Polymer packages for food – materials, concepts and interactions
A literature review

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1. **INTRODUCTION**

1.1. **Selection of a food packaging system**

Many factors must be considered when selecting a package system for a given application. These include the cost of the total system, marketing requirements, such as convenience, and barrier properties to maintain expected shelf-life. Shelf-life is defined as the length of time that a container and the material in the container will remain in an acceptable condition under specified conditions of storage. The assurance that food quality will be maintained during the expected shelf-life is as important as any consideration of costs.

If packages do not possess the necessary mechanical properties to maintain integrity during manufacture, handling and transport it may get pinholes, flex cracks or weak areas which could result in loss of integrity (Hotchkiss, 1988; Oswin, 1982).

Maintainance of the package barrier properties towards oxygen, water vapour and organic species is also critical to the shelf-life of the product. The ability of a packaging material to protect and preserve food products depends on how well it inhibits or prevents the transport of gases, vapours, and other low molecular weight compounds through the packaging and prevents the migration of substances from the package to the food (Koros, 1990).

Packaging materials are used extensively to protect and preserve food products in the storage and distribution environments.

Product shelf-life is controlled by three factors (Gray and Harte, 1986).

1. Product characteristics
2. The environment to which the product is exposed during distribution.
3. The properties of the package.

Foods can be classified according to the amount of protection required, **Table 1.** Data like this serve as an estimate of the protection needed which can be used to determine the requisites of a barrier.
Table 1. Degree of permeation protection required by various foods and beverages (one year shelf-life assumed at 25°C). (Harte and Gray, 1986).

<table>
<thead>
<tr>
<th>Food/Beverage</th>
<th>Estimated Max. Ant. of O₂ Gain Tolerable (ppm)</th>
<th>Other Gas Protection Needed</th>
<th>Estimated Maximum Degree of Water Gain or Loss Required</th>
<th>Requires High Oil Resistance</th>
<th>Requires Good Barrier to Volatile Organics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Canned Milk, Canned Meats Canned Fish, Poultry</td>
<td>1 - 5</td>
<td>-</td>
<td>5% Loss</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>2. Baby Foods</td>
<td>1 - 5</td>
<td>-</td>
<td>5% Loss</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>3. Bisc, Alc. Wine</td>
<td>1 - 5</td>
<td>&lt;20% CO₂ (or SO₂) Loss</td>
<td>5% Loss</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>4. Instant Coffee</td>
<td>1 - 5</td>
<td>-</td>
<td>5% Gain</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>5. Canned Vegetables, Soups, Spaghetti, Catup, Sauces</td>
<td>1 - 5</td>
<td>-</td>
<td>5% Loss</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6. Canned Fruits</td>
<td>5 - 15</td>
<td>-</td>
<td>5% Loss</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7. Nuts, Snacks</td>
<td>5 - 15</td>
<td>-</td>
<td>5% Gain</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>8. Dried Fruits</td>
<td>5 - 15</td>
<td>-</td>
<td>5% Gain</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9. Fruit Juices, Drinks</td>
<td>10 - 40</td>
<td>-</td>
<td>5% Loss</td>
<td>-</td>
<td>x</td>
</tr>
<tr>
<td>10. Carbonated Soft Drinks</td>
<td>10 - 40</td>
<td>&lt;20% CO₂ Loss</td>
<td>5% Loss</td>
<td>-</td>
<td>x</td>
</tr>
<tr>
<td>11. Oils, Shortenings</td>
<td>50 - 200</td>
<td>-</td>
<td>10% Gain</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>12. Salad Dressings</td>
<td>50 - 200</td>
<td>-</td>
<td>10% Gain</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>13. Jams, Jellies, Syrups, Pickles, Olives, Vimegars</td>
<td>50 - 200</td>
<td>-</td>
<td>5% Loss</td>
<td>-</td>
<td>x</td>
</tr>
<tr>
<td>14. Liquors</td>
<td>50 - 200</td>
<td>-</td>
<td>5% Loss</td>
<td>-</td>
<td>x</td>
</tr>
<tr>
<td>15. Condiments</td>
<td>50 - 200</td>
<td>-</td>
<td>5% Gain</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16. Peanut Butter</td>
<td>50 - 200</td>
<td>-</td>
<td>10% Gain</td>
<td>x</td>
<td>-</td>
</tr>
</tbody>
</table>

Most plastics can be considered to be barriers to certain substances. Plastics differ, however, widely in their characteristic permeabilities to water vapour, oxygen, carbon dioxide and volatile substances. Furthermore, these permeability characteristics are affected by temperature, humidity and other environmental conditions as well.

Food products may undergo loss of quality due to failure of the package and/or due to product/package interactions. Package failure can result from inadequate barrier properties (against oxygen, water vapour, light etc.) for the intended shelf-life or from loss of integrity during distribution (Mannheim and Paasy, 1990).

Product/package interactions result from one of several modes, Figure 1. Product components may penetrate the structure of the packaging material, causing loss of aroma, barrier and/or mechanical properties. Packaging materials can absorb flavour components, scalping, from products, the loss of which results in a reduced perception of quality.
Further, the migration of low molecular weight components (e.g. additives) from packaging materials to a contained product can result in a flavour and/or colour change (Crosby, 1981; Brown, 1986).

Improper use of packaging materials can increase the risk associated with packaged foods.

When selecting a packaging system with appropriate barrier properties for a food product, a number of criteria must be considered;

1. The stability of the food product itself, such as food component changes as a result of exposure to light, oxygen and changes in the water activity of the product.

2. Environmental factors such as temperature, relative humidity (RH%), light intensity to which the product/package system is exposed during distribution and storage and the desired shelf-life of the product.

3. The compatibility of the package with the method of perservation selected.

![Diagram showing interactions between environment, package, foodstuff, and problem.](image)

**Figure 1.** Interactions between foods and packaging. (Paxéus, 1988).
Flavour degeneration is a complex issue, and various modes of loss can occur. Of primary importance is oxidation resulting from invasion of oxygen from the atmosphere through the container and subsequent reaction with the food (Harte, 1986). Elimination of this type of flavour deterioration requires that the package restrict the transport of oxygen. Since it is critical that dry foods remain dry and that moist foods do not dehydrate, it may also be necessary to limit the flux of water vapour.

Contamination of the food from an external source is another mode of flavour deterioration. An example of this process is the migration of solvents used in printing inks and adhesives into foods during storage. Another area of great concern is the migration of flavour compounds from the food into the food packages. Flavour molecules are present in extremely small quantities. However, these molecules are responsible for the unique flavour of a particular food, and small losses can result in a dramatic "off" taste. Losses can involve anything from removal of all flavours to an imbalance caused by selective removal of only a few flavour components.

Flavour losses that result from the interaction with the polymer package can be classified into two categories: first, losses occurring by permeation through or migration from the package, and, second, those from sorption or scalping by the container. Many plastic packages contain a barrier polymer to minimize flavour losses. Barrier polymers are polymers that inhibit mass transport.

In view of the growing use of plastics as food packaging materials and the complexity of food flavour, an important issue to focus on would be to be able to predict the mass transport parameters of flavour molecules in polymers.
2. PLASTIC PACKAGING MATERIALS FOR FOODS

Packages can be classified into two categories: primary, where the packaging material is in contact with the packed product, and secondary, where the main function is mechanical protection. The two cases could also be combined in one packaging system.

The primary packages can be flexible, i.e. films, papers and thin laminates, and cardboard, or rigid, i.e. thick plastics, metal and glass (Miltz, 1992).

With the exception of aluminium in the form of foil in laminates, only polymer materials will be discussed in this section.

Most polymers used for food packaging are thermoplastics, i.e. they can be repeatedly softened by heating and hardened on cooling. Thermosets, on the other hand, undergo an irreversible change on heating and are not able to be softened and reconstructed. This is due to their molecular structure, which is a three-dimensional bonded network, Figure 2.

![Figure 2. Linear, branched, and cross-linked polymer chains.](image)
The foremost advantage of polymers is their wide diversity and broad spectrum of properties. Most polymers have a density around 1 g/cm$^3$, making them lightweight packages. They are relatively cheap, easily processed and shaped.

The major drawback is that they do not provide an absolute barrier to gases and vapours and that they might interact with the packed food.

2.1. Polyolefines

The most widely used polymers for food packaging applications are polyolefins. Many kinds of plastic films are used in food plastic packaging applications, particularly in flexible pouches or box-type containers for beverages (Shorten, 1982). In such containers, polyolefine films, i.e. PE or PP, are used as an interior lining because of their characteristic heat sealability properties.

2.1.1 Polyethylene (or polyethene, PE)

The molecular formula of PE is (CH$_2$)$_n$ and, although the chains in the macromolecule are referred to as linear, the carbon atoms in the chain are lined in a zig-zag fashion. The carbon atoms are linked by strong covalent bonds at a distance of 1.54 Å and at an angle of 109°. In addition, neighbouring chains are stabilised by much weaker van der Waals' forces.

The presence of branched chains prevents close packing of the polymer chains so that the density of the finished product is low. The degree of crystallinity has a major effect on some of the polymer properties.

The irregularity introduced by the presence of many branched chains also lowers the overall degree of crystallinity and the softening point, since less energy in the form of heat is required to break the secondary bonding forces between the chains which are less closely and regularly packed. Crystalline regions of the polymer consist of parallel chains of linked monomers, while amorphous regions are randomly oriented chains irregular in configuration.
There are many hundred grades of PE available, most of which differ in their properties in one way or another. Such differences arise from the following variables (Brydson, 1982):

* Variation in the degree of short and long chain branching in the polymer.
* Variation in the average molecular weight.
* Variation in the molecular weight distribution (MWD).
* The presence of small amounts of comonomer residues.
* The presence of impurities or polymerization residues.

There are, however, four main versions of polyethylene available, which differ in structure and properties, as well as in the manufacturing process, Figure 3.

1) high-density polyethylene (HDPE), 2) low-density polyethylene (LDPE), 3) medium-density polyethylene (MDPE), and 4) linear-low-density polyethylene (LLDPE).

![Diagram of HDPE, LDPE, and LLDPE structures](image)

**Figure 3.** Structure of three of the main polyethylene versions. (Miltz, 1992).

2.1.1.1. Low density polyethylene (LDPE)

This variety accounts for the largest proportion of packaging plastics. Relatively inert chemically, its permeability is moderately low for water vapour, but high for oxygen. In general, the gas permeability is high, with poor odour barrier characteristics. LDPE can be laminated, extrusion coated, or, in some cases, coextruded.
The main attractive features of PE, in addition to its low price, are good processability, toughness, flexibility, relatively few additives and, in thin films of certain grades, transparency.

LDPE has good heat sealability and is easily coated onto other materials such as paper and aluminium.

There are no strong intermolecular forces, and most of the strength of the polymer is due to the fact that crystallization allows close chain packing. Because it is a crystalline material and does not enter into specific interactions with any liquids, there are no solvents for it at room temperature. At elevated temperatures the thermodynamics are more favourable to solution, and the polymer dissolves in a number of hydrocarbons with similar solubility parameters.

2.1.1.2 High Density Polyethylene (HDPE)

Compared to LDPE, HDPE is stiffer, harder, less transparent, and has a less waxy feel. It has better resistance to oils and greases, a higher softening point but lower impact strength and permeability to water vapour.

2.1.2 Ionomers

Ionomers are defined as linear organic polymers that are copolymerized with a minor portion of an acid function, which is neutralized to varying degrees by a metal or quarternary ammonium ion, Figure 4.

![Planar representation of ionic domains in an ionomer.](image-url)
The ionizable carboxylic groups of the ionomer create ionic cross-links between chains at ambient temperatures. They are flexible, tough, transparent, and of excellent heat sealability. One of the trade names of ionomers is Surlyn.

2.1.3 Polypropylene (PP)

Polypropylene is the next member in the series of polyolefines with the structural formula shown below:

\[
\begin{align*}
  &\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
  &\text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} -
\end{align*}
\]

Generally, polymerization of such a molecule will produce an irregular macromolecule with the \(\text{CH}_3\)-groups randomly distributed on either side of the main chain as shown below:

\[
\begin{align*}
  &\text{H} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \quad \text{H} \\
  &\text{I} \quad \text{I} 
\end{align*}
\]

This structure is known as the atactic form.

It is also possible to prepare an isotactic form of polypropylene in which the \(\text{CH}_3\)-groups are largely arranged on the same side of the polymer chain:

\[
\begin{align*}
  &\text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \\
  &\text{I} \quad \text{I} 
\end{align*}
\]
The regular arrangement of the methyl groups produces a polymer with a higher crystallinity. In the isotactic form the carbon atoms are arranged in a helical chain with all the methyl groups projecting on the outside of the helix.

This polymer is harder and has a higher softening point than HDPE and greater resilience. It has a permeability intermediate between LDPE and HDPE. Further use of this polymer arises in the form of biaxially oriented films. These films are stretched in two directions at right angles under suitable temperature conditions. The resulting film has improved clarity, impact strength and barrier properties to water vapour and oxygen. Commercially available polypropylenes have a density of 0.90 to 0.91 g/cm³, one of the lowest among polymers.

2.2. Polyvinyl Chloride (PVC)

A number of plastics are available in which one hydrogen atom of ethylene has been substituted by a halogen or other group. These constitute the vinyl plastics. Vinyl chloride monomer has the following structural formula:

```
  H   H
 /    /
 C - C
 /    /
 H   Cl
```

The polymer exists in the atactic form and, therefore, has a low crystallinity. The substitution of chlorine atoms into the polymer chain increases the polarity of the molecule and the formation of stronger interchain forces.

It is hard, stiff and clear, with excellent moisture resistance and low gas permeability. Incorporation of plasticisers softens the resulting film and makes it more flexible but lowers its tensile strength, to a degree depending on the amount of plasticiser added. PVC is widely used in the biaxially oriented form and offers good resistance to oils and fats.
2.3. Polyvinylidene Chloride (PVDC)

The monomer contains an additional chlorine atom substituted into the ethylene molecule:

\[
\begin{align*}
&H & Cl \\
&C & - & C \\
&H & Cl
\end{align*}
\]

The polymer is hard with a high degree of crystallinity. It is insoluble in most solvents and has a very low water absorption. It produces a clear film with very low permeability to vapours and good strength properties. Saran is a common trade name for PVDC.

2.4. Ethylene vinyl alcohol (EvOH)

Ethylene-vinyl alcohol (EvOH) films are commonly used as plastic packaging material because of their high gas barrier properties.

There are two polymers used in the majority of high barrier food packages, namely PVDC (Saran) and EvOH (Alger et al., 1990). Packages where either PVDC or EvOH provides the barrier are invariably multilayered, since neither of these polymers offers the properties required to make a good monolayer structure.

EvOH - trade name EVAL - is an excellent gas barrier and commercially available in several grades with different ratios of ethylene/vinyl alcohol in the chain (Tsai and Wachtel, 1990). The major limitation of EvOH is that, at elevated humidity, its barrier effectiveness is severely reduced because of disruption of the polymer-polymer hydrogen bonds. Also, because of the hydroxyl groups in the polymer backbone, water tends to be extremely soluble in EvOH.

The polarity of EvOH may be changed by varying the ethylene content. Figure 5.
\[ \text{Ethylene units} \quad \text{Vinyl alcohol units} \]

**Figure 5.** The structural formula of ethylene vinyl alcohol (EvOH).

Retortable food packages using EvOH as the oxygen barrier are multilayer structures which are formed by coextrusion. A representative five-layer structure is shown in **Figure 6**.

Retortable food packages are steam retorted typically from 105° to 132°C to sterilize the content (Alger et al., 1990). The retort operation greatly stresses the package and subjects it to high water activity. Since EvOH has a very high water affinity, it has been found that a significant quantity of water can be absorbed during the retort process. Also, the generally excellent oxygen barrier effectiveness of EvOH is seriously reduced at high humidity. **Figure 7**.

**Figure 6.** Five-layer structure with PP/tie/EvOH/tie/PC. (Alger et al., 1990).
Figure 7. Effect of relative humidity on oxygen permeability of EvOH and nylons. (Miltz, 1992)

Therefore, immediately following retort, the wet EvOH offers a reduced resistance to oxygen permeation. As the EvOH dries, the barrier properties substantially recover, but a significant amount of oxygen can pass through the package wall during the drying-out stage.

2.5. Polystyrene (PS)

Styrene consists of an ethylene molecule in which one of the hydrogens has been substituted by a phenyl group:

\[
\text{--CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 -
\]

Polymerisation of styrene produces the atactic form, and the bulky nature of the phenyl group prevents close packing of the macromolecular chains. Hence, it is amorphous. The polymer is transparent and possesses good barrier properties to gases, except water vapour. It is brittle, but this may be overcome by copolymerisation with butadiene and or acrylonitrile (ABS, respectively SAN).
Another way of modifying PS is making a blend of polystyrene and rubbery materials, i.e. polystyrene SBR blend. This high impact polystyrene (HIPS) has a higher impact strength than ordinary polystyrene but a lower tensile strength, lower hardness and a lower softening point.

2.6. Polyamides (Nylons)

These comprise a series of polymers prepared by the condensation of a diacid and a diamine, Figure 8. An example of this is the reaction between adipic acid and hexamethylene diamine, giving nylon 6,6.

\[
\begin{align*}
2nH_2N\text{-}CH_2\text{-}R\text{-}CH_2\text{-}NH_2 + nHOOC\text{-}R_1\text{-}COOH & \rightarrow \\
H & \quad H\text{O} \quad O \\
H\text{(-N-CH}_2\text{-R-CH}_2\text{-N-C-R}_1\text{-C)}\text{OH} + 2(n - 1)H_2O
\end{align*}
\]

Figure 8. The reaction of a diacid and a diamine giving a polyamide.

Other forms of nylon exist and are distinguished by a figure denoting the number of carbon atoms in each molecule of amine and acid used for synthesis. Some polymers are obtained from the self-condensation of one aminoacid, e.g. nylon 6 prepared from amino caproic acid, Figure 9.

\[
\begin{align*}
nH_2N\text{-}R\text{-}COOH & \rightarrow \\
H\text{(-N(-R-C-NH)}\text{H} + nH_2O
\end{align*}
\]

Figure 9. Self-condensation of an aminoacid giving a polyamide.

