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Modelling the moisture vapour transmission rate through segmented block co-poly(ether–ester) based breathable films

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Abstract

Water permeability is an important property of films used in, for instance, protective clothing or construction applications. There are a number of standardised test methods available for evaluating the permeability of films. In one class of tests, there is a direct contact between the polymer film and water; in another class of tests there is an air layer between water and the film. This paper deals with the modelling of water permeability of two commercial types of segmented block co-poly(ether–ester). Water transport in the films is modelled assuming a simple Fickian diffusion behaviour, sorption isotherms are described in terms of either a Zimm–Lundberg based cluster model or Henry's law. Mass transport in the air layer is described in analogy with heat transport for the classical Bénard problem. Using this analysis it is shown that water permeability for both films and for both types of tests can be predicted as a function of the film thickness. There is a good agreement between the model predictions and the experiment. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Modelling; Water permeability; Block co-poly(ether–ester) films

1. Introduction

In many film applications barrier properties are considered to be vital. In these cases a controlled level of permeability to one or more media is required. When barrier properties against media with large differences in solubility parameter are necessary, often material combinations (e.g. via co-extrusion) have to be used to fulfil the demands. Examples of the latter are polyamide polyethylene combinations that are applied when a barrier against water and oxygen is required.

There is, however, an increasing number of film applications where a high permeability is an asset. In most of these cases, permeability of water vapour, while still acting as a barrier against liquid water, is required. Films that posses this property are called breathable films. Examples of applications for breathable films are: clothing, protective apparel, diapers and feminine hygiene, roofing membranes, etc.

There are two classes of breathable film, which are set apart by principal differences in transport mechanism. The first class consists of microporous membranes. These membranes can be biaxially stretched films (often polyethylene filled with calcium carbonate) or dense non-wovens. If the pore size is sufficiently small, water does not pass through due to the high surface energy involved, but water vapour can permeate through the pores. Disadvantage of such systems is that the pores tend to get blocked in use and that they are not selective to water (in the case of protective medical apparel, bacteria and viruses will also pass through the pores).

An alternative route to get a breathable membrane, which does not have these disadvantages, is to make a monolithic film out of a material that intrinsically has a high permeability for water. Such a film, if produced properly, will be without holes and, since the transport mechanism is solution-diffusion, only lower molecular weight species that are sufficiently soluble in the polymer will permeate through the film.

In order to get a high water permeability the material needs to have a high water absorption and/or a high water diffusion coefficient. Thermoplastic elastomers (TPEs) based on segmented block copolymers are particularly suitable to fulfil at least one of these requirements. The reason for this is basically the same as why these materials behave as a TPE. Both functions require a continuous amorphous phase that is far above T_g at the temperature of use; in the case of a breathable film to get a high diffusion coefficient and for a TPE to get rubbery behaviour. Both functions also require a way to keep this amorphous structure together; in the case of a breathable film to prevent the

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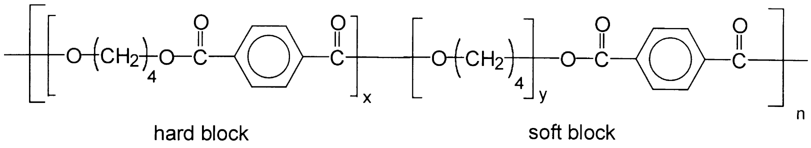

Fig. 1. Structure of a co-poly(ether–ester), based on PBT and PTMO.

material from swelling or dissolving in water and for a TPE to get mechanical strength.

Examples of TPEs, which are often used for breathable film applications, are the segmented block co-poly(ether–esters) or TPE-Es. DSM Engineering Plastics is one of the main mondial suppliers of this class of TPEs (marketed under the tradename Arnitel®). These polymers are based on alternating polyether and polyester segments, for instance, as shown in Fig. 1 [1].

Within certain limits, variations can be made in the hard/soft ratio, the block length of the polyether and the type of polyether. Especially, the amount and the type of soft block are expected to affect the breathability strongly.

In the molten state, TPE-Es typically form a homogeneous mixed phase of polyether and polyester segments. Upon cooling, at a certain temperature the polyester segments start to crystallise. There is evidence that crystallisation starts from a homogeneous melt and that the crystallisation process is the driving force for phase separation [2–4]. In most literature it is assumed that after crystallisation the material can be described by a two-phase model: a crystalline polyester phase and an homogeneous amorphous phase of the poly (ether) and the non-crystalline polyester [5–7]. Recent work, however, shows that in many cases two amorphous phases (an almost pure polyether phase and a mixed polyether–polyester phase) are present and, at low temperatures, sometimes a crystalline polyether phase exists [8,9].

There is a large variety of test methods that can be used for measuring the water permeability or Moisture Vapour Transmission Rate (MVTR) of breathable films. Usually, different market segments require different test methods. Most of these test methods are quite pragmatic in nature and differ strongly in conditions like humidity on both sides of the film, temperature, direct contact of water with the film or not, etc. Due to these differences in conditions, the MVTR values vary strongly from one method to another. In order to prevent measuring films under all these different conditions, we attempted to derive a model that is capable of predicting the MVTR values for different conditions. This model will be described in this paper.

2. Experimental procedure

Measurements were performed on two commercial TPE-E grades supplied by DSM Engineering Plastics: Arnitel EM400 and Arnitel PM380. Arnitel EM400 has a structure as shown in Fig. 1, i.e. the soft block is poly(tetramethylene-oxide). In the case of Arnitel PM380, the polyether is poly(-propylene-oxide) endcapped with poly(ethylene-oxide). Poly(butylene-terephthalate) forms the hard segment in all cases. Both grades have a similar hard/soft ratio, and have a Shore D hardness that is on the lower end of the commercially available range.

Cast film was produced on a Battenfeld 45 mm extruder, equipped with a Verbruggen 250 mm slit die with a die opening of 300 μm. The film was cast on a chill roll, which was set at a temperature of 12°C. The film thickness was varied by changing the speed of the chill roll and wind-up unit. In all cases, the neck-in was reduced by applying an air knife. In this way films with a thickness down to 10 μm could be produced.

Blown film was produced on a Schwabenthan 45 mm extruder equipped with an annular die with a diameter of 50 mm. The die opening was constant at 500 μm. The film thickness was varied by changing the blow up ratio and the draw speed. In this way films were produced down to 15 μm.

Compression moulded films were produced in a standard press. Compression moulding was done between Teflon sheets at a temperature of 240°C. The press was set at the maximum cooling rate of 40°C/min. Minimum film thickness, which could be obtained using this method, was approximately 40 μm.

