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The Effect of Liquid Absorption on Gas Barrier Properties of Triplex Film Coated with Silicon Oxide

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Summary

Polymeric triplex film with SiO_x deposit (polyethylene terephthalate/polyethylene terephthalate+SiO_x/polyethylene) was analysed for its gas permeance characteristics. For this purpose the permeance of triplex film to oxygen, nitrogen and carbon dioxide was analysed before and after the immersion into the test solutions (ethanol, acetic acid and distilled water). Gas permeance measurements were performed in temperature range from 20 to 60 °C. The permeability of the treated triplex film (181–241 $cm^3\ m^{-2}\ d^{-1}\ bar^{-1}$) showed negligible changes in comparison with the untreated ones (164–257 $cm^3\ m^{-2}\ d^{-1}\ bar^{-1}$). Due to the existence of inflection point at 40 °C, the Arrhenius equation was applied in narrow temperature ranges (20–35 °C and 40–60 °C). The obtained activation energies for the permeance of gases were correlated with different physical characteristics of permeates.

Key words: barrier properties, SiO_x, temperature, test solutions, triplex film

Introduction

Polyethylene terephtalate (PET) is the basic material for vacuum coated films. It represents an industrial reference for the process of physical vapour deposition (PVD) as well as plasma-enhanced chemical vapour deposition (PECVD). These processes allow improvements of the barrier properties of the basic films. To achieve significant barrier improvements upon thin film coating with aluminium or silicon oxide, surface pretreatment process with active oxygen is usually applied (*1,2*).

One of the newly introduced food packaging materials is plastic coated with a barrier film of an oxide such as silicon oxide. This type of coated plastic is often referred to as »flexible glass«, and silicon oxides used as barrier coating are referred to as SiO_x (*1*). This is because the high vacuum evaporation process yields a mixture of silicon mono- and dioxide (*1,2*). The x-values range between 1.5 and 1.8, where low x-values give the best oxygen barrier effect, but also the highest tendency toward yellowing. A good compromise with respect to these two contradictory properties is to choose an x-value of about 1.7 (*2*). Furthermore, SiO_x is very inert and fulfills the EU Directive on migration (*3*). Silicon oxide barrier is offered as a laminate with very thin SiO_x layer between polymeric films (*1,2*). This technology is still in the development stage and is trying to cross many hurdles like cost effective coating process. Better understanding of food/packaging interaction is needed to recognize the factors that influence the transport mechanism through this material. These include temperature (*4*) and relative humidity (*5,6*). It was shown that relative humidity had considerable influence on permeability and sorption characteristics in low-density linear polyethylene (PE-LLD), high-density polyethylene (PE-HD) and ethylene/vinyl-alcohol (E/VAL) (*5,6*). The aim of this work was to establish gas permeance characteristics

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of newly introduced food packaging material (triplex film with SiO_x deposit) prior to and after the exposure to different temperature and food simulants.

Experimental

The used laminate system, obtained directly from the producer, is composed of polyethylene terephthalate/polyethylene terephthalate+SiO_x/polyethylene (PET/PET+SiO_x/PE) with total thickness of 0.095 mm.

Acetic acid 3 %, alcohol solution 15 % and distilled water were used as food simulants, according to the EU rules (*7*). Gas permeance was determined by manometric method using permeability testing appliance, Type GDP-E (Brugger Feinmechanik GmbH), and was calculated according to the following equation (*8*):

$$q = k_1 \frac{V}{N\,T} \qquad /1/$$

where q = permeance (cm^3 m^{-2} d^{-1} bar^{-1}), V = measurement volume (cm^3), N = slope of the measurement curve (s/scale division), T = temperature (K) and $k_1 = 3.41 \cdot 10^7$.

Permeability constant

$$P = k_2\; q\; l \qquad /2/$$

where: P = permeability constant (cm^2 s^{-1} bar^{-1}), k_2=1.16 · 10^{-9} and l = polymer thickness (cm).

