

Water Vapor Permeation Through Polymer Films at Elevated Temperatures

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ABSTRACT

Measurements of the water vapor transmission rate (WVTR) are important for polymers, which are used in a variety of applications including food packaging and substrates for electronic components. Polymers such as Polyetheretherketone (PEEK) has a continuous use temperature of 260°C, which is well above the limits of conventional permeation testers. We have developed a novel permeation measurement method that is capable of measuring rates of permeation through film materials at elevated temperatures. Measurements were carried out on film samples of Polyethylene terephthalate (PET), Polyethylene naphthalate (PEN) and PEEK at temperatures up to 210°C. The experiments were carried out in a saturated water vapor atmosphere. The water vapor pressure is an exponential function of temperature and therefore the samples are exposed to severe pressures during measurements at elevated temperatures. This pressure increase appears to be the main driving force for the increase of WVTR with temperature. At a constant pressure a temperature increase usually leads to a higher rate of permeation because the polymer chains become more mobile. In a saturated atmosphere of water vapor a temperature increase leads to a higher vapor pressure, which appears to be the main contribution to an increased WVTR. The effect of an increased temperature on the WVTR is much less pronounced and the corresponding activation energy for permeation was found to be in the range of 10-20 kJ/mol.

INTRODUCTION

Polymers such as Polyethylene Terephthalate (PET), Polyethylene Naphthalate (PEN) and Polyether- etherketone (PEEK) find application in high-value added products. Examples are substrates for flexible electronics (organic light-emitting displays photovoltaics). Permeation experiments at elevated temperatures have been mainly carried out on gases [1]. The particular challenge for permeation experiments with water vapor at elevated temperatures is the fact that its vapor pressure is an exponential function of the absolute temperature rather than a linear function as in the case of the ideal gas. Figure 1 shows the vapor pressure of water vapor as function of temperature at 100% relative humidity (RH) At 100°C the vapor pressure of water is 1 bar, at 200°C it is already 15.3 bar [2]. This causes considerable mechanical stress on the sample. Approximating the curve shown in Figure 1 with a function:

$$p_{WV} = const \cdot \exp\left(\frac{-\Delta E}{kT}\right)$$

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yields an exponential parameter ΔE of about 41 kJ/mol.

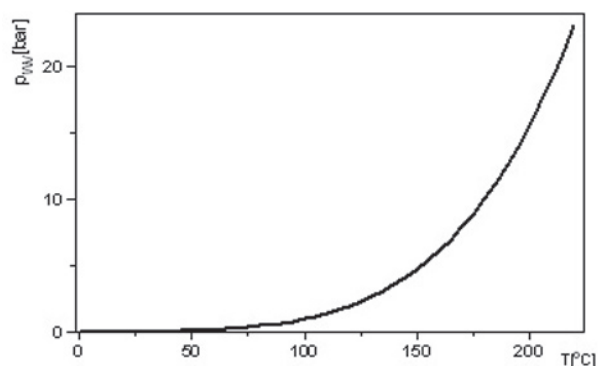


Figure 1: Vapor pressure of water as function of temperature [1].

To quantify the permeation of water vapor the term Water Vapor Transmission Rate (WVTR) is used, which is usually given in units of g/m²/d at a certain RH and temperature T. For the calculation of activation energies for permeation the WVTR should be divided by the vapor pressure. Published activation energies for water vapor diffusion vary widely [3, 4]. The lack of accurate data for activation energies and uncertainties about the functional dependence of permeation on temperature make experimental determination of WVTR for polymers necessary at elevated temperatures. The purpose of this paper is to present WVTR for different polymers in the temperature range up to 210°C.

EXPERIMENTS

Figure 2 shows a schematic view of the principle used in the experiment. The polymer sample is mounted on a gas container. The gas container is filled with a few droplets of water, which creates a saturated water vapour atmosphere inside the gas container. The filled gas container with the polymer sample is then introduced into a chamber. Water molecules, which have

permeated through the polymer sample, contribute to a pressure increase in the vacuum chamber. This pressure increase is measured with a pressure sensor (Figure 2). Depending on the surface structure of the polymer film (hydrophilic, hydrophobic) small water droplets may form on the upstream side of the sample. Previous studies indicate that this makes little or no difference to the amount of water that permeates through the film [5].