The amido groupe \((-\text{NH.CO-})\) is strongly polar and promotes strong hydrogen bonding between CO and NH groups on adjacent polymer chains.
Hence, the nylons are strong, though highly crystalline, materials with high melting and softening points and low gas permeability.

They absorb moisture depending on the relative portions of hydrocarbons and amido groups in the polymer chain.

2.7. Polyesters

Polyester resins are encountered in many forms. The most widely used polyester is polyethylene terephthalate (PET) with the following molecular formula:

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

PET has good mechanical properties, excellent transparency, and relatively low permeability to gases.

Biaxially oriented PET is often used in the production of bottles for carbonated beverages. Laminates with PET as one of the components are also very common as are sterilizable pouches and "boil-in-bag" applications.

2.8. Polycarbonates (PC)

Polycarbonates are linear polyesters of carbonic acid with aromatic or aliphatic dihydroxy compounds with the general formula:

\[
\left[ \text{R} - \text{O} - \text{C} - \text{O} \right]_n
\]

Most commercial polycarbonates are tough, stiff, hard and transparent. The disadvantages are high cost and the fact that they absorb moisture, with resulting deterioration of mechanical properties and processability. An additional disadvantage, for packaging, is their poor gas barrier quality.
2.9. Other constituents of plastics

All plastics contain, in addition to the basic polymer, a number of other substances to a higher or lower extent (Kim-Kang, 1990; Birley, 1982). These substances may be either added deliberately during manufacturing and processing (1) or unavoidably as residues from polymerisation reactions (2) (Brydson, 1982).

1) Processing aids such as antioxidants, antiblock agents, antistatic agents, heat and light stabilisers, plasticisers, lubricants and slip agents, pigments, fillers, mould release agents and fungicides.

2) Polymerisation residues including monomers, oligomers, catalysts, solvents emulsifiers, raw material impurities, plant contaminants, inhibitors, decomposition and side reaction products.

3. VARIABLES OF THE POLYMERS

3.1. Mechanical properties

The mechanical properties are very dependent on the molecular weight and on the degree of branching of the polymer. These properties are also dependent on the rate of testing, the test temperature, the method of specimen preparation, the size and shape of the specimen and, in some cases, the conditioning of samples before testing. The general effects of changing rate of testing, temperature and density on the tensile stress-strain curves are shown schematically in Figures 10-12.
Figure 10. Effect of strain rate on the stress-strain curve of a polymer. (Miltz, 1992)

Figure 11. Effect of temperature on the stress-strain curve of a polymer. (Miltz, 1992)
3.2. Thermal properties

The most important thermal properties of polymeric materials in the context of packaging are the glass transition temperature $T_g$, and the melting point $T_m$.

These properties may be represented by the modulus of elasticity, a typical curve of which is shown in Figure 13.

**Figure 12.** Stress-strain curves for different kinds of polymers. (Miltz, 1992)

**Figure 13.** Effect of temperature on modulus of elasticity of polymers. (Miltz, 1992)
The modulus of elasticity curve may be divided into four regions.

1. The first region represents an interval of low temperatures in which the polymer has a very high modulus. The polymer is very strong but also highly brittle, such as glass. This is called the glassy region.

2. In the second region, referred to as the leathery region, the polymer is still strong but also flexible. The modulus decreases very rapidly as temperature increases.

3. In the third region the polymer behaves like a rubber; this is denoted the rubbery region.

4. In the fourth region, called the flow region, the viscosity decreases rapidly and the polymer flows under stress. This region is absent in thermoplastics, which decompose at elevated temperatures.

The difference between amorphous and crystalline polymers is that the crystallites act as reinforcement and extend the glassy region to higher temperatures, the modulus in the rubbery state is higher, and the transition to the flow region is sharper, due to melting of the crystallites. The temperature where the crystallites in a semicrystalline polymer melt is called the melting point, $T_m$.

3.3. Molecular structures of the polymer

There are certain specific molecular structures which give good barrier properties to polymers (Salame and Steingisser, 1977).

1. Some polarity
2. Regularity of molecular structure
3. Close chain-to-chain packing in the solid state.

The regularity of the molecular structure, and the close chain-to-chain packing that it permits, provide a restricted pathway for permeants. These demands are actually the same as for the ability of a polymer to crystallize.
However, a structure that leads to a good gas barrier often results in a poor water vapour barrier.

The high content of hydroxyl groups in EvOH and PvOH permits interactions that retard permeation through the polymer when dry. However, when water enters the polymer, it preferentially interacts with the hydroxyl groups and thereby diminishing retardation of the permeants, and also swells the structure to increase interchain distances, and thus free volume (Halek, 1988).

Similar behaviour is observed for Nylon 6,6 with its amide groups. It is thus not restricted only to hydroxyl groups.

The interacting effect with water is not observed for PVDC, PAN or PET, which also have polar groups.

3.4. The rubbery and glassy state

The rubber-like region, which lies above $T_g$, appears when the rotation about segment links is free enough to enable the chains to assume any of the large number of equi-energetic conformations available.

In the rubber-like state the chains are in relatively rapid motion, but as the temperature is lowered the movement becomes progressively slower, until eventually the available energy is insufficient to overcome the rotational energy barrier in the chain.

At this temperature, which is known as the glass transition temperature $T_g$, the chains become locked in whichever conformation they possessed when $T_g$ was reached. Below $T_g$ the polymer is in the glassy state and is, in effect, a frozen liquid with a completely random structure.

Mainly three factors determine whether a polymer is glassy, rubbery or fibre-forming under a given set of conditions. These are the chain flexibility, the interchain interaction and the regularity of the polymer. This relationship has been expressed diagrammatically by Swallow (1951), Figure 14.
Figure 14. Effect of structure regularity, molecular stiffness and intermolecular attraction on polymer properties.
(Swallow, 1951)

3.5. Factors affecting the glass transition temperature $T_g$

The magnitude of $T_g$ varies over a wide temperature range for different polymers, Table 2. As $T_g$ depends largely on the amount of thermal energy required to keep the polymer chains moving, a number of factors which affect rotation about chain-links will also influence $T_g$.

There are a number of structural features which have an appreciable effect on the value of the glass transition temperature. Since $T_g$ is a temperature at which molecular rotation about single bonds becomes restricted, it is obvious that these structural features are those which influence the ease of rotation.

The factors which affect the glass transition temperature according to Bryden (1982) are:

1. Groups attached to the backbone of the polymer which increase the energy required for rotation.
2. Rigid structure, e.g. phenylene groups, incorporated in the backbone of the molecule.

3. The packaging of substituents around the main chain.

4. Secondary bonding between chains, e.g. hydrogen bonding.

5. Primary bonding between chains, e.g. cross-linking.


7. Molecular weight.

8. Copolymerisation


3.6. Factors affecting the ability to crystallise

The types of chains which might be expected to crystallise are those which have the following characteristics:

1. Symmetrical chains which allow the regular close packing required for crystallite formation.

2. Chains possessing groups which encourage strong intermolecular attraction, thereby stabilizing the alignment.
<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>Features of interest affecting Tg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(dimethyl siloxane)</td>
<td>-123</td>
<td>-85 to -65</td>
<td>Flexible backbone</td>
</tr>
<tr>
<td>cis-1,4-Polybutadiene</td>
<td>-107</td>
<td>4</td>
<td>Flexibility enhanced by occasional c=c bond</td>
</tr>
<tr>
<td>trans-1,4-Polybutadiene</td>
<td>-107</td>
<td>+145</td>
<td>cis-trans effect</td>
</tr>
<tr>
<td>cis-1,4-Polyisoprene</td>
<td>-73</td>
<td>+25</td>
<td>Stiffening effect of methyl group</td>
</tr>
<tr>
<td>trans-1,4 Polyisoprene</td>
<td>-53</td>
<td>+65</td>
<td>trans-isomer</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>-20</td>
<td>+120</td>
<td>Flexible backbone</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>+5</td>
<td>+150</td>
<td>Stiffening effect of methyl group</td>
</tr>
<tr>
<td>Polybut-1-ene</td>
<td>-20</td>
<td>+120</td>
<td>Plasticising effect of alkyl side chain</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>-73</td>
<td></td>
<td>Symmetry</td>
</tr>
<tr>
<td>Polypent-1-ene</td>
<td>+24</td>
<td>+70</td>
<td>Plasticising effect of alkyl side group</td>
</tr>
<tr>
<td>Poly(3-methyl-but-1-ene)</td>
<td>+60</td>
<td>+240</td>
<td>Branched side chain</td>
</tr>
<tr>
<td>Poly(4-methylpent-1-ene)</td>
<td>+53</td>
<td>+245</td>
<td>Branched side chain</td>
</tr>
<tr>
<td>Poly-n-heptylbutadiene</td>
<td>-83</td>
<td></td>
<td>Long side chain</td>
</tr>
<tr>
<td>Poly-n-decylbutadiene</td>
<td>-53</td>
<td></td>
<td>Interaction in long side chain</td>
</tr>
<tr>
<td>Polyoxyethylene</td>
<td>-30</td>
<td>+160</td>
<td>Flexible backbone</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>+115</td>
<td>+327</td>
<td>Stiff backbone</td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>+70</td>
<td></td>
<td>Polar interaction</td>
</tr>
<tr>
<td>Poly(vinyl acetate)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>+30</td>
<td></td>
<td>Weak polar interaction</td>
</tr>
<tr>
<td>Poly(vinylidene chloride)</td>
<td>+80</td>
<td>+190</td>
<td>Polar interaction</td>
</tr>
<tr>
<td>Polyacrylonitrile</td>
<td></td>
<td></td>
<td>Symmetry</td>
</tr>
<tr>
<td>Polystyrene (atactic)</td>
<td>+80-104</td>
<td></td>
<td>Polar interaction</td>
</tr>
<tr>
<td>Polystyrene (isotactic)</td>
<td>+90-100</td>
<td></td>
<td>Stiffening by benzene ring</td>
</tr>
<tr>
<td>Poly(ethylene adipate)</td>
<td>+100</td>
<td>+230</td>
<td>Regular structure</td>
</tr>
<tr>
<td>Polyethylene therephthalate</td>
<td>-70</td>
<td>+256</td>
<td>Flexible backbone</td>
</tr>
<tr>
<td>Polymethacrylates</td>
<td></td>
<td></td>
<td>Stiffening by phenylene group</td>
</tr>
<tr>
<td>Methyl (free radical)</td>
<td>+99</td>
<td>+160</td>
<td>Stiffening effect of methyl group</td>
</tr>
<tr>
<td>Methyl (isotactic)</td>
<td>+45</td>
<td>+200</td>
<td>Side-chain plasticisation</td>
</tr>
<tr>
<td>Methyl (syndiotactic)</td>
<td>+115</td>
<td></td>
<td>Branched side chain</td>
</tr>
<tr>
<td>Ethyl</td>
<td>+65</td>
<td></td>
<td>Side-chain plasticisation</td>
</tr>
<tr>
<td>Isopropyl</td>
<td>+81</td>
<td></td>
<td>Branched side-chain</td>
</tr>
<tr>
<td>n-Butyl</td>
<td>+20</td>
<td></td>
<td>Side-chain plasticisation</td>
</tr>
<tr>
<td>Isobutyl</td>
<td>+53</td>
<td></td>
<td>Branched side chain</td>
</tr>
<tr>
<td>Octyl</td>
<td>-20</td>
<td></td>
<td>Side-chain plasticisation</td>
</tr>
<tr>
<td>Polymethacrylates</td>
<td></td>
<td></td>
<td>Stiffening effect of methyl group</td>
</tr>
<tr>
<td>Methyl (free radical)</td>
<td>+99</td>
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</tr>
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<td>Methyl (isotactic)</td>
<td>+45</td>
<td>+200</td>
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</tr>
<tr>
<td>Methyl (syndiotactic)</td>
<td>+115</td>
<td></td>
<td>Branched side chain</td>
</tr>
<tr>
<td>Ethyl</td>
<td>+65</td>
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<tr>
<td>Isopropyl</td>
<td>+81</td>
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<td>Branched side-chain</td>
</tr>
<tr>
<td>n-Butyl</td>
<td>+20</td>
<td></td>
<td>Side-chain plasticisation</td>
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<tr>
<td>Isobutyl</td>
<td>+53</td>
<td></td>
<td>Branched side chain</td>
</tr>
<tr>
<td>Octyl</td>
<td>-20</td>
<td></td>
<td>Side-chain plasticisation</td>
</tr>
<tr>
<td>Polycarbonate of bis-phenol A</td>
<td>+149</td>
<td>+225</td>
<td>Stiffening by phenylene group</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>+50</td>
<td>+215</td>
<td>H-bonding</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>+60</td>
<td>+264</td>
<td>H-bonding</td>
</tr>
<tr>
<td>Poly(vinyl ethers)</td>
<td></td>
<td></td>
<td>Flexible backbone</td>
</tr>
<tr>
<td>Methyl</td>
<td>-31</td>
<td>+144</td>
<td>Side-chain plasticisation</td>
</tr>
<tr>
<td>Ethyl</td>
<td>-86</td>
<td>+86</td>
<td>Flexible backbone</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td>-55</td>
<td>+66</td>
<td>Flexible backbone</td>
</tr>
<tr>
<td>Poly(propylene oxide)</td>
<td>-62</td>
<td>+65</td>
<td>Flexible backbone</td>
</tr>
</tbody>
</table>
4. FOOD PACKAGING INTERACTIONS

As polymer packaging is becoming more widely used for direct contact with foods, product compatibility with the packaging material must be considered. The sorption of flavour compounds, or scalping, is one of the most important compatibility problems. The problem of aroma absorption by plastic packages has been recognized for many years. The tendency for absorption varies with polymer type. For example, polymers, such as polyolefins, can selectively sorb certain flavour constituents from products (Foster, 1987).

Early works focused on volatile absorption from sources external to the package (Gilbert and Pegg, 1969). Haydanek et al. (1970) and Gilbert et al. (1982) examined volatile uptake by various packaging polymers. Polyethylene (PE) and polypropylene (PP) are especially susceptible to pervasion by organic vapours. Because of their low cost, heat sealability and lack of additives, PE and PP have been widely used in contact with food in packages. The use of PE and PP in plastic packages has raised questions concerning sorption of intrinsic food flavours (Durr et al., 1981).

4.1. Flexible packaging materials

The aseptic packaging of juices in flexible cartons is a growing high value industry (Hirose et al., 1988). A typical aseptic carton laminate material from inside to outside is generally composed of PE/PE ionomer/aluminium foil/PE ionomer or other laminating layer/paperboard/PE.

The Brik-Pak, a commonly used package, consists of a six or seven-layer laminate pouch of polyolefins, paper, paperboard, and aluminium foil (Marin et al., 1992).

LDPE is the food contact surface of the most common brick-type aseptic package, and this material sorbs a wide variety of flavour compounds.

Another popular packaging system for juices and concentrates is the "bag-in-the-box". The structure of the bag is generally a laminate made of PE/metallized polyester/PE with an inner PE liner (Mannheim et al., 1988). The metallized polyester may be replaced by a non-metallized high barrier film.
Milk-based products, fruit juices and drinks are the major aseptic products on the market (LaBell, 1986; Swientek, 1984). Other food products being considered for aseptic packaging include tomato-based products, soups, wine and mineral water (Arora et al., 1991).

4.2. The influence of scalping on food quality

The quality of the juices packed in aseptic cartons has been the subject of intensive research over the past few years. Most juices that are filled aseptically are packed into laminated carton packages such as the Brik-Pak or combibloc, in which the food contact material is PE (Mannheim et al., 1987). Mannheim et al. found that the product shelf life of orange and grapefruit juices was significantly shorter in laminated cartons than in glass jars.

This difference is considered to depend on the following parameters:

1. Absorption of d-limonene by a PE contacting surface. A rapid loss of d-limonene from about 80 to 60 mg/L was observed in carton packs with juices during the first days of storage. Similar results were obtained by Durr et al. (1981) and Marshall et al. (1985).

2. Acceleration of ascorbic acid degradation and browning due to contact with the PE film. It has been reported that the PE contact surface accelerated the rate of degradation, with oxidized PE having a greater effect, Figure 15.

![Figure 15. Change in d-limonene content in model solutions with and without contact with polyethylene film. (Mannheim et al., 1997).](image-url)
3. Transmission of oxygen through the package.

A longer product shelf life can be predicted for commercial containers having a smaller surface to volume ratio than in smaller containers having a larger surface-to-volume ratio.


Fruit juices in general, and orange juice in particular, are extensively packed aseptically (Graumlich et al., 1986; Hansen and Arora, 1990).

Citrus flavour has often been used in model systems for flavour absorption studies (Ahmed et al., 1978; Durr and Schobinger, 1981; Marshall et al., 1985; Hirose et al., 1988; Kwapong and Hotchkiss, 1987; Moshonas and Shaw, 1989; Mottar, 1989). d-Limonene, the predominant volatile in citrus oils and essences, is often used as a probe compound in such studies.

Composititionally, limonene is a non-polar, unsaturated terpene hydrocarbon (Shaw, 1979).

As can be seen in Figure 16, many flavour compounds contain ester, alcohol, and other polar functional groups. Essential oils from citrus consist of terpenes, sesquiterpenes, oxygenated compounds, and non-volatile components.

The oxygenated compounds are important contributors to citrus flavours (Moshonas and Lund, 1969). Many research groups have reported that polar compounds are sorbed to a much lower extent in PE than limonene and other hydrocarbon volatiles.
\begin{center}
\begin{tabular}{|l|l|}
\hline
\textbf{Compound} & \textbf{Class} \\
\hline
1-Carvone & Ketone \\
\hline
Citral a+b & Aldehyde \\
\text{\begin{tabular}{l}
\text{(a = geranial)} \\
\text{(b = neral)}
\end{tabular}} & \\
\hline
Ethyl Butyrate & Ester \\
\hline
d-Limonene & Hydrocarbon \\
\hline
dl-Linalool & Alcohol \\
\hline
Myrcene & Hydrocarbon \\
\hline
\text{alpha-Pinene} & \text{Hydrocarbon} \\
\hline
\end{tabular}
\end{center}

\textbf{Figure 16.} Structures of aroma compounds found in citrus fruits.
(Halek and Meyers, 1989)

Understanding the differences in sorption of oil constituents in various polymeric materials could help processors to reduce flavour absorption problems.

