



Improved oxygen barrier performance of poly(vinyl alcohol) films through hydrogen bond complex with poly(methyl vinyl ether-co-maleic acid)

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ABSTRACT

Hydrogen bonding between poly(methyl vinyl ether-co-maleic acid) (PMVE-MA) and poly(vinyl alcohol) (PVOH) has resulted in films with lower oxygen transmission rates (OTR) than pure PVOH. In the range 20–30% (w/w) PMVE-MA, complexation between the two polymers in the blend was maximized, as shown by viscometry, Fourier Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC) analysis. OTR measurements have shown that the maximum interpolymer complexation ratio also correlates with the lowest OTR values of the resulting film. The improved oxygen barrier properties are believed to be a combination of the relatively intact PVOH crystalline regions as shown with X-ray diffraction (XRD) and a higher degree of hydrogen bonding in the amorphous regions of the PVOH and PMVE-MA films as indicated by glass transition temperature (T_g) shifts. This leads to denser amorphous regions that reduces the rate of gases diffusing through the polymer film, hence the reduced OTR.

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1. Introduction

Interpolymer complexes stabilised through hydrogen bonding can be described as the association of a polyacid with a polybase [1]. Unique properties of these complexes include increased impact and tensile strength and controlled swelling, useful in a wide range of applications. In particular, considerable attention is given to the application of polymer complexes as drug carriers, in which advantage is taken of their controlled release capabilities [2,3].

Poly(vinyl alcohol) (PVOH) exhibits a complexation ability with complimentary polymers [4,5]. A previous study has shown that an interpolymer complex is formed owing to hydrogen bond interaction between the hydroxyl (—OH) groups of PVOH and the carboxylic acid (—COOH) and ether (—O—) groups of poly(methyl vinyl ether-co-

maleic acid) (PMVE-MA) [6]. The interaction between the PVOH and PMVE-MA, and thus the resulting physical properties, are sensitive to the molar ratio of the two polymers, with a maximum interaction occurring at a specific ratio.

PVOH is also known for its good gas-barrier properties [7]. Low polarity gas molecules such as oxygen and carbon dioxide exhibit only weak interactions with the highly polar hydroxyl groups in PVOH. This weak interaction combined with the presence of crystalline regions reduces the permeability rates of the gases, resulting in the good gas-barrier properties of PVOH [8].

Through complexation with another polymer it might be possible to modulate the oxygen barrier properties of PVOH. In this paper the influence of complexation between PVOH and PMVE-MA on oxygen transmission rates (OTR) was studied to determine whether a correlation exists between optimum interpolymer complexation ratios and oxygen barrier properties. In addition, viscometry, X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy

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(FTIR) analysis and Differential Scanning Calorimetry (DSC) were used to interpret the OTR results.

2. Experimental

2.1. Materials

A commercial grade of PVOH was supplied by Celanese Chemicals, USA (Celvol 107; 98.4% hydrolysed; DP: 350–650). The PMVE–MA alternating copolymer was supplied by ISP Corporation, USA (Gantrez S97; M_w 1,500,000 g/mol).

A two-component thermoset overcoat was used on all barrier coated bottles to protect the barrier coating from moisture during OTR measurements. The components of the thermoset overcoat were supplied by Spies Hecker, Germany. These are an acrylic based resin (MS Vario Clearcoat 8000) and a hardener (MS Hardener Plus 3040-Medium).

In all cases freshly moulded PET bottles (500 ml) supplied by Container Corporation of Canada (Toronto, Canada) was used for the experiments.

2.2. Sample preparation

PVOH and PMVE–MA solutions were prepared by adding 100 g of the respective polymer powder to 900 g of water in a sealable glass container under continuous stirring. The polymer/water blends were placed in an oven until complete hydration occurred (5 h at 90 °C for PVOH and 12 h at 60 °C for PMVE–MA). The solutions were then removed from the oven and stirred continuously until the solution was homogenous.

Samples for DSC, FTIR and XRD analysis were prepared from the 10% PVOH and PMVE–MA solutions. Eleven blend solutions were prepared in mass ratios of 0:100, 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10, 100:0, PMVE–MA to PVOH. The solutions were then cast onto a polyethylene terephthalate (PET) surface. These were dried over 2 days at 60 °C. The films were then dried for another 8 h at 60 °C with full vacuum using a Vismara 65 Vacuum Oven.

