Packaging as it Relates to Core Storage and Preservation

What follows is an attempt to synthesize current information from a wide variety of sources into a useful guide to methods of core storage and preservation. It must be stressed that the focus of the packaging industry is twofold. The first is the relatively short term preservation of, mostly, food and medical products. The second is packaging for protection and display purposes. Clearly, neither of these industries address the specific needs and requirements of IODP, so we must be creative and eclectic in our selection of the most suitable products for our application. Moreover, we must be actively involved in the research, testing and development of new products and methods by partnership/involvement with other institutions, so that IODP can be at the forefront of this technology as befits our ethos.

Section 1 - Vacuum Packaging

Vacuum packing (or vacuum sealing) is a form of packaging that involves the removal of air (and sometimes its replacement) from a pouch or plastic container. Vacuum packaging provides several benefits: protection against dehydration; barrier against air or moisture; tamper evident protection; compressed packaging for fragmented cores; protection from dust and moisture.

Types of Vacuum Sealing Equipment

Non Chamber Vacuum Sealers

These units vacuum and seal the pouches externally. Some units also come equipped with special external nozzles to allow for the vacuum packaging using plastic containers. Non Chamber Vacuum sealers are meant for low volumes, and are suitable for vacuum sealing products that have little or no moisture. However some units do have special collectors for products that have excess moisture. Not recommended for vacuum sealing liquids, or powdered products.

Chamber Vacuum Sealers

Chamber Vacuum Sealers are designed for sealing higher volumes of products than their non chamber counterparts. The vacuum pouches are placed within a box-like chamber, the desired amount of air is pulled from the machine, and the pouch is then sealed. Some chamber vacuum sealers have the option of gas flush kits.

Chamber vacuum sealers are an economical solution for high volume vacuum applications because the vacuum pouches are more economical than the micro layered pouches used in non chamber sealers. Additionally, chamber vacuum sealers can seal a wider variety of vacuum pouches and bags. Units must include an oil-based vacuum pump. This type of equipment is commonly used in the food packaging industry to pack meats, fish, and dried products.

Required Maintenance

Chamber Vacuum Sealers require routine maintenance. The vacuum pumps are oil-based, so the vacuum oil needs to be changed regularly. Additionally, since these units use an impulse mechanism to heat seal the pouches, Teflon tape and seal wires also need periodic replacement.

Vacuum Sealer options

MAP, Modified Atmosphere Packaging

MAP is a packaging method in which an altered atmosphere inside a package is used to retard chemical deterioration of the product, and the growth of unwanted microorganisms. Vacuum packaging itself (i.e. the removal of air) is a form of MAP. However, the most familiar usage of the term describes the creation of an artificial atmosphere of mixed gases inside a package. Such a method is usually used in conjunction with a non-barrier type film, in order to let the food product respire naturally. An Inert Gas Kit or Gas Flush Kit, is required for vacuum sealers to allow the user to modify the atmosphere within their vacuum pouches. Inert gas is injected into the package allowing the package to obtain a 'pillow effect' or a packaging of the product without the tight rigidity that may destroy or compromise the product.

Seal Bar Options

Most Chamber Vacuum Sealers come with a seal bar consisting of one 4mm seal wire and a trimmer wire. However, other seal configurations may be available including: Double seal: one bar with two 4mm seal wires; Wide seal: One bar with 6mm bar.

Vacuum Pouches

Also known as food vacuum pouches or barrier pouches, provide a barrier against atmosphere and moisture.

Vacuum Pouches for Non-Chamber Machines

These pouches are designed specifically for machines that perform an external vacuum. The micro layered vacuum bags are made from food grade plastic material. Each pouch consists of 3 layers of construction:

Two smooth outer layers of 3mil polyamide (nylon)-polyethylene barrier material and one polyethylene mesh layer of material in the middle of the pouch. The mesh middle layer is the most important component of the pouch. It allows the air inside the pouch to be directly vacuumed out of the pouch.

Vacuum Pouches for Chamber Machines

These pouches consist of two smooth layers of 3mil polyamide (nylon)-polyethylene barrier material. 3mil is the most common thickness for vacuum pouches in the industry and meets USDA standards for food packaging. These pouches do not have a layer of mesh, since the chamber vacuum machines will evacuate the air once the pouch is within the chamber.

Other Types of Vacuum Pouches

There are other special vacuum pouches including light barrier bags, boilable vacuum pouches, and bone guard pouches that are commercially available.

Vacuum Containers

These high barrier, and durable plastic containers are an excellent choice when the application requires a durable vacuum storage.

Case Studies

1. Maplewood Meats;

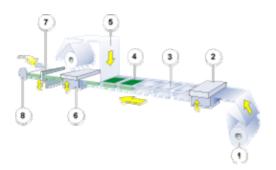
- slow speed of conventional vacuum packaging
- problems with seals
- introduces the process of thermoforming

Maplewood originally utilized a vacuum chamber system to package its savory products. The system required that company personnel place portion-sized meats into a preformed pouch and then accurately place the pouch on the machine to be vacuum-sealed and trimmed. The process was time-consuming, and the system would sometimes produce leaky packages, necessitating that the production cycle be repeated. "If you combined the amount of time it took us to package our products the first time, and then add in the time for repackaging the faulty ones, the system was extremely time and labor intensive," says Van Hemelryk the CEO.