Permeance measurements of solvent treated samples are performed in temperature range from 20 to 60 °C (HAAKE, F3 thermostat). Permeance measurement of triplex film was also analysed after the immersion in the test solutions (ethanol 15 %, acetic acid 3 % and distilled water) at 40 °C for 24 h. Afterwards, the treated samples were placed on thick, absorbent paper for a few seconds to soak up excess liquid before permeability measurements. The amount of absorbed solvent in triplex film was determined gravimetrically and expressed as the mass increase (Δm/g) for an exposed area of A/cm^2. The mean value of 5–7 measurements for the permeance was taken. In order to calculate the amount of absorbed solvents, 24 samples were analysed for each test solution.

The temperature dependence of permeability (P) is described according to the Arrhenius expression:

$$P = P_0 \exp\left(-\frac{E}{RT}\right) \qquad /3/$$

where: P_o = permeability constant extrapolated to infinitely low temperature (cm^2 s^{-1} bar^{-1}), E_p = activation energy for permeation (J mol^{-1}), T = temperature (K), R = gas constant (J mol^{-1} K^{-1}).

Results and Discussion

Fig. 1 shows the results of gas permeance through triplex film with SiO_x deposit at different temperatures. The permeance values are between 164 and 257 cm^3 m^{-2} d^{-1} bar^{-1}. These values are higher compared to the minimum achieved permeation rates, from 2 to 4 cm^3 m^{-2} d^{-1} bar^{-1}, reported for PET film with SiO_x deposit (*9*).

According to Nelson (*10*) permeability dependence on coating thickness is not applicable to SiO_x films because it does not take into account defects such as pinholes, which are always present in the structure. It was also reported that the barrier is enhanced as the coating thickness is increased (*11*). The exact thickness for the SiO_x layer of the investigated triplex film is not indicated and according to literature data it could be from 60 nm (*11*) to 120 nm (*2*).

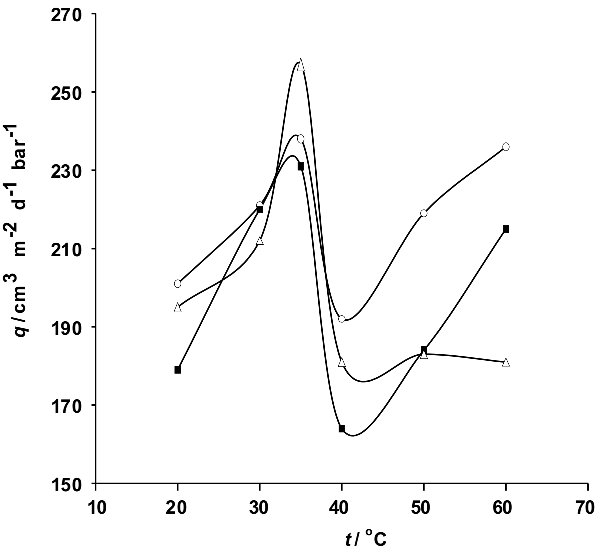

Fig. 1. Permeance (*q*) values through triplex film with SiO_x deposit at different temperatures ○ N_2, ■ O_2, △ CO_2

Generally, permeance values were not affected by either temperature or solvent treatment (181–241 cm^3 m^{-2} d^{-1} bar $^{-1}$). Similar values were obtained for the same samples after the exposure to 30–150 stress cycles (*12*). According to literature data (*13,14*) the oxygen permeation through vacuum web coated barrier layers, like Al, AlO_x, SiO_x and melamin, occurs predominantly at macroscopic defects about 0.1 μm in diameter. Differ-

