

# Blending and oxygen permeation properties of the blown films of blends of modified polyamide and ethylene vinyl alcohol copolymer with varying vinyl alcohol contents

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**Abstract** The oxygen permeation and blending properties of the MPAEVOH blends of modified polyamide (MPA) and ethylene vinyl alcohol copolymer (EVOH) with varying vinyl alcohol contents were systematically investigated in this study. The oxygen permeation rates of EVOH film specimens are dramatically slower than that of the PE specimen and reduce significantly as their vinyl alcohol contents increase. After blending EVOH in MPA resin, the oxygen permeation rates of each MPA-EVOH series film specimens reduce significantly as their EVOH and/or vinyl alcohol contents increase, respectively. At some optimum compositions, the oxygen permeation rates of the MPAEVOH film specimens are even lower than that of the pure EVOH film specimen with a vinyl alcohol content of 52 wt%. On the other hand, the average radius ( $R_f$ ), volume ( $V_f$ ) of the free-volume-cavities and fractional free-volume ( $F_v$ ) values of each MPAEVOH series specimens reduce significantly as their EVOH and/or vinyl alcohol contents increase. These interesting barrier and free-volume properties of the EVOH and MPAEVOH specimens with varying vinyl

alcohol contents were investigated in terms of the intermolecular interaction and/or free-volume properties in the amorphous phases of the EVOH and MPAEVOH specimens obtained in this study.

## Introduction

It is well known that organic liquids such as non-polar hydrocarbon solvents and gas molecules can easily permeate through polyolefin polymers (e.g. polyethylene and polypropylene). In contrast to polyolefin resins, polyamide (PA) and ethylene vinyl alcohol copolymer (EVOH) exhibits good barrier resistance against the permeation of non-polar hydrocarbon solvent and/or gas molecules, which are often co-extruded with polyolefin resins to enhance the barrier resistance of the polyolefin contained multilayer films or containers [1–3]. In comparison with PA, EVOH exhibits even better transparency, oil resistance, and barrier properties against non-polar gas and solvent permeations, and is recognized as the oxygen-barrier material in food and other packaging applications that require protection from oxygen [4–6]. However, the relatively brittle, expensive and moisture absorbable properties of EVOH reduce its merit [7, 8]. In order to reduce the cost and moisture absorption of using EVOH, EVOH resins are often co-extruded with cheaper and water-proof polymers, such as lower-density polyethylene (LDPE), high-density polyethylene (HDPE) and PP resins to make multilayer films and/or containers.

In contrast to the co-extrusion process, the “laminar-blend-blow-molding process” forms a layered structure containing numerous discontinuous, overlapping platelets of barrier resins such as polyamide (PA) and/or ethylene

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vinyl alcohol (EVOH) in a PE matrix, which is one of well proven barrier technologies to enhance the resistance of PE containers to non-polar hydrocarbon permeation [9–16]. Our latest studies [17–20] further indicated that the type and content of compatibilizer precursor (CP) and PA present in a modified polyamide (MPA) have significant effects on the barrier, morphology and rheological properties of MPA resins and the corresponding PE/MPA blends. In fact, by using proper compositions and processing conditions, the PE/MPA laminar blends structured bottles exhibited excellent permeation resistance against non-polar hydrocarbon solvents (e.g. xylene) and mixtures of non-polar hydrocarbon solvents (e.g. paint thinner) [21–25]. However, significantly poor permeation resistance was found [13, 25–26] on these laminar blends structured bottles when the PE/MPA bottles were filled with mixtures of polar and non-polar solvents (i.e. gasoline and paint mixed solvents). For instance, much worse barrier improvement (<15) against paint mixed solvent permeation was found on the PE/MPA bottles, when the polar solvents are in certain range [25]. Our latest effort [27–31] found that, after blending proper amounts of EVOH in MPA, the mixed solvent permeation rates of PE/MPAEVOH bottle specimens are dramatically reduced and are very close to the summation permeation rates calculated using the simple mixing rule. Presumably, this dramatically improved permeation resistance was attributed to the good enough barrier properties of MPAEVOH laminas that present in the PE/MPAEVOH bottles. In fact, after blending proper amounts of EVOH in MPA, the oxygen permeation rates of MPAEVOH film specimens are significantly reduced and are about five times smaller than that of the MPA film specimens prepared with the optimum processing condition and composition [28]. However, as far as we know, the influence of the vinyl alcohol contents of EVOH resins on oxygen permeation properties of the film-blown MPAEVOH specimens have never been reported.

In this study, the blending and oxygen permeation properties of the MPAEVOH blends with varying vinyl alcohol contents were systematically investigated. Three types of EVOHs with varying vinyl alcohol contents were used to prepare the MPAEVOH resins by melt blending them with varying amounts of MPA resin, respectively. In order to clarify the underlying mechanisms accounting for the interesting barrier properties of MPAEVOH blends, FT-IR and free volume analysis were carried out to investigate their blending properties in a molecular level. Possible mechanisms accounting for the interesting barrier properties of MPAEVOH blends with varying vinyl alcohol contents are proposed.

## Experimental

### Materials and sample preparation

The polyamide (PA) and CP used in this study were obtained from Formosa Chemicals and Fiber Corporation, Taiwan, wherein PA is nylon 6 with a trade name of Sunylon 6N and CP is a 40% zinc-neutralized ethylene/acrylic acid (95:5) copolymer. The MPA resin was prepared by reactive extrusion of the melt blending of CP and PA. The polyethylene (HDPE Taisox 9003), EVOHs with varying vinyl alcohol contents and antioxidant (Irganox B225) used in this study were obtained from Formosa Plastic Corporation (Taipei, Taiwan), Kuraray Corporation (Osaka, Japan) and Ciba-Geigy Corporation (Basel, Switzerland), respectively. For convenience, the EVOH resins with 68, 56 and 52 wt% vinyl alcohol contents will be referred to as EVOH<sup>a</sup>, EVOH<sup>b</sup> and EVOH<sup>c</sup> resins, respectively, in the following discussion.

Before melt blending, PA was dried at 80 °C for 16 h, while EVOH and CP were dried at 60 °C for 16 h in a vacuum oven. About 1,500 ppm of antioxidant was dry-blended with the dried PA/CP blend of varying weight ratios. The dry-blended PA/CP blends together with antioxidant were then fed into an Ekegai PCM 45 co-rotating twin-screw extruder to make MPA resin. The extruder was operated at 220 °C in the feeding zone and at 240 °C towards the extrusion die with a screw speed of 100 rpm. The CP MPA obtained from twin-screw extruder was quenched in cold water at 15 °C and cut into the pellet form. Formation of CP-grafted-PA copolymers through the reaction of carboxyl groups of CP with the terminal amine groups of PA has been reported during the preparation of MPA [16, 17]. The blends of MPA and EVOH (MPAEVOH) were prepared by melt blending of the MPA and EVOH using a Fure Shuen 40SP-H single-screw extruder. The dried components of MPA/EVOH at varying weight ratios were fed into the single-screw extruder which was operated at 220 °C with a screw speed of 400 rpm in the feeding zone and 235 °C towards the extrusion die. The extruded MPAEVOH resins were then quenched in cold water at 15 °C and cut into the pellet form. The compositions of the three groups of MPAEVOH specimens prepared in this study are summarized in Table 1.

