Modeling of water permeability through the polymer nanocomposites

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Abstract. The influence of chemical and physical parameters of polymer nanocomposites on the water permeability is analyzed. The chemical structure of the matrix polymer and the polar groups grafted onto the surface of the nanoparticles lead to the greatest influence. A large influence is exerted by the concentration of nanoparticles, their shape and size distribution. The direction of the penetration front in the nanocomposite sample has a lesser effect.

1. Introduction

An analytical model for predicting the water permeability of polymer nanocomposites should take into account a number of physical and chemical characteristics of the system under consideration. These characteristics include the chemical structure and concentration of the polymer, the chemical structure of the nanoparticle surface, the concentration of nanoparticles in the composite, the concentration of polar functional groups at the surface, and the nanoparticle size and shape. The concentrations of nanoparticles and polar groups have the most profound effect on permeability. The effects of the size distribution and orientation of anisometric nanoparticles on permeability also should be analyzed.

The problem of control over the permeability of nanocomposites has attracted careful attention from specialists over the last several decades. Special attention has been given to nanocomposites containing long planar nanoparticles, because they create “tortuous” paths for the motion of liquid molecules, thereby significantly decreasing the diffusion rate and permeability. The water permeability of a series of polylactic acid (PLA)–based nanocomposites containing up to 6 wt. % phyllosilicate, i.e., montmorillonite (nanoclay), have been studied [1]. The measured values of permeability were found to decrease with an increase in the nanoclay content up to 5 wt. %, a result that agrees well with the predictions of Nielsen’s model [2]. The penetration of gases through nanocomposites was reviewed in [3]. A geometrical model for the prognosis of efficient diffusion through composite membranes with impermeable anisotropic domains depending on their orientations and volume fractions was described in [4]. The predictions of the model were compared with the experimental data. Works [5-9] were dedicated to different models for the description of the permeability of composites containing layered fillers in the polymer matrix. The experimental properties of nanocomposites containing nanoclays were studied in [8, 9].

The studies performed in [6, 7, 10], where the theory of the prediction of the properties of barrier membranes was verified, are closest in regard to the topics of this paper. Permeability was predicted to
change with changes in the concentration and the ratio of the sides of planar particles used to fill composite materials. The polymer films with parallel-packed planar impermeable particles of filler were shown in [7] to possess permeability 2-3 orders of magnitude lower than those of the same-size films containing no filler. However, if the planar particles of filler have a size distribution, the decrease in permeability can result from a compromise between the shorter diffusion paths in any region containing fine particles and the particle concentration. The theoretical and experimental data show that the diffusion resistance of films containing 3 vol. % planar particles is 20% higher than that of films containing 6 vol. % of such particles. A geometrical model for the prediction of efficient diffusion through nanocomposites as depending on the orientation and volume fraction of the polymer nanoclay, as well as on its interaction with the polymer matrix, was proposed in [10]. Good agreement between the predictions of the model and the numerical-simulation data was observed. In regard to the already existing theoretical models, the authors believe that the proposed model is more adequate for the description of the diffusion in conventional nanocomposites. In the case when the inorganic lamellas agglomerate into clusters, the model ceases to work.

The most detailed analysis of gas permeation through nanocomposites was performed in [11], where a great number of references are given, and which considers how 19 versions of various models are dependent on the nanocomposite morphology and the polymer–filler interaction. Although these studies are dedicated to gas permeability, the experimental studies on water permeability in nanocomposites (for example, see [1]) use analogous models to explain the results. All these models and the corresponding equations utilize such parameters as the outer diameter, the diffusion coefficient, the nanoparticle length, the molecular mass, the form factor of a nanoparticle, the membrane thickness, the diameter–length ratios of fibrous fillers, the volume fraction or the filling, the orientation angle, and the thickness of the polymer layer. All these models allow a prediction of the barrier properties of nanocomposites. However, such a prediction does not involve the chemical structures of matrix polymers, the chemical structure of the nanoparticle surface, and the concentration of functional groups on this surface. Therefore, this study is dedicated to the design of such a calculation scheme that makes it possible to predict the water permeability of nanocomposites on the basis of the chemical structure of the matrix polymer and the chemical structures of modifying agents added to improve the compatibilities of nanoparticles with the matrix. For this purpose, we propose, first and foremost, a simplified version of the calculation scheme that allows the calculation of water permeation through matrix polymers and copolymers, while taking into account their chemical structures and the ratio of components. Then, this scheme is applied to analyze the water permeability of nanocomposites with consideration for the sizes and shapes of nanoparticles and their concentrations and orientations in the polymer matrix.