Water absorption was measured following ISO 62. The absorption was measured at 50% relative humidity and after immersion in water. MVTR was measured following the ASTM E96 standard. In this standard different methods are described. Two of these are generally used and are shown schematically in Fig. 2.

In the ASTM E96BW test (inverted cup) the film is in direct contact with water, while in the ASTM E96B test (upright cup) an air layer between film and water exists. The distance between the water surface and the film in the upright cup method was close to 7.5 cm for all tests. Cups, partly filled with water, were placed in a conditioned

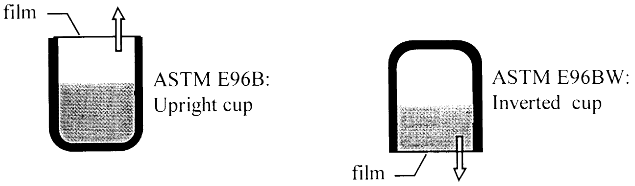

Fig. 2. Schematic representation of MVTR tests according to ASTM E96.

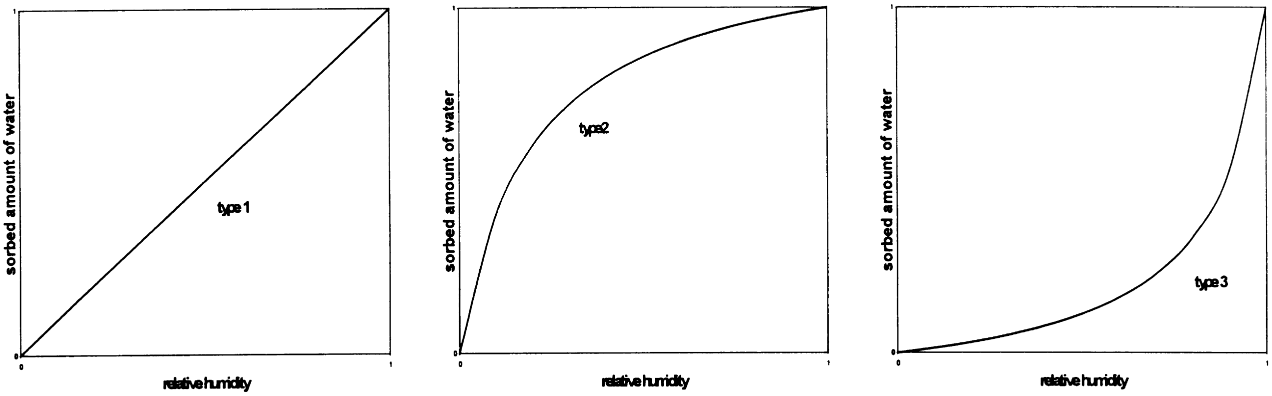

Fig. 3. Examples of linear (type1), concave (type2) and convex (type3) sorption isotherms.

chamber that was set at 38°C and 50% relative humidity. The air in the conditioned chamber was circulated with an electric fan. In both test methods the weight loss is measured as a function of time. After a certain time the weight loss becomes constant with time. The MVTR is taken in this steady state regime and is given in the unit g/m^2 day.

3. Theory

3.1. Description of equilibrium sorption isotherm

Basically three types of equilibrium sorption isotherms for water in polymer materials are possible, see Fig. 3. For ideal systems, the amount of sorbed water in the polymer is linear with respect to the applied pressure and Henry's law is applicable (type 1). Concave sorption behaviour (type 2) is often explained in terms of the Langmuir sorption accounting for chemisorption of water to specific hydrophilic functionalities of the polymer. This mechanism of chemisorption leads to a non-random distribution of water in the polymer and results in already relatively high amounts of sorbed water at low pressure. A convex sorption isotherm (type 3) can be interpreted in terms of the Flory–Huggins type of sorption behaviour, which implies a random distribution of water in the polymer material. With this Flory–Huggins approach only a rather weak convex behaviour of the sorption isotherm can be anticipated applying a concentration independent interaction parameter. Stronger convexity is mostly explained in terms of cluster models [10–12], based on the idea that water molecules are not solved as single molecules but as aggregates or clusters. This self-association of water is frequently interpreted in terms of Zimm and Lundberg's cluster theory [13,14].

In practice, not only these three types of sorption behaviour are encountered but also combinations of these types are possible. This has led to the development of dual- or multi-mode models, mainly based on the above basic concepts.

The water absorption as a function of relative humidity for Arnitel EM400 and PM380 is shown in Fig. 4. In this paper, sorption behaviour of the Arnitel EM400 film is described by Henry's law because of the linear nature of the sorption isotherm. The behaviour of Arnitel PM380, exhibiting a convex sorption isotherm, is modelled by a method developed by Brown [15]. In fact, this method is a combination of the Flory–Huggins approach and Zimm and Lundberg's cluster concept. This method allows one to extract a χ-parameter reflecting the enthalpic balance between similar (polymer segment/polymer segment and water/water) and dissimilar (polymer segment/water) contacts. This χ-parameter is composition independent in the approach taken because compositional effects are incorporated in the cluster functions as will become clear from the following. Further, one can quantify the deviation from the Henry sorption behaviour at each value of the relative humidity by computing the total amount of sorbed water and compare this with the amount of water sorbed in a strict Henry's fashion.

Brown's method links the amount of sorbed water ϕ to the activity of water in the vapour phase. The activity is approximated by the partial pressure of water or alternatively the relative humidity (rh) of the gas phase.

$$\frac{1}{\phi} = \frac{k_1}{\mathrm{rh}} - k_2 \tag{1}$$

Eq. (1) represents Henry's law for $k_2 = 0$, the Langmuir type behaviour for negative k_2 values and a Flory–Huggins and/or a Zimm–Lundberg isotherm for positive k_2 values. In Brown's approach the total amount of water sorbed is considered to consist of two types. Water sorbed by a normal random mixing process and water sorbed in the form of clusters. The essential postulate in Brown's approach is that the water sorption at very low concentrations (in the limiting case for infinite dilution) is normal in behaviour and can be described in the classical Flory–Huggins terms. According to Flory–Huggins [16]:

$$\mathrm{rh} = \exp\left[\ln\phi + \left(1 - \frac{1}{s}\right)(1-\phi) + \chi(1-\phi)^2\right] \tag{2}$$

