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MODEL BASED DESIGN OF BARRIER COATINGS FOR PAPER BASED MATERIALS

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ABSTRACT

Paper based materials have limited vapour barrier properties. Several techniques have been developed to overcome this limitation. One of such technique is the use of barrier dispersion coatings. These barriers are continuous and solid layers normally applied on the surface of paper materials. Dispersion coatings are normally composed of two materials; a latex binder and filler particles. The interaction between these materials creates tortuous pathways that reduce the diffusion of the permeant. The main objective of this study was to develop an understanding of how the dispersion coatings can be designed to optimise the barrier properties of paper materials. In particular, the aim was to comprehend the effect of fillers added into dispersion coatings on the permeability with the purpose of developing of a model for predicting permeability.

A number of models have been developed to predict the permeability of barrier films such as thermoplastic composites but none have been applied or developed for use on barrier dispersion coatings. These models are normally based on idealised geometries, where the fillers are arranged in either oriented or random ways. The heterogeneous characteristics of the barrier dispersion coatings, such as uneven coating thickness, particle size and the lower elongation of the fillers used in dispersion coatings limit the use of the existing models for the prediction of dispersion coating barrier performance.

To develop a predictive model, the characterisation of aspects such as shape, size distribution and volume fraction of fillers in barrier coatings and their effect on the barrier performance were studied. The analysis of the geometry of fillers was carried out by image analysis from microscopy (scanning electron and light microscopes). This was carried out on three types of kaolin clays. The shapes, Feret diameters, and thicknesses of the clays were characterised. The filler shapes were elongated with an average ratio between the major and minor diameter being no larger than two. The Fourier series descriptor approximates the filler shape at the second harmonic. The Feret diameter and thickness were fitted to distribution curves. These distributions were used to define the fillers for generation of particle populations required for modelling. The particle populations can be based on either assuming representative filler shapes such as rectangular or elliptical plates or by the Fourier series descriptor.

Characterisation of dispersion coatings were also carried out. The dispersion coatings were formulated by styrene-butadiene latex and mixed with the selected clays at several filler volume fractions and applied on 160 $g \cdot m^{-2}$ linerboards. The characterisation was based on the measurement of water vapour transmission rate (WVTR) and oxygen transmission rate (O_2TR).

The coating thickness was also measured by scanning electron microscopy image analysis. The WVTR and O_2TR were shown to be sensitive to the type of filler, volume fraction of filler, and thickness of the coatings. Both the WVTR and O_2TR tended to be lower as the filler size, filler volume fraction, and coating thickness increased. The thickness of the coating was found to be dependent on the coating process (coated rod), coating formulation, and its variability on the linerboard topography.

The proposed model predicted the relative permeability based on the estimation of permeant flux by the Fick's first law through three dimensional coating geometries. The coatings were filled with rectangular plates randomly located. These plates were defined by distribution curves of maximum Feret diameter, elongation, and thickness of the selected clays. The amount of fillers in the coating was determined by part of filler volume fractions used for measurements of WVTR and O_2TR. The sizes of the geometries were defined by the representative elemental volume estimated from the filler volume fraction and the variation of the predictions. The geometries were generated by programming in Matlab under particular conditions of coating formulation and exposure.

The mathematical solution of the model was carried out by finite element method and solved by Comsol Multiphysics. As expected from the experimental characterisation of the coatings, the predictions indicated that the relative permeability reduced as the volume fraction of filler and the size of the clay increased; however, overestimation of the barrier properties were predicted. To understand the reasons for the discrepancy, several factors, that were not included in the conceptual model, were analysed. It was observed that the filler agglomeration and uncoated areas was the most significant factor that may affect the prediction of the relative permeability. Other factors such the uniformity of coating profile, and filler shape were found to have an effect on the prediction. Despite the discrepancy, the model was suitable for prediction of how to improve barrier performance trend. Thus, it was possible to evaluate different factors related to the barrier performance to find their best combination.

In order to optimise the formulation of barrier dispersion coatings, sensitivity analyses were carried out based on factors that affect the permeability. Filler settling in the coating or coatings with two layers were found to provide a reduction of relative permeability. This technique also may reduce the material used for coating preparation and the occurrence of uncoated areas. However, these effects were smaller than the effect of filler agglomeration on the barrier performance. For this reason, future studies should be focused on the improvement of dispersion of fillers in the coating binder. The application of the model in other coating formulations must consider the definitions of the concepts used in the study in order to apply the correct

information for running simulations.