Briefly consider the design scheme proposed in the work [12]. The basic equation for describing the permeability $P$ of polymers is as follows:

$$P = P_0 e^{\frac{\Delta E}{RT}} ,$$

(1)

where $P_0$ is the constant, $\Delta E$ is the activation energy of the permeability process, $R$ is the universal gas constant, and $T$ is the absolute temperature.

In accordance with the principles of construction of calculation schemes for the prediction of polymer properties [13, 14], the value $\Delta E$ is described as follows:

$$\Delta E = \sum \Delta E_i^{**} ,$$

(2)

where $N_A$ is the Avogadro number, $\sum \Delta V_i$ is the van der Waals volume of the repeating unit of the polymer, $\sum \Delta E_i^{**}$ is the activation energy of the permeability process multiplied by the van der
Waals volume of the repeating unit, formed from the van der Waals volumes of each atom or a specific polar group, which causes dipole-dipole interactions or hydrogen bonding. Then

$$\ln P = \ln P_0 - \frac{\sum \Delta E^*_i}{N_A R T \sum \Delta V'_i}.$$  \hspace{1cm} (3)

The set of atomic constants, as well as to a number of parameters characterizing the energy of strong intermolecular interactions for a number of individual groups are listed in Table 1. Value $\ln P_0 = 3.002$ (barrer).

**Table 1.** Atomic constants and parameters describing specific intermolecular interactions.

| Atom and type of intermolecular interaction | Designation   | $\Delta E^{**}_{i}/RT_{298}$ | $\Delta E^{**}_{i}$, (kJ/mol) |
|-------------------------------------------|--------------|-----------------------------|-----------------------------|
| Carbon                                    | $\Delta E_C^{**}$ | 42.75                       | 105.85                     |
| Hydrogen                                  | $\Delta E_H^{**}$ | -36.65                      | -90.75                     |
| Oxygen                                    | $\Delta E_O^{**}$ | -8.20                       | -20.3                      |
| Hydrogen bond for the NHCO-group          | $\Delta E_{NHCO}^{**}$ | -385.2                      | -953.7                     |
| Double bond                               | $\Delta E_d^{**}$ | -182.8                      | -452.6                     |
| Chlorine                                  | $\Delta E_{Cl}^{**}$ | 44.1                        | 109.2                      |
| Fluorine                                  | $\Delta E_F^{**}$ | -60.1                       | -148.8                     |
| Hydrogen bond                             | $\Delta E_h^{**}$ | -28.3                       | -70.1                      |
| Aliphatic cycle (skeleton)                | $\Delta E_{al,c}^{**}$ | -234.5                      | -580.6                     |
| Dipole-dipole interaction                 | $\Delta E_d^{**}$ | -109.8                      | -271.9                     |
| Aromatic cycle (skeleton) located in the back bone | $\Delta E_{ar,c,b}^{**}$ | -203                        | -502.6                     |
| Nitrogen                                  | $\Delta E_N^{**}$ | 29.8                        | 73.8                       |
| Silicon                                   | $\Delta E_{Si}^{**}$ | -156.9                      | -388.5                     |
| Sulfur                                    | $\Delta E_S^{**}$ | -62.1                       | -1538                      |
| Aromatic cycle (skeleton) located in the side chain | $\Delta E_{ar,c,s}^{**}$ | -326.3                      | -808                       |

2. **Theoretical analysis**

Solid particles added to amorphous polymers are not involved in transport processes. For this reason, we write:

$$P = P_0^* (1 - \alpha_{d,f}),$$  \hspace{1cm} (4)

where $P$ is the permeability of a composite comprising a polymer and nanoparticles, $P_0^*$ is the permeability of the starting polymer, and $\alpha_{d,f}$ is the volume fraction of nanoparticles.

