A review of the water barrier properties of polymer/clay and polymer/graphene nanocomposites

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ABSTRACT

This paper reviews the literature on moisture barrier properties of polymer/clay and polymer/graphene-based nanocomposites. The various models proposed to predict the effects of nanofillers in reducing water vapour permeability through polymers are outlined. These models are based on a range of different factors such as; tortuosity, geometry, platelet stacking, orientation, polymer chain confinement and plasticization. Published experimental studies of water vapour permeability in both polymer/clay and polymer/graphene nanocomposites are then reviewed. The extent to which the models are validated by the results of these studies is discussed, together with the degree to which the potential for water barrier improvement in polymer nanocomposites has been realised.

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1. 1. Introduction

Studies of the sorption and transport properties of water and water vapour in polymeric materials are of considerable importance in many industry sectors. These include diverse applications ranging from packaging materials for consumer products (e.g. food, pharmaceuticals and micro-electronics) through to damp-proofing materials, corrosion barrier films and reverse osmosis membranes. In the polymer packaging industry, especially the food sector, the water vapour barrier property provided by polymer films is a key factor in determining performance.

In recent years a number of interesting new technologies have emerged to enhance the barrier properties of polymer films. One of these is polymer nanocomposites. These novel materials contain relatively small amounts (typically less than 5 wt%) of nanometre-sized filler particles, which, if properly dispersed, have been found to cause significant reductions in both gas and water vapour permeability [1,2].

The latest development in this field is polymer/graphene nanocomposites [3]. Graphene-based nanofillers have much higher aspect ratios than clay-based nanofillers, and so these materials have the potential to provide barrier films for very sensitive applications, such as electronic devices.

The aim of this paper is to outline the various models that have been proposed to predict and/or to explain the effects of nanofillers in improving polymer barrier properties, to review the published experimental results of water vapour permeability in both polymer/clay and polymer/graphene nanocomposites, to review the extent to which the various models have been validated and also to comment on the extent to which the potential improvement in water barrier properties of the materials has been realised.

2. Fundamental principles

2.1. Theory, definitions and units

The fundamental principles describing the permeation of gases or vapours through polymer films have been discussed in numerous publications [4–11]. These principles underpin the work reviewed in this paper, and therefore will be briefly summarised below.

Permeation across a polymer film or coating involves both solubilisation of the penetrant molecule into the polymer matrix and diffusion through it [4,5].

Fick's first and second laws describe diffusion in many polymer systems. They are given in Eqs. (1) and (2) below: -

$$J = - D(c)\frac{dc}{dx} \tag{1}$$

$$\frac{dc}{dt} = \frac{d}{dx}\left[D(c)\frac{dc}{dx} \right] \tag{2}$$

Here, J represents the amount of penetrant moving through unit area per unit time (i.e. the flux), c is concentration, x is the direction of diffusion and D is the diffusion coefficient [4].

The flux can be described by Eq. (3), if there is a linear concentration gradient under steady state conditions.

$$J = D\frac{(c_1 - c_2)}{l} \tag{3}$$

Here, l is the thickness of the film, and c_1 and c_2 represent the penetrant concentrations at the two film surfaces. However, rather than measuring concentration in the surfaces of the film, it is usually easier to measure the partial pressures of the vapour or gas on either side of the film. Hence flux is more often represented by Eq. (4).

$$J = P\frac{(p_1 - p_2)}{l} \tag{4}$$

Here, p_1 and p_2, are the vapour pressures on either side of the polymer film. P is the permeability coefficient, which is the rate per unit area at which gas or vapour moves through unit thickness of the film under a single unit of pressure difference [4,5].

The concentration of gas or vapour in the polymer film surface is related to its vapour pressure in the gaseous state by means of the solubility coefficient (S), as given in Eq. (5).

$$c = S \cdot p \tag{5}$$

A relationship is derived between the permeability coefficient (P), diffusion coefficient (D) and the solubility coefficient (S) by combining Eqs. (3), (4) and (5):

$$P = D \cdot S \tag{6}$$

This simple and well known equation shows that permeability is the product of diffusivity and solubility [4–6]. Eq. (6) provides a good basis for a conceptual understanding of the basic principles of permeability through polymer films. Once the penetrant molecule has adsorbed onto the surface of the polymer, it must dissolve in the polymer matrix and then diffuse down a concentration gradient through the film, before desorbing from the opposite surface. Either the diffusivity, D, or the solubility, S, may be the rate controlling process. Meares [6] first reported that the permeation of gases, such as CO_2 and O_2, through polymer films is usually dominated by the diffusion coefficient. However, it is found that the water permeability through polymer films is likely to be controlled by the solubility of water in the polymer [5,7]. Hence, highly polar polymers have poor water barrier properties because of the high solubility of water in these polymers. On the other hand, non-polar polymers, like polyethylene, have very good water barrier properties because water has a low solubility in hydrophobic polymers.

The units of permeability require some consideration. As defined in Eq. (4), permeability has the following dimensions:

$$P = \frac{(amount\ of\ permeant) \times (film\ thickness)}{(area) \times (time) \times (pressure\ \ drop\ across\ film)}$$

This applies to the transport of most gases through most polymer films. However, for organic vapours and water, permeability can vary with both pressure drop and the thickness of the film. Hence, in these cases, data are usually expressed in terms of a transmission rate, Q, which has the dimensions:

$$Q = \frac{(amount\ of\ permeant) \times (film\ thickness)}{(area) \times (time)}$$

It is important to quote both the test temperature and the vapour pressure applied [8].

2.2. Fickian and non-Fickian diffusion

'Ideal' Fickian behaviour is exhibited by simple gases (e.g. O_2, H_2 and CO_2), which diffuse by random jumps between the polymer chains. Henry's law is obeyed and D is independent of both concentration and time. Water vapour diffusing through hydrophobic polymers can exhibit 'ideal' diffusion behaviour [4,5].

There are many polymer/penetrant systems for which D depends strongly on concentration. Examples of these involve solvents or organic vapours that need co-operative movement of a polymer chain segment to create an appropriately-sized 'hole'.