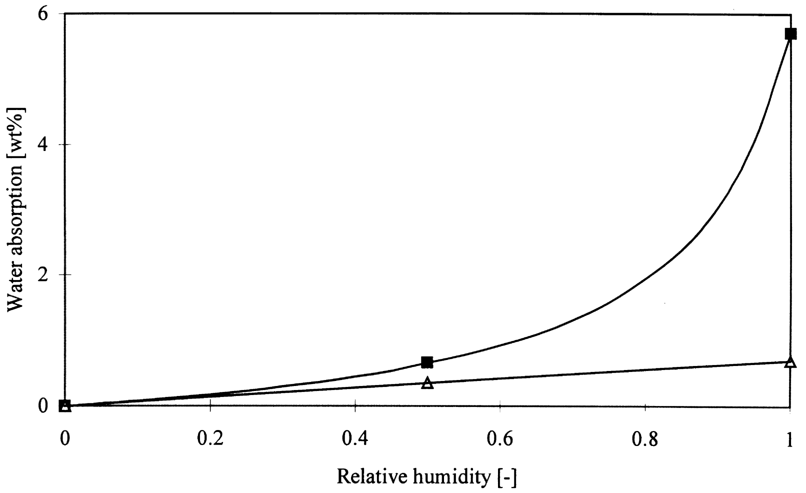

Fig. 4. Water absorption of Arnitel EM400 and Arnitel PM380, measured at 50 and 100% rh. (B) Arnitel PM380; (K) Arnitel EM400; and (lines) computed sorption isotherms.

where s is the number of lattice sites per polymer molecule or the chain length of the polymer.

In the case of infinite polymer molar mass and infinite dilution, i.e. $s \rightarrow \infty$ and $\phi \rightarrow 0$, Eq. (2) reduces to

$$\mathrm{rh} = \phi \exp[1 + \chi] \tag{3}$$

Under infinite dilution conditions, Eq. (3) can be expressed in terms of Henry's law

$$\frac{1}{\phi_{\mathrm{H}}} = \frac{k_1}{\mathrm{rh}} \tag{4}$$

where ϕ_{H} is the amount of sorbed water according to Henry's law. Combining Eqs. (3) and (4) for infinite dilution conditions ($\phi \rightarrow 0, \phi_{\mathrm{H}} \rightarrow 0$) enables one to extract the interaction parameter χ

$$\chi = \ln k_1 - 1 \tag{5}$$

Another interesting property forms the enhancement number N_{e}, which is an indication for the deviation from the Henry type of sorption. This number is defined as the ratio of the amount of total sorbed water to the amount of sorbed water according to Henry's law

$$N_{\mathrm{e}} = \frac{\phi}{\phi_H} = 1 + k_2 \phi \tag{6}$$

The cluster concept has been successfully applied to water sorption in acrylates [15], polyurethane block copolymers [17], polyamide 6 [10] and polyamide 66 [12].

3.2. Description of transport of water in film

The transport of water in the film is described in terms of a simple Fickian diffusion behaviour with an overall diffusion coefficient independent of the location in the film or alternatively the water concentration. So

$$\mathrm{MVTR} = D_{\mathrm{film}} \frac{\partial \phi}{\partial l} = D_{\mathrm{film}} \frac{\Delta \phi}{\Delta l} \tag{7}$$

where l is the co-ordinate perpendicular to the film surface. As will become clear from the next paragraph, there is no actual need to revert to more elaborate approaches.

3.3. Description of transport of water in atmosphere

Two types of ASTM tests are described earlier: the ASTM E96B and the E96BW test. In the E96BW test, the barrier for water transport forms the polymer film and not the liquid water phase inside the cup or the atmosphere outside the cup, because forced convection is ensured. The situation for the E96B test, however, is different. In this test two barriers towards water transport have to be distinguished. One potential barrier is formed by the atmosphere inside the cup, the other is formed by the polymer film itself.

Mass transfer in the atmosphere for the E96B test can be described in analogy with heat transfer for the classical Bénard problem [18,19] that deals with the stability of heat transport of a liquid or a gas between two horizontal walls. We use the same analogy between transport of mass and heat [20] and further, we reduce the cup geometry to the situation of two horizontal plates. Consider a cavity containing an atmosphere consisting of air and water vapour, see Fig. 5. Plate 1 represents the liquid water surface that is in direct contact with an atmosphere with a relative humidity of 1. Plate 2 is the polymer film that is downward in contact with an atmosphere with a lower relative humidity. Upwards, the relative humidity of the atmosphere is 0.5. There is an upward driving force for water transport due to a difference in water activity (water activity or alternatively relative humidity in upward position decreases). The transport of water may take place via a diffusion process in a stable situation or by free convection induced by instabilities in the system. The essential drive for instabilities to occur is the density difference of the gas in vertical position and gravity. Under isobaric conditions the density of the

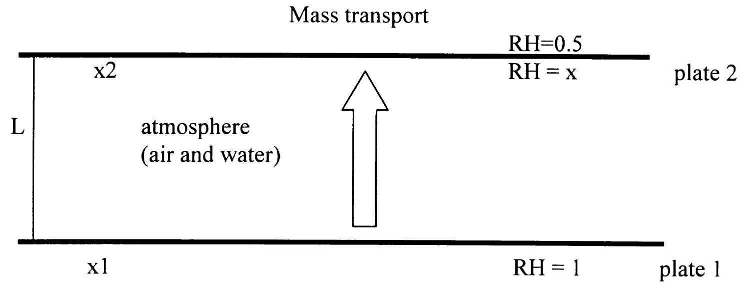

Fig. 5. Schematic representation of the atmosphere layer between two horizontal parallel plates.

atmosphere at plate 1 is lower than the atmosphere at plate 2 because of the higher relative humidity at plate 1. Stabilising factors are the diffusion process, which tends to dampen perturbations, and the viscosity of the gas. For small differences in relative humidity, the stabilising factors are dominant over the destabilising ones resulting in a diffusional transport mechanism for water into the atmosphere. For somewhat larger differences in relative humidity, destabilising factors start to take over resulting in free convection manifesting itself by the occurrence of stable vortices laminar in nature. For even larger differences, free convection will become turbulent manifested by irregular and unstable vortices. These stabilising and destabilising factors can be expressed in a single dimensionless number, the so called Rayleigh number, which is defined as the product of the Grashof and Schmidt number [20]

$$\mathrm{Ra} = \mathrm{Gr}_{\mathrm{ab}} \times \mathrm{Sc} \tag{8}$$

$$= \frac{\rho^2 \xi g L^3 (x_1 - x_2)}{\mu^2} \frac{\mu}{\rho D} \qquad \text{where } \xi = \frac{-1}{\rho}\left(\frac{\partial \rho}{\partial x}\right)_{\mathrm{p,T}}$$

$$= \frac{-\left(\frac{\partial \rho}{\partial x}\right)_{\mathrm{p,T}} g L^3 (x_1 - x_2)}{\mu D}$$

The symbols are defined in Table 1.