2.3. Polymer Characterization Techniques

2.3.1. Viscosity measurement

PVOH and PMVE–MA blend solutions with concentrations ranging from 0:100 to 100:0 (w/w) PMVE–MA/PVOH were prepared. The viscosities of the blend solutions were then measured using a Brookfield digital viscometer (model DV-1). The readings were taken with spindle RV-4 at a speed of 100 rpm.

2.3.2. FTIR analysis

Spectra of the films were obtained using a Perkin Elmer Spectrum 100 FTIR spectrometer, with wavenumbers ranging from 4000 cm^{-1} to 650 cm^{-1} .

2.3.3. DSC analysis

A Perkin Elmer DSC-7 differential scanning calorimeter (DSC), which was calibrated with Indium, was used to

study the glass transition (T_g) behavior of the dried PMVE–MA/PVOH samples. Samples, approximately 3 to 5 mg, were placed in aluminum pans and scanned from 20 to 140 °C at a heating rate of 30 °C/min.

2.3.4. OTR Measurement

OTR measurements were conducted using a fiber-optic oxygen meter (FB3-Trace-03-044, PreSens GmbH, Germany). Oxyfluorinated PET bottles were first coated on the outsides with PMVE–MA/PVOH ratios ranging from 0:100 to 100:0, dried, and then coated with a moisture resistant overcoat to limit the amount of moisture permeating into the barrier coat. Bottles were then filled with water containing at least 0.02 g AgNO_3 that acted as a biocide. Nitrogen was then bubbled through the water until the oxygen content was below 0.5 mg/L. Afterwards the bottles were sealed with oxygen tight closures (ensuring no headspace was created), each fitted with a trace oxygen-sensor spot (Type TOS7). A fiber optic probe was attached to the closures to read oxygen content in the filled bottles. The sealed bottles were kept at a constant 30 °C and 50% relative humidity for the remainder of the test.

The rate of change of the oxygen content in the water was observed twice a day over a 5-day period, excluding an initial 48 h conditioning period. The period at which the rate of change of oxygen content was constant was used to calculate the OTR.

Permeability coefficients were calculated from OTR values. The coating thicknesses were calculated using the surface area of the bottles, the mass and the density of the dried barrier coatings.

2.3.5. Relative crystallinity measurement

XRD was used to determine the Crystallinity Index (CI) of the various polymer films. The samples were mounted on a zero background sample holder. They were analysed with a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits each set at 15 mm, scanned from 10 to 60° 2θ at a scanning speed of 9 sec/step. The radiation was Fe-filtered Co K α radiation. The phases were identified using X'Pert Highscore plus software.

2.3.6. Coating thickness increase measurement

Oxyfluorinated PET strips (0.3 mm average thickness) were coated on one side with PMVE–MA/PVOH ratios ranging from 0:100 to 100:0 and then dried. The average thicknesses of the strips were measured before and after coating using a Mitutoyo Digimatic Indicator. Coating thickness was obtained by subtracting the coated thickness from the uncoated thickness. To calculate the coating thickness increase factor (CTIF), the thickness of the various ratios was divided by the thickness of the 100% PVOH film.

2.4. Oxyfluorination of PET bottles

Surface treatment was performed using industrial equipment manufactured by Oxyfibre (Pelindaba, South Africa). The bottles were placed into a reactor and sealed.

A proprietary gas mixture containing oxygen and fluorine was charged into the reactor. The bottles were exposed to the gas mixture for approximately 3 min before the gas was flushed and the bottles removed. For control purposes, the OTR of uncoated bottles were tested before and after oxyfluorination. Oxyfluorination did not show any significant effect on OTR. For an uncoated PET bottle, OTR improved from 0.0361 to 0.0335 cm³/bottle/day.

3. Results and discussion

3.1. PMVE-MA/PVOH complexation

Fig. 1 shows the viscosity of PMVE-MA/PVOH blend solutions with concentrations ranging from 0% to 100% (wt/wt) PMVE-MA in PVOH.

