Influence of Aspect Ratio on Barrier Properties of Polymer-Clay Nanocomposites

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The barrier properties of polymer-clay nanocomposites, with far less inorganic contents of layered-silicate fillers, are remarkably superior to those of neat polymers or their conventional counterparts. A simple renormalization group model is proposed to assess the influence of geometric factors (such as aspect ratio, orientation, and extent of exfoliation) of layered-silicate fillers on the barrier properties of polymer-clay nanocomposites. The results show that the aspect ratio of exfoliated silicate platelets has a critical role in controlling the microstructure of polymer-clay nanocomposites and their barrier properties. The estimated percolation thresholds of clay content for minimum permeability are in good agreement with experimental data.

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Recently, the intriguing microstructure and excellent properties of polymer-clay nanocomposites (PCNs) have stimulated much interest and research within both the scientific and engineering communities [1,2]. PCNs are a new emerging class of organic-inorganic hybrid materials. With much less inorganic contents of clay (layered-silicates such as montmorillonite, saponite, kaolinite, hectorite, etc.,) than comparable glass- or mineral-reinforced polymers, PCNs exhibit physical and mechanical properties significantly different from their more conventional counterparts. They have good thermal stability, high heat distortion temperature, superior barrier properties (gas/liquid permeability, flammability), and high specific stiffness (or strength) at low concentrations of clay (< 5 wt %) in a range of polymer matrices (polyimide, polyester, polycaprolactone, etc.,) [3–7]. Clay particles like montmorillonites are crystalline materials with a sandwich structure (one octahedral sheet of alumina between two tetrahedral sheets of silica), which are composed of stacked platelets with thickness 1 nm, diameter from 10 to 1000 nm, and the spacing between platelets less than 1 nm. It is generally believed that the improvements of their barrier and other mechanical properties are mainly caused by the high aspect ratio (10–1000) or large surface area of exfoliated clay particles and the strong interfacial interaction between the silicate platelets and the polymer matrix [1–7].

The dependence of barrier properties on the extents of intercalation (or exfoliation), orientation, and dispersion of nanometer-sized silicate platelets in a polymer matrix is not well understood to date. Let us consider the gas/liquid permeability of PCNs, a typical measurement of barrier property, as an example. It is well known that the permeability k of gas/liquid molecules through a homogeneous medium can be described by Darcy's law, $k = ud/\Delta p$, where u is the flow rate and Δp is the pressure difference across a specimen with thickness d. The permeability problem is, however, actually more complicated than Darcy's law predicts. For instance, in C_{18}-montmorillonite poly (butylenes succinate) nanocomposites, there was a sharp decrease of the O_2 gas permeability at 1.25 vol % concentration of the montmorillonite [5]. A very similar phenomenon was also discovered in polyester-clay nanocomposites [6]. It is clear that Darcy's law for the prediction of permeability cannot explain these anomalous barrier behaviors observed in PCNs. In this Letter, a simple renormalization group model is proposed to assess the influence of geometric factors (such as aspect ratio, orientation, and extent of intercalation or exfoliation) of exfoliated clay fillers on the barrier properties of PCNs.

In terms of morphology and cohesive strength between silicate platelets and the polymer matrix, there are three representative types of PCNs: *intercalated, flocculated,* and *exfoliated* nanocomposites [4,5]. In intercalation, the polymer chains swell the interplatelet or gallery spacing of clay particles and lead to a well-ordered alternating polymer-clay nanostructure. In exfoliation, the clay particles are fully separated or delaminated from cubical to flat