Before film-blowing, MPA and MPAEVOH resins were dried at 80 °C for 16 h, while EVOH resin was dried at 60 °C for 16 h. These barrier resins were co-extruded with the HDPE resin and then film-blown using a Queen QN-35/2E-650 double layer blown-film machine, since it is well known that the melt viscosities of these barrier resins are too low to blow film alone. The extruder used for HDPE and barrier resins were operated at 195 °C in the feeding

**Table 1** The compositions of MPAEVOH specimens prepared in this study

Specimens	MPA (%)	EVOH <sup>a</sup> (%)	EVOH <sup>b</sup> (%)	EVOH <sup>c</sup> (%)
MPA <sub>2</sub> EVOH <sub>1</sub> <sup>a</sup>	66.67	33.33		
MPA <sub>1</sub> EVOH <sub>1</sub> <sup>a</sup>	50.00	50.00		
MPA <sub>1</sub> EVOH <sub>2</sub> <sup>a</sup>	33.33	66.67		
MPA <sub>1</sub> EVOH <sub>4</sub> <sup>a</sup>	20.00	80.00		
MPA <sub>2</sub> EVOH <sub>1</sub> <sup>b</sup>	66.67		33.33	
MPA <sub>1</sub> EVOH <sub>1</sub> <sup>b</sup>	50.00		50.00	
MPA <sub>1</sub> EVOH <sub>2</sub> <sup>b</sup>	33.33		66.67	
MPA <sub>1</sub> EVOH <sub>4</sub> <sup>b</sup>	20.00		80.00	
MPA <sub>2</sub> EVOH <sub>1</sub> <sup>c</sup>	66.67			33.33
MPA <sub>1</sub> EVOH <sub>1</sub> <sup>c</sup>	50.00			50.00
MPA <sub>1</sub> EVOH <sub>2</sub> <sup>c</sup>	33.33			66.67
MPA <sub>1</sub> EVOH <sub>4</sub> <sup>c</sup>	20.00			80.00

zone, 230 °C towards the extrusion die with a screw speed of 150 rpm. The co-extruded films were then blown up at a blow-up ratio of 3, wherein HDPE and the barrier resins were in the inside and outside layer, respectively. After film-blowing, the barrier layers were separated from the HDPE layer. The barrier film specimens prepared in this study had a thickness of 50 µm.

#### Oxygen permeation properties

The oxygen permeation rates of PE, MPA, three series of EVOH and MPAEVOH films were determined using a Lyssy L100–4002 manometric gas permeability tester in accordance with ASTM D-1434 standard. All film specimens were cut into a circular shape with a diameter of 10 cm and a thickness of about 50 µm. The oxygen permeation rates of the EVOH and MPAEVOH specimens at varying humidities were not determined in this study, although it is well known that the gas permeability of EVOH polymers containing hydrophilic groups is strongly influenced by moisture. In order to investigate the oxygen permeation properties of the MPAEVOH blends with varying vinyl alcohol contents, all the permeation tests were carried out at 25 °C and 50% relative humidity as suggested by ASTM D-1434 standard test method. The oxygen permeation rate of each film specimen was estimated based on the average permeation rate of at least three film specimens.

#### Free-volume properties

The free-volume characteristics of polymer were determined using a positron annihilation life-time (PAL) instrument equipped with a fast-fast coincidence spec-

trimeter and a <sup>22</sup>Na source that was sandwiched between one layer of hot-pressed film with 1 mm thickness on both sides to ensure complete annihilation of positron in the sample. A short-lived component ( $\tau_1$ ; ca. 0.12 ns), an intermediate-lived component ( $\tau_2$ ; ca. 0.35–0.4 ns), and a long-lived component ( $\tau_3$ ; ca. 1.8–2.5 ns), are the three resolved life-time components obtained, that are attributed to the para-positronium (*p*-Ps), free positron, and ortho-positronium (*o*-Ps) states, respectively. The longest life-time component  $\tau_3$  with intensity  $I_3$  is attributed to the pick-off annihilation of the *o*-Ps in the free-volume sites present mainly in the amorphous regions of the polymer matrix [32]. The annihilation of *o*-Ps in the spherical free-volume-cavities can be described by a simple quantum mechanical model, which assumes the *o*-Ps atom to be localized in a spherical potential well with an electron layer of thickness  $\Delta R$ . This model provides the relationship between the radius  $R_f$  of the free-volume hole and the *o*-Ps life-time ( $\tau_3$ ) as follows [33]:

$$\frac{1}{\tau_3} = 2 \left[ 1 - \frac{R_f}{R_0} + \frac{1}{2\pi} \sin \left( \frac{2\pi R_f}{R_0} \right) \right] \quad (1)$$

where  $R_0 = R_f + \Delta R$ . Parameter  $\Delta R$  was determined by fitting the experimental values of  $\tau_3$  obtained for materials of known hole size such as zeolites. The  $\Delta R$  value of 0.166 nm was used in this study [32].

The fractional free-volume, defined as the ratio of free-volume to the total volume of polymer, was calculated using following equation [34, 35].

$$F_v = C \cdot V_f \cdot I_3 \quad (2)$$

where the coefficient  $C$  is a structural constant, one way of calculating  $C$  is from a measurement of the thermal expansion coefficient of the free-volume. The unit of the  $C$  constant is  $\text{nm}^{-3}$ ,  $I_3$  (%) is the intensity of *o*-Ps life-time, and  $V_f$  ( $\text{nm}^3$ ) is the mean volume of the free-volume holes calculated using mean radius  $R_f$  obtained as follows:

$$V_f = 4/3 \pi R_f^3 \quad (3)$$

#### Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopic measurements of PA, EVOH, MPA and MPAEVOH specimens were recorded on a Nicolet Avatar 320 FT-IR spectrophotometer at 25 °C and 50% relative humidity, wherein 32 scans with a spectral resolution  $1 \text{ cm}^{-1}$  were collected during each spectroscopic measurement. Infrared spectra of the film specimens were determined by using the conventional NaCl disk method. The 1,1,1,3,3,3-hexafluoro-2-propanol

solutions containing the PA, EVOH, MPA and MPAEVOH were cast onto NaCl disk and dried at 60 °C for 30 min, respectively. The cast films used in this study were prepared sufficiently thin enough to obey the Beer-Lambert law.

