

Recent research and future developments in barrier films (long-term storage)

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Introduction

This paper reviews recent on-going research work in the Conservation Unit, Natural History Museum that has been undertaken as a student project with Imperial College, Material Science Department. The information that has been gathered is currently being assessed as part of the development of the project. The aims of this PCU research project is to identify suitable low cost barrier films that meet the requirements of a conservation grade material and will allow conservators to store specimens for periods of up to 20 years.

This project will also establish a benchmark barrier film that meets the relevant criteria as below

- Low oxygen migration
- Low water vapour migration
- Stability in range of humidities
- Stability in contact with high pollutant concentrations
- Good tear strength
- Good tensile strength
- Clear
- Easy to seal with good seal properties
- Known composition
- Flexible
- Low cost

Low cost The Barrier film industry

Barrier Films are used extensively for packaging most humidity and oxygen sensitive materials and come in a vast range of specifications and compositions dependant on their use and shelf-life. All films are multi-layer containing at least individual layers that can be heat sealed or welded and that can reduce the rates of oxygen and/or water vapour migration. The compositional range can include thermosetting and thermoplastics, polymers that have been processed to be highly aligned as well as layers consisting of ceramic and metallic substances. There are new developments occurring such as new materials but also design aspects such as sealing technologies and improved processing.

Films are made for packaging of foodstuffs and pharmaceuticals as well as the protection of building materials and conservation artefacts. The electronics industry uses barrier films to protect its products and materials handling of any sort can include flexible packaging.



Figure 1. Image showing a macro view of all the films in the study

Scanning Electron Microscopy, Infrared Spectroscopy, Topographical analysis using Zygo and Confocal Microscopy were undertaken on these products.

Characterisation of a range of films

The first section of this report reviews the range of barrier films available from supplier companies. Although commercial information on the composition and mechanical and physical properties are available it is felt that an independent assessment of the barrier films is required.

The samples of films were acquired by contacting companies and suppliers either by telephone or email. The materials collected were as follows:

Commercial Name	Origins
Corrosion Intercept	Conservation By Design
Low Barrier Film	Conservation By Design
Archipress (pouch)	Conservation By Design
Marvelseal 360	Conservation By Design
Aclar	Honeywell, USA
Escal	Mitsubishi Gas and Chemicals
Foil o Wrap	Bell Fibre Products
Saran	DOW
Film o Wrap	Bell Fibre Products
Vaposhield	Techniplex
Escal Seal	(Mitsubishi Gas and Chemicals)
Moistop	Barrier Foil Products Co, Manchester

Table1. List of films investigated as part of characterisation tests.

Table 1 Analytical techniques undertaken on each film

Film ID	List of all films	SEM Surface image	SEM X-section image (s =side view of x sect)	IR	Zygo	Confocal x-no results ok-results recorded
1	Corrosion Intercept	✓	✓	✓	✓	
2	Low Barrier Film	✓	✓	✓	✓	Tried unsuccessful x
3	Archipress (pouch)	✓	✓	✓	✓	Tried unsuccessful x
4	Marvelseal 360	✓	✓	✓	✓	Tried unsuccessful x
5	Aclar	✓	✓	✓	✓	
6	Escal	✓	✓	✓	✓	✓
7	Foil o wrap	✓	✓	✓	✓	
8	Saran	✓	✓	✓	✓	
9	Film o Wrap			✓	✓	✓
10	Vaposhield	✓	✓	✓	✓	
11	Escal Seal	✓	✓		✓	
12	Moistop	✓	✓		✓	

Scanning Electron Microscopy Imaging

Introduction

A LEO 1445VP low vacuum scanning electron microscope was used to image the films. SEM images were taken to investigate the structure, composition and to identify any defects that could effect performance of the material.

Low vacuum SEM microscopy has the advantage of allowing non-conducting polymers to be viewed at very high resolution. It was therefore concluded that it was a useful method for characterising and comparing the film.

Aim

The barrier films, which could be used in the long-term storage of specimens, need to be fully understood in terms of their structure and this type of microscopy can provide information that will contribute to this.

- Develop preparation methods- what gives the best images of the films
- Identify number of layers and match composition of layers to information acquired from manufacturers/ suppliers
- Measure layer thickness within the multi-layer films
- Compare the structures of different films and how this relates to their properties.

The images captured were mainly viewed in backscatter mode although secondary electron mode allowed confirmation of surface topography when necessary.

Abstract

A series of films were successfully imaged using SEM. The films were best viewed when mounted using a polypropylene plug in comparison to gluing the film up against a steel washer. Many of the layers could be measured to an accuracy of within 5 micron and separate layers were often visible allowing for further characterisation. The films with a greater variety of composition in general responded better under microscopy. Other features that were viewed qualitatively showed that Aclar™ had very few defects and Saran contained high levels of contamination.

Method

The following films were imaged using a low vacuum scanning electron microscope:

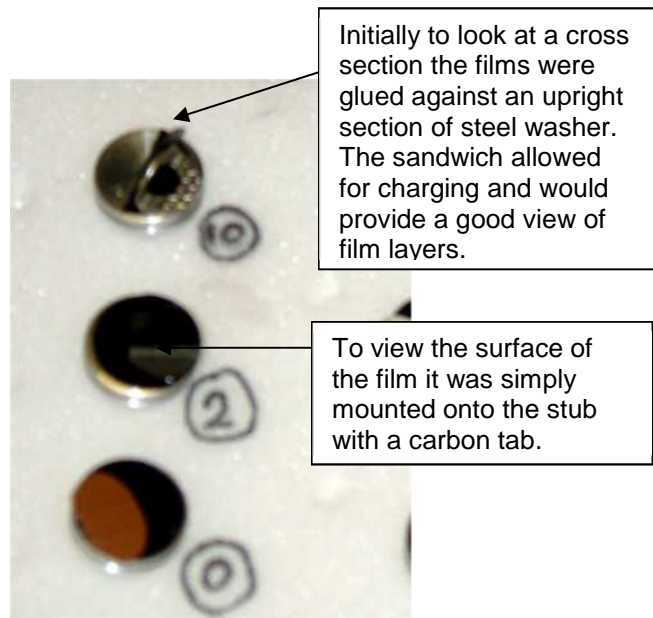
- Corrosion Intercept
- Low Barrier Film
- Archipress (pouch)
- Marvelseal 360
- Aclar
- Escal
- Saran
- Film o Wrap
- Vaposhield
- Escal- Heat Sealed area
- Moistop

Each film was studied qualitatively looking particularly at number of layers, thickness of layers, contamination within the film, regularity of structure, porosity and composition all of which will affect the performance of the film as a barrier material.

Microscopy Preparation

Using Scanning electron microscopy on plastics can be difficult since the nature of this type of microscopy is that electrons are bombarded at a surface. Plastics are non conductive so this tends to burn the surface of the material which results in poor or non-existent images.

However, in this investigation the microscope used was a low vacuum SEM which means the plastics samples are effected little or not at all and



can be imaged accurately. A low vacuum SEM works because the electron stream is able to discharge adequately rather than building up on the polymer.

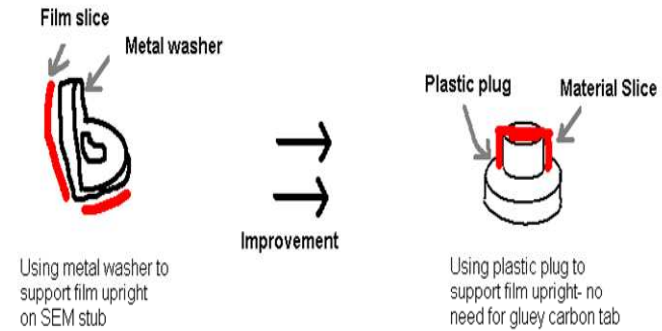
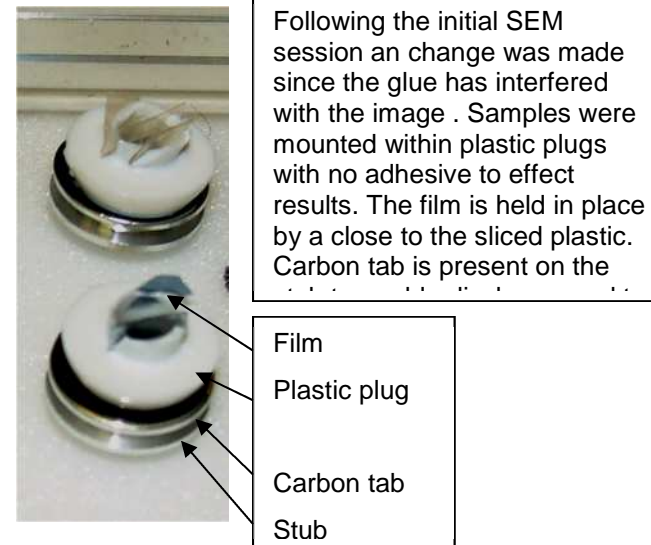


Figure 2 Schematic showing the preparation improvement made for the 2nd SEM session

Session 2 Preparation



Results

Several images were taken of each film in a range of views. The following are a selection of the images which best describe the main features of each material. Each one has been annotated for the information it provides about the barrier film.

Aims of Project

- Identify Component Layers of a broad range of commercially available Oxygen Barrier Films
- Identify composition of oxygen and moisture barriers within films
- Establish long-term reactivity of barrier films to varying relative humidity in anoxic environments
- Establish long-term reactivity of barrier films to SO₂, H₂S, Formaldehyde and other products off-gassed from stored objects
- Identify potential new directions and commercial relationships for developing moisture and oxygen barrier films for museum applications

Expectations

- Put things into the bags and seal them in for long periods of time
- 20 years
- Long term holding storage for archives and museum objects
- Stable environments

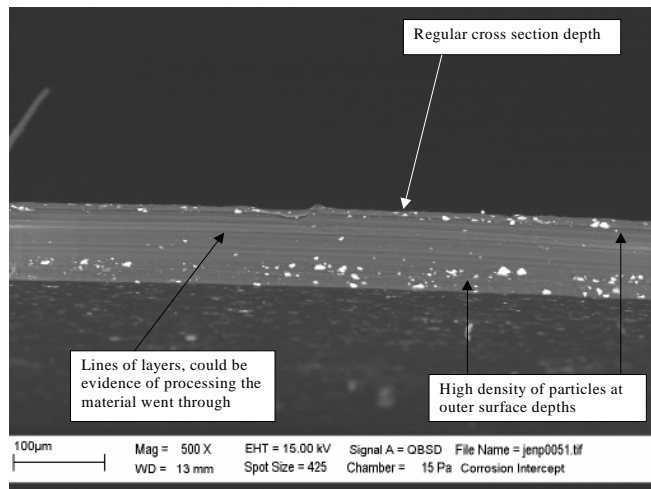
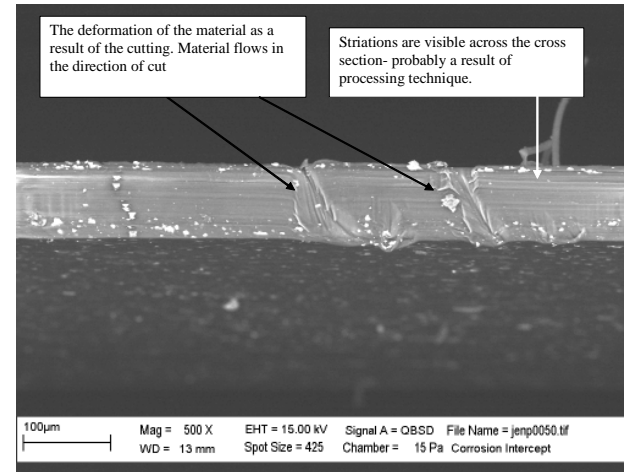
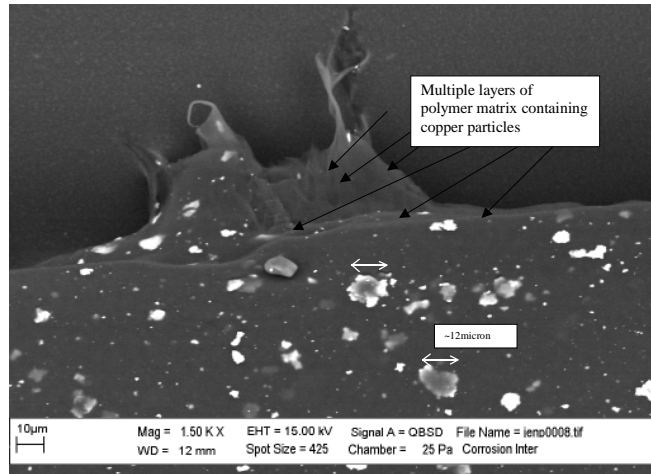
Commercially sensitive

- Combination of proprietary materials
- Designed for specific function
- Shelf life
- Conservation Combination – Expensive!