The critical Rayleigh number, marking the transition from diffusional transport to transport by free convection, is given by [19]:

$$\mathrm{Ra}_{\mathrm{c}} \cong 1700 \tag{9}$$

For Rayleigh numbers above this critical value, the instability factors start to dominate and free convection sets in. The Rayleigh number, marking the transition from free convection with a laminar character to a turbulent nature, for our specific case is [19]

$$\mathrm{Ra}_{\mathrm{t}} = 2 \times 10^7 \tag{10}$$

Following from the dimensional analysis of free convection [19] the Nusselt number for mass transport can be expressed as a function of the Rayleigh number

$$\mathrm{Nu}_{\mathrm{ab}} = \mathrm{Nu}_{\mathrm{ab}}(\mathrm{Ra}) = \frac{kL}{D} \tag{11}$$

where k is the mass transfer coefficient.

For our specific case, the following empirical relations can be applied [19]:

$$\text{Diffusional transport :} \qquad \mathrm{Nu}_{\mathrm{AB}} \approx 1 \tag{12}$$

$$\text{Free convection, laminar :} \ \mathrm{Nu}_{\mathrm{AB}} = 0.54\ \mathrm{Ra}^{1/4} \tag{13}$$

$$\text{Free convection, turbulent :} \mathrm{Nu}_{\mathrm{AB}} = 0.14\ \mathrm{Ra}^{1/3} \tag{14}$$

Now that we are in a position to estimate the Nusselt

Table 1
Explanatory table/values for parameters as used in the analysis of water transport in the atmosphere

Abbreviation	Explanation	Numerical value[a] [dimensions]
ρ	Density atmosphere	1.1347×10^3 [g/m^3] Ref. [22]
g	Gravitational acceleration	9.8 [m/s^2]
L	Distance between parallel horizontal plates	0.075 [m]
μ	Viscosity atmosphere	189.1×10^{-4} [g/(ms)] Ref. [22]
D	Diffusion coefficient of atmosphere	2.683×10^{-5} [m^2/s] Ref. [22]
c_1	Concentration water in atmosphere at plate 1 for which rh = 1	46.24 [g/m^3] Ref. [23]
c_2	Concentration water in atmosphere at plate 2	A priori unknown
rh_1	Relative humidity at plate 1	1 [–]
rh_2	Relative humidity at plate 2	A priori unknown
x_1	Mole fraction of water in atmosphere at plate 1 (rh = 1)	–
x_2	Mole fraction of water in atmosphere at plate 2	–

[a] Values are given for the experimental conditions, i.e. 38°C and 1 bar.

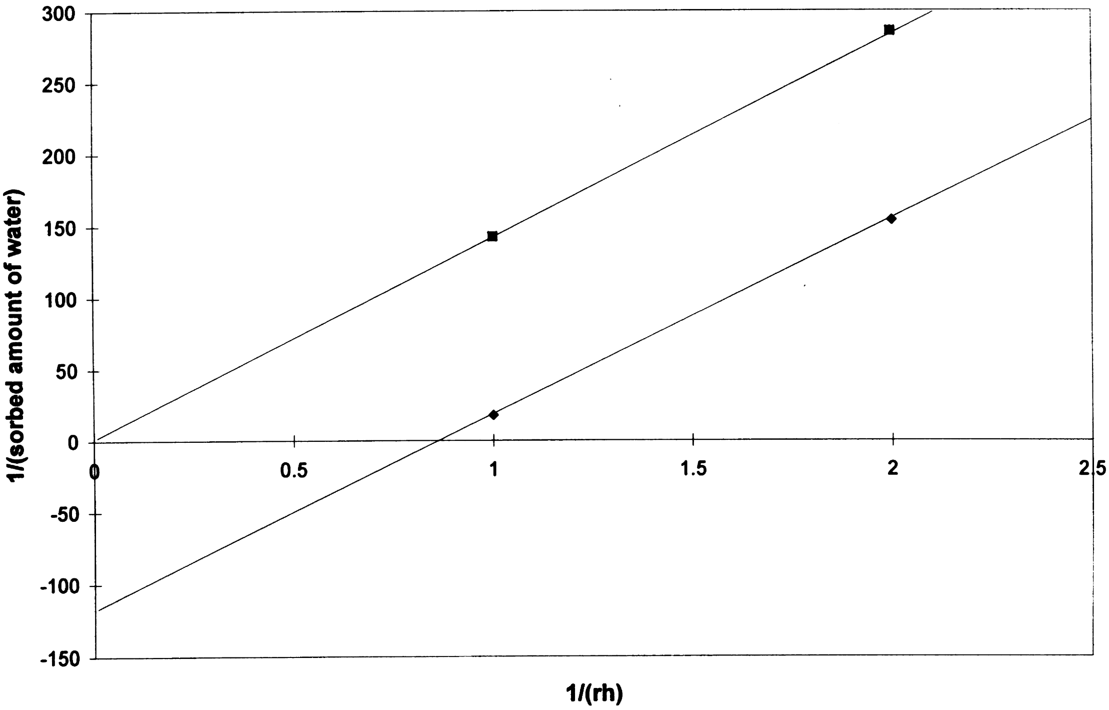

Fig. 6. Reciprocal weight fraction of sorbed water versus reciprocal relative humidity for: (V) Arnitel PM380; and (B) Arnitel EM400 films.

number, it is possible to express the transport phenomena in the air layer in terms of a mass transfer coefficient. The flux in the air layer is described by

$$\mathrm{MVTR}_{\mathrm{atm}} = k\Delta c \tag{15}$$

where Δc is the concentration difference of water in the atmosphere at plates 1 and 2.

This enables us to predict the resistance for mass transport in the air layer and compare it with the resistance for mass transport in the film, as will be shown in the next paragraph. Further, we can predict the effect of the presence of the air layer in the E96B test on the overall MVTR and compare it with the MVTR of the E96BW test.

4. Results and discussion

The following procedure is followed:

1. The experimental equilibrium sorption isotherms for water in EM400 and PM380 are fitted to Henry's model (EM400) and the cluster model (PM380) and characteristic parameters are extracted.
2. From the experimental E96BW test results, the values of the diffusion coefficients for water in EM400 and PM380 are quantified and water fluxes can be computed as a function of film thickness for the E96BW test.
3. For the E96B test, the mass transport resistance in the air layer is estimated. The mass transport in the film is described analogous to the E96BW test, applying identical values for the diffusion coefficients. A coupled analysis of the water transport in the film and water transport in the atmosphere enables one to extract the relative humidity at the cup side of the film and to predict the water flux for the complete test without any additional parameter.