## Results and discussion

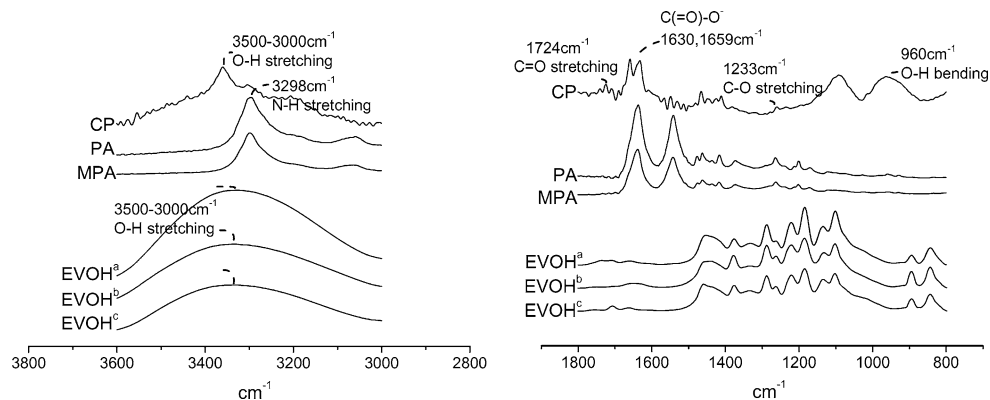
### Fourier transform infrared spectra

Typical Fourier transform infrared (FT-IR) spectra of CP, MPA and EVOH specimens with varying vinyl alcohol contents are shown in Fig. 1. The distinguished absorption bands of CP specimens centered at 960, 1,233, 1,630/1,659 and 1,724 and 3,360  $\text{cm}^{-1}$ , are most likely corresponding to the motions of O–H out-of-plane bending, C–O stretching of the carboxylic acid, carboxylate anion stretching, C=O stretching of the carboxylic acid and O–H stretching vibration present in CP molecules, respectively. Similar to those found by Coleman and coauthors [36], the FT-IR spectra of MPA specimen exhibit three distinguished absorption bands centered at 1,542, 1,636 and 3,298  $\text{cm}^{-1}$ , which are attributed to the motions of N–H bending vibration, C=O stretching vibration and N–H stretching of PA molecules, respectively. However, the 960 and 1233 (O–H out-of-plane bending and C–O stretching of the carboxylic acid) and 3360  $\text{cm}^{-1}$  (hydroxyl stretching vibration) absorption bands originally shown on the FT-IR spectra of CP specimens almost disappeared completely. Presumably, this disappearance is due to the formation of CP-grafted-PA copolymers through the reaction of carboxylic acid groups of CP with the terminal amine groups of PA molecules during the reactive extrusion of MPA resins [17, 18].

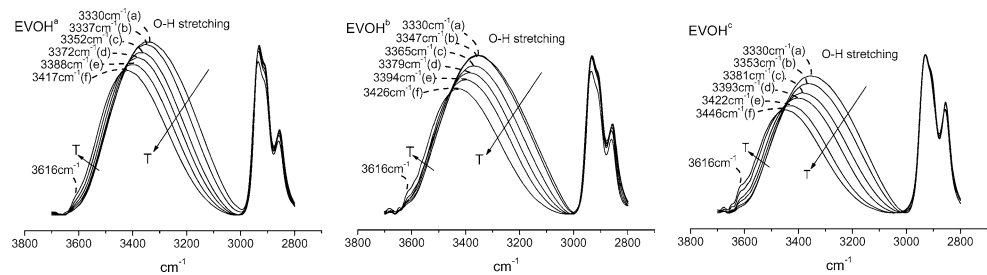
As shown in Fig. 1, an intense broad band centered at approximately 3,330  $\text{cm}^{-1}$  corresponding to hydroxyl stretching was found on the spectra of EVOH specimens with varying vinyl alcohol contents, which is attributed to a distribution of intermolecular and/or intramolecular

hydrogen-bonded OH dimer and multimers [37]. It is worth noting that the intensity and size of the hydrogen-bonded band of the EVOH specimen increase significantly as their vinyl alcohol contents increase (see Fig. 1). Presumably, this increasing intensity and size of the spectra is due to the gradually strengthened inter and intramolecular hydrogen-bonded OH dimer and multimers present in EVOH molecules as their vinyl alcohol contents increase. Typical FT-IR spectra of EVOH specimens determined at varying temperatures are shown in Fig. 2. The peak maximum of EVOH<sup>a</sup> specimen shifted into higher frequency (from about 3,330 to 3,417  $\text{cm}^{-1}$ ) and the intensity of this band reduced significantly as the testing temperatures increased from 35 °C to 210 °C. In fact, a new small band centered at 3,616  $\text{cm}^{-1}$  corresponding to free (non-hydrogen-bonded) hydroxyl groups was found as the temperatures increase. As shown in Fig. 3, the frequency difference ( $\Delta\nu$ ) between the absorption bands of hydrogen-bonded hydroxyl and free hydroxyl groups reduces significantly with increasing temperatures. Presumably, as suggested by several investigations [38], this decrease in  $\Delta\nu$  suggests gradual weakening of hydrogen-bonded hydroxyl groups present in the EVOH molecules, which, hence, causes the absorption band of free hydroxyl groups to become more pronounced as the temperature increases. Similar tendency was found on the FT-IR spectra of EVOH<sup>b</sup> and EVOH<sup>c</sup> specimens, however, the  $\Delta\nu$  values at a fixed temperature appear to increase significantly as the vinyl alcohol contents of EVOH specimens increase (see Fig. 3). Moreover, it is worth noting that the intensities of the free hydroxyl band centered at 3.616  $\text{cm}^{-1}$  of EVOH specimens determined at higher temperatures reduce significantly as their vinyl alcohol contents increase (see Fig. 2). These results clearly suggest that the inter and intramolecular hydrogen-bonded hydroxyl groups present in the EVOH molecules are somewhat strengthened as their vinyl alcohol contents increase, and hence, causes a significant increase in  $\Delta\nu$  values and reduction in the intensity of the free hydroxyl band at a fixed high temperature, respectively.

