Barrier Films

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1.0 INTRODUCTION

Let me start off by using a few phrases: low cost, low maintenance, bangs for bucks, preventive conservation, flexible enclosures, non-interventive stabilisation ! These are all criteria that have nudged Us, well at least me ! down the road to using barrier films in a system to develop some form of micro-environmental management for an object. Barrier films are produced in bulk for the food, pharmaceutical, packaging and military industries and are therefore available at low cost! But, they are not designed for conservation purposes and do not necessarily meet our standards for stability. If proven reliable within the museum environment, they could provide a cost effective and importantly non-interventive solution to many museum storage and stabilisation problems – which in my area means keeping as much of the original data in the object as possible ! Lets also add the word, enclosure, because in the context of this talk, these things are in the main useless unless sealed up into a bag of some sort !

Barrier Films can mean many things to many people; Burke uses the phrase 'vapour barriers'. Probably we should use the phrase environmental barriers as we are using them to protect specimens from a range of environmental factors that can cause material deterioration. Their older use has been to allegedly protect specimens by putting a lacquer across specimens to protect them from vapour, or gaseous phase pollutants. In my own profession of geology there was a misconception that for instance lacquering geological specimens that had pyrite decay with a poly (vinylacetate) would prevent the process from happening.

In the 1970s and 80s, it was suggested that some of the resin forms of the polymers we now find in barrier films were used as lacquers to prevent water vapour transfer between object and environment (Lafontaine and Wood, 1982). We know that this does not work of course, and can in some instances be more destructive than constructive. More recently we have used barriers to protect objects from low quality materials in storage. By lining MDF with aluminised polyethylene (which was heat sealed or bonded) on the inner surface of drawers and cabinets, a barrier between specimen and storage material was made which protected specimens from vapours and gases off-gassed by low quality woods. This made the use of lower quality woods more acceptable when cost, as it always is, was an issue ! At its most basic form we used polythene to bag specimens to protect specimens from pollutants and us from specimens.

Where a 'Bang for Bucks' approach in conservation is required low cost barrier films are seen as a cost effective method when higher quality materials cannot be afforded. They are also often a more reliable lower technology approach when high tech is not always the best solution!

We also use barriers to establish micro-environments (Thomson 1978, Horie and Francis, 1984, Greenspan 1977). One of the main preventive conservation techniques is the use of silica gel (or Artsorb™) conditioned to a particular RH that is used to buffer the humidity within an enclosed environment. We traditionally use 'stewart boxes' as the enclosure for these microenvironments and rely on the thickness of the plastic (polyethylene or more recently polypropylene) and a good seal to reduce water vapour transmission between the interior of the box and the outside. Within the enclosure the conditioned silica gel buffers the relative humidity. The water vapour transmission rates for polythene (between about 1 and 5 $g.H_2O/m^2/day$ for HD polythene) indicate that polyethylene is not necessarily the most efficient material for building enclosures, relying on its thickness and seals to prevent water vapour transmission! Neither is this approach low cost or flexible for large numbers or large specimens and specimens cannot be seen through the thicker poly(ethylene)s.

So hopefully we are all familiar with the concept of enclosures or containers as barriers to water vapour and other vapour phase, gas and particulate pollutants to which a material can be susceptible.

In the mid 1980s we started looking at controlling humidity within sealed enclosures made from flexible materials such as aluminised polythene. The flexible aluminium laminates work because of the way small overlapping platelets of aluminium are deposited on top of each other to block the path for the water vapour penetration (Burke 1993). These were successful, having low moisture (and oxygen) migration rates (moisture 0.01 g/m^{-2} /24hrs; Oxygen 0.05 cc/m^{-2} /24hrs), but suffered from the fact that people needed to see the specimens. It should also be noted that for the thinner aluminized films (use in the food industry) the transmission figures are much lower. Fine for short term applications but not necessarily for longer term ones ! A 'clear' alternative was needed.

In the early '80s King (King 1983) adapted materials used in the forensics industry for carting off body parts from scenes of crime for storing mineralogical material in buffered environments. Using a material produced by Kapak Ltd., called G-pak, a polypropylene/Nylon laminate and building bags or enclosures he succeeded in establishing relatively stable buffered environments for specimens. While these were successful once the laminate was scratched or abraded the environment in the bag broke down quickly. At the time the problems of gas(oxygen)migration through the barrier were not considered. We had little information on low-cost methods of controlling oxygen transmission (or even any technical data on oxygen migration rates) so these were the first attempts to build specimen specific flexible laminate microenvironments for specimens without having to rely on good seals and a thick layer of polyethythene!