The potential problem of flavour scalping into polymeric packaging materials has been studied by several research groups.

Ikegami \textit{et al.} (1987) and Shimoda \textit{et al.} (1988) have examined absorption of polar volatiles diluted in aqueous solutions by PE.

Shimoda \textit{et al.} (1984) reported loss of volatiles from mandarin orange juice kept in plastic pouches. They found that nonpolar constituents, such as limonene, are more readily absorbed by polyolefins than polar ones. Kwapong and Hotchkiss (1987) confirmed these results.
In his MS thesis Kwapong (1986) examined the absorption rates of limonene and other volatile components from pure standards and orange oil into plastic polymers.

Buchner (1985) also showed that there exists a sorption of aroma-bearing orange oil into the polyolefin layer of an aseptic package.

Several workers have reported that the shelf life of juices in carton packs is shorter (about half) than in glass packages and is usually not more than 3-4 months at ambient storage temperature (Mannheim and Havkin, 1981; Gherardi, 1982; Granzer, 1982).

4.3. The influence of pulp content on scalping

Gherardi (1982) and Granzer (1982) both investigated the quality changes of fruit juices in carton packs as compared with those in glass packages. Both found that juices deteriorated faster in carton packs than in glass bottles. In products with a low fruit content, the difference between the packages was small.

This is in accordance with the results of Shimoda et al. (1984) showing that in juice from satsuma mandarins limonene sorption by polymers is lower in the presence of juice pulp. Maeda et al. (1984) and Osajima et al. (1983) reported that a low pulp content in orange juice resulted in higher absorption of aroma compounds.

Yamada et al. (1992) reported that, with LDPE, the d-limonene retention of the sample juice (mandarin orange juice) was 50%, but that of a diluted citrus mix (97.5% ethanol solution of citrus mix diluted 1/1000 with dechlorinated water) was only 4%. This effect was attributed to the pulp content.

Fruit juice volatiles remain stable in the juice, while they are adsorbed by or suspended on the pulp. However, the amount of pulp, such as cellulose powder, which must be added if it is to be used to control the sorption of volatiles by LDPE is large. In such a case, the volatiles are adsorbed by the pulp itself.
4.4. **Methods of suppressing scalping**

Yamada *et al.* (1990) suggested methods of suppressing the sorption of volatiles by the contact layer.

1. Sorption of volatiles could be reduced considerably by reducing the thickness of the sealant layer. This could, however, cause the sorbed compounds to permeate the polyolefine layer and change the structure and properties of the barrier layer, or result in delamination of the laminate.

2. Sorption of volatiles could also be reduced by having a sealant adsorbing some fruit juice essence beforehand (i.e. presorption).

3. The sorption of volatiles can be reduced if the glass transition temperature is much higher than the storage temperature.

It is revealed that CPP absorbed volatiles to a lesser extent than LDPE during storage at 3°C. This difference is considered attributable to the difference in $T_g$ between the two materials. The glass transition temperature of LDPE is -120°C and that of CPP is -150°C. During storage at 3°C, CPP shows smaller micro-Brownian movements of molecular segments and is closer to the glass state than LDPE. This may be why CPP showed less sorption of volatiles. From this result it can be deduced that the sorption of volatiles can be reduced if the glass transition temperature is much higher than the storage temperature. Since there is no suitable material of high $T_g$ among polyolefin resins, Yamada *et al.* (1990) selected PET and PAN as packaging materials because of their heat-sealing property and usability as a sealant. The glass transition temperature of PET is 81°C and that of PAN 87°C. These materials showed no sorption at all. As regards sorption of organic compounds, Imai *et al.* (1990) found that co-PET would be better than LDPE and EvOH as a contact layer for orange juice, Figure 7.

Charara *et al.* (1992) found that sorption of apple aromas by co-PET and EvOH was significantly less than for LDPE. As regards sorption of volatiles from apple juice, EvOH and co-PET would be less sorptive than LDPE.
McLellan et al. (1987) showed that an oriented polyethylene terephthalate container provided a satisfactory shelf life as compared to glass packaged samples over a 6-9 months period. Difference and preference tests were used to establish the shelf life comparison.

![Graph showing sorption of d-limonene by LDPE, EVOH, and co-PET](image)

**Figure 17.** Sorption of d-limonene by LDPE, EVOH and co-PET. (Imai et al., 1990)

Sorption of hydrocarbons in amorphous nylon has been found to be less than 1/34 of the sorption into MDPE (Ikegami et al., 1991). In the same study, thermoplastic polyester was found to absorb esters more readily (1.7-9.1 times) than MDPE.

A few treatments of polymer surfaces and judicious selection of polymers, such as use of crystalline polymers (Shimoda et al., 1988) use of polymer blends (Subramanian, 1990), flourination of polymer surfaces (Hobbes et al., 1990), and inert coatings, i.e. silica, of the polymer surfaces (Charara, 1987) have been proposed in the literature to circumvent the scalping of flavour compounds from food products.
Baner et al. (1991) found that the food contact layer, usually polyethylene, largely controls the sorption behaviour. This means that any improvements in flexible materials regarding aroma sorption must come from new food contact layers and not from new barrier layers.

While studying differences between PE and PP, Ikekami et al. (1988) noted that, although PP had a greater sorption at equilibrium, it required a longer time to reach equilibrium than the PE because of its lower diffusion in the polymer.

Gherardi (1982) found high oxygen and low carbon dioxide contents in the headspace of carton packs versus low oxygen and high carbon dioxide content in glass bottles. The carbon dioxide was attributed to ascorbic acid degradation. Therefore, Gherardi (1982) concluded that the main cause of the differences in keeping quality between products in carton packs and glass bottles was the higher oxygen transfer into the former package. Granzer (1982) also claimed that the oxygen permeability into carton packages caused a faster deterioration of the juices packed in them.

4.5. Comparison of instrumental and sensory analysis

Mannheim et al. (1985) documented changes in aseptically packed citrus juices by sensory as well as chemical analysis. They related loss of orange juice flavour to the absorption of d-limonene into polyolefin packaging. However, in a comparison of the sensory quality of orange juice stored in polyethylene-lined paperboard cartons at different temperatures, Durr et al. (1981) reported temperature to be the main variable affecting flavour. In addition, they found that orange oil, expressed in terms of limonene, was absorbed by the polyolefin contact layer.

They proposed that limonene absorption was an advantage, since limonene was known to be a precursor to off-flavour compounds. They also reported that desirable aroma volatiles were practically unabsorbed.

Although it is well documented that certain orange juice constituents are absorbed by polymeric materials and that the absorption of flavour compounds changes the aroma profile (Mannheim et al., 1985), it is not clear that these changes are caused by absorption of odour-active orange juice constituents (Marin et al., 1992).
Most reported studies on flavour scalping in orange juice were performed with model solutions, not representing actual orange juice, or with orange juice which had not been commercially produced and packaged (Pieper et al., 1992). Many of the investigations were performed without sensory evaluation.

Pieper et al. (1991) showed that a sensory panel could not distinguish between orange juice stored in glass bottles and juice stored in laminated cardboard packages with LDPE as the food contact polymer, even though absorption of up to 50% of d-limonene and small amounts of aldehydes and alcohols by the packaging materials was seen.

Marin et al. (1992) exposed plastic packaging materials, i.e., PE and Surlyn, to orange juice and measured the changes in the limonene content of the juice using a gas chromatograph equipped with a flame ionization detector (GC-FID). They determined the components which were most important to the aroma using gas chromatography - olfactometry (GCO).

More than 70% of the limonene content was absorbed by the polymers in 24 hours at 25°C. However, results from the GCO analysis indicated that limonene had only trace odour activity. Furthermore, the plastic polymers did not substantially alter the odour-active components detected in orange juice.

These reports emphasize the importance of using actual food systems, when possible, and comparing instrumental analysis with organoleptic evaluation.

4.6. Influence of scalping on barrier and mechanical properties

As has been shown in the reports mentioned above, the scalping process may not alter the sensoric quality of the packed juice. However, absorption of flavour components by the package may alter the mechanical properties of the polymer, cause delamination, or alter the barrier properties of the package (Schroeder et al., 1990; Olafsson et al., 1993). Marshall et al. (1985) reported absorption of limonene from orange juice into polyolefins. They found that the loss of limonene into the contact layer was directly related to the thickness of the polyolefin layer and not to its oxygen permeability. They also quantified the absorption of several
terpenes and other flavourings from orange juice into LDPE. The predominant compounds absorbed were the terpenes and sesquiterpenes. More than 60% of the d-limonene in the juice was absorbed by LDPE, but only 45% was absorbed by Surlyn. Other terpenes, such as pinene and myrcene, were absorbed to even greater extents. Infrared spectra of LDPE showed that the terpenes were absorbed rather than adsorbed. Also, the presence of d-limonene in the polymer aided the absorption of other compounds, such as carotenoid pigments, thus reducing the colour of the juice.

Scanning Electron Microscope (SEM) pictures of a polymer after exposure to orange oil revealed significant swelling of the polymer, inferring severe localized internal stresses in the polymer (Marshall et al., 1985). These stresses indicated a possible cause of delamination problems occasionally encountered in LDPE-laminated board structures. The adhesion between LDPE and foil was much lower than between Surlyn and foil.

Absorption of limonene has been shown to have an effect on the mechanical properties of LDPE and two ionomers, i.e. Surlyn of sodium and zinc type, respectively (Miltz et al., 1990; Hirose et al., 1988). The plasticising effect of limonene, as represented by the strength of the sealants, is shown in Figure 1B. Miltz et al. (1990) also showed that the absorption of d-limonene increased the oxygen permeability of the three polymer films used.

Several approaches to the assessment of scalping have appeared in the literature. Most frequently, containers with a known quantity of essence in aqueous solution have been monitored for the loss of volatiles with time (Dürr and Schobinger, 1981; Ikegami et al., 1987; Shimoda et al., 1988).
4.7. Sorption of liquids and vapours in polymers

Sorption studies concerning the loss of volatiles from an aqueous medium have inherent limitations. They are influenced by container geometry, volatile diffusion properties, and degree of convection.

Many volatiles can not be accurately measured at naturally occurring concentrations, and solubility limits restrict addition levels for many compounds. The several weeks required for aqueous studies raise questions concerning the true pathway of loss, since decomposition and absorption may be difficult to discriminate. Moreover, tests which measure loss of volatiles from aqueous media provide limited information on their solubility or diffusion coefficient within the polymer. Also, adsorption cannot be distinguished from absorption (i.e. volatile incorporation into the polymer matrix) (Meyers, 1987).

Direct measurement of organic vapour sorption by the polymer would circumvent many of the problems associated with liquid-phase absorption tests. Compared with the aqueous sorption approach, vapour sorption studies are more amenable to mathematical evaluation. They can also indicate the true mechanism of sorption (e.g. ad- or ab-sorption). However, studies of aroma vapour sorption are not a realistic process for the simulation of food scalping in many cases.
Whether volatiles are adsorbed or absorbed by a polymer, loss of flavour would be expected. The limits of adsorption loss are defined by volatile partitioning between food and polymer surfaces. Absorptive loss of volatiles is more invasive and may result in volatile loss to the external environment, delamination, and barrier compromise.

4.8. Oxygen permeability

The oxygen permeability is the determining factor for the shelf-life of some foods. There are some standard devices such as Dow Cells, Linde Cells and Mocon Oxtran units available for measurements of oxygen transmission rates through polymers. They all require gas environments on both sides of the test material, i.e. an atypical arrangement for containers holding liquids. Sadler and Nelson (1988) developed a method for measurements of oxygen transport from a gaseous environment into liquids and a technique to calculate the oxygen solubility in aqueous media from permeation data.

4.8.1. Oxygen electrode method

Sadler and Braddock (1990) reported a method of determining limonene scalping by measuring oxygen permeability. Organic vapours often solvate host polymers. Plasticized membranes usually exhibit higher permeability to oxygen and other gases than nonplasticized membranes (Salame and Steingisser, 1977). This suggests that oxygen permeability might provide information on volatile scalping. Increased oxygen permeation would reflect absorption of volatiles. Desorption of volatiles would reduce oxygen permeation.

In their study Sadler and Braddock (1990) used sheets of LDPE positioned on an oxygen electrode (OE) (YSI 5331, Yellow Springs, OH) instead of the manufacturer's membrane. The probe of the OE was placed in a 125 ml flask which contained a mixture of air and saturated limonene vapour.

The absorption-induced increase in oxygen permeation was monitored with time. When stable readings indicated maximum sorption, the probe was withdrawn and placed in an air stream. The air stream forced desorption of limonene from the probe membrane, and a decreased oxygen permeability was monitored, Figure 19.
4.8.2 Weight method

For comparison, absorption was also measured by the more traditional weight method (WM). Tared LDPE sheets were stored in limonene vapour. After one week samples were re-weighed. The sheets were immediately attached to a vertical shaft and rotated to desorb the limonene from the sheets. Samples were re-weighed at 15 min intervals. Crank’s equation for membrane sorption and desorption was used to determine the diffusion coefficient of limonene in LDPE:

Sadler and Braddock (1990) showed that $M_t / M = P_t / P$, where $M_t$ and $P_t$, respectively, are the absorbed volatile weight of and oxygen permeation rate through the polymer at time $t$, and $M$ and $P$ are the corresponding weight of volatile absorbed and rate of oxygen permeation through the polymer at $t = \infty$, i.e., oxygen permeability is directly proportional to penetrant concentration.

The OE method permits distinction between absorption and adsorption. Increased oxygen permeability of the membrane could only be explained by polymer solvation, i.e., absorption. According to Sadler and Braddock (1991) attachment of volatile molecules at the polymer surface could hinder oxygen permeation, that is, adsorption would lower the oxygen permeation, or at best leave it unchanged.
4.9. Influence of polymer morphology on scalping

An understanding of the interactions between food ingredients and polymeric packaging materials requires knowledge of the chemical and physical structures of both the food ingredients and the polymers (Halek, 1988).

It is well established that sorption of flavour compounds does occur, but little data have been reported on the effect of structure and polarity of the sorbants and of polymers on the sorption process, and even fewer interpretative explanations of these behaviours have been published.

Often, flavour compounds are sorbed to a lesser extent in low density polymer films than in the same type of film with a higher density (Letinksii and Halek, 1992; Charara et al., 1992; Ikegami et al., 1987, 1988; Shimoda et al., 1988).

Density values can be converted to the degree of crystallinity in the polymer from the following relationship (Runt, 1986):

\[
W_c = \frac{1/D - 1/D_a}{1/D_c - 1/D_a}
\]

\(W_c\) is the weight-fraction degree of crystallinity; \(D\), \(D_a\), and \(D_c\) are the total, completely amorphous and completely crystalline densities of the polymer, respectively. Values of \(D_a\) and \(D_c\) can be obtained from the Encyclopedia of Polymer Science and Engineering (Vol. 4, p. 487).

The degree of crystallinity may also be determined by differential scanning calorimetry (DSC).

The crystalline areas are thought to be impermeable to permeants. The diffusion of permeants through a polymer occurs solely in the amorphous regions of the polymer. Since the polymer chains in these regions are not held in a fixed arrangement, as they are in the crystalline areas, small vibrational movements occur along the polymer chains. These micro Brownian motions can result in "hole" formation as parts of the polymer chains move away from each other. It is through such "holes" that permeant molecules can diffuse through the polymer.
Polymer crystallinity can affect sorption in several ways (Rogers, 1985). Crystalline regions can act as excluded volumes and reduce sorption, or as impermeable barriers for diffusion through the polymer. In addition, they can act as crosslinks to prevent swelling of the polymer. These crystalline regions can also restrain polymer segmental mobility, thereby affecting the size available for solute penetration of the amorphous region.

Charara et al. (1992) studied the sorption of citrus flavour compounds into four different packaging materials. They also measured the volume and crystallinity changes of the polymers as a result of their contact with citrus oil. The crystallinity was determined using a differential scanning calorimeter (DSC). The polymers were tested before and after exposure to juice with both cold-pressed orange oil and orange oil without terpenes.

The crystallinity was calculated as follows (Collins et al., 1973):

\[
\% \text{ crystallinity} = \frac{\text{dH (J/G)}}{\text{dH of 100% crystalline polymer}} \times 100.
\]

The DSC indicated that only loosely packed crystals were affected by orange oil, while the more ordered crystals were not, unless the polymers were placed in pure orange oil. Cold-pressed oil and oil without terpenes in the orange juice samples slightly lowered the percentage crystallinity and melting point of the polymers. Table 3.

Swelling factors show that highly crystalline polymers (HDPE and PP) swell less than lower crystalline polymeric materials (LDPE).