**Fig. 1** FT-IR spectra of CP, PA, MPA and EVOH<sup>a</sup>, EVOH<sup>b</sup> and EVOH<sup>c</sup> specimens determined at 35 °C



**Fig. 2** FT-IR spectra of three EVOH specimens (EVOH<sup>a</sup>, EVOH<sup>b</sup> and EVOH<sup>c</sup>, from left to right) determined at (a) 35 °C, (b) 80 °C, (c) 120 °C, (d) 150 °C, (e) 180 °C and (f) 210 °C

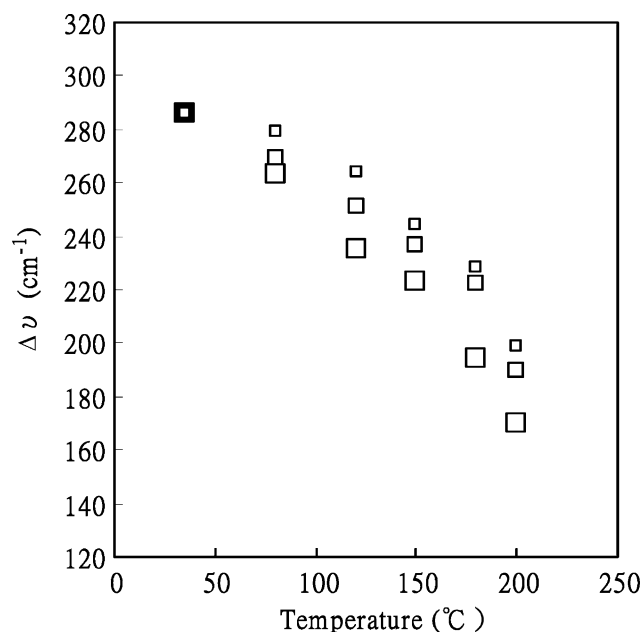


The FT-IR spectra of the three MPAEVOH series specimens (i.e. MPAEVOH<sup>a</sup>, MPAEVOH<sup>b</sup> and MPAEVOH<sup>c</sup>) with varying EVOH contents are shown in Fig. 4(1–3). As shown in Fig. 4(1), after blending EVOH<sup>a</sup> in MPA, the widths ( $\Delta w$ ) shown in the half-height of C=O stretching bands of MPAEVOH<sup>a</sup> specimens reduce significantly with increasing the EVOH<sup>a</sup> contents. Similar tendency was found on the FT-IR spectra of MPAEVOH<sup>b</sup> and MPAEVOH<sup>c</sup> specimens (see Fig. 4(2, 3)). In fact, at a fixed EVOH content, the  $\Delta w$  values of C=O stretching bands of the MPAEVOH specimens appear to reduce significantly as their vinyl alcohol contents of EVOH resins increase (see Fig. 5). It is generally recognized that this reduction in  $\Delta w$  of the C=O stretching band can be attributed to the decreasing amounts of allowed C=O stretching vibrations [39]. Presumably, the decreasing allowed C=O stretching vibrations can be attributed to the gradually strengthened interaction between carbonyl and hydroxyl groups in the MPAEVOH series specimen, as the EVOH and/or the vinyl

alcohol contents of the MPAEVOH series specimens increase. Based on these premises, it is reasonably to suggest that the presence of EVOH in MPA can interfere, break the hydrogen-bonded carbonyl groups originally present in MPA resins, and even form new interaction between carbonyl and hydroxyl groups, as the EVOH and/or the vinyl alcohol contents of MPAEVOH series specimens increase.

