Oxygen Permeability at High Temperatures and Relative Humidities

Lena Axelson-Larsson

PACKFORSK, Box 9, S-164 93 Kista, Sweden

It is a well-known fact that the permeability of polymer materials increases as the temperature increases. As the temperature drops to its original level, the permeability in many instances does the same. When packages are processed in an autoclave, the material will be exposed to both high temperature and high relative humidity. This can strongly affect the barrier of some materials, e.g. ethylene vinyl alcohol (EVOH) and polyamide (PA), because the water will act as a plasticizer.

A current project is now studying the permeability of different materials after sterilization. The aim of the project is to determine the permeability of different materials during sterilization at autoclave conditions and during storage. Factors that can reduce the negative effect on the barrier are also examined.

INTRODUCTION

All polymer materials are to some extent permeable to oxygen and if the temperature increases, the permeability increases. As the temperature drops to the original level, the permeability in many cases does the same. When packages are sterilized in a retort, the material will be exposed to both high temperature and high relative humidity. This will strongly affect the barrier of some materials, e.g. ethylene vinyl alcohol (EVOH) and polyamide (PA), even after the temperature has dropped to the original level, since the water will act as a plasticizer. The effect on the barrier is at its greatest immediately after sterilization, i.e. at the beginning of storage and distribution. The permeability will vary with the relative humidity.

Generally, EVOH materials are produced as multilayer materials consisting of at least five layers. The outer layers are generally polyethylene (PE) or polypropylene (PP), then there is an adhesive layer and in the middle is placed the EVOH layer. This structure will assure a very good oxygen and water vapour barrier as long as the EVOH layer is dry. But when the package is retort processed the barrier of the outer layer against moisture will be lowered because of the high temperature used in the retort. This will give a higher moisture content in the EVOH layer and reduce its oxygen barrier. As the temperature drops after the sterilization process, the barrier of the outer layer will go back to normal, which means that water will be trapped in the EVOH layer.

During storage the moisture content in the EVOH layer decreases. If, as in most cases, there is a high relative humidity in the package, the moisture content is at first the same or higher than the moisture content at equilibrium. So in this case moisture is transported from the EVOH layer and out through the outer layer. When we reach the point where the moisture content in the EVOH layer is the same or lower than the humidity in the environment, moisture will be transported into the EVOH layer from the inside of the package and then diffuse out through the outer layer.

The time it will take for the barrier to 'dry out' can be reduced by using polyethylene terephtha-

late (PET) or (PC) as an outer layer. The water barrier of PET is about four times lower than the water barrier of PP. This means that water will leave the material about four times faster. Another important factor is where the barrier layer is placed in the structure. The thicker the outer layer, the longer it will take before equilibrium is reached. But for some products an asymmetric construction might not give a shelf-life that is long enough. One way to reduce the barrier loss is to make the barrier layer thicker. Which construction we should choose is a combination of what is economically most advantageous and what the product demands. An asymmetric structure might be good for products that are sensitive to high concentrations of oxygen under a short period of time, e.g. fruit juices. Other products might be more sensitive to the total amount of oxygen penetrating the package during its shelf-life.

THEORY OF PERMEATION

EVOH is a semicrystalline polymer and permeation takes place in the amorphous regions. Under dry conditions the resistance to permeation is very good, since interchain hydrogen bonding prevents oxygen diffusion by reducing the mobility of chain segments. But when EVOH is exposed to water, it becomes plasticized, undergoing a reduction in the degree of hydrogen bonding. Above relative humidities of 80%, EVOH is plasticized to a point where its glass transition temperature drops below room temperature.[1]

Permeability is an activated process and as a function of temperature can be described by an Arrhenius equation

$$P = P_0 \, e^{(-E/RT)}$$

where P is the permeability, P_0 is a constant, E is the activation energy, R is the molar gas constant and T is the absolute temperature. If the temperature is increased, than the permeability will increase because the free volume in the material will increase. A common rule of thumb is that the permeability increases 30–50% for a rise in temperature of 5°C. Plots of $\ln P$ vs. $1/T$ are linear, but the slope changes when the polymer reaches a transition temperature.

The permeability coefficient is independent of the gas pressure if the gas does not interact with the polymer. But if there is a strong interaction,

the permeability will be dependent on the pressure and generally will increase as the pressure increases. This is the case, for example, when water dissolves in the material, the water has a plasticizing effect and the diffusion coefficient increases.

EXPERIMENT (see Table 1)

The aim of the project was to measure the permeability before and after the retorting process and to determine the permeability at retort conditions and during storage. The materials (A–F) studied were different combinations of PP/EVOH/PP and PP/PA6/PP, as follows:

A   PP/EVOH(32%)/PP 90/35/165
B   PP/EVOH(32%)/PP 90/35/505
C   PP/EVOH(32%)/PP 100/15/335
D   PP/EVOH(44%)/PP 234/29/242
E   PP/PA6/PP   131/66/134
F   PP/PA6/PP   179/85/202

The permeability of the material was measured before retorting. All permeability measurements were carried out in a Mocon Ox-Tran Twin. The gas streams were humidified by letting the gases pass through bubblers with a glass-bead and a controlled amount of water.

