not expected to have good predictive power for nanocomposites based on semi-crystalline polymers. However, it is expected to work great for amorphous polymers, for elastomers, and for semi-crystalline polymers whose crystallites –*e.g.*, spherulites– are substantially smaller than the inter-particle distance, *i.e.*, the filler-filler separation.

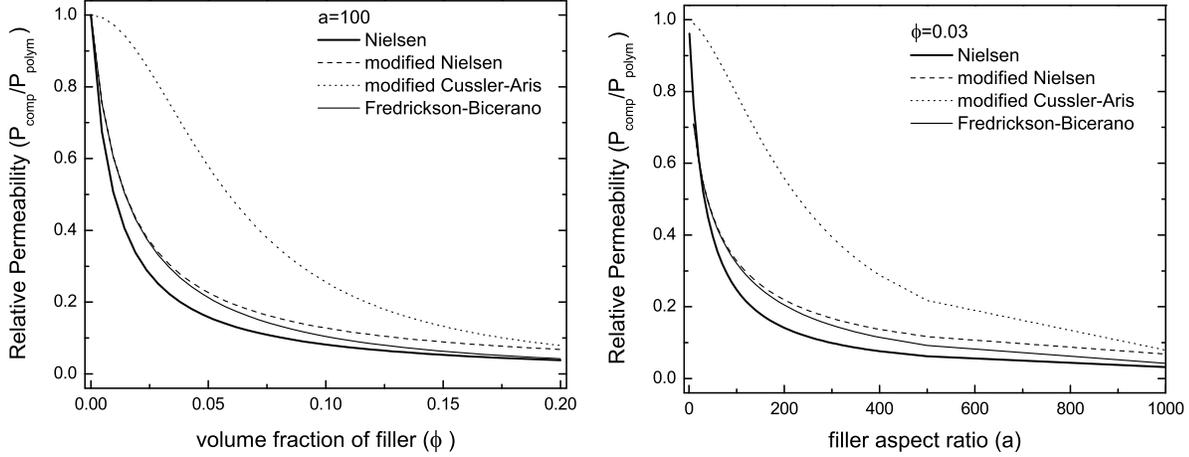


Figure 1: Comparison of theoretical models quantifying the effect of path tortuosity on the permeability of a composite: Nielsen model<sup>14</sup> (eq. 1), Fredrickson-Bicerano<sup>16</sup> (eq. 3), and modified<sup>16</sup> Nielsen and Cussler-Aris (eq. 4).

for the filler orientation:

$$\frac{P_{\text{comp}}}{P_{\text{poly}}} = \frac{1 - \phi}{1 + a\phi\frac{2}{3}(S + \frac{1}{2})} \quad \text{with } S = \frac{1}{2}\langle 3\cos^2\theta - 1 \rangle = \begin{cases} 1 & \parallel \text{ surface} \\ 0 & \text{random} \\ -\frac{1}{2} & \perp \text{ surface} \end{cases} \quad (2)$$

which reduces to the Nielsen equation for perfectly aligned fillers ( $S=1$ ). In a more detailed approach, Fredrickson and Bicerano derived<sup>16</sup> the same path tortuosity effects for circular fillers (radius  $R$  and thickness  $2W$ ), obtaining:

$$\frac{P_{\text{comp}}}{P_{\text{poly}}} = \frac{1}{4} \left( \frac{1}{1 + a\phi\beta_1} + \frac{1}{1 + a\phi\beta_2} \right)^2 \quad \text{with } \begin{cases} \beta_1 = (\pi/\ln a)(2 - \sqrt{2})/4 \\ \beta_2 = (\pi/\ln a)(2 + \sqrt{2})/4 \end{cases} \quad (3)$$

which can cover a wider  $\phi$  range –from dilute to semi dilute– than the ‘modified Nielsen’ and ‘modified Cussler-Aris’ relations (as presented in this same work<sup>16</sup>, modified to address circular fillers):

$$\frac{P_{\text{comp}}}{P_{\text{poly}}} = \frac{1}{1 + a\phi\pi/\ln a} \left( \begin{array}{c} \text{modified} \\ \text{Nielsen} \end{array} \right), \quad \frac{1}{1 + (a\phi\pi/(4\ln a))^2} \left( \begin{array}{c} \text{modified} \\ \text{Cussler-Aris} \end{array} \right) \quad (4)$$