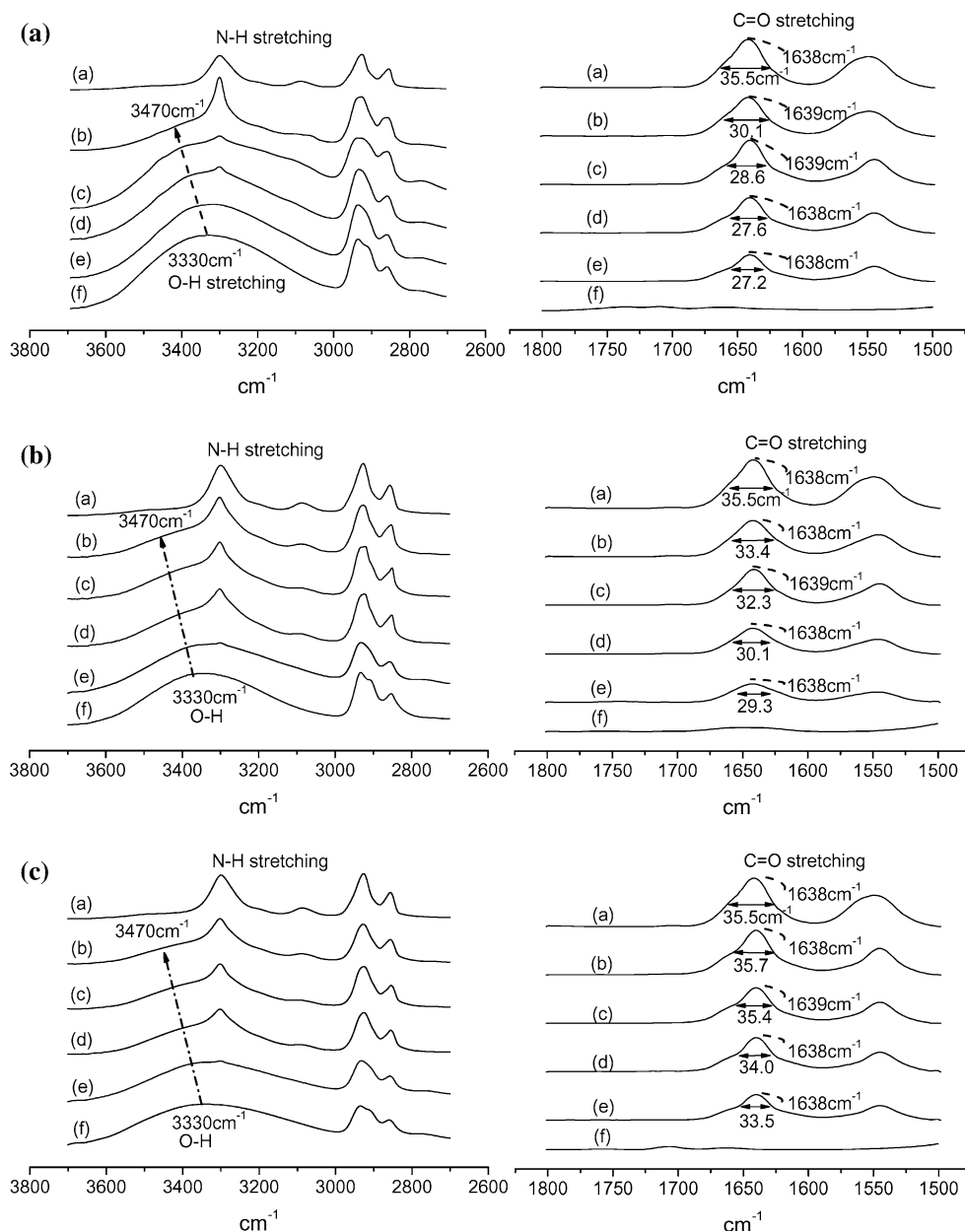
#### Free-volume properties

Table 2 summarized the evaluated free-volume properties of PE, MPA and EVOH specimens. As expected, the average radius ( $R_f$ ) and volume ( $V_f$ ) values of the free-volume-cavities of the MPA resins are significantly lower than that of the PE specimen. The fractional free-volume ( $F_v$ ) of MPA is also significantly lower than that of the PE specimen, since  $I_3$  values of PE and MPA specimens are nearly the same, wherein the  $I_3$  values reflect the relative average numbers of the free-volume-cavities per unit volume. In contrast, the  $R_f$ ,  $V_f$  and  $F_v$  values of the EVOH resins are significantly lower than those of the MPA resin, although the  $I_3$  values of the EVOH specimens are slightly higher than that of the MPA specimens. Moreover, it is worth noting that the  $R_f$ ,  $V_f$ ,  $I_3$  and  $F_v$  values of EVOH specimens all reduce significantly as their vinyl alcohol contents increase. As shown in Table 2, the  $V_f$  and  $F_v$  values of EVOH specimens reduce from 0.0394 nm<sup>3</sup>/8.0% to 0.0371 nm<sup>3</sup>/7.3% and then to 0.0320 nm<sup>3</sup>/6.1%, as their vinyl alcohol contents increase from 52 to 56 and then to 68 wt%, respectively, which are significantly smaller than the  $V_f$  and  $F_v$  values (i.e. 0.0619 nm<sup>3</sup>/10.5% and 0.1177 nm<sup>3</sup>/20%) of MPA and PE specimens, respectively. After blending EVOH in MPA, the  $R_f$ ,  $V_f$  and  $F_v$  values of each MPAEVOH sample series tend to reduce, as the EVOH contents increase, respectively, although the  $I_3$  values increase slightly as the EVOH contents increase (see Fig. 6). Similar to those found in EVOH sample series, at a fixed EVOH content, the  $R_f$ ,  $V_f$ ,  $I_3$  and  $F_v$  values of MPAEVOH sample series reduce significantly as their vinyl alcohol contents increase. However, the beneficial effect of the vinyl alcohol content on reducing the  $R_f$ ,  $V_f$ ,  $I_3$  and  $F_v$  values of MPAEVOH samples persists but become less demarcated as their EVOH contents reduce.



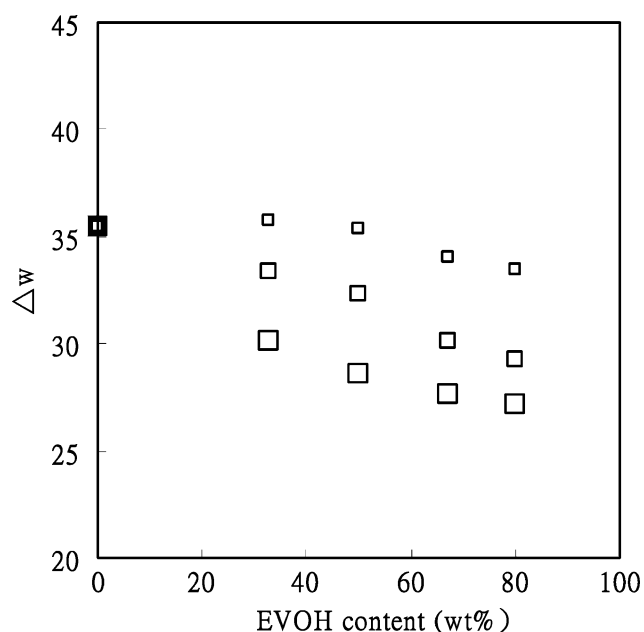
**Fig. 3** Frequency difference ( $\Delta\nu$ ) between the absorption bands of hydrogen-bonded hydroxyl and free hydroxyl groups of EVOH<sup>a</sup> (■), EVOH<sup>b</sup> (□) and EVOH<sup>c</sup> (□) specimens determined at varying temperatures

**Fig. 4** (1) FT-IR spectra of (a) MPA, (b) MPA<sub>2</sub>EVOH<sub>1</sub><sup>a</sup>, (c) MPA<sub>1</sub>EVOH<sub>1</sub><sup>a</sup>, (d) MPA<sub>1</sub>EVOH<sub>2</sub><sup>a</sup>, (e) MPA<sub>1</sub>EVOH<sub>4</sub><sup>a</sup> and (f) EVOH<sup>a</sup> specimens determined at 35 °C (2) FT-IR spectra of (a) MPA, (b) MPA<sub>2</sub>EVOH<sub>1</sub><sup>b</sup>, (c) MPA<sub>1</sub>EVOH<sub>1</sub><sup>b</sup>, (d) MPA<sub>1</sub>EVOH<sub>2</sub><sup>b</sup>, (e) MPA<sub>1</sub>EVOH<sub>4</sub><sup>b</sup> and (f) EVOH<sup>b</sup> specimens determined at 35 °C. (3) FT-IR spectra of (a) MPA, (b) MPA<sub>2</sub>EVOH<sub>1</sub><sup>c</sup>, (c) MPA<sub>1</sub>EVOH<sub>1</sub><sup>c</sup>, (d) MPA<sub>1</sub>EVOH<sub>2</sub><sup>c</sup>, (e) MPA<sub>1</sub>EVOH<sub>4</sub><sup>c</sup> and (f) EVOH<sup>c</sup> specimens determined at 35 °C



It is generally recognized that the size and distribution of the free-volume-cavities of polymers are related to the molecular structure and molecular interaction present in their amorphous phases. Strong molecular interaction, such as inter and/or intramolecular hydrogen bondings can attract and hold the polymer molecules in a more condensed way in their amorphous phases and, hence, cause a relatively small  $R_f$  and  $V_f$  of the free-volume-cavities. In contrast, only weak secondary molecular interaction (i.e. van der Waals' attraction) but no strong molecular interaction is present between non-polar PE molecules, which can only hold the PE molecules in a relatively loose way in their amorphous regions. It is, therefore, PE exhibits significant larger  $R_f$ ,  $V_f$  and  $F_v$  values than polar MPA and

