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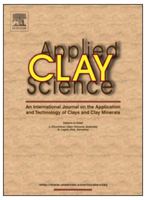

Research paper

Tortuosity model to predict the combined effects of crystallinity and nano-sized clay mineral on the water vapour barrier properties of polylactic acid

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ABSTRACT

The combined effects of crystallinity and nano-sized clay mineral (montmorillonite) fillers on the water vapour barrier properties of poly(lactic acid) (PLA) nanocomposites are investigated. Both amorphous and semi-crystalline PLA nanocomposites containing 0 to 5 wt% montmorillonite clay are prepared by melt compounding followed by compression moulding with two different thermal treatments: quenching and annealing. Thermal properties and morphology are investigated using differential scanning calorimetry (DSC), polarised light microscopy, transmission electron microscopy (TEM) and wide-angle X-ray diffraction (WAXD). It is confirmed that the nanocomposite structures are intercalated and the montmorillonite aspect ratio is measured to be 40 in both quenched and annealed samples. Water vapour transmission rates (WVTR) through the film samples are measured. A new tortuous path model is developed that fits the WVTR data and accounts for the effects of crystallinity as well as montmorillonite aspect ratio, concentration and orientation.

1. Introduction

The development of bio-based and compostable polymers in recent years has been in response to growing concerns about the environmental impact of plastic waste. Poly(lactic acid) (PLA) is one of the most commercially successful bio-plastics. Its monomer, lactic acid, is derived from renewable sources, such as starch or maize sugar, through fermentation (Garlotta, 2002). Since lactic acid has an asymmetric carbon atom, it has two optically active configurations (L- and D-lactic acid). Commercial PLA is produce by ring-opening polymerization of the lactide (Lim et al., 2008), which is a dimer of lactic acid. The two configurations can form into three forms of lactide: L-lactide (a dimer of L-lactic acid); D-lactide (a dimer of D-lactic acid) and meso-lactide (a dimer of L- and D-lactic acid). The crystallisability of PLA is dependent on the ratio of L-, D- and meso-lactide in the polymer backbone: higher crystallinities are obtained with the more optically pure polymers because of their higher chain symmetry (Madhavan Nampoothiri et al., 2010). PLA resin that contains 50%–93% L-lactic acid is amorphous and PLA with L-lactic acid higher than 93% is semi-crystalline (Auras et al., 2004).

A challenge posed by compostable polymers is that they tend to have poor water barrier properties compared with conventional thermoplastics. This is because they are polar polymers and therefore have high water vapour solubility and hence high permeability. One way of addressing this problem is through the development of clay mineral polymer nanocomposites, which have been very successful in improving barrier properties (LeBaron et al., 1999; Neppalli et al., 2014; Tan and Thomas, 2016). At relatively low additions of nano-sized clay mineral, it is possible to achieve quite dramatic reductions in permeability to both gases and water vapour. For example, Yano et al. reported a reduction of 83% in water vapour permeability in a polyimide/montmorillonite nanocomposite with a montmorillonite loading of 8 wt% (Yano et al., 1993). In a further study (Yano et al., 1997), a reduction of water vapour permeability of up to 90% was reported for a polyimide/mica composite with a mica content of only 2 wt%. These researchers demonstrated that the barrier properties of the nanocomposites are greatly affected by the length of the clay mineral filler particles.

It is generally accepted that the mechanism by which the barrier properties of polymer nanocomposites are improved is by a so-called 'tortuous path' effect. In this model, the diffusion path length of gas or water vapour molecules is dramatically increased due to obstacles created by impervious particles, as illustrated in Fig. 1. The model was first proposed by Nielsen (1967), who quantified the permeability of polymer/filler composites. In the 'Nielsen model', the single layers of

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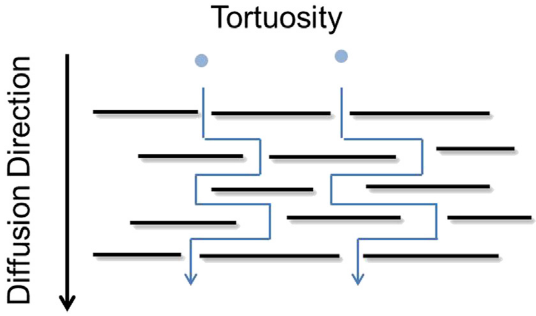

Fig. 1. Schematic diagram of the tortuous path model.

clay mineral are assumed to be circular or rectangular, evenly dispersed and aligned perpendicular to the diffusion direction. The Nielsen model is given in Eq. (1).

$$\frac{P_F}{P_u} = \frac{\varnothing_P}{\tau} \tag{1}$$

where P_F represents the permeability of the polymer composite, P_u represents the permeability of the unfilled polymer, $\varnothing_P$ is the volume fraction of the polymer, τ is the tortuosity factor as defined below:

$$\tau = \frac{\text{distance a molecule must travel to get through film}}{\text{thickness of film}}$$

In the Nielsen model the tortuous path is assumed to be the maximum distance that a diffusing molecule must travel, therefore τ is expressed as:

$$\tau = 1 + (L/2D)\varnothing_F \tag{2}$$

where L and D are the average length and thickness of the filler platelets, respectively, and $\varnothing_F$ is the volume fraction of the filler.