REXAM MEDICAL PACKAGING LEGEND RED = Not Recommended YELLOW = Limited Recommendation GREEN = Strongly Recommended WHITE = Not Evaluated	DISCOVERY PROCESS												Notes/Comments							
	TYPICAL OUTER WEB						TYPICAL SEALANT WEB							TYPICAL PROCESS						
Mark Items	PET	Paper	Foil	Nylon	Callo	OPP	ME PET	EVA	Suryl®	LDPE	ULDPE	HDPE	CPP	Liq. HSC	Peelable Film	Est Cost	Est Lead	Auth Item	Print	
PRODUCT CHARACTERISTICS																				
• Liquid (Alcohol)																				Requires foil or Metallized barrier
• Oily (Paracetamol)																				Typically an adhesive lamination
• Chemically Active (Iodine)																				Typically Box Nylon and/or LDPE
• Shape/Size (Sharp Edges)																				
• Solvents																				
PERFORMANCE REQUIREMENTS																				
• Moisture Sensitive (MTR)																				Foil and Oils: not preferred for oils and greases. Some coated film or Co-Ex materials with EVOH
• Gas Sensitive (Oxygenation, O ₂ IR)																				Requires foil and/or Me Barrier
• Light Sensitive																				HSC in exceptional circumstances
• Abrasion Resistance																				
• Flex Crack / Flexure Resistance																				
PROCESS REQUIREMENTS																				
• Transformable – Shallow (<1/2")																				
• Transformable – Deep (>1/2")																				
• High Packing Speed; Short (low dwell time)																				Recommend Suryl® for Hot Tack
• Soft "Head" or Feed																				Box PET, Paper and Callo Typically Best
• Surface Printed/Tight register; Race, rate																				Best Serviced with PET, Callo
• Reverse Printed/Tight register; Race, rate																				Paper Best, Consider Chemically treated PE
• Product may be visible																				
• Customer no inline print																				
SEAL/OPENING CHARACTERISTICS																				
• Seal through contaminants																				Typically associated with Suryl®
• Peelable but gas impermeable																				Oils: Typically poor Gas Barriers
• Peelable, no Tear																				Consider Steamer Resist CPP when Steam Sterilisation process involved
• Strong Hermetic Seal; no notch – laser heat																				
• Strong Hermetic Seal; with notch																				
• Seal to PETG/PVC, etc.																				Paper & Callo begin to degrade at over 1. MegaPa
STERILIZABLE																				Requires a porous material or open pouch
• Gamma																				
• EO																				
• Ethanol																				
• Steam/Retort																				High temperature process usually CPP or HD
USABLE MATERIALS																				

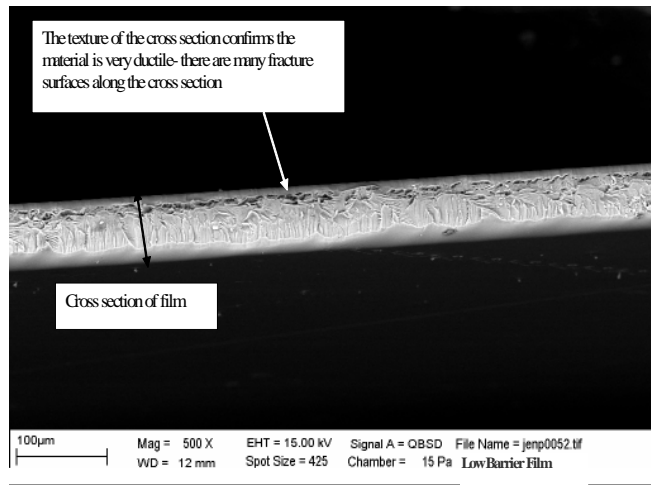
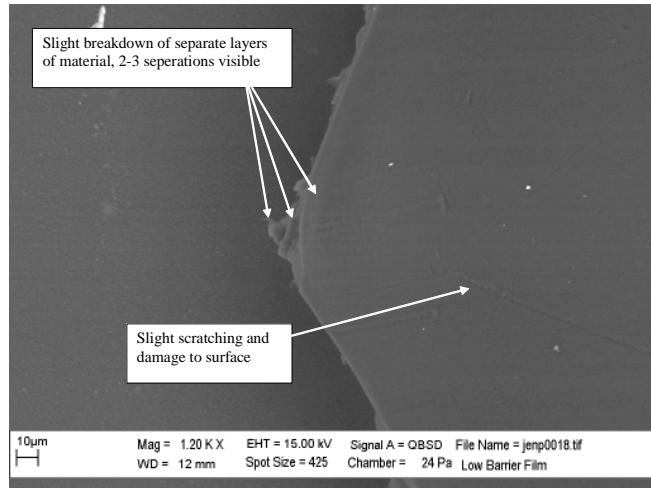
Note: This chart and the information contained is based on the typical situation. There will be certain instances that the information contained would make your choice different from the obvious stated.

SEM Images of Corrosion Intercept

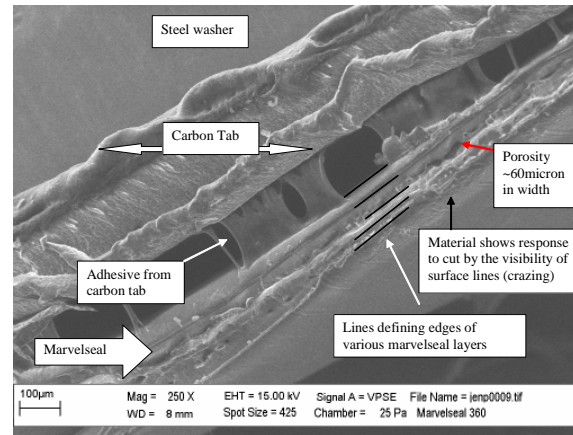


SEM Images of Low Barrier Film™

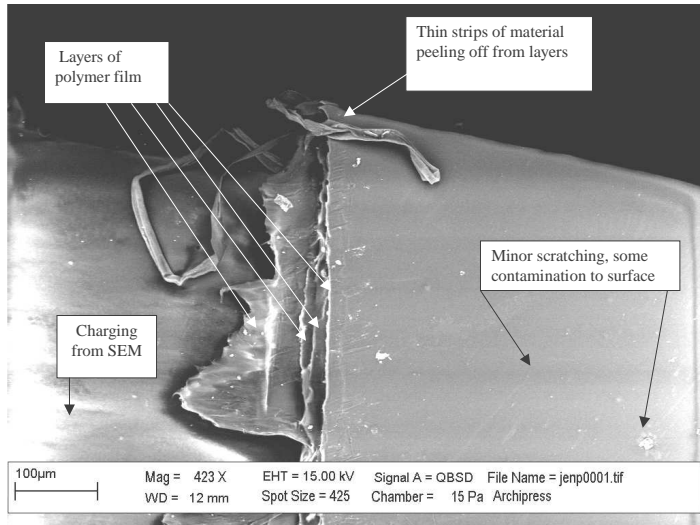
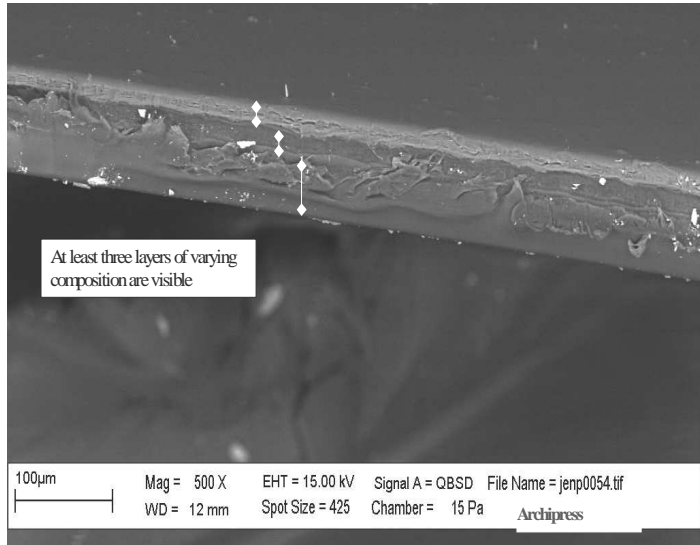
(Supplier - Conservation by Design)



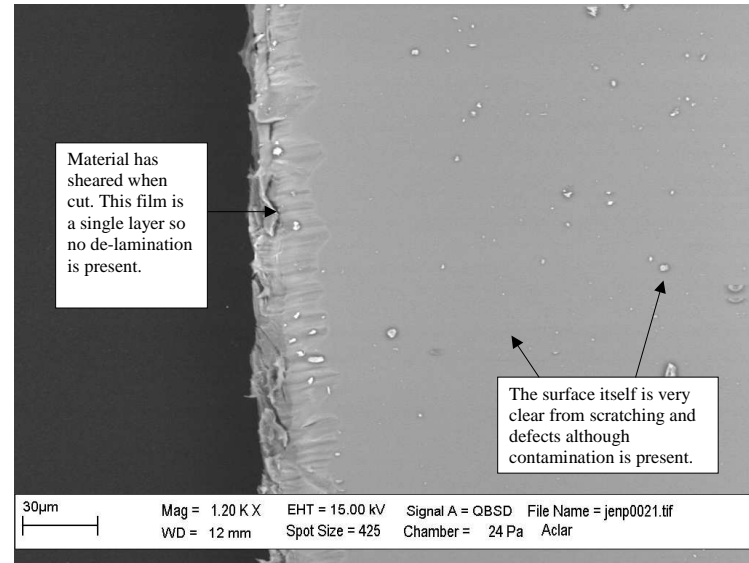
SEM Images Marvelseal™



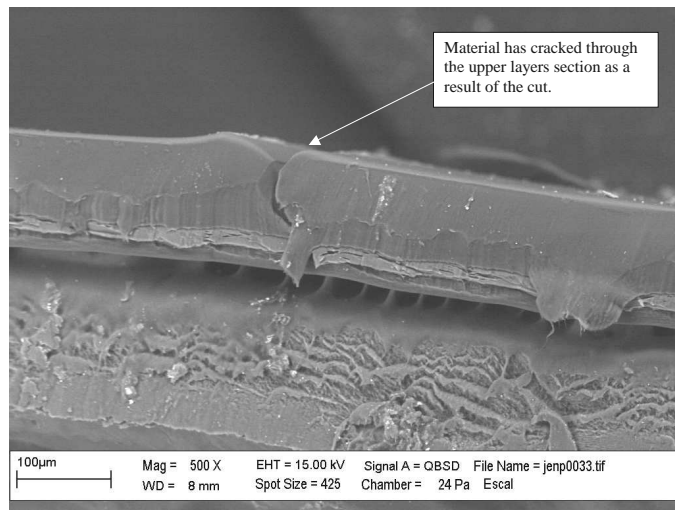
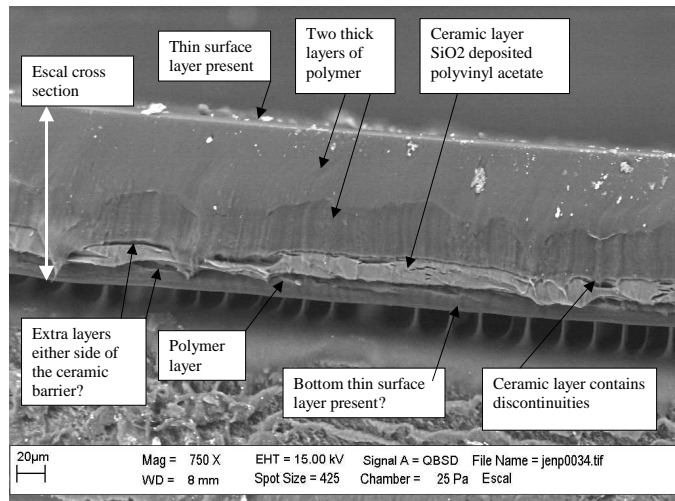
Archipress™



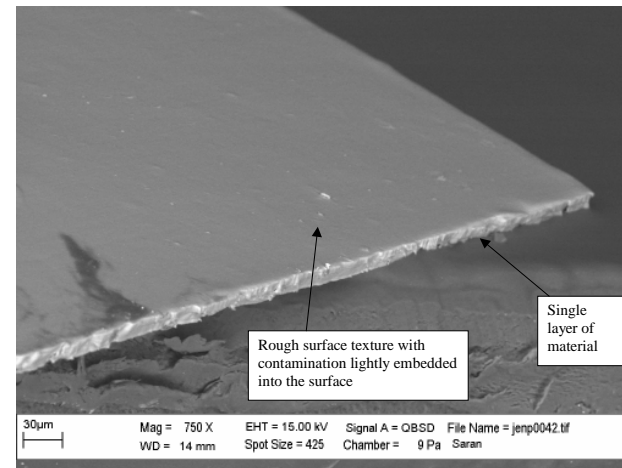
Aclar™



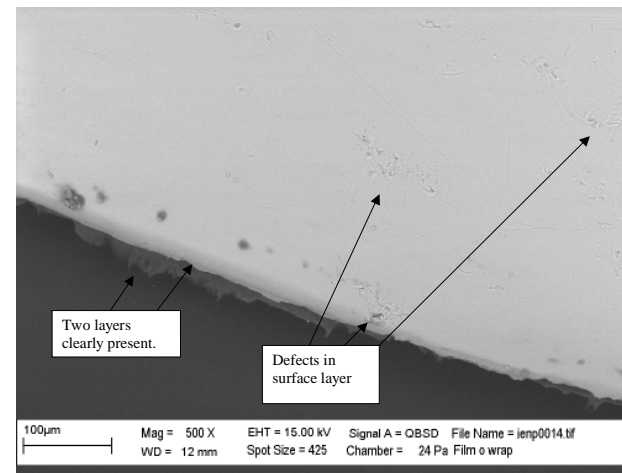
Escal



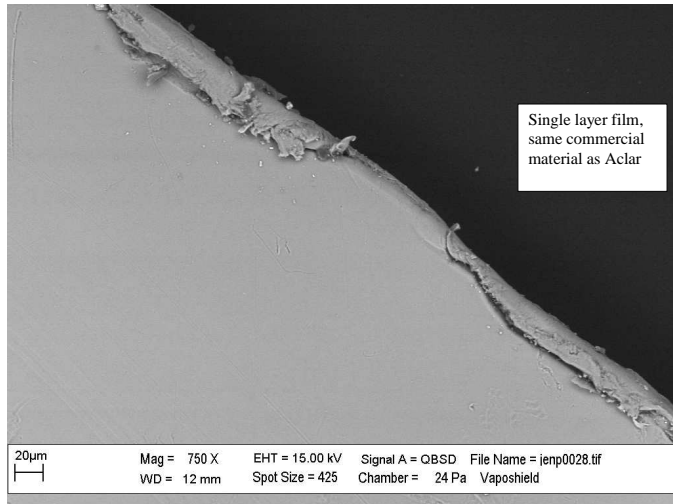
Saran (polyvinylidene chloride)