4.1. Application of cluster model for Arnitel PM380 and Henry's model for Arnitel EM400

As discussed earlier, the PM380 and EM400 Arnitel materials consist of different phases, a crystalline and one or two types of amorphous phases. Water transport will mainly take place through the continuous ether-rich amorphous phase. However, we do not know exactly the amount of this phase in both Arnitel materials. For this reason, in the next analysis we do not take into account the multi-phase character of the materials and model the water sorption process for the sample as a whole.

The sorption isotherms of the Arnitel PM380 and EM400 films were already presented in Fig. 4. In Fig. 6 the sorption isotherms of the Arnitel PM380 and EM400 are plotted in reciprocal units, in order to fit Eq. (1) and extract values for k_1 and k_2. This procedure leads to the following values for k_1 and k_2, see Table 2.

The computed sorption isotherms for PM380 and EM400, according to Eq. (1) and with the values for the constants given in Table 2, are shown in Fig. 4. For infinite dilution conditions, one is able to extract the values of the χ-parameters from Eq. (5), these values are given in Table 2. The values for the χ-parameters of the Arnitel PM380/water and EM400/water systems are very alike and suggest a repulsive interaction between water and the polymer material.

Table 2
Values for characteristic parameters in the cluster model

Sample	k_1	k_2	χ	N_e at rh = 1
PM380	136.31	118.77	3.91	7.77
EM400	142.86	0	3.96	1

First we would like to comment on the apparent hydrophobic character of the materials, based on the values of the χ-parameters. For the Arnitel EM400 material it is clear that under humid conditions ($\mathrm{rh} = 1$) less than 1 wt% of water is solved in the polymer indicating hydrophobic character of the material. For PM380 the situation is somewhat more complex. The χ-parameter is estimated in the regime of infinitely low water composition. The experimental sorption isotherm (see Fig. 4) indicates that for the regime of rather low and moderate relative humidities the water uptake is rather low ($\mathrm{rh} = 0.5$, $\phi = 0.65$ wt%) while for the regime of high relative humidity a vast increase in water uptake is observed ($\mathrm{rh} = 1$, $\phi = 5.7$ wt%). Such a sorption behaviour cannot be described with a Flory–Huggins sorption expression as given by Eq. (2) with a composition independent χ-parameter. However, it could be described with a χ-parameter that is strongly composition dependent, i.e. a χ-parameter that decreases with increasing relative humidity indicating that the material becomes more hydrophilic as it moves towards more humid conditions. We did not follow this approach, which requires a fitting of the χ-parameter over the composition regime. We choose for the application of a cluster concept that is generally used for the description of convex sorption isotherms. With this cluster concept in mind, the upswing of the sorption is explained in terms of an increase of the water cluster size. In resume, we want to remark that the extracted χ-parameter for the PM380 material is indicative of the hydrophobic character of the material only for the low water concentration regime.

Secondly, we want to speculate on the fact that the χ-values for infinite dilution for the EM400/water and PM380/water systems are similar. The relative amounts of soft and hard block for both Arnitel systems are similar, the type of hard block is identical. The basic difference is the chemical nature of the soft block. The soft block of Arnitel EM400 consists of poly(tetramethylene-oxide), the soft block of PM380 of poly(propylene-oxide) and poly(ethylene-oxide). The χ-parameter reflects the interaction between an ‘averaged, imaginary’ Arnitel segment and a water molecule, which is a consequence of the fact that the Arnitel materials are modelled as homogeneous materials. Similarity of the extracted χ-parameters for infinite dilution indicates, for these conditions, that the interaction between tetramethylene-oxide and water is similar to the interaction between a propylene-oxide/ethylene-oxide segment and water. This implies that the repulsive nature between water and the ether increases for the ether series ethylene oxide/tetramethylene oxide/propylene oxide. This effect can be anticipated on the basis of the aliphatic character of the soft blocks combined with steric effects. It is known that the interaction between ethylene-oxide and water is more favourable than the interaction between propylene-oxide and water. Linse has quantified this effect by interpreting the phase behaviour of poly(ethylene oxide)/poly(propylene oxide)/water in terms of a mean field model [21]. Going from propylene-oxide to poly(tetramethylene-oxide) the aliphatic character further increases and one would expect a further decrease of the favourable interaction with water. This cannot explain the similarity of both χ-parameters as discussed before. However, it can be explained by taking shielding effects into account. Poly(propylene-oxide) has a non-linear structure while poly(ethylene-oxide) and poly(-tetramethylene-oxide) are of a linear nature. This leads to a steric shielding effect of the ether functionality by a pendant methyl functionality in the case of poly(propylene-oxide) leading to a reduced interaction with water. This rather speculative hypothesis supports the idea that the interaction between poly(tetramethylene-oxide) and water is less repulsive than the poly(propylene oxide)/water interaction and could explain the similarity of both χ-parameters.

In Fig. 7 the enhancement number N_e is plotted versus the relative humidity, as computed according to the cluster model (see Eq. (6)). For low values of the relative humidity, most of the water sorption can be expressed in Henry’s terms. From a relative humidity of approximately 0.6 ($N_e = 2$), non-random mixing or cluster effects start to dominate and water sorption increases strongly for even higher values of the relative humidity. With the cluster model for PM380 and Henry’s model for EM400 we can now compute the amount of sorbed water as a function of the relative humidity of the atmosphere. We will use this in the modelling of the E96B and E96BW test.

4.2. Modelling the E96BW test for EM400 and PM380 Arnitel films

The ASTM E96BW results for PM380 and EM400 are used to extract a diffusion coefficient for water in these films. The diffusion coefficient is assumed to be independent of position in the film (or alternatively local amount of water solved), moreover a simple Fickian diffusion behaviour is assumed implying linearity between the water flux (MVTR values) and reciprocal film thickness. Equilibrium concentrations at each side of the film are extracted from the cluster model for Arnitel PM380 and Henry’s model for Arnitel EM400. Using a linear regression technique, the following values for the diffusion coefficients are extracted, see Table 3.

