

Water Vapor Transmission of Poly(ethylene oxide)-Based Segmented Block Copolymers

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Received 2 September 2008; accepted 9 November 2008

DOI 10.1002/app.29677

Published online 13 February 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This article discusses the rate of water vapor transmission (WVT) through monolithic films of segmented block copolymers based on poly(ethylene oxide) (PEO) and monodisperse crystallisable tetra-amide segments. The polyether phase consisted of hydrophilic PEO or mixtures of PEO and hydrophobic poly(tetramethylene oxide) (PTMO) segments. The monodisperse tetra-amide segments (T6T6T) were based on terephthalate units (T) and hexamethylenediamine (6). By using monodisperse T6T6T segments the crystallinity in the copolymers was high ($\sim 85\%$) and, therefore, the amount of noncrystallised T6T6T dissolved in the polyether phase was minimal. The WVT was determined by using the ASTM E96BW method, also known as the inverted cup method. By using this method, there is direct contact between the polymer film and the water

in the cup. The WVT experiments were performed in a climate-controlled chamber at a temperature of 30°C and a relative humidity of 50%. A linear relation was found between the WVT and the reciprocal film thickness of polyether-T6T6T segmented block copolymers. The WVT of a 25- μm thick film of PTMO₂₀₀₀-based copolymers was 3.1 kg m⁻² d⁻¹ and for PEO₂₀₀₀-based copolymers 153 kg m⁻² d⁻¹. Of all the studied copolymers, the WVT was linear related to the volume fraction of water absorbed in the copolymer to the second power. The results were explained by the absorption-diffusion model. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2143–2150, 2009

Key words: poly(ethylene oxide); segmented; monodisperse; water vapor transmission

INTRODUCTION

Segmented block copolymers are often used in breathable film applications applied in markets like construction, medical, hygiene, textile, and food packaging. A breathable film is characterized by a high permeability toward water vapor and is at the same time waterproof.

One type of breathable film is a monolithic (homogeneous) film made from a hydrophilic polymer. These films are nonfouling, have a selective permeability and good mechanical properties. However, hydrophilic polymers often swell in the presence of water and with an increased amount of absorbed water, the mechanical properties like modulus and fracture stress are reduced.^{1–7}

The transport of water vapor molecules through a monolithic film is usually described by the solution-diffusion model [eq. (1)].⁸

$$P = S \times D \quad (1)$$

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Contract grant sponsor: Dutch Polymer Institute (DPI, The Netherlands); contract grant number: 313.

where P is the transport of water vapor, S is the solubility of water in the polymer, and D is the diffusion rate. Water will be absorbed at the film side with the highest concentration of water molecules. Subsequently, water diffuses through the film and desorbs at the side with the lowest concentration of water molecules. The driving force for diffusion is the concentration difference across the film. The transport of water vapor molecules through a monolithic film can be described by Fick's first law [eq. (2)]⁹:

$$J = -P \frac{dc}{dx} \quad (2)$$

where J is the water vapor flux through the film, P is the permeability coefficient, and dc/dx the concentration (c) gradient over the film with a certain thickness (x).

According to the solution-diffusion model, the permeability of water vapor through a polymer film is the product of diffusivity and solubility. The solubility of water in segmented block copolymers is strongly influenced by the interaction between water and the polar groups, the crosslink density and the amount and type of a filler phase.^{9–11} Diffusivity is a kinetic parameter that indicates how fast water vapor molecules are transported through the polymer film.⁹ Generally, the diffusivity of polar

TABLE I
WVT of Some Commercially Available Segmented Block copolymers (ASTM E96BW,
 $T = 38^{\circ}\text{C}$, $\text{RH} = 50\%$)^{17,24}

| Polymer | Trade name | Type of polyether | WA (wt %) | WVT (25 μm) ($\text{kg m}^{-2} \text{d}^{-1}$) |
|-------------------|----------------------------|-------------------|-----------|--|
| Poly(ether ester) | Arnitel EM400 ^a | PTMO | 0.5 | 1.9 |
| Poly(ether ester) | Arnitel PM380 ^a | PPO | 5.7 | 4.0 |
| Poly(ether amide) | PEBAX 3533 ^b | PTMO | – | 2.5 |
| Poly(ether amide) | PEBAX MV1041 ^b | PEO | – | >10 |
| Poly(ether amide) | PEBAX MV3000 ^b | PEO | – | >15 |
| Poly(ether amide) | PEBAX MV1074 ^b | PEO | – | >20 |

^a Manufactured by DSM.