From the material, plastic pouches were formed. The pouches were filled with distilled water and placed in the retort. The heating up time was

---

Table 1. Experiment

(1) Permeability measurements made before and after retorting

Retort process
Heating up time: 20 min
Retort time: 20 min
Cooling and emptying: 15 min
Outgassing: 15 min

Measurements carried out at 23°C.

(2) Permeability during the retort process

Measurements carried out at 45° and 50°C.

$\ln P = f(1/T)$ gives an oxygen transmission rate at other temperatures, based on the assumptions that:

(a) the polymer does not reach a transition temperature;
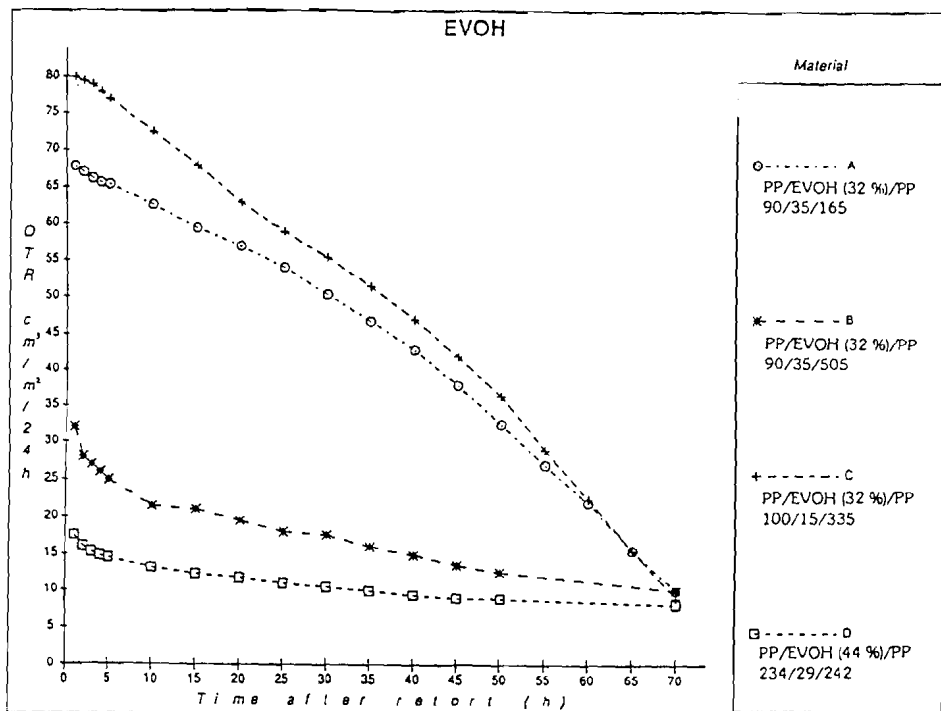(b) the water content in the material on retorting is the same as when the permeability measurement starts.

Figure 1.

·20 min, then the temperature was maintained for 20 min and the time for cooling and emptying the retort was ca. 15 min. After an additional 15 min, the Ox-Tran was outgassed from room air and the actual measuring of the permeability started. The permeability was measured on material cut out from the pouches.

The permeability depends on how much water the material absorbs, which in turn depends on the material thickness, the outer layer, the sterilization time, the sterilization temperature, etc. Advanced mathematical models are needed to calculate the permeability at high temperature and high relative humidity, but extensive measurements for input data would be needed. Instead of using mathematical models, it might be possible to use permeability measurements carried out directly after retort processing in order to determine the permeability during the retort processing.

The permeability directly after retorting was measured at two different temperatures, and the fact that the logarithm of the permeability is linear vs. $1/T$ is used to determine the permeability at a third temperature. This might be possible if the polymer does not reach a transition temperature and also includes the assumption that the water content in the material at sterilization in the retort is the same as the water content 30 min later while measuring the permeability. This approximation was checked by weighing the material continuously after retorting. The transition temperatures were measured by differential scanning calorimetry (DSC) directly after retort processing.

Within the project, different factors affecting the barrier were studied: the influence of different time–temperature relationships, the influence of the total pressure, the influence of the relative humidity during the permeability measurements and the influence of drying the package immediately after retort processing.

RESULTS

Figure 1 shows the measured permeability of four EVOH laminates directly after retort processing. Materials A, B and C contained 32 mol.% ethylene in the EVOH layer, while material D contained 44 mol.% ethylene. Therefore, it is not possible to compare directly the results between the different samples.