Scanning electron micrograph of LDPE beads before and after absorption of cold-pressed oil demonstrated that physical changes occurred at the surface during absorption, Figure 20.
Table 3. Melting point and percent crystallinity of four polymers. (Charara et al., 1992)

<table>
<thead>
<tr>
<th>Polymer (treatment)</th>
<th>Melting point</th>
<th>% crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>107.4</td>
<td>21.8 ± 0.1</td>
</tr>
<tr>
<td>LDPE (O.J. + terpeneless)</td>
<td>105.6</td>
<td>21.2 ± 0.1</td>
</tr>
<tr>
<td>LDPE (O.J. + cold-pressed)</td>
<td>104.7</td>
<td>22.7 ± 0.1</td>
</tr>
<tr>
<td>LDPE (pure oil)</td>
<td>103.8</td>
<td>19.6 ± 0.1</td>
</tr>
<tr>
<td>HDPE</td>
<td>136.2</td>
<td>43.8 ± 1.0</td>
</tr>
<tr>
<td>HDPE (O.J. + terpeneless)</td>
<td>135.2</td>
<td>40.1 ± 2.0</td>
</tr>
<tr>
<td>HDPE (O.J. + cold-pressed)</td>
<td>136.0</td>
<td>40.1 ± 2.0</td>
</tr>
<tr>
<td>HDPE (pure oil)</td>
<td>129.8</td>
<td>38.1 ± 0.5</td>
</tr>
<tr>
<td>PP</td>
<td>165.6</td>
<td>39.2 ± 0.5</td>
</tr>
<tr>
<td>PP (O.J. + terpeneless)</td>
<td>154.9</td>
<td>37.6 ± 0.1</td>
</tr>
<tr>
<td>PP (O.J. + cold-pressed)</td>
<td>155.1</td>
<td>37.0 ± 0.1</td>
</tr>
<tr>
<td>PP (pure oil)</td>
<td>162.7</td>
<td>36.2 ± 1.0</td>
</tr>
<tr>
<td>S</td>
<td>100.0</td>
<td>14.0 ± 1.0</td>
</tr>
<tr>
<td>S (O.J. + terpeneless)</td>
<td>100.0</td>
<td>13.9 ± 0.1</td>
</tr>
<tr>
<td>S (O.J. + cold-pressed)</td>
<td>97.0</td>
<td>13.9 ± 0.1</td>
</tr>
<tr>
<td>S (pure oil)</td>
<td>90.0</td>
<td>13.8 ± 0.1</td>
</tr>
</tbody>
</table>

* Average of duplicates ± standard deviation, repeated twice.

Figure 20. Scanning electron micrograph of LDPE beads before (I) and after (II) soaking in cold-pressed oil. (Charara et al., 1992.)
The barrier properties of polymers are altered by the chemical environment which they are exposed to.

Eftring and Nielsen (1991) used olive oil and acetic acid as food simulants to study the effect of fatty foods and acidic foods, respectively. They measured the change in oxygen permeability between the virginial polymer films and the polymer films that had been in contact with the food simulants. From their result, it could be seen that in some cases sorption of olive oil or acetic acid could alter the barrier characteristics of the polymer.

Comparing different polymeric sealant films has shown that polyolefins usually sorb the various aroma compounds to the highest extent. Polymer films made of polyester (PET) or polyamides (PA) usually sorb aroma compounds to a very low extent.

Polyolefins and EvOH also sorb aromas much faster than other polymers.

Several authors have reported that sorption into polyolefins occurs within hours and reaches equilibrium after a few days. Durr et al. (1981) reported that 40% of the limonene content in orange juice was sorbed in a PE lining within 6 days. Osajima (1983) and Marshall et al. (1985) both reported 60% absorption of terpene hydrocarbons into PE films.

Baner et al. (1991) studied sorption into four different flexible packaging materials with barrier layers of aluminium foil, PVDC (Saran), metallized polyester (MPET) and EvOH. They found that the inner polyolefine layer determined the aroma sorption behaviour.

The solubility coefficients make a large contribution to the permeability. Leufvén and Stöllman (1992) showed that the solubility plays a more important role than the diffusion as regards the overall permeability of aldehydes in a variety of polymer films.

Hauser et al. (1989) showed that the sorption process of alcohols and water in polyvinylalcohol (PvOH) and polyetherimide (PEI) is faster at higher temperatures. However, the total amount absorbed, in the range investigated, was practically independent of temperature.
4.10 Influence of penetrant molecular size on permeability, diffusion and solubility in polymers

Several reports have stated that the sorption of low molecular compounds is greatly influenced by the functional groups of the compounds (Ikegami et al., 1988; Shimoda et al., 1987).

In PE the distribution ratios generally increase as follows:

alcohols < aldehydes < esters < terpene hydrocarbons

In homologous series of esters and aldehydes, the distribution ratios increase threefold for each additional methylene group in the carbon chain (Ikegami et al., 1988). However, for the compounds composed of ten or more carbon atoms, the increments in distribution ratios were less or negative, Figure 21.

![Figure 21](image)

**Figure 21** Distribution of homologous series of ethyl alkanoates and alkanals in different polypropylene films at 20°C. (Ikegami et al., 1988)

The diffusion coefficient decreases modestly as the size of the permeating esters increases in LDPE, EvOH and co-VDC films (Strandburg et al., 1990).

The solubility coefficient undergoes a greater change with increasing ester size.
The permeability thus increases with increasing ester size. Consequently, the amount of flavour lost to the packaging depends on both diffusion and solubility.

Arora et al. (1991) also found a higher degree of sorption into LDPE films as the carbon number in the flavour compounds, i.e. aldehydes, methyl ketones, and methyl esters, increased, Figure 22. They also found that straight chain aldehydes and methyl esters were sorbed to a greater extent than branched chain methyl ketones in LDPE films.

Besides chain length, unsaturation of aldehydes has been shown to affect the degree of sorption into LDPE. Aldehydes which had a double bond, perillaldehyde and geranial, were absorbed in PE to a much lesser extent than saturated aldehydes (Charara et al., 1992).

![Figure 22. Distribution ratios for the sorption of aldehydes, methyl ketones and methyl esters by low density polyethylene as a function of carbon number. (Arora et al., 1991)](image)

4.11. Plastization of polymer films

The molecular configuration of a polymer is altered through solvation of organic penetrants (Takeuchi and Okamura, 1976). Plasticized membranes normally exhibit increased permeability to gases (Salame and Steingisser, 1977). Sadler and Braddock (1990) showed that the oxygen permeability of LDPE was proportional to the mass of absorbed limonene.
Usually a mixture of compounds will be absorbed in a polymer to a different extent compared to when they are alone (Lettinski and Halek, 1992; DeLassus et al., 1988; Kwapong and Hatchkiss, 1987; Nielsen et al., 1992). This difference is due to interactions either by competition of the species for space on the surface and in the polymer or plasticization.

Also, interactions may occur between the flavour compounds, thereby altering partitioning behaviour (Kwapong and Hatchkiss, 1987).

Ethyl butyrate and hexyl acetate have been shown to be sorbed in PE twice as much when alone in an aqueous solution compared to when ten different aroma compounds were present (Nielsson et al., 1992). As a result of this antagonistic effect, the amounts of a substance that will be lost from a real foodstuff will be lower compared to a model solution with only one or a few different probe compounds present.

However, with a headspace method no significant interactions between aroma vapours and different aseptic packaging materials were observed by studying partition coefficients (Baner et al., 1991).

The permeation behaviour of gas mixtures through non-porous polymeric membranes has attracted much attention. If component gases exhibit very low solubilities in the polymer, each gas permeates independently through the polymer. Thus, permeation characteristics of the gas mixture are predicted from the permeation data of pure gases.

The absorption or organic vapours can result in polymer swelling and thus change the configuration of polymer chains. These configurational changes are not instantaneous but are controlled by the retardation times of the polymer chains. If these times are long, stresses may be set up, which relax slowly. As a result, in permeation of more soluble gases and vapours, the permeation of one component affects the permeation of another component, i.e. the plasticizing effect within the polymeric membrane becomes apparent. The absorption and diffusion of the components can be accompanied by concentration as well as time-dependent processes within the polymer, which are slower than the micro-Brownian motion of polymer chain segments which promote diffusion (Meares, 1965).
The degree of plastization of a glassy polymer caused by sorption may be expressed as the depression of the glass transition temperature, which can be directly measured by DSC determinations of $T_g$ on polymer samples containing known concentrations of penetrant (Berenst, 1990).

The depression of $T_g$ can also be calculated through a theoretical expression derived by Chow on the basis of thermodynamics (Chow, 1980).

Chow's treatment, as well as empirical results, shows that the plasticizing efficiency increases with the decreasing molecular weight and size of the penetrant.

Several authors have reported that the amounts of transferred aroma compounds are related to feed concentration (Potey et al., 1992; Mohney et al., 1988; Charara et al., 1992; Matsui et al., 1989; Sadler and Braddock, 1991).

At relatively low permeant concentrations, mass transport follows a Fickian-type behaviour. At higher permeant concentrations, the polymer structure is swollen and the mass transport becomes concentration-dependent and is therefore not well represented by the theoretic equations that apply only for a constant diffusion coefficient (Koszynowski, 1986; Mohney et al., 1988).

As can be seen in Figure 23, the permeability coefficient is exponentially concentration-dependent for the diffusion of d-limonene in both the laminate structures used. Other authors have reported the same type of behaviour in other polymer/permeant combinations (Baner et al., 1986; Hernandez et al., 1986; Zobel, 1982, 1985; Potey et al., 1992).

Below a d-limonene vapour concentration of 5 ppm (w/v) a linear relationship obeying Henry's law was observed.

Nielsen et al. (1992) showed that the partition coefficients between LLDPE and ten aroma compounds in an aqueous solution showed no significant difference in the concentration range 0.1 - 10 ppm.
Matsui et al. (1989) studied the permeation of volatile compounds from aqueous solutions through PE films. They reported that both the diffusion and permeability increased with increasing concentration of the volatile compounds, while the solubility (i.e., distribution coefficient) was unchanged.

**Figure 23.** Transmission rate profile curves for d-limonene through HDPE as a function of vapour concentration (23°C). (Mohney et al., 1988)

4.12. **Effect of moisture on barrier properties**

For some polymers, exposure to moisture has a strong influence on their barrier properties (Chao and Rizvi, 1988; Taoukis et al., 1988). **Figure 24** shows the effect of relative humidity on oxygen permeability for some common barrier polymers.
Figure 24. The effect of humidity on $O_2$ permeability (24 h at 1 atm) of some polymers, MXD-6 = polymetaxylyenediamine. (Perdikoulias and Wybenga, 1989).

The temperature also affects the oxygen permeability rate, as shown in Figure 25 (Perdikoulias and Wybenga, 1989).
Figure 25. The effect of temperature on $O_2$ permeability of some polymers, MXD-6 = polymetaxylylenediamine. (Perdikoulias and Wybenga, 1989).

The water vapour permeability constants of LDPE, PET and a laminate of both films were determined at three different temperatures and from 55 to 90% relative humidities by Samaniego-Esguerra and Robertson (1991). The relationship between permeability and temperature followed the Arrhenious model and, further, the relative humidity influenced the permeability of the films.

The presence of water vapour often accelerates the diffusion of gases and vapours in polymers with an affinity for water. Long and Thomson (1953) observed that the sorption rates for acetone in PVAc and cellulose acetate were greatly accelerated in the presence of water vapour, but this was not the case for sorption of benzene in PS.
Similar effects were observed with other small molecules, such as methanol, provided they could be sorbed to appreciable amounts in the polymers. It was concluded that the water diffused rapidly into the film and acted as a plasticizer. However, the water molecule itself had no special plasticizing effect, as shown by the fact that approximately equal amounts of water and acetone led to the same increase in the diffusion coefficient of the organic vapour.

Plasticized resins are several orders of magnitude more permeable than the nonplasticized resins. Even so, for most of the plasticized polymers, the ratio of $O_2$ to $CO_2$ permeability remains essentially constant, or shows some enhancement favouring $CO_2$. Whenever the presence of water results in a high degree of plasticization of the polymer, e.g., cellulosics or vinyl alcohol, the enhancement of $CO_2$ transfer should become intensified. This is because the $CO_2$ becomes more soluble in the water-swollen polymer than the $O_2$. This effectively lowers the sorption barrier of the water plasticised film to $CO_2$ and thereby increases its transfer rate. Laminating a hydrophobic film to the high moisture side of a hydrophilic film results in barriers with greater resistance to $CO_2$ transfer. This has been done in a number of commercially available laminated packaging films (Tock, 1983).

Theory predicts that the plasticizing effect of water on a hydrophilic film, such as EvOH or PVOH would increase the permeability by increasing the diffusivity because of the higher mobility acquired by the polymer network (Landois-Garza and Hotchkiss, 1988; Martin-Polo et al., 1992).

Results by Ito (1961) showed that this is actually the case for the permeation of $CO_2$ through PVOH.

DeLassus et al. (1988) showed that permeation of trans-2-hexenal through EvOH, both above and below $T_g$, also agreed with theory, in that permeability was increased at higher relative humidities. Above $T_g$ for EvOH the solubility remained constant when the humidity was increased, while below $T_g$ the solubility coefficient decreased. This implies some competition for sorption sites when the polymer is below $T_g$. 
Transport of various organic vapours through various multilayer films showed contradictory behaviour, i.e. for some of them permeability increased at higher relative humidities, while for others the opposite occurred (Hatzidimitriu et al., 1987).

An earlier study made by Pye et al. (1976) found that water vapour reduced the permeability of gases, i.e. methane and hydrogen, through amorphous polyamides.

In co-VDC film, Saran, no effect of humidity on the permeability of trans-2-hexenal was observed (DeLassus et al., 1988).

Landois-Garza and Hotchkiss (1988) showed that the permeability of ethyl propionate through PEOH decreased with increasing relative humidity. These results were explained by analysis of diffusion and solubility data. Diffusion coefficients remained constant and showed a slight downward trend only at high relative humidities. Solubility coefficients showed a clear trend towards lower solubilities at higher relative humidities. Thus, the decrease in permeability was mainly a result of the lowering of the solubility as relative humidity increased.

The decrease in solubility was explained by the same theory as DeLassus et al. used, i.e. a competition effect between the water molecules and the ethyl ester molecules.

Within the framework of dual-mode sorption theory, the water molecules may compete for the Langmuir sorption sites better than the permeate molecules in hydrophilic polymers. The presence of water molecules in the polymer matrix occupies "holes" that otherwise would be available for the diffusion of permeant molecules, effectively increases the length of the viable diffusion paths, and diminishes the permeant diffusivity (Landois-Garza and Hotchkiss, 1988). Furthermore, water molecules present throughout the polymer represent a lipophobic barrier to non-polar molecules. These effects were thought to counteract the relaxation of the polymer network brought about by the plasticization effect of water (Landois-Garza and Hotchkiss, 1988).
The basic of transmission of water vapour through a flexible film is governed by Fick's first law of diffusion combined with Henry's law for gas solution at low concentration (Gerlowski, 1990). Under steady-state conditions for water vapour, the rate of transport across a membrane becomes

$$\frac{dW}{dP} = \frac{(k) A (p_1 - p_2)}{x}$$

where $dP$ = amount of moisture passing through per unit of time, e.g., grams/day; $k$ = film permeability in (amount x thickness)/(unit area x time x driving force), usually grams-millimeter per square meter X day X mm Hg; $x$ = film thickness in appropriate units such as thousandths of a millimeter (or inch).

Using the units which are approved by ATSM gives the following units for the permeability coefficients and WVTR, respectively:

Permeability coefficient:

$$P \ (cm^3 \ STP/24 \ hrs) \ \frac{mil}{100 \ in^2 \ atm}$$

Water vapour transmission rate:

$$WVTR \ (g/24 \ hrs) \ \frac{mil}{100 \ in^2}$$

A table of conversion factors for many of the unit systems used internationally is given in Table 4.
Table 4. Conversion factors for units of permeability coefficients. (Tock, 1983).

\[
P = \frac{1.0 \text{ (cm}^3\text{g/mil)}}{(24 \text{ hrs})/100 \text{ in}^2/\text{atm}} = 6.00 \times 10^{-11} \frac{(\text{cm}^3/\text{cm})}{(\text{sec/cm}^2/\text{cm Hg})} = 4.56 \times 10^{-11} \frac{(\text{cm}^3/\text{cm})}{(\text{sec/cm}^2/\text{atm})} = 3.94 \times 10^{-11} \frac{(\text{cm}^3/\text{mm})}{(24 \text{ hrs)/(m}^2/\text{atm})} = 3.89 \times 10^{-11} \frac{(\text{cm}^3/\text{mm})}{(24 \text{ hrs}/(m}^2/\text{kPa})} = 3.89 \times 10^{-12} \frac{(\text{cm}^3/\text{mm})}{(24 \text{ hrs}/(m}^2/\text{kPa})} = 2.68 \times 10^{-17} \frac{\text{Nm}^2/\text{cm}}{(\text{sec/cm}^2/\text{cm Hg})}
\]

here M is the molecular weight of the permeating gas or vapor.

\[
\text{WVTR} = \frac{1.0 \text{ (g/mil)}}{(24 \text{ hrs})/100 \text{ in}^2} = 1.02 \times 10^{-3} \frac{1/\text{(cm}^3/\text{cm})}{\text{W/(sec/cm}^2)}
\]

here M is the molecular weight of the permeating vapor and P is the partial pressure gradient across the film.

VTR: for water vapor at

\[
100 \degree F = 1.15 \times 10^{-4} \frac{(\text{cm}^3/\text{cm})}{(\text{sec/cm}^2/\text{cm Hg})} = \frac{1.0 \text{ (g/mil)}}{(24 \text{ hrs})/100 \text{ in}^2}
\]

Table 5 gives the permeability and WVTR for a wide range of polymers, and Table 6 gives the short-hand notation used to represent different types of polymers. The values shown in Table 5 either represent the only available value or the averages from two or more sources. These average values are then followed by the range of the reported values (Tock, 1983).
### Table 5. Carbon dioxide, oxygen and water transfer rates for commercial polymer films.