^b Manufactured by Arkema.

polymers increases with increasing amount of water absorbed in the polymer due to the plasticizing effect. However, it was reported that when clustering of water molecules in the polymer takes place the diffusivity decreases.^{9,10,12,13} Adriaensens et al.¹⁴ reported that the diffusion coefficient of water in copolyamides, as determined by sorption isotherms, increased with the water absorption (WA) of the copolymer (4–12 wt %).

Generally, the rate of water vapor transmission (WVT) is used to quantify the breathability and is expressed as amount of water vapor transported through one square meter of film per day ($\text{kg m}^{-2} \text{d}^{-1}$). Several methods can be used for determining the WVT, which differ in test conditions like indirect or direct contact of the film with water, the humidity on both sides of the film, the temperature.¹⁴ The test methods and conditions are often adjusted to the demands of the application market of the film. It was found that the WVT results obtained with different test methods were not comparable.^{15,16} However, it is possible to make a correlation between these WVT results.^{15,16}

Some methods have been standardized (ASTM E96) and two of these methods are frequently used; the E96BW (inverted cup) and the E96B (upright cup) method. By using the inverted cup method the water in the cup is in direct contact with the film, while using the upright cup method an air layer between the film and water in the cup exists. This air layer acts as an extra resistant boundary layer that affects the WVT values. Consequently, the WVT values obtained with the E96BW method are significant higher than when the E96B method is applied. To obtain WVT values that are characteristic for the polymer, the diffusion of water vapor through the film must be the rate determining step. Therefore, the E96BW method is more suitable than the E96B method. However, it has been reported that the ASTM E96BW method is not suitable for measuring the WVT of highly permeable thin films due to an increase in the resistance of the boundary layers.^{17,18}

For the use as breathable film material several segmented block copolymers are available, like poly(ether urethane)s,^{12,19–21} poly(ether ester)s,^{22,23} and poly(ether amide)s.²⁴ The permeability of these copolymers is expected to increase with the hydrophilicity, which increases in the order of poly(tetramethylene oxide) (PTMO), poly(propylene oxide) (PPO), and poly(ethylene oxide) (PEO).

Metz et al.¹³ studied the water vapor flux through a film of poly(ether ester) segmented block copolymers (PEO₁₀₀₀-PBT). The flux increased with the water activity at the feed side and the hydrophilicity of the copolymer.

In Table I, the WVT of some commercially available segmented block copolymers are listed.^{17,24} The WVT of these materials, having a film thickness of 25 μm , was measured in a climate chamber ($T = 38^{\circ}\text{C}$, $\text{RH} = 50\%$) using the ASTM E96BW method. The use of a more hydrophilic polyether segment resulted in increased WA and WVT.

Generally, the crystallinity of the rigid segments in segmented block copolymers is rather low, around 30%. This means that a relatively high amount of rigid segments is necessary to obtain good mechanical properties of the copolymer. Moreover, a large amount of noncrystallised rigid segment is present in the polyether phase, which might affect the rate of WVT.

With the use of short monodisperse crystallisable segments one can improve the crystallinity of the rigid segments in the copolymer.^{25–30} A typical example for this are the PEO-T6T6T segmented block copolymers (Fig. 1).^{28–30}

The T6T6T segments are based on terephthalic acid (T) and hexamethylenediamine (6) and T6T6T had in the copolymers a high crystallinity ($\sim 85\%$). The morphology of the T6T6T crystallites is that of nanoribbons with a thickness of about 4 nm and a length >300 nm.³⁰ Because of the short highly crystalline T6T6T segments had the copolymers with a high PEO concentration still had good mechanical properties.^{6,7,29,30} The WA of these well-defined

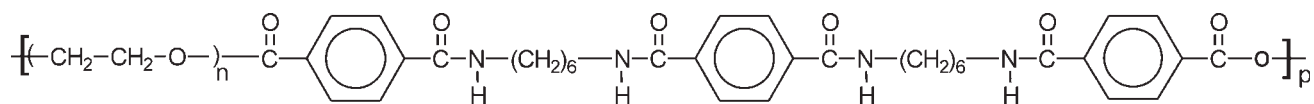


Figure 1 Chemical structure of PEO-T6T6T.