Materials A, B and C have about the same outer layer thickness but the inner layer thickness varies from 165 μm in material A to 505 μm in material
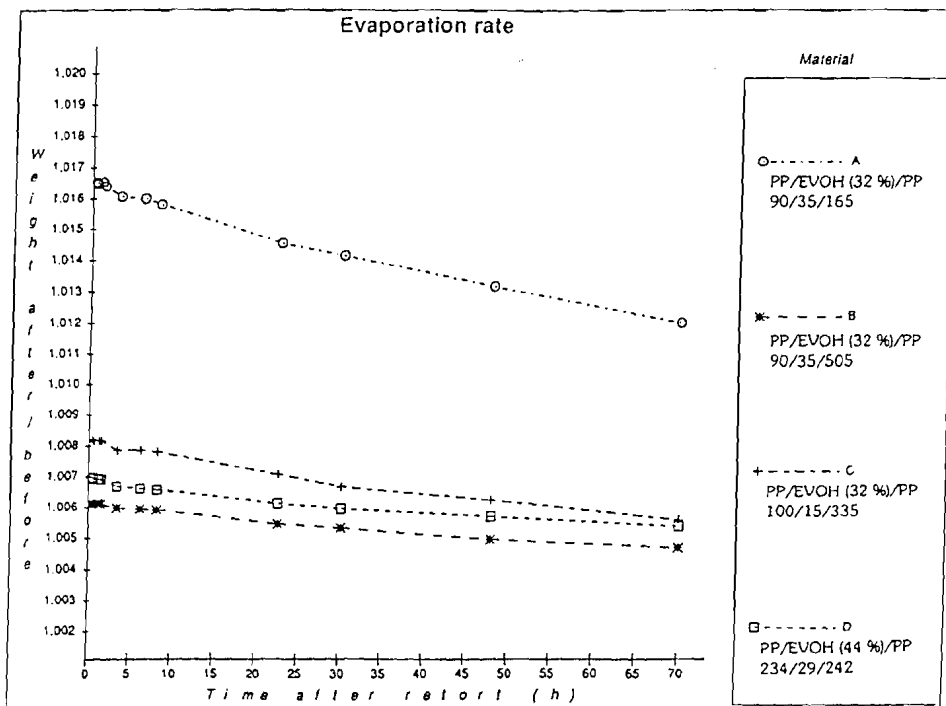
Figure 2.

B. In all three materials the EVOH layer is asymmetrically placed. One big difference between them is that the barrier layer is only 15 μm in material C and 35 μm in materials A and B.

The permeability before retorting for materials A and B was ca. 0.1 and for C and D ca. 0.2 cm^3/m^2/24 h. For all materials the processing had a severe effect on the barrier, which means that after 3 days (70 h) the permeability was still 50–100 times higher than before. The oxygen transmission rate (OTR) of material B after 1 month had decreased to ca. 0.2 cm^3/m^2/24 h.

Material B provides a better barrier than material A directly after sterilization. In this case the thicker inner layer must protect the EVOH layer. On the other hand, it takes longer for material B to 'dry out'.

Material C, because of its thinner barrier, achieves the highest OTR directly after sterilization but recovers faster than the other materials.

In material D the barrier layer is symmetrically placed and the outer layer is much thicker than for the other materials. Although the barrier layer is thinner than in materials A and B, directly after retort sterilization the barrier is better. One reason

for this is the higher concentration of ethylene in the barrier layer. We have to wait 70–80 h before materials A and B catch up. But the thinner outer layer of materials A and B results in a faster evaporation rate. This can be seen in Figure 2.

This figure shows the ratio between the weight of the material after and before retorting vs. time after retorting. The y-axis shows that the water uptake in material A is very high, ca. 1.65%, and is lowest in material B, ca. 0.6%. The reason why the water uptake is higher in material D than in material B must be because of the very much thicker inner layer in material B, which protects the barrier very well.

Figure 3 shows the OTR directly after retort processing for the two PA6 materials. As can be seen in the figure, the thicker material gives an almost linear relation between time and OTR but the thinner material does not.

As mentioned in the Experimental, the logarithm of the permeability is linear vs. the reciprocal temperature if the polymer does not reach a transition temperature. The glass transition temperature (T_s) of EVOH is, under normal conditions, ca. 70°C, but the high relative humidity in the retort lowers the T_g.
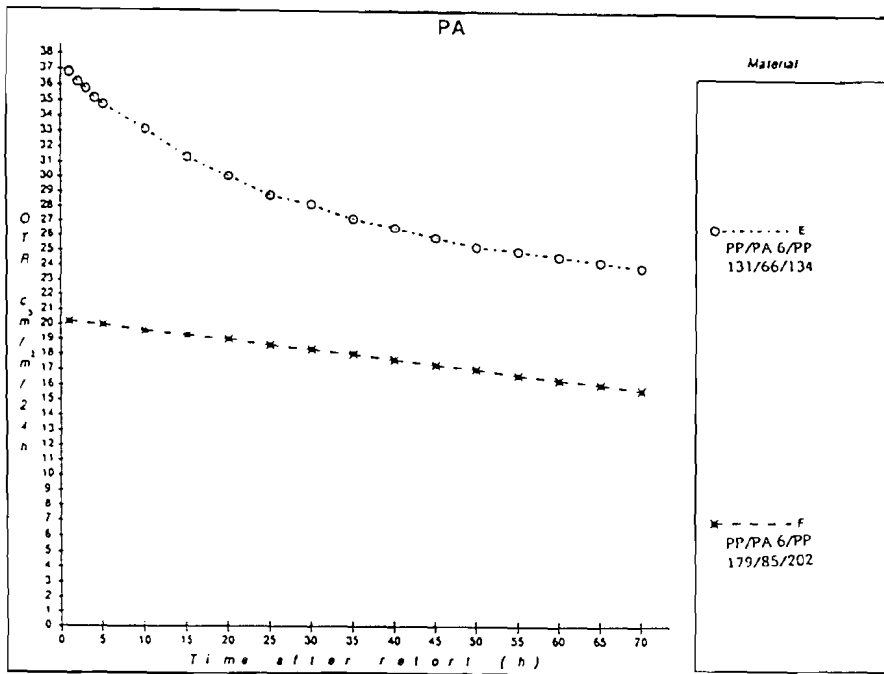
Figure 3.

