

Diffusion Barrier Performance in Real Transformer Operation

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Abstract - This report gives a summary of the basic theory of gas transport in polymer membrane. It outlines important parameters influencing the transport processes in polymer membrane. With the theoretical background in mind, some commercial membranes are compared and discussed with the focus on the oxygen transmission.

Key words: sealed transformer, air bag, rubber bladder, permeation, polymer, permeability.

I. INTRODUCTION

In order to extend lifetime or increase temperature endurance of transformers in operation, different methods to prevent oxygen to enter the transformers are used. Oxygen is the main reason for the degradation processes and the recent increase in hot-spot (design) temperatures make transformer sealing imperative. The use of different materials in the diffusion barrier gives rise to very different permeability to (primarily) oxygen. Material thickness and structure is of utmost importance for the success of the investment made.

Experience from recently delivered transformers seem to suggest that manufacturers of transformers do not have an applicable standard specification with sufficiently stringent requirements to produce transformers with as good properties in this aspect than was done 50 years ago.

After a summary of the diffusion theory based of the works of Fick and Crank [1], the material properties of some commercial barriers in transformers will be compared and discussed with focus on the oxygen permeability.

II. THEORETICAL BACKGROUND

A The diffusion process

Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions.

When there is a concentration gradient present in the system, the random molecular motions result in a net transport of molecules from high to low concentration.

Transfer of heat is also due to random molecular motions. This analogy was recognized by Fick (1855) who adopted the mathematical equation of heat conduction derived by Fourier (1822). This resulted in two laws.

Fick's first law: The rate of transfer of diffusing substance through unit area of a section is proportional to the concentration gradient measured perpendicular to the section (1), see Fig. 1.

$$J = -D \frac{\partial c}{\partial x} \quad (1)$$

J is the mass or molar flux, (rate of transfer per unit area of section), c the concentration of diffusing substance, x the space coordinate measured normal to the section, and D the diffusion coefficient.

The negative sign arises because diffusion occurs in the direction opposite to that of increasing concentration.

Equation 1 is applicable to the diffusion in the steady state, i.e. when the concentration does not vary with time. On the other hand Fick's second law describes the non-steady state for the diffusion of a substance, which is given by the rate of change of the substance concentration ($\frac{\partial c}{\partial t}$) per unit area of section:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

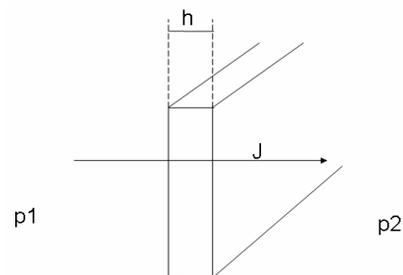


Fig. 1. Permeation through a membrane submitted to a concentration gradient ($p_1 > p_2$)

B Gas transport in a plane sheet (membrane)

One model to describe gas transport in a non porous barrier is the solution diffusion model. The gas permeation is seen as a three-stage process:

1. Adsorption and dissolution of the gas at the polymer membrane interface.
2. Diffusion of the gas in and through the bulk polymer. (The diffusion process in a membrane could be visualized as a series of thermally activated jumps.)
3. Desorption of the gas into the external phase.

The transport process is characterized by an initial non-steady state when the gas concentration profile in the membrane is building up. During this time the process is described by Fick's second law. After some time, the concentration profile within the membrane remains constant with time (steady state). The transport through the membrane is then described by Fick's first law.

In the most common experimental arrangement the membrane is initially at zero concentration and the concentration at the face through which diffusing substance emerges is maintained effectively at zero concentration. The penetration of a gas in a membrane could be described by one-dimensional diffusion in a medium bounded by two parallel planes, e.g. the planes at $x=0$, $x=h$ (the membrane's thickness). This means that in practice the material is so thin that effectively all the diffusing substance enters through the plane faces and a negligible amount through the edges.

Steady state

In the steady state (1) is integrated to give:

$$J = \frac{D(c_1 - c_2)}{h} \quad (3)$$

where h is the membrane's thickness. In the case of transport of gases and vapours, Henry's law describes the distribution of the penetrant between the penetrant and the polymer phase,

$$c = Sp \quad (4)$$

where c is the concentration within the membrane. That is the concentration of sorbed penetrant in equilibrium with the vapour pressure p of non-sorbed penetrant. S is the solubility coefficient.