The viscosity of the blend solution increases rapidly with PMVE-MA concentration and reaches a maximum at around 20% PMVE-MA. Interpolymer complexation due to hydrogen bonding is usually associated with viscosity decrease of the solution, due to complex precipitation. In such systems, a very compact structure is formed as a result of favourable geometries such as: high chain flexibility, limited steric hindrance, and an equal match of proton donors to proton acceptors. The result is a much reduced hydrodynamic volume, resulting in precipitation of the complex [9]. The viscosity increase in the PMVE-MA/PVOH mixture could be attributed to a combination of factors relating to chain geometry and interaction strength [10]: the bulky PMVE-MA repeat unit does not allow for a compact structure allowing water molecules to interact freely with non-interacting hydrophilic groups; the bulky side-groups of PMVE-MA gives increased steric hindrance leading to lower chain mobility; each PMVE-MA repeat unit contains several proton acceptors compared to the one proton donor of the PVOH repeat unit; polymers with hydroxyl groups as interacting sites generally have low complexation ability [4]. The combination of these factors yields a product in which the hydrodynamic volume is still sufficiently large to result in an interpolymer complex that remains in solution.

FTIR spectroscopy also provides insight into the degree of interpolymer complexation that takes place due to hydrogen bonding between the carbonyl (=O) groups of the PMVE-MA and the hydroxyl (–OH) groups of the

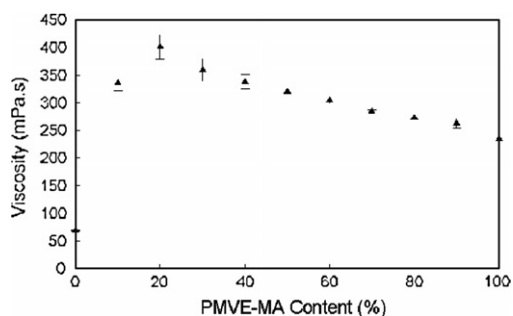


Fig. 1. Viscosity profile of PMVE-MA/PVOH blend solutions at different weight ratios. The data points represent $n = 3$ independent experiments.

PVOH. During interpolymer complexation, the hydrogen bonds that form between the =O and –OH groups cause a shift in their respective wavenumbers. The –OH absorbance band of PVOH is expected to shift to lower wavenumbers on the formation of hydrogen bonds [11], whereas the =O absorbance band of PMVE-MA is expected to shift to higher wavenumbers [12]. Figs. 2 and 3 show the shift in the –OH and =O absorption bands, respectively, while in Fig. 4 the absolute wavenumbers of both the –OH and the C=O absorption bands over the same composition range are plotted for comparison.

The –OH stretching peak shifts from 3272 cm⁻¹ in 0% PMVE-MA films (100% PVOH), to about 3326 cm⁻¹ in 50% PMVE-MA films (beyond 50% the –OH absorbance band becomes too indistinct to make an accurate analysis). With initial addition of PMVE-MA (10%), –OH wavenumbers increase abruptly by 20 cm⁻¹ to 3292 cm⁻¹. Further addition of PMVE-MA (up to 40%) shows only an 8 cm⁻¹ –OH wavenumber increase. Increasing PMVE-MA from 40% to 50% shows another abrupt increase of 26 cm⁻¹ to 3326 cm⁻¹. With initial addition of PMVE-MA to PVOH the main result is possibly the breaking of PVOH intramolecular hydrogen bonds. It can also be expected that this action occurs in the amorphous regions of PVOH, since it has previously been shown that in a miscible crystalline/amorphous blend, the amorphous polymer is rejected from the crystalline regions [13]. Further addition of PMVE-MA (up to 40%) does not show any further increase in –OH wavenumber, indicating the possibility that while additional intramolecular hydrogen bonds might be broken, new intermolecular hydrogen bonds between the PVOH and PMVE-MA molecules are formed in the amorphous regions. At 50% PMVE a net rapid reduction in hydrogen bonds occur. This could be attributed to the combined effect of inappropriate stoichiometry for complexation and that the PVOH crystalline regions are being destroyed by the PMVE-MA molecules.