(Tock, 1983)

<table>
<thead>
<tr>
<th>Film Classification</th>
<th>Permeability 25 °C (77 °F) (cm³/cm²mil)(24 hr)/(100 in²)/(atm)</th>
<th>Water Vapor Transmission (g/mil)/(24 hr)/(100 in²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASTM D-1600</td>
<td>35 °C (100 °F) 50−100% RH ASTM E-96</td>
</tr>
<tr>
<td></td>
<td><strong>O₂</strong></td>
<td><strong>CO₂</strong></td>
</tr>
<tr>
<td>ABS</td>
<td>60 = 10</td>
<td>175 = 25</td>
</tr>
<tr>
<td>Poly (Vinyl Alcohol)</td>
<td>0.3</td>
<td>0.3−900 (9000) (atm) (psig) (psi)</td>
</tr>
<tr>
<td>Cellulosic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CA</td>
<td>134 = 17</td>
<td>930 = 70</td>
</tr>
<tr>
<td>CTA</td>
<td>150</td>
<td>550</td>
</tr>
<tr>
<td>CAB</td>
<td>800 = 200</td>
<td>8000 = 2000</td>
</tr>
<tr>
<td>EC</td>
<td>2000</td>
<td>5000</td>
</tr>
<tr>
<td>C</td>
<td>0.65 = 0.15</td>
<td>3.2 = 3.8</td>
</tr>
<tr>
<td>C*</td>
<td>0.6</td>
<td>−</td>
</tr>
<tr>
<td>Fluoroplastics</td>
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<td></td>
</tr>
<tr>
<td>ECTFE</td>
<td>25</td>
<td>110</td>
</tr>
<tr>
<td>ETFE</td>
<td>100</td>
<td>250</td>
</tr>
<tr>
<td>FEP</td>
<td>750</td>
<td>1670</td>
</tr>
<tr>
<td>CTFE</td>
<td>11 = 4</td>
<td>23 = 12</td>
</tr>
<tr>
<td>PVF</td>
<td>3.3</td>
<td>11.1</td>
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<tr>
<td>PVDF</td>
<td>367</td>
<td>851</td>
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<tr>
<td>Polyamides</td>
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<tr>
<td>PA6</td>
<td>2.6</td>
<td>11 = 1.0</td>
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<tr>
<td>PA6*</td>
<td>1.3</td>
<td>−</td>
</tr>
<tr>
<td>PA11, PA12</td>
<td>63 = 29</td>
<td>245 = 92</td>
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<tr>
<td>PA*</td>
<td>0.5</td>
<td>1.4</td>
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<td>PA**</td>
<td>0.05</td>
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<td>Polyesters</td>
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<tr>
<td>PC</td>
<td>234</td>
<td>925 = 55</td>
</tr>
<tr>
<td>PET</td>
<td>4.5 ± 1.5</td>
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</tr>
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<td>PET*</td>
<td>0.4</td>
<td>−</td>
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<td>PET**</td>
<td>0.08</td>
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<tr>
<td>Polyolefins</td>
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<tr>
<td>LDPE</td>
<td>500</td>
<td>2700</td>
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<tr>
<td>LLDPE</td>
<td>545 ± 29</td>
<td>2748 ± 2230</td>
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<tr>
<td>MDPE</td>
<td>393 ± 145</td>
<td>1750 ± 750</td>
</tr>
<tr>
<td>HDPE</td>
<td>185</td>
<td>580</td>
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<tr>
<td>E-VAe Copolymer</td>
<td>380</td>
<td>6000</td>
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<tr>
<td>Ionomer</td>
<td>350 ± 20</td>
<td>800 ± 200</td>
</tr>
<tr>
<td>PP</td>
<td>250 ± 160</td>
<td>925 ± 425</td>
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<tr>
<td>pp**</td>
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<td>PP**</td>
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<tr>
<td>PS</td>
<td>330 ± 165</td>
<td>1160 ± 520</td>
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<tr>
<td>Chloroacrplastics</td>
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<td></td>
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<tr>
<td>PVC</td>
<td>17 ± 13</td>
<td>27 = 23</td>
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<tr>
<td>PVC*</td>
<td>450 ± 150</td>
<td>4500 ± 1500</td>
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<tr>
<td>PVDC</td>
<td>3.9 ± 3.0</td>
<td>24 ± 20</td>
</tr>
<tr>
<td>PVCA</td>
<td>17.5 ± 2.5</td>
<td>55 ± 15</td>
</tr>
<tr>
<td>PVCA*</td>
<td>85 ± 65</td>
<td>435 ± 165</td>
</tr>
<tr>
<td>Miscellaneous</td>
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<td></td>
</tr>
<tr>
<td>Nitriles</td>
<td>60 = 10</td>
<td>175 = 25</td>
</tr>
<tr>
<td>PI</td>
<td>25</td>
<td>45</td>
</tr>
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<td>PSUL</td>
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<td>PES</td>
<td>90</td>
<td>405</td>
</tr>
<tr>
<td>PB</td>
<td>385</td>
<td>825</td>
</tr>
</tbody>
</table>

**Superscript:**
- * = Saturated Coated;
- ** = Metalized Coated;
- o = Oriented (Biaxial);
- p = Plasticized Polymer
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Polymer Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>Acrylonitrile-Butadiene-Styrene</td>
</tr>
<tr>
<td>CA</td>
<td>Cellulose Acetate</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly (Vinyl Alcohol)</td>
</tr>
<tr>
<td>CTA</td>
<td>Cellulose Triacetate</td>
</tr>
<tr>
<td>CAB</td>
<td>Cellulose Acetate Butyrate</td>
</tr>
<tr>
<td>EC</td>
<td>Ethyl Cellulose</td>
</tr>
<tr>
<td>C</td>
<td>Cellophane (Regenerated Cellulose)</td>
</tr>
<tr>
<td>C*</td>
<td>Saran Coated Cellophane</td>
</tr>
<tr>
<td>E-CTFE</td>
<td>Ethylene-Chlorotrifluoroethylene Copolymer</td>
</tr>
<tr>
<td>ETFE</td>
<td>Ethylene-Tetrafluoroethylene Copolymer</td>
</tr>
<tr>
<td>FEP</td>
<td>Fluorinated Ethylene Propylene Copolymer</td>
</tr>
<tr>
<td>CTFE</td>
<td>Poly (Chlorotrifluoroethylene) Copolymer</td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly (Tetrafluoroethylene)</td>
</tr>
<tr>
<td>PA*</td>
<td>Poly (Vinylidene)</td>
</tr>
<tr>
<td>PVDF</td>
<td>Poly (Vinylidene Fluoride)</td>
</tr>
<tr>
<td>PA6</td>
<td>Nylon 6</td>
</tr>
<tr>
<td>PA6*</td>
<td>Nylon 6 (oriented)</td>
</tr>
<tr>
<td>PA11; PA12</td>
<td>Nylon 11 and 12</td>
</tr>
<tr>
<td>PA*</td>
<td>Saran Coated Nylon 6</td>
</tr>
<tr>
<td>PA**</td>
<td>Metallized-Coated Nylon 6</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>PET</td>
<td>Poly (Ethylene Terephthalate)</td>
</tr>
<tr>
<td>PET*</td>
<td>Saran Coated</td>
</tr>
<tr>
<td>PET**</td>
<td>Metallized Coated</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low-Density Polyethylene</td>
</tr>
<tr>
<td>LLDPE</td>
<td>Linear Low Density</td>
</tr>
<tr>
<td>MDPE</td>
<td>Medium Density</td>
</tr>
<tr>
<td>HDPE</td>
<td>High Density</td>
</tr>
<tr>
<td>E-VAc</td>
<td>Ethylene-Vinylacetate Copolymer</td>
</tr>
<tr>
<td>PP</td>
<td>Poly (Propylene)</td>
</tr>
<tr>
<td>PP*</td>
<td>Oriented Poly (Propylene)</td>
</tr>
<tr>
<td>PP**</td>
<td>Metallized Poly (Propylene)</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly (Vinyl Chloride)</td>
</tr>
<tr>
<td>PVC*</td>
<td>Plasticized PVC</td>
</tr>
<tr>
<td>PVDC</td>
<td>Poly (Vinylidene Chloride)</td>
</tr>
<tr>
<td>PVCA</td>
<td>Poly (Vinyl Chloride-Acetate) Copolymer</td>
</tr>
<tr>
<td>PVCA*</td>
<td>Plasticized PVCA</td>
</tr>
<tr>
<td>PI</td>
<td>Poly (Imide)</td>
</tr>
<tr>
<td>PSUL</td>
<td>Poly (Sulfone)</td>
</tr>
<tr>
<td>PES</td>
<td>Poly (Ether Sulfone)</td>
</tr>
<tr>
<td>PB</td>
<td>Poly (Butylene)</td>
</tr>
</tbody>
</table>

Superscripts:
* = Saran Coated  
** = Metallized Coated  
O = Oriented (Biaxial)  
p = Plasticized Polymer
The average range for a transmission value was plus or minus 38 per cent of that reported in Table 5. This appears to allow for a considerable degree of variation, which is typical of transmission in polymeric films. The fact that transmission values are complex functions of both solubility and diffusion, and at the same time dependent on the time-temperature history of the polymers, will account for much of the scatter in the data (Tock, 1983).

Liu et al. (1988) studied the effect of relative humidity on the diffusion of toluene vapour through a multi-layer film structure containing moisture-sensitive hydrophilic layers (nylon and EvOH). A scanning electron micrograph of the film is shown in Figure 26.

![Figure 26](image)

**Figure 26.** Scanning electron micrograph of coextrusion film: cross sectional view at approximately 2000x magnification. (Liu et al., 1988)
Two different methods were used. One method (method 1) evaluated the effect of relative humidity on the diffusion of toluene vapour through the film being preconditioned to the required relative humidity. The other method (method 2) evaluated the effect of water vapour as a co-permeant in the diffusion of toluene vapour through the film, i.e., both water vapour and toluene vapour permeated simultaneously.

A comparison of the permeability constants determined by the two methods, under similar conditions of relative humidity and toluene concentration, shows that P values obtained by method 1 are three to four orders of magnitude greater than those obtained by method 2.

In contrast to the extensive studies conducted on the permeability of gases, i.e., oxygen and carbon dioxide, water vapour and organic vapours through plastic materials, less has been done on the transport of a combination of these compounds.

4.13 Effect of temperature on barrier properties

The components of a barrier - the permeability, the diffusivity, and the solubility - are strongly dependent on temperature.

The permeability and the diffusivity are expected to be represented by straight lines both above and below the glass transition temperature, \( T_g \). However, these lines are expected to have different slopes. The magnitude of the slope above \( T_g \) should be greater than the slope below \( T_g \), meaning that extrapolation through \( T_g \) is not possible, Figure 27.
4.13.1 Vapours

Temperature has been reported to have a significant effect on the partitioning of aroma compounds (Baner et al., 1991).

In general, the higher the temperature, the smaller the partition coefficient, i.e. a decrease in the amount of a component sorbed by the material. This has been commonly observed for organic vapours in polymers as temperature increases (Rogers, 1964).

The effect of chain length on the solubility of aldehydes in polymer films is most obvious at low temperature and on the diffusion at high temperatures (Leufvén and Stöllman, 1992), Figures 28 and 29.
Figure 28. The solubility coefficients (S) at 5°C, room temperature, and 75°C for aldehydes in five different polymer films as a function of the number of carbon atoms in the aldehydes.
(Leufvén and Stöllman, 1992)

In general, the diffusion of the aldehydes in the different polymers increased and the solubility decreased with increasing temperature, i.e. 5-75°C. That is the same behaviour as for permanent gases.

Figure 29. The diffusion coefficients (D) at 5°C, room temperature and 75°C for aldehydes in five different polymer films as a function of carbon atoms in the aldehydes.
(Leufvén and Stöllman, 1992)
4.13.2. Liquids

Typical sorption isotherms obtained for limonene in model systems show that sorption increases with increasing temperature, Figure 30. This is a characteristic of absorptive processes (Kwapong and Hotchkiss, 1987).

Studying the sorption of esters, aldehydes and alcohols in LLDPE, Nielsen et al. (1992) showed that significantly larger amounts were sorbed at 75°C compared to 5°C. The partition coefficients of the esters were approximately doubled at the higher temperature, while for the aldehydes and alcohols, the difference was even greater.

The reason for the increasing partition coefficients at higher temperatures might be the greater mobility of molecules, or that the polymer might be affected in some way, the crystallinity decreases and the polymer might swell at high temperatures (Billmeyer, 1971).

Figure 30. Ionomer 1652-limonene sorption isotherms. (+ = 6°C, o = 25°C; * = 38°C; initial concentrations = 50 ppm to 500 ppm). (Kwapong and Hotchkiss, 1987)
5. SOME PACKAGING CONCEPTS

In the past, production of foods was a major concern for the majority of the population. Today, in urbanized countries people are dependent on a food supply chain. Since most foods are perishable, the food processing/packaging industry provides an essential link in this long chain by ensuring that the consumers have a constant supply of various foods that are shelf-stable, safe and nutritious.

Over the past 20-30 years there have been many changes in the life-styles and food preferences of consumers. Today, most households own a microwave oven and a freezer. The result is that many consumers buy shelf-stable heat-and-serve meals. In most cases packaging must facilitate easy handling.

5.1. Trends in packaging materials

The speed of development of new packaging materials in recent years is remarkable. Some areas will be briefly discussed here. The four most interesting areas that have seen the most rapid advances in recent years are summarized in Table 7. Many of the new packaging materials have been developed to meet the increased demands for new packaging/preservation techniques, such as modified atmosphere packaging (MAP), controlled atmosphere packaging (CAP), microwavable foods or an increased demand for recyclability or other environmental considerations (Yoshii, 1989).

5.2. Active packaging technologies

Active packaging systems involve an interaction between the packaging material itself, the internal atmosphere, and the food (Katsura, 1989). The intention is to extend the shelf-life of foods. New technologies that couple active packaging to controlled atmosphere packaging (CAP) or modified atmosphere packaging (MAP) are being developed (Sneller, 1986; Wolpert, 1987).
Table 7. Four interesting areas that have seen rapid advances in recent years. (Yokoyama, 1992).

<table>
<thead>
<tr>
<th>Classification</th>
<th>Usages</th>
<th>Types of packaging materials</th>
<th>Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshness keeping packaging materials</td>
<td>Vegetables, fruits</td>
<td>Polyelefin films into which CaCO₃, zeolite and ceramics are mixed.</td>
<td>Absorption of ethylene gas from vegetables and fruits.</td>
</tr>
<tr>
<td></td>
<td>Fresh meats and fishes</td>
<td>Multi-layer films and sheets in which PVDC or EVOH is used as a barrier layer.</td>
<td>Gas replacement packaging by oxygen and carbon dioxide for meats and by nitrogen and carbon dioxide for fishes.</td>
</tr>
<tr>
<td>Selectively permeable packaging materials</td>
<td>Processed meat products</td>
<td>Single-layer tubular films in which selectively permeable resins are used as mainmaterials.</td>
<td>Permeation of smoke ingredients under high temperatures and pressures and the excellent barrier under room temperatures. Permeation of carbon dioxide generating while it is packaged and aged.</td>
</tr>
<tr>
<td></td>
<td>Natural cheese</td>
<td>Multi-layer films with carbon dioxide permeability in which PVDC is used as a barrier layer.</td>
<td></td>
</tr>
<tr>
<td>Microwavable packaging materials</td>
<td>Retortable foods</td>
<td>Barrier containers composed of PP/PVDC/PP or PP/EVOH/PP, PP, PP + CaCO₃, C-PET.</td>
<td>Heat resistance of up to 120°C for more than 10 minutes. Microwavability. Cold resistance of down to -30°C. Microwavability.</td>
</tr>
<tr>
<td></td>
<td>Frozen foods</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Processed meat products</td>
<td>High-barrier or polymer alloy film in which PVDC or EVOH is blended with other resins.</td>
<td></td>
</tr>
</tbody>
</table>

5.2.1 Freshness-maintaining packaging materials

Freshness-maintaining packaging materials are one group of materials which recently have been attracting attention (Iwata, 1989). For vegetables and fruits, packaging materials with the function of adsorbing ethylene, ammonia, etc. have been developed. The active material used is often activated carbon.

5.2.2 Packaging materials with preferential permeability

Selectively permeable packaging materials can be regarded as highly functional gas-barrier packaging materials. In general, gas transmission rates of gas barrier resins such as PVDC, EVOH and PAN increase in the order of nitrogen, oxygen and carbon dioxide, and their transmission ratios (CO₂/O₂ etc.) are constant for each barrier resin.
Some foods require not only the permeation of unfavourable gas generated from the inside but also require the maintenance of the oxygen barrier. Demands for packaging to meet these contradictory requirements have risen recently. An example of this is a packaging material which allows compounds from the smoking process to penetrate into the surface of for example, sausage under high temperature. After the processing this material extends high barrier characteristics below ambient temperature, keeping the quality of the product (Yoshii, 1990).

Another example, this time from the dairy industry, is a packaging material with preferential permeability during the ageing of cheese. This material allows permeation of carbon dioxide formed during the ageing process of cheddar and gouda cheese, yet prevents oxygen permeation from the outside.

5.2.3. Packaging of microwaveable foods

Unique features of microwave energy are its ability to penetrate a food product and its efficient conversion to heat.

Common microwaveable packing materials, such as paperboard, facilitate microwave penetration, so that foods heat and cooks directly in the package. However, a common complaint about microwave cooking is its inability to produce a browning and crisping surface in packaged products (Higo, 1989; Ohlsson, 1989). To overcome such a limitation susceptor films are being developed. A susceptor is a material that is able to absorb and convert the electrical component of microwave energy into infrared or radiant energy (Smith et al., 1990). The most common susceptors are made of aluminium-coated polyester films. The aluminium absorbs microwave energy and acts as a secondary heat source. Second-generation susceptors, which will be based on other materials, are being developed.

5.2.4. High barrier packaging materials

Table 8 shows the conditions required of packaging materials for foods.

High barrier resins can not solely satisfy all the requirements of the packaging. The barrier layers are arranged between structural and sealing layers. At present, materials belonging to the barrier resin category are: Polyvinylidene (PVDC), Ethylene vinyl-alcohol (EvOH), Polycrylonitrile (PAN), Methaxylyene-diamine (MXD-6), nylon etc.
Table 8. The conditions required to packaging materials for foods.