Nevertheless, eq. 3 generally gives results similar to the Nielsen approach (eq. 1), when a geometric correction of  $\sqrt{\pi}/2$  is applied to the filler aspect ratio (*i.e.*, comparing equal area fillers, square for Nielsen and circular for Fredrickson-Bicerano). The comparison of the theoretical models is illustrated in figure 1. Given that all models

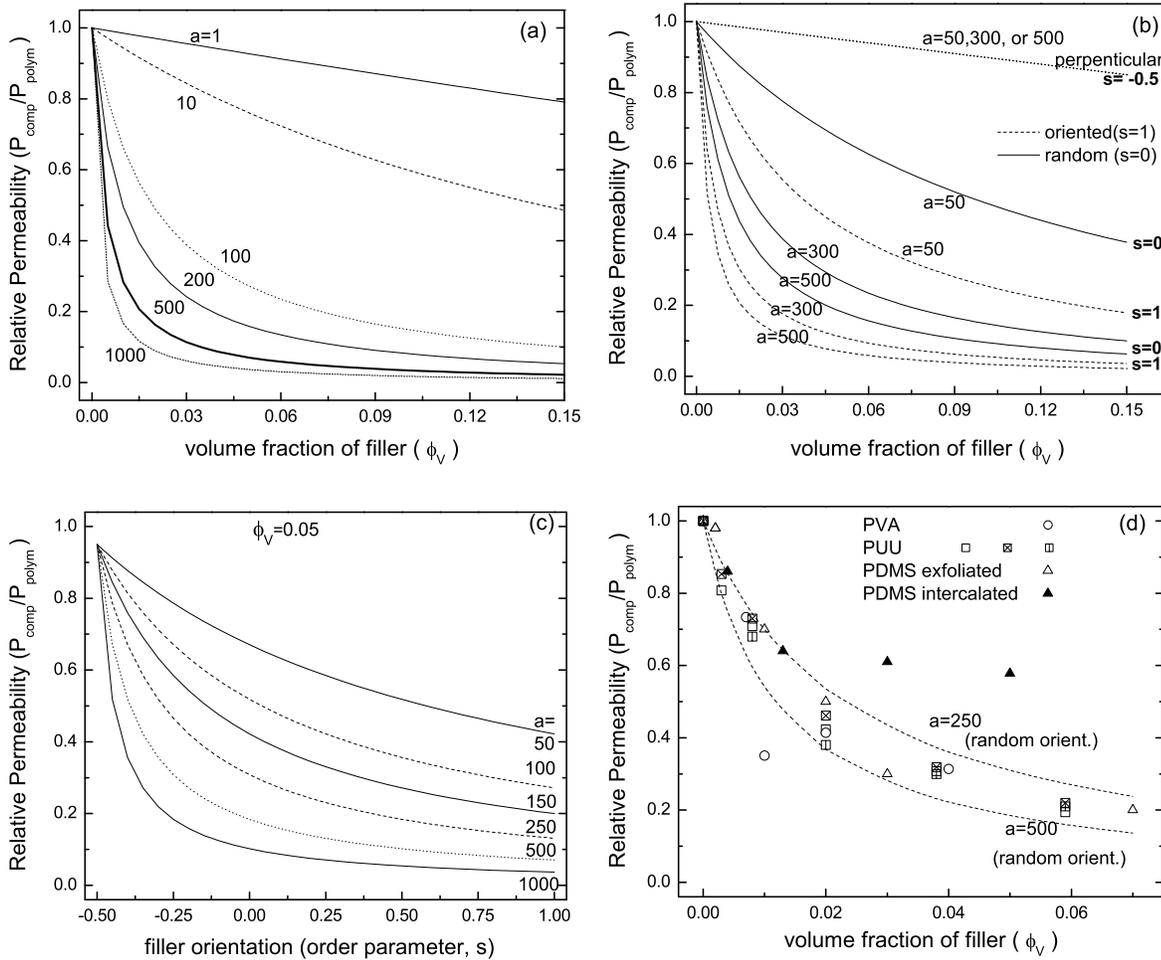


Figure 2: Theoretical predictions based on path tortuosity, as a function of: (a) filler aspect ratio  $a=1..1000$ ; (b) filler aspect ratio and alignment,  $S=1$ : perfect smectic alignment /dashed lines,  $S=0$ : random orientation /solid lines; (c) filler aspect ratio for a constant volume fraction  $\phi_V=5\%$ . (d) Comparison of theoretical predictions –parameters as indicated– with experimental values for water vapor permeabilities in various polymer/montmorillonite nanocomposites<sup>18–20</sup>.