The values for the regression coefficients indicate that rather good linear fits are obtained. At this point it should be noted that the values for the diffusion coefficients are relatively high. Earlier, we have stated that the EM400 material has a rather hydrophobic nature, while the PM380 material is somewhat more hydrophilic. Further, both materials are breathable, i.e. the water permeability

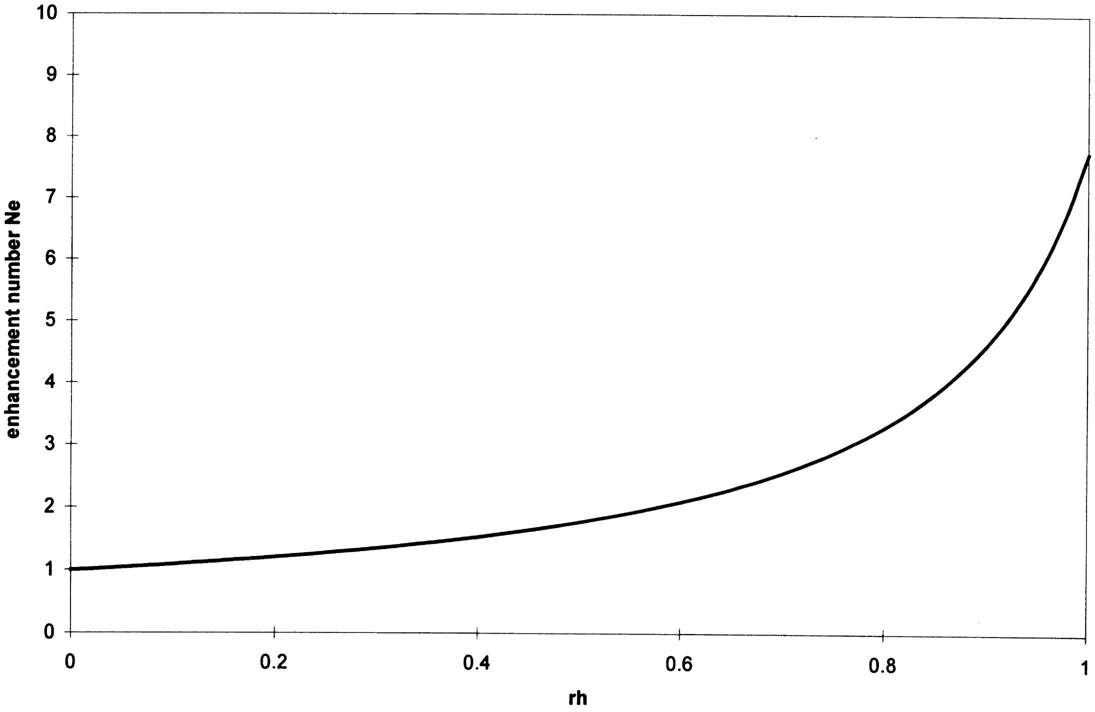

Fig. 7. Enhancement number N_e versus the relative humidity for PM380.

is relatively high. Permeability is the reflection of two distinct physical features: solubility and diffusion. The relative high value of water permeability is caused, in the first place, by the low resistance of the films towards water transport as reflected by the intrinsic high values of the water diffusion coefficients (see Table 3). Water solubility does not contribute that much to the high values of the water permeability. This especially holds for the EM400 material and to a lesser extent for PM380.

The diffusion coefficients are taken to be water concentration independent. However, especially for the cluster based system, one expects the diffusion coefficient to vary with water concentration. However, in the ASTM E96BW test, the amount of water at each side of the film is kept constant and only the film thickness is changed. This means that the fractions of solved water in the films are in the same regime for all experiments weakening the necessity to apply water concentration dependent diffusion parameters.

The predicted MVTR values for the E96BW test for Arnitel PM380 and EM400 films are shown in Figs. 8 and 9, together with the experimental values. The predictions of the E96BW test are quite satisfactory. For both Arnitel systems a quantitative level of description is reached indicating that the assumption of a Fickian diffusion behaviour with a water concentration independent diffusion parameter is quite acceptable.

Table 3
Diffusion coefficients for water in PM380 and EM400 films

Arnitel type	D_{film} in (m^2/s)	Number of experimental points	Regression coefficient
PM380	2.3644×10^{-11}	13	0.9935
EM400	1.5017×10^{-10}	5	0.9918

4.3. Modelling the E96B test for Arnitel EM400 and PM380 films

For the E96B test, the barriers for water transport are formed by the Arnitel film and by the atmosphere in the cup. In Figs. 8 and 9 the experimental MVTR-values for the E96B test are plotted together with the experimental MVTR values for the E96BW test for PM380 as well as EM400. The observation is that with decreasing film thickness the difference in MVTR values for both tests increases. This can be attributed to the fact that with decreasing film thickness the mass transport resistance in the atmosphere dominates over the resistance in the film.

The water transport in the film is again described by a simple Fickian diffusion model with diffusion coefficients for PM380 and EM400 as given in the previous paragraph. This model, however, requires solved water concentrations at each side of the film, which in their turn are coupled to the relative humidity at each side of the film by the theoretical description of the sorption isotherm. However, for the E96B test, the relative humidity at the Arnitel film surface at the cup side is not known a priori because of the fact that the atmosphere in the cup also forms a barrier for water transport. The water transport in this atmosphere is described by the dimensionless analysis as described before. A coupled

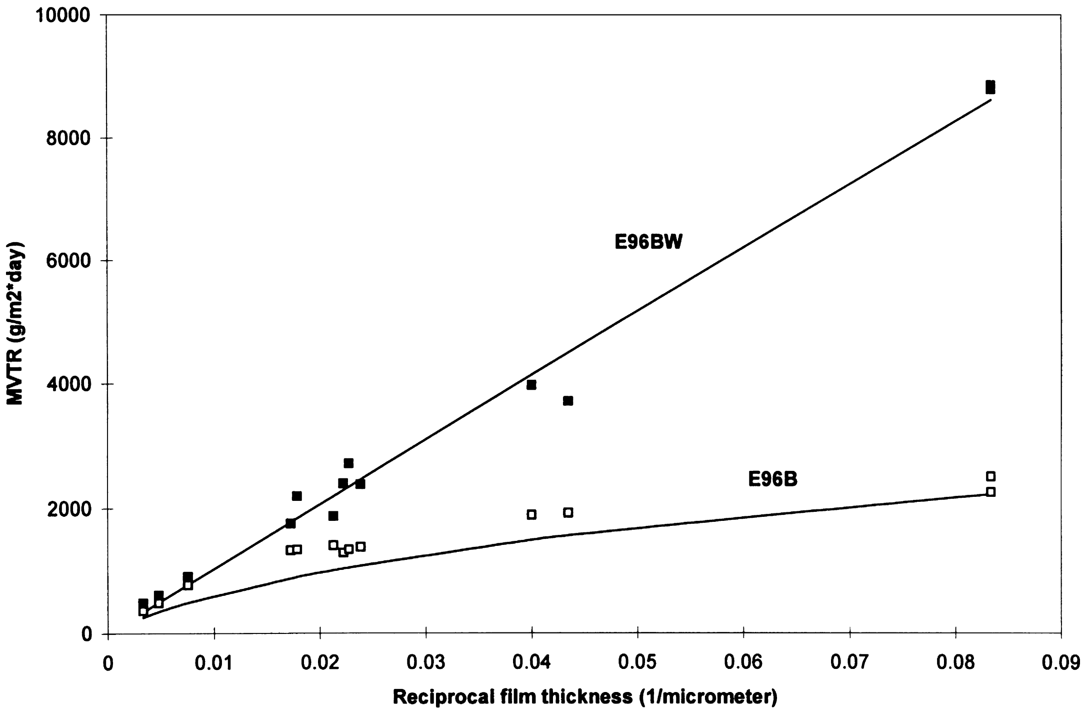

Fig. 8. Experimental MVTR values for: (B) PM380 for the E96BW; and (A) E96B tests versus film thickness and the predicted values are given by the lines.