In the case of the =O shift of PMVE-MA, from 100% down to 60% PMVE-MA virtually no shift occurs. Only from

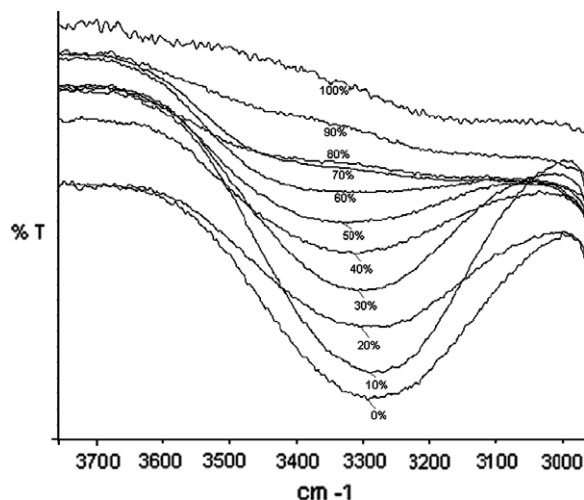


Fig. 2. The shift in the –OH absorption bands with increasing PMVE-MA content (%).

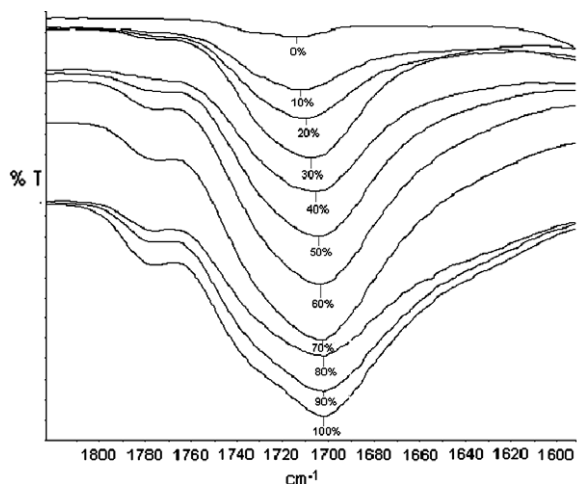


Fig. 3. The shift in the =O absorption bands with increasing PMVE-MA content (%).

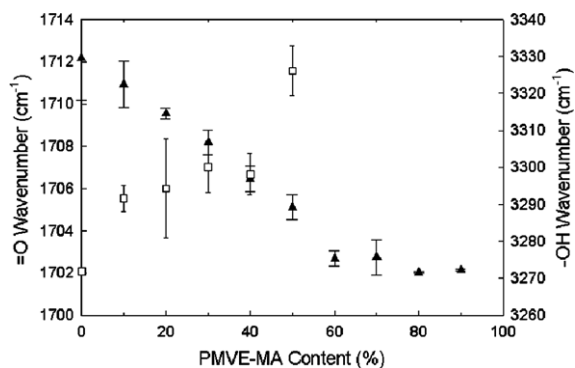


Fig. 4. The shift in the wavenumbers of the =O (▲) and -OH (□) groups as a function of PMVE-MA concentration. The data points represent $n = 3$ independent experiments.

50% PMVE-MA do the =O wavenumbers gradually increase, from 1705 cm^{-1} to 1711 cm^{-1} at 10% PMVE-MA. At low concentrations of PVOH it can be assumed that PVOH intramolecular interactions are preferred, or that the number of interactions is too low to cause a shift in the =O wavenumbers. Only once the PVOH concentration is sufficiently high (from 50%) does intermolecular interaction become apparent. As the PVOH concentration increases, the optimum stoichiometric conditions for interaction are approached, resulting in increased =O wavenumber shifts. The FTIR results thus show that maximum interaction between PVOH and PMVE-MA occurs between 70–80% PVOH, which compares well with the maximum solution viscosity found in the same region.

3.2. Effect of PMVE-MA/PVOH complexation on OTR

PET bottles were first oxyfluorinated to ensure optimum contact between the PMVE-MA/PVOH films and the PET substrate. Oxyfluorination is a process whereby the surface of a polymeric product is chemically modified

by a combination of the penetration of fluorine atoms into the polymer surface and the presence of oxygen atoms, to improve adhesion of the coating [14].