<table>
<thead>
<tr>
<th>Sanitation</th>
<th>Non-toxicity</th>
<th>No reaction to ingredients of foods. No sign to the toxicity caused by the ageing.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical strength</td>
<td></td>
<td>Tensile strength, elongation, burst strength, tearing strength, impact, bending strength, impact strength, puncture strength, friction strength.</td>
</tr>
<tr>
<td>Protection</td>
<td>Barrier</td>
<td>Moisture-permeability, water vapor permeability, gas permeability, flavor retention, thermal insulation, light interception, UV interception.</td>
</tr>
<tr>
<td>Stability</td>
<td></td>
<td>Water-resistance, light resistance, chemical resistance, organic solvent resistance, cold resistance, heat resistance.</td>
</tr>
<tr>
<td></td>
<td>Consistency</td>
<td>Packaging operationability, machinability, breaking property, stiffness, non-electroconductivity, heat scalability, blocking resistance, heat shrinkability, create tension, non-cumbersome property.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Contactability. Glass, transparency, smoothness, whiteness, printability.</td>
</tr>
<tr>
<td></td>
<td>Economy</td>
<td>Price, productivity, transportation, storage.</td>
</tr>
</tbody>
</table>

In high-barrier packaging materials PVDC or EvOH have often been used as the barrier layer. However, the consumption of these polymers is relatively small. Lately, much attention has been paid to silica-coated materials (Mäschig, 1990).

5.2.5 Silica-coated film

To achieve added food-protecting barrier properties, films can be coated with SiO₂. Silica-coated plastics, also referred to as glass-coated, have several benefits, being clear barrier materials, microwaveable, retortable, and recyclable without any step to separate components being required. Thus far, SiO₂ coating has been deposited on polyester and LDPE films, PET containers and PP films. The film requires no pretreatment in order to achieve good adhesion of the SiO₂ coating to the film. Further, there is no optical absorption, i.e., yellowing, of the packaging material (Rice, 1992b). A 300 A SiO₂-coated LDPE film exhibits a 0.65 cc/100 in²/day oxygen transmission rate. Oxygen permeability rates for coated BOPP (Biaxial Oriented Polypropylene) are said to be comparable to those exhibited by metallized BOPP. Silica-coated PET films exhibit 0.06 cc/100 in²/day oxygen transmission rates.

These coated films could, consequently, offer barrier properties approaching those provided by multi-layer plastic structures, foil laminates or metallized films. Using silica-coated plastics, one is able to have a monolayer plastic film with an extremely thin SiO₂ layer.

Table 9 shows oxygen and WVTR for glass-coated films manufactures by PC Materials Corpr. (Rice, 1992a).
Table 9  Oxygen and water vapour transmission rates for glass-coated films manufactured by PC Materials Corp. (Rice, 1992a).

<table>
<thead>
<tr>
<th>FILM TYPE</th>
<th>RELATIVE THICKNESS</th>
<th>OTR</th>
<th>WVTR</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET - 1 mil</td>
<td>2000</td>
<td>.0015</td>
<td>.0380</td>
</tr>
<tr>
<td>Control</td>
<td>1000</td>
<td>.0600</td>
<td>.0770</td>
</tr>
<tr>
<td>PET - 5 mil</td>
<td>2000</td>
<td>.1400</td>
<td>.0600</td>
</tr>
<tr>
<td>Control</td>
<td>0.0000</td>
<td>.0000</td>
<td>2.0000</td>
</tr>
<tr>
<td>OPP - .8 mil</td>
<td>2000</td>
<td>.6100</td>
<td>.0000</td>
</tr>
<tr>
<td>Control</td>
<td>1.0500</td>
<td>.0000</td>
<td>.0000</td>
</tr>
<tr>
<td></td>
<td>150.0000</td>
<td>.4000</td>
<td>.0000</td>
</tr>
</tbody>
</table>

Oxygen and water vapor transmission rates are not normalized with respect to film gauge.

At this point there seem to be three factors slowing down the commercial application of glass-coated packaging material (Rice, 1992a):

1. Economics
2. Technical difficulties in ensuring good silica adhesion to certain substrates
3. Lack of converter and packager experience with these new packaging materials.

However, silicon oxide-coated composites are said to be less expensive than composites containing EvOH or PVdC for similar applications, but silica-coated films are more expensive than aluminium-metallized films (Rice, 1992a).

Early developmental problems reported were yellowing and fragility of the glass coatings. However, these problems seem to have been overcome now (Rice, 1992a). Not surprisingly, Japan has been in the forefront in silica-coated plastics research, development and commercialization. In 1988 a multilayer microwaveable pouch with a glass coated polyester barrier was introduced. Today, several other applications are seen. These are discussed by Rice (1992a). There have also been reports of micro-cracks in the SiO_x coatings. These cracks make tunnels through which oxygen can diffuse into the container (Yoshii, 1992).
5.2.6 Oxygen scavenging

Another new trend in barrier packaging materials concerns chemical barriers or oxygen absorbing materials. These chemical barriers are used together with so-called physical barriers such as PVDC, PAN or EVOH.

One example is the "OXBAR" system, comprising PET as the main component (96%), MXD-6 as the oxidizable component (4%) and with organic cobalt salt added as oxidizing catalyst at a 50-200 ppm level. The synthetic process used to make the MXD-6 film is shown in Figure 31.

![Chemical structure of MXD-6](attachment:image)

**Figure 31.** Synthetic process of MXD-6.
(Sadamoto, 1989)

This composition can be extruded to make blown bottles, which are said to be able to maintain the oxygen level inside the container as low as zero for two years (Yoshii, 1992).

Barrier lifetime is a function of two main variables: scavenge capacity and rate of consumption. The former depends on the composition of the blend (MXD-6 and Co content) and the wall thickness of the container.

One key to the MAP technology is the controlled permeation of O₂ and CO₂, as well as the scavenging of ethylene, or controlled release of other compounds which could have a preservative effect on the food (Labuzza and Breene, 1989). One way to directly control oxygen levels in a package is through the use of an oxygen scavenger system (Takahashi et al., 1984). The simplest scavenger is reduced iron. The amount of iron that needs to be used depends on the initial oxygen level in the headspace, the amount dissolved in the food and the oxygen permeability rate through the film (Labuzza and Breene, 1989). One gram of iron will react with 300 cc of oxygen. The iron is separated from the food by keeping it in a small highly oxygen-permeable pouch.
Another example is an oxygen-absorbing plastic called "Long Life", which can extend the shelf-life of oxygen-sensitive drinks. This material is said to be insoluble in water and of a similar structure to hemoglobin (Yoshii, 1992). The hydroxyl groups of the base polymer is reacted with silica and combined with a metal complex.

Another method to actively control the oxygen level in a food package is the use of an enzyme reactor surface, which will react with some substrate to scavenge incoming oxygen.

A new active packaging system developed by PharmaCal Co. (USA) utilizes glucose oxidase and catalase enzymes for the removal of oxygen from liquid products, Figure 32 (Yoshii, 1991).

![Figure 32. Oxygen removal from liquid products by glucose oxidase and catalase enzymes (Yoshii, 1991)](image)

Other chemical scavenger systems include reactive dyes, ascorbic acid and catechol based reducers.

There is one commercial application that uses a mixed iron powder–calcium hydroxide sachet in which both oxygen and carbon dioxide are scavenged (Labuza and Breene, 1989). It is being used to pack fresh-ground coffee in flexible bags. This packaging system is said to more than triple the shelf-life.
5.2.7. Edible films

Recently, an edible film of polysaccharides has been used in certain packaging applications (Labell, 1991). The polysaccharide films look like plastic films. The edible polysaccharide beads are seamless spheres of polysaccharides measuring 1-3 mm in diameter, and they will be dissolved by heat and moisture. Dry ingredients such as spice and seasoning mixes can be portion packed in edible film pouches. The entire pouch can be added to, for example, a soup, and the package will quickly dissolve. However, the polysaccharide films are more permeable to gases than plastic films. In addition, their tensile strength is not as high as that of plastic films. This will be a problem in automatic form/fill/seal machines.

In Japan, edible polysaccharide film has already found wide use in the meat industry for packing of processed smoked meats such as hams and poultry products (Labell, 1991). Processors can wrap the meat in edible film before smoking and steaming. The smoke flavour permeates the film during the smoke process and the film dissolves during steaming. The surface structure and texture of the finished ham are improved. Also, yields are better because less moisture is lost during processing.

The shelf-life of fresh fruits and vegetables can be extended by using an edible film. Plastic films provide a gas barrier to protect the products, but moisture from the packed product will be collected inside the packaging. Edible film packaging gradually absorbs the moisture given off from the product, preventing its accumulation in the packaging.

This could lead to a reduced growth of mould. Over time, this moisture absorption may cause the film to dissolve.

5.3. Aseptic/ultra-high temperature (UHT) packaging

Heat sterilization is the heating of foods at a sufficiently high temperature for a sufficiently long time to destroy microbial and enzymatic activity. As a result, sterilized foods have a much longer shelf-life.

Packaging material for aseptic processing/packaging must be sterilizable, be suitable for aseptic filling, and should permit the application and maintenance of sterility of the product during storage and handling (Smith et al., 1990).
Rigid, semi rigid and flexible packaging materials have all been used for aseptic packaging. The sterilization and sealing techniques are somewhat different for each application. Basic packaging materials used in aseptic packaging include metal sheet and foil, glass, plastic films and paper. Metal has been used because it is a durable barrier that can be sterilized and hermetically sealed. However, metal containers are also expensive, have poor adaptability to non-cylindrical shapes, and can not be heated in microwave ovens.

Glass containers offer advantages similar to metal containers, but suffer from the additional disadvantages of fragility and density.

Plastic materials offer versatility, but cannot be used alone since they do not possess all of the required properties. Consequently, they must be laminated to other materials to give packages with the appropriate requirements.

At present, the Tetra-Pak concept, a paperboard-foil-plastic laminate, is widely used for aseptic packaging. This laminated structure consists of as many as six layers of materials: PP, Surlyn, foil, PE, paperboard, and PE as the inner food contact layer. Other combinations that can be used include laminations of Saran, EvOH, PE and PS; or a metallized polyester, which consists of vinyl ethyl acetate, nylon, foil and PE.

Aluminium foil is the most commonly used barrier material. PP or PE, i.e. polyolefins, are the most common heat sealing and food contact materials used.

Foil needs to be protected from mechanical damage, and protection is usually provided by paperboard, which also gives rigidity. All of the composite materials described act as barriers to moisture, oxygen, light and microbes, and have the strength and heat sealability needed for aseptic packaging. However, as will be discussed later, scalping to the polyolefin food contact layer has been reported by several authors. The effect of this scalping process has been a source of disagreement between different research groups. A review of aseptic processing has been provided by Lopez (1987). Historical perspectives of aseptic packaging technology and the use of plastic packaging materials are described further in other publications (Downes, 1989; Eidman, 1989; Fox, 1989; Kern, 1989).
5.4. Modified atmosphere packaging

MAP is defined as the enclosure of food products in an atmosphere inside gas-barrier materials, in which the gaseous environment has been changed to slow down respiration rates, reduce microbial growth and retard enzymatic spoilage, all with the intent of extending shelf-life (Parry, 1993). Such modifications usually result in a reduced oxygen content of the air inside the package headspace, and an increased carbon dioxide and nitrogen level.

Gas packaging is an extension of vacuum packaging technology. This technique involves removal of air from the packaging and replacing it with a mixture of gases. This is achieved either by continuous forming or thermoforming gas packaging equipment.

Carbon dioxide is the most important gas in the gas mixture. Several factors influence the antimicrobial effect of carbon dioxide, specifically microbial load, gas concentration, temperature and packaging film permeability.

To be effective against aerobic spoilage microorganisms, a concentration of 20-60% carbon dioxide is required in the package headspace (Smith et al., 1990).

One of the most important factors influencing the antimicrobial effect of carbon dioxide is packaging film permeability (Parry, 1993). The success or failure of MAP for foods depends on both the oxygen and the carbon dioxide impermeability of packaging materials in order to maintain the correct gas mixture in the package headspace. In addition, films used in gas packaging should have low WVTRs, to prevent changes in moisture content.

Polymers commonly used for the gas packaging of foods include polyester (nylon), PP, PVDC, EvOH and PE. Since all of the desired characteristics of a packaging film, i.e. strength, impermeability, and heat sealability, are seldom found in one polymer, individual polymers are laminated to one another to produce films with the desired characteristics for gas packaging of foods.
Examples of such laminated structures include nylon-PE, nylon-PVDC-PE and nylon-EvOH-PE. Such composite structures have the desired characteristics for the gas packaging of food products: strength is provided by the outermost layer of nylon; gas and moisture vapour impermeability is provided by EvOH and PVDC; heat sealability is provided by PE (Brody, 1989).

For fruits and vegetables the production of the correct packaging materials is even more challenging, due to the fact that these products respire. The ideal packaging material for gas packaging of these products must be able to keep a balance of low oxygen concentration within the package headspace and prevent a high carbon dioxide concentration from building up.

Packaging films commonly used to achieve such a balance include LDPE and PVC (Zagory and Kader, 1988).

Certain active packaging techniques have similarities to MAP, since many additives incorporated into packaging film or within packaging containers, such as oxygen scavengers, carbon dioxide scavengers/emitters and ethylene absorbers, are capable of altering the composition of the atmosphere surrounding the food.

Packaging film of the correct permeability must be chosen to overcome the depletion of oxygen and the accumulation of carbon dioxide caused by respiring products. Newly developed highly permeable microperforated films such as P-Plus and Crop appear to be most suitable at present (Gill, 1990; Geeson et al, 1988). These films allow the product to breathe while it ripens inside the package.

The use of ethylene scavengers is a complementary approach to this problem. Ethylene scavengers, using a silica gel which contains permanganate are commercially used in Japan (Labuza and Breene, 1989). The latter oxidizes the ethylene and has been commercially successful with many fruits. As with the oxygen system, the scavenger is put in a sachet that is highly permeable to the ethylene.
5.4.1 Temperature compensating films

A newly developed film called Intelimer has a temperature "switch" point at which the permeation of the film changes abruptly. The switching mechanism is accomplished by the long-chain fatty alcohol-based polymeric side chains patented by the Landec Corporation, Figure 33.

Below a preset temperature, these side chains are crystalline and provide a relative gas barrier. However, above this preset temperature, these side chains reversibly convert to an amorphous structure, which is up to 1000 times more permeable to gas and may be tailored to the very large increase in respiration rates of fresh produce at temperatures above 5°C (Day, 1993).

Because the change is physical and not chemical, this process is continuously reversible. The transition point can be moved by increasing or reducing the average number of carbon atoms in a chain. The switch point may be set anywhere between 0 and 45.5°C, and controlled within 2°C. The switch also changes the adhesiveness and viscosity of the film. Intelimer films are intended to be used for packaging highly respiring produce, but commercialization is still several years away (Anon., 1992).

Figure 33. Intelimer films show a 1000 fold change in permeability at a preset temperature.
Another temperature-compensating film for produce has recently been patented and relies on the same principle as a bimetallic strip, but uses two different plastic films instead of two metals. Temperature-sensitive apertures are cut into laminated plastic film in the form of small strips or "petals". At a selected temperature, the laminated film is flat and gives minimal opening areas. However, at higher temperatures the free area for gas exchange increases as the petals curl, and the permeability of the film can be engineered to increase in proportion to the rise in respiration rates of produce.

The rate of curl is a function of the coefficient of expansion of the two separate films, and the extent of opening is controlled by the length and shape of the petals surrounding the aperture.

5.4.2 Moisture absorbers

Since metabolism of fat and carbohydrates produces water, the humidity in the headspace of a food package will build up and allow the growth of moulds and yeasts (Hirata, 1986). A dessicant film or sachet can be used to overcome this problem (Geeson et al., 1985). A Japanese company has developed a film which is in the form of a pillow with entrapped propylene glycol (Labuza and Breene, 1989). When placed in contact with the surface of meat or fish, it absorbs water and causes injury to spoilage bacteria.

5.5. Sous-vide (vacuum cooking/packaging) technology

There has been a tremendous growth in recent years in the use of sous-vide processing technology to extend shelf-life and maintain the quality of fresh food (Smith et al., 1990). The development of such technology is in response to consumer demands for ready-to-eat, microwaveable, convenience foods with extended shelf-life that retain "closer to fresh" characteristics. The term sous-vide means 'under vacuum'. In sous-vide processing, foods are cooked in sealed, evacuated, heat-stable pouches or thermoformed trays, in such a way that the natural flavour, aroma and nutrient qualities are retained by the product. This technique needs a highly controlled packaging/cooking condition.
5.6. Lamination and coextrusion

Many new packaging materials or combinations of materials have been used in food packaging during recent years. The main driving force has been to increase the barrier properties of the package and therefore the protection given to food products with more complex material structures.

A single polymer is often not able to provide all the properties necessary to create suitable barrier characteristics. This creates a need for multi-layer structures and techniques such as lamination and coextrusion. Coextrusion is not simply a competitive alternative to lamination. There are laminate properties that coextrusion is unable to meet, and non-thermoplastic materials such as paper and aluminium foil, which are often used in the lamination process, can obviously not be coextruded. In addition, printing ink can be protected if within a laminate, but must be on the surface of a coextruded film. There are also applications where the two technologies are combined, i.e. when a coextruded film is used in a lamination.

For example, ionomers have excellent sealing characteristics, but are relatively expensive. A PE/ionomer coextrusion can give the sealing properties needed in a more cost-effective way than an ionomer monofilm (Meadows, 1991). Production of such a structure may be by adhesive lamination of the coextruded PE/ionomer or by coextrusion coating of the other material.

The principal advantage of coextrusion over lamination is that the materials are extruded simultaneously, without the separate lamination process (Meadows, 1991).

In flexible packaging, laminates and metallized films have replaced single structure materials. This has greatly improved the light and oxygen barrier properties of the materials, and thus extended shelf-life. A drawback of metallized laminates is the environmental load, even though only tiny amounts of metal are being used. The long established tendency towards laminates may be hit by recycling legislation when the industry is controlled by requirements to make packaging products recyclable. Even though laminates exhibit many advantages such as flexibility in terms of stiffness, strength, barrier and sealing qualities, many structures may have to be simplified, and there may have to be an increased use of compatible base films so that the whole structure can be recycled by the same path (Meadows, 1991).
There is a growing need for high-performance barrier packaging to give shelf stability over a wide range of environmental conditions.