Over the last few years oxygen free environments have been built within glass enclosures. These have either relied on a forced nitrogen system, which requires maintenance and can be costly or on pulling a vacuum on sealed glass vials (Waller 1995).

2.0 WHERE ARE THEY FROM ?

In Industry, in particular the food, pharmaceutical, forensics and electronics industry there is/has been a requirement to control water vapour and gas levels around materials for transport and short term storage. After all the public would not like their crisps or cereals soggy! These environments have been passive and enclosures built traditionally from aluminized polythene or polyester laminates. For certain applications, clear laminates have been and are being developed for specific applications (electronics packaging and military applications). The production of specific micro-environments within these were mainly produced by flushing the bags with humidity controlled nitrogen. Once these were sealed up, low migration rates for vapour and gas phase meant that the environments within these bags were maintained within suitable criteria for short periods of time. Marketing interests also mean that these laminates were produced using materials which can be printed onto with 'popular' advertising slogans, which are also happen to be acceptable for use in museums.

The barrier films that we are using today are developments on these ideas. As new demands come along for stability or flexibility, they improve. As in most areas of conservation these materials are not built for the conservation business. We have adapted them for our own use. Our demand for the material is rarely going to be to the same level as the food or packaging industry and it is unlikely therefore that a barrier film will be developed specifically to our own requirements. We must either rely on the criteria for stability in other high user industries to improve so that higher quality products will become available to the conservation profession, or persuade the manufacturers that barrier films built to conservation standards will be of commercial use to other industries. The laminates are composed of a variety of polymers, each of which has a specific function.

3.0 BARRIER FILMS – WHAT ARE THEY ?

Barrier films are multiple layer laminates which are composed of a water vapour and gas barrier film, a heat sealable layer and a structural or protective layer.

The vapour barrier is normally sandwiched between two layers of polyethylene. The internal layer is used to (heat) bond the barrier film together melting these two layers together. The second or outer layer is used to bond the outer surface to a protective layer that also serves to increase the barrier properties of the laminate. This can be polyethylene, but other materials such as polypropylene or nylon are becoming common e.g. Hy-Bar produced by BP uses LLDPE and Capran Oxyshield produced by Allied Signals uses BO Nylon 6. This outside surface material is chosen to provide additional properties to the completed structure, such as low gas permeability, puncture or tear resistance or printability. In the simplest laminated structure using aluminium foil as the water vapour barrier, an outer layer of oriented polypropylene or nylon protects the metal layer from being stretched or broken and further serves to decrease permeability to oxygen, nitrogen, and carbon dioxide. In more complex structures layers are adhered together to build up multi-layer laminates with separate gas and moisture barriers, structural support and protection and heat sealable layers.

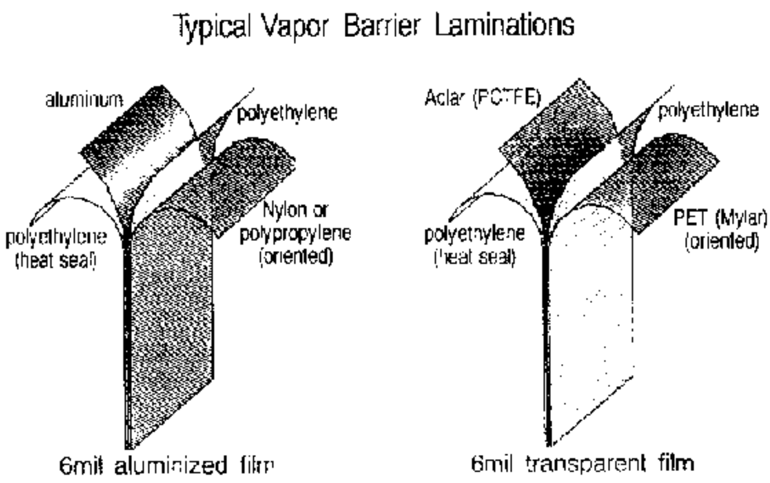


FIG. 1 STRUCTURE OF BARRIER FILMS (FROM BURKE 1990)

Commonly one or more of the outer layers has been "oriented" by stretching and annealing. . Polymers that undergone this process are normally referred to as being uniaxial, biaxial or linear. This "drawing" process aligns the random molecular bundles into a tighter, more crystalline arrangement and makes the film both tougher and less permeable to atmospheric gases. Films that have been stretched in two perpendicular directions are called "biaxially oriented" and are the most efficient barriers to atmospheric gases, as well as being exceptionally resistant to stretching, puncturing or tearing.