Maplewood spends a great deal of time focusing on the quality of its products, and the company did not feel the original system was producing a package that did justice to the product inside. The company decided to partner with Multivac to formulate a new strategy that would heighten the efficiency of its operation as well as the quality and attractiveness of its packages. Upon assessing the company's needs and current operation, Multivac's food packaging team recommended using a compact, rollstock system.

Rollstock Machines

Thermoformed packs are produced on rollstock machines automatically by sealing the formable lower web to an upper web. Product is loaded manually or automatically into the pocket or transformed on the lower web before sealing to the upper web takes place.



- 1. Packaging material for the base web (thermoformable film) is unwound from the reel.
- 2. It is heated in the forming die and formed into pockets/trays.
- 3./4. The formed pockets are loaded manually or automatically
- 5. The top web of packaging material (lid film) covers the filled pockets/trays.
- 6 The air is evacuated from the sealing die and protective gas is added if required. Then the pack is sealed by the application of heat and pressure.
- 7. The web of packs is cut across the machine direction initially.
- 8. Production of the individual packs has been completed after the longitudinal cutting operation.

Within days of the integration, Maplewood noticed a considerable difference in its packaging. Product is easily loaded into customized compartments that are formed from a bottom web of roll-fed, flexible film that is heated and stamped. Then the machine's top web securely seals each package in-line.

With its new automated thermoforming technology, Maplewood has dramatically simplified its packaging process, boosted productivity and eliminated the problem with leakers. "We are now packaging the same amount of product in three hours that would normally have taken a full nine- to ten-hour cycle," remarks Roger Van Hemelryk. "Our production speed has increased by 200 percent."



Plates, compartment sizes and films can be changed over in as little as ten minutes.

Simplifying this process has also helped Maplewood move forward with its food-safety initiatives. By quickly placing product into the thermoformed sections, the amount of time the meat needs to be handled is minimized, and any opportunity for product to come into contact with machine components is eliminated. "I worry less about contamination because of the machine's engineering. The stainless-steel, washdown design really gives us peace of mind," says Roger Van Hemelryk.

The new system has also afforded Maplewood greater operational flexibility. With the company's expansive product line, it often needs to package more than one type of meat over the course of a production day. The quick and easy changeover procedure on the rollstock system enables plant personnel to change the plates, compartment sizes and appropriate films in roughly 10 minutes. Depending on the day, this switching can occur multiple times, making the simplicity of the changeover feature essential to minimizing downtime.

The integration was not only beneficial to Maplewood, but also to its customers. The speed and accuracy of the new rollstock machine allows the company to sell a more compact and convenient package. To outweigh the material costs and time it took with the previous process, the company used to portion its products in 1-lb assortments to reach its cost-per-unit target. "The new system efficiently utilizes the packaging material so we can offer our customers more convenient half-pound portions," notes Van Hemelryk. "Customers appreciate the added value of our smaller packages."

- 2. Food sell-by dates criticized;
 - Temporal limitations on Shelf Life (2 years on vacuum packed goods)

• Long term sell-by dates on some packaged foods are not justified, research has suggested.

Olives with a claimed shelf-life of up to three years can be "unacceptable" to eat long before, agricultural researchers in Greece found.

They said the move towards plastic packaging has led to some "arbitrary" sell by dates. Food manufacturers said standards were high and firms were complying with guidelines and regulations.

About 10 million tonnes of olives are consumed worldwide each year, most of which are produced in Europe.

Suggested shelf-life for olives

Packed in air - nine months Packed in a "modified atmosphere" - 15 months Vacuum-packed - 23 months

There is a growing trend towards using polyethylene pouches which are either vacuumpacked, filled with brine, air, or packed in a combination of gases.

The study, published in the Journal of the Science of Food and Agriculture, suggested only vacuum pouches could justify a claim to a shelf-life of almost two years, while olives packed in air were only good for nine months.

Olives in Greece were tested over a six-month period for micro-organisms, acidity, color and firmness.

Smell

A ten-member panel then rated the product on smell, taste, and general acceptability. No harmful bacteria were found in any of the olives but the overall quality was found to be "unacceptable" in the air-packed olives and those in a "modified atmosphere" of 40% carbon dioxide, 30% nitrogen and 30% oxygen.

Those in brine were found to be of "medium acceptability".

Dr Efstathios Panagou, of the National Agricultural Research Foundation in Athens, led the research.

He said: "The shelf-life of these products is not yet clearly defined, although the majority of Greek industries state a shelf-life of two to three years on the labels based on the fact that olives are a fermented product of high quality.

"However, this period is quite arbitrary and is not supported by relevant studies." The National Food Processors Association (NFPA) in the US said it was the

manufacturer's responsibility to determine the shelf life of their product.

Whether the researchers' findings agreed with the claims of the manufacturers "would depend on the storage conditions they used," said Allen Matthys, vice-president for federal and state regulations at the NFPA.

Regulators would be keeping a check on the shelf-life claimed by the manufacturers and would intervene if they were not correct, Mr Matthys added.

Information

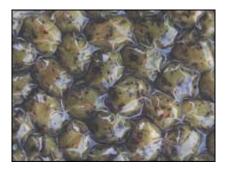
A spokeswoman for the Food and Drink Federation in the UK said it had information on short-term chilled foods which were vacuum packed (VP) or modified atmosphere products (MAP), but not on those with a long shelf-life.

