



Research paper

The influence of clay orientation and crystallinity on oxygen permeation in dispersion barrier coatings



Å. Nyflött^{a,c,*}, E. Moons^b, C. Bonnerup^c, G. Carlsson^a, L. Järnström^a, M. Lestelius^a

^a Department of Engineering and Chemical Sciences, Karlstad University, SE-651 88 Karlstad, Sweden

^b Department of Engineering and Physics, Karlstad University, SE-651 88 Karlstad, Sweden

^c Stora Enso, Karlstad Research Centre, SE-650 09 Karlstad, Sweden

ARTICLE INFO

Article history:

Received 13 November 2015

Received in revised form 23 February 2016

Accepted 24 February 2016

Available online 5 March 2016

Keywords:

Barrier coating

Kaolin

Polyvinyl alcohol

Permeability

Dynamic mass transport

Crystallinity

Kaolin orientation

ABSTRACT

In this study oxygen permeability in dispersion barriers produced from poly(vinyl alcohol) (PVOH) and kaolin clay blends coated onto polymeric supports was investigated. To determine the oxygen permeability, two measurement methods were used: the oxygen transmission rate (OTR) and the ambient oxygen ingress rate (AOIR). It was found that with increasing kaolin content the oxygen permeability increased, up to about 5 wt% kaolin, whereafter the oxygen permeability decreased, as was expected. The increased (>5%) kaolin loading lowered the diffusion because of an increased tortuosity. Structural information about the dispersion-barrier coatings, such as kaolin orientation and polymer crystallinity, was obtained from Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Kaolin orientation was influenced by the drying temperature, the thickness of the samples, and the kaolin concentration. The polymer crystallinity increased in thicker samples. The drying temperature did not show any clear effect on the crystallinity of thin samples, while for the thicker barriers, combined with a kaolin concentration lower than 20 wt%, a higher crystallinity was achieved at lower drying temperatures. This study demonstrates the strong influence of chemical and physical structures on the permeability of the investigated coatings.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In addition to being easy to handle, food packages should ensure food safety, quality, and freshness by regulating moisture, grease, and gas transport through the packaging material. Oxygen, for example, compromises the quality of packed food, especially if the food contains lipids (Lopez-Cervantes et al., 2003). Lipid oxidation is one of the most common causes of deterioration of food quality (Huis in't Veld, 1996). Other food products, such as baked goods, may also be sensitive to oxygen (Guynot et al., 2003).

Oxygen barriers are mostly based on non-renewable materials, such as poly(vinyl alcohol) (PVOH), aluminium, polyamides (PA), or ethylene vinyl alcohol copolymer. Occasionally, the barrier polymers are filled with clay particles. Different techniques can be used to provide paperboard with a barrier, such as lamination, extrusion, or dispersion coating. The performance of the oxygen barrier depends on the substrate, processing conditions, the polymer used, and on fillers (Bollström et al., 2013; Johansson et al., 2012).

The mass transport of oxygen through a barrier is affected by the polymer's characteristics as well as the barrier's free volume, porosity, and voids (Crank, 1979). The crystallinity of the polymer affects the

permeability, since more crystalline regions have lower solubility (Vieth, 1991) and can act like a tortuous path for the oxygen molecules (Grunlan et al., 2004; Hu et al., 2002). However, the presence of water can lower the effect of the crystalline phases and the tortuous path (Grunlan et al., 2004). Clay fillers increase the tortuosity, or the length of the pathway for the diffusant (Nielsen, 1967). Barrier properties are improved when the clay is oriented parallel to the basal plane and the platelets overlap (Minelli et al., 2009, 2011). However, if the clay is oriented perpendicular to the basal plane, clay fillers would not give any contribution to lowering the permeability compared to a pure polymer film (Sorrentino et al., 2006).