segmented block copolymers increased with PEO length, PEO concentration and decreasing T6T6T concentration.¹¹ The WA of the PEO-T6T6T copolymers decreased also with increased amount of dissolved nonpolar groups like PTMO and/or terephthalic groups.¹¹ As the WA increased, the number of water molecules per EO unit ($\text{H}_2\text{O}/\text{EO}$) also increased and in systems with long PEO segments ($>1000 \text{ g mol}^{-1}$) clustering of water molecules was taking place.¹¹

In dry conditions, PEO segments with a length $>2000 \text{ g mol}^{-1}$ have a crystalline PEO phase at room temperature. It is expected that the presence of polyether crystals in the copolymer have an adverse effect on the WVT. However, on wetting the copolymer the PEO melting temperature decreased strongly. At 54% RH, the PEO melting temperature was 6°C and at 85% RH the PEO melting temperature was $\sim 35^\circ\text{C}$ lower.¹¹

The influence of the soft phase composition on the rate of WVT of polyether-T6T6T segmented block copolymers was studied. The WVT was determined by using the ASTM E96BW method at a temperature of 30°C and a relative humidity of 50%. Three different copolymer series were studied, which vary in the PEO concentration, the hydrophobic concentration (PTMO or terephthalate units) and the T6T6T concentration.

EXPERIMENTAL

PEO₁₀₀₀/PTMO₁₀₀₀-T6T6T and PEO₂₀₀₀/PTMO₂₀₀₀-T6T6T block copolymers

The PEO/PTMO-T6T6T block copolymers have been synthesized by a polycondensation reaction using a mixture of PEO and PTMO segments and T6T6T.⁶ The PEO and PTMO molecular weight was 1000 or 2000 g mol^{-1} .

PEO_x-T6T6T block copolymers

The PEO_x-T6T6T copolymers have been synthesized by a polycondensation reaction using PEO segments with a molecular weight (x) of $1000\text{--}3400 \text{ g mol}^{-1}$ and T6T6T.²⁹

(PEO_x/T)_y-T6T6T block copolymers

The (PEO_x/T)_y-T6T6T copolymers have been synthesized by a polycondensation reaction using PEO seg-

ments, which are extended with terephthalic units (T), and T6T6T.³¹ The PEO molecular weight (x) and the total molecular weight of the flexible segment (y) were varied.

Film preparation

Films of $\sim 100 \mu\text{m}$ have been made from dried copolymers using of a 40 ton Lauffer 40 press. The temperature was set $\sim 40^\circ\text{C}$ above the melting temperature of the copolymer. First, air was removed from the polymer in the mold by quickly pressurizing the samples followed by depressurizing. This procedure was repeated three times before actually pressing the samples at 10 MP ($\sim 8.5 \text{ MPa}$) for 5 min. Subsequently, the samples were cooled to room temperature while maintaining the pressure. It was possible to vary the film thickness from 50 to $300 \mu\text{m}$ by using metal molds of appropriate thickness. To prevent sticking of the polymer onto the metal mold, glass fiber reinforced PTFE sheets was used (Benetech type B105). The dry film thickness was the average measured on 10 different places and the standard deviation (SD) was $\pm 15 \mu\text{m}$.

Water absorption

The equilibrium WA was measured using pieces of injection-molded polymer bars. The samples were placed in a desiccator filled with demineralized water for 4 weeks at room temperature. The WA was defined as the weight gain of the polymer according to eq. (3).

$$\text{WA} = \frac{m - m_0}{m_0} \times 100\% \text{ (wt \%)} \quad (3)$$

where m_0 is the weight of dry sample and m is the weight of the sample after conditioning to equilibrium. The measurements were performed in duplicate. After 4 weeks, the samples were dried and m_0 was measured again to exclude weight loss during the experiment. The volume fraction of water in the polymer (ϕ_{water}) was determined by using a PEO, PTMO, DMT, and T6T6T density of 1.13, 0.98, 1.20, and 1.32 g cm^{-3} , respectively.¹⁰

Rate of WVT

The WVT through films was determined using the ASTM E96BW method (inverted cup method). A