Figure 4 shows the results from a DSC analysis of material D after retorting. We can see that the T_g is lowered to ca. 38°C. In the Ox-Tran we can measure permeability up to a temperature of 50°C, which makes it possible for us to measure the permeability above the T_g.

Figure 5 shows the permeability directly after retorting for material D, measured at 45°C.

Figure 6 shows the permeability at 50°C. By extrapolation of the slope, the intercept with the y-axis gives the permeability at time zero, which is the retort time, and at the humidity level that this material had reached in the retort (121°C for 20 min).

These measurements at two different temperatures give us Figure 7, which also shows the logarithm of the permeability vs. the reciprocal temperature at a very high OTR value of 2760 cm^3/m^2/24 h at 121°C for this material under these specific retort conditions.

The same experiment was carried out at another retort temperature. In this case the material was retorted at 115°C but all other variables were the same. The result is shown in Figure 8, which

gives an OTR of ca. 1100 cm^3/m^2/24 h in the retort.

If we take a look at Figure 7 again and read off the value corresponding to 115°C, this gives us an OTR of ca. 2200 cm^3/m^2/24 h, which is twice as big as the real value of 1100. It is interesting to note also that the material absorbs twice as much water at 121°C than at 115°C. A very small increase in temperature and corresponding total pressure is needed to make a severe increase in the water uptake and OTR.

The permeability of the thinner PA material was also evaluated at 45°C (Figure 9) and at 50°C (Figure 10) and the intercepts gave an extremely high OTR of 36 300 cm^3/m^2/24 h on retorting at 121°C for 20 min (Figure 11).

To evaluate to what extent the humidity in the Ox-Tran affects the measured value directly after retorting, measurements of the OTR were carried out under both humid and dry conditions. Figure 12 shows that if extrapolation to time zero is carried out, there is no difference between the values measured under dry or humid conditions. Weighing the samples and studying the evaporation rate verifies this result, which means that it is
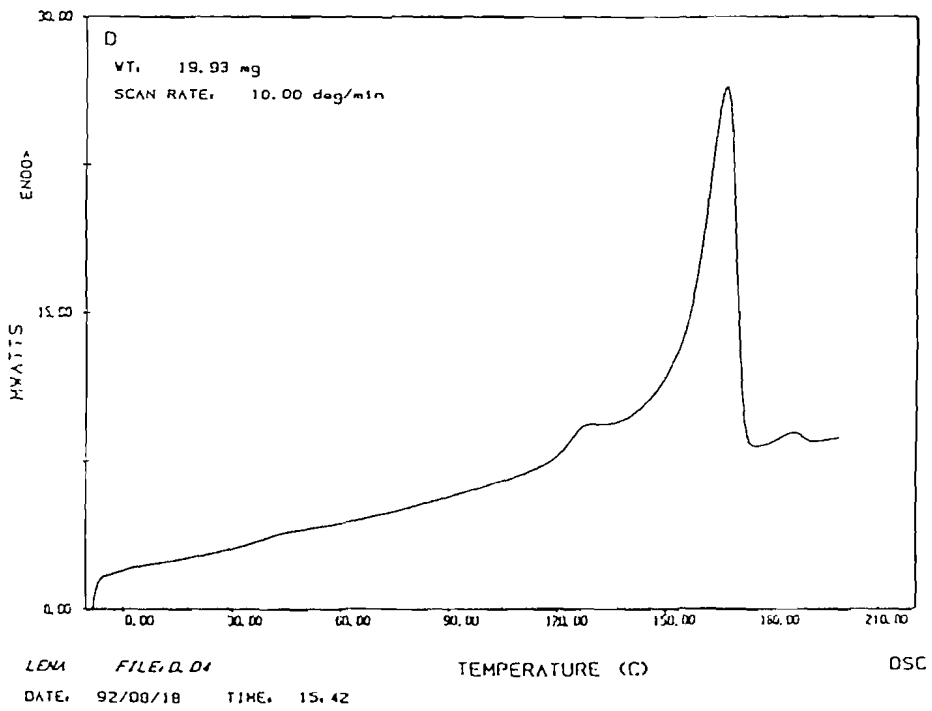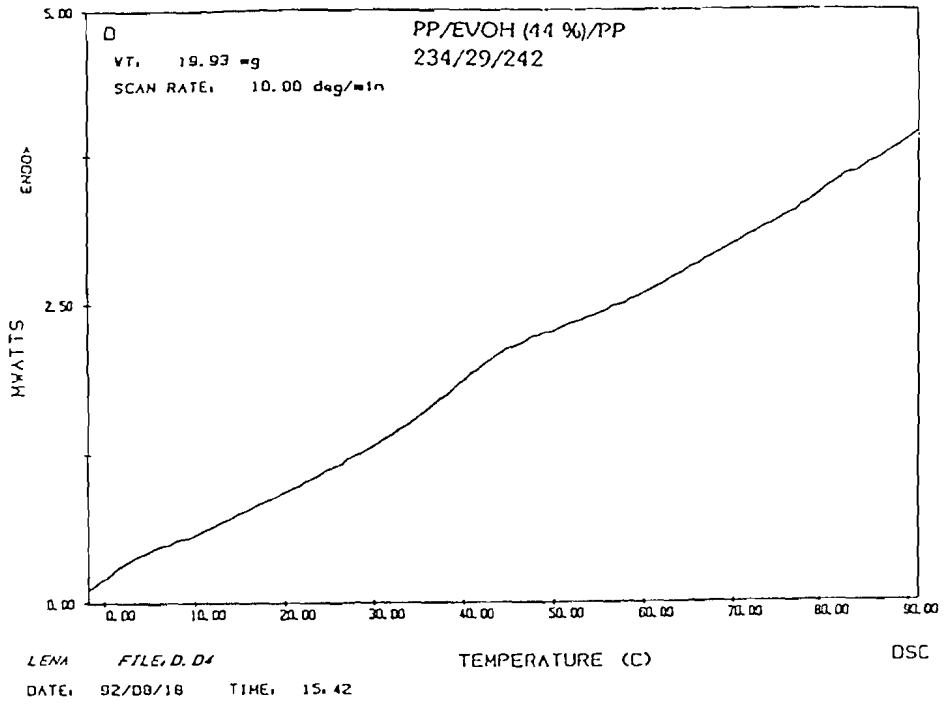
Figure 4.