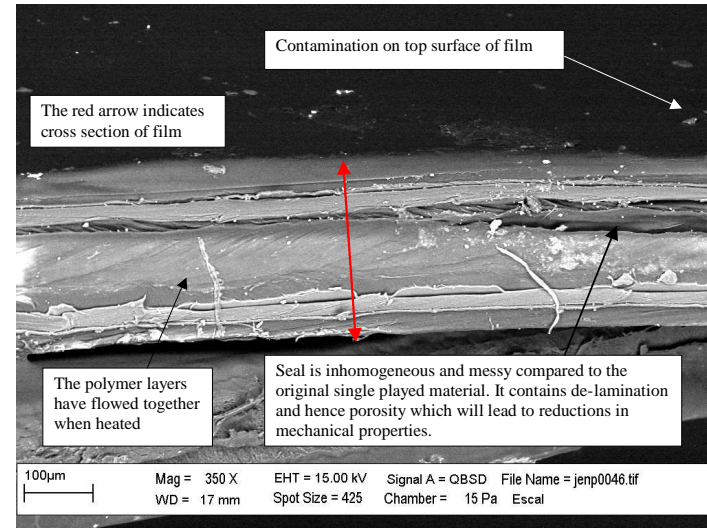
Film o Wrap



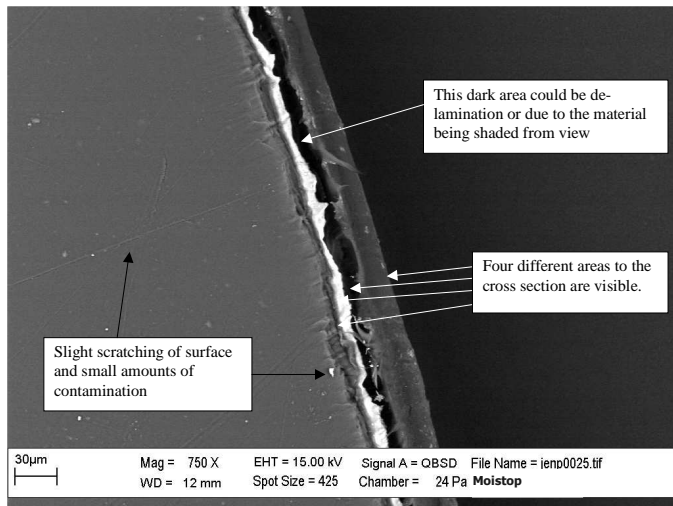
Vaposhield



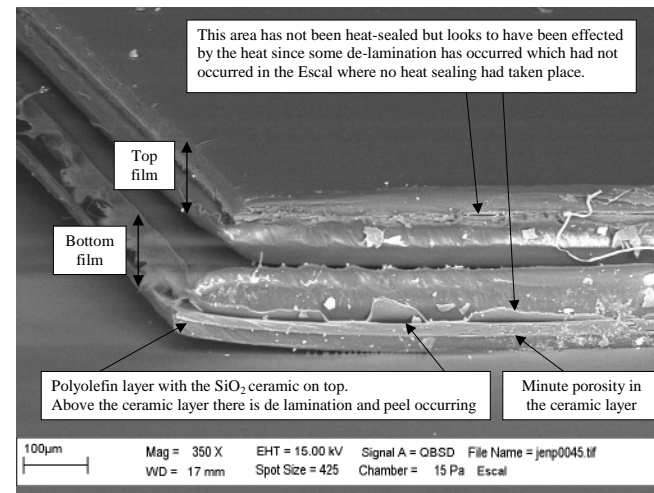
Escal™ (heat sealed cross section)



Moistop



Escal-area next to a heat sealed section



Film	Number of layers/striations visible	Thicknesses of inner layers (where measurable and taking into account film was on tilt)	Average thickness of cross section of film from image-could be tilted (micron)	Measured thickness of film using micrometer (micron)
Corrosion Intercept	>10 striations (overall a monolayer)	Polyethylene striations spaced at ~3micron	85.9	90
Low Barrier Film		3 Top layer~8micron, Central layer~48.3micron, Bottom layer~16.1micron	72.5	100-105
Archipress (pouch)		3 Light coloured top layer~17.4micron, First central layer~18.8micron, Second central layer~28.2micron, Bottom layer~20.1micron	84.6	90
Marvalseal 360		4 Top polyethylene layer~17.5micron, Polyester~52micron, Aluminised Polyethylene~53micron, Bottom polyethylene layer~17.5micron	131.6	140
Aclar		1 n/a	not possible to estimate	~40
Escal		6 Polyethylene~4micron, Polypropylene~55micron, Polyvinyl Acetate~30micron, Silica~13micron, Polypropylene~13micron, Polyethylene~4micron	123.5	120
Saran		1 n/a	10.7	10
Film o Wrap	2 visible	not possible to estimate from image	not possible to estimate	110
Vaposhield		1 not possible to estimate from image	not possible to estimate	75~80
Escal Seal		10	207	230-240
Moistop		(at an angle) Polyester ~7micron, Alu foil ~6 micron, Polyethylene ~14 micron, White LDPE/LLDPE Film ~20micron	47micron	130

Figure 3 Qualitative results from SEM Images

Discussion

SEM imaging of barrier films was successful in detailing the structure and investigating the interlayer areas. The films were handled well by the low vacuum microscope and the images are mainly clear with little evidence of charging. By modifying the preparation of the samples the cross sections captured in the second session the images were improved since there was no cross contamination from the carbon tabs.

The images could also have been improved in some cases by taking more care with handling since the contamination can deter from the material itself. Although gloves were used and contamination is never going to be completely avoided the samples could've been gently air blown in order to remove more particles. These films will attract dust particles due to static forces and the constant presence of particulate in the environment.

Each film imaged in this set is designed as a polymer or multi-layered packaging material designed either for , however, the construction of the films has depended upon the specific application and design. For example Corrosion Intercept has been produced to prevent corrosion yet Escal is marketed to protect specimens from oxygen environments. I am going to summarise each film using the images created here and commenting qualitatively on a range of materials features seen from this analysis.

Corrosion Intercept

Examination of the first film, Corrosion Intercept shows what is most likely to be a film which has been extruded as one layer. There are striations clearly visible and running parallel to the film surface. The striations could be evidence of a series of layers however the economics of producing a singular layer suggest this is more likely. The copper particles that are embedded within the cross section are in much higher density at the surfaces and one side appears to contain a larger volume than its opposing side. This may be intentional by the manufacturer in order to prevent the majority of corrosive product being eliminated by the particles before the designated inner surface is reached. However it could also be a consequence of the processing. The particles are likely to be coated whilst the polymer is still close to its melting point and in the processes of just being polymerised and extruded. The copper is flake like in shape suggesting they are designed with a large surface area to capture oxygen in greater volumes. Although they are at different heights within the surface they do not seem to cluster on certain levels but are spread

homogeneously. The size of the particles appears to range up to a maximum particle size of around 12-15microns, with anything below acceptable for the processing. The main purpose of this film is to prevent oxidation during the storage of metallic objects. The polymer matrix is yet to be confirmed for composition and is concluded to be present to support the particulate, be low cost, with flexibility and ability to transmit light.

Low Barrier film

This film appears to be a single layer. In terms of the storage of museum artefacts it would only be of use in the mechanical protection of specimens rather prevention of oxygen diffusion since the material contains "low barrier" properties, as described by the manufacturer. The material is seen as failing in a ductile manner as there are a high number of fracture surfaces seen. SEM imaging in this example has described the mechanism of failure of the material which gives information about the mechanical properties of the film. Compared to a multi layer substance this film cannot exhibit failure by peeling layers but its material properties alone are limited.

Archipress

This film in contrast is multiple layer, with at least 3 layers visible from the SEM image. The top surface had failed in a different manner to the upper edge- the base polymer appears to have a weaker structure as it has flowed and curled. The base is presumably the heat-sealing layer that will have a lower melting point and is likely to be polyethylene or polypropylene. Both the middle and upper film layers appear less mechanically pliable and there are possibly areas of micro porosity visible as open sections across the layers.

Marvelseal

This film has not been as well imaged using this technique since the cross sections have been contaminated with carbon tab adhesive. Individual layers are difficult to separate visually. Despite this it can be observed that there appears to be porosity between the layers of this film. Edges of the layers where the material has been cut are seen to have fractured with some material flow and the result of this is some surface marks on the base side of the film near the edge.

Aclar

This film under first inspection appears very clean of surface defects and striations although contamination has been attracted onto the material. The cut edge had fractured as would be expected from a ductile substance; it is rough and full of fracture surfaces. The film is a mono-layer and the material it is composed doesn't seem to flow in any significant way showing the presence of a strong polymer, which is therefore likely to have a high melting point. These properties would suggest a better ability to be a barrier film since the structure is likely to be more closely packed and impermeable. The exact composition of the material will be confirmed later in this report using Infrared Spectroscopy.

Escal

Imaging the cross section of Escal has worked well using this analysis technique. The edge cut has moved the material a little making measuring the thickness of the layers more difficult. However it is possible to decipher between at least 6 different layers by studying the change in shading (due to compositional change). The range of properties of those layers can also be seen. The layers likely to be polyolefin's (polyethylene and polypropylene) are those, which are thicker and have flowed down onto other layers. They have these properties because they are produced for the heat-sealing property of the films and are low cost substances so using larger amounts is more likely. They are lower melting point materials compared to the ceramic layer and so will be softer and more likely to flow. The ceramic layer is thinner, it is a heavier material and if too thick would reduce the flexibility of the film. It seems to be capable of fracture and porosity, which would reduce its barrier properties.

It is important to note the film is not symmetrical but does have two distinctly different top and bottom surfaces. This means it is essential to be aware which side needs to be on the inside when heat sealing. The bulk of the polymer layers would need to be on the inside so to allow for the thickest and most effective seal. On the very top and bottom surface on many of the images taken is a very thin layer of film. This may be protective to assist the film in its barrier property. This layer needs to be scratch resistance and be a low melting point polymer since it will be involved in the heat seal.

A cleaner cut through the Escal may help discover a better estimate on the number and thickness of the various layers. Creating different cuts through the film gives information about the way a material fails and therefore indicates material properties.

Saran

This film is another monolayer substance and is a lot thinner than the other films. Although it is therefore more flexible this will reduce its barrier properties since species will take less time to diffuse through the material (according to Fick's law of diffusion. The film has failed as a flexible and ductile material with a rough fracture surface. There appears to be contamination almost embedded within the surface, suggesting the film is fairly soft or the processing has been poorly. Saran is better known as cling film and is produced in large quantities for short term use. Its properties for conservation are that it is transparent and cheap. Although as part of a barrier films where it is a relatively good oxygen and water barrier its properties are limited due to its poor stability low. The quality of the production compared to a film such as Escal or Aclar can be easily seen identified as lower from the film- it's rougher and less uniform. This comparison is useful in comparing the value of the films in relation to performance.

Film o Wrap

The individual layers were clearly visible within this film using scanning electron microscopy. There are at least two layers although there may be more since there seems to be space between where the two films have peeled apart. Both films appear relatively thin and flexible and the top surface contains many defects. The bottom layer appears as a low-grade thin low density polyethylene. The top layer on closer inspection has not pulled away from the cut with such flow and appears to be a stronger and higher melting point polymer. The composition of the layers changes which is seen as different tones of grey on the image. The lighter the material appears on the image the heavier it is so the top layer consists of a heavier polymer. The defects seen look like a result of minor impacts of the surface and subsequent cracking. The material has responded by plastically deforming beyond the crack as the crack grows. This deformation decreases its tear strength and reduces the overall mechanical strength of the film. The form of the impact crack suggests the material can respond in a brittle manner- this could be a sign that the polymer has degraded and become embrittled.

Vaposhield

The shading of his film is fairly similar to those seen previously. It is a monolayer substance, which has cut fairly cleanly. The material has not become wispy or pulled thin but has remained close to the broken edge. This suggests again a higher melting point material with a greater strength than a polyolefin. The surface shows a few striations and defects although relatively few compared to a film such as the low barrier film studied previously. The layer curled over at the edge show the material to be continuous with no porosity that suggest as well processed film with good barrier properties.

Escal Seal

Imaging the seal was of interest since this area has been researched in order to check mechanical integrity and barrier properties. This seal was performed at a setting of around 3-4, a fairly high value compared to the melting points of the polymers and layers involved. As can be seen from the image this means the cross section of the film shows several areas of de-lamination and peel.

If the seal is going to be effective it really needs to combine the two layers of material without affecting the structure of them so as to not change the property of the film. De-lamination is a serious change to the film and would result in the barrier properties being significantly reduced. This method of analysis can give an accurate description of the accuracy of a heat seat, which is supportive to the research already carried out. It would be possible to associate the best sealing temperature with mechanical integrity and a structural check using SEM.

Moistop

This is the final film viewed under this analysis technique. It is a multiplayer film of various materials seen from the differences in grey scale shading as a response to compositional change. Low mass elements appear darker, for example metals appear bright and polymers dull (unless they contain metal atoms). The brightest film in this structure is likely to be the metallic layer. It is thin compared to some of the other layers and is well bonded to the layer below it. That layer is likely to be polymer which is fairly tough and not showing much plastic flow when cut. In comparison the top layer to the right of the cross sectional image seems soft and pliable. It is unclear what has occurred to the layer one in from the right since there appears to be blank space. The layer could be shaded from view due to

the angle of imaging or be free space due to de-lamination of the film. By tilting the SEM platform at different angles it may be possible to view the layers from a better place, giving more information on numbers of layers and the thickness.

Summary

This technique proved successful since it provided a quantity of information on each film such as whether they were mono or multi layer (and if multi how many), details of the surface defects and levels of contamination visible on the upper layers and initial indications of composition since fractures of the films suggests properties such as mechanical strength and plastic flow.

The large range of compositions within this series of films is demonstrated from this analysis and will correspond to a variety of properties and capabilities. The comparison of several films shows a range of quality of films that can be directly related to cost and performance.

For example the films which appear more consistent in structure, such as Escal and Aclar, are likely be more expensive to process and will have better mechanical and barrier properties. Although you cannot differentiate between different polymers using SEM the metallic and ceramic coatings of Moistop and Marvelseal were easily visible due to the compositional difference. The imaging was successful in confirming details and re-establishing a micro view of the films which will correspond to the associated material properties.

Infrared Spectroscopy

Introduction

Infrared spectroscopy is an analytical tool used for the identification of polymers. It works by detecting the changes that occur to the wavelengths in an IR beam when it is transmitted through a polymer.

This type of analysis may also be able to indicate changes in the polymer structure. For example research has been published which uses a ratio of two peak heights (which are associated with particular chemical bonds) to make predictions about how much a polymer may have aged (oxidised)¹. More details about this topic are covered in the "Ageing Polymers" section.

Aim

The analysis using IR covers two distinct sections:

- Identifying the composition of the layers of the barrier films
- Comparing the spectra of identical films that have been exposed to a variety of environments

Abstract

The range of films were analysed using IR spectroscopy and the peaks from the spectra associated with polymers from the reference text. Highly transparent, mono-layer films responded better to the analysis, opaque films such as Marvelseal did not recover results. This technique successfully identified the 'Low Barrier Film' as being nylon. No information had been available as to what composition this film was, and the spectra confirmed the polymer composition.

The second part of the experiments using IR exposed the film Escal to several different environments some of which were intended to induced ageing. The spectra were compared to assess whether IR spectroscopy of this sort could be useful in showing changes to the polymer to relate to ageing processes. Very slight differences in the spectra were seen

however it cannot be concluded at this point to attribute these peak differences to ageing processes.

Method

IR was performed in transmission mode and spectra generated for each film. These spectra were then analysed using comparison with standard spectra from a reference text. The peaks associate with specific atomic bonds and therefore particular groups known to exist within a polymer. Peaks are eliminated using the reference polymers (effectively removing them from the spectra); the remaining peaks can be matched to other polymers resulting in multiple film compositions being identified.