However, she added: "In general, for a longer shelf-life, products will need to meet specific controlling factors or manufacturers will need to undertake a risk assessment to determine the maximum safe shelf-life.

"The food and drink manufacturing industry has maintained an excellent safety record in respect of VP and MAP chilled foods and is satisfied with the current industry code of practice."

The UK's Food Standards Agency said a "use by" or "best before" date was a legal requirement but shops and manufacturers could decide whether to add a "sell by" or "display until" date.

A spokeswoman added: "The sell by date is more for quality, it is the use by date that is more important as it refers to the safety of the food."



3. Vacuum-Packing and its Implications for Library, Archive, and Related Materials;

• concerns about the possibility of desiccation

Last year a new method of drying wet books was used on seventy leather-bound books that had been damaged by water and mold from a leaking drainpipe in the Fitzwilliam Museum in Cambridge, England. Some of the books had been seriously weakened, so a staff member looked for a drying method that would be gentler than freeze drying, and decided to use one that Stuart Welch had been experimenting with, vacuum packing with absorbent materials. For comparison, he sent some books for freeze-drying. Welch's method allowed nearly half of the books to be returned to the shelf after three or four days of drying, cleaning and stabilizing. The leather did not shrink off the cover boards, the boards did not become distorted, and the thread did not pull through the wet paper.

The rest of the volumes required either minimal paper conservation and board reattachment, or, for the most deteriorated volumes, boxing without immediate treatment. The authors describe the procedure: books are vacuum-packed individually in plastic, with blotting paper or other desiccant which is changed periodically. Modern books with coated paper can be inspected briefly at these times to see if the pages are blocking; if so, pages can be easily separated. A number of tests were done to confirm that this method does prevent blocking of coated paper. [One is reminded of the method used by volunteers for drying books by hand after the St. Petersburg fire--wrapping them in a blanket or something similar, with plenty of dry sawdust.]

Conservation by Design Ltd. says, "Vacuum sealed wet objects quickly transfer moisture to any dry absorbent material such as blotting paper, until they reach an equilibrium. At this stage the bag is opened, the wet blotter replaced by dry blotter and the bag sealed again. This process is repeated until the object, book etc. is dry.... Because the wet object is held in an oxygen free package no mould grows and the vacuum holds the object's shape while drying." The web site is <u>http://www.conservation-by-design.co.uk/</u>.

Observations

Vacuum Pouches

- Are time and labor intensive
- Risk smearing core when inserting into pouch
- Pouch side seals are large and will make for difficult core storage
- Every time a core is sampled a new pouch will be required

Chamber Sealers

• Are not commercially available with the size of chamber that core sections would require.

Unsuitable Lithologies for Vacuum Packaging

- Muds, sediments with any moisture content.
- Sands, friable rocks, any rock type with a week matrix

Suitable Lithologies for Vacuum Packaging

• Rocks and hard sediments where it is desirable to store them in an anoxic environment to reduce the possibility of oxidation.

Discussion

Neither vacuum pouches, nor Chamber Sealers offer an off the shelf solutions to meet all our core storage needs. Most of IODP's cores have a high moisture content which makes vacuum sealing an unsuitable method of preservation. However, vacuum packaging does offer significant benefits in terms of the preservation of specialty cores where a modified atmosphere is required. Oxygen scrubbers can be incorporated into packages, the atmosphere inside the package can either be flushed with inert gas, or fully evacuated. The question raised is; does modifying the atmosphere and storing cores long term at well below atmospheric pressure have any long term effects on the physical and geochemical properties of the cores? This requires further investigation.

As we can see from the Maplewood case study, Thermoforming is a relatively new technology that may offer distinct advantages for core preservation.

Section 2 - Shrink Wrapping

Shrink wrapping is a particularly well-established form of packaging that has developed over the past four to five decades. Essentially, material is produced such that molecules are stretched as part of the manufacturing process. When this material is subjected to heat, the elastic memory of the plastic is activated, causing the material to shrink around the product. The type of shrink film to be used is determined by the type of equipment used and by the needs of the customer.

L-bar Sealer

The most popular wrapping and sealing machine is the "L" bar sealer. The name derives from the fact that the sealing bar is in the shape of a backward "L". The L-Bar sealer

trims and seals the film with each down stroke or cycle of the sealing bar. By using a center folded film, side seals of the package are simultaneously formed, producing a fully sealed individual bag around each product - ready to be heated and shrink-wrapped. The sealer allows continuous production of wrapped packs that are then processed through a shrink tunnel. L sealers are found in a variety of forms – manual, semi and fully automatic. A large part of the manual and semi automatic market has been taken by combined seal and shrink machinery. These machines are commonly referred to as chamber machines. Fully automatic L sealers have found increasing use as their cost and versatility have improved.

Applying heat

The most common method of applying heat is a hot air circulating chamber, with a conveyor to move the product, otherwise known as the heat tunnel. Products travel through the tunnel, and are exposed to heat for only a few seconds. While traveling through the tunnel, shrinkage occurs. Since this only takes a few seconds, only the shrink film will be affected by the heat, not the product. Occasionally heat guns are used for applying heat and shrinkage.