EVOH specimens. On the other hand, as reported in the previous section, the inter and intramolecular hydrogen-bonded hydroxyl groups present in the EVOH molecules are somewhat strengthened as their vinyl alcohol contents increase, as evidenced by a significant increase in  $\Delta\nu$  values and reduction in the intensity of the free hydroxyl band at a fixed high temperature, respectively. Based on these premises, it is reasonable to understand that the significant amounts of hydrogen-bonded OH dimer and multimers can attract and hold the EVOH molecules in a relatively condensed way in their amorphous phases, and cause smaller  $R_f$  and  $V_f$  values of the free-volume-cavities as their vinyl alcohol contents increase. In contrast, formation of hydrogen bondings in MPA molecules between N–H and



**Fig. 5** The widths ( $\Delta w$ ) shown in the half-height of C=O stretching bands of MPAEVOH<sup>a</sup> (□), MPAEVOH<sup>b</sup> (□) and MPAEVOH<sup>c</sup> (□) specimens

C=O groups is expected to be fewer and slightly weaker than those in EVOH molecules. These fewer and weaker hydrogen bondings can attract and hold the MPA molecules in a more sparse way in their amorphous phases, and hence, cause larger  $R_f$  and  $V_f$  values than those of the EVOH molecules.

On the other hand, it is not completely clear what accounts for the interesting free-volume properties of MPA-EVOH specimens described above. As evidenced by the FT-IR spectra reported in the previous section, the reduction of the widths shown in the half-height of C=O stretching bands of MPAEVOH specimens is attributed to the decreasing amounts of allowed C=O stretching vibrations and the gradually strengthened interaction between carbonyl and hydroxyl groups in the MPAEVOH series specimen, as the EVOH and/or the vinyl alcohol contents of the MPAEVOH series specimens increase. Based on these premises, it is reasonably to understand after blending EVOH in MPA resin, the relatively loose molecular

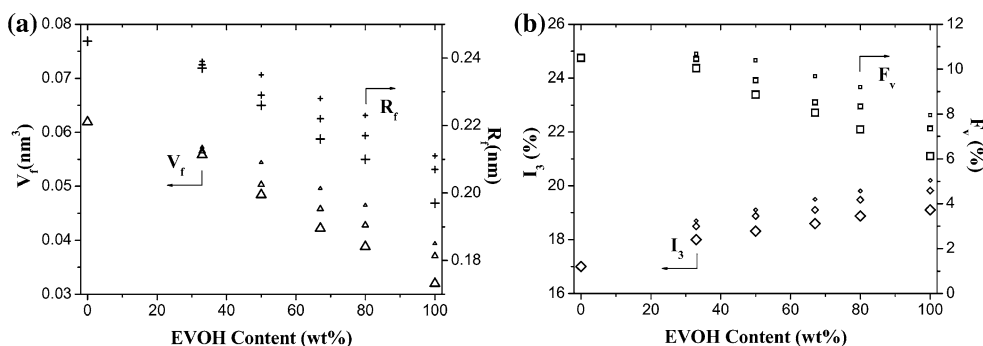
structure originally present in the amorphous regions of MPA specimens can be disrupted and changed into denser structure as the EVOH and/or vinyl alcohol contents increase. Consequently, the  $R_f$ ,  $V_f$  and  $F_v$  values of the MPAEVOH specimens reduce significantly as their EVOH contents increase, and further reduce significantly as the vinyl alcohol contents present in the virgin EVOH resins increase.

#### Oxygen permeation rates of MPA, EVOH and MPAEVOH film specimens

The oxygen permeation rates of MPA, EVOH and MPA-EVOH film specimens at 25 °C are summarized in Table 3 and Fig. 7. The oxygen permeation rate of MPA film specimen reaches only about 154 ( $50 \mu\text{m cm}^3/\text{m}^2 \text{ day - atm}$ ), which is significantly slower than that of the PE film specimen (i.e. 4840 ( $50 \mu\text{m cm}^3/\text{m}^2 \text{ day atm}$ )), but is still higher than those of the EVOH film specimens with varying vinyl alcohol contents. As shown in Table 3, the oxygen permeation rates of the EVOH film specimens are less than 2 ( $50 \mu\text{m cm}^3/\text{m}^2 \cdot \text{day} \cdot \text{atm}$ ) and reduce from 1.5 to 0.48 and to 0.29 ( $50 \mu\text{m cm}^3/\text{m}^2 \text{ day atm}$ ) as their vinyl alcohol contents increase from 52 to 56 and then to 68 wt%, respectively. After blending EVOH in MPA, the oxygen permeation rates of each MPAEVOH series specimens reduce significantly as their EVOH contents increase. As shown in Table 3, the oxygen permeation rates of MPAEVOH<sup>c</sup> series film specimens reduce significantly to 35.9, 13.4 and 6.5 ( $50 \mu\text{m cm}^3/\text{m}^2 \text{ day atm}$ ) as their EVOH<sup>c</sup> contents increase to 33.3, 66.7 and 80 wt%, respectively. Similar tendency of the oxygen permeation properties was found for the MPAEVOH<sup>a</sup> and MPA-EVOH<sup>b</sup> series film specimens (see Fig. 7). Moreover, it is interesting to note that, the oxygen permeation resistance of the MPAEVOH specimens with the same EVOH contents improves significantly as their vinyl alcohol contents increase. For instance, at an 80 wt% EVOH content, the oxygen permeation rates of the MPA<sub>1</sub>EVOH<sub>4</sub> specimens reduce from 6.5 to 1.2 and to 0.58 ( $50 \mu\text{m cm}^3/\text{m}^2 \text{ day - atm}$ ) as their vinyl alcohol contents increase from 52 to 56 and then to 68 wt%, respectively. In fact, it is worth noting that the oxygen permeation rates of the MPA<sub>1</sub>EVOH<sub>4</sub> and

**Table 2** Free-volume properties of PE, MPA and EVOH film specimens

Sample	Annihilation intensity $I_3$ (%)	Radius of the average free-volume-cavity $R_f$ (nm)	Average free-volume-cavity size $V_f$ ( $\text{nm}^3$ )	Fractional free volume $F_v$ (%)
PE	16.95	0.304	0.1177	20.0
MPA	17.00	0.245	0.0619	10.5
EVOH <sup>a</sup>	19.11	0.197	0.0320	6.1
EVOH <sup>b</sup>	19.82	0.207	0.0371	7.3
EVOH <sup>c</sup>	20.20	0.211	0.0394	8.0



**Fig. 6** (a) Average radius ( $R_f$ ) (+) and free-volume ( $V_f$ ) ( $\Delta$ ) values of the free-volume-cavity of MPAEVOH<sup>a</sup>, MPAEVOH<sup>b</sup> and MPAEVOH<sup>c</sup> specimens; (b) annihilation intensity ( $I_3$ ) ( $\diamond$ ) and

fractional free-volume ( $F_v$ ) ( $\square$ ) values of MPAEVOH<sup>a</sup>, MPAEVOH<sup>b</sup> and MPAEVOH<sup>c</sup> specimens. (The sizes of symbols increase with the increasing vinyl alcohol contents present in virgin EVOH resins)

MPA<sub>1</sub>EVOH<sub>4</sub><sup>b</sup> film specimens are even lower than that of the pure EVOH<sup>c</sup> film specimen.