4.0 BARRIER FILMS AND OXYGEN SCAVENGERS

By sealing up the bags, as in a crisp or juice packet, enclosing a controlled or set environment we can establish micro-environments that can help to reduce the rates of deterioration for specimens. If nothing is sealed into that environment then the environment will slowly equilibrate to that of the outside at a rate dictated by the characteristics of the barrier film. By buffering the environment in some way we can prolong the environment in the bag. However we are now exploring more fully the potential for developing specialist barrier films. The production of these is however dependant on their commercial viability.

There are several methods of controlling and removing the oxygen from the bag. These are generally nitrogen flushing and oxygen removal either through chemical or physical methods. Finally it is no use having clear bags with alleged oxygen free environments inside them if we cannot monitor the oxygen levels. This needs to be undertaken as simply and cheaply as possible. The current system used for monitoring oxygen levels inside anoxic enclosures are ‘Ageless Eyes’ that are produced by Mitsubishi Gas Chemicals Ltd.

5.0 OXYGEN FREE ENVIRONMENTS

When used in association with an oxygen scavenger and a relatively low cost oxygen monitor we can establish a monitored, low cost oxygen free environment. These will help us to reduce the rates of deterioration in much of our unstable material and help us to reduce the amount of interventive treatment that we need to undertake on specimens.

6.0 PEST CONTROL

Besides their use as barrier films around low quality storage materials much of the early use of barrier films has been to build enclosure for Pest Control. Their use has been reported widely. Either through extracting the oxygen using a system such as the ‘Veloxy™’ system, flushing with controlled humidified nitrogen or through using Oxygen scavengers (or a combination of all three) oxygen levels below 0.01% can be maintained for short periods. These can be maintained by continuous flushing or by using oxygen scavengers. The barrier films that have been used have mainly been EVOH based films that have low to middling migration rates (1-4 ml $O_2/m^2/24$ hr), but would require higher amounts of buffering for use over longer periods. The demands of pest control do not stretch their short-term designs of the laminates and for short periods of up to 8 months they can provide stable enclosures with minimal buffering.

7.0 LONG TERM OR SHORT TERM STORAGE

Long-term storage will depend on the stability of the laminates and an ability to buffer the environments within these enclosures over a long period of time! The attraction of using stable, low transmission rate, barrier films and efficient oxygen scavengers is that they are low cost and low maintenance over long periods of time!

Horie (1987) lists specific properties and requirements of a polymer that can be used in conservation. While these are aimed at applications as resins and lacquers some criteria can be applied to the polymers which we are assessing in barrier films. These must be applied to any polymers that come into contact with materials, to prevent contamination and deterioration of the specimens and to also ensure that we don't have to continuously keep monitoring the enclosure.

- Plasticisers should not be used if possible
- Polymers which deteriorate rapidly on ageing by yellowing or oxidation e.g. poly(vinyl chloride, PVC) are not suitable
- Optically the films should not deteriorate

8.0 HEAT SEALABLE LAYER

- Polyethylene (LDPE, LLDPE, MDPE, HDPE),
- ACLAR (PCTFE)
- Polyester (PET)

The vapour barrier is normally sandwiched between two layers of polyethylene. The internal layer is used to (heat) bond the barrier film together melting these two layers together.

Care should be taken to use the correct temperature, pressure and time constants for the particular film that you are trying to bond. They vary greatly and should be checked with your manufacturer. The use of an accurately controlled hot spatula or crimping tool is recommended.

8.1 POLYTHENE (PE) is made from polymerizing ethylene gas. Two forms are made;

LDPE	Low density polyethylene	highly branched
HDPE	High density polyethylene	uniform, closely packed, more crystalline

Polyethylene undergoes photo-oxidation leading to cross-linking, embrittlement and discolouration. The lower the density of the PE, the lower the T_g and therefore the greater the likely hood that it will pick up dirt. Care should be taken to keep materials having PE on their surfaces clean and stored in a dust free environment.