Oxyfluorinated PET bottles were coated with PMVE/PVOH solutions ranging from 0 to 100% (wt/wt) PMVE-MA in PVOH, and the OTR measured at each PMVE-MA concentration is presented in Fig. 5. The OTR decreased from $0.013 \text{ cm}^3/\text{STP}/\text{bottle}/\text{day}$ for a 100% PVOH film to 0.003 and $0.004 \text{ cm}^3/\text{STP}/\text{bottle}/\text{day}$, respectively, for 20% and 30% PMVE-MA content. The OTR's increased again with further increase in PMVE-MA content. All the coatings, up to 80% PMVE-MA content showed a significant decrease in OTR compared to the uncoated PET. In order to compare these results with commercial barrier polymers [15], the oxygen permeability coefficients of key barrier coatings were calculated from OTR values obtained from a series model intended for multilayer systems [16].

$$\text{OTR}_{\text{coating}} = \frac{1}{\frac{1}{\text{OTR}_{\text{total}}} - \frac{1}{\text{OTR}_{\text{bottle}}}}$$

The results are summarized in Table 1.

The total amount of permeant that will pass through a film of area A after time t is given by [17]:

$$Q = Pat(p_2 - p_1)/\ell$$

where P is the permeability coefficient, p_1 and p_2 are the permeant partial pressures on either side of the film and ℓ is the film thickness. Thus, the OTR values would be inversely proportional to film thickness. To determine if the reduced OTR values are simply due to increased coating thickness, thickness increase and OTR improvement over 100% PVOH for each PMVE-MA ratio was calculated. Table 2 compares the coating thickness increase factor (CTIF) with the OTR improvement factor (OIF) over 100% PVOH. Although the coatings of the PMVE-MA ratios which showed the greatest reduction in OTR's are thicker, the OIF greatly exceeds the CTIF in the 10 to 50% PMVE-MA range, with a maximum OIF around 20% PMVE-MA. Thus, while some of the improvement in OTR's can be attributed to increased coating thickness other effects have a greater impact.

A good correlation is shown between lowest OTR's and the ratios at which maximum interaction between PVOH

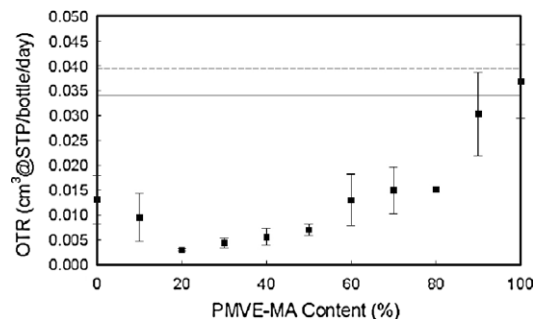


Fig. 5. The OTR of oxyfluorinated PET bottles coated with various PMVE-MA/PVOH ratios (■). Also shown are the OTR of PET without any barrier coating (---), and the OTR of only the overcoat on PET (---). The error bars represent $n = 3$ independent experiments.

Table 1

Oxygen permeability coefficients of selected coatings compared to various commercial barrier polymers [15]

Material	Permeability coefficient $\frac{(\text{cm}^3)(\text{cm})}{(\text{cm}^2)(\text{s})(\text{Pa})}$
100% PVOH	0.00036
20% PMVE-MA	0.000089
30% PMVE-MA	0.000086
Poly(vinylidene chloride) Saran	0.00383
Poly(acrylonitrile) Barex	0.0041
Poly(amide) 6	0.0285
PET	0.03

Table 2

Dried film thickness of each composition including a comparison of the coating thickness increase factor (CTIF) with the OTR improvement factor (OIF) over 100% PVOH

% PMVE-MA	Thickness (mm)	CTIF	OIF
0	0.024	1.00	1.00
10	0.027	1.12	1.37
20	0.041	1.72	4.43
30	0.029	1.20	3.02
40	0.025	1.04	2.35
50	0.028	1.16	1.88
60	0.024	1.00	1.01
70	0.024	1.00	0.88
80	0.021	0.88	0.87
90	0.032	1.32	0.43
100	0.030	1.24	0.35

and PMVE-MA was found based on the viscosity increase. Since no modification in the chemical structure of the components occurred after complexation, the reduced OTR could be related to physical effects on the molecular level.