It is generally recognized that the crystallinity values, sizes and fractional free volumes of the free volume cavities in the amorphous regions of the polymers can greatly affect their barrier properties, because the gas or liquid permeant molecules can hardly diffuse through crystalline regions but can only permeate through the amorphous regions of the polymer resins, wherein the permeant paths in the amorphous regions offer enough space allowing permeant molecules to enter and diffuse. In addition, the non-polar polymer molecules are expected to absorb more non-polar permeant molecules into their amorphous regions,

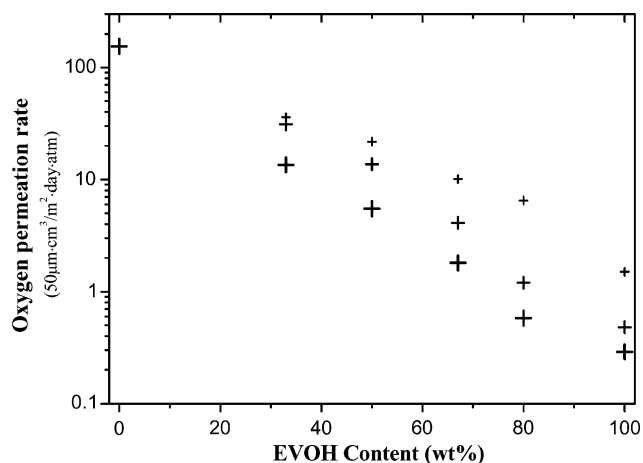
and hence, enhance the permeation rates of the non-polar permeant molecules than the polar polymers with about the same sizes or fractional free volumes of the free volume cavities. The influence of the vinyl alcohol contents on the crystallinity values of EVOH and MPAEVOH resins were discussed in our previous investigation [31]. The crystallinity values of EVOH resins increase from 31.1% to 40.8% as their vinyl alcohol contents increase from 52 wt% to 68 wt%. However, the crystallinity values of the MPAEVOH series specimens with varying vinyl alcohol contents remain relatively unchanged. For instance, the crystallinity values of MPA<sub>1</sub>EVOH<sub>2</sub>, MPA<sub>1</sub>EVOH<sub>1</sub>, MPA<sub>4</sub>EVOH<sub>1</sub> and MPA<sub>5</sub>EVOH<sub>1</sub> series specimens only increase by about 2%, as the vinyl alcohol contents of EVOH resins present in the MPAEVOH specimens increase from 52 wt% to 68 wt%, respectively. On the other hand, as shown in the previous section, the  $R_f$ ,  $V_f$  and  $F_v$  values of the EVOH and MPA resins are significantly lower than that of the PE resin, wherein the  $R_f$ ,  $V_f$  and  $F_v$  values of the EVOH specimens are even lower than that of the MPA specimens, and reduce further with increasing their vinyl alcohol contents. Apparently, the small, non-polar oxygen molecules with an effective radius of about 0.2 nm can easily permeate through the amorphous regions of the non-polar PE resins with relatively large  $R_f$  and  $F_v$  values of 0.304 nm and 20.0%, respectively, but can barely enter into and permeate through the amorphous regions of the EVOH resins, since their  $R_f$  or  $F_v$  values are nearly equal to 0.2 nm or less than about 8%, respectively. Based on these premises, it is not hard to understand that the oxygen permeation rates of EVOH film specimens are dramatically and significantly lower than that of the PE and MPA film specimens, respectively, and reduce further as their vinyl alcohol contents increase.

**Table 3** Oxygen permeation rates of PE, MPA, EVOH and MPA-EVOH film specimens

Films	Oxygen	
	Permeation rate (50 $\mu\text{m cm}^3/\text{m}^2 \text{ day atm}$ )	Barrier improvement
PE	4840	1.0
MPA	154	31.4
MPA <sub>2</sub> EVOH <sub>1</sub> <sup>a</sup>	13.5	359
MPA <sub>1</sub> EVOH <sub>1</sub> <sup>a</sup>	5.5	880
MPA <sub>1</sub> EVOH <sub>2</sub> <sup>a</sup>	1.8	2689
MPA <sub>1</sub> EVOH <sub>4</sub> <sup>a</sup>	0.58	8345
EVOH <sup>a</sup>	0.29	16690
MPA <sub>2</sub> EVOH <sub>1</sub> <sup>b</sup>	31	156
MPA <sub>1</sub> EVOH <sub>1</sub> <sup>b</sup>	13.7	353
MPA <sub>1</sub> EVOH <sub>2</sub> <sup>b</sup>	4.1	1180
MPA <sub>1</sub> EVOH <sub>4</sub> <sup>b</sup>	1.2	4033
EVOH <sup>b</sup>	0.48	10083
MPA <sub>2</sub> EVOH <sub>1</sub> <sup>c</sup>	35.9	135
MPA <sub>1</sub> EVOH <sub>1</sub> <sup>c</sup>	21.8	222
MPA <sub>1</sub> EVOH <sub>2</sub> <sup>c</sup>	10.1	479
MPA <sub>1</sub> EVOH <sub>4</sub> <sup>c</sup>	6.5	745
EVOH <sup>c</sup>	1.5	3227

As mentioned in the previous section, after blending EVOH in MPA, the  $R_f$ ,  $V_f$  and  $F_v$  values of the MPAEVOH specimens reduce significantly as their EVOH contents increase, and further reduce significantly as the vinyl





**Fig. 7** Oxygen permeation rates of MPAEVOH<sup>a</sup> (+), MPAEVOH<sup>b</sup> (+) and MPAEVOH<sup>c</sup> (+) series specimens

alcohol contents present in the virgin EVOH resins increase. It is, therefore, reasonable to suggest that the significant reduction in the oxygen permeation rates of MPAEVOH specimens with increasing EVOH and/or vinyl alcohol contents is due to their gradually reduced  $R_f$  and  $F_v$  values, as the EVOH and/or the vinyl alcohol contents of MPAEVOH series specimens increase.