Side Seal Wrappers

The highest output speeds are offered by flow wrappers using side seal or overlap mechanisms. The conventional L-bar is replaced with a side seal wheel and a seal bar. The seal bar is activated by a light sensor when the products leading edge is detected. Once the bar has made the seal, the product automatically advances on a conveyor while at the same time the seal wheel is sealing and trimming the sides of the film. Once the optical sensor detects the end of the package the bar seals and cuts the trailing edge. The product is then free to advance on a conveyor through the heat tunnel.

Maintenance

L-bar sealers are relatively simple in construction and require little maintenance other than the periodic replacement of sealing wire and tape. Side Seal machinery is more complex and requires some technical knowledge and ability on the part of the user to keep it running smoothly. Seal bars and side seal wheels need periodic replacement and are not inexpensive. However, this is leading edge technology and the future will provide modular units that are more reliable, and more easily maintained.

Case Study

ODP/IODP Experience

In 2003 IODP purchased a used L-bar sealer and heat shrink tunnel. The objective was to move away from the labor intensive method of hand wrapping cores, to a speedier more automated process. At the same time, the film we chose to use with the machine offered superior barrier properties in terms of oxygen and water vapor transmission rates. The

actual unit cost to wrap each section was roughly the same for either method; hand or shrink wrapping.

Plastic Wrap Properties	Glad Wrap	Cryovac BDF-2001	Cryovac BDF-2001
Thickness	~0.5	0.75 mil	1 mil
Water Vapor Transmission Rate (gm/day/100 in ²)	1-3	1	0.75
Oxygen Transmission Rate (cc/day/m ²)	400-1000	5.7	4.2
Composition	Polyethylene w/vegoil derivative	,	multilayered polyethylene w/interior laminate layer

The unit we acquired was basic and had little in the way of technological features. The Lbar was raised and lowered by hand, so efficient operation usually required three people; one to load core, one to operate the sealing bar, and one to collect the wrapped and processed core. Even though the L-bar was counter balanced, operator fatigue was a problem and, after hours of sustained usage, sore shoulders were reported with some regularity. However, the machine was successful in achieving its objectives; it increased productivity dramatically, and gave us a much better end product.

The L-bar sealer we purchased allowed us to incorporate industrial packaging technology onto our operations, at a nominal cost (\$4,800), and evaluate the technology for our specific needs. The machine we purchased was used (@20yrs old), and did not represent the latest technology in the packaging industry. Therefore the decision was made to purchase a new shrink packaging system especially tailored for IODPs' requirements. In October of 2005 we took delivery of a TPA Model 3000I Automatic Intermittent Motion Side Seal Wrapper and Eastey Model ET 1608 Heat Tunnel. This machine is fully automatic, and does not require anyone to operate a sealing bar. The same operator can load and retrieve the product making 1-man operation possible. The rate-determining step with the L-bar sealer was how quickly one could operate the bar sealer. With the side seal machine, pacing is set by the rate that cores can be fed through, and removed from, the machine.

Although technologically more advanced the automatic sealer fell short of our performance goals. When operating and running smoothly, it is an excellent piece of equipment. However, the initial fit and finish of the machine was very poor leading to numerous breakages and delays. Replacement of consumable parts requires the removal of intricate mechanisms. This requires that a skilled person be available in order to maintain and trouble shoot the equipment.

Observations

Shrink packaging has been used with great success in the wrapping and preservation of cores at the Gulf Coast Repository. For the bulk of the cores recovered by the JR that have significant moisture content, or are weekly bound, shrink packaging has obvious benefits over vacuum packaging. It is also a much quicker and cleaner method. However,

vacuum packaging has its niche in IODPs operations. For specialized cores requiring modified atmospheric packaging, or the complete removal of air, vacuum sealing is an excellent solution.

Section 3 – Film Materials

There often are long, and pointless, discussions about the various definitions contained in the terms of "films" versus "sheet", and the not completely consistent dividing lines between flexible, semi rigid, or semi flexible, and rigid.

In common use, films are planar forms of plastics that may be thick enough to be selfsupporting, but thin enough to be flexed, folded or creased without cracking. The dividing line between film and sheet is sometimes given as:

2 to $200 \,\mu\text{m}$, flexible

200 to 400 μ m, semi rigid, or semi flexible Over 400 μ m, rigid.

A Note on Chemistry

(Excerpt from "A Guide to Polyolefin Film Extrusion", Equistar Chemicals, LP (Formerly Quantum Chemical Corp.)

Polyolefins Are Thermoplastics Derived From Petrochemicals

Polyolefins are plastic resins polymerized from petroleum-based gases. The two principal gases are ethylene and propylene. Ethylene is the principal raw material for making polyethylene (PE) and ethylene copolymer resins; and propylene is the main ingredient for making polypropylene (PP) and propylene copolymer resins.

Molecular Structure and Composition Affect Properties and Processability Three basic molecular properties affect most of the properties essential to high quality film extrusion:

average molecular weight

molecular weight distribution

crystallinity or density.

These molecular properties are determined by the materials used to produce the Polyolefins and the conditions under which they are manufactured.

Density

Polyolefin resins have a mixture of crystalline and amorphous areas. Molecular chains in crystalline areas are arranged somewhat parallel to each other. In amorphous areas, they are randomly arranged. This mixture of crystalline and amorphous regions is essential to the formation of good film products. A totally amorphous polyolefin would be rubber-like and have poor physical properties; a totally crystalline polymer would be very hard and brittle.