9.0 OXYGEN\WATER VAPOUR BARRIERS

When exploring the stability of these materials commercial information is relatively useless as all commercial information says that ' … our material is the best thing since sliced bread…' or herring, depending on where you come from! There is little comparative published information on oxygen transmission rates for individual polymers, so much of our information is derived from commercial sources on complete laminates that include a particular gas barrier. Figures can vary greatly between similar materials, for instance ACLAR (see below) and TEFLON (water vapour transmission 1.0 gm-mm/m2/24hrs@23C@90%RH O2 transmission rate 0 .55 cc(STP)-mm/m2/24hr-ATM@25C Burke pers. Comm.) and even between barrier films from different suppliers. The grade of a material and associated polymers can also affect its properties to allow water vapour or a gas to migrate through it !

Below we discuss some of the more current oxygen and water vapour barrier films on the market!

- ACLAR (PCTFE)
- SARAN (PVDC)
- Metallized Polyester (METPET),
- EVOH
- TEFLON (PTFE)
- TEDLAR (PFE)
- ESCAL (Ceramic coated PVOH)

9.1 ETHYLENE VINYL ALCOHOL COPOLYMER (EVOH)

Ethylene vinyl alcohol copolymer (EVOH) is a commonly used relatively stable gas barrier polymer that many of the European barrier films, examples of which include, Archipress™, Cryovac BDF 200 and Hy-Bar™ use this as their gas barrier.

As an example transmission rates for Hy-Bar (BP) are:

Oxygen Migration transmission	:	$2\ cm^3/m^2/24$ hr/atm (@23°C, 50% RH)
Water Vapour transmission	:	0.4-0.8 $g//m^2/24$ hr/atm (@23°C, 50% RH)

Materials using EVOH as an oxygen\moisture barrier such as CAPRAN (Allied signals) are hydrophilic, or water-sensitive material. Moisture and water act as plasticizers. The higher the moisture content of the film, the more flexible and rubbery it behaves. The lower the moisture content, the stiffer and tougher it behaves. The level of moisture content in for instance, CAPRAN at time of use is therefore an important criterion for successful performance.

When shipped, films such as CAPRAN barrier films for instance produced by Allied Signals is preconditioned to a moisture level which provides suitable handling characteristics at its time of use. Because of this it is important that after shipping this film is stored in a protective box or covered with the protective wrap in which it is shipped. Dry environments tend to dehydrate these materials. Ideal storage is at 20-25°C and 45% - 55% R.H.

9.2 POLYVINYLIDENE CHLORIDE (PVDC)

O_2 migration rates	0.2 ml/100 sq. in./24 hours
H_2O vapour migration rates	0.5 gm/100 sq. in./24 hours
(for Saran HB 1 mil	

Polyvinylidene chloride is formed by polymerisation of vinylidene chloride. It is unstable to heat and UV degrading in the same way as PVC. PVDC degrades by losing HCl from the chain, producing double bonds. Hence it is not an ideal polymer to be used in a barrier film despite its excellent properties.

9.3 ACLAR (POLY(TRICHLOROFLUOROETHYLENE) PCTFE)

Poly(trichlorofluoroethylene (PCTFE) is similar to Teflon (but has higher migration rates) and has been used widely in US clear barrier films such as Marvelseal 1177 and Bell Fibre's Film O-Rap FR 7750. Aclar is not a good oxygen barrier (7 c.c./100 sq. in./24 hours/atm.), but a good water vapour barrier so must be allied with other materials to bring the migration rates down to an acceptable level.

H_2O vapour migration rates:	0.035 gm/100 sq. in./24 hours
O_2 migration rates	7 ml/100 sq. in./24 hours

Up until the advent of ESCAL™ this sort of figure was considered good for an oxygen barrier film.

9.4 METALLISED FILMS

Metallised films consist of an aluminium oxide rather than an aluminium layer deposited onto polyester. These are more stable than aluminium layers in the long term, but as individual laminates have substantially lower oxygen and water transmission rates (see below). Metallised films tend to be the standard material used to make snack packets etc. such as crisps or cereal bars.

Barrier figures for materials metallised barrier films e.g. Camclear RHB (pers. Comm. G. Chalkley, Rexam Mettalising) are:.

Moisture transmission:	1.0g/m^2/24 hrs at 38°C/90% RH
Oxygen transmission:	1.0cc/m^2/24 hrs at 23°C/50% RH

There are discussions on-going on producing a double laminate of this material which should have much lower migration rates. However as always the production of this material depends on there being enough commercial interest.