Combination of (3) and (4) gives the permeation equation:

$$J = \frac{DS(p_1 - p_2)}{h} \quad (5)$$

where p_1 and p_2 are the ambient pressures on two sides of a film of thickness h . The product DS is called the permeability coefficient, P_e , so that

$$P_e = DS \quad (6)$$

In terms of permeability, the flux (5) can be written as

$$J = P_e \frac{(p_1 - p_2)}{h} \quad (7)$$

Non-steady state

Fig. 2. displays the plot of a permeability test. The amount of penetrant that has passed through a membrane is plotted as a function of time. Initially there is a transient non-steady state, described by Fick's second law. Finally the curve approaches the line (derived from Fick's second law for $t \rightarrow \infty$):

$$Q_t = \left(\frac{Dc_1}{h}\right)\left(t - \frac{h^2}{6D}\right) \quad (8)$$

where Q_t is the total amount of penetrant which has passed through the membrane, D the diffusion coefficient, h the thickness of the membrane and, c_1 the concentration of the penetrant at the face of high concentration. This line has an intercept θ , time-lag, on the t -axis (Fig. 2.) given by:

$$\theta = h^2 / 6D \quad (9)$$

If D is supposed to be independent of concentration it could be determined by (9). P_e is deduced by using (7), and S follows from (6). This procedure to determine D , P_e , and S by analysing the stationary and non-stationary flow is referred to as the time-lag method, introduced by Barrer 1951.

From (5) and (6) it is obvious that the flux J or the transmission rate is dependent on the pressure difference over the membrane and the thickness of the membrane. The permeability coefficient, P_e , on the other hand, is normalized for the pressure and the thickness. Thus it is convenient to use the P_e coefficient to compare transport properties in different membranes.

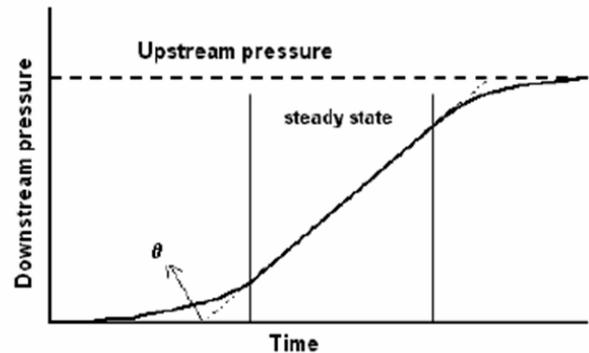


Fig. 2. Determination of time-lag from steady state permeation [2].

C Parameters influencing the transport properties

There are many parameters that influence the transport of gases in a membrane. Here, the most important ones will briefly be described. Generally these parameters influence each other.

Temperature

The diffusion of small molecules in rubbery polymers is a thermally activated process. At a given pressure and in a narrow temperature interval, the transport coefficients S , D , and Pe can be expressed by Arrhenius law:

$$S(T) = S_0 \exp(-\Delta H_S/RT) \quad (10)$$

$$D(T) = D_0 \exp(-E_D/RT) \quad (11)$$

$$Pe(T) = Pe_0 \exp(-E_P/RT) \quad (12)$$

The pre-exponential factors represent the limit values, infinite molecular agitation (T approaches infinity), of each transport coefficient. E_P represents the apparent activation energy for the permeation process and is equal to the sum of E_D , the apparent activation energy for the diffusion process, and ΔH_S , the heat of solution needed for the dissolution of a penetrant mole in the polymer matrix [3]:

$$E_P = E_D + \Delta H_S. \quad (13)$$

Pressure

Two opposite effects may occur when the pressure on the upstream side of a membrane is increased.

-An increased hydrostatic pressure leads to a compaction of the polymer, thereby reducing the free volume. The diffusion is therefore retarded

- An increased penetrant concentration which could lead to a more plasticised polymer and a larger diffusion.

Free volume

The specific free volume V_F is defined by Vrentas and Duda [4] as:

$$\widehat{V}F - \widehat{V}0 = \widehat{V} - \widehat{V}(0). \quad (14)$$

\widehat{V} is the specific volume of the equilibrium liquid structure at any temperature T . $\widehat{V}0$ is defined to be the specific volume of the equilibrium liquid at 0 K (this quantity can be estimated by a variety of methods [4]).

Glass transition temperature, T_g

A polymer with a temperature higher than the glass transition temperature, T_g , is in its rubbery region and behaves like a rubber. Rubbery polymers are characterised by segmental mobility and unsaturation. This results in smooth and easy diffusion of small molecules. A low T_g implies large segmental mobility and high diffusivity. In addition the increase of D with decreasing T_g is accompanied by a decrease in concentration dependence of D .