Because this model was the first approach developed for dispersion coatings, several aspects were fully not explored in this study. In future research may be focused on the improvement of filler geometry characterisation, dispersion of fillers in the coating binder, incorporation of coating irregularities in the conceptual model, and incorporation of commercial coatings additives in the model. These points may increase the complexity of the model; however, it is expected that such complexity will be practical to be included in the model in the near future due to advances in computing capability for FEM simulations.

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LIST OF NOMENCLATURE

$\left(\frac{P_f}{P_u}\right)_{pinhole}$: Relative permeability of coating with one representative pinhole

$TR_f\big|_{z=0}$: Transmission rate of the coating at $z = 0\ \mu m$

$TR_f\big|_{z=K}$: Transmission rate of the coating at $z = K\ \mu m$

$\frac{P_f}{P_u}$: Relative permeability from simulation with even coating profile (normal simulations)

$Pf/Pu_{\alpha E}$: Relative permeability across the third dimensional aspect ratio

$\dot{m}_{N_2}$: Mass flow rate of nitrogen in the inlet ($g \cdot min^{-1}$)

$\dot{m}_{air_{in}}$: Mass flow rate of air in the inlet ($g \cdot min^{-1}$)

$\frac{\sigma_x}{\sigma_{N_2}}$: Ratio of the collision diameter of the permeant and nitrogen

$\emptyset_{F_1}$: Volume fraction of the first layer of the coating

$\emptyset_{F_2}$: Volume fraction of the second layer of the coating

$\emptyset_{F_{final}}$: Final volume fraction of coating formed by two layers

$\emptyset_F$: Volume fraction of fillers

Δp_f: Partial pressure of permeant for filled coatings (Pa)

Δp_u: Partial pressure of permeant for unfilled coating (Pa)

A_{O_2TR}: Area of permeability for O_2TR (m^2)

A_{f_i}: Surface area of the fillers assuming a regular shape

A_{f_i}: Surface area of fillers assuming a regular shape

A_{WVTR}: Area of permeability for WVTR (m^2)

A_d: Area of filler

$A_{exposure}$: Exposure area (m^2)

$A_{reference}$: Reference area (m^2)

C_{10}: Constant for calculation of partial pressure at saturation of the air

C_{11}: Constant for calculation of partial pressure at saturation of the air

C_{12}: Constant for calculation of partial pressure at saturation of the air

C_{13}: Constant for calculation of partial pressure at saturation of the air

C_8: Constant for calculation of partial pressure at saturation of the air

C_9: Constant for calculation of partial pressure at saturation of the air

D_f: Fractal dimension

D_{filled}: Diffusivity of permeant through the filled coating ($m^2 \cdot s^{-1}$)

$D_{unfilled}$: Diffusivity of permeant through the unfilled coating ($m^2 \cdot s^{-1}$)

E_D: Activation energy of diffusion ($J \cdot mol^{-1}$)

E_i: Elongation of the *i* filler

E_t: Theoretical elongation

F_{N_2}: Flow of oxyfree nitrogen ($mL \cdot min^{-1}$)

J_P: Permeant flux ($mol \cdot s^{-1} \cdot m^{-2}$)

J_{cyl}: Permeant flux through the coating when the cross section shape is assumed as cylinder ($mol \cdot m^{-2} \cdot s^{-1}$)

K_f: Coating thickness for a particular formulation (m)

$K_{layer\,1}$: Thickness of the first layer of the coating

$K_{layer\,2}$: Thickness of the second layer of the coating

$K_{no\,sed}$: Thickness of the unfilled region (m)

K_{sed}: Thickness of the settling region(m)

K_{sv}: Stern-Volmer constant

L_i: Length of the *i* filler (m)

L_i: Maximum Ferert diameter of the *i* filler (m)

P_f: Permeability of filled coatings ($mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$)

P_u: Permeability of unfilled coating ($mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$)

RH_{in}: Relative humidity inside of the gravimetric cup

RH_{out}: Relative humidity outside of the gravimetric cup

$RP_{no\,sed}$: Relative permeability of the unfilled region

RP_{obs}: Relative permeability of analysed barrier dispersion coatings

RP_{sed}: Relative permeability of the settling region

$RP_{settling}(\emptyset_F)$: Relative permeability at filler volume fraction $\emptyset_F$

$RP_{settling}$: Relative permeability of a barrier dispersion coating with filler sedimentation

TR_f: Transmission rate of permeant for filled coatings ($mol \cdot m^{-2} \cdot s^{-1}$)

TR_{fk}: Transmission rate of the permeant through the coating for a particular coating formulation and conditions of exposure ($mol \cdot m^{-2} \cdot s^{-1}$)