When different chemical groups are localized on the surface of each nanoparticle, these groups have an effect on the water permeability. Because of this circumstance, each nanocomposite can be represented as a mixture comprising a starting polymer (free of nanoparticles) and chemical groups localized on the surfaces of nanoparticles. Let us consider the effect of localized chemical groups on the water permeability of nanocomposites with consideration for such factors as the chemical structure and the concentration of the polymer, the chemical structure of the nanoparticle surface, the concentration of nanoparticles in the composite, the concentration of functional groups on the surfaces of nanoparticles, and the sizes and shapes of nanoparticles. Let us calculate the number of chemical groups, $\beta$, localized on a nanoparticle surface per repeating unit of the polymer. Value $\beta$ can be determined as follows. The number of nanoparticles, $n_{np}$, contained in one gram of the nanocomposite is

$$n_{np} = \frac{c_{np}}{g_{np}} = \frac{c_{np}}{\rho_{np} v_{np}},$$  \hspace{1cm} (5)
where \(c_{np}\) is the mass of the nanoparticles in the nanocomposite, \(g_{np}\) is the mass of one nanoparticle, \(\rho_{np}\) is the density of a nanoparticle, and \(v_{np}\) is the volume of one nanoparticle.

The number of chemical groups, \(N_{cg}\), for all nanoparticles in a nanocomposite is

\[
N_{cg} = \frac{n_{cg} \cdot c_{np}}{\rho_{np} v_{np}},
\]

where \(n_{cg}\) is the number of polar groups on the surface of one nanoparticle.

The total number of repeating units, \(N_{ru}\), in the considered system is

\[
N_{ru} = \frac{c_{p} \cdot 0.6022 \cdot 10^{24}}{M_{0}},
\]

where \(c_{p}\) is the mass of the polymer and \(M_{0}\) is the molecular mass of the repeating fragment of the polymer.

Hence, the number of chemical groups per repeating unit of the linear polymer or per repeating fragment of the polymer network is calculated as

\[
\beta = \frac{n_{cg} c_{np} M_{0}}{\rho_{np} v_{np} c_{p} 0.6022 \cdot 10^{24}}.
\]

The values (water permeation through the polymer free of nanoparticles) are calculated with the program “Cascade”. Let us consider some examples of the calculation. First, it is necessary to estimate the possible content range of the polymer in the nanocomposite, which depends on both the chemical structure of the polymer and the parameters of nanoparticles. It is obvious that

\[
\alpha_{m,p} = \frac{1}{1 + \beta} \quad \text{and} \quad \alpha_{m,cg} = \frac{\beta}{1 + \beta},
\]

where \(\alpha_{m,p}\) is the molar fraction of the polymer and \(\alpha_{m,cg}\) is the molar fraction of the chemical groups.

Substituting Eq. (8) into formula (9), we obtain

\[
\alpha_{m,p} = \frac{1}{1 + \beta} \cdot \frac{n_{cg} c_{np} M_{0}}{1 + n_{cg} \rho_{np} v_{np} c_{p} 0.6023 \cdot 10^{22}}.
\]

Let us suggest a simplified equation for the estimation of water permeability \(P_{0}^{*}\).

\[
\ln P_{0}^{*} = \frac{\sum_{i} \Delta E_{i}^{**}}{N_{A} \sum_{i} \Delta V_{i}},
\]

where \(\sum_{i} \Delta E_{i}^{**}\) is the reduced energy of intermolecular interaction, \(N_{A}\) is Avogadro’s number, and \(\sum_{i} \Delta V_{i}\) is the van der Waals volume of the repeating unit (or the repeating fragment of the network).