acceptable to assume that the humidity level in the material at the start of measurements in the Ox-Tran is the same as the humidity level in the material after retorting.

REFERENCE

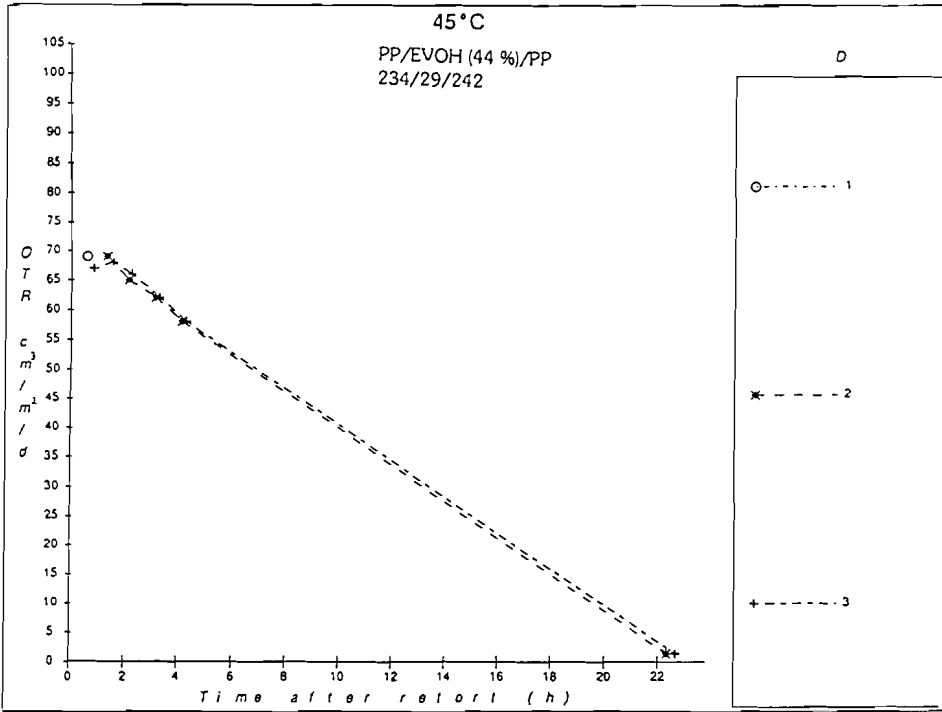1. Wachtel, J. A., Tsai, B. C. and Farrell, C. J. Retortable plastic cans keep air out, flavor in. *Plas. Eng.* Feb. (1985).