–except for the Cussler-Aris– give similar behavior for the range of parameters relevant to polymer/layered-inorganic nanocomposites ( $10 < a < 1000$  and  $\phi \leq 15$  vol.%) we henceforth use the much simpler Nielsen model, including the addition of the orientation term (eq. 1 and eq. 2). According to this model, the obvious expectations can be quantified: higher aspect ratio fillers provide substantial lower permeabilities for a given filler volume fraction (fig. 2a), and aligned fillers are much more effective barriers for a given aspect ratio and filler loading (fig. 2c). Additionally, some

not-so-obvious conclusions can also be drawn:

- High aspect ratio fillers are as effective as smaller aspect ratio fillers but at a slightly higher loading. For example, for aligned fillers –fig. 2a– a completely exfoliated montmorillonite ( $a=500$ ) at  $\phi=2$  vol.%, has comparable permeability with a partially exfoliated montmorillonite ( $a=200$ ) at  $\phi \sim 3\%$ , or a mostly-intercalated montmorillonite ( $a=100$ ) at  $\phi \sim 5\%$ . This observation has important implications in designing a barrier nanocomposite: for the same example, instead of completely exfoliating a given filler –a task that is usually difficult to achieve– the same filler in a partially-exfoliated or mostly-intercalated morphology could achieve the same barrier performance at slightly higher filler loadings.
- Perfectly aligned fillers result in similar permeabilities with randomly oriented fillers of higher aspect ratio and/or higher loading. For example, fig. 2b, for a  $a=300$  filler, perfect alignment at  $\phi=1.5\%$  results in the same barrier performance as the same filler when randomly oriented at  $\phi \sim 4.3\%$ ; and for a  $a=500$  filler, perfect alignment at 1.5 vol.% is comparable in permeability with a 4.5 vol.% composite with random filler orientation. Along the same lines, a perfectly aligned filler nanocomposite with  $a=300$  at  $\phi=1\%$  has similar barrier performance as  $a=500$  at 2%. This observation provides also important guidance on how to overcome the difficult task of perfectly aligning the fillers parallel to the film surface (fig. 2c).
- The effect of filler orientation on permeability is decreasing in importance with higher filler aspect ratio (fig. 2c). For example, permeability improvement for  $a=1000$  is only 5% better with perfect alignment ( $S=1$ ) compared to a random orientation ( $S=0$ ), and for  $a=500$  this difference is about 10%.
- Ultimate barrier performance is predicted for those cases where the fillers are arranged in networks. For example, “house-of-cards” type of filler networks would result in  $a \gg 1000$  reducing the permeability by 2 to 4 orders of magnitude compared to the unfilled matrix, whereas a percolated filler network would correspond to  $a \rightarrow \infty$  and, thus, permeability approaching zero (a perfect barrier structure!).

Finally, the favorable comparison of these theoretical predictions against experimental data (fig. 2d) gives some credibility to the conclusions above. In figure 2d we plot experimental water vapor permeabilities of various solvent cast nanocomposite films. The experimental behavior follows well the theoretical trend, and is enclosed between the response of exfoliated systems –especially for low filler loadings– and the one of intercalated systems –for moderate and higher loadings. This reflects

the “effective filler aspect ratio”, which accounts for both the filler geometry but also for the filler dispersion. This agreement persists for all composites based on amorphous or elastomeric polymers and that have good filler dispersion. However, this agreement diminishes for most semicrystalline polymers, and disappears when filler dispersion is poor (compare PDMS with intercalated and exfoliated dimethyl-dialkyl-montmorillonite). Finally, this agreement is rather independent of polymer and filler hydrophilicity –ranging from very hydrophilic poly(vinyl alcohol) reinforced by Na<sup>+</sup> montmorillonite, to moderate poly(urethane-co-ureas), to rather hydrophobic poly(dimethyl siloxane) and dialkyl-modified montmorillonite.

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