By setting up a redundant system of equations based on Eq. (11), we obtain the following values of the van der Waals volume of the repeating unit (or the repeating fragment of the network), the atomic constants and a small number of increments for dipole–dipole interactions, hydrogen bonds, and aliphatic and aromatic rings (Table 2). The increment value of the hydrogen bond energy for the \(-\text{NHCO}–\)amide groups was introduced separately.

Table 2. Atomic constants and increments with allowance made for specific interactions.

| Atom and type of intermolecular interaction | Designations | \(\Delta E_{i}^{**}\)kJ/mol |
|------------------------------------------|-------------|-----------------|
| Carbon                                   | \(\Delta E_{C}^{**}\) | -27.85          |
| Hydrogen                                 | \(\Delta E_{H}^{**}\) | 44.84           |
| Oxygen                                   | \(\Delta E_{O}^{**}\) | 19.5            |
Nitrogen $\Delta E_{N}^{\bullet\bullet}$ -19.5
Silicon $\Delta E_{Si}^{\bullet\bullet}$ 194
Chlorine $\Delta E_{Cl}^{\bullet\bullet}$ -9.5
Fluorine $\Delta E_{F}^{\bullet\bullet}$ 77.3
Sulfur $\Delta E_{S}^{\bullet\bullet}$ 637
Hydrogen bond for the $–$NHCO$–$ groups $\Delta E_{NHCO}^{\bullet\bullet}$ 353
Double bond $\Delta E_{d}^{\bullet}$ 190
Hydrogen bond $\Delta E_{h}^{\bullet\bullet}$ 30.5
Aromatic ring (skeleton) in the main chain $\Delta E_{ar.c,b}^{\bullet\bullet}$ 219
Aromatic ring (skeleton) in the side chain $\Delta E_{ar.c.s}^{\bullet\bullet}$ 123
Aliphatic cycle (skeleton) $\Delta E_{al.c}^{\bullet\bullet}$ 239
Dipole–dipole interaction $\Delta E_{d}^{\bullet\bullet}$ 122

The increment value of the hydrogen bond energy for the $–$NHCO$–$ amide groups was introduced separately.

For nanocomposites where the surfaces of nanoparticles are modified with chemical groups of a certain chemical structure, the relationship is:

$$P^\ast = \frac{\alpha_{m,p} \left( \sum \Delta E_{i}^{\bullet\bullet} \right)_{p} + (1 - \alpha_{m,p}) \left( \sum \Delta E_{i}^{\bullet\bullet} \right)_{cg}}{N_{A} \left[ \alpha_{m,p} \left( \sum \Delta V_{i} \right)_{p} + (1 - \alpha_{m,p}) \left( \sum \Delta V_{i} \right)_{cg} \right]},$$

where $\left( \sum \Delta E_{i}^{\bullet\bullet} \right)_{p}$ and $\left( \sum \Delta E_{i}^{\bullet\bullet} \right)_{cg}$ are the reduced energies of intermolecular interaction for the repeating unit of the polymer and the chemical group localized on the nanoparticle surface, respectively, and $\left( \sum \Delta V_{i} \right)_{p}$ and $\left( \sum \Delta V_{i} \right)_{cg}$ are the van der Waals volumes of the repeating unit of the polymer and the chemical group localized on the nanoparticle surface, respectively.

Since the volume of the nanoparticle $V_{np}$ depends on the shape (spherical, cylindrical, rectangular), according to equation (8), the permeability will also depend on the shape.