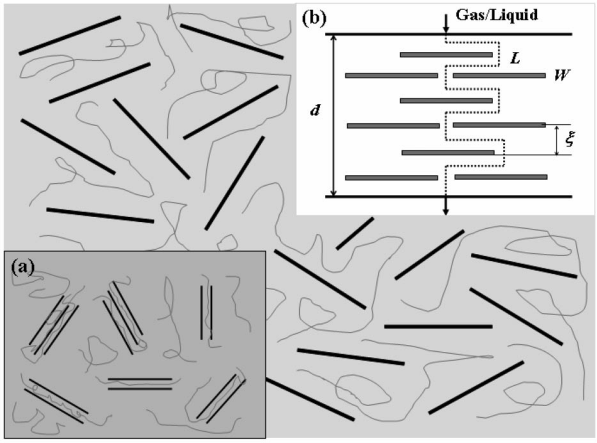

FIG. 1. Schematic of exfoliated clay morphologies of PCNs, where inset (a) shows the state of intercalation and inset (b) is a simple tortuosity-based model to describe the gas/liquid permeability in filled polymers. Note the concentration of clay is much lower than that shown in the sketch.

platelets and individually dispersed in the matrix (see Fig. 1). The flocculated structure lies between intercalation and exfoliation. To achieve full exfoliation of clay in a polymer matrix, the clay particles must be premodified with an organic ammonium surfactant. Since silicate platelets are impenetrable to diffusing gas/liquid molecules, the influence factors on barrier properties of PCNs mainly depend on the degree of exfoliation (or intercalation), the state of aggregation and dispersion of silicate platelets in the matrix, such as aspect ratio L/W (L and W are length and thickness of silicate platelets, respectively), dispersion distance ξ, orientation θ, volume fraction ϕ, etc., (see Fig. 1). Other physical polymer matrix properties (such as crystallinity and affinity) also affect the barrier properties of PCNs. Here, for simplicity, we only consider the effects of geometric factors of clay particles in a polymer matrix, and assume the motion of gas/liquid molecules in PCNs is steady and stable. From dimensional analysis, the relative permeability k' is given by $k' = k_{\mathrm{PCN}}/k_{\mathrm{P}} = f(L/W, \xi/W, \theta, \phi)$, where k_{PCN} and k_{P} are the permeability of PCNs and polymer, respectively, and f is a dimensionless function of four parameters: L/W, ξ/W, θ, and ϕ.

Because a diffusing gas/liquid molecule cannot permeate the silicate platelets, it must go around them thus leading to a tortuous path. Based on a *tortuosity* argument, a simple model was developed, and widely used to describe the permeability of filled polymers [8]. In an ideal case, where clay particles are completely exfoliated and uniformly dispersed along the preferred orientation ($\theta = 0°$) in the polymer matrix (inset in Fig. 1), the tortuosity factor τ (defined as the ratio of actual distance d' to shortest distance d) becomes

$$\tau = \frac{d'}{d} = 1 + \frac{L}{2W}\phi. \tag{1}$$

Clearly, the relative permeability k' decreases as the aspect ratio L/W (degree of exfoliation) and concentration ϕ of the clay fillers increase, that is, $k' \sim \tau^{-1}$. However, recent experimental results showed that, in C_{18}-montmorillonite poly (butylenes succinate) nanocomposites, the gas permeability decreased systematically with increasing clay content up to 1.1 vol % (2.8 wt %) as expected from Eq. (1), and then there was a sharp drop in gas permeability with a clay content of 1.4 vol % (3.6 wt %) [5]. These test results proved that there was a *percolation* threshold of clay content. Similar behaviors were also observed for other physical properties of PCNs [3–6]. In fact, the gas/liquid permeation process in PCNs can be viewed as a typical percolation phenomenon [9]. But, in contrast to classical percolation, it is more like an aspect ratio-controlled percolation in the pressure difference direction [10]. As the clay content increases, the correlation size of barrier clusters increases monotonically, and at a critical value, the correlation length approaches infinity. Hence, the critical value of clay content in PCNs can be studied using *renormalization group* (RG) theory, which provides a powerful method for modeling large heterogeneous systems [11]. Several simple models based on the real (position) space RG approach have been successfully applied to studies of earthquake prediction, transport in porous media, microcrack connectivity, and fragmentation of rocks [12,13].