Part 1

The following films were prepared by being stretched across a plate with central hole for transmission:

Corrosion Intercept
Low Barrier Film
Archipress (pouch)
Marvelseal 360
Aclar
Escal
Saran
Film o Wrap

Part 2

The second part of the IR investigation involved several pieces of the same polymer that had been stored or treated differently were run through the IR spectrometer. A detail of the differences between these films is described below;

(Film investigated= Escal)

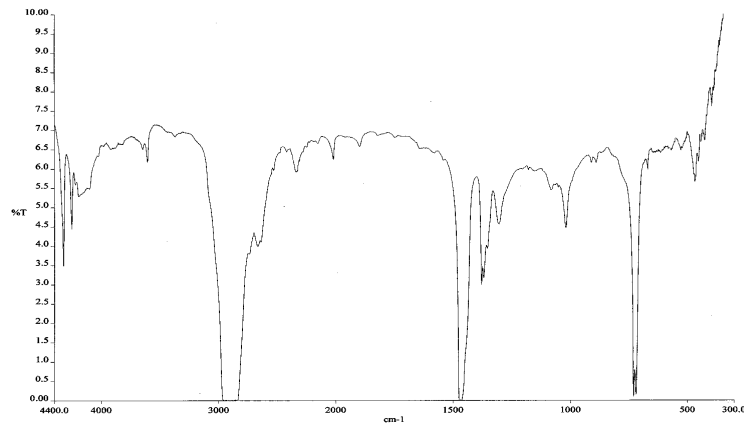
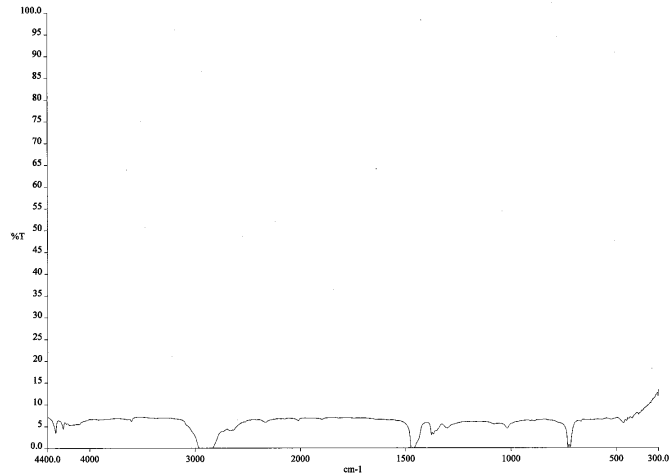
- Control sample- stored at NHM
- Stored at Conservation by Design
- Oven heated at 150°C for 20mins
- Oven heated at 110°C for 1min

- Heated and exposed to a UV pen for 1 hour, (200-260watts/ 50/60Hz/0.25amps)

Results

The following results display the spectra generated from the various polymer films under investigation as well as the reference spectra in comparison. A summary is included of the major peaks

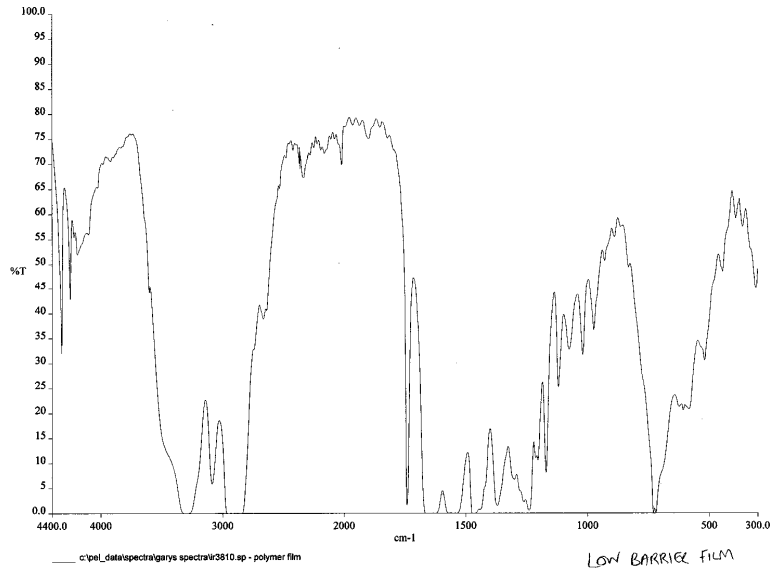
Corrosion Intercept



Identifying the peaks

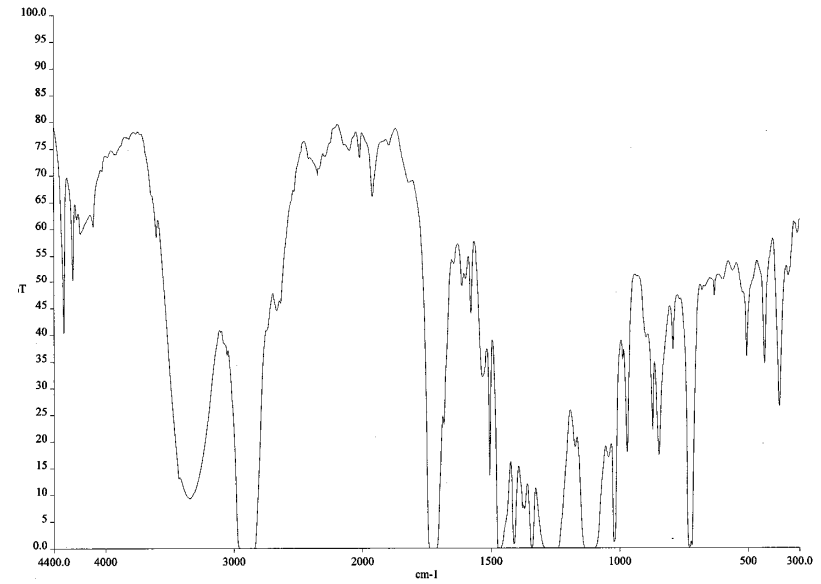
Peak Type	Wavenumber (cm ⁻¹)	Material
Sharp Peak	2900	Polyethylene
Sharp Peak	1450	Polyethylene
Weak Peak	1375	Polyethylene
Doublet Peak	725	Polyethylene

Low Barrier Film



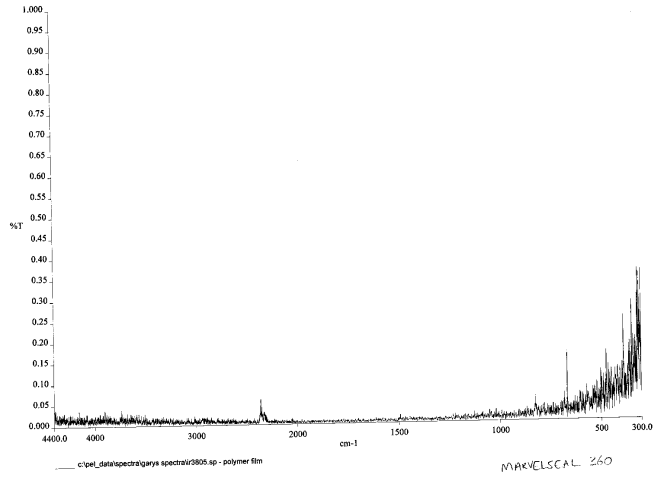
Identifying the peaks		
Peak Type	Wavenumber (cm^{-1})	Material
Sharp Peak	3400	Nylon
Sharp Peak	2900	Nylon
Series of peaks	1650-1175	Nylon
Wide Peak	650-750	Nylon
Sharp Peak	1740	PVA?

Archipress (pouch)



Identifying the peaks		
Peak Type	Wavenumber (cm^{-1})	Material
Sharp Peak	2900	Polyethylene
Sharp Peak	1720	Polymethyl Acrylate (Polyester)
Series of peaks	1000-1500	Polyester
Doublet Peak	725	Polyethylene
Doublet Peak	725	Polyethylene
Sharp Peak	3400	Polyvinyl acetate or Nylon?

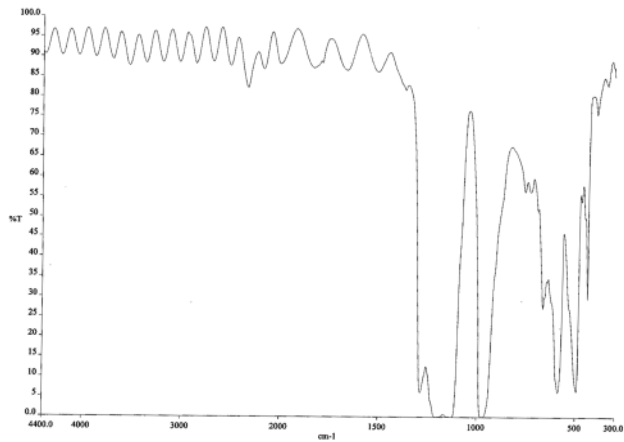
Marvelseal 360



As would be expected the spectrum from this material which is an aluminised polyethylene shows no characteristic peaks

Aclar

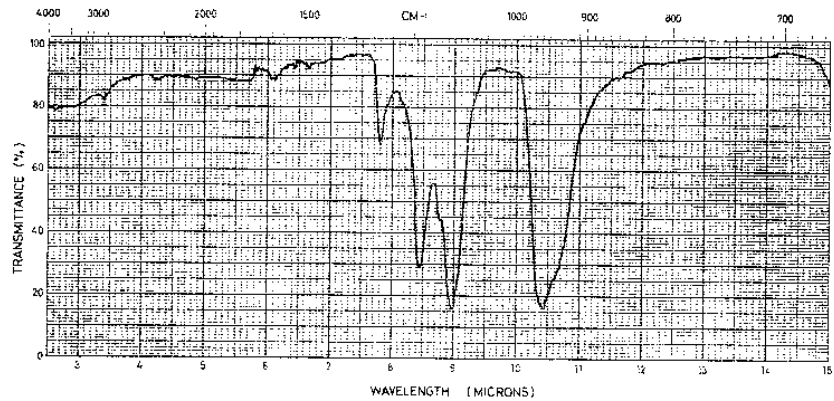
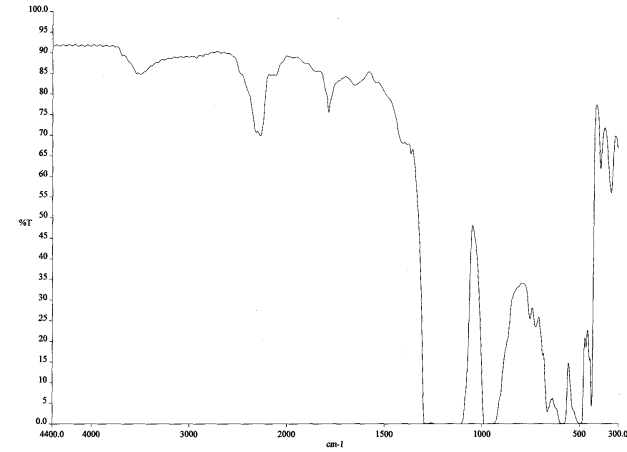
Aclar film, 0.8mm width



Identifying the peaks

Peak Type	Wavenumber (cm ⁻¹)	Material
Weak Peak	1290	Polytrifluorochloroethylene (PTFCE)
Doublet Peak	1160	PTFCE
Sharp Peak	950	PTFCE

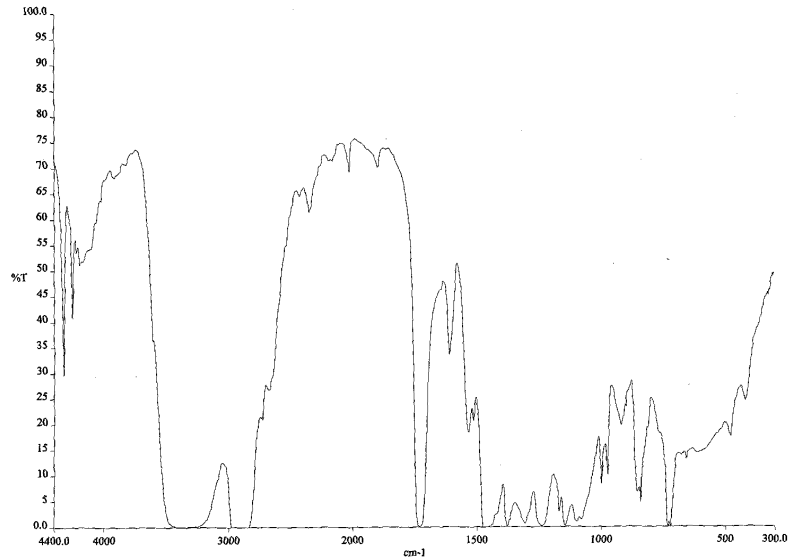
Aclar film 2mm thick



*Spectrum 7-2(b) - Polytetrafluoroethylene
A.T.R. spectrum of hot-pressed film*

Figure 4. Example of the reference spectrum for PTFCE

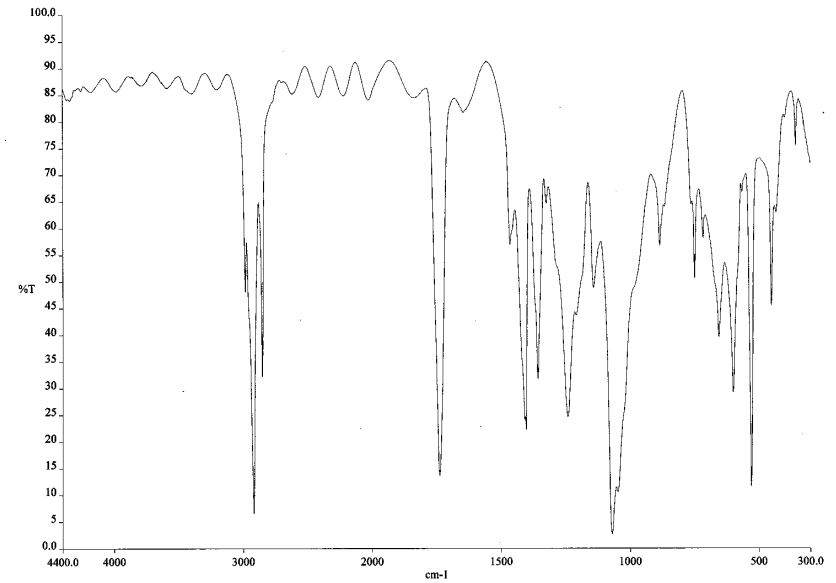
Escal



Identifying the peaks

Peak Type	Wavenumber (cm ⁻¹)	Material
Wide peak	3250-3450	Polyvinyl Alcohol
Sharp Peak	2900	Polyvinyl Alcohol
Sharp Peak	1740	Polyvinyl Acetate?
Sharp Peak	1450	Polyethylene
Series of Peaks	1500-1000	Polypropylene
Series of Peaks	1500-1000	Polyvinyl Acetate?
Small Peak	730	Polypropylene/ Polyethylene

Saran



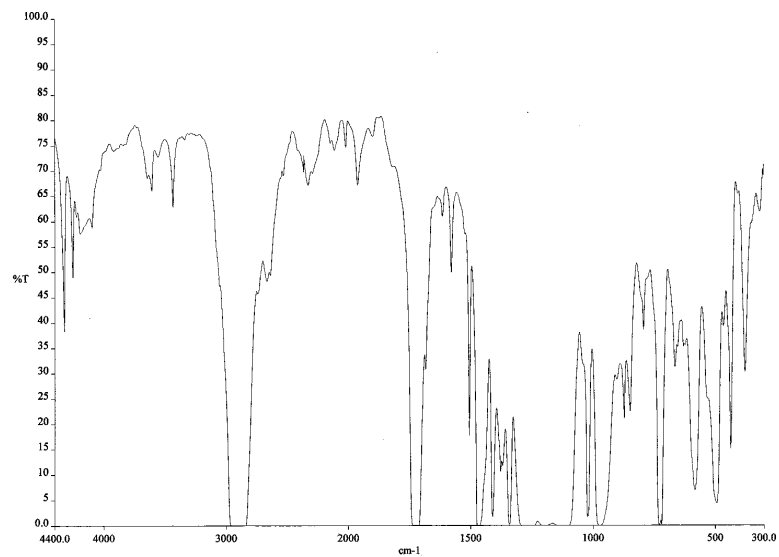
Identifying the peaks

Peak Type	Wavenumber (cm ⁻¹)	Material
Sharp Peaks	2900	Polyvinyl Chloride
Sharp Peak	1740	Polyvinyl Acetate
Doublet Peak	1050	Polyvinyl Acetate
Sharp Peak	1425	Polyvinyl Chloride
Sharp Peak	1350	Polyvinyl Chloride
Sharp Peak	1250	Polyvinyl Chloride

Notes:

Peaks on the results from IR show a much sharper profile than the peaks from the reference spectra. This could be a result of orientation playing a factor.