TR_n: Normalised TR for either WVTR or O_2TR ($mol \cdot m^{-2} \cdot s^{-1}$)

$TR_{pinhole}$: Transmission rate through the pinhole ($mol \cdot m^{-2} \cdot s^{-1}$)

TR_u: Transmission rate of permeant for unfilled coating ($mol \cdot m^{-2} \cdot s^{-1}$)

T_g: Glass transition temperature of the coating ($°C$)

$V_{coating}$: Volume of coating after drying and consolidation of the substrate (mL)

V_{filler}: Volume of fillers (mL)

$V_{latex\,dry}$: Volume of dried latex (mL)

$V_{solid\ part\ binder}$: Volume of solid part of the binder (mL)

$WVTR_{filled}$: Normalised water vapour transmission rate of barrier dispersion coatings filled at different volume fraction of filler

$WVTR_{unfilled}$: Normalised water vapour transmission rate of unfilled barrier dispersion coatings

Xf_{solid}: Solid content of the latex

X_{max}: Maximum average of the relative permeability for the previous five estimations of the relative permeability

X_n: Average of the relative permeability at iteration n

a_n: Magnitude of each harmonic

b_{f_i}: Thickness of fillers assuming a regular shape

b_i: Thickness of the i filler (m)

b_n: Phase of each harmonic

c_{N_2}: Concentration of oxygen of the nitrogen inlet (0%)

c_{N_2/O_2}: Concentration of oxygen in the outlet of the carrier gas chamber (%)

$c_{air_{in}}$: Concentration of oxygen in the air inlet (21 %)

$c_{air_{out}}$: Concentration of oxygen in air inlet (%)

c_{bottom}: Concentration of permeant on the bottom surface of coating $(mol \cdot m^{-3})$

c_{top}: Concentration of permeant on the top surface of coating $(mol \cdot m^{-3})$

c_{wv}: Concentration of water vapour at either bottom or top coating surface $(mol \cdot m^{-3})$

$d_{F_{max}}$: Maximum Feret diameter of the filler

$d_{F_{min}}$: Minimum Feret diameter of the filler

d_F: Statistical diameter defined as the distance between pairs of parallel tangents to the projected outline of the particle in some fixed direction

d_M: Statistical diameter defined as chord length, parallel to some fixed direction, which divides the particle projected outline into two equal area

d_a: Diameter of a circle having the same projected area as the particle in stable orientation

d_c: Diameter of a circle having the same perimeter (P) as the projected outline of the particle

d_p: Diameter of a circle having the same projected area as the particle in random orientation

$d_{pinhole}$: Diameter of the pinhole (m)

d_s: Diameter of a sphere having the same surface (S) as the particle

d_{sv}: Diameter of a sphere having the same external surface to volume ratio as the particle

d_{trial}: Diameter of the coating trial (m)

d_v: Diameter of a sphere having the same volume (V) as the particle

f_{bR}: Bulkiness of fillers

$gsm_{linerboard}$: Grammage of the linerboard $(g \cdot m^{-2})$

gsm_n: Coat weight for normalisation $(g \cdot m^{-2})$

gsm: Coat weight of the coating trials $(g \cdot m^{-2})$

k_e: Shape parameter

$m_{V_{solid\ part\ binder}}$: Mass of the solid part of the binder (g)

m_{perm}: Molecular weight of any permeant gas $(g \cdot mol^{-1})$

m_{WV}: Molecular weight of water vapour $(18.02\ g \cdot mol^{-1})$

m_{filler}: Mass of the fillers (g)

$m_{latex\ dry}$: Mass of the dried latex (g)

m_p: Mass of pycnometer (g)

m_{pf}: Mass of pycnometer and fillers (g)

m_{pf}: Mass of pycnometer and filler sample (g)

m_{pl}: Mass of pycnometer raised with reference liquid (g)

m_{plf}: Mass of pycnometer raised with reference liquid and filler sample (g)

m_{total}: Total mass of filler in a given sample

m_{trial}: Mass of the coating trial sample (g)

nx_i: Initial number of segments of coating grid through x-axis

ny_i: Initial number of segments of coating grid through y-axis

nz_i: Initial number of segments of coating grid through z-axis

p_{atm}: Atmospheric pressure

p_{bottom}: Partial pressure on bottom coating surface (Pa)

p_{sat}: Saturated pressure (Pa)

p_{top}: Partial pressure on top coating surface (Pa)

p_v: Current partial pressure at either bottom or top surface of the coating (Pa)

p_{vs}: Partial pressure at saturation at either bottom or top side of the coating (Pa)

r_1: Radius of the shortest distance between a coating surface and the imaginary centre of the cylinder (projection of the radius) (m)

r_2: Radius of the largest distance between a coating surface and the imaginary centre of the cylinder (projection of the radius) (m)

sd_{max}: Maximum standard deviation of the relative permeability for the previous five

estimations of the relative permeability

sd_n: Standard deviation of the relative permeability at iteration n

x_e: Elongation of the filler

x_f: Thickness of filled coatings (m)

x_f: Length (m) or thickness (m) of the fillers at a particular probability

x_{max}: Maximum length(m) or thickness (m) of the fillers at a particular probability

x_{min}: Minimum length(m) or thickness (m) of the fillers at a particular probability

x_u: Thickness of unfilled coating (m)