In use these materials are water clear (as against the metalic appearance of the thinner aluminised barrier films), and the materials suggest that they will be much more stable than similar materials.

9.5 ESCAL™ CERAMIC COATED POLY VINYL ALCOHOL (PVAL OR PVOH)

ESCAL™ is a ceramic coated poly vinyl alcohol (PVAL). The basic structure for this barrier film is orientated polypropylene (OPP)\Silica deposited PVAL\ LLDPE. No plasticisers are used in ESCAL ™ (Pers. Comm. Kikuko Iwai 1998)

Oxygen migration rates for ESCAL™ are very close to aluminized polythene;

Moisture barrier: 0.01 g/m^2.day @ 25°C 60%RH
Oxygen barrier: 0.05 cc/M^2.day.atm @ 25°C 60%RH

Stunning figures for a clear barrier film.

Little information is available on how silica (ceramic) later is deposited onto the PVAL. However it should be stable dependant on the overall and individual structures. Currently no independent age testing results are available on this material.

The material does have one of the best transmission rates for any clear barrier film currently available on the market. These figures are close to those published for the thicker grades of aluminized polyethylene and make the laminate suitable for use in long term storage projects.

The use of PVAL (or PVOH) is of a little more of a concern. Formed by removal of acetate groups from PVAC and replaced by OH groups by alcoholysis, the reaction does not always go to completion leaving some acetate groups attached (a sort of vinyl alcohol – vinyl acetate copolymer). Full polymerisation of PVAL leads to a polymer which is very stable to UV/Oxygen ageing. However you will get slow chain scission. (Ciabach 1983)

One of the major problems that we have identified for this material is that optically this is very yellow. This has affected the appearance of colour sensitive materials and is therefore an undesirable property.

Structurally the laminate is thicker than others and does appear to suffer from abrasion fairly readily. In some of our tests we have found that very fine scratches that have appeared on the laminate and have cause breakdowns in the controlled environment of the enclosure.

10.0 STRUCTURAL OR PROTECTIVE LAYERS

Structural layer materials are there to strengthen the laminate and to provide protection for more delicate gas barriers. Examples include:

- Polypropylene (PP),
- Oriented Polypropylene (OPP),

- Biaxially Oriented Polypropylene (BOPP),
- Biaxially Oriented Nylon (BON),

10.1 POLYETHYLENE TEREPHTHALATE (PET OR PETP)

Forms of PET such as Mylar are commonly used in conservation and have been recognised as some of the more stable polymers. They are prone to some yellowing and embrittlement. In this context they have slighly lower transmission rates than recognised barrier polymers. In this context they are being used as structural and protective materials, having better tear strength and puncture resistance.

Water Vapour Transmission Rate	2.8gm/100 sq. in./24 hours
Oxygen transmission rate	9c.c./100 sq. in./24 hours/atm

Nylon is also commonly used as a structural material (commonly nylon 66).

10.2 NYLON 66 (N, BON)

Oxygen Transmission Rate	13.1	cc/m ^{2}/day	@ 70°F(25°C)/0%RH
Water Vapour Transmission Rate	388–131	gms/m^2 /day	@100°F(37.0°C)/100%RH

This again provides the laminate with good tear strength and puncture resistance. However these are prone to yellowing and embrittlement with age and probably reduce the long term stability of the barrier film.

11.0 COMPARATIVE TRANSMISSION RATES

Respective transmission rates are shown for different proprietary laminates in the figures below. As you will see they can vary considerably, depending on the guage, types of polymers and mix of polymers used.

11.1 ACCEPTABLE TRANSMISSION RATES

To date gas transmission rates between 1 –4 cc.m^{-2}/24hrs have been seen as being acceptable. These are fine for the short term pest control but can mean migration of an over 100 times as much oxygen per annum into a container as in enclosures designed using glass or more modern laminates such as ESCAL™ . This extra oxygen transmission will be reflected in the amount (and cost of) the oxygen scavenger that has to be used to control the oxygen levels over a set period.

- O^2 1-4 cc.m^{-2}/24hrs
- O^2 0.05 cc.m^{-2}/24hrs

Moisture vapour transmission rates below 1 cc.m^{-2}/24hrs have been industry standards for some time. Most Barrier films are designed with these transmission rates in mind.