Film o Wrap



Identifying the peaks		
Peak Type	Wavenumber (cm ⁻¹)	Material
Sharp Peak	2900	Polymethyl Acrylate (Polyester)
Sharp Peak	1740	Polyester
Sharp Peak	1460	Polyethylene
Wide Peak	1100-1300	Polyester
Sharp peak	960	Polytrifluorochloroethylene (PTFCE)

Part 2: Results

The spectrum below shows the sample stored and not exposed to any extra form of ageing process. The arrows on this spectrum indicate the peaks which appear to alter in shape and depth as different samples are analysed.

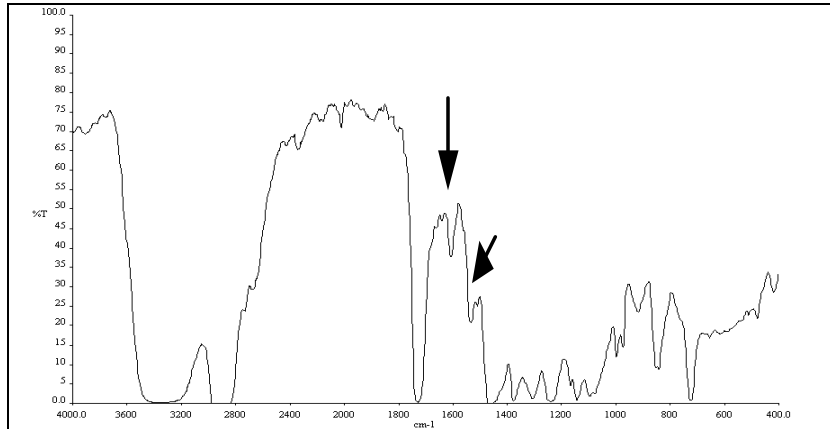


Figure 5. Control sample- stored at The Natural History Museum. The arrows indicate the peaks that change shape when analysing different samples.

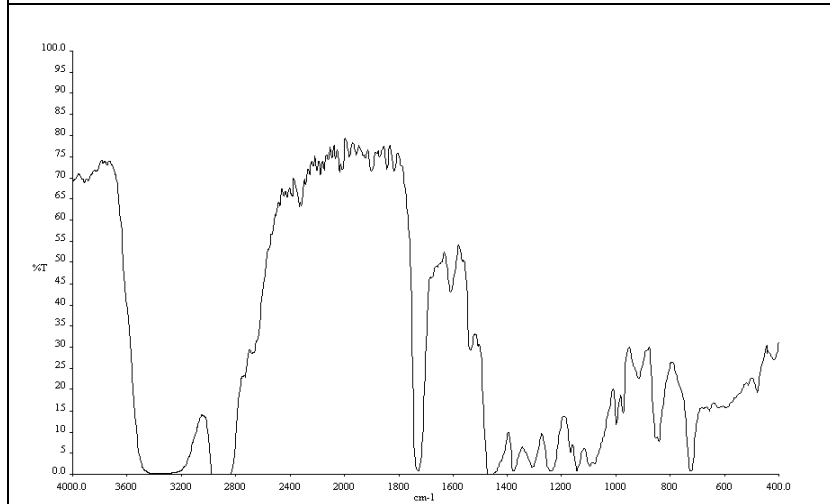


Figure 6 Stored at Conservation by Design (supplier)

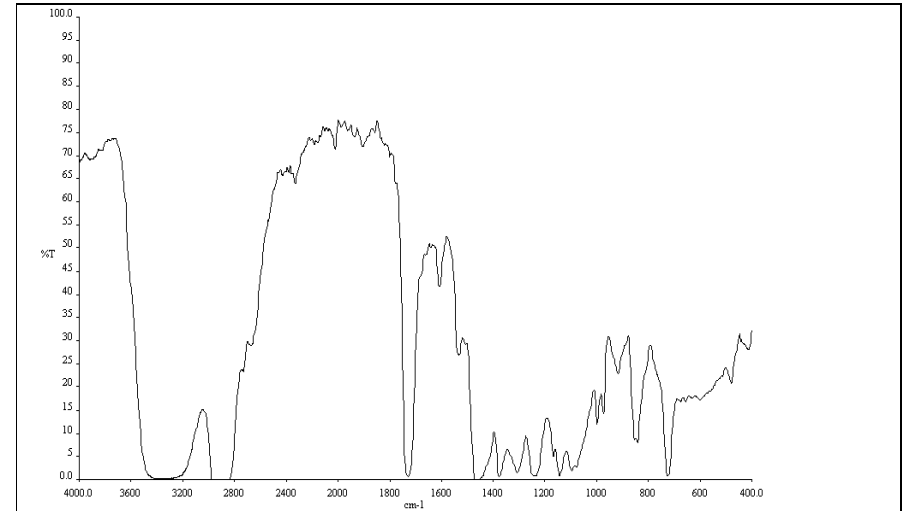


Figure 7 Oven heated at 110°C for 1 minute

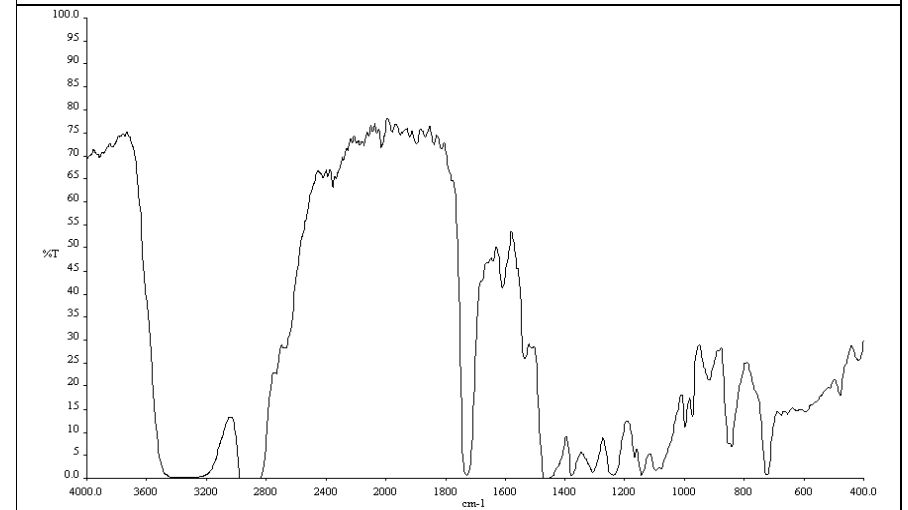


Figure 8 Exposed to UV pen for 1 hour (Heat and UV degradation)

Note: Identical material that had been stored in different environments were both analysed by the spectra. By holding the printouts up to light is it possible to see the spectra are identical apart from a slight shape difference in the doublet at 1520cm^{-1} .

Discussion

The spectra obtained from this type of analysis show transmittance on the y-axis and wavenumber on the x-axis. The spectrum is a result of the beam being affected by the materials it comes in contact with. These spectra show that at certain wave numbers the beam is being absorbed and therefore transmission falls. These peaks can be associated with the specific groups within known polymers and combinations of peaks can also confirm compositions. The table below gives a brief summary of the association of peaks with chemical groups;

Table 2 Characteristic infrared absorptions of some common bonds^K

Each film is now discussed in terms of the IR spectra obtained in part 1.

Corrosion Intercept

This material, due to its opaque nature has given spectra with low transmission values. Despite the spectra being confined to low transmissions the peaks are still clear and able to confirm the polymer within this material to be polyethylene. This supports the SEM image that indicated the material to be very soft and flexible it was seemed to become thin and wispy when cut.

Low Barrier Film

This film shows a perfect match to the reference spectra of Nylon. It suggests, as the SEM image did, that the film is mono-layer and since the spectra is so well matched it is concluded to have a relatively pure composition. Knowing these features of the film helps understand the

material- giving information about overall properties which will match that of a nylon itself (being strong but with low barrier properties).

Archipress (pouch)

This spectra is much more complicated and seems to be a multiplayer film including polyethylene and polyester as well as something else. By studying the other fundamental peaks there are other peaks that remain once these materials are "ticked off". A major peak which remains is the peak at 3400cm^{-1} which could be associated with polyvinyl acetate or nylon. To establish which one the other peaks need to be confirmed to conclude which is more likely.

Marvelseal

Since this film is completely opaque the beam could not penetrate and thus the spectra is seen as showing zero transmittance. This shows a limitation of the analysis and a need for another technique. This will be covered later in the report.

Aclar

This single layer film is clearly identifiable as Polytrifluorochloroethylene. The form of the spectra clearly follows the pattern of the reference spectra. Another interesting thing about the analysis of aclar is that two spectra were recorded one of a 0.8 thick sample and the other 2mm thick. The spectrum of the thicker sample is obviously showing more absorbance.

This could be used as a method for measuring thickness of films if the peak depths could be calibrated to certain known thickness of film. The obvious effect of having a thinner film is a change in properties. The film will become more flexible and a reduction on material means less cost but the barrier properties would drop since more material as shown here reduces species getting through the material.

Escal

This film is another multi layer substance so the peaks need to be associated one by one. The identification is done in conjunction with the general commercial information also available. A peak at 1450cm^{-1} and identifies polyethylene and the series of peaks between $1500-1000\text{cm}^{-1}$ show the presence of polypropylene. The other polymers identified include Polyvinyl Alcohol and Polyvinyl Acetate. From commercial information the presence of both of these material seems unlikely and the peaks could be due to other materials.

However the material is said to be composed of Silica deposited on PVA, the PVA could refer to either of these material. Polyvinyl alcohol has good gas barrier properties but is not effective as a moisture barrier. It is a

polymer used more commonly in the barrier film industry compared to polyvinyl acetate. The acetate peaks may be other species, the 1740cm^{-1} peak is classically associated with the carbonyl group which is often due to oxidation of the polymer. The spectra is complex and so compositional analysis has been only partially successful.

Saran

This material is identified as polyvinyl chloride the identification is due to the number of peaks matching the reference spectra. There also seem to be traces of another polymer such as polyvinyl acetate. This is relatively unsurprising since the film under SEM analysis looks fairly full of impurities that will affect the IR spectra. This material is clearly thinner than the rest since the peaks all remain above the y-axis showing more transmission due to less material blocking the beam.

Film o Wrap

This material is again full of many polymers making the spectra fairly complex to break down. The four constituent parts are recovered and this corresponds well to the commercially released data. The polymers found were polyester, polyethylene and PTFCE.

Part 2

The second part of the results show results of the barrier film Escal exposed to a variety of different environments. The spectra all seem very similar despite at least one of the materials (the film sample exposed to the highest temperature and longest time in the oven) becoming very curled up and slightly brittle after heat treatment.

The only differences that can be seen amongst the films are the series of peaks around 1600cm^{-1} , described by the arrows in the first figure above. Here the peaks are seen to change shape. This may indicate oxidation taking place in the film. Further work is to be undertaken to establish whether this is an issue in the stability and oxygen diffusion properties of the material. In order to establish whether the changes in the peaks noted here are relevant the material could be exposed to stronger levels of change by ageing.

Summary

IR spectroscopy has successfully identified many of the polymers in the films in this study. However, it failed to work when used on opaque samples and it was difficult to determine precise results when considering multi-layer samples. The advantage of the technique was that it was readily available and laws quick to do. The reference spectra for polymers characterised in this way are also well established compared to other methods making it better for common polymers as were found in this study.

Zygo- topography study

Introduction

The surface structure of the barrier film will have an effect on its performance as a barrier film. Polymers at their surface will be different from the structure in the central regions. On the surface polymer chains have end groups which are exposed and will respond differently to the interior that is likely to contain the main backbone of the chains. Literature describes how a polymers surface affects such properties as adhesion and wetability (relating to heat sealability), electrical behaviour (static and the chance of the film therefore collecting dust), wear properties and optical properties (haze, gloss and stains)^M.

Film surfaces are also important in protecting specimens. This method of analysis is being used to measure the micro-topography of the films. Looking at the surface will allow for comparison between the films in terms of shape, form, defects and structure leading to conclusions about processing quality and film capabilities.

Aims

- Record topographical images of the films
- Evaluate this method for characterisation and measurement.