Fig. 6 shows the XRD plots of the polymer films as a function of film composition.

A gradual decrease in crystallinity with PMVE-MA addition is shown. To highlight the crystallinity difference measured, the crystallinity index (CI) was calculated using the method described by Jaworska et al. [18] as well as by Focher et al. [19] and adapted here by measuring the inten-

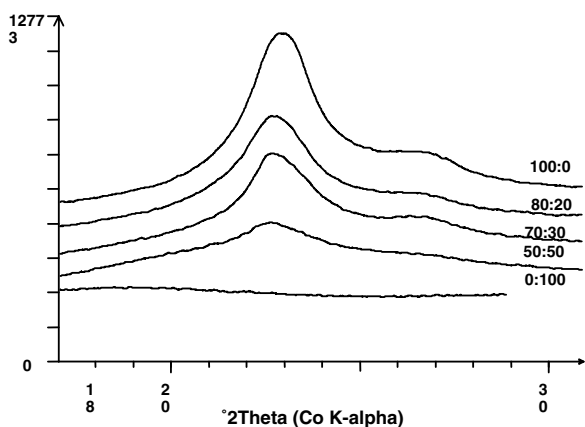


Fig. 6. XRD results as a function of polymer film composition (PVOH:PMVE-MA). The intensity of the diffracted X-rays (Y-axis) is plotted against the diffracted angle of diffraction (2θ) (X-axis).

sity of the highest peak (I_{peak}) at around $22.7^\circ 2\theta$ and that of the amorphous diffraction intensity (I_{am}) at about $18^\circ 2\theta$. The CI was then calculated using the following formula:

$$\text{CI} = (I_{\text{peak}} - I_{\text{am}}) / I_{\text{peak}} \times 100$$

Values are presented in Fig. 7 and show a decrease in crystallinity with increase in PMVE-MA content. However, the decrease is not linear. At 20% PMVE-MA crystallinity is reduced only by 8%. Only at 30% PMVE-MA content does crystallinity drop rapidly.

A number of examples in literature demonstrate the relationship between crystallinity and permeability, where higher crystallinity results in decreased permeability [20–22]. The crystalline regions of the polymer film act as an impermeable barrier that increases the path-length of diffusing permeant. While crystallinity was still relatively intact up to 20% PMVE-MA, crystallinity generally decreased with increased PMVE-MA content. Since the reduced OTR of the PMVE-MA/PVOH mixtures could not be attributed to increased crystallinity, the amorphous regions were studied for a possible explanation.

The T_g of a polymer represents the amorphous regions of a polymer and is therefore a useful technique to study changes that occur in these regions. While miscible blends of two polymers are characterized by the formation of a single T_g , miscible blends that form as a result of hydrogen bonding usually show T_g 's with a positive deviation from the linear additive value [23]. This is mainly because hydrogen bonding reduces the mobility of the polymer chains.

Fig. 8 shows T_g 's measured for various PMVE-MA:PVOH ratio's. Only one T_g is found in the dry blends indicating miscibility over the entire composition range. The T_g 's of each composition were also compared to the linear additive value in order to highlight deviations (Fig. 9).

At low PMVE-MA concentrations (10–40% wt) a positive deviation from the linear additive value occurs, with a maximum positive deviation of about 20°C at 20% wt PMVE-MA. With further increase in PMVE-MA content, the positive deviation decreases until a negative deviation occurs in the 70–90% wt PMVE-MA. The PMVE-MA wt% at which the maximum positive deviation occurs coincides with the wt% PMVE-MA at which maximum solution viscosity and the lowest OTR values were found. This positive deviation would indicate that the hydrogen bond density

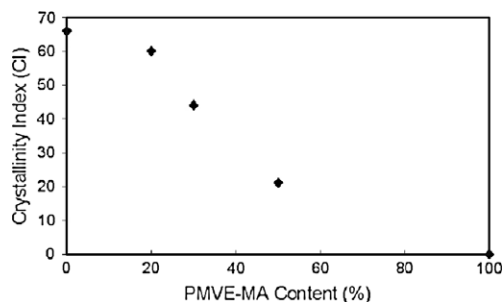


Fig. 7. Crystallinity Index as measured by XRD for films with increasing PMVE-MA content.