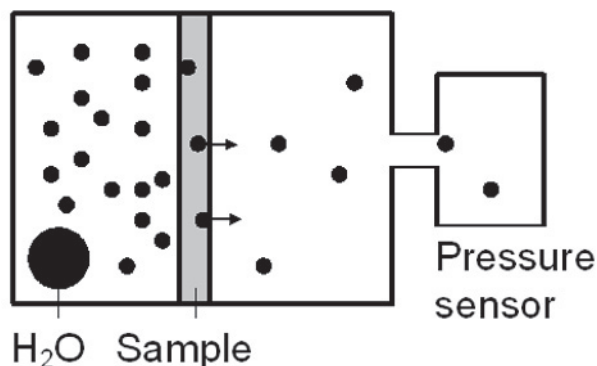


Figure 2: Experiment set up.

The increase of the pressure inside the vacuum chamber is a measure for the amount of water vapour that has permeated through the polymer sample. The method is called the Total Pressure Method [6]. The vacuum chamber can be heated up to 210°C. The sample is mechanically supported by a metal grid.

RESULTS

Figure 3 shows an Arrhenius plot of the water vapor pressure as function of temperature for PET, PEN and PEEK. The measured WVTR data in g/m²/d as summarized in Table 1 have been divided by the water vapor pressure to give values in g/m²/d/bar, which are plotted in Figure 3.

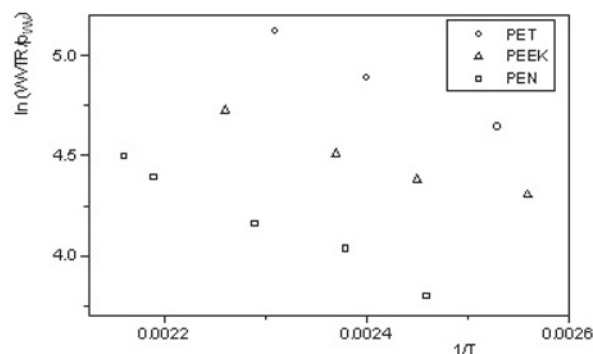


Figure 3: Arrhenius plot of WVTR/ p_{wv} as function of inverse temperature.

Table 1: WVTR for PET, PEN and PEEK films in units of g/m²/d @ RH=100%.

	PEN	PEEK	PET
120°C	90	180	300
160°C	470	760	1400
190°C	1300	1900	-

Film thickness was 125 μ m for PEN and PEEK and 100 μ m for PET.

As the number of data points is limited, further data points are required to decide to what extent the points shown in Figure 3 obey an exponential law or may be influenced by the glass transition of the polymers. Activation energies obtained from the data shown in Figure 3 are 11 kJ/mol for PEEK and 18 kJ/mol for PEN and PET. These values are obtained from the measurements at elevated temperatures and may not be extrapolated to low temperatures as a value of about 3g/m²/d for PEEK measured at RT indicates. The data base in the literature about permeation at elevated temperatures is rather thin and further studies might be required to establish whether activation energies obtained in a different temperature range can be compared as the water vapor pressure may vary by up to three orders of magnitude. The values for the activation energy for water vapor permeation determined from the data discussed in this paper are considerably smaller than the effect the pressure increase of saturated water vapor (41 kJ/mol, see Figure 1) has. It should be noted that apart from the temperature increase and the exponential pressure increase, the transformation between the glassy and the rubbery state of the polymers may contribute to the dependence of the WVTR on temperature.

CONCLUSION

We have shown a novel method to measure rates of permeation at elevated temperatures up to 210°C. WVTR has been estimated for water vapor transmission (permeation) through PET, PEN and PEEK. In a saturated water vapor atmosphere the amount of water permeating through the polymer films is mainly determined by the pressure increase due to the increased temperature. Activation energies for water vapor permeation are in the range 10-20 kJ/mol in the temperature range studied and may be different at lower temperatures.

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