- H_2O 0.1-0.05 g. m^{-2}/24hrs

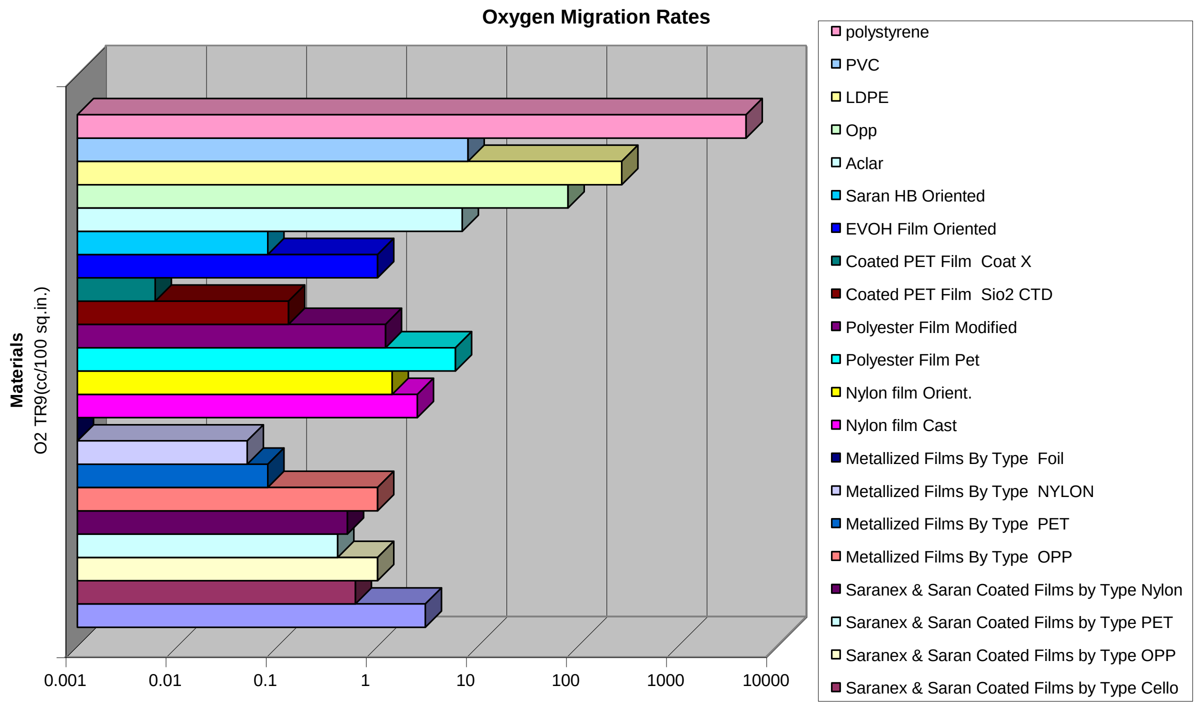


Fig 2. Oxygen transmission for proprietary laminates

Fig 3. Oxygen Migration Rates (Burke 1992)