3. Effect of the orientation (ordering parameter) of filler elements

The uniform distribution of nanoparticles in the composition is a simple case for analysis and is rarely encountered in practice. The random distribution of nanoparticles is of a general nature and, therefore, we consider it in detail. In this case, the cumulative distribution function over $\Delta l$ is described by the relationship

$$F(\Delta l) = 1 - e^{-\Delta l / \bar{\Delta l}},$$

where $\Delta l$ is the linear space available for the penetration of water molecules and $\bar{\Delta l}$ is the average size of the linear space.

If water molecules penetrate through the accessible space of the membrane, when the nanoparticles are stacked in thickness perpendicular to the penetration front, we denote this as case 1, if in width, we denote it as case 2. The plots of $F(\Delta l)$ versus $\Delta l$ at different $\bar{\Delta l}$ values are shown in Fig. 1.
It is seen that portion $\Delta l$ depends on the average distance between neighboring nanoparticles. If case 2 is considered, the average distance between neighboring nanoparticles is longer. For this reason, the plots of $F(\Delta l)$ versus $\Delta l$ have the shapes shown in Fig. 1b.

In order to calculate the portion of the distance available for the penetration of water molecules, $\alpha_{\text{avail}}$, it is necessary to take into consideration that the diameter of this molecule is equal to $D = 3.2$ Å. The size of the areas accessible for water penetration should be twice as large as the diameter of the water molecule. Therefore, $\alpha_{\text{avail}}$ is calculated through the formula

$$\alpha_{\text{avail}} = 1 - F(\Delta l) = e^{-\frac{0.64}{\Delta l_{av}}}.$$  \hspace{1cm} (14)

The plots of $\alpha_{\text{avail}}$ versus $l_{av}$ are shown in Fig. 2.

It is obvious that the portion of the distance available for water penetration increases with an increase in $l_{av}$.

When there is a distribution of nanoparticles over rotation angles $\alpha$, the problem becomes more complicated. Let us consider the Poisson distribution:

$$P(k) = \frac{\lambda^k \exp(-\lambda)}{k!},$$ \hspace{1cm} (15)

where $k = 1, 2, 3, \ldots, n$; and $\lambda$ is the anticipated average value.

The plots of $P(k)$ versus $\alpha$ are shown in Fig. 3. It is evident that the maxima of dependences shift with regard to the rotation angle when the $\lambda$ value increases.

Now let us calculate the $\Sigma P(k)\Delta l$ values. The $P(k)\Delta l$ values were calculated preliminarily at $l_0 = 54.3$ nm and placed in Table 3.
Table 3. $P(k)\Delta l$ values at $a = 40$ nm, $b = 4$ nm, and $l_0 = 54.3$ nm

| $\alpha$ | $\lambda = 1$ | $\lambda = 2$ | $\lambda = 3$ | $\lambda = 4$ | $\lambda = 5$ | $\Delta L$ |
|----------|--------------|--------------|--------------|--------------|--------------|-----------|
| 10       | 5,2286       | 3,8470       | 2,1228       | 1,0413       | 0,4788       | 14,212    |
| 20       | 2,8221       | 4,1527       | 3,4373       | 2,2481       | 1,2922       | 15,342    |
| 30       | 1,0825       | 3,1857       | 3,9554       | 3,4491       | 2,4782       | 17,655    |
| 40       | 0,3231       | 1,9018       | 3,5419       | 4,1181       | 3,6987       | 21,079    |
| 50       | 0,0782       | 0,9207       | 2,5721       | 3,9873       | 4,4765       | 25,512    |
| 60       | 0,0157       | 0,3707       | 1,5535       | 3,2113       | 4,5069       | 30,819    |
| 70       | 0,0027       | 0,1266       | 0,7958       | 2,1933       | 3,8475       | 36,838    |
| 80       | 0,0004       | 0,0373       | 0,3515       | 1,2916       | 2,8322       | 43,387    |
| 90       | 5.1E-05      | 0,0096       | 0,1357       | 0,6651       | 1,8230       | 50,268    |

The plots of $P(k)\Delta l$ versus $\alpha$ are shown in Fig. 4, while the plots of $\Sigma P(k)\Delta l$ versus $\lambda$ are shown in Fig. 5.