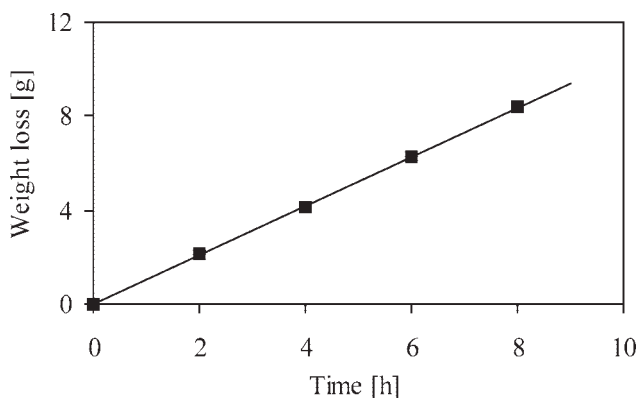


Figure 2 Weight loss (g) as a function of the time (h) in steady-state conditions of PEO₂₀₀₀/PTMO₂₀₀₀-T6T6T (40/60) (dry film thickness ~ 119 μm).

cup filled with demineralized water (250 mL) was sealed with a swollen polymer film and placed upside-down in climate-controlled chamber. In this chamber, the temperature was $30 \pm 1^\circ\text{C}$ and the relative humidity $50 \pm 2\%$ and there was a constant air circulation. A sealant (butyl rubber) is used to prevent leakage of water when the cup is placed in the inverted position. After steady-state conditions were reached in ~ 2 h, the weight of the cup was periodically measured (periods of ~ 2 h) for at least five times. The WVT was calculated using eq. (4).

$$\text{WVT} = \frac{(G/t)}{A} \text{ (kg m}^{-2} \text{ d}^{-1}) \quad (4)$$

where G is the weight loss (kg), t is the time in days (d), A is the test area of the cup (0.00503 m^2), and WVT is the rate of WVT ($\text{kg m}^{-2} \text{ d}^{-1}$). The WVT experiments were performed in duplicate.

At high water fluxes an under pressure was created in the cup which disturbed the measurement. This side effect at high WVT can be prevented by using thick films and short time intervals.

RESULTS AND DISCUSSION

The effect of the type of polyether, the polyether molecular weight, the polyether concentration and the rigid segment concentration on the WVT was studied. Three copolymer series were investigated: PEO/PTMO-T6T6T, PEO_x-T6T6T, and (PEO_x/T)_y-T6T6T. In this study, the films were saturated with water before measuring and therefore the polyether phase was completely amorphous during the test.

WVT measurements

The WVT measurements were performed using the inverted cup ASTM E96BW method, where there is direct contact between the water in the cup and the polymer film. When a dry polymer film is placed on

the cup filled with water and subsequently the cup is inverted, the film absorbs water and swells and thereby enlarges its size. Consequently, the exact film area is unknown and the WVT cannot be calculated precisely. To prevent this, the film was first allowed to swell in water before it was placed on the cup. For the calculation of the WVT, the thickness of the dry film was used. The measurements were for practical reasons carried out at 30°C .

After steady-state conditions were obtained the weight loss of the cup as a function of time was measured (Fig. 2). From the slope of this plot, the vapor flux through the film was determined. By dividing the water vapor flux by the test area, the rate of WVT was calculated using eq. (4).

Influence film thickness on WVT

According to Fick's first law [eq. (2)], the water vapor flux is inversely related to the thickness of a monolithic film,³² assuming that the diffusion coefficient is constant. The influence of the film thickness on the WVT was examined using the PEO₂₀₀₀/PTMO₂₀₀₀-T6T6T (40/60) copolymer, which consists of mixed PEO₂₀₀₀ and PTMO₂₀₀₀ segments with a weight percentage ratio of 40/60 and monodisperse crystallisable T6T6T segments. The WVT of the films with varying thicknesses between 69 and 216 μm are given in Figure 3. As expected, a linear relation was observed between the reciprocal film thickness and the WVT (Fig. 3). The diffusion coefficient of this copolymer is constant and independent of the water vapor flux.