Combining Eqs. (1) and (2), the permeability equation becomes:

$$\frac{P_F}{P_u} = \frac{1-\varnothing_F}{1 + (L/2D)\varnothing_F} \tag{3}$$

Many models have been proposed to explain water vapour transport behaviour in polymer nanocomposites films. Tan and Thomas (2016) have reviewed the existing models for the prediction of moisture barrier properties of polymer nanocomposites and discussed anomalous phenomena that influence moisture barrier properties. Among these models, that due to Nielsen is the most commonly used to predict permeability and, despite its simplicity, the Nielsen equation has proved to be remarkably successful. For example, Yano et al. (1993) used the Nielsen equation to model the gas permeability of polyimide/montmorillonite nanocomposites. It was reported that the experimental results of gas permeability fitted the theoretical line predicted from the Nielsen model. In a recent study, Duan et al. (2013) showed that water vapour transmission rates through films of poly(lactic acid)/montmorillonite nanocomposites fitted well with the Nielsen equation.

It is generally agreed that the barrier properties of polymer membranes are related to crystallinity because impervious crystallites can act as barriers to the diffusion path of gases and water vapour molecules (Drieskens et al., 2009). One of the earliest papers on this was by Michaels et al. (1963), who studied diffusion of various gases in glassy and rubbery polyethylene terephthalate in the temperature range 25 to 130 °C. They found that below the glass transition temperature (T_g), diffusion was impeded by the presence of crystallites to an extent dependent on the reciprocal of the amorphous volume fraction. The effects of crystallisation polymorphism and crystallinity on the water vapour permeability of poly(L-lactic acid) has been studied by Cocca et al. (2011). They reported that water vapour permeability decreased slightly at low degrees of crystallinity but suddenly dropped dramatically when the crystallinity reached a certain range between 0.39 and 0.4. This rapid decrease in water vapour permeability was attributed to the change of crystal conformation from α′ to α.

Duan and Thomas (2014) have modified the Nielsen equation to predict the water vapour permeability of semi-crystalline PLA films by assuming that the spherulites are impermeable spherical particles. Hence, in Eq. (3) if $L = D$ and the volume fraction ($\varnothing_F$) is replaced by the degree of crystallinity (X_c), then the Nielsen model becomes

$$\frac{P_{\text{crystalline}}}{P_{\text{amorphous}}} = \frac{1-X_c}{1+\frac{1}{2}X_c} \tag{4}$$

In their study, a series of semi-crystalline PLA samples with crystallinity ranging from 0 to 50% was tested and the experimental results of water vapour permeability were found to fit well with the modified Nielsen model in Eq. (4).

In terms of gas permeation, Picard et al. (2011) predicted the effect of crystallinity on the oxygen barrier properties of semi-crystalline PLA nanocomposites using the Nielsen model (with $L = D$), and found good agreement between the theoretical and experimental permeability for semi-crystalline PLA films.

The effect of nano-sized clay mineral on the water vapour barrier properties of PLA nanocomposites has been reported in a number of studies (Gorrasi et al., 2004; Rhim et al., 2009; Sanchez-Garcia et al., 2008; Thellen et al., 2005; Zenkiewicz and Richert, 2008; Zenkiewicz et al., 2010; Duan et al., 2013; Espino-Pérez et al., 2013; Tenn et al., 2013). However, there is a limited number of studies on the combined effect of crystallinity and clay mineral on the barrier properties. Only Picard et al. (2011) investigated the effect of nano-sized montmorillonite on the gas barrier properties of both amorphous and annealed PLA nanocomposites. A reduction of 60% in oxygen permeability in an annealed PLA nanocomposite sample was shown to result from the respective contribution of the montmorillonite and the crystalline phase. Johansson and Clegg (2015) investigated oxygen permeability of both annealed and non-annealed nanocomposites of ethylene-modified poly(vinyl alcohol), with three different bentonites. It was found that the most effective bentonites for the reduction of oxygen permeability was Na-montmorillonite and that the combined effects of annealing and the nano-sized clay mineral caused a further reduction in the oxygen permeability.

The aim of this paper is to investigate the combined effects of crystallinity and montmorillonite concentration on the water barrier properties of PLA films and to quantitatively model the results. PLA nanocomposites containing 0 to 5 wt% montmorillonite are prepared by melt compounding followed by compression moulding with two different thermal treatments (i.e. quenching and annealing) to obtain amorphous and semi-crystalline samples. The morphology, thermal properties, and water vapour transmission rates of these samples are investigated. The combined effects of crystallinity and montmorillonite concentration on the water vapour barrier properties of PLA are investigated and a new tortuous path equation is derived to model the results.

2. Experimental

2.1. Materials

Two grades of polylactide (PLA) polymer (Ingeo™ 4060D and 4032D) were supplied by Natureworks LLC (Minnetonka, MN, USA). 4060D is an amorphous polymer with an average D-lactide content of 12 wt% and a glass transition temperature (T_g) of 55–60 °C, whereas 4032D is semi-crystalline with an average D-lactide content of 1.4 wt% and a melting point in the range 155–170 °C. The weight average molar mass (M_w) of the two polymers as determined by gel permeation