The basic hypothesis of the RG approach is the probability p that a cell acts as a barrier, is the same at all orders. The essential step is construction of a renormalization transformation, $p' = R_b(p)$, between original probability p and renormalized probability p' when the degree of coarse graining in observation is changed [11]. Let us consider a b^d-site Kadanoff cell with a ratio of *coarse graining* $b = 2$ and *dimension* $d = 3$. Figure 2 shows a Kadanoff cell comprising 8 elements. In each cell, there can be zero to eight elements occupied (by silicate platelets), and hence there are $2^8 = 256$ possible combinations [12]. Excluding multiplicities, there are 22 topologically different configurations, in which the barrier elements are indicated by solid dots at their corners (see Fig. 2). Here, an element in a cell is considered a barrier when it contains silicate platelets. To specify whether a cell is a barrier or not, the simplest way is to find if there is a permeation path through the cell. As exemplified in Fig. 3, cells (a) and (b) with 4 barrier elements are permeable and impermeable, respectively, corresponding to cases 4c and 4d in Fig. 2. Thus, in all 256 combinations, partial or whole configurations 4a, 4d, 4e, 4f, 5a, 5b, 5c, 6a, 6b, 6c, 7, and 8 are barrier cells, which are highlighted in bold letters beneath the relevant configurations (see Fig. 2). It is noted that since permeation is mainly along the pressure difference direction (from top to bottom), only partial combinations in configurations 4a, 4d, 4e, 5a, 5b, and 6a can act as barriers. Let us use again a cell with 4 barrier elements as an example. The probability that the cell is a barrier can be represented by $16p^4(1 - p)^4$, where 16 is the number of barrier combinations (4a, 4d, 4e, and 4f in Fig. 2).

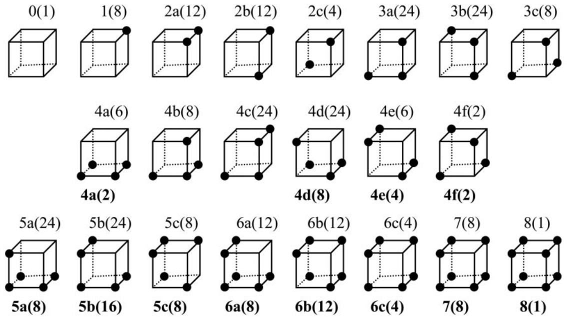

FIG. 2. An n-order cell is shown as a simple cube with its corners representing eight constitutive $(n - 1)$-order elements. Each corner is marked by a solid dot when the corresponding $(n - 1)$-order element acts as a barrier. There are 22 different topological configurations labeled 0, 1, 2a,…, 8, with their multiplicities given in parentheses. Of all $2^8 = 256$ combinations, there are 81 cases in which the silicate platelets act as barriers (and these are highlighted in bold letters below the relevant configurations).

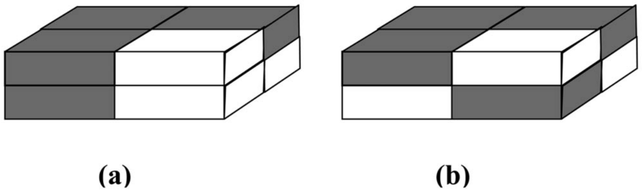

FIG. 3. Illustration of two typical topologies referenced to Fig. 2: (a) represents case 4c in which the gas/liquid molecules can easily pass through the matrix; and (b) is for case 4d, where the silicate platelets (marked in gray color) act as barriers.

Considering all possible configurations with 5, 6, 7, and 8 barrier elements and summing up all the probabilities as noted in Ref. [14], the renormalization transformation $R_2(p)$, that is, the probability p' that a cell of order $(n + 1)$ is a barrier *versus* the probability p that a cell of order n (i.e., an element of order $n + 1$) is a barrier, follows the equation

$$p' = R_2(p) = 16p^4 - 32p^5 + 24p^6 - 8p^7 + p^8. \quad (2)$$

The iterative relation in Eq. (2) crosses the straight line, $p' = p$, at $p' = p = p_c = 0.718$, which is an unstable fixed point that separates the region of stable behavior from the region of unstable behavior. If $p < p_c$, the solution iterates to one stable point $p = 0$ as n increases, and no barrier occurs. On the contrary, if $p > p_c$, the solution iterates to another stable point $p = 1$ as n increases, and the system acts as a barrier. Bifurcation of the solution occurs at $p = p_c$, which is the critical value of clay content for minimum permeability [15].