To compare the WVT of films with different thicknesses (l), a normalized WVT can be calculated by using a reference thickness (l_{ref}) according to eq. (5).

$$\text{WVT}_{25\mu\text{m}} = \text{WVT} \times \left(\frac{l}{l_{\text{ref}}} \right) \text{ (kg m}^{-2} \text{ d}^{-1}) \quad (5)$$

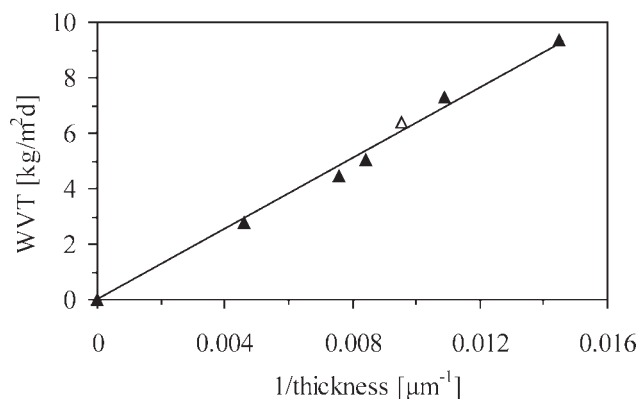


Figure 3 Influence of film thickness (dry) and water content in the cup on the WVT of PEO₂₀₀₀/PTMO₂₀₀₀-T6T6T (40/60); \blacktriangle , 250 mL water; Δ , 75 mL water.

TABLE II
WVT_{25μm} of PEO/PTMO-T6T6T Copolymers

| PEO/PTMO (ratio) | Conc. T6T6T (wt %) | Conc. PEO (wt %) | Conc. PTMO (wt %) | $G'_{20^\circ\text{C}}^a$ (MPa) | WA (wt %) | H ₂ O/EO (-) | ϕ_{water} (vol %) | WVT _{25μm} ± SD (kg m ⁻² d ⁻¹) |
|--|-----------------------|---------------------|----------------------|------------------------------------|--------------|----------------------------|----------------------------------|---|
| PEO ₂₀₀₀ /PTMO ₂₀₀₀ -T6T6T | | | | | | | | |
| 0/100 | 23.8 | 0.0 | 76.2 | 34 | 1.2 | - | 1.2 | 3.1 ± 0.5 |
| 20/80 | 23.8 | 15.2 | 61.0 | 38 | 9.8 | 1.6 | 10 | 7.5 ± 1.4 |
| 40/60 | 23.8 | 30.5 | 45.7 | 31 | 24 | 1.9 | 22 | 25 ± 2 |
| 50/50 | 23.8 | 38.1 | 38.1 | 33 | 33 | 2.1 | 28 | 42 ± 7 |
| 60/40 | 23.8 | 45.7 | 30.5 | 33 | 42 | 2.3 | 33 | 62 ± 10 |
| 80/20 | 23.8 | 61.0 | 15.2 | 33 | 60 | 2.4 | 41 | 101 ± 17 |
| 100/0 | 23.8 | 76.2 | 0.0 | 38 | 91 | 2.9 | 52 | 153 ± 12 |
| PEO ₁₀₀₀ /PTMO ₁₀₀₀ -T6T6T | | | | | | | | |
| 0/100 | 38.4 | 0.0 | 61.6 | 89 | 1.1 | - | 1.2 | 1.7 ± 0.2 |
| 30/70 | 38.4 | 18.5 | 43.1 | 80 | 8.1 | 1.1 | 8.8 | 3.5 ± 0.2 |
| 40/60 | 38.4 | 24.6 | 37.0 | 111 | 11 | 1.1 | 12 | 6.2 ± 0.9 |
| 60/40 | 38.4 | 37.0 | 24.6 | 103 | 20 | 1.3 | 19 | 14 ± 2 |
| 100/0 | 38.4 | 61.6 | 0.0 | 85 | 41 | 1.4 | 33 | 57 ± 9 |

^a Storage modulus determined at 20°C using dynamic mechanical analysis.⁶

The rate of WVT (kg m⁻² d⁻¹) was normalized to a film thickness of 25 μm (WVT_{25μm}). The calculated average WVT_{25μm} values had a standard deviation of about 10%.

For films with high WVT values, the amount of water in the cup decreased strongly and reduced the pressure in the cup. To prevent this effect with high WVT values thicker films were used and short measuring times were applied. With the used experimental setup, it was not possible to measure the WVT of films that were thicker than 300 μm since the sealing of the cup failed and leakage of water took place.