analysis of the water transport in the film and water transport in the atmosphere enables one to compute the relative humidity at the cup side of the film and to predict the MVTR for the complete test without a single adjustable parameter. The values for the parameters in the dimensionless analysis of water transport in the atmosphere are given in Table 1. On the basis of the values given in Table 1 it is easily shown that under the given conditions (38°C and 1 bar) the mole fraction water, x, of a saturated atmosphere (rh = 1) equals 0.06565 and its density is 1106.511 g/m^3. So

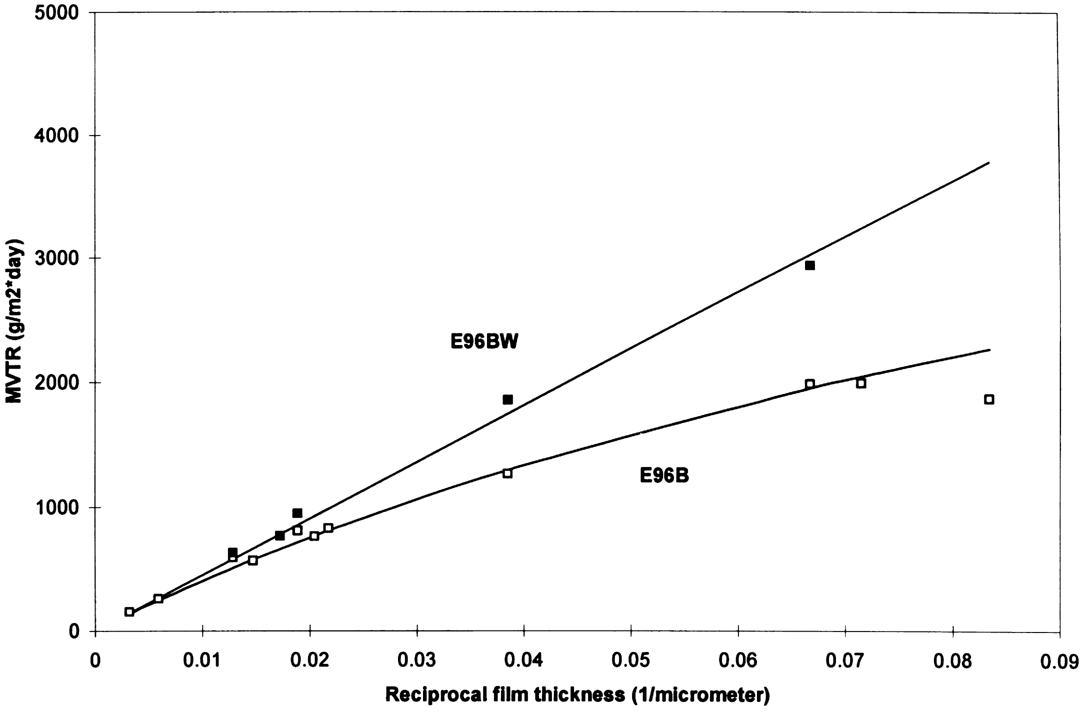

Fig. 9. Experimental MVTR values for: (B) EM400 for the E96BW; and (A) E96B tests versus film thickness and the predicted values are given by the lines.

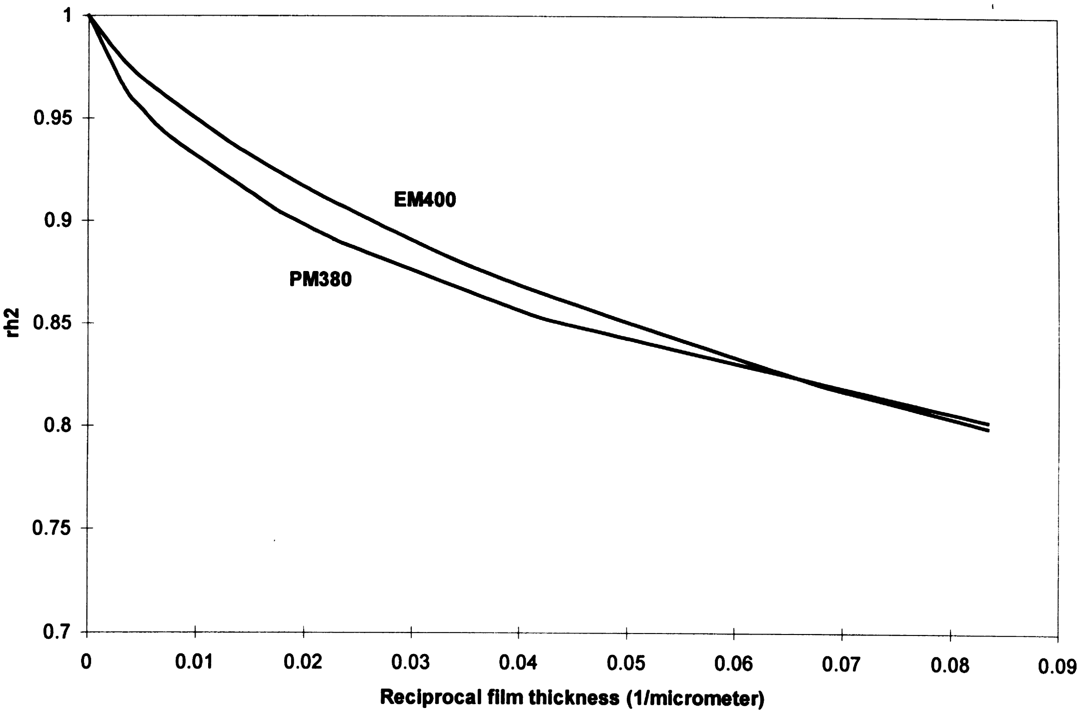

Fig. 10. Predicted relative humidity of the atmosphere in contact with the film at the cup side (rh_2) versus reciprocal film thickness for the E96B test.

$$x = 0.06565\mathrm{rh} \tag{16}$$

and

$$\left(\frac{\partial\rho}{\partial x}\right)_{\mathrm{p,T}} = -429.40\ \mathrm{g/m^3} \tag{17}$$

This gives, combined with the earlier expression for the Rayleigh number, the following expression for this number as a function of the relative humidity at the atmosphere in direct contact with the Arnitel film:

$$Ra = 2.29717 \times 10^5(1 - \mathrm{rh}_2) \tag{18}$$

Only for a very small regime of rh_2 close to 1 ($0.9926 < rh_2 < 1$), the Rayleigh number does not exceed Ra_c and the transport of water in the atmosphere will be governed by a diffusion process. For all other values of rh_2 the water transport takes place by a free convection process under laminar conditions because the value for Ra_t is never exceeded. So, the Nusselt number is directly related to the Rayleigh number by relation 13 and for each experimental point the mass transport coefficient k can be computed.