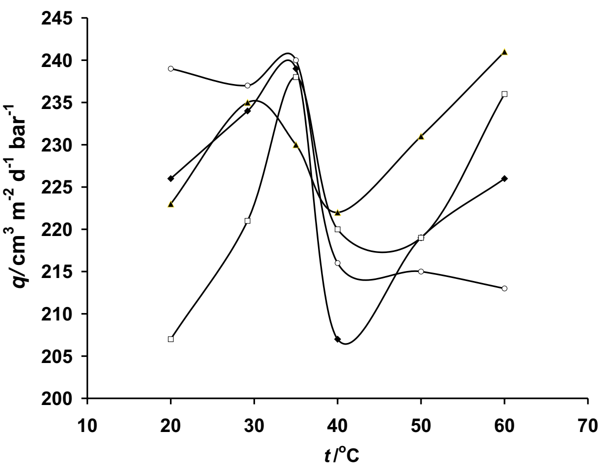

Fig. 2. Temperature dependence of O_2 permeance in triplex film with SiO_x deposit ◆ ethanol, ○ acetic acid, ▲ water, □ dry

ences in barrier properties are explained by the nature of the coating material, coating thickness and surface morphology (*11*).

The main characteristic of the analysed samples is the existence of an inflection point, most frequently at 40 °C (Figs. 2–4). Due to the existence of the inflection point the Arrhenius behaviour of gas permeability constant, predicted by equation /3/, *vs.* the inverse temperature is not applicable in the investigated temperature range (Figs. 2–4). In order to display the Arrhenius behaviour and to calculate the activation energy for permeation permeability constant *vs.* inverse temperature in close temperature ranges (20–35 and 40–60 °C) is used and the activation energy for permeance is calculated (Table 1). Literature data on gas properties (*15–17*) were used in order to find which property (Table 2) of the permeates correlates with the activation energies (Ea_I and Ea_{II}) for permeation through triplex film (Table 1).

Generally, better correlation (Table 1) is obtained at lower temperature interval (20–35 °C). This is especially evident for the molecular diameter, average velocity, mean free path and gas density. Identical behaviour is obtained with van der Waals constant *a*, which is a measure of the attraction force between the molecules, while the term *b* is due to the finite volume of the molecules and to their general incompressibility (*15*). Diffusion coefficient and molecular volume of gases showed better correlation (r = 0.71–0.99), both for dry and solvent treated samples at higher temperature interval (40–60 °C) in comparison with low temperature interval (20–35 °C).

The lowest amount of absorbed solvent (Fig. 5) is obtained with an acetic acid treatment (average of 0.0038 g cm^{-2}), where slightly higher values are obtained with ethanol and water treatment (0.0046 and 0.0045, respectively).

The activation energy for the permeation of gases decreases when triplex film is treated with a solution. This could be due to the water molecule and its ability to form extensive hydrogen-bonded networks with itself and to hydrogen-bond strongly to other polar materials.

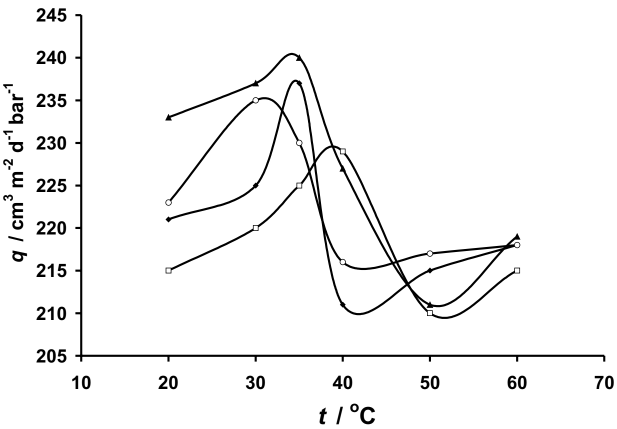

Fig 3. Temperature dependence of N_2 permeance in triplex film with SiO_x deposit ◆ ethanol, ○ acetic acid, ▲ water, □ dry