Next, let us consider the nanostructure of exfoliated clay particles and determine the probability p of an element that is a barrier. As already mentioned, p is determined by many factors such as aspect ratio L/W, dispersion distance ξ, orientation θ, clay content ϕ, etc. From the classical theory of suspension rheology [16], in order to distribute uniformly exfoliated silicate platelets in a polymer matrix, the dispersion distance ξ between two platelets should be equal to or greater than its length L, i.e., $\xi \geq L$. Thus, the critical volume fraction can be estimated by $\phi_c = L^2W/L^3 = W/L$. For layered silicates with thickness $W = 1$ nm and length $L = 100$ nm, its critical volume fraction is about 1%. But it is noted that this is a locally sufficient (but not necessary) condition for exfoliation. Based on this crude estimate, when the clay filler concentration is small, the geometric influence factors (such as L/W, ξ/W, θ, etc.) on the barrier properties in exfoliated PCNs can be considered as independent of each other, and the probability for an element that is a barrier is described by $p = \Pi p_i$, where p_i is the probability of the ith influence driver. The following are the three main influence factors:

(a) The influence of the extent of *exfoliation* or *intercalation* can be simply represented by the *aspect ratio* L/W. As the extent of intercalation increases, the thickness W of exfoliated platelets increases and the aspect ratio L/W decreases. (b) The influence of the *orientation* θ of the silicate platelets in a polymer matrix can be represented by an orientation parameter S, which is defined by: $S = \langle 3\cos^2\theta - 1\rangle/2$. Here, $S = 1$ $(\theta = 0°)$ indicates perfect alignment, and $S = 0$ $(\theta = 54.74°)$ for random distribution [17]. Thus, the effective aspect ratio with perfect alignment becomes $L/W\langle\cos^2\theta\rangle$ [18]. (c) The influence of the *dispersion distance* ξ between two silicate platelets can be considered by the volume fraction ϕ. In exfoliated PCNs, $\phi = W/\xi$ since the silicate platelets are randomly dispersed in the polymer matrix.

Now, the barrier probability for an element in a Kadanoff cell can be written as

$$p = \frac{L}{W}\langle\cos^2\theta\rangle\phi = \frac{2S + 1}{3}\frac{L}{W}\phi. \quad (3)$$

At the critical point, the percolation threshold of clay content ϕ_c is obtained by

$$\phi_c = \frac{3}{2S + 1}\frac{W}{L}p_c, \quad (4)$$

where $p_c = 0.718$ in terms of the RG model discussed above.

The theoretical critical volume fraction ϕ_c *versus* aspect ratio L/W $(S = 0)$ and orientation S $(L/W = 100)$ of the silicate platelets are shown in Figs. 4 and 5 respectively. ϕ_c for several typical clay fillers (hectorite, saponite, montmorillonite, and synthetic mica) can be estimated from their aspect ratios L/W [3] (see Fig. 4). Also, experimental critical thresholds for O_2 gas permeability of C_{18}-montmorillonite poly (butylenes succinate) $(L/W = 150$ and $\phi_c = 1.25\%$ [5]) and polyester-clay nanocomposites $(L/W \approx 200$, $\phi_c = 1.4\%$ [6]) are plotted in Fig. 4