$y_{settling}$: Fraction of the coating thickness where the settling occurs

γ_1: Angle formed between the centre of the rotated filler and a corner with the original position as references

γ_2: Angle formed between the centre of the filler and a corner

γ_F: Maximum angle of filler orientation

$\frac{\varepsilon}{k}$: Lennard-Jones temperature (K)

μ_e: Location parameter

μ_e: Location parameter

μ_f: Average of the logarithm of length(m), or thickness (m) of the fillers

μ_f: Average of the logarithm of length or thickness of the fillers

$\rho_{V_{solid\ part\ binder}}$: True density of the solid part of the binder $(g \cdot mL^{-1})$

ρ_{filler}: True density of the filler $(g \cdot mL^{-1})$

ρ_l: Density of the reference liquid $(g \cdot mL^{-1})$

$\rho_{latex\ dry}$: True density of the dried latex $(g \cdot mL^{-1})$

ρ_{latex}: True density of the liquid latex $(g \cdot mL^{-1})$

ρ_{liquid}: True density of liquid part $(g \cdot mL^{-1})$

σ_e: Scale parameter

σ_e: Scale parameter

σ_f: Standard deviation of the logarithm of length(m) or thickness (m) of the fillers

σ_f: Standard deviation of the logarithm of length or thickness of the fillers

τ_0: Fluorescence lifetime at 0% of oxygen

ψ_{Ap}: Circularity of fillers

ψ_s: Sphericity of fillers

ΔH_S: Heat of solution $(J \cdot mol^{-1})$

Δc: Variation in concentration between surfaces $(mol \cdot m^{-3})$

Δm: Variation in mass of the gravimetric cup during time (g)

Δp: Difference in partial pressure of permeant on both sides of the barrier dispersion coating

Δp: Difference of partial pressure between coating trials surfaces (Pa)

c: Concentration of permeant on the surface of the dispersion coating $(mol \cdot m^{-3})$

A: Area of permeability (m^2)

A: Area of the matrix

C: Roundness of fillers

C: Length of fillers in the width direction

D: Diffusivity coefficient $(m^2 \cdot s^{-1})$

E: Elongation of fillers

$F(x_f; \mu_f, \sigma_f)$: Cumulative distribution function of the length, or thickness of fillers

F: Flatness of fillers

J: Length of coating (m)

K: Thickness of coating (m)

L: Length of fillers

M: Width of coating (m)

N: Number of fillers for coating definition

P: Permeability of coating trials of such as WV or O_2 $(mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa)$

Q: Amount of permeant passing through the barrier coating (g)

$R(\theta)$: Radius generated from Fourier shape descriptor

R: Ideal gas constant $(8.314\ J \cdot mol^{-1} \cdot K^{-1})$

RH: Relative humidity at either bottom or top coating surface

S_{order}: Parameter of order of the Bharadwaj model

TR: Transmission rate of permeant $(mol \cdot m^{-2} \cdot s^{-1})$

a, s: Space between two parallel filler layers and the slit between two filler particles

b: Thickness of fillers

c: Concentration gradient of the gas $(mol \cdot m^{-3})$

$f(x_f; \mu_f, \sigma_f)$: Probability density function of the length or thickness of fillers

n: Number of harmonics

p: Partial pressure of the permeant (Pa)

r: Diagonal (hypotenuse) formed between any corner and the centre of a filler

s: Solubility of the permeant $(mol \cdot m^{-3} \cdot Pa^{-1})$

t: Time of measurement (day)

x: Thickness of the barrier (m)

α: Aspect ratio of fillers

δ: Ratio between A_d and A

θ: Temperature $(°C)$

λ: Linear fraction or the ratio between the thickness of the fillers and the total thickness of the barrier

μ: Mean of the natural logarithm of the Fourier shape descriptor parameters

σ: Standard deviation of the natural logarithm of the Fourier shape descriptor parameters

τ: Fluorescence lifetime of the sample

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