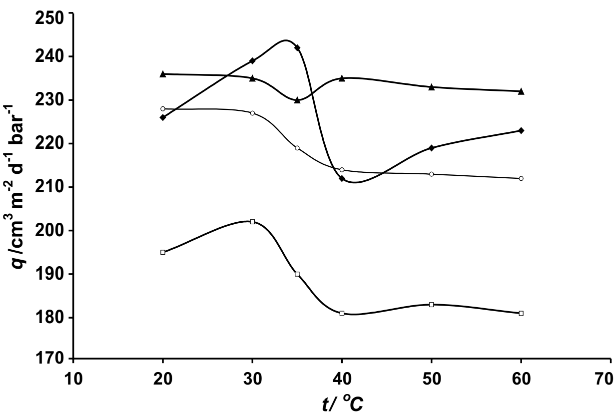

Fig. 4 Temperature dependence of CO_2 permeance in triplex film with SiO_x deposit ◆ ethanol, ○ acetic acid, ▲ water, □ dry

Table 1. Correlation (r) between the activation energy (*Ea*/ J mol^{-1})* for permeation and the gas properties obtained for triplex film with SiO_x deposit before (dry) and after the treatment with ethanol (EtOH), acetic acid (AcOH) and distilled water (H_2O)

	Gases	EtOH		AcOH		H_2O		Dry	
		Ea_I	Ea_{II}	Ea_I	Ea_{II}	Ea_I	Ea_{II}	Ea_I	Ea_{II}
Gas properties	N_2	3258	1423	1993	403	1497	–1484	2260	–2673
	O_2	2861	3820	77	–616	1992	3592	6846	3208
	CO_2	3665	2200	–1804	–411	–1171	–558	–691	–17
		Correlation coefficient (r)							
Molecular diameter /cm ·10^{-8}		**0.99**	**–0.64**	**–0.52**	0.19	**–0.94**	**–0.75**	**–0.99**	**–0.52**
Average velocity /cm s^{-1} ·10^2		**–0.67**	–0.12	**0.98**	**0.60**	**0.89**	0.03	**0.57**	–0.26
Mean free path /cm·10^{-8}		**–0.97**	0.35	**0.77**	0.17	**0.99**	0.49	**0.88**	0.22
Critical volume / cm^3 mol^{-1}		**0.96**	**–0.85**	-0.23	0.46	**–0.79**	**–0.92**	**–0.99**	**–0.76**
Viscosity / μP		**–1**	**0.65**	**0.50**	-0.18	**0.93**	**0.76**	**0.99**	**0.54**
Diffusion coeff. of gases in water at 20 °C cm^2 s^{-1}·10^5		–0.17	**0.85**	**–0.77**	**-0.99**	–0.19	**0.77**	0.29	**0.92**
Gas density / kg m^{-3}		**0.73**	0.04	**–0.96**	**-0.54**	**–0.93**	–0.11	**–0.63**	0.18
van der Waals constant *a* / bar L^2 mol^{-2}		**0.99**	**–0.56**	**–0.60**	0.06	**–0.97**	**–0.68**	**–0.97**	–0.43
van der Waals constant *b* / L mol · 10^{-2}		**0.98**	**–0.79**	–0.31	0.38	**–0.84**	**–0.88**	**–0.99**	**–0.70**
Molecular volume / cm^3 mol^{-1}		**0.82**	**–0.97**	0.09	**0.71**	**–0.56**	**–0.99**	**–0.89**	**–0.93**

Table 2. The most important properties of gases used in the experiments

Properties	Nitrogen	Carbon dioxide	Oxygen	Ref.
Molecular diameter / cm · 10^{-8}	3.15	3.34	2.98	(*15*)
Mean free path / cm · 10^{-6}	9.29	6.15	9.93	
Average velocity / cm s^{-1} · 10^{2}	471	376	440	
van der Waals constant *a* / bar L^2 mol^{-2}	1.39	3.59	1.36	
van der Waals constant *b* / L mol · 10^{-2}	3.91	4.27	3.18	
Critical volume /cm^3 mol^{-1}	90.1	94	78	(*16*)
Viscosity / μP	176	147	204	
Gas density / kg m^{-3}	1.25	1.98	1.43	(*17*)
Molecular volume / cm^3 mol^{-1}	31.2	30.7	25.6	
Solubilities of gases in water at different temperatures/ cm^3 dm^{-3}	16.0 (20 °C) 12.5 (40 °C) 10.2 (60 °C)	878 (20 °C) 530 (40 °C) 360 (60 °C)	31 (20 °C) 23 (40 °C) 19 (60 °C)	
Diffusion coefficients of gases in water / cm^2 s^{-1} · 10^5	1.64	1.77	1.8	