For homopolymer polyethylenes, the higher the resin density, the higher the degree of crystallinity. High density PE resins (HDPE) have molecular chains with comparatively few side chain branches. This allows the chains to pack more closely together. The result is crystallinity up to 85%. Low density PE resins (LDPE) generally have crystallinity from 35 to 55%. Linear low density PE (LLDPE) resins have crystallinity from 35 to 60%. Polypropylene resins are highly crystalline, but they are not very dense.

LLDPE resins' densities range from 0.900 to 0.939 grams per cubic centimeter (g/cm3) LDPE resins range from 0.916 to 0.925 g/cm3

MDPE (medium density) resins range from 0.926-0.940 g/cm3

HDPE resins range from 0.941 to 0.965 g/cm3

PP resins range from 0.890 to 0.905 g/cm3

EVA copolymers' densities are functions of the proportion of comonomer incorporated into the resin; as comonomer increases, density increases, but crystallinity decreases. Higher density, in turn, influences numerous properties. With increasing density, some properties increase. However, increased density also results in a reduction of some properties, e.g., stress cracking resistance and low temperature toughness.

Molecular Weight

Atoms of different elements, such as carbon, hydrogen, etc., have different atomic weights. For carbon, the atomic weight is 12, and for hydrogen it is 1. Thus, the molecular weight of the ethylene unit, is the sum of the weight of its six atoms (2 carbon + 4 hydrogen) or 28.

Every polyolefin resin consists of a mixture of large and small chains, i.e., chains of high and low molecular weights. The molecular weight of the polymer chain generally is in the thousands. The average of these is called, quite appropriately, the average molecular weight.

As average molecular weight increases, resin toughness increases. The same holds true for tensile strength and environmental stress cracking resistance (cracking brought on when film is subjected to stresses in the presence of liquids such as solvents, oils, detergents, etc.)

Melt Viscosity

Melt viscosity generally is expressed for polyethylene resins by their melt indices (tested under standard conditions of temperature and pressure). Melt index (MI) is inversely related to the resin's average molecular weight; as average molecular weight increases, MI decreases. Generally, a polyolefin resin with high molecular weight has a low MI, and vice versa.

Molecular Weight Distribution

The relative distribution of large, medium and small molecular chains in a polyolefin resin is important to its properties. When the distribution consists of chains close to the average length, the resin is said to have a "narrow molecular weight distribution". "Broad molecular weight distribution" Polyolefins are those resins with a wider variety of chain lengths. In general, resins with narrow molecular weight distributions have greater stress cracking resistance and better optical properties. Resins with broad molecular weight distributions generally have greater impact strength and greater ease of processing.

Comonomers

Polyolefins made with one basic type of monomer are called homopolymers. There are, however, many Polyolefins which consist of two or more monomers -- each called a comonomer -- and these combinations are called copolymers. Many film extrusion grades of LLDPE, LDPE, HDPE and PP are made with Comonomers. These side chain groups provide specific property improvements.

The Comonomers used most often with LLDPE and HDPE are collectively called alpha olefins. They include butene, hexene and others. Other Comonomers used with ethylene to make EMA copolymers, and VA to produce EVA copolymers.

The addition of small amounts of VA to polyethylene results in a resin which extrudes similarly to a polyethylene homopolymer but has the additional properties of increased toughness, lower stiffness and potentially higher clarity. A wide range of properties is possible, depending upon the proportion of VA incorporated and the synthesis conditions used to make the modified resins.

Modifiers, Additives and Tie-Layers

Numerous chemical modifiers and additives are compounded with polyolefin film extrusion resins. In some grades, the chemical modifiers are added during resin manufacture. These include thermal stabilizers, anti-static agents and slip/anti-block agents.

A Note on Shrink Films and Fumes

Some years ago, the conventional film used for shrink wrapping was PVC – polyvinylchloride with plasticizer; an amorphous crystalline structure. PVC has largely been replaced by polyolefin shrink film although PVC continues to be offered. PVC has particular benefits in that it is the easiest of any films to seal and shrink but it suffers from problems on sealing, whilst it also has strength and storage issues. PVC's sealing temperature is very close to its degradation temperature at which a number of by-products are created. These include very small quantities of hydrogen chloride gas and carbon deposits on the sealer. The HCL may be dealt with through ventilation. All materials should be used with regard to good safety practices and therefore polyolefin films also require ventilation in the same way.

Carbon deposits require regular removal, whilst the presence of HCL will give rise to a need for regular maintenance of the sealer. As polyolefin's have no chlorine, this does not arise with their use.

The plasticizer in PVC will harden in cold conditions and soften in hot conditions and this may well cause strength problems in cold weather and equally machineability problems in hot. Again, as polyolefin material has no plasticizer, these are not issues where this film is concerned. PVC requires storage at normal room temperature, failing which, it is likely to start to shrink. Polyolefin will tolerate higher storage temperatures.

Polyolefin films offer a variety of attributes so that a very large range of applications can be made. In general, these are not found in food applications, although polyolefin is used in certain applications notably pizza and egg wrapping as well as produce packaging. However, a more precise definition might be that polyolefin is not used to extend the shelf life of a food product unless a shrink barrier film is used. Display applications for polyolefin have almost no limits as materials have been engineered to deal with any given requirement. At a more specialized level, slip and anti-fog treatments are also available. There are a few notable ranges of polyolefin shrink film that offer better machineability and performance than the majority of the market and these are particularly distinguished by technical differentiation in manufacturing. These lead to irradiated grades which offer enhanced strength and multi-layer complexes that may be tailored to a particular requirement. Polyolefin manufacture typically uses three or five layer extrusion and this confers performance benefits as a consequence.