Glassy polymers ($T < T_g$) are non equilibrium solids that are characterised by hard and brittle moiety with restricted chain mobility. Rotation around the chain axis is limited and the motion within the structure is dominated by vibration. Glassy polymers have a specific volume larger than the specific volume of equilibrium. These characteristics lead to a more complicated and less understood diffusion process than for rubbery polymers.

Explanation of T_g by looking at the specific volume

If a polymer in the rubbery region is cooled, the equilibrium specific volume will decrease linearly with the temperature.

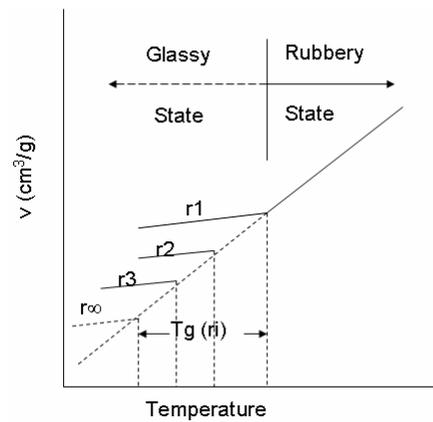


Fig. 3. Schematic illustration of the effect of quench rate (r_i) on glass density [5]

At a certain point, there will be a deviation from the extrapolation of the equilibrium v versus T curve applicable in the high temperature rubbery region. This point is defined as T_g . At slower cooling rates this point will be at lower temperature until a minimum at "infinitely slow" cooling rate, shown as r_∞ in Fig. 2.

This inflection occurs when the potential energy for rotation around a bond becomes of the same magnitude or greater than the thermal energy available for motion because the main chain is no longer able to undergo free gyration and loses its rubber-like qualities.

Further reduction in volume can only be achieved by small vibrations. The material then follows the less steep thermal contraction curve characteristic of an equilibrium glass.

Fig. 3. also displays that rapidly quenched glasses (curve r_1) are less dense than slowly cooled or pressure densified samples of the same material (curves r_2 or r_3). Lower density glasses are said to have higher amounts of frozen free volume due to the incomplete volume relaxations [5].

Degree of saturation

It has been found that the diffusivity decreases when the degree of unsaturation is lowered by hydrogenation [6]. Saturated chains are more restricted and therefore they have less segmental mobility than unsaturated ones.

Degree of cross linking

At low levels of cross linking, the diffusivity decreases linearly with increasing cross linking. However higher levels of cross-linking result in a smaller dependence on cross linking of diffusivity.

Nature of substituents

The introduction of bulky or polar groups in the polymer chain also influences the transport properties. Rubbers containing large numbers of substituent methyl groups have lower diffusivities. The bulky groups reduce the mobility of the polymer chains and the free volume available for diffusion of penetrant molecules. Studies have shown [6] that bulky groups in the side chains have greater influence on decreasing the diffusivity than bulky groups in the backbone.

Functional groups

The permeability of penetrants which interact weakly with functional groups in a polymer can be expected to decrease when the cohesive energy of the polymer increases. For example, by increasing the polarity of the substituent group on a vinyl polymer backbone, oxygen permeability was reduced by almost 50000 times [6].

Plasticizer

The addition of plasticisers results in an increased segmental mobility and generally an increased penetrant transport.

It is important to note that water could act as a plasticiser in some materials (hydrophilic).

Molecular weight

Increased molecular weight decreases the diffusivity significantly in glassy polymers. The number of chain ends decrease with increasing molecular weight. The chain ends are discontinuities that may form sites where the penetrant could be sorbed. However, it has been found [7] that in thermoplastic polyurethane elastomers, which are block copolymers, composed of soft segments and hard segments, the permeability of oxygen and carbon dioxide increased with the chain length of the soft segments. This displays the fact that it is not only one single parameter that influences the transport processes but a combination of several factors.

Nature of the penetrant

The penetrant's size and shape affect its transport rate within the polymer matrix. An increase in penetrant size results in a decrease of the diffusivity. The shape of the penetrant also influences the transport. A flattened or elongated molecule has higher diffusion coefficients than spherical molecules of equal molecule volume.

The effects of the penetrants size and shape are more marked in glassy than in rubbery polymers. This is because the polymer-penetrant mixing processes are different. In rubbery polymers, energy is required to create holes for the penetrant molecules. Larger penetrants tend to increase the heat of sorption resulting in increased sorption leading to an enhanced plasticisation of the polymer chains. Thus the

smaller diffusion coefficients for larger molecules will be compensated for by increased sorption.