Abstract

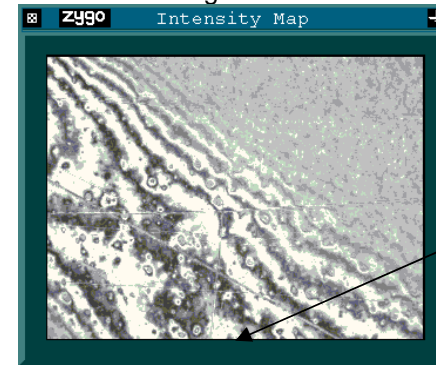
Using this method for surface measurements is rarely done in the analysis of polymers. They are flexible, non flat materials yet this method did give information about the micro surface details and could distinguish well between smooth and defected films. Aclar (vaposhield) was found to be the smoothest film with least defects, in comparison saran and foil o wrap were seen to have very varied surface topography shown by the ~10micron difference in the surface heights across the material. T should be noted that the material being worked on was a pure commercial sample and therefore more likely to have a higher level of production quality.

Method

All the films in the study were analysed using this method.

The materials were fixed to metal washers for support during these experiments. The washers were viewed under an optical microscope with a

special optical system that allows interference fringes from the surface of the material to be seen. Te purpose of the fringes is to see where the material is flat by adjusting the sample platform appropriately. Below is an example of the interference fringes on a film:



Interference fringes show the material is not flat but the form follows a curve.

Once the material has been brought to a point where the interference fringes are strong in contrast and stretched out the material is presumed to be as flat as is possible. A scan of the surface is then completed and the data available for analysis. The scans were completed at 25seconds with a x10 lens.

The data that is drawn from the topographical scan includes depth profiles over the surface of the material presented in 3D. The value used for comparison of the barrier films in this investigation is the bearing ratio. This graph records the number of points collected at certain heights across the surface as a cumulative data set. For example a perfectly flat sample would be recorded as a flat line at a certain height. This measurement can give comparison of height ranges across a sample.

Results

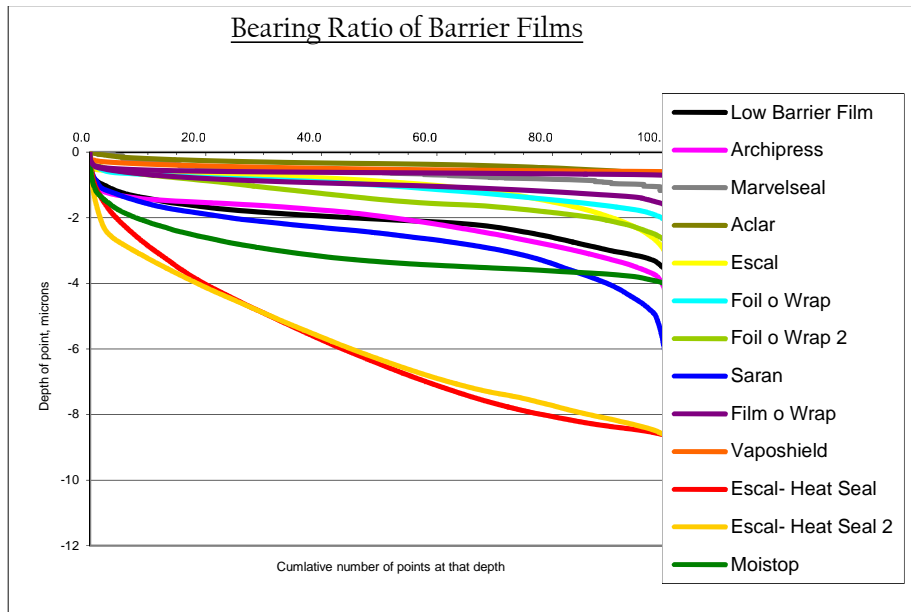


Figure 9 Bearing Ratio plot of all barrier films

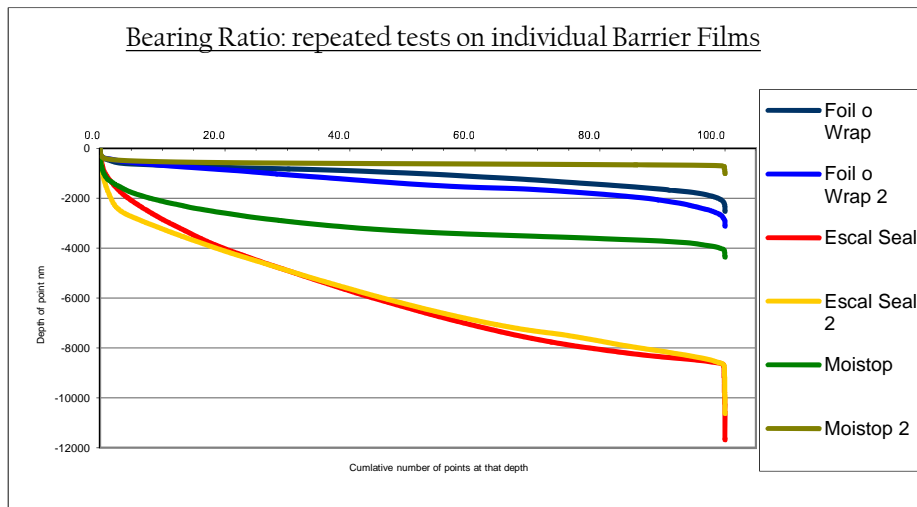


Figure 10. Bearing Ratio plot of selected barrier films

Below are a selection of images and graphical representations of the films.

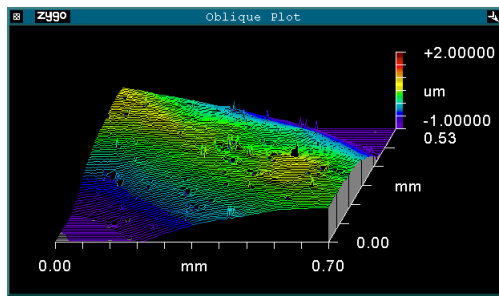


Figure 11. Escal (nhm store)

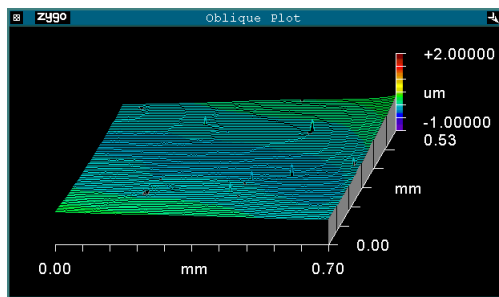
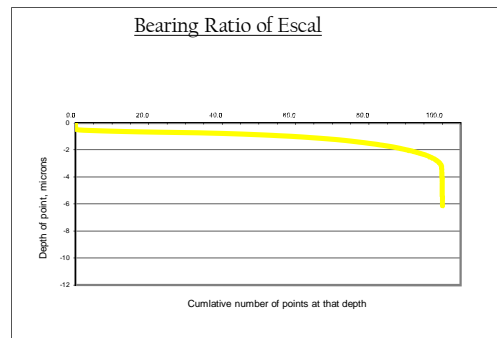


Figure 12. Vaposhield (Aclar)

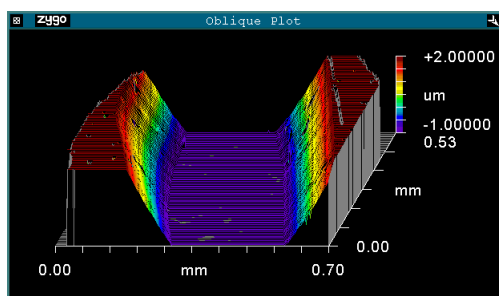
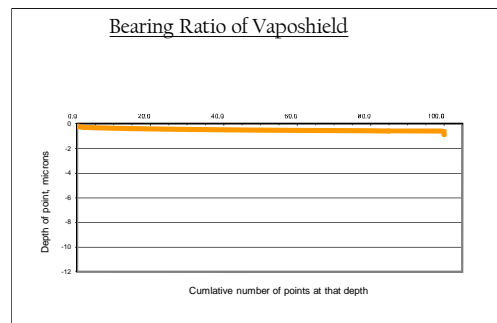
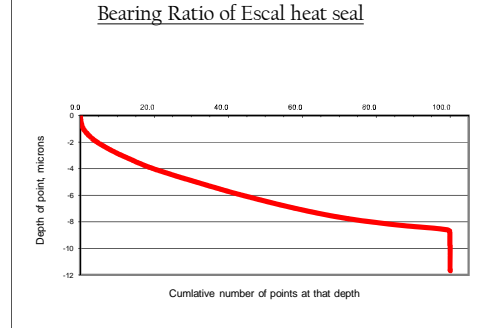


Figure 13. Escal Heat Seal



Discussion

The bearing ratio graphs describe a wide range of surfaces from the different barrier films. A bearing ratio plot represents the roughness of the surface by measuring points at different heights taken from the reference at the highest peak. A plot that is relatively flat would suggest an even surface with few defects and pits. The gradient of the plot suggests how much variance there is between the heights in the surface and the previous point. A steeper gradient refers to a more sudden change in depth.

It is important to note that the bearing ratio also includes the depth effect created by the fact that polymer films are flexible and so have a profile inherent even when held onto a flat washer. The surface detail of the barrier films is visible using the 3D surface images shown in the results section above.

The bearing ratio plot showing all the barrier films shows the films have a variety of flexibilities and surface heights. The smoothest films are noted to be Aclar and Vaposhield. These materials were confirmed to be of the same composition by IR spectroscopy. This makes this result relatively unsurprising yet assuring that the zygo measurements can be considered consistent.

The smoothness of the structure is likely to be assisted by the fact that the films are mono-layer allowing the material to settle alone and not be affected by interfacial forces present in multiple layer films. The topography of these films is also supported by the middle figure in the second page of results.

This type of smooth surface suggests good barrier film properties since it describes a surface with a few defects (these could allow species to propagate more easily through the film). A flat surface also houses fewer protrusions, which could make for good sites for build up in concentration of dust particles- thus reducing light transmission. A rough surface could also suggest a more random inner structure. A homogenous structure would have a lower its surface energy and so be less likely it is to react strongly to its environment (not exhibit long term stability).

Going back to the first graph the film Marvelseal is also fairly smooth. It is a thicker film compared to Vaposhield and Aclar that could suggest it is more capable of laying flat under its own weight. Again its smoothness suggests good properties since there are few deep defects shown since there is little fall at the end of the curve.

The metallic films in this study include Moistop, Foil o Wrap and Marvelseal. All are seen to have surface plots that fall within similar profiles suggesting the surface properties do relate to the physical properties and composition of the films. A metallic film will be denser than a polymeric substance and therefore be capable of sitting flatter across the washer. The plot also proves the a metallic film is less likely to contain deep defects, since the graph doesn't have a large number of points at the deepest point of the measurements (at the end of the plot).

Displaying a wider range of surface depths (a greater difference in plot height) is Escal as a single film section. This material shows in particular a great number of points (deep into the material) towards the end of the plot. The graph falls off suddenly suggesting steep sided surface defects. Compared to the smooth Vaposhield (Aclar) film the Escal plot appears to show a rough surface finish with a regular array of holes.

The surface depths of the films Archipress and Low Barrier Film are shown on the bearing ratio plot as having a greater range of surface heights. This is due to the materials being thinner and more flexible and also containing more defects. Scratches were clearly seen on the surface of these films looking through SEM analysis. However, the performance of the films does not solely depend on surface features. Defects play a crucial role in ease of diffusion and permeability plus thinner more flexible films are going to be permeated more quickly and easily by species.

Saran being an especially thin film results in the graph showing the flexibility in a wide range of height measurements. This film also appears to have many defects since the plot falls steeply at the end of the plot. These features would contribute to a poor performance in terms of mechanical and barrier properties.

Finally a heat sealed region between two Escal films was measured using this technique. The depth of the heat seal can be measured at 1 micron below the original surface height. Compared to the overall thickness of a single layer of Escal (~120micron) this is a small impact. Imaging the heat seal shows its profile to be regular making its ability to be structurally sound good. At the deepest point where the seal becomes flat, the width is

measured using the Zygo analysis as being 3mm on average. The image of the seal shows how drastic its profile is compared to the standard section of barrier film. It is clearly an area that will respond differently compared to the bulk of the film.

The effect of heat sealing causes the polymer to cross-link so a compositional change will alter structure and strength. Accurately measuring the dimensions of the heat seal could be used to analyse forces across the seal such as that which could break. If the width of the Escal changes significantly this could alter the mechanical strength of the material, however it is also important to note that the heat sealed area has structurally and compositionally altered from the original film. Measuring the heat seal dimensions of other films is clearly possible using this technique.

Comparing the films has mainly contributed to classifying the films in terms of roughness, flexibility and defect concentration. Using information previously discovered from SEM analysis and compositional knowledge the films are able to be compared more extensively. The metallic films are stiffer and able to lay flatter. The polymer film that performs the best in terms of remaining flat and containing few defects was Aclar. The most flexible and roughest films of the films were Archipress, Low Barrier film and Saran. The Escal heat seal was successfully measured using Zygo, these measurements could be used to assist in calculations of the tensile properties of the film.

Confocal Microscopy

Introduction

The films have been characterised by various methods but so far a very accurate method of measuring the separate layers of the multiple layer films. This technique is known as a method to study different layers through a material.

Confocal microscopy uses laser light of a specific wavelength to induce fluorescence within the object it is imaging. The microscope is designed to record multiple images of surfaces through a material. The material being studied needs to be able to transmit light otherwise the laser beam cannot propagate through the substance it is looking at. This type of microscopy is traditionally used at the museum in order to image sub surface structure of biological samples, building up 3D structures of objects.

Aims

- Summarise the information this analysis can give about barrier films
- Identify which films, if any, give a fluorescent response from the laser light
- Investigate whether this analysis can be used to measure layer thickness by looking for changes in imaging as the surfaces are analysed in a series
- Evaluate this method for characterisation and measurement.

Abstract

Although Confocal microscopy on the Marvelseal film did not recover any information (the beam was reflected), fluorescence was detected within the Escal and Film o Wrap films. The shape of the fluorescence was ring like suggesting it was due to stressed areas of material as a response to shape changes around a defect or piece of contamination present in the film.

The fluorescence areas seen t a sequence of depths would appear to suddenly change in distribution and array at certain points within the sequence of images taken. However the graphs tracking the presence of this fluorescence did not show these jumps in image clearly enough for measurements to be accurately made.

Although the is method did give more information about the material in and amongst the layers of film than other techniques used so far it was not possible to make any clear conclusions about layer thickness from the measurements.

Introduction to Confocal Microscopy

The fluorescence is due to the chemistry of the material; certain substances can emit a photon of light (fluorescence) in response to the high energy of the laser beam. The fluorescence can help describe profiles within the film. It was hoped that separate layers may respond differently to others which could be related to changes in the films such as layer differences.