Multilayer Films, definitions

There are innumerable constructions for multilayers, many that seem practically custom designed for their specific use. Plastics can be most easily associated with traditional materials, boosting overall performance to fit almost all packaging needs. Multilayers may be all plastics films, or include paper, board, and aluminum foil.

The requirements for the selection of multi-layers are machinability, speed, strength, functions, barrier, and protection. The idea is that the price/performance ratio is better achieved with the synergy of the layers than with a single material.

Simply put, the basic, most frequent structure of multilayer films is made of three basic types of components:

- 1. An outer layer, to provide protection against abrasion and scratches during processing and packaging operations. It must be printable, direct or reverse, and resistant to temperatures required to melt the sealant.
- 2. The middle layer provides the barrier to gas permeation. It may be ethylene vinyl alcohol (EVOH) or polyvinylidene chloride (or Saran film, PVDC) and others. In the case of EVOH used with polyolefins, there must be a tie-layer between the polyolefins and EVOH.
- 3. The inner layer provides a hermetic seal by melting at selected temperatures. The most used sealants are PE, ethylene-vinyl acetate (EVA), and ionomers.

To put some order into the many types of multilayers, a description is often used to define the type of multilayers. The various layers are defined by letters, to describe the symmetrical or non symmetrical type of construction. For instance five layers will commonly be defined as:

ABCBD, like PE-LLD/tie/PA/tie/PE-LD, or another order of letters, showing asymmetrical structures.

The multilayer construction concept is applicable to flexible films, sealable into bags and pouches, to rigid sheet, thermoformable into trays, dishes and cups, and to blow molded containers.

Multilayer constructions of films and sheet aim at combining a number of properties, each particular to the various layers used, to arrive at a set of performances which could not be obtained by any of the composing materials used alone. A better barrier is insured because of the interface between possible defects of each single layer. Better mechanical properties can also be obtained.

Multilayer construction of films and sheet can be obtained by a number of processes: Lamination or adhesive lamination

Coextrusion

Extrusion lamination Coating Metallizing Etc.

Barriers, definitions

With the exception of pinhole free aluminum foil, all flexible packs have some level of permeability to oxygen, carbon dioxide and water vapor. Achieving a good moisture barrier is relatively easy for plastics. Barrier to gases is more difficult. It is rarely

economic to use solid single film as barrier, although there are a number of more or less polymer barriers which provide suitable levels of performance for particular situations. The barrier concept really applies to plastics whose performances approach total barrier but never achieve it.

There are a number of barrier materials/processes designed to achieve the best balance of cost/performance for the applications as selected.

The very first barrier materials were aluminum foil, various coated papers and cellophane.

The main polymer-based barrier materials are:

PVDC polyvinylidene chloride

EVOH ethylene vinyl alcohol

Oxide coated films, SiOx, AlOx

LCP - Liquid crystal polymers

Nylon MXD6

PCTFE - polychloro-trifluoroethylene

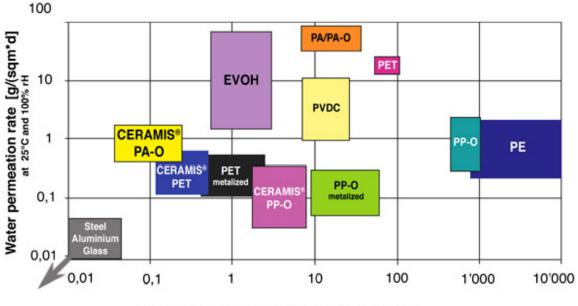
PET/PEN - polyethylene terephthalate/ polyethylene naphthalate

Nano films, latest entrants in barriers

Plasma techniques, so far more for blown containers

And semi barriers such as oriented PA 6 OPA - Polyamide 6 layer biaxial nylon

The diagrams below shows some of the physical properties of various barrier materials.



Oxygen permeation rate [cm3/(sqm*d*bar] at 25°C and 50% rH

	Oxygen Permeability (cc mil / 100 in ² day atm)		
EVOH 29 mol	0.02		
EVOH 44 mol	0.07	PA w/	
PVdC	0.75 +	- Nanoclay	
PA	2.50	2.0 - 0.50	
O-PET	5.00		
HDPE	110		
PP	150		
LDPE	450		
EVA	800		

Oxygen Permeability of Polymers

Lamination, Adhesive Lamination

Lamination is a process that makes multi-layers by taking and putting together different layers of materials, with adhesives and possible association of partial extrusion and coating.

Lamination permits an almost unlimited range of multilayer structures, made of infinite combinations of different and incompatible materials, with almost complete freedom regarding thickness, as long as it is less than 400-500 μ m.

Laminates often offer a gas barrier better than that of coextrusion. Moreover, lamination is the only process that can be used with non plastics materials, aluminum foil and paper.

Coextrusion

Coextrusion is a process of extruding a multi ply structure with several layers of resins in it, through one die simultaneously, so that all the different resins come together as a single integral structure.