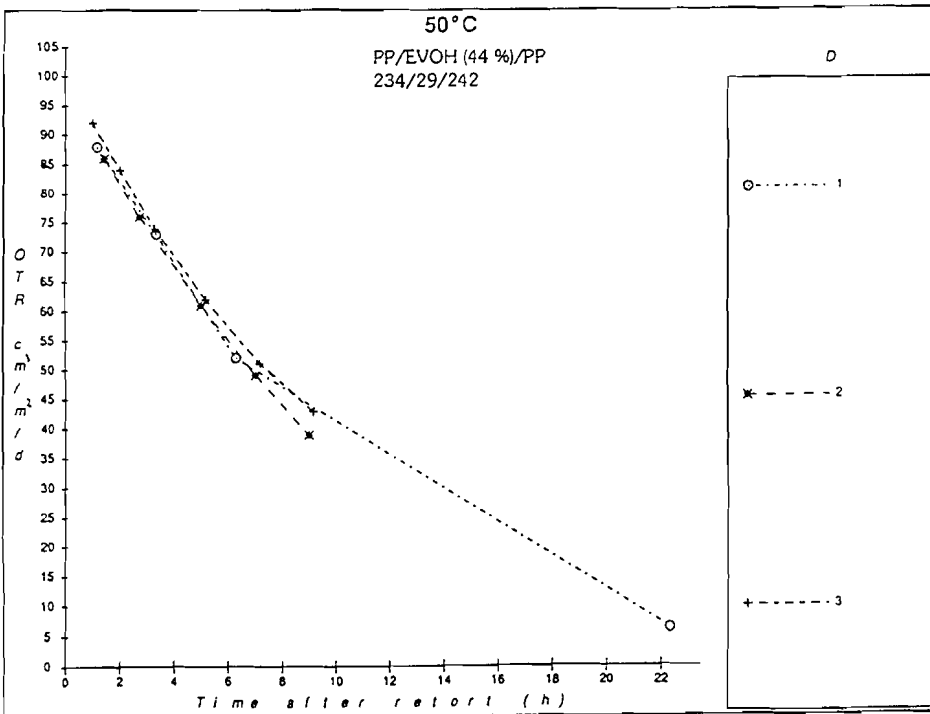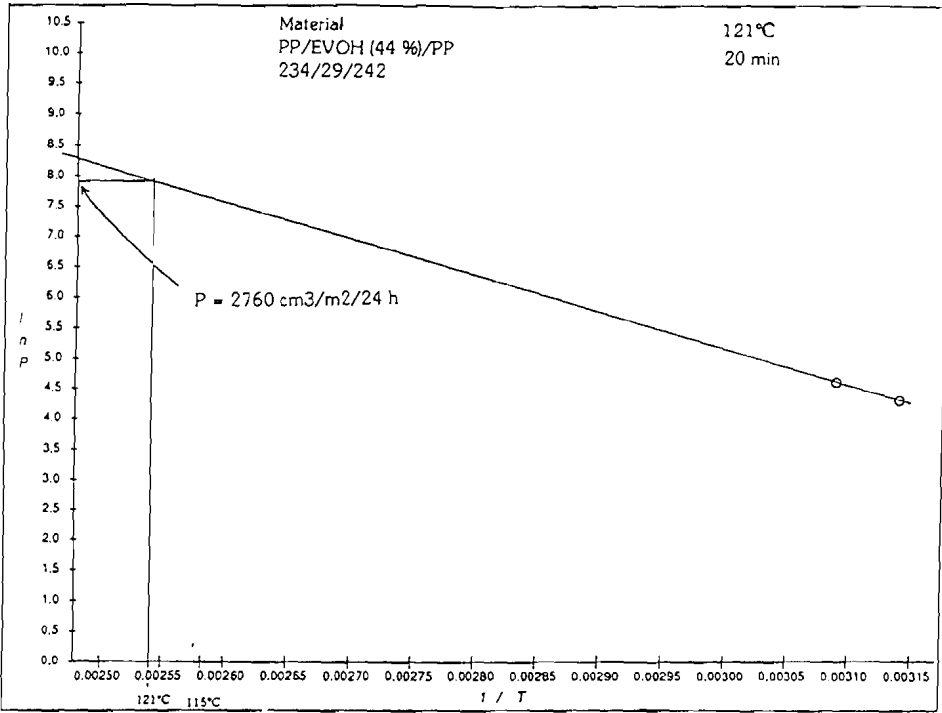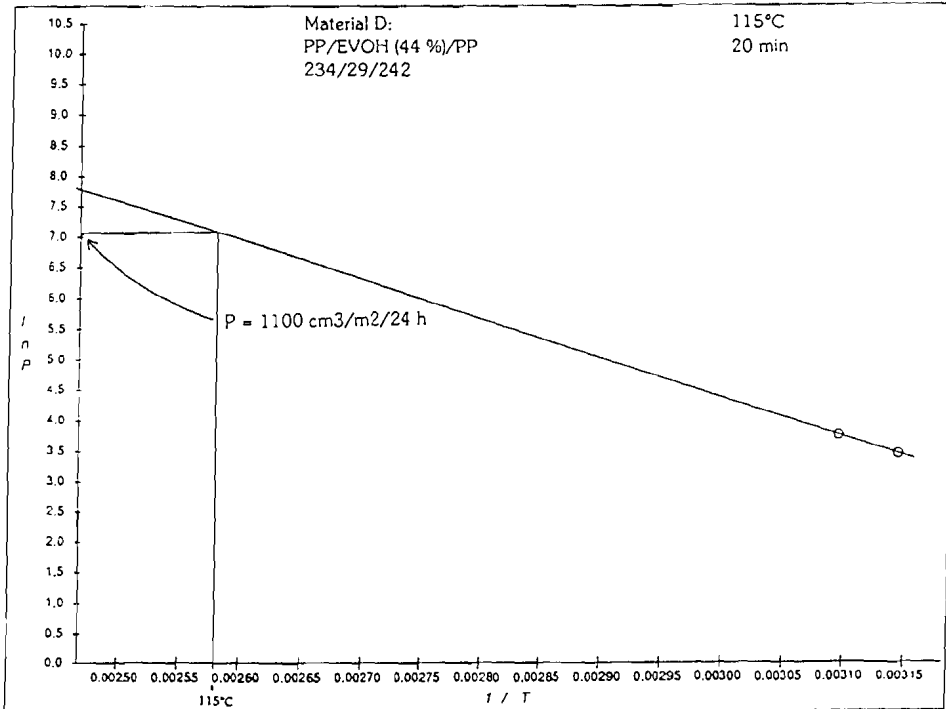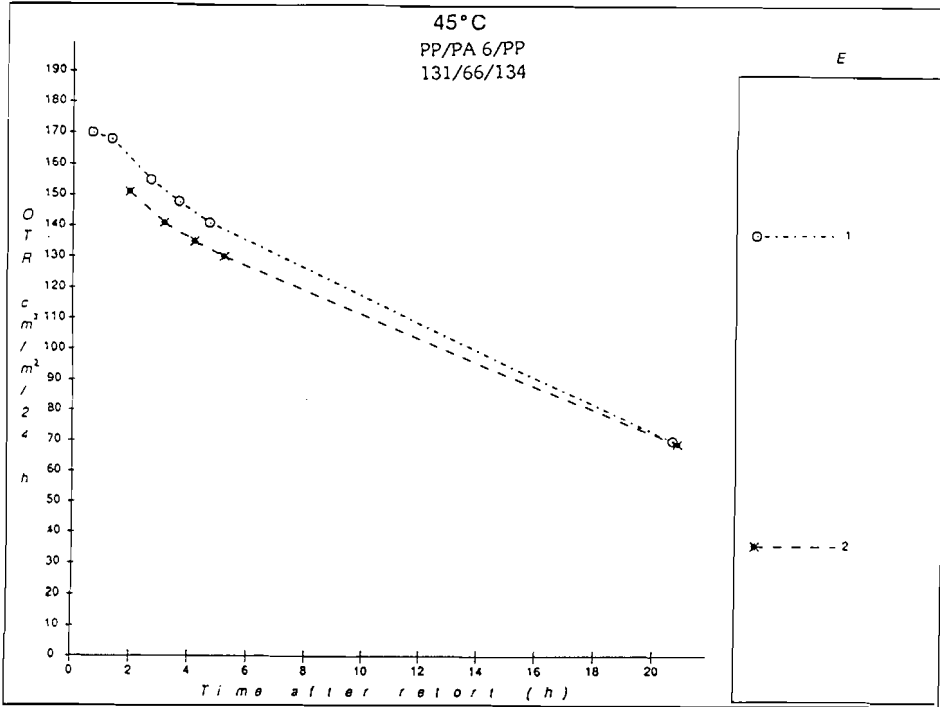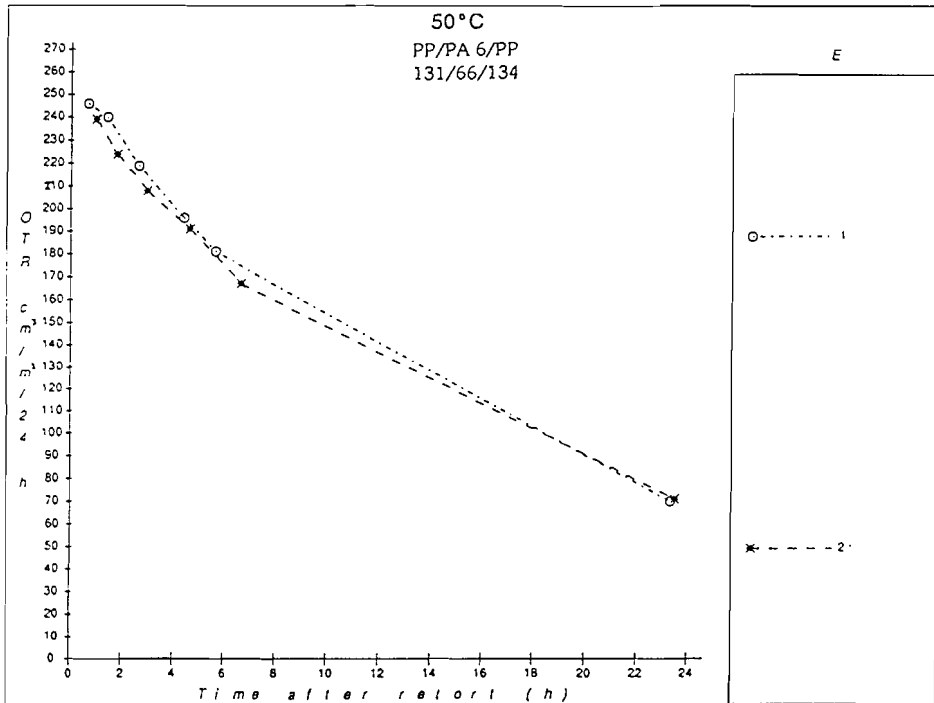