Different layers can be viewed because the working distance within the setting of the microscope changes. Each working distance at which the image will focus corresponds to a certain depth within the material. It relies on the beam being able to penetrate through the film and return to the detector. Only a particular depth in the material becomes focused at one time since the working distance of each wavelength is unique.

Method

The following films were prepared by minimal handling (avoiding extra contamination) and placed between two glass slides to enable the film to sit as flat as possible.

- Low Barrier Film x
- Archipress (pouch)x
- Marvelseal 360 x
- Escal ok
- Film o Wrap ok

To improve the results the analysis was conducted using an oil immersion.

The samples were examined using a Leica SP NT confocal microscope in reflected light mode. With this microscope simultaneous images can be collected at several different wavelengths that correspond to different depths within the film.

An initial test was carried out on each film to determine if any autofluorescence took place using a wavelength (λ) scan. The section was scanned at a single focal plane with each laser in turn to give the wavelength with the best response.

The best results for the barrier films were obtained with the 476nm laser, which was used for all subsequent imaging. The films which did fluoresce were imaged through depths of up to ~40micron with steps of around ~4micron.

Marvelseal showed no auto fluorescence and the film reflected the beam resulting in no sub surface information being gained. Escal and Film o wrap showed auto fluorescence using the 476nm laser. The fluorescence in the films is coloured green whereas the transmitted light images (taken of Escal) are displayed as a greyscale.

Each frame was scanned twice and run through a frame-averaging filter to reduce background noise. For single images, the z-axis (depth) data from the entire stack was combined and the brightest pixel from each point was computed and displayed (maximum projection image).

The results collected include images through the top regions of the films. When areas of fluorescence appear they can be measured for relative brightness and position through the film, producing graphs representing

the fluorescence as brightness peaks. The highest point on the peak indicates the position of the fluorescence.

Results

Escal

Below is a selection of confocal images taken of Escal™. Each image describes a distance of 250 microns across the material. Each image is taken intervals of 0.5 micron in depth. The black images are showing the fluorescence from reflectance and the greyscale images represent a transmitted image through the sample.

Figure 14 Stack of images from imaging the top layers of Escal. Light grey images are optical transmission; the laser fluorescence is shown as green pixels on black the screen. The images in this selection have been taken in pairs; one optical and one showing fluorescence.

Figure 15 These images are taken from the same sample as the figure above but are from a different depth from the surface. This shows different areas of fluorescence appearing at different places within the material.

Escal

The following graphs record the points of fluorescence within the films depth. The plots show depth in microns along the x axis with relative fluorescence on the y axis. By looking at the peaks on the graphs this shows the brightest areas of fluorescence and the relative location through the films thickness. All the areas of fluorescence are selected whilst the microscopy is taking place and recorded on the computer. Each selection on an area of fluorescence gives rise to a peak on the graph.

Figure 16 Image showing the fluorescence within Escal film. The green fluorescence is seen to form in a similar shape and form; a ring of fluorescence surrounding a circle of no fluorescence.

Figure 17 This graph shows a series of peaks describing the fluorescence recorded within the sample. The total depth that was measured in this sequence was ~48micron.

Figure 18 This graph shows the series of fluorescence seen through the Escal film looking from the other side of the film. This depth profile covers a smaller distance throughout the material than the previous graph ~20micron.

Escal

The graph below shows fluorescence peaks in Escal recorded during a different analysis session to the previous two graphs. The peaks were similar to those recorded previously except for the profile described by the major peak. It suddenly drops to a minimum, this graph is shown cropped to describe this feature.

Figure 19 The axis are the same on this graph as those previously. The graph shows sudden drop in fluorescence at a certain depth in the material.

Marvalseal 360

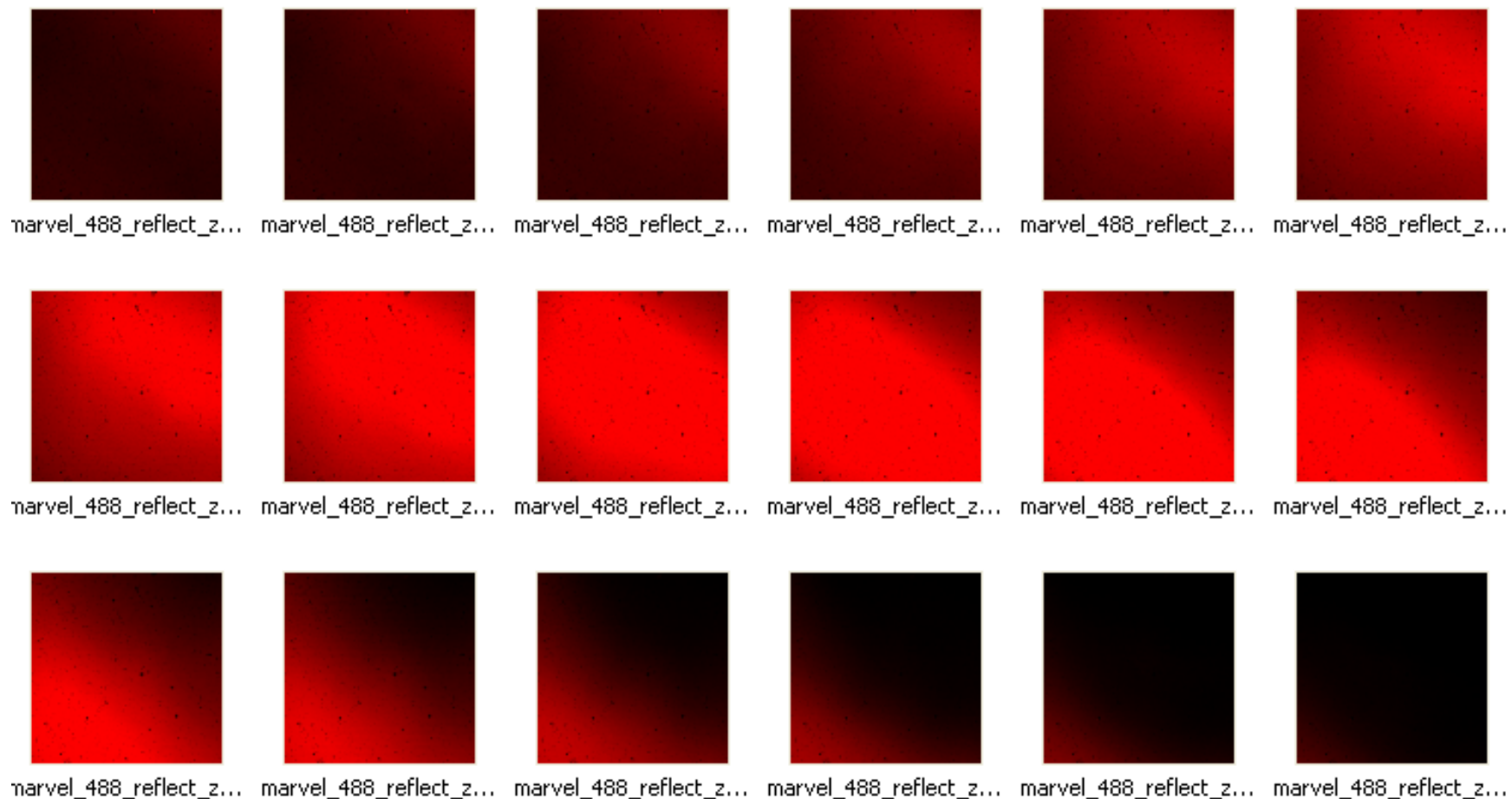


Figure 20 Marvalseal images showing the surface coming in and out of focus. No other areas of fluorescence were acquired. Width of each image is 250micron

Film o Wrap

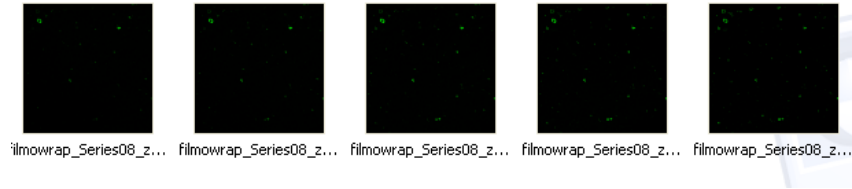


Figure 21 Part of the fluorescence image series in film o wrap. Width of each image is 250micron

Figure 22 Plot of fluorescence within film o wrap, showing equal distribution of peaks throughout the depth analysed. The areas of fluorescence appear to increase in brightness

Discussion

It is not common to look at barrier films under this type of microscopy. Literature on plastic films does not describe the films being viewed in this way, yet it is an aim of this project to discover more about the internal structure of the films to help assess barrier performance.

The first material studied under the confocal microscopy was Escal. It has been shown that Escal is a multi-layer film by the SEM analysis and IR spectroscopy. The results above show there to be a reasonable level of fluorescence coming from the film at depths of up to ~48micron. Each area of fluorescence seems to follow a similar shape- that of rings around a dark circle. The areas do differ in size but all follow this similar pattern, suggesting it is one type of structure or feature that is causing this response.

Fluorescence is caused by interactions of between the laser beam and electrons within the material. When an electron is bombarded this causes it to increase energy levels, it then quickly loses energy and falls back down to the lower state. As the electron falls energy level, it releases energy which is seen as fluorescence. An electron in a particular bond is only affected by a specific wavelength of light corresponding to a certain amount of energy. Different chemistry determines whether or not an area of material fluoresces or not. It is due to the different levels of energy a bond exhibits which can be a result of different atoms and the conditions they are under.

It could be that the rings of fluorescence seen here are due to impurities and contamination. The chemistry of impurities would be different from the material itself giving a different response to the laser light. However, the rings could also be showing areas where the material is under stress. When a substance is stressed it's energy will be increased possibly introducing energy levels which are more effected by the wavelength of the laser beam. Some of the rings appear to be repeated around the dark centre giving the impression that the effect is like a stress pattern seen on polymers when they are put under force. Another explanation of the shapes described by the fluorescence are that the dark section is an area of porosity within the film surrounded by a stressed region of film. The circular shape of the defects could also be created by trapped gas or fluid.

Defects such as those described above are likely to have occurred during the processing since it was the last time the material was exposed to significant change. Gas or particulate could've been trapped in the melt and not completely removed by the extrusion process, unpolymerised monomer (material which had not been exposed to enough heat to react sufficiently enough) could also be a source of contamination.

During the generation of the images it was noted that after viewing a certain groups of fluorescent areas at a certain point the image would seem to "jump" to show a different array of fluorescence. This seemed to suggest that the defects could be located in certain depths of the material. It was felt this could be an indication of a change in the material such as an interface of two layers or a group of fluorescent sections each being associated with a specific layer.

By studying the graphs describing the locations of fluorescence within the Escal film it could be suggested that the peaks fall into groups. The first graph shows nine peaks describing nine areas of fluorescence within a layer thickness of about ~48micron. The central group of peaks seem very collected and either side are areas where the fluorescence drops to nothing. The width of the area in which these middle peaks collect is around 7 micron in thickness. This doesn't seem to correspond to other suggestions for layer thickness that have been measured using SEM analysis. The other peaks seem fairly evenly spaced and not necessarily grouped.

It would seem logical that if processing in a certain thickness that the defects would become trapped in certain areas and therefore could be associated with a structural characteristic of the film. The fact that defects can be seen give information about the films performance- porosity would reduce barrier capabilities and impurities weaken the mechanical properties of the film.

It is also noted that rings seen on the confocal images appear slightly squashed and orientated in the same direction. If these rings are measured at the point at which they are most stretch the largest is around 50 micron whereas the smallest are barely 5 micron across. If compared to the size of defects seen in Escal using SEM they correspond to the flecks of particles seen within the cross section and measuring approximately 5micron across. The SEM images help to support the view that the defects

here appear to be particulate rather than porosity. This complicates the structure of the polymer and could result in changes to the chemical responses of the film.

The range of brightness from the areas of fluorescence within the film can be seen from the relative heights of the peaks in the graphs. The heights are fairly randomly distributed suggesting the range of defects is spread homogeneously. Remembering the results are taken every 0.5micron change in depth proves again that the peaks are quite evenly distributed. By counting the number of peaks in a certain depth of material a quick estimate of defect concentration can be calculated. The concentration of the defects from the top graph is ~0.2 per micron depth. In comparison, the other side of the film has a defect the defect concentration of ~ 0.5 per micron depth.

The final graph generated from imaging Escal shows a defect concentration of ~0.4 per micron depth. There therefore doesn't seem to be a great difference in the concentration of these defects within the film. This could be due to good processing creating a homogeneous material. Looking at the distance between the top of the peaks can give information about the defects relative to the layer thickness of the films they are contained within. The maximum distance apart between two peaks is around 5 micron, which is equivalent to the thickness of the least thick film in the multi-layer structure.

The Marvelseal imaging is featured to explain why the technique is not suitable for this type of film. It was hoped that the upper transparent layers of Marvelseal would recover some information about the films structure. However the metallic layer simply reflects the beam and no information (fluorescence) was recovered above or below this surface.

The final film that did recover information from this type of microscopy was Film o Wrap. This is a transparent and multiple layer film composed of Aclar and Polyolefin layers. The depth of film analysed was 18 micron which really only covers a small percentage of the overall thickness which is ~110micron. The peaks show a definite increase in height (fluorescence) as the depth increases. This seems counterintuitive since the energy returning to the detector may expect to decrease as distance increases. However it is could be due to there being a change in material,

which actually contains material which when stressed responds more strongly to the laser. The peaks also appear to have a profile. A flat peak shows the fluorescence levels change less over the depth whereas the sharp peaks indicate a thinner area of fluorescence. Either side of the peaks are shadows of the main source of fluorescence so the location of the defect is assumed to be where the peak is at a maximum. The shapes as you look down on the film of the defects within Film o Wrap also follow the ring pattern seen within Escal. The defects in Film o wrap compared to Escal are generally smaller in width and show a greater range of thickness as described by the range of peak profiles.

This analysis showed there to be defects within the surface layers of Escal and Film o Wrap. By comparing the fluorescence with the optical images and SEM views the areas glowing are concluded to be stressed sections of polymer film. This change in shape resulting in a stressed area could be due to porosity or particulate regions within the film. Since this area of the film has not been exposed to an external environment since its production these defects must have come from processing. Escal and Film o wrap differ in the defects they contain, Escal has a lower concentration of defects in the upper layers of the film compared to film o wrap. If more imaging were to be completed there would be better range of data to draw average values and measurements from. The defects in general seem regular in terms of distribution and size.