This technique permits the use of melt heat to bond the various plastics, or using the center layer as an adhesive. Coextrusion is an economical competitor to conventional laminating processes, as it reduces material handling costs, raw material cost and machine time costs. Pin holing is also reduced with coextrusion, even when it uses one extruder and divides the melt into a two-layer structure. Other advantages are the elimination of delaminating and air entrapment.

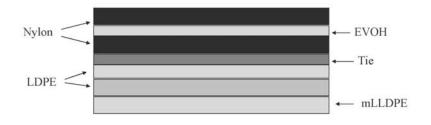
The more recent coextrusion structures, developed in the early 1980s, are generally made of five layers minimum. Most barrier materials require tie layers to prevent delaminating from olefinic outer layers, making a minimum of 5 layers a virtual necessity for large coextruded barrier film markets. The advantages of barrier coextrusion are to obtain a multilayer material in one operation and to use only a thin layer of expensive barrier material coextruded with cheaper supports and dry adhesives.

Examples of co-extruded laminates are shown below

Co-ex Five Layer Buried Nylon Diagram



Co-ex Seven Layer Surface Nylon Diagram



The multiplication of layers permits an almost custom made adaptation of materials, but that the intrinsic higher productivity of the coextrusion equipment requires large volume output of few single types of multilayers. As time passes, since coextrusion began, this conflict has been reduced, in favor of more coextrusion, as the film suppliers are fewer, concentrated, and offering a more streamlined supply of multilayer combinations, adapted to many end-use markets.

This is definitely why coextrusion is more commonly used for commodity plastics, PE and PP, than for lower volume carefully designed barrier multilayer materials. And even this is not entirely true in the sense that multilayer materials often are obtained by two or more operations, like using a coextruded relatively commodity film of polyolefins, then further laminated, or coated, still expanding the range of possibilities.

The coextrusion process only permits surface printing. Most multilayer film producers want to protect the printing by sandwich printing or reverse printing.

Extrusion Lamination

Extrusion lamination, to extrude a resin which then acts as a bond between two layers, is a variant from the extrusion coating process, when the resin extrusion is made on the surface of another material. In this latter process the supporting materials may be paper or aluminium foil, as well as plastics films.

Coating

Coating is more versatile than coextrusion. It can be combined with coextrusion and lamination in the broad range of possible multilayer film constructions.

In extrusion coating, an extruder forces melted plastics through a horizontal slot die onto a moving substrate or web of material. The rate of application controls the thickness of the continuous film deposited on the web. The melt stream, extruded in one layer or coextruded layers, can be used as a coating or as an adhesive to laminate or sandwich two or more materials together such as plastic film, foil or paper.

PVDC coating is one of the oldest gas barriers, having first been used on cellophane, for many years.

Coating is widely used on commodity films such as OPP. The coating process makes the basic OPP film, generally coex, transparent, with 3 layers, sealable on both sides, a more specialty film.

Metallizing

Metallizing originally was a replacement technique, to offer a substitute for aluminum foil. A very thin layer of aluminium deposited on plastics or paper appeared attractive as the price of aluminium increased. Metallization thus is just a coating, metal powder deposit, but the adhesion is more difficult to achieve than with inks. Metallized films have a number of advantages over foil, such as overall cost, higher converting machine speeds, availability, flexibility and even brighter appearance. On the other hand, the main advantage of aluminium foil is the deadfold ability.

Multilayer film applications

In general, for most films, the main end-using industry is packaging. However, the other end-uses may be quite important for some films, like, magnetics, optics, telectronics for PET, consumer goods, medical for PVC, automobile and construction for PVB. In packaging applications, in earlier days, the very first flexible multilayers, with paper and foil, were developed for biscuit and butter, back in the thirties. Then the concept developed for all sorts of packaged foods, in parallel with the development of self-service stores and super markets, starting in Europe in the sixties, and, later on, in the eighties/nineties, with the overwhelming change brought by ready-to-eat and ready-to-cook prepared foods.

High barrier films are used for CAP, controlled atmosphere packaging, MAP, modified atmosphere packaging, for all kinds of longer shelf life packaging under gas flush.

The coextruded barrier films, the dominating and still fastest growing segment at the moment, are used in:

- Bag in box for wines, fruit juices, milk, tomato paste, medical products, from 2 to 1000 liters
- Wrap for processed meat, delicatessen packaging
- Packages for the keeping and aging of cheese
- Controlled atmosphere flush packs for supermarket fresh meat cuts

The true success for barriers in the association of a shallow tray and a barrier lid film came from the tremendous success of prepared dishes, with the concept of single portions, microwaveable. A number of segments have thus appeared, along these main lines:

- Shelf stable, 3 months to one year, high barrier plastics using PP/EVOH or CPET/EVOH.
- Chilled dishes in trays of HDPE, PP, CPET, with or without barrier.
- Chilled dishes either in pouches of barrier films, high or medium barrier, put into a carton, or in thermoformed trays. The chilled dishes, now the most popular presentation for prepared recipes, can either be pasteurized or vacuum cooked.
- "Fifth generation" of cooked vegetables, with a shelf life of 10-12 days.
- And many others...