The water flux in the atmosphere can now be expressed by

$$\mathrm{MVTR_{atm}} = k(c_1 - c_2) = 0.54\frac{D}{L}Ra^{1/4}46.24(1 - rh_2) \tag{19}$$

with rh_2 the only unknown parameter.

The water flux in the film is described by

$$\mathrm{MVTR_{film}} = D_{\mathrm{film}}\frac{\Delta\phi}{\Delta l} = D_{\mathrm{film}}\frac{\phi_2 - \phi_3}{l} \tag{20}$$

where ϕ_2 and ϕ_3 are the amounts of solved water at both sides of the film (ϕ_2 is the cup side). The film thickness l is an experimental input parameter and the diffusion coefficients of the films are given in Table 3. Under equilibrium conditions, the solved amounts of water at both sides of the film are related to the relative humidity in the atmosphere by the sorption isotherm of the film. These are given by

$$\frac{1}{\phi} = \frac{142.86}{\mathrm{rh}} \quad \text{for EM400} \tag{21}$$

and

$$\frac{1}{\phi} = \frac{136.31}{\mathrm{rh}} - 118.77 \quad \text{for PM380} \tag{22}$$

The fraction ϕ_3 is in equilibrium with an atmosphere with $\mathrm{rh} = 0.5$ and can be directly extracted from the sorption isotherms. The fraction ϕ_2 is in equilibrium with rh_2, which is the only unknown parameter left in the expression for $\mathrm{MVTR_{film}}$. Under stationary conditions

$$\mathrm{MVTR_{atm}} = \mathrm{MVTR_{film}} \tag{23}$$

which enables one to solve rh_2 and MVTR. We solve Eq. (23) for each experimental point (varying in film thickness and type of film) and compute MVTR and rh_2. So, for the E96B test we are in a position to predict the water flux (MVTR) without applying a single adjustable parameter. These predictions for MVTR, together with the experimental MVTR values, are shown in Fig. 8 for PM380 and in Fig. 9 for EM400. Predicted values for rh_2 are shown in Fig. 10.

First of all we indeed predict that the difference between the flux in the E96BW test and E96B test increases with decreasing film thickness indicating that the mass transfer resistance of the atmosphere becomes more important going to thinner films. This is reflected by the fact that the relative humidity, directly at the cup side of the film (rh_2), deviates more from unity going to thinner films, as shown in Fig. 10. For relatively thick films (300 μm), rh_2 is of the order of 0.97 and decreases to approximately 0.80 for the thinnest films (12 μm). It should be remarked that for all the values of rh_2 mass transport in the atmosphere is indeed governed by a laminar type of free convection and not by a diffusional process.

For EM400, a quantitative prediction of the E96B test results (see Fig. 9) is obtained without any adjustable parameter which is quite satisfactory. For PM380, a semi-quantitative prediction is reached, see Fig. 8. The predicted MVTR values are somewhat lower compared to the experimental ones but the result is still gratifying. We have shown that we can now predict the MVTR value of an E96B test in a (semi)-quantitative manner based on information extracted from the E96BW test.

References

[1] Adams RK, Hoeschele GK, Witsiepe WK. In: Holden G, Legge NR, Quirk R, Schroeder HE, editors. Thermoplastic elastomers, 2nd ed. Munich: Hanser, 1996. p. 191.
[2] Miller JA, McKenna JM, Pruckmayr G, Epperson JE, Cooper SL. Macromolecules 1985;18:1727.
[3] Soliman M, Dijkstra K, Borggreve RJM, Wedler W, Winter HH. Poster at Makromolekulares Kolloquium Freiburg 1998.
[4] Veenstra H, Hoogvliet RM, Norder B, Posthuma de Boer A. J Polym Sci B 1998;36:1795.
[5] Zhu LL, Wegner G. Makromol Chem 1981;182:3625.
[6] Vallance MA, Cooper SL. Macromolecules 1984;17:1208.
[7] Phillips RA, McKenna JM, Cooper SL. J Polym Sci B 1994;32:791.
[8] Dijkstra K, Martens H, Soliman M, Borggreve RJM. Europhysics Conference Abstracts, vol. 21A. European Physical Society, 1997. p. 31.
[9] Schmidt A, Veeman WS, Litvinov VM, Gabriëlse W. Macromolecules 1998;31:1652.
[10] Hernandez RJ, Gavara R. J Polym Sci, Polym Phys Ed 1994;32:2367.
[11] Hsu WP, Li RJ, Myerson AS, Kwei TW. Polymer 1993;34:597.
[12] Starkweather Jr. HW. In: Rowland SP, editor. Water in polymers, ACS Symposium Series, vol. 127. Washington, DC: American Chemical Society, 1980.
[13] Zimm BH, Lundberg JL. J Phys Chem 1956;60:425.
[14] Zimm BH. J Chem Phys 1953;21:934.
[15] Brown GL. In: Rowland SP, editor. Water in polymers, ACS Symposium Series, vol. 127. Washington, DC: American Chemical Society, 1980.
[16] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press, 1953.
[17] Pissis P, et al. J Polym Sci, Phys Ed 1996;34:1529.
[18] Bénard H. Rev Gen Sci Pures Appl 1900;11:1261.
[19] Agassant J-F, Avenas P, Sergant J-Ph, Carreau PJ. Polymer processing, principles and modeling, Hanser Publishers, 1991. p. 369.
[20] Bird RB, Stewart WE, Lightfoot EN. Transport phenomena. New York: Wiley, 1960.
[21] Malmsten M, Linse P, Zhang KW. Macromolecules 1993;26:2905.
[22] Landolt-Börnstein. In: Hellwege KH, editor. Zahlenwerte und functionen am Naturwissenschaften und Techniek, Berlin: Springer, 1975.
[23] Schmidt E. In: Grigull H, editor. Properties of water and steam in SI-units, Berlin: Springer, 1989.