To determine whether the amount of water on top of the film had an influence on the WVT, the water level was varied from 50 mm (250 mL in the cup) to 15 mm (75 mL in the cup) (Fig. 3). These results indicate that the water level in the cup had no measurable influence on the WVT.

PEO/PTMO-T6T6T copolymers

The hydrophilic nature of the polyether segments has a large influence on the WVT of segmented block copolymers (Table I). The WVT of PEO-based copolymers were significantly higher compared with PTMO-based copolymers. A way to vary the hydrophilicity of the copolymers is by using a mixture of hydrophilic PEO and hydrophobic PTMO segments.¹¹ Several copolymers based on mixtures of PEO and PTMO segments were prepared and these copolymers are denoted as PEO/PTMO-T6T6T (Table II).⁶ In these copolymers, the soft phase composition can be varied in two ways; by changing the PEO/PTMO ratio and by changing the polyether molecular weights.

The WVT results of the PEO₂₀₀₀/PTMO₂₀₀₀-T6T6T and PEO₁₀₀₀/PTMO₁₀₀₀-T6T6T series are given in Table III. Increasing the PEO concentration increased

TABLE III
WVT_{25μm} of PEO_x-T6T6T and (PEO_x/T)_y-T6T6T Copolymers

| x or y (g mol ⁻¹) | Conc. T6T6T (wt %) | Conc. PEO (wt %) | Conc. T (wt %) | $G'_{20^\circ\text{C}}^a$ (MPa) | WA (wt %) | H ₂ O/EO (-) | ϕ_{water} (vol %) | WVT _{25μm} ± SD (kg m ⁻² d ⁻¹) |
|---|-----------------------|---------------------|-------------------|------------------------------------|--------------|----------------------------|----------------------------------|---|
| PEO _x -T6T6T | | | | | | | | |
| 1000 | 38.4 | 61.6 | - | 86 | 35 | 1.4 | 33 | 57 ± 9 |
| 1500 | 29.4 | 70.6 | - | 57 | 69 | 2.4 | 45 | 117 ± 10 |
| 2000 | 23.8 | 76.2 | - | 38 | 91 | 2.9 | 51 | 153 ± 12 |
| 3400 | 15.5 | 84.5 | - | 18 ^b | 127 | 3.7 | 60 | 188 ± 14 |
| (PEO ₃₀₀ /T) _y -T6T6T | | | | | | | | |
| 2500 | 19.9 | 58.4 | 21.7 | 46 | 14 | 0.6 | 14 | 13 ± 3 |
| (PEO ₆₀₀ /T) _y -T6T6T | | | | | | | | |
| 1250 | 33.3 | 60.4 | 6.3 | 68 | 30 | 1.2 | 26 | 25 ± 5 |
| 2500 | 20.0 | 69.0 | 11.0 | 32 | 49 | 1.7 | 36 | 58 ± 8 |
| 5000 | 11.1 | 74.8 | 14.2 | 12 | 69 | 2.2 | 43 | 124 ± 11 |