Metallized flexible films are a niche of their own. Both in the case of the metallized PET film and of the metallized OPP film, there only are three or four major applications, all in foods and beverages (labels), namely:

- Metallized PET: Coffee, frozen foods, powder and dehydrated foods
 - Metallized OPP: Snacks, chips, confectionery

Metallized OPA: Fresh foods, processed fish

Metallized PVC: Sweet package twisting, decorative paper

There are no real large volume new applications for metallized films, the growth of consumption has been fueled both by the intrinsic growth of the products put into metallized films, and most importantly, by the replacement of aluminum foil and other flexible materials.

Metallized PET films are mostly used for barrier, eventually combined by the marketing appeal of gloss, and metallized OPP is mostly used for marketing lower cost reasons.

The Future

Engineering at the nanoscale is now a reality and big news for packaging. New areas of application and research include:

- Nano reinforcement: using nanotechnology in fibre engineering to enhance the strength of board and thus reducing materials.
- Nanocoatings: to enhance barrier properties.
- Nanocomposites.
- Nano barcodes and taggants: for track and trace and brand protection of packaging

- Nanotechnology in paper-like electronic displays: which can be used to display information to the retailer/consumer about the freshness or condition of the product
- Intelligent inks: nanotech-enabled oxygen indicators.

Conclusions

Cryovacs BDF 2001 film will (although yet to be field tested) perform on vacuum or shrink equipment. However, as research moves forward in this field it is recommended that IODP partners with an experimental test lab, such as Michigan State University School of Packaging, Packaging Contract Research and Testing Lab, in developing the best possible film for our application. MSU, for example, has the expertise and testing facilities required to contribute substantially to this effort. See below;

Test 1. Drop Testing

Test 2. Compression Testing

Test 3. Shock Testing

Test 4. Vibration Testing (Sine and Random)

Test 5. Cushion Testing

Test 6. Friction Testing

Test 7. Tensile Testing

Test 8. Conditioning

Test 9. Water Vapor Permeability

Test 10. Carbon Dioxide Permeability

Test 11. Oxygen Permeability

Test 12. Organic Vapor Permeability

Test 13. Closure Testing

Test 14. Izod Impact Testing (Notched)

Test 15. Testing of Insulated Shipping Containers

Test 16. Pallet & Container Testing

MSU testing services and contract research are also available in the following areas of package analysis and evaluation:

Distribution environment measurement and simulation.

Dynamic Testing to predict performance.

Shock and vibration Testing of products and packages.

Fragility Testing.

Testing of pallets, reusable racks, and containers.

Oxygen, carbon dioxide and water vapor Permeability of packaging materials and packages.

Organic vapor Permeability of packaging materials and packages.

Package integrity.

Mechanical property evaluation.

Light transmission of polymeric packaging materials.

Ultraviolet degradation of plastics.

Product shelf life.

Product package compatibility

Package ergonomics.

Thermal properties of insulating containers. Package or material storage under controlled temperature and humidity Closure Testing. Legibility of labeling. Package burst Testing.

Section 4 – Summary and Recommendations

As both shrink and vacuum packaging have attributes that are desirable for the preservation of cores, it is also desirable that the equipment we purchase is capable of performing both functions.

Observations

- Ready made vacuum pouches are not a practical method of preservation for most cores.
- Commercial vacuum chambers are not large enough to accommodate our cores.
- Fully automatic side seal shrink wrappers are overly complicated and prone to high maintenance costs and breakdown.
- Cryovac BDF2001 is an adequate film for our current needs although its usefulness as a vacuum film has yet to be verified by field testing. Such testing is currently being carried out by Maryland Packaging.

Recommendations

- 1. Combination vacuum and shrink wrap machines are available. An L-bar sealer is used to create the pouch which is then either evacuated and sealed, or sealed and shrunk.
- 2. Although Cryovac BDF2001 is an adequate film in terms of both vacuum and shrink wrap performance, future joint research with a packaging research lab, such as MSU, on new films is recommended.

Potential Vendors

Ulma Packaging Shrink Packaging Systems

Appendices

Shrink Film Manufaturers

AEP Industries Alcan Incorporated Alcoa Incorporated **Applied Extrusion Technologies Atlantis Plastics** Bemis Company (Bemis Clysar) (Curwood) Bollore Diamant Art DuPont (EI) de Nemours Exopack LLC Exxon Mobil Firstline Corporation Formosa Plastics Group (Inteplast Group) Fuji Seal International Hood Companies Illinois Tool Works (Signode Packaging Systems) Impaxx Incorporated (Gilbreth Packaging Systems) Intertape Polymer Group Kloeckner Pentaplast GmbH & Company Mercury Plastics Mitsubishi Chemical MRI Flexible Packaging **Okura Industrial Company** Paragon Films **Pinnacle Films Pliant Corporation** Poly-America LP Seal-It Incorporated Sealed Air (Cryovac) Seneca Enterprises (Salem Label) Sigma Plastics Group (FlexSol Packaging) SKC Company Smyth Companies Sonoco Products Company Syfan-Saad Tyco International VIBAC Group (Vifan) Western Plastics

Compilation of Film Data Sheets

See attached folder

Applicable Standards

API Recommended Practice 40 for Core Analysis Section 3 Core Screening and Core Preservation. ASTM F1219 ASTM Active Standard: F1980-02 Standard Guide for Accelerating Aging of Sterile Medical Device Packages.

Further Reading

Principles and Applications of Modified Atmosphere Packaging of Foods By Barbara A Blakistone Nanotechnology in Plastics Packaging Edited by Andy Garland