5.7. Milk packaging

The traditional material for milk packaging is glass or carton packages. Because of their environmental benefits, refillable plastics milk bottles are becoming increasingly popular. Two and three litre bottles of polycarbonate have been on the market in Switzerland for some years, and an one litre polycarbonate bottles is being tested in Sweden by Arla. The polycarbonate bottles are made of brown tinted polycarbonate to protect the milk from UV degradation. However, critics claim that refillable plastic milk bottles are less hygienic and, of course, as always the case with reused packages, there might be a problem with compounds being sorbed in the packaging material and not being completely removed during the washing process.

5.8. Ketchup packaging

Recently, Heinz developed a new ketchup bottle called Enviropet to meet the increased demand for recycling and other environmental considerations. Figure 34 shows the original bottled and the Enviropet bottle. This new container is based on a PET/EvOH/PET/EvOH/PET structure, eliminating the adhesives which cause a problem with materials not being able to separate later (Yoshii, 1992). According to Heinz, recyclability is its sale point.
Original Technology:
Gamma Bottle by American National Can.

**ORIGINAL TECHNOLOGY**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene (P.P.)</td>
<td>55-65 %</td>
</tr>
<tr>
<td>P.P. Regrind</td>
<td>25-30 %</td>
</tr>
<tr>
<td>Adhesive</td>
<td>4-6 %</td>
</tr>
<tr>
<td>Barrier</td>
<td>6-8 %</td>
</tr>
</tbody>
</table>

Purpose:
- Product Protection
- Consumer Convenience

Imported Technology:
Enviropet by Sidel/Husky co-injection bottle

**IMPROVED TECHNOLOGY**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.E.T.</td>
<td>98.5 %</td>
</tr>
<tr>
<td>Barrier</td>
<td>1.5 %</td>
</tr>
</tbody>
</table>

Purpose:
- Product Protection
- Consumer Convenience
- Recyclability
- Clarity
- Breakage Resistance

*Figure 34.* The original and the improved Enviropet Ketchup bottles. (Yoshii, 1992)
6. THEORIES OF SORPTION AND TRANSPORT IN POLYMER MEMBRANES

The interest in the sorption and transport behaviour of gases and vapours in non-porous membranes is growing because of its many important practical applications, which include packaging materials, separation membrane systems, industrial gas separation systems, drug delivery systems and reverse osmotic applications (Odani and Uyeda, 1991).

6.1. Transport processes

The permeation of gases through a non-porous membrane is governed by the coupled solution-diffusion mechanism proposed by Graham one hundred and twenty eight years ago (Graham, 1866).

Permeability \(P\) = Solubility \(S\) x Diffusivity \(D\)  

\[ (1) \]

First, sorption of gas molecules occurs in the surface layer on the upstream side of the membrane, then the molecules diffuse across the membrane in response to a concentration gradient, and finally evaporate from the surface on the downstream side, Figure 35, where \(L\) is the thickness of the membrane, \(p\) is the partial pressure of the permeant and \(J_s\) is the total flow of permeant through the membrane. Also shown in Figure 35 is the total flow up to time \(t\) of permeant per unit membrane area out of the membrane as a function of \(t\).

---

**Figure 35.** Permeation cell experiment.  
(Frisch, 1991)
The total flow rate increases steadily until a constant steady-state value \( J_s \) (the derivative of the linear portion of the curve in Figure 35) is achieved. \( J_s \) is the steady-state flux (amount gas/per unit area and time) out of the membrane at \( x = 1 \).

Transport processes can be divided, rather arbitrarily, into Fickian and non-Fickian categories. In Fickian processes, transport is described by Fick's law.

\[
Q = -D(c) \frac{dC}{dx}
\]  
(2)

where

\( Q \) is the flux of permeant in amount/cm\(^2\) x sec

\( C \) is the concentration

\( x \) is the coordinate dimension in the direction of transport

\( D \) is the diffusion coefficient in cm\(^2\)/sec

Fick's second law gives the change in concentration as a function of distance and time if the diffusion coefficient is assumed to be constant.

\[
\frac{dc}{dt} = -D \frac{d^2c}{dx^2}
\]  
(3)

The non-Fickian category includes systems in which transport can not be described by equation No. 2 (Ahn, 1985).

Fickian diffusion can be visualized as a series of jumps in which Brownian motion of the polymer chain segments produces transient voids in the vicinity of the penetrant, enabling it to move through the polymer matrix. The size of the voids required to permit a jump is, of course, related to the size of the penetrant. The thermal energy which must be localized near the penetrant is related to the volume of the fluctuation, the cohesive energy density of the polymer, and the presence of nearby penetrants which can facilitate the motion of the surrounding chains (Stannet, 1986).

Particularly at high concentrations of sorbed penetrant, the plasticizing effect of neighboring penetrants can cause pronounced concentration dependence of the diffusion coefficient, D.
For low penetrant concentration in rubbery polymers, the concentration of the sorbed penetrant can be determined by Henry's law.

\[ C = k_d \times p \]  

(4)

\( k_d \) is the Henry's law solubility coefficient.

At sufficiently high penetrant concentration, there exists a deviation from behaviour according to Henry's law.

Although there are similarities between gaseous and liquid transport in a polymer, there are also a number of differences. In general, the affinity between liquids and polymers is much greater than that between gases and polymer, i.e. the solubility of a liquid in a polymer is much higher than that of a gas. Another difference between liquids and gases is that the gases in a mixture permeate through a polymer in a quite independent manner, while with liquid mixtures the transport of the components is influenced by flow coupling and thermodynamic interaction (Mulder, 1991).

It is well known that amorphous polymer-penetrant systems generally exhibit very different sorption behaviour above and below the glass transition temperature of the polymer, \( T_g \). Figure 36 (Koros and Paul, 1978; Frisch, 1991).

While solubility and transport of small molecules in rubbery polymers are relatively well understood, much less is known about the mechanism of sorption and transport in glassy polymers.

![Figure 36](image-url)  
Figure 36. Comparison between sorption in glasses and rubbers. (Lipscomb, 1990).
It is believed that the inability of the sub-$T_g$ matrix to relax to thermodynamic equilibrium can lead to local inhomogeneities in the penetrant environment (Cabonell and Sarti, 1990).

For a penetrant-polymer system, whose $T_g$ differs at least somewhat from that of the pure polymer and depends on concentration, the segmental micro-Brownian motion of some fractions of the polymer chains slows down just below the glass transition. As the temperature is further reduced, an increasingly large fraction of the chains in the sample have backbone micro-Brownian motion which is "frozen" out (Paul and Koros, 1976; Sefcik et al., 1983; Astrarita et al., 1989).

When the solubility of penetrants is very low, i.e. gases in polymers, it can be described by Henry's law. However, with organic vapours or liquids, which can not be considered ideal, Henry's law no longer applies.

The diffusivity is a kinetic parameter which indicates how fast a penetrant is transported through the membrane.

The diffusivity is dependent on the geometry of the penetrant; as the molecular size increases the diffusion coefficient decreases (Bicerano et al., 1990).

However, the diffusion is concentration dependent with interacting systems and even large organic molecules which have the ability to swell the polymer can have large diffusion coefficients (Chen and Edin, 1980).

Two separate cases must therefore be considered, ideal systems or case 1 diffusion, where both the diffusivity and the solubility are constant, and concentration-dependent systems where the solubility and the diffusivity are functions of the concentration (Saxena and Stern, 1982; Choy et al., 1984; Alger et al., 1989).

Other cases can be distinguished where the solubility and the diffusivity are functions of other parameters such as time and place. These phenomena, often termed anomalous, can be observed in glassy polymers where relaxation occurs, or in heterogeneous types of membranes.
For ideal systems, where the solubility is independent of concentration, the sorption isotherm is linear (Henry's law), i.e., the concentration inside the polymer is proportional to the applied pressure, Figure 37a. With glassy polymers the sorption isotherm is generally curved rather than linear, Figure 37b. Where strong interactions occur between organic vapours or liquids and polymers, the sorption isotherm is highly non-linear, especially at higher vapour pressures, Figure 37c. Such non-ideal sorption behaviour can be described by free volume models or Flory-Huggins thermodynamics.

For glassy polymers where the solubility of a gas often deviates in the manner shown in Figure 37b, such behaviour can be described by the dual sorption theory, in which it is assumed that two sorption mechanisms occur simultaneously, i.e., sorption according to Henry's law and via a Langmuir type sorption, Figure 37.

![Figure 37. Schematic drawing of sorption isotherms for ideal and non-ideal systems. (Mulder, 1991)](image)

6.2. Dual sorption theory

For the dual-mode model, first suggested by Meares, it is assumed that there exist two distinct molecular populations of penetrant in the polymer. One population (the Henry's law mode) dissolves directly into the polymer matrix, and a second population (the Langmuir mode) is sorbed into microvoids or holes in the polymer, Figure 38. The microvoids are frozen into the glass at $T_g$, where the mobility of the polymer chains drastically decreases (Vliet al., 1976; Fredrickson and Helfand, 1985; Vrentas et al., 1989; Vrentas and Vrentas, 1991).
The penetrant is believed to be sorbed into the polymer:

1. by ordinary dissolution in a continuous amorphous matrix; The concentration of this mode, $c_D$, is represented by Henry's law, and
2. by sorption in a limited number of fixed preexisting microvoids, or at fixed sites, in the polymer; The concentration of this mode, $c_H$, is represented by the Langmuir equation.

The total concentration of sorbed penetrant is given by the dual mode sorption model as:

$$ c = c_D + c_H = k_D \times p + c'_H \times b \times p/(1 + b \times p) $$

where:

- $c_D$ is the concentration of dissolved molecules
- $k_D$ is the Henry's law constant
- $p$ is the penetrant pressure at equilibrium
- $c'_H$ is the Langmuir capacity constant (the concentration in the holes at saturation)
- $b$ is the Langmuir affinity constant (hole affinity constant)
- $c_H$ is the concentration of molecules adsorbed in microvoids (Langmuir concentration)

Figure 39 shows the permeability coefficient as a function of permeant pressure.

![Diagram showing the penetrant pressure and the concentration of different modes of sorption](image)

*Figure 38. Typical dual-mode sorption isotherm and its components. (Stern and Trochalaki, 1990).*
Figure 39. Permeability coefficient for small molecules in glassy polymers as a function of penetrant pressure. (Stern and Trohalaki, 1990)

For cases involving little penetrant-penetrant interaction, it may be expected that sorption of a binary gas mixture A/B in the polymer matrix in the absence of a plasticizing effect will occur essentially additively, that is, the Henry-mode solubility of a given gas is independent of the existence of another component (Sanders and Koros, 1986). In the Langmuir-mode of sorption, on the other hand, there will be competition between A and B for the fixed number of sites. This effect may cause significant sorption depression of both penetrants (Odani and Uyeda, 1991).

6.3. The free-volume model

The free-volume model which has been developed by Stern et al. represents permeation through membranes of rubbery polymers.

A number of physical parameters are changed at the glass transition temperature, i.e. in the rubbery state, one of these is the density or specific volume, Figure 40.
Figure 40. Specific volume of an amorphous polymer as a function of the temperature. (Mulder, 1991)

The free volume $V_f$ may be defined as the volume generated by thermal expansion of the initially closed packed molecules at $0\degree K$.

$$V_f = V_t - V_0$$  \hspace{1cm} (6)

where $V_t$ is the observed volume at a temperature $T$, and $V_0$ is the volume occupied by the molecules at $0\degree K$. The fractional free volume $v_f$ is defined as the ratio of the free volume $V_f$ and the observed volume $V_t$.

$$v_f = \frac{V_f}{V_t}$$  \hspace{1cm} (7)

Using the free volume concept based on viscosity, a fractional free volume $v_f = 0.025$ has been found for a number of glassy polymers, and this value is considered to be a constant, $v_f = v_{f,T_g}$ (Mulder, 1991).

Above $T_g$ the free volume increases linearly with temperature, according to

$$V_f = v_{f,T_g} + da (T - T_g)$$  \hspace{1cm} (8)

where $da$ is the difference between the value of the thermal expansion coefficient above $T_g$ and below $T_g$.

The theory assumes that the mobility of a diffusing species, $D_{T_1}$, is a function of the average fractional free volume of the penetrant-polymer system, $v_f$. 

If the size of the penetrant increases, the amount of free volume must also increase. The probability of finding a hole whose size exceeds a critical value is proportional to \( \exp\left(-B/v_f\right) \), where \( B \) expresses the local free volume needed for a given penetrant and \( v_f \) is the fractional free volume.

The mobility of a given penetrant depends on the probability of finding a hole of sufficient size that allows its displacement.

\[
D_T = R x T x A_f \exp\left(-B/v_f\right)
\]

(9)

where \( A_f \) is dependent on the size and the shape of the penetrant molecule, while \( B \) is related to the minimum local free volume necessary to allow a displacement (Mulder, 1991; Odani and Uyeda, 1991). Equation No. 9 shows that the diffusion coefficient increases with increasing temperature, and also that the diffusion coefficient decreases as the size of the penetrant molecule increases, since \( B \) increases.

For non-interacting systems, Equation No. 9 predicts a straight line when \( \ln D \) is plotted versus the reciprocal of the fractional free volume, assuming that \( A_f \) and \( B \) are independent of the polymer type. Such behaviour has been observed, suggesting that the diffusivity of a non-interacting gas molecule can be determined from density measurements alone (Muruganandan et al., 1987; Barbari et al., 1988; Min and Paul, 1988).

However, other data deviate from this linear behaviour, suggesting that the assumptions behind Equation No. 9 are not completely correct, and that \( A_f \) and \( B \) may be a function of the polymer type, or that polymer-dependent parameters need to be incorporated in the equation (Tanaka et al., 1989).

A more sophisticated approach to free volume theory has been presented by Vrentas and Duda, but that theory contains a number of additional parameters that have to be determined experimentally.

Table 10 is a summary of diffusion behaviour in homogeneous polymer membranes.
Table 10. Diffusion behaviour of penetrants in homogenous polymer membranes.
(Stern and Trohalaki, 1990)

<table>
<thead>
<tr>
<th>$T&gt;T_g$</th>
<th>$T&lt;T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal or Case I diffusion $k_0$ independent of $p$</td>
<td>Dual Mode Sorption</td>
</tr>
<tr>
<td>$D=D_0$ independent of concentration.</td>
<td></td>
</tr>
<tr>
<td>For $T&gt;&gt;T_g$, Arrhenius temperature dependence of D</td>
<td>Non-Fickian Diffusion</td>
</tr>
<tr>
<td>Concentration dependent diffusion $D=D(c)$ $k_0$ can depend on $p$.</td>
<td>Memory effects and &quot;time dependent&quot; diffusion.</td>
</tr>
<tr>
<td>Sorption equilibrium generally attained at boundaries.</td>
<td>Diffusion anomalies in sorption and permeation</td>
</tr>
<tr>
<td>Fickian diffusion</td>
<td>Concentration dependent dual mode sorption</td>
</tr>
<tr>
<td>Free volume behavior</td>
<td>Cracking and mechanical failure of polymers in which diffusion occurs.</td>
</tr>
</tbody>
</table>

6.4. Determination of the diffusion coefficient

The diffusion coefficient can be determined by a permeation method, the so-called time-lag method. If the polymer is free of penetrant at the start of the experiment, the amount of penetrant, $Q_t$, passing through the polymer membrane in the time $t$ is given by

$$
\frac{Q_t}{\ell c_i} = \frac{D c_i}{\ell^2} \cdot \frac{1}{6} \cdot \frac{2}{\pi} \sum \frac{(-1)^n}{n^2} \exp \left[ -\frac{D n^2 \pi^2}{\ell^2} t \right]
$$ (10)

where $C_1$ is the concentration on the feed side and $n$ is an integer (Crank, 1967).

When $t \rightarrow \infty$, the exponential term in Equation No. 10 can be neglected and simplifies the equation to

$$
Q_t = \frac{D c_i}{\ell} \left| \frac{\ell^2}{6D} \right|
$$ (11)
The apparent diffusion coefficient can be calculated from the following expression:

\[ \theta = \frac{D}{\delta D} \]  \hspace{1cm} (12)

where \( D \) is the apparent diffusion coefficient (in \( \text{cm}^2/\text{s} \)), \( \theta \) is the time lag (in s) and \( \delta \) is the film thickness (in cm).

The time-lag required by the aroma vapour to dissolve in and permeate through the polymer is related to the apparent diffusion coefficient or diffusivity of the permeant through the film (Crank, 1967).

The permeability coefficient \( P \) can be obtained from the steady-state part of the permeation curve in Figure 41. This means that both the diffusion coefficient and the permeability coefficient can be determined with one experiment.

More complex relationships for the time-lag diffusion must be used in concentration-dependent systems (Frisch, 1957).

\[ \frac{Q_t}{Z c} \]

transient state

steady state

\[ \theta \]

\[ t \]

**Figure 41.** Time-lag measurement of gas permeation.  
(Mulder, 1991).

The time-lag might be dependent on the concentration of the permeating species.

An example is given by Apostolopoulos and Winters (1991) concerning the permeability of d-limonene in plastic packaging films. As the concentration of d-limonene decreased, the diffusivity of d-limonene de-
creased and the time-lag became longer (i.e. at concentrations lower than 0.54 ppm, d-limonene had not been detected after 20 days). Conversely, an increase of the d-limonene concentration resulted in greater diffusivities and shorter lag-times, (i.e. with 14.4 ppm limonene vapour concentration, the observed time-lag was less than a few hours).

In Figure 42 the relationship of the time-lag-diffusivity found by Apostolopoulos and Winters (1991) is shown.

![Figure 42. Permeation curves of d-limonene vapour at different concentrations with OPP film. (Apostolopoulos and Winters, 1991)](image_url)

Apparently, the diffusion coefficient is not constant over the concentration range (i.e. 0.54-14.4 ppm).

Also, the permeation rate was found to be concentration-dependent in a similar manner, Figure 43.
Figure 43. Permeation rate of d-limonene for OPP film as a function of d-limonene vapour concentration gradient. (Apostolopoulos and Winters, 1991)

A linear relationship between concentration and permeability, obeying Henry's law, was observed at d-limonene concentrations lower than 3 ppm, while at higher concentrations the permeation rate increased very rapidly.