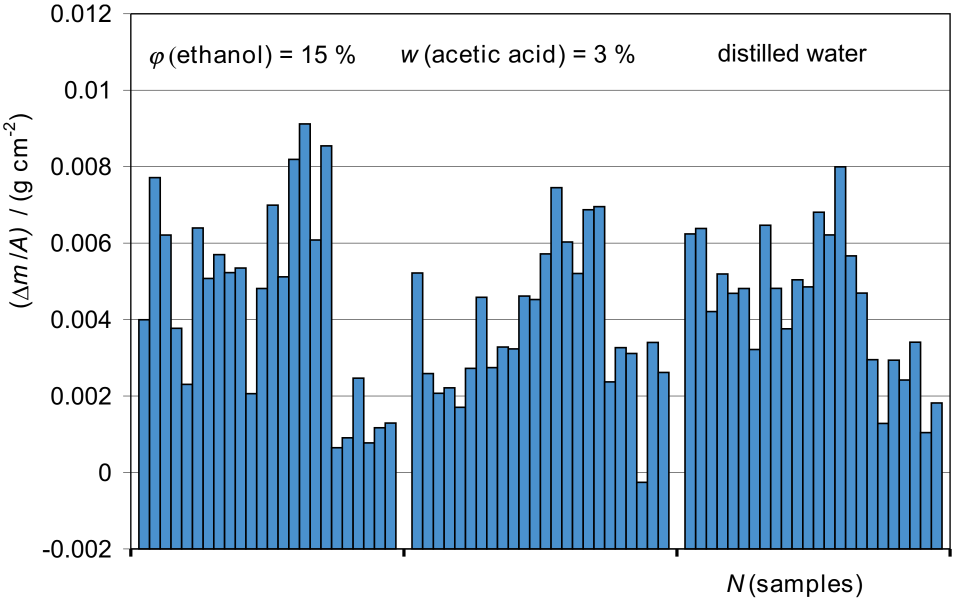

Fig. 5. The amount of absorbed solvent in triplex film with SiO_x deposit during 24 h at 40 °C for different samples

Similar effect is observed with alcohols, although the bond energy is much lower compared to that of water (*18*). At this point, further research on different solvent absorption mechanisms is needed in order to explain the effect of Si-O network and the resulting barrier effect.

Conclusion

Taking into account all treatments, *i.e.* temperature and immersion tests, to which triplex film with SiO_x deposit has been submitted and the resulting permeance values, one can conclude that this film is able to maintain the original barrier properties to protect the product against gases during processing, handling and in contact with liquid media.

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Utjecaj apsorpcije otapala na propusnost plinova kroz tripleks-film s prevlakom silicijevog oksida

Sažetak

U radu je istraživana propusnost plinova kroz tripleks-film s nanosom SiOx (polietilentereftalat/polietilentereftalat+SiOx/polietilen). U tu je svrhu određena propusnost kisika, dušika i ugljikova dioksida kroz tripleks-film prije i nakon uranjanja u test-otopine (etanol, octena kiselina i destilirana voda). Ispitivanja propusnosti plinova provedena su u rasponu od 20 do 60 °C. Propusnost obrađenog tripleks-filma (181–241 $cm^3\ m^{-2}\ d^{-1}\ bar^{-1}$) pokazuje zanemarive promjene u usporedbi s filmom koji nije bio izložen djelovanju test-otopina (164–257 $cm^3\ m^{-2}\ d^{-1}\ bar^{-1}$). Zbog postojanja točke infleksije, pri 40 °C, Arrheniusova jednadžba primijenjena je za usko temperaturno područje (20–35 i 40–60 °C). Dobivene vrijednosti energije aktivacije za propusnost plinova uspoređene su s različitim fizikalnim parametrima permeata.