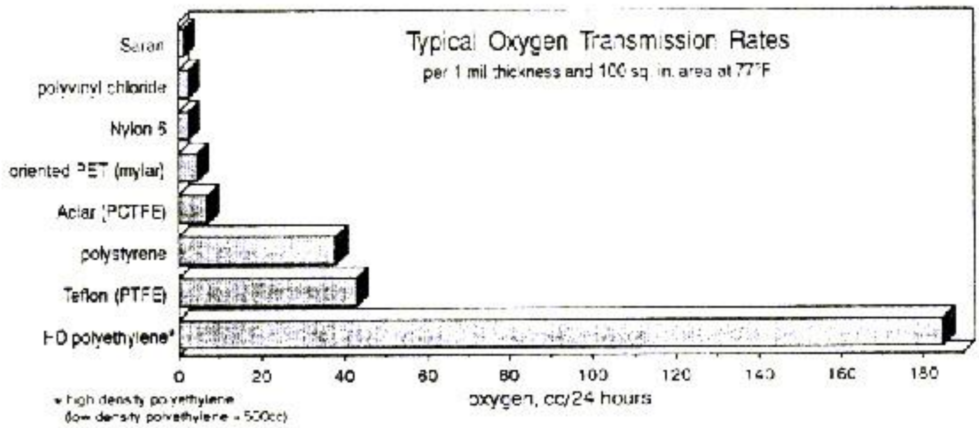
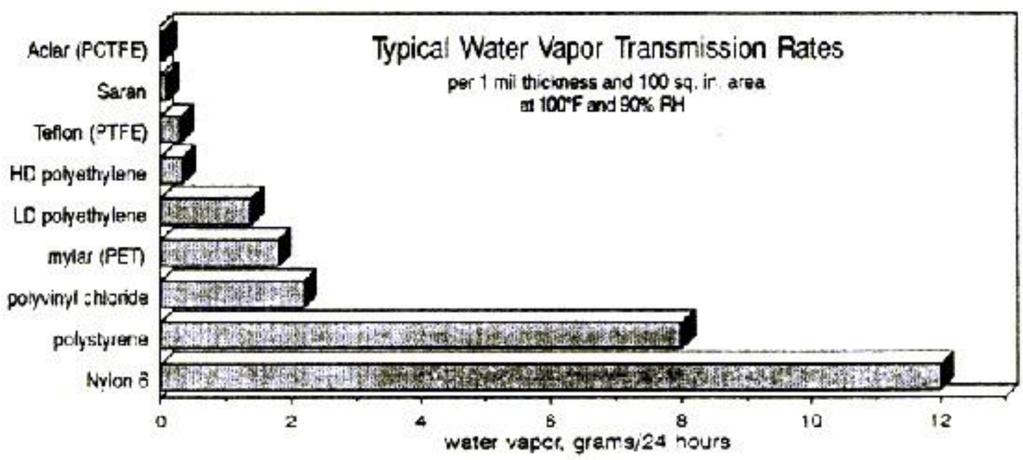


Fig. 4 Moisture vapour migration rates (Burke 1992)