The permeability of oxygen through films and coatings made from polymers such as poly(lactic acid) (PLA), poly(hydroxyalkanoates) (PHA) or poly(caprolactones) (PCL), have been shown to decrease when filled with nanoclay when the concentration of nanoclay is <5 wt% (Sanchez-Garcia et al., 2010). Nanoclay also affects the crystallinity of the polymer (Sanchez-Garcia et al., 2010). Nanoclay fillers improve the oxygen barrier performance of poly(propylene) (PP) and affect the morphology, especially the exfoliation of the clay in the polymer matrix (Zehetmeyer et al., 2012). PVOH mixed with nanoclay was reported to have similar advantages in oxygen barrier performance and the morphology (Strawhecker and Manias, 2000; Yu et al., 2003).

The confined space, induced by the coating thickness, and drying temperature affect the barrier performance. The fillers and additives are able to orient in the confined space of the coating (Alam et al., 2006; Sand et al.,

* Corresponding author at: Department of Engineering and Chemical Sciences, Karlstad University, SE-651 88 Karlstad, Sweden.

2009a,b). The coating thickness define the confined space, which becomes smaller while drying (Sand et al., 2009a). A quick drying of the coating might be disadvantageous since it immobilises the structure (Andersson et al., 2002; Johansson et al., 2012).

Oxygen permeability can be measured using several techniques, such as luminescent dye, OxySense (Kerry et al., 2006) and Fibox (Galdi et al., 2008), and chromatographic methods (Andersson et al., 2002). We have chosen to use the oxygen transmission rate (OTR) method (the most commonly used technique) and the ambient oxygen ingress rate (AOIR), a method that captures mass transport, especially in the initial stage (Larsen et al., 2000; Nyflött et al., 2015).

The aim of this study is to investigate the effect of kaolin and crystallinity on the barrier properties of PVOH. The orientation and distribution of kaolin platelets were examined by variation of the concentration of clay in the coating, the barrier layer thickness, and the drying temperature. Crystallinity was varied, as a consequence of the film preparation and composition. This study was performed in laboratory scale to elucidate the influence of kaolin concentration and drying conditions on polymeric barrier coating films. However, the relationship between the studied process parameters and properties of the film constituent materials are complex as they are interdependent. For instance, the crystallinity depends on clay content, temperature and thickness of the films. Therefore this study focused on monitoring the structural properties for relevant scientific and industrial applications to understand the mechanism of oxygen mass transport process.

2. Material and methods

2.1. Materials

This study used barrier materials made from PVOH (Mowiol 15-99 from Kuraray, Frankfurt, Germany) and kaolin from USA with aspect ratio 60 (IMERYS, Sandersville, US). The kaolin particles were pre-treated with sodium polyacrylate (NaPAA). Sodium hydroxide (NaOH) (99.9% purity) and magnesium nitrate ($Mg(NO_3)_2$) (99.9% purity) were purchased from Merck (Darmstadt, Germany). Polyethylene terephthalate (PET) sheets (23- μm thick) were purchased from HiFi Industrial Films (Hertfordshire, UK).

2.1.1. Preparation of PVOH and kaolin dispersions

PVOH was dissolved in deionized water at 95 °C under gentle stirring for 1.5 h and then cooled to room temperature before film preparation. The concentration of the final PVOH solution was 15.3 wt%, the pH 6.1 and the conductivity $0.7 \cdot 10^{-3} S cm^{-1}$. The kaolin was dispersed in deionized water during stirring to a concentration of 60 wt% and then diluted to concentrations needed to receive the target concentration in the dry state. Some of the concentrations were above the calculated critical pigment volume concentration (CPVC) (theoretical CPVC 63 wt%) (Andersson, 2008; Asbeck and Loo, 1949). This produces at kaolin:PVOH ratios for some dispersion in which the PVOH will not be capable to fill all interstitial voids between the kaolin platelets. The pH and the conductivity of the kaolin suspension at 60 wt% were 6.3 and $1.9 \cdot 10^{-3} S cm^{-1}$, respectively.