4. Calculations of the membrane area available for water penetration

The orientation angle $\alpha = 0$. First of all, it is necessary to calculate the area of nanoparticles corresponding to case 1. The area of nanoparticles is $S_{n.p.} = n^2 \cdot a \cdot b$, where $n$ is the number of nanoparticles on a straight line; $a$ is the length of the nanoparticle, $b$ is its width. Using the formula (16)

$$n = \sqrt[3]{N} = \frac{10^7 \sqrt[3]{V}}{\sqrt[3]{abc}}$$

we obtain (taking into account, that $V = \Phi$):

$$S_{n.p.} = \frac{10^{14} ab}{\sqrt[3]{abc}} = \frac{\sqrt[3]{ab}}{\sqrt[3]{abc}} \cdot \sqrt[3]{c} \cdot \frac{1}{\sqrt[3]{\Phi}}, \text{ cm}^2$$

(17)

The portion of the region occupied by all nanoparticles in the plane of the membrane is $S_{np}$ because the total area of the membrane is $1 \text{ cm}^2$. The region between neighboring nanoparticles is estimated as $\Delta l_{av} \cdot b$ (case 1) and as $\Delta l_{av} \cdot a$ (case 2). In case 1, the region that is unavailable for the penetration of water molecules is...
\[ S_1 = \frac{3}{2} \sqrt[3]{\frac{\Phi}{abc}} \Delta l_{av, 1} b (1 - \alpha_{av}) = \frac{3}{2} \sqrt[3]{\frac{\Phi}{abc}} \Delta l_{av, 1} b \left(1 - e^{-0.64 / \Delta l_{av, 1}}\right). \]  

For case 2, the analogous value is determined as

\[ S_2 = \frac{3}{2} \sqrt[3]{\frac{\Phi}{abc}} \Delta l_{av, 2} a (1 - \alpha_{av}) = \frac{3}{2} \sqrt[3]{\frac{\Phi}{abc}} \Delta l_{av, 2} a \left(1 - e^{-0.64 / \Delta l_{av, 2}}\right), \]

where \( \Delta l_{av, 1} = \sqrt[3]{\frac{a b c}{\Phi}} - a \) and \( \Delta l_{av, 2} = \sqrt[3]{\frac{a b c}{\Phi}} - b \)

Thus, the total portion of the region that is unavailable for the penetration of water molecules is described as

\[ \alpha_{unav} = \frac{3}{2} \sqrt[3]{\frac{ab}{\Phi}} + \frac{3}{2} \sqrt[3]{\frac{c}{\Phi}} \left[ \Delta l_{av, 1} b \left(1 - \exp\left(-0.64 / \Delta l_{av, 1}\right)\right) + \Delta l_{av, 2} a \left(1 - \exp\left(-0.64 / \Delta l_{av, 2}\right)\right) \right] \]  

5. Conclusion

The proposed calculation scheme makes it possible to predict the permeability of polymeric nanocomposites containing planar nanoparticles with different shapes and concentrations to small molecules (in particular, water molecules). Disc-like and rectangular nanoparticles were considered. In the latter case, we paid attention to anisometric particles, which simulate the particles of nanoclay and other planar fillers. The permeability was shown to depend mainly on the concentrations of nanoparticles, their lengths, and their orientations in the polymer matrix. The given calculated scheme takes into account all these factors, the main point being that the proposed calculation scheme takes into account the chemical structure of the matrix polymer as well as the chemical structures of the modifying agents added to improve the compatibility of nanoparticles with the matrix. For this purpose, we proposed first and foremost a simplified version of our calculation scheme that allows the calculation of water permeation through matrix polymers and copolymers with consideration for their chemical structures and the ratio of components. The experimental verification showed good agreement between the calculated and experimental data on the change in the relative permeability during a change in concentration.

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