6.5. Diffusion

Diffusion of gases in polymers is an important, and in some cases, controlling factor in a number of applications, such as protective coatings, membrane separation processes, and packaging of food and beverages. Therefore, a better understanding of the mechanism of gas and vapour diffusion in polymers is highly desirable in order to achieve significant improvements in these applications and in developing new ones.

From a macroscopic viewpoint, the diffusion process can be described in many cases of practical interest by Fick's two laws.

The equilibrium concentration (solubility), \( c \), of a penetrant gas or vapour dissolved in a polymer can be related to the pressure, \( p \), of the penetrant by the relation:

\[
c = S(c) \times p
\]  

(13)

where \( S(c) \) (or \( S(p) \)) is a solubility coefficient. When the concentration of the penetrant in the polymer is very low, Eq. No. 13 is a form of Henry's law, and the solubility coefficient is then independent of \( c \) (or \( p \)). In such cases, the diffusion coefficient may also become independent of \( c \).
Equation No. 14 indicates that the permeability coefficient is a product of a diffusion coefficient (a kinetic factor) and of a solubility coefficient (a thermodynamic factor).

Considerable effort has been made to develop a microscopic description of gas and vapour diffusion in polymers which is more detailed than the simplified viewpoint given by Fick’s laws. The mechanism of diffusion is very different in "rubbery" and "glassy" polymers.

6.6. Sorption

The simplest case is that of ideal solution behaviour with sorbed penetrant randomly dispersed within the polymer in such a way that Henry’s law is obeyed.

The solubility coefficient is then a constant independent of sorbant concentration at a given temperature, and the sorption isotherm is linearly related to concentration. The term "randomly dispersed" refers to a molecular scale such that neither polymer-penetrant nor penetrant-penetrant pairs are preferred. This means that a penetrant molecule excludes its own site from other penetrant molecules but does not otherwise affect their distribution.

In practice, ideal sorption behaviour is observed when permanent gases are sorbed by polymers, provided the gas pressure does not exceed about one atmosphere.

This behaviour is readily understood, since the solubility of permanent gases is very small (<0.2%) due to the lack of strong polymer-penetrant interactions. As a result, gas-gas interactions are also negligible, and ideal solution behaviour is observed.

The solubility coefficient is a vapour/polymer or liquid/polymer equilibrium partition coefficient. The extent of distribution of penetrant vapour in the polymer is dependent on the energy required to keep the penetrant in the vapour phase.
Within a homologous series of compounds, an increase in methylene units along the backbone will increase the heat of vapourization and lead to larger solubility coefficients (Strandburg et al., 1991). Figure 44 shows the solubility coefficients as a function of boiling points (K) of linear esters, n-alkanes and linear ketones at 85°C. As expected, the trend is consistent within each series, but much lower solubility coefficients are realized for the n-alkane family at a specified boiling point (heat of vapourization).

In this plot boiling points represent, as a first approximation, heats of vapourization. While it is advantageous to use heats of vapourization to explain the thermodynamic process, these have generally not been reliably reported. Boiling points, on the other hand, are reasonably reliable.

![Figure 44. Solubility coefficients for linear esters, n-alkanes and linear ketones in co-VDC at 85°C.](image)

This observation can be explained by examination of the van't Hoff type equation:

\[ S_T = S_0 \exp \left(-\frac{\Delta H_S}{RT}\right) \]  

(15)

where \(S_0\) is a preexponential factor, \(R\) is the ideal gas law constant, \(T\) is the absolute experimental temperature, and \(\Delta H_S\) is the heat of solution. The thermodynamics involved in the heat of solution can be expresses as:
\[ \Delta H_S = \Delta H_{\text{cond}} + \Delta H_{\text{mix}} \]  

or

\[ \Delta H_S = - \Delta H_{\text{vap}} + \Delta H_{\text{mix}} \]  

The solubility coefficients are not only dependent on heats of vaporization, but the partitioning is also dependent on the thermodynamics of the resulting mixture. Heats of mixing are generally not available. However, \( \Delta H_{\text{mix}} \) can be estimated using Hildebrand's approximation.

6.7. Permeability

There are many dimensions and units found in the literature for the general expression permeability (e.g. the transmission of molecules through polymer films).

\[
P = \frac{\text{(quantity of permeant)}}{\text{(area) x (time) x (pressure drop across the film)}}
\]  

Permeability is not only a function of the chemical structure of the polymer, but also varies with the morphology of the polymer and depends on many physical factors such as density, crystallinity and orientation. However, the chemical structure of the polymer can be considered to be the predominant factor controlling the magnitude of the permeability.

Below some general trends in permeability in relation to a few factors influencing permeability will be briefly discussed.

Density can be regarded as a measure of the free volume between the molecules of the polymer structure. In general, the higher the density, the lower the permeability.

Crystallinity of a semicrystalline polymer reduces the permeability compared to a completely amorphous polymer. The crystallinity and density of a polymer are closely related.

Molecular mass of a polymer has been found to have little effect on the permeability through polymers, except in the very low range of molecular mass.
Orientation of polymer molecules reduces permeability.

Crosslinking decreases the permeability, especially for high degrees of crosslinking and for large molecular size permeants.

Plasticizers, such as additives or sorbed compounds, increase the permeability.

Humidity alters the permeability, especially for hydrophilic polymers.

Thickness does not, in principle, affect the permeability coefficient (P), diffusion coefficient (D) and solubility coefficient (S). In practice, different values may be obtained from films of varying thickness. The reasons for this are different physical properties of the films obtained by differences in drawing, orientation and crystallinity.

The penetrant size, shape and polarity, of course, also affect the degree of permeability through a polymer.

An increase in the size (e.g. average diameter) of a penetrant in a series of similar penetrants generally leads to an increase in solubility, S, and a decrease in diffusion, D. This is true up to a certain molecular size (Shimoda et al., 1987). Since the permeability coefficient is the product of the diffusion coefficient and the solubility coefficient, its dependence on penetrant size is generally much less than for the other two variables.

The increase in solubility usually results in an increase in the concentration dependence of S, D and P with increasing penetrant size due to plasticization.

The increase in solubility is related to the dependence of S on boiling temperature and related parameters.

The decrease in D is a reflection of the need to create or utilize a critical activation volume in the polymer proportional to that of the penetrant molecule.
Temperature generally affects the permeability in the way shown in Figure 45. Since the permeability coefficient is the product of the diffusion and solubility coefficients, it is temperature-dependent according to:

\[ P = D_0 \times S_0 \exp\left(-\frac{E_D + \Delta H_T}{RT}\right) = P_0 \exp\left(-\frac{E_P}{RT}\right) \]  

(19)

If a permeant does not interact with the polymer under investigation, the permeability coefficient is characteristic of the permeant-polymer system. This is the case with the permeability of many gases, such as H\(_2\), He, O\(_2\), N\(_2\) and CO\(_2\), through many polymers. On the other hand, if a permeant interacts with the polymer, the permeability coefficient is no longer a constant and may be dependent on the measurement technique and the history of the polymer film. In such cases, a single value of the permeability coefficient does not represent the characteristic permeability of the polymer for a specific penetrant, and it is necessary to know the dependency of the permeability coefficient on all possible variables in order to obtain the complete profile of the permeability through the polymer.

For practical reasons, the transmission rate, Q, is often used in these cases.

\[ Q = \text{(quantity of permeant) / (area) x (time)} \]  

(20)

Since the transmission rate includes neither pressure of permeant nor thickness of the polymer, it is necessary to know either the concentration or pressure of the permeant during a specific measurement procedure.

Figure 45. Effect of temperature on permeation curves.  
(Miltz, 1992)
7. **EXPERIMENTAL METHODS**

A variety of experimental methods exists for evaluating the permeability through polymers. A comprehensive discussion of experimental methods used for the permeation, diffusion and sorption of gases and vapours in polymers may be found in Felder and Huvard (1980). They also outline methods of data analysis and theories for the experimental methods used. More detailed discussions of the theory may be found in the work of Crank and Park (1968).

Only a brief discussion of different approaches will be given here.

Most experimental techniques for studying the diffusion of gases and vapours in polymers involve one of three modes of transport: (1) sorption into or out of a polymer, (2) permeation through a membrane into a closed chamber, and (3) permeation through a membrane into a flowing stream.

All of the permeation and sorption methods mentioned above have the need for precise pressure (concentration) and temperature control in common. Further, the membrane thickness, polymer morphology and the thermal history of the polymer need to be defined. A common source of error in permeation cell measurements is leakage between the upstream and downstream compartments of the cell.

7.1. **Sorption methods**

Sorption measurements may be performed using a gravimetric or a barometric technique. Only gravimetric techniques will be discussed here.

7.1.1. **Gravimetric techniques**

No standard method for predicting the amount of sorption occurring for any polymer-flavour combination has been developed. Several sorption studies have utilized sorption cell methods where the penetrant is dissolved or suspended in a liquid and brought into contact with a polymer. The polymer and the liquid are either placed in an inert container (Hirose et al., 1988), or the liquid is placed in a polymeric container (Durr et al., 1981). Sorption is measured by quantitative evaluation of the aroma compound(s) remaining or by quantitative headspace evaluation after certain times (Becker et al., 1983; Mannheim et al., 1987; Halek and Meyers, 1989; Aithal et al., 1990).
Alternatively, polymer samples immersed in a liquid penetrant, or exposed to vapours, are removed, blotted, weighed and returned at intervals. Shortcomings of these methods include disturbances during weighing (Roland and Hotchkiss, 1991).

Measurements at high or saturated vapour pressures may not reflect sorption from foods where aromas are well below saturation.

In direct weighing methods, sorption or desorption rates are determined directly by following the change in weight of a polymer sample. These methods are generally used for measurements at subatmospheric pressures (Felder and Huvard, 1980).

Micro-gravimetric methods for quantifying the sorption of aroma compounds by polymeric films have been used by several authors (Roland and Hotchkiss, 1991; Baner et al., 1986; Mohney et al., 1988). Roland and Hotchkiss (1991) described a vacuum micro-gravimetric technique, shown in Figure 46.

Polymer samples are placed on the balance in a sealed chamber and out-gassed to $10^{-4}$ torr. The aroma compounds are admitted to the evacuated chamber, and the sorption-induced mass increase of the polymer and the pressure within the vessel are recorded. Additional aroma compound was admitted to the chamber after equilibrium was achieved, and a new equilibrium mass-pressure combination recorded, Figure 47.

Sorption isotherms were calculated from these results.

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Figure 46. The vacuum microbalance apparatus described by Roland and Hotchkiss (1991).
Figure 47. Mass gain for d-limonene sorption by polyethylene. Final vapour pressure (mm Hg):
a) 0.101, b) 0.154, c) 0.293, d) 0.413, e) 0.549, f) 0.684 and
g) 0.752.
(Roland and Hotchkiss, 1991)

This method only allows determination of a single aroma compound at a
time, or can not distinguish between different compounds. The method
provides, however, ways of obtaining sorption isotherms and solubility
coefficients for individual aroma/polymer combinations at penetrant
concentrations which are representative of food systems.

7.1.2 Extraction methods

To determine the level of volatiles sorbed by polymer films, extraction
procedures have been used to remove the penetrating compound from the
polymer (Hirose et al., 1988). Extraction of the polymer films which had
been in contact with a permeating species can be performed using either
an organic solvent, such as methylene chloride or hexane, (Kwapong and
Hotchkiss, 1987), simultaneously distillation-extraction (Shimoda et al.,
1988) or, as recently reported, using supercritical carbon dioxide (Nielsen
et al., 1991; Johansson et al., 1993).

Imai et al. (1990) reported a very rapid desorption of sorbed d-limonene
from the film following its removal from the test media (e.g. orange
juice). Apparently, the desorption of d-limonene occurred during the
sampling and washing process prior to extraction. To circumvent this
problem the difference method used by Kashtock et al. (1980) was
proposed.

Often, the solubility coefficient is calculated from permeability and
diffusion coefficients. This could, however, result in unrealistical values
of the solubility, since large errors in the estimate of diffusion coefficients may occur (Siegel, 1970).

7.2. Permeation methods

A large number of measuring devices exists for studying gas phase permeation of organic compounds. The permeability cell usually consists of two parts, between which the studied material is positioned (Demorest, 1992). In a dynamic device a carrier gas, usually nitrogen, is flushed through the permeability cell transporting the permeants, either directly to a detector (on-line) or to an adsorbent material (off-line).

In a static device the penetrant permeates into a closed cell initially containing a gas other than the penetrant. Gas samples are then withdrawn at intervals. Alternatively, a penetrant permeates into an initially evacuated chamber, and the resulting increase in pressure at constant volume, or the rise in volume at constant pressure, is measured (Felder and Huvard, 1980).

7.2.1 Mass-spectrometric techniques

In 1966 Bredeweg and Caldecourt reported an electron impact mass spectrometric technique for the measurement of permeation rates. Their method require, however, that the permeating side of a membrane is exposed to high vacuum. This requirement may alter the permeation characteristics of a membrane due to physical changes resulting from the vacuum seal and support (Tou et al., 1990).

Caldecourt and Tou (1986) developed two additional techniques based on atmospheric pressure ionization mass spectrometry and photoionization.

The photoionization technique, however, suffers from a drawback, since the window on the photoionization detector tends to be coated with the photodecomposition products from the permeating molecules, resulting in a loss of sensitivity (Tou et al., 1990).

The atmospheric pressure ionization mass spectrometric technique is restricted by its inherently narrow dynamic range and competitive ion-molecular reactions (Kallas et al., 1982).
A new sophisticated mass spectrometric technique was developed by Caldecourt and Tou (1986) and Tou et al. (1990). Tou et al. (1990) described an MS system consisting of an MS, a flow through hollow fiber interface and a permeation device for the measurement of aroma/flavour permeability rates across polymeric films.

Use of the flow through hollow fiber enabled enough sensitivity to be reached for monitoring volatile organics, in air or nitrogen, in the parts-per-billion range.

Both the feed side and the permeating side of the polymer film are at an ambient pressure with a feed concentration down to the parts-per-million level.

DeLassus et al. (1988) used an electron impact mass spectrometric method to determine the transport of apple aromas through different polymer films at different temperatures, relative humidities and aroma concentrations. The instrument (Hewlett-Packard 5970 MS) was used in a selected ion mode. Typically, three ions were monitored for each of the aromas involved. Figure 4.8 shows the results of a typical experiment using a co-VDC film with trans-2-hexenal as the permeant. The intensity of three ions added together is displayed. The first response is due to calibration.

![Figure 4.8](image)

Figure 4.8. Permeation experiment for trans-2-hexenal in a vinlylidene chloride copolymer film at 110°C. (DeLassus et al., 1988)

The above described technique could measure the barrier properties of packages efficiently, but the equipment required is expensive.
7.2.2. Gas chromatographic techniques

A typical gas chromatographic system, as applied to permeability, consists of a gas transmission cell either coupled directly (on-line) through a metering valve and a separating column to a detector, or via an adsorbent device (off-line) with subsequent desorption of the permeant into the gas chromatograph.

Gas chromatographic techniques using a variety of detectors have been described in the literature.

The selection of a separating column and detector is determined by the type of permeant used. The sensitivity of detection is also governed by the column and its operating conditions, together with the type of detector employed.

7.2.3. Dynamic methods

The dynamic approach is based on the principle of allowing a permeant gas to flow on one side of a film and allowing the permeate to be picked up by an inert carrier gas flowing past the other side of the film and being transported to an analysis system.

Leufvén and Stöllman (1992) have described a dynamic permeation cell, modified from Niebergall (1968), Figure 49. The permeating species were diluted and pumped through the upstream side of the polymer film at a specific flow rate. A similar flow rate was kept at the downstream side to recover the permeated species. An adsorbent material (e.g. Chromosorb 102) was used to collect both the permeants that had passed the film without being sorbed in it and those that had passed through the film.

Quantification of the permeants was made after thermal desorption of the species from the adsorbent material, cryofocusing in a cold-trap and injected on a gas chromatographic column connected to a flame ionization detector (FID).
According to Pasternak et al. (1970) the carrier gas passed through a thermal conductivity detector. The output was registered as an integral curve showing the dynamic approach of the permeation to steady-state conditions. This makes the contribution of more than one permeate difficult to separate, unless their diffusion times are significantly different. Nor can the method be adapted for measurements under a low vapour pressure because of the monitoring by a thermal conductivity detector.

Pye et al. (1976) described a similar approach with the additional use of a gas chromatograph to sample the carrier gas. Both on-line analysis by gas chromatography and gas sampling for special off-line analysis were possible.

Shimoda et al. (1987) described an on-line gas chromatographic technique using a flame ionization detector for measurement of diffusion, permeation and solubility coefficients.
Figure 50. Diagram of a measuring system for permeation experiments; NV1, NV2 are flow control valves, V is a three-way valve, FID1, FID2 are flame ionization detectors. (Shimoda et al., 1987)

Baner et al. (1986) developed two test methods for the determination of diffusion rates through polymer membranes. The first method is similar to the one described above and based on a continuous flow or isostatic procedure. This method utilizes gas chromatographic analysis to quantify the amount of organic vapour that has permeated through a membrane.

7.2.4 Static methods

The second method described by Baner et al. (1986) involves an iso-static procedure based on accumulation of permeants and also utilizes gas chromatography for the quantification of permeating species. In such an apparatus, headspace samples are withdrawn periodically with a gas-tight syringe and injected directly onto a gas chromatograph. The withdrawn headspace is replaced by an equal amount of air to maintain a constant total pressure of 1 atm inside the permeation cell.
Caldecourt and Tou (1985) have developed a permeation instrument which relies on a photo-ionization detector. Matsui et al. (1989) used a new method for measuring the permeability of volatile compounds in aqueous solution into PE films. The amount of a volatile compound permeating the PE film was detected by use of a gas chromatograph equipped with a FID, Figure 51.

Figure 51. Schematic representation of a permeation apparatus for aqueous solutions. (Matsui et al., 1989)
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