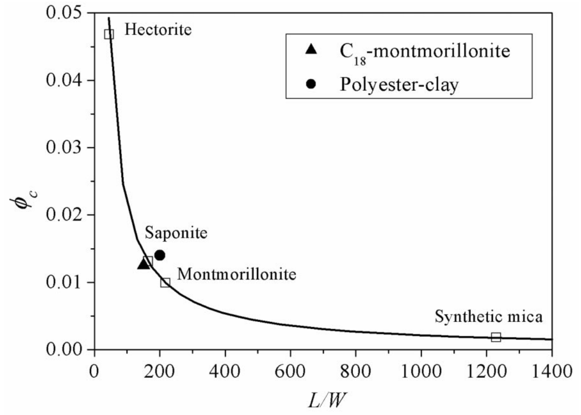

FIG. 4. Critical volume fraction ϕ_c *versus* aspect ratio L/W of silicate platelets with $S = 0$. Thresholds for several typical clay fillers are obtained directly from Eq. (4) based on their aspect ratios [3] (open symbols). Two solid symbols indicate the test data of O_2 gas permeability in C_{18}-montmorillonite $(L/W = 150$ and $\phi_c = 1.25\%$ [5]) and polyester-clay $(L/W \approx 200$, $\phi_c = 1.4\%$ [6]) nanocomposites. There is good agreement with the theoretical curve.

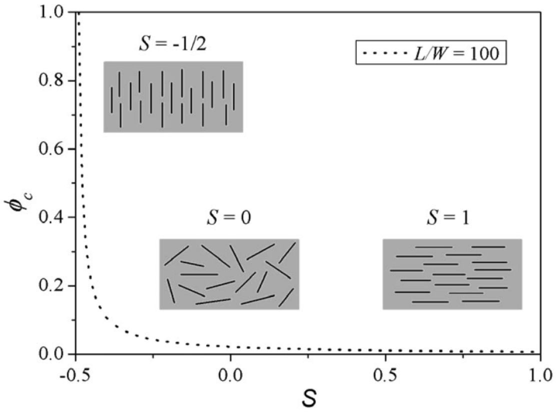

FIG. 5. Critical volume fraction ϕ_c *versus* orientation S of silicate platelets with $L/W = 100$. The insets are three typical patterns of silicate platelets in a polymer matrix for cases of $S = -1/2$, 0, and 1, respectively.

and they agree well with the theoretical predictions. It is obvious that the aspect ratio L/W (extent of exfoliation) of clay particles plays a key role in controlling the barrier properties of PCNs. In Fig. 5, the critical volume fraction ϕ_c *versus* orientation S of silicate platelets with $L/W = 100$ is shown, where the insets represent three typical patterns ($S = -1/2$, 0, and 1) of silicate platelets in a polymer matrix. In many real cases, S varies from 0 to 1.

Finally, it is suggested that the RG approach can also be used to study other anomalous properties of PCNs, such as strength and toughness, in which renormalization transformation is more complex due to stress transfer and interaction [19]. Much further work is needed to obtain optimal parameters (or percolation thresholds) of clay fillers to improve the barrier and other physical properties.

In summary, a simple renormalization group model has been proposed to study the effects of geometric factors of clay fillers, such as aspect ratio, orientation, and extent of intercalation or exfoliation on the barrier properties of the PCNs. The results show that the aspect ratio of exfoliated silicate platelets is a most critical parameter, and the permeation of gas/liquid molecules in the PCNs can be viewed as an aspect ratio-controlled percolation. The predicted percolation thresholds of clay contents for the minimum permeability are in good agreement with experimental data.

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[14] The barrier probabilities for the other cases, as highlighted in bold letters in Fig. 2, can be similarly derived. By summing up all these probabilities, the renormalization transformation $R_2(p)$ is given by: $R_2(p) = 16p^4(1-p)^4 + 32p^5(1-p)^3 + 24p^6(1-p)^2 + 8p^7(1-p) + p^8$. Then, by simplifying the right hand side, we obtain Eq. (2).

[15] To reduce the errors, the Kadanoff cell size should be as large as possible. Instead of calculating R_b analytically, the Monte Carlo RG method can be used to estimate the percolation threshold for a large lattice.

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