^a Storage modulus determined at 20°C using dynamic mechanical analysis.³⁰

^b Storage modulus of the rubbery plateau determined at 55°C.³⁰

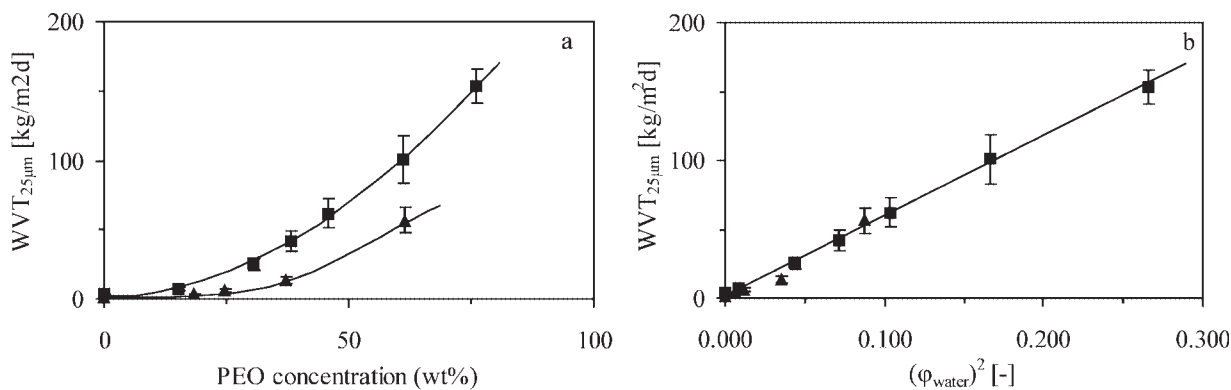


Figure 4 WVT_{25μm} as a function of the PEO concentration (a), the volume fraction of water to the second power (b): ■, PEO₂₀₀₀/PTMO₂₀₀₀-T6T6T; ▲, PEO₁₀₀₀/PTMO₁₀₀₀-T6T6T.

the WA of PEO_x/PTMO_z-T6T6T copolymers. Also the number of water molecules per ethylene oxide unit (H₂O/EO) increased. The water content (φ) increased linearly with PEO content and the slope was higher for the PEO₂₀₀₀/PTMO₂₀₀₀-T6T6T series compared with that of the PEO₁₀₀₀/PTMO₁₀₀₀-T6T6T series.¹¹ This effect is probably due to the polyether segment length and/or the T6T6T concentration. The swelling of rubbers depends both on the network density and on the presence of reinforcing fibers (i.e., T6T6T crystals) which reduces the swelling of the material.^{33,34}

The WVT_{25μm} increased with increasing PEO concentration in the PEO/PTMO-T6T6T copolymers and this increase was exponential [Fig. 4(a)]. The WVT_{25μm} of PEO₂₀₀₀-T6T6T (153 kg m⁻² d⁻¹) was much higher than for PTMO₂₀₀₀-T6T6T (3.1 kg m⁻² d⁻¹). The continuous increase in WVT_{25μm} with PEO concentration indicates that no phase inversion between the PEO and PTMO is noticeable or else an S-shape curve would have been observed.²¹ The WVT_{25μm} values were higher for PEO₂₀₀₀/PTMO₂₀₀₀-T6T6T copolymers than for PEO₁₀₀₀/PTMO₁₀₀₀-T6T6T copolymers, even at similar PEO concentrations. The WVT_{25μm} values had a similar trend as the WA (Table II). This suggests that the WVT is correlated to the amount of water in the copolymer.

When the WVT_{25μm} of both series are given as a function of the volume fraction of water in the copolymer (φ_{water}), the data coincide in one exponential curve (not plotted). This was also the case when the WVT_{25μm} was plotted as function of WA, but not when plotted as function of the H₂O/EO values. This indicates that water clustering (high H₂O/EO values) had for the studied copolymer systems not a good correlation with the WVT and thus the effect of the clustering of water on the WVT was not strong.

A linear relation is observed when the WVT versus (φ_{water})² is given [Fig. 4(b)], indicating that the

WVT is related to the volume fraction of water to the power of two [eq. (6)].

$$\text{WVT}_{25\mu\text{m}} = A (\phi_{\text{water}})^2 \quad (6)$$

The parameter A (kg m⁻² d⁻¹) is expected to be dependant on the test conditions and had in our case a value of 600. The water transport through films is according to the solution-diffusion model a function of WA and water diffusion rate [eq. (1)]⁸ The WA is normally given as [H₂O]/[Polymer] and the water concentration as [H₂O]/[H₂O + Polymer]. At low WAs values, the WA and the water concentration values are identical, however at high WAs (>30%) the concentration values are lower. If the water concentration is used in eq. (1), which does not seem illogic, than the results mean that the water diffusion rate is increased linearly with the water concentration in the film. This is in line with the results obtained on copolyamides.¹⁴ It needs to be sorted out whether in the solution-diffusion model, the water concentration is allowed to be used to calculate the diffusivity parameter.

PEO-T6T6T copolymers

From the previous series, it appears that the PEO segment length is an important parameter for the WA and WVT values. Two series were studied where the PEO segment length was varied: PEO_x-T6T6T and (PEO_x-T)_y-T6T6T (Table III).