## Conclusions

The oxygen permeation rate of EVOH film specimens are dramatically slower than that of the PE and MPA specimens and reduce significantly as their vinyl alcohol contents increase. After blending EVOH in MPA resin, the oxygen permeation rates of each MPAEVOH series film specimens reduce significantly as their EVOH and/or vinyl alcohol contents increase. In fact, at an EVOH content of 80 wt%, the oxygen permeation rates of the MPA<sub>1</sub>EVOH<sub>4</sub> film specimens are even lower than that of the pure EVOH film specimen with a vinyl alcohol content of 52 wt%, wherein the vinyl alcohol contents present in the virgin EVOH of MPA<sub>1</sub>EVOH<sub>4</sub> film specimens are equal to or more than 56 wt%. The free volume investigations indicate that  $R_f$ ,  $V_f$  and  $F_v$  values of the EVOH resins are significantly lower than those of the PE and MPA resins and reduce significantly with increasing their vinyl alcohol contents. After blending EVOH in MPA, the  $R_f$ ,  $V_f$  and  $F_v$  values of each MPAEVOH series specimens reduce significantly as their EVOH and/or vinyl alcohol contents increase. Presumably, the significant reduction in the oxygen permeation rates of MPAEVOH specimens with increasing EVOH and/or vinyl alcohol contents is due to their gradually reduced  $R_f$  and  $F_v$  values, as the EVOH and/or the vinyl alcohol contents of MPAEVOH series specimens increase.

Further FT-IR studies found that at a fixed elevated temperature, the  $\Delta\nu$  values and the intensity of the free hydroxyl band of EVOH specimens increase and reduce significantly as their vinyl alcohol contents increase, respectively. These results clearly suggest that inter and intramolecular hydrogen-bonded hydroxyl groups present in the EVOH molecules are somewhat strengthened as their vinyl alcohol contents increase, that can attract and hold the EVOH molecules in a relatively condensed way in their amorphous phases, and cause smaller  $R_f$  and  $V_f$  values of the free-volume-cavities as their vinyl alcohol contents increase. On the other hand, the widths shown in the half-height of C=O stretching bands of MPAEVOH specimens reduce significantly with increasing the EVOH and/or vinyl alcohol contents. Presumably, these interesting FT-IR results are attributed to the decreasing amounts of allowed C=O stretching vibrations and the gradually strengthened interaction between carbonyl and hydroxyl groups in the MPAEVOH series specimens, as their EVOH and/or the vinyl alcohol contents increase. As a consequence, the relatively loose molecular structure originally present in the amorphous regions of MPA specimens can be disrupted and changed into denser structure and hence, causes a significant reduction in the  $R_f$ ,  $V_f$  and  $F_v$  values of the MPAEVOH specimens, as their EVOH and/or vinyl alcohol contents increase.

## References

- Iwanamy T, Hiral Y (1983) *Tappi J* 66:85
- Tanaka Y (1989) *Jpn Food Sci* 7:49
- Ozeki Y, Kim J (1996) In: Salamone JC (ed) *Polymeric materials encyclopedia*, vol 3. CRC, New York, p 2284
- Finch CA (1992) In: *Polyvinyl alcohol*. John Wiley and Sons, New York, p 258
- Tsai BC, Wachtel JA (1989) In: Koros WJ (ed) *Barrier polymers and structures*, ACS symposium series 423. American Chemical Society, Washington, DC, p 192
- Brown WE (1992) In: *Plastics in food packaging*. Marcel Dekker, New York, p 301
- Odorzynski TW (1982) U.S. Patent no. 4347332
- Pottsville AD (1984) U.S. Patent no. 4427825
- Subramanian PM (1983) U.S. Patent no. 4410482
- Subramanian PM (1984) U.S. Patent no. 4444817
- Yeh JT, Jou WS, Su YS (1999) *J Appl Polym Sci* 9:2158
- Yeh JT, Wang LH, Chen KN, Jou WS (2001) *J Mater Sci* 36:1891
- Yeh JT, Shyu WD, Chen CH (2001) *J Appl Polym Sci* 80:1122
- Subramanian PM (1985) *Polym Eng Sci* 25:483
- Subramanian PM (1987) *Polym Eng Sci* 27:663
- Diluccio RC (1983) U.S. Patent no. 4416942
- Yeh JT, Fan-Chiang CC (1995) *Cho MF Polym Bull* 35:371
- Yeh JT, Fan-Chiang CC, Yang SS (1997) *J Appl Polym Sci* 64:1531
- Yeh JT, Fan-Chiang CC (1997) *J Appl Polym Sci* 66:2517
- Yeh JT, Fan-Chiang CC (1996) *J Polym Res* 3:211
- Yeh JT, Jyan CF (1998) *Polym Eng Sci* 38:1482

22. Yeh JT, Jyan CF, Chou S (1998) *SPE Antec* 3:3567
23. Yeh JT, Yang SS, Jyan CF, Chou S (1999) *Polym Eng Sci* 39:1952
24. Yeh JT, Chao CC, Chen CH (2000) *J Appl Polym Sci* 76:1997
25. Yeh JT, Shih WS, Huang SS (2002) *Macromol Mater Eng* 287:23
26. Yeh JT, Chang SS, Yao HT, Chen KN, Jou WS (2000) *J Mater Sci* 35:1
27. Yeh JT, Huang SS, Yao WH (2002) *Macromol Mater Eng* 287:532
28. Yeh JT, Yao WH, Du QG, Chen CC (2005) *J Polym Sci Part B Polym Phys* 43:511
29. Yeh JT, Huang SS, Chen HY (2005) *Polym Eng Sci* 45:25
30. Yeh JT, Huang SS, Chen HY (2005) *J Appl Polym Sci* 97:1333
31. Yeh JT, Chen HY, Tsai FC (in press) *J Appl Polym Sci*
32. Nakanishi H, Jean YC, Smith EG, Sandreczki TC (1989) *J Polym Sci Polym Phys Ed* 27:1419
33. Nakanishi H, Wang SJ, Jean YC (1988) In: Sharma SC (ed) *Positron annihilation in fluids*. World Scientific, Singapore, p 753
34. Deng Q, Sundar CS, Jean YC (1992) *J Phys Chem* 96:492
35. Wang YY, Nakanishi H, Jean YC, Sandreczki TC (1990) *J Polym Sci Polym Phys Ed* 28:1431
36. Skrovanek DJ, Howe SE, Painter PC, Coleman MM (1985) *Macromolecules* 18:1676
37. Coleman MM, Yang X, Zhang H, Painter PC (1993) *J Macromol Sci Phys B* 32:295
38. Moskala EJ, Varnell DF, Coleman MM (1985) *Polymer* 26:228
39. Person WB, Zerbi G (1982) In *Vibrational intensities in infrared and Raman spectroscopy*. Elsevier, New York, p 159