2.1.2. Preparation of barrier coatings of PVOH and kaolin

The coatings were prepared with the same procedure as Nyflött et al. (2015). The nominal thicknesses of the wet films were 6, 12, 24, 50, and 100 μm , and the dried weight proportions of the dispersions are given in Table 1. These sheets were dried at 60, 95, or 160 °C in a heating chamber until the barrier coatings contained only 5% water. The barrier coating reached temperatures of approximately 50, 70, or 100 °C during drying (which are similar to temperatures used in the industrial manufacturing), as measured with an IR temperature sensor (Thermopoint TPT 62, FLIR system AB, Danderyd, Sweden). The water content in the barrier during drying was measured with a contactless NIR moisture sensor (FIBRO MCA 1410, FIBRO System AB, Hågersten,

Table 1

The dry PVOH and kaolin content for the different samples. The dashed line indicates the critical pigment volume concentration (CPVC).

Sample code	PVOH content / wt%	Kaolin content / wt%
PVOH100	100.0	0
PVOH98.9	98.9	1.1
PVOH98	98.0	2.0
PVOH94.3	94.3	5.7
PVOH89.8	89.8	10.2
PVOH80	80.0	20.0
PVOH72.1	72.1	27.9
PVOH62.2	62.2	37.8
PVOH47.6	47.6	52.4
PVOH27.9	27.9	72.1
PVOH24.6	24.6	75.4

Sweden). The dispersions were also poured into Petri dishes to make free-standing films (i.e., films without PET support); these films were dried at 23 °C and 50% RH.

Table 2 shows the thicknesses of the dry barrier coatings coated on PET, independent of kaolin concentration, measured using the procedure described by Nyflött et al. (2015). The PET sheet thickness of $22 \pm 0.1 \mu m$ was subtracted from the recorded thickness values to obtain the thickness of the barrier film layer. The free-standing films had a thickness of $30 \pm 3.3 \mu m$.

2.1.3. Kaolin analysis

The organic compounds in the kaolin were identified using thermogravimetric analysis (TGA) (TGA/SDTA851e, Mettler-Toledo, Schwerzenbach, Switzerland). The sample was heated at a rate of 25 °C/min from 50 to 525 °C and was kept at 525 °C for 40 min. The same heating rate was maintained up to 900 °C and the sample was kept at 900 °C for 10 min. The airflow was 50 ml/min during the whole process. The used kaolin contained $12.6 \pm 0.1\%$ organic parts.

The structure of the kaolin was analysed using X-ray diffraction (XRD) (D8 Advance, Bruker AXS, Karlsruhe, Germany) with Cr K (α) source in the 2θ -range from 2° to 65° (2θ is the total angle between the incident beam and the reflected on the crystal plane), Fig. 1. (Powder Diffraction Files, 2013).

The particle size distribution of dispersed kaolin with concentrations 0.43% and 0.22% were analysed using the sedimentation method (LUMiSizer, LUM GmbH, Berlin, Germany) according to ISO 13318-2. The results, presented in Fig. 2, revealed that the kaolin has at least two particle sizes (smaller size = 0.1–1 μm and dominating larger size = 1–5 μm). The different sizes of the platelets affect the packing in the PVOH matrix.

2.2. Methods

2.2.1. Fourier transform infrared spectroscopy

The FTIR spectra were collected with a Thermo Nicolet FTIR Nexus spectrometer (Madison, US) in attenuated total reflectance (ATR)

Table 2

Nominal wet film thickness and corresponding average dry thickness of the barrier coatings dried at 60, 95, and 160 °C (the kaolin concentration is omitted, since no thickness dependency was observed). Error margins are given as 95% confidence intervals.

Wet film thickness [μm]	Dry thickness @ 60 °C [μm]	Dry thickness @ 95 °C [μm]	Dry thickness @ 160 °C [μm]
6	1.8 ± 0.8	1.7 ± 0.6	2.4 ± 0.9
12	2.0 ± 0.8	2.1 ± 0.5	2.8 ± 0.8
24	2.3 ± 0.9	2.9 ± 0.7	3.0 ± 0.6
50	3.6 ± 0.8	4.2 ± 0.8	4.1 ± 0.6
100	5.3 ± 1.1	6.3 ± 1.2	5.9 ± 0.7

Download English Version:

<https://daneshyari.com/en/article/1694038>

Download Persian Version:

<https://daneshyari.com/article/1694038>

[Daneshyari.com](https://daneshyari.com)