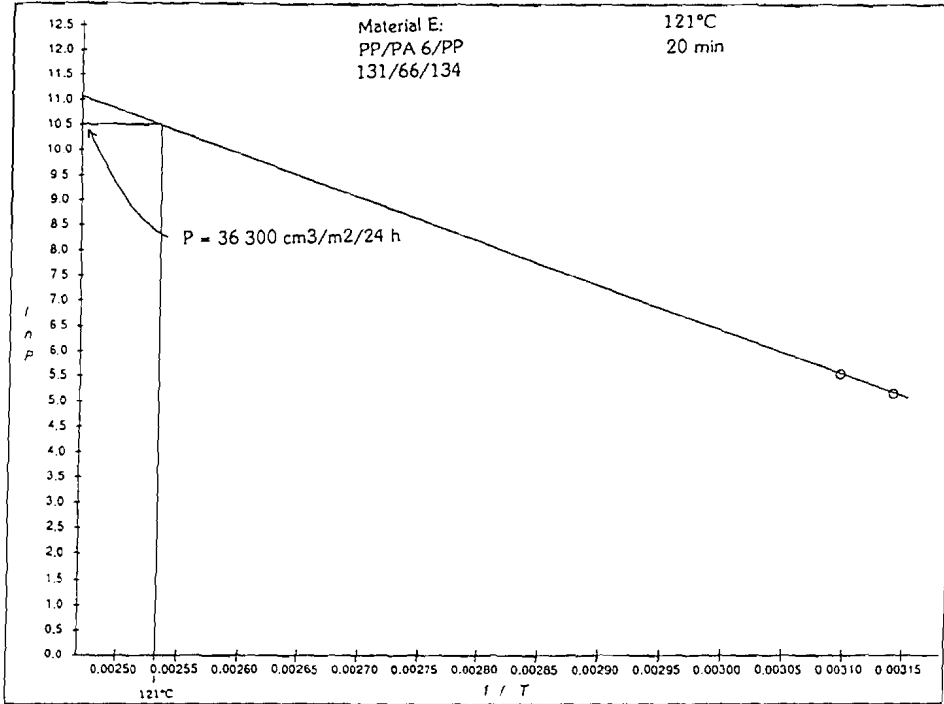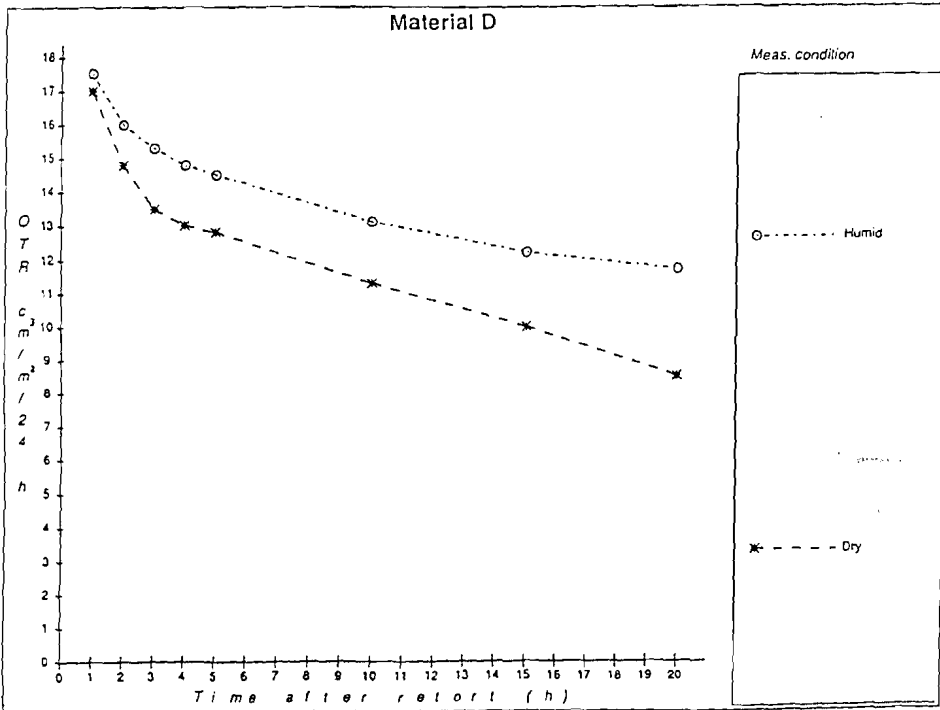

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Figure 11.

Figure 12.