In the PEO_x-T6T6T series, the PEO molecular weight (x) was varied from 1000 to 3400 g mol⁻¹.⁶ It was not possible to make a polymer film by compression molding with a PEO molecular weight below 1000 g mol⁻¹ as the film was brittle. When the PEO molecular weight was higher than 3400 g mol⁻¹, the WA of the copolymer was very high (>127 wt %) and the wet film tiered during clamping on the cup.

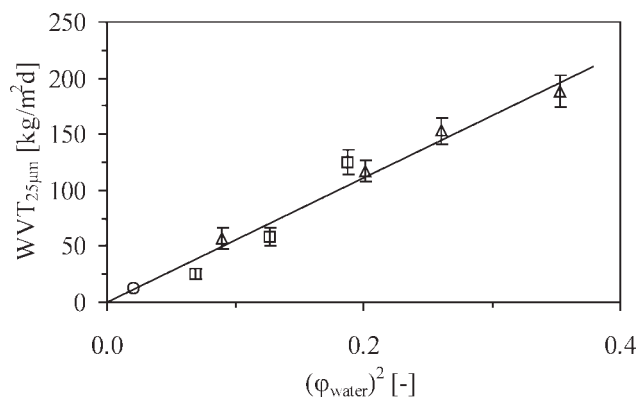


Figure 5 $WVT_{25\mu m}$ as a function the volume fraction of water to the power of two: Δ , PEO_x -T6T6T; \square , $(PEO_{600}/T)_y$ -T6T6T; \circ , $(PEO_{300}/T)_y$ -T6T6T).

In the $(PEO_x-T)_y$ -T6T6T series the PEO_x is extended with terephthalic units to create long polyether segment lengths (y).³¹ These copolymers could be made with high soft segment length (high PEO concentrations) while still having a homogenous melt. The WA of the PEO_x -T6T6T copolymers was influenced by the PEO_x length, the PEO concentration and T6T6T concentration. As the PEO length increased, the PEO concentration increased and the T6T6T concentration decreased. These three parameters are directly related in this series. With increasing soft segment length and thus PEO concentration, the WA was increased. A linear relation was found between the volume fraction of water and the PEO concentration when the PEO concentration was above 49 wt %⁶. The WA of the $(PEO_x-T)_y$ -T6T6T as function of PEO concentration were slightly lower. The reduction of WA was stronger when copolymers contain higher concentrations of terephthalic unit. The presence of hydrophobic terephthalic groups in the soft phase lowers the H_2O/EO values in a similar way as was observed when PTMO was presence.

In Figure 5, the $WVT_{25\mu m}$ of the PEO_x -T6T6T and $(PEO_x-T)_y$ -T6T6T copolymers are given as a function of the volume fraction of water to the power of two and again a linear relationship was observed. The slope of the line, value A in eq. (6), was the same as for the PEO/PTMO-T6T6T series. This indicates the strong correlation between the water concentration in the copolymers and the WVT.

CONCLUSIONS

The rate of WVT through polyether-T6T6T films was determined by using the ASTM E96BW (inverted cup) method. The experiments were performed in a climate-controlled chamber at a temperature of 30°C and a relative humidity of 50% in the climate chamber.

A linear relation was found between the WVT and the reciprocal film thickness of the polyether-T6T6T copolymers. As a consequence, it is possible to calculate a normalized WVT data for a 25- μm thick film.

With increasing PEO concentration in the copolymer, a strong increase in $WVT_{25\mu m}$ was observed. The $WVT_{25\mu m}$ for $PTMO_{2000}$ -T6T6T and PEO_{2000} -T6T6T is 3.1 and 153 $kg\ m^{-2}\ d^{-1}$, respectively. A linear relation was found between the WVT and the volume fraction of water in the copolymer to the second power. The composition of the copolymers had no effect on this relationship. With the absorption-diffusion model [eq. (1)], the solubility parameter (S) changes linearly with the water concentration. The WVT is the permeability parameter (P) and changed with the quadrupole of the water concentration. As a result of this, the diffusion parameter (D) must change linearly with the water concentration in the copolymer. Thus, it was found that the water diffusion parameter increased linearly with the water concentration in the sample.

The authors thank Drs A. Stroeks, K. Dijkstra, and A. Smidt of DSM research in Geleen, The Netherlands, for their advice and Professors J. Feijen and M. Wessling of Twente University for their discussions.

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