Fillers

The diffusion and the transport in filled polymers depend upon the nature of the filler. If the filler is inert and compatible with the polymer matrix, the filler will occupy part of the free volume resulting in a decreased permeability.

On the other hand, if the filler is incompatible with the polymer, voids are created at the interface, leading to an increased free volume and permeability [6].

Crystallinity

The sorption and diffusion take place only in the amorphous regions. The crystalline regions have two effects, they increase the effective path length of diffusion and they reduce the mobility of the polymer chains. This results in higher activation energy of diffusion.

Orientation

Uniaxially drawing of the polymer, changes its morphology and could both increase and decrease the transport parameters.

Diffusion in polymer blends

The transport through a blend depends on its composition, miscibility and phase morphology. In homogenous blends the diffusion is influenced by the interaction between the component polymers, while for heterogeneous blends, the interfacial phenomena and the rubbery or glassy nature of the phases are important. Most polymer blends are heterogeneous.

III. CHOOSING MATERIAL IN POWER TRANSFORMER SEALING BAGS

To obtain a membrane with a low oxygen diffusion rate it is important to obtain a material that possesses both high barrier properties and high flexibility to avoid material rupture. It is difficult to find a single material that combines both of these properties. High flexibility generally means high permeability because of large segmental motions. Similarly a high barrier often means a rigid material. Therefore one is directed to blends or laminates that combine the required properties.

IV. THE REALITY

In the commercial application people responsible for ordering the rubber bags seem to have forgotten WHY they are ordered. This is also the case with the suppliers.

Attempts to obtain gas diffusion data from various suppliers have failed because the data are not available and maybe never have been available. This means that materials are chosen based on cost and flexibility rather than performance and cost which is more to be expected in technical applications.

As a consequence today's rubber bag sealed transformers have very low sealing tightness, especially in comparison

TABLE I
NITROGEN ANNUAL INCREASE

Sealing quality	Annual N ₂ increase	Years to N ₂ -saturation
Good	1 000 ppm	> 50
Acceptable	2-3 000 ppm	20- 40
Unacceptable	> 5 000 ppm	10
Today's best	5 000 ppm	10
Today's worst	1 000 000 ppm	2 weeks

with sealed transformers from the 1950's and 1960's. In fact some of the very recent transformers tested during commissioning/warranty period has made it necessary to investigate whether they actually had a rubber bag.

It is easy to measure the tightness against atmospheric gases as nitrogen, the most abundant of atmospheric gases, is inert. Oxygen is not suited for this as the oxygen level in a faulty and sealed transformer can become very low as oxygen is consumed due to the heat generated by the fault.

TABLE I displays the annual increase of nitrogen for some transformers in different condition. "Good" are measured data from 50 years old transformers from Iceland. Iceland's volcanic foundation and its H₂S-rich atmosphere convinced the Icelandic engineers to choose sealed designs to avoid sulphur corrosion. On the same time they received an extra bonus of extreme life times as oxygen was also excluded from the transformers.

Today's best and worst are measured very recently and range from 20 MVA to HVDC transformers of >500 MVA.

V. DISCUSSION AND SUGGESTIONS

The decline in chemical performance (=life time parameters) need to be addressed by the purchasing side by specifications that include the life time aspects such as rubber bag seals (extending life time by not allowing oxygen to enter the insulation system).

The development towards lower and lower quality rubber bag sealing materials can be handled when ordering the transformer by simply state the requested maximum annual in-flow of air gases and state that it should be measured by monitoring the N₂-content rate of change according to a standardized test method. Because of the influence of several parameters on the permeability, the method should specify the pre conditioning of the membrane. This means that the membrane is kept at constant conditions, temperature, pressure, (and relative humidity. The relative humidity should not be an important parameter, because the material should be chosen not be sensitive to humidity.), prior to measuring. The test should also be run under these constant conditions and the results should be reported in permeability units, which make it possible to compare different materials. Then it will be up to the transformer designer to ensure this is done. By this

method any other leaky points e.g. at bushings, circulation pumps etc. will also have to be addressed by the designer and better sealing would be chosen there too.

It is essential to understand that carefully monitoring air gases levels in insulating oil systems require very stringent sampling procedures, sample transportation methods and analytical techniques. Syringes and Head-Space laboratory analytical methods have proven to be extremely vulnerable to contamination of the sample by atmospheric gases rendering the analytical results always to come out to high. Thus that methodology is not suited for diagnosing diffusion of atmospheric gases into the insulation system of a transformer.

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