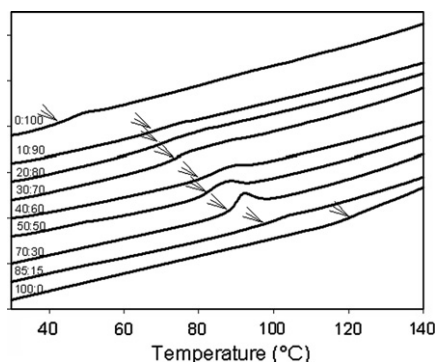


Fig. 8. DSC thermograms of PMVE-MA/PVOH blends with ratio's as indicated, showing T_g positions (arrows).

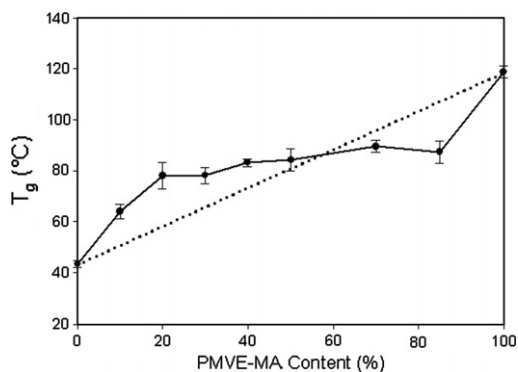


Fig. 9. T_g 's of dry blends of PMVE-MA/PVOH as a function of PMVE-MA content by weight, compared to the linear additive T_g values (dotted line).

in the amorphous region at low PMVE-MA content is greater than that found in pure PVOH. Many studies have shown that intermolecular interactions lead to more compact packing of the molecules, resulting in lower free-volumes [24–27]. Fig. 10 is a schematic illustration of the amorphous regions before and after interpolymer complexation. A reduction in free-volume of the amorphous regions would reduce the diffusion rate for diffusing gas molecules. Since PVOH crystallinity with 20–30% PMVE-MA addition is not inhibited dramatically, the presence of the impermeable crystalline regions together with the

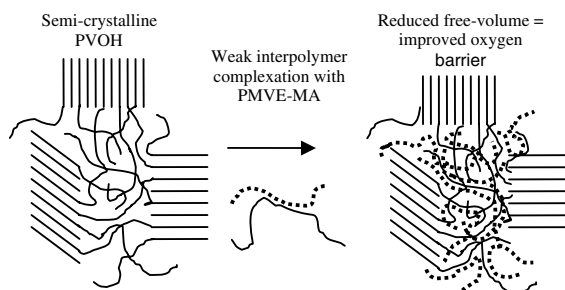


Fig. 10. Formation of a semi-crystalline structure with reduced free-volume through weak interpolymer complexation between PVOH and PMVE-MA.

denser amorphous region would lead to higher gas barrier properties. With further addition of PMVE-MA, crystallisation of PVOH becomes severely inhibited and the concentration of hydrogen bonds decreases, leading to poorer gas barrier properties.

4. Conclusion

Interpolymer complexation between PMVE-MA and PVOH can produce coatings with oxygen barrier properties superior to those of the individual components. Viscosity measurements and FTIR analysis have shown the presence of hydrogen bonding between PMVE-MA and PVOH, specifically in the 20–30% PMVE-MA content range. This is confirmed with thermal analysis which shows a large positive T_g deviation from the linear additive value. XRD analysis has shown that the complexation was not strong enough to destroy PVOH crystallinity completely in the 20–30% PMVE-MA range, allowing the formation of a low free-volume complexed structure interdispersed with impermeable PVOH crystalline regions. It is proposed that the improved barrier properties originate from the combined effect of the lower free-volume in the amorphous regions and the mostly intact PVOH crystallites.

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