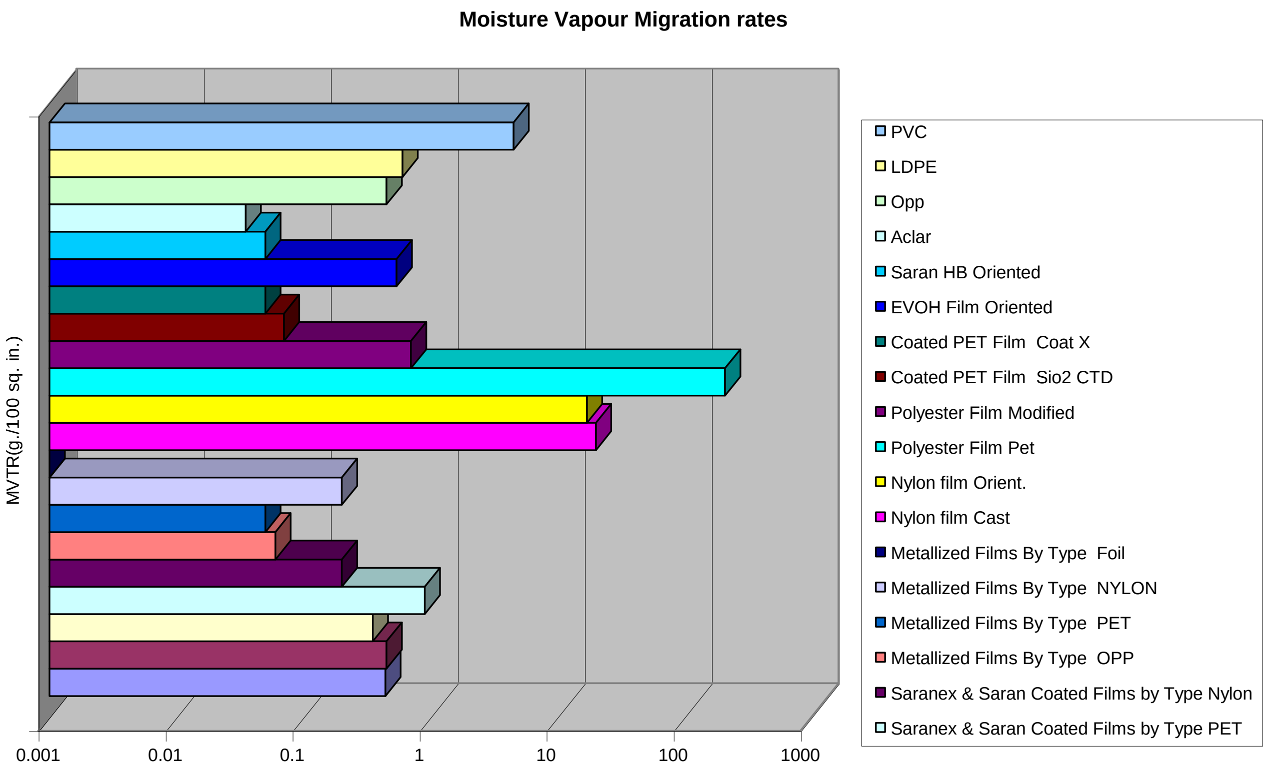


Fig. 5 Water Vapour Transmission Rates

12.0 AFFECTS ON BARRIER FILMS AND DETERIORATION

Because some barrier films especially those based around EVOH (AL), come preconditioned at ambient RH and temperature it is important that they are protected and stored in an RH of around 50% and at about 18°C. Otherwise, they will tend to shrink and their mechanical properties deteriorate (Allied Signals 1999). EVOH and PVOH can also be susceptible to yellowing, and shrinkage related to UV and Photo-deterioration including chain scissioning and crosslinking. Materials such as ACLAR (PCTFE) and SARAN (PVDC) degrade releasing HCl and are therefore, unsuitable for medium to short term storage but may have uses in pest control. Materials using the EVOH gas and moisture barrier can also lose their optical properties (pers. Comm).

All are susceptible to puncture and abrasion, despite the inclusion of polymers that are included to protect and strengthen the laminate (LLDPE, BON etc.). In our tests this has been the major problem with barrier films, especially this on open storage, or subject to higher pollution levels.

Current work in our unit is looking at the affect of off-gassing from specimens (H_2S, SO_x etc.) on the stability of barrier films and the affect on geological specimens stored in these unusual environments.

12.1 DETERIORATION OF BARRIER FILMS

- Pollutants
- UV
- Light
- Oxidation
- Relative Humidity
- Physical Abrasion

12.2 AFFECTS ON BARRIER FILMS FROM SPECIMENS

The affects of off-gassing from specimens has not been investigated however it is proposed that off-gassing could affect the barrier films. Investigations are currently underway on this.

- Off-gassing by specimens
  - H_2S
  - SO_x
  - H_2O

12.3 Physical Deterioration

Abrasion and puncturing are major causes of deterioration of the barrier films. This is caused both internally by specimens and storage materials and externally by storage drawers\trays and particulate pollutants.

12.4 Affects on specimens

There is no clear evidence that these barrier films have any affect on specimens stored inside them or in oxygen (anoxic) free environments. There is some anecdotal evidence of colour instability in some pigments stored in anoxic environments. Barrier films containing PCTFE and PVDC are potentially hazardous for specimens held in enclosures made of barrier films containing these polymers as they deteriorate releasing HCl into the enclosure – undesirable !

13.0 What do we want ?

We want a clear flexible laminate that we can adapt and build into different sized enclosures. It is important that the laminates that we use do not age and deteriorate to release chemicals into the enclosure or yellow to reduce the optical properties of the barrier film. They should be easy to heat seal. Importantly they should be resistant to abrasion and puncturing. They should be low cost and low maintenance.

14.0 Solutions

At the moment the commercial barrier film with the best transmission figures is probably ESCAL™ . The laminate is however very yellow so where optical properties are important this is not necessarily desirable. The use of PVOH as a substrate for the deposition of the silica (ceramic) barrier film must also be questioned. The potential developments in double layer metallised barrier films could answer some of the problems. If the theoretical transmission rates for these can be confirmed in practice then they should prove suitable for building long term storage environments for specimens. For sealed systems in use with high-grade seals and glass they may already provide a solution to long term storage problems. Systems that rely on polyester being bonded rather than polyethylene should be even more stable.

In some instances glass containers sealed with bituminous sealants such as Shell Tixophalte may be a less flexible long-term solution to certain problems, particularly in display. In practice they have been age tested and proved stable over tens if not hundreds of years (A.J. van Damme 1999). This solution may be appropriate for certain materials.

For short-term treatments such as pest control then the EVOH barrier films seem to provide a stable alternative. For longer term use their long term stability must be questioned.

In terms of research we are currently investigating the affects of specimens and oxygen free environments on specimens and barrier films alike. We are also trying to establish relationships with companies in Europe involved with the development of barrier film technology with a view to developing suitable barrier films that comply with conservation standards

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