	Manufacturer	Composition
Corrosion Intercept	Lucent Technologies/ Bell Labs, DuPont [18]	Copper particles bonded into a polymer matrix [10] polymer=polyethylene [15]
Low Barrier Film	Supplied by Conservation By Design	Nylon- from IR Spectra done at NHM
Archipress (pouch)	Multipak BV Netherlands	Reinforced Polyester Film [5], Polyethylene + Barrier Layer (1), Archipress 1000, 1500 and 2900 vacuum pouches are made from a five layer co-extrusion of 92 micron, plasticiser free, pure polyester, pure polyethylene and a special gas barrier
Marvalseal 360	DuPont	Aluminised Polyethylene + Polyester + PP [1,2], Aluminised polyethylene and nylon barrier film [8]
Aclar	Honeywell (was Allied Signal)	PTCFE Homopolymer
Escal	MGC	PP/ Ceramic deposited PVA/ PE
Foil o Wrap	Bell Fibre Products	Polyester, Polyethylene, Aluminium Foil, Polyethylene [24]
Saran	DOW	Polyvinylidene Chloride
Film o Wrap	Bell Fibre Products	Polyethylene/ Polyester/ Polyethylene/ PCTFE (aclar) [11]
Vaposhield	Honeywell (was Allied Signal)	Aclar, PVC? Could just be aclar. (190micron PVC, 50 micron PCTFE, 190micron PVC) [22]
Moistop 622	Fortifiber [31]	*polyester film, 12 micron; polyethylene bonding layer, 16 micron; Alu Foil, 7 micron; white LDPE/ LLDPE Film, 70 micron [23]
Barex Resins [33]	BP	Acrylonitrile-butadiene-methyl acrylate copolymer, Acrylonitrile, Methyl acrylate, Water
Super Escal	MGC	"the outer layer is orientated polypropylene, and the barrier layer is a vacuum deposited ceramic on a PVA substrate. A layer of Orientated Nylon has been added to the inside of the barrier layer; the inner sealing layer is linear low density
EVAL	EVAL	Ethylene (27-48%) and Vinyl Alcohol [29]

Analysis

- Confocal Microscopy
 - Surface characteristics
- Zygo-topography
 - Surface characteristics and depth profiling
- Raman Spectroscopy
 - Composition of barrier film
- FTIR
 - Composition of barrier film
- SEM

Confocal Raman Spectroscopy

- Depth profiling (surface – 18 microns)
- Change at material interface
 - Polyethylene/polypropylene interface

spectra in 2d and 3d describing the top layer of Escal film and the change in composition as material depth increases

Current Favourites

- Barrier Films
 - Escal®
 - Aclar (PTFCE)

Preliminary Research Results

- Have been able to identify components of barrier films
- Surface integrity seems to be changeable dependant on product
- Differences in quality of production leads to changes in thickness of polymer layers
- Ductility of polymers, cutting and welding can lead to loss of integrity of barrier film
- Impurities in films can cause loss of integrity of barrier films

Future Areas of Research

Seal

Heat sealable: polyethylene
Impulse weld: Polyester (PET)

Oxygen barrier: PTFCE (Aclar)
Ceramic Coated Polyester

Water Vapour : PTFCE (Aclar)
Barrier Ceramic Coated Polyester

Tear Strength: Nylon
Protection Polyester (PET)
Polypropylene

Future Developments

Conservation grade materials
Polyester (PET)
Ceramic coating (SiO₂ or Al₂O₃)
Polyethylene (heat sealable layer)

Explore use of PTCFE (Aclar®)

Working relationship with barrier film company
Improved quality control

Overall Conclusion

This report covers a wide range of features and aspects of barrier film materials. It aimed to investigate the business and industrial side of films as well as look at the materials from a more scientific perspective. Finally a review was conducted to look at methods and research, which have been conducted on polymers and aspects of barrier films.

Several barrier films companies were contacted mainly via the internet and email contact. Companies contacted included Honeywell, EVAL, MGC, DOW, BP and Rexam Flexibles. These are new contacts, which have been made between the museum and industry. The strongest link was made with the barrier film processing company, Rexam Flexibles. Following a preliminary meeting Rexam, the company seemed enthusiastic to work with projects conducted here in the future. The facilities at Rexam include a wide range of film manufacturing techniques as well as a laboratory dedicated to the testing and analysis of barrier films. Rexam are closely connected with Honeywell in America, a company, which produces the expensive, but high quality moisture barrier film, Aclar. It is recommended that a contact with Rexam be retained in order to gain knowledge and possible use of facilities. It has been recently advertised that an Aclar/ Barex composite barrier films has been produced. Barex is manufactured by BP and is specifically an oxygen barrier material. The combination of both these films may offer one of the best films for the application of specimen storage. The film is likely to be expensive but have superior barrier properties and if included with a sealing layer could satisfy most of the original

material properties required. Rexam is a company likely to have access to this material because of the contact with Honeywell.

The next stage of the report aimed to characterise a range of barrier films. The SEM imaging proved especially successful at describing the layers in multiplayer structures and worked best when dealing with films containing different compositions. The imaging showed contamination and defects upon and within the surfaces of the films. Aclar film looked the best in terms of least surface and internal contamination. Other important features to note from this analysis included being able to see the different layers amongst Escal film as well as de-lamination within the Escal heat seal.

FTIR spectroscopy determined the composition of Low barrier film to be Nylon which was previously unknown. It also confirmed the composition of most of the films in the study. The limitation of IR was that it would not work on opaque films and the peaks were not always easily assigned to certain polymers.

Zygo surface analysis of Aclar showed it to have a very smooth surface with few defects compared to Escal which had some deep surface pin holes. Zygo was able to give dimensional measurements of the heat seal in Escal. Finally, confocal microscopy showed Escal and Film o Wrap both to contain defects and contamination below the surface. This contamination was concluded to be spread fairly homogeneously throughout the area viewed.

and subsequent carbonyl index measurements acquired using an ATR-IR spectrometer..

In the latter stages of the project Confocal Raman spectroscopy was trailed on Escal to compare the characterisation technique to the others in this study. The confocal Raman gave the composition and layer thickness of the first layer of Escal successfully. It is recommended that further work use this technique if available.

The final section of the report was a review into polymer ageing. The major agents and modes, which can cause polymers to degrade, were listed and discussed. A review of papers on ageing gave details of how a standard ageing experiment may be constructed using the correct wavelength lamp and a turntable. The changes which occur to the polymer can be analysed using FTIR and by measuring the carbonyl index. Although the research relates in detail to the materials at a micro level there seemed to be a lack of information as to how this correlated to real time scales for physical change.

Overall, it is recommended that contact be continued with Rexam flexibles, with particular focus on developing Aclar and derivatives to compete with Escal as a conservation film. To analyse the barrier films Confocal Raman spectroscopy, ATR-FTIR and AFM are all recommended to recover more information about the micro and sub micron material structure. Collaboration with Imperial College Chemical Engineering department would allow the museum more access to a larger range of analysis equipment. Ageing experiments could be conducted on polymeric materials using the information in this report, a uv lamp and turntable equipment needs to be purchased

References

- A. Doyle, A.M. 2003. A large scale 'microclimate' enclosure for pyretic specimens. The Geological Curator 7(9):329-335.
- B. Heat Sealing of Escal, E Lam, A M. Doyle 1999
- C. Barrier films- unpublished work, Chris Collins, Cambridge University, 1999.
- D. Barrier Polymers, University of Texas, www.mrw.interscience.wiley.com/epds/articles/pst025/sect7-fs.html, 106.2003
- E. Plastic Films Technology and Packaging of applications, Kenton R. Osborne and Wilmer A. Jenkins, 1992, pg 31
- F. <http://www.rutanpoly.com/tour-2.htm>, 19.6.2003
- G. Rexam Healthcare flexibles, www.rexam.com/flexibles, Aug 2003, CDROM from marketing department.
- H. Polymer Permeability, Ed by J Comyn, 1985, Pg 23
- I. http://www.chem-mats.mmu.ac.uk/Chemistry/Chem_staff/Edge.htm, 24.8.2003
- J. FTIR Reference Text.
- K. Chemistry in context, 4th Ed, Graham Hill and John Holman, 1995, pg 434
- L. Rosales-Jasso, N.S. Allen. Polym Degrad Stab 1999; 65:199-206
- M. Surface analysis of polymers by XPS and Static SIMS, D Briggs, 1998, pg 1,2
- N. Materials Science and Engineering, An Introduction, William D. Callister, Jr. 2000
- O. Plastic Film; Technology and Packaging Applications, K Osborn/ W Jenkins, 1992
- P. http://www.mse.arizona.edu/classes/mse435/Polymer_degradation.pdf, 28.8.2003
- Q. <http://www.chem-mats.mmu.ac.uk/Research/Polymer/normanpublicat.htm>, 28.8.2003
- R. <http://www.polymers.tudelft.nl/research/poleng.html>, 28.8.2003
- S. Edge, M, Allen, NS, Wiles, R, McDonald*, W and Mortlock*, SV, Characterisation of the Species Responsible for the Yellowing in Melt Degraded Aromatic Polyesters: Part I: Yellowing of Polyethylene terephthalate', Polym Deg & Stabil, 53, 141-151, 1996.

References (Polymer Degradation Research)

1. Gugumus F. Polym Degrad Stab 2002; 77:147-155
2. Joao Carlos Miguez Suarez, Eloisa Biasotto Mano. Polym Degrad Stab 2001; 72:217-221
3. Hitoshi Kuota, Yayoi Hariya, Shin-ichi Kuroda, Takashi Kondo. Polym Degrad Stab 2001;72:223-227
4. The use of oxygen-free environments in the control of museum insect pests, Shin Maekaura, Kerstin Elert, The Getty Conservation Institute, Los Angeles, 2003
5. Materials Science and Engineering, An Introduction, William Callister, Jr., 5th ed Wiley.
6. C.M. Liauw, A Childs, N.S. Allen, M. Edge, K.R. Franklin, D.G. Collopy. Polym Degrad Stab 1999; 65:207-215
7. http://fire.nist.gov/bfrl_pubs/build95/art006.html 5.9.03
8. Kenneth Moller, Thomas Gevert, Arne Holmstrom Polym Degrad Stab 2001;73:69-74
9. (Article in press) F. Fallani, G Ruuggeri, S. Bronco, M. Bertoldo Polym Degrad Stab, accepted May 2003
10. A. Rosales-Jasso, N.S. Allen. Polym Degrad Stab 1999; 65:199-206
11. Kato, Z.Osawa. Polym Degrad Stab 1999;65:457-461
12. Gabriela Botelho, Arlete Queiros, Pieter Gijnsman. Polym Degrad Stab 2001;73:431-435
13. R.S.Lehrle, I.W. Parsons, M. Rollinson. Polym Degrad Stab 2000;67:21-33
14. Dan Forsstrom, Torjorn Reitberger, Bjorn Terselius. Polym Degrad Stab 2000;67:255-261
15. Nazdaneh Yarahmadi, Ignancy Jakubowicz, Thomas Hjertberg. Polym Degrad Stab 2003;82:59-72
16. H Havebratt, E Ostman, SJ Persson. J Appl Polym Sci Appl Polym Symp. 1992; 44:83.
17. Gui-Yang Li, J.L. Koenig. Polym Degrad Stab 2003;81:377-385
18. AG Erlat, RJ Spontak, RP Clarke, TC Robinson. PD Haaland, Y Tropsha, NG Harvey, EA Vogler. J Phys Chem B. 1999; 103:6047
19. Meng Ouyang, Peter P Klemchuk, Jeffrey T Koberstein. Polym Degrad Stab 2000;70:217-228

Appendices

Film and Polymer Melting points

<i>Commercial Name</i>	<i>Tm/ oC</i>
Corrosion Intercept	140
Low Barrier Film	250
Archipress (pouch)	
Marvelseal 360	130
Aclar	211
Escal	140
Foil o Wrap	140
Saran	
Film o Wrap	140
Vaposhield	211
Escal Seal	
BF unknown name	140
Escal	

<i>Polymer</i>	<i>Tm/ oC</i>
Polyethylene	140
Ester	122
Nylon	250
Polypropylene	187
PCTFE	211

General Web References

June 4th-13th 2003

<http://www.toppan.co.jp/aboutus/overview/accounts/setsume4/english/setsu5.html#2>
http://www.wipak.com/tech_support/index.html
[http://www.packstrat.com/FILES/HTML/Marketing_and_Tech_Studies/Study_TOCs/PS
TOC - barrier films and coatings 2001-2005/0.4976,,00.html](http://www.packstrat.com/FILES/HTML/Marketing_and_Tech_Studies/Study_TOCs/PS_TOC_-_barrier_films_and_coatings_2001-2005/0.4976,,00.html)
<http://www.sealedair-emea.com/eu/en/products/food/films.html>
<http://www.keepsafe.ca/>
<http://www.dow.com/medfilm/products/prod13.htm>
<http://www.dow.com/stickwithus/product/products/saranex.htm>
http://www.boedeker.com/pctfe_p.htm
[http://www.sciencedirect.com/science?_ob=QuickSearchListURL&_method=list&_as
et=W-WA-A-A-AUUU-MSAYWW-UUA-AUCVEYWUWB-YDAVVUAZ-
BACW-
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BACW-
U&_sort=d&view=c&_acct=C000011279&_version=1&_userid=217827&md5=d179
20590481d88b72300fab74269bb2)
<http://www.aclar.com/>
<http://www.conservation-by-design.co.uk/oxyfree/oxyfree10.html>
<http://www.2spi.com/catalog/photo/aclar-film.shtml>
<http://store.preservationequipment.co.uk/store/show-product.cfm?p=320>
<http://www.honeywell.com/>
http://www.surrey.ac.uk/PRC/publications/JC_2000_AME_AWE.pdf
<http://www.surrey.ac.uk/PRC/current.html#Ageing>
<http://www.polymers.tudelft.nl/research/poleng.html>
<http://www.npl.co.uk/npl/cmmt/polydeg/>

http://www.npl.co.uk/npl/cmmt/polydeg/esc_guide_cmmta288.pdf
<http://www.elsevier.com/locate/inca/405941>
<http://www.mse.arizona.edu/classes/mse435/Polymerdegradation.pdf>
http://www.chem-mats.mmu.ac.uk/Chemistry/Chem_staff/Edge.htm
<http://www.chem-mats.mmu.ac.uk/Research/Polymer/photodegr.htm>
<http://www.staff.ncl.ac.uk/owen.bradford/technique.html>

General Text References

- Plastic Films, J H Briston, 1974
- Engineering Materials 1; An introduction to their properties and applications, M Ashby and D Jones, 1996
- Polymer Permeability, Ed by J Comyn, 1994
- Surface Analysis of Polymers by XPS and static SIMS, D Briggs, 1998
- The Chemistry of Polymers, J W Nicholson, 1991
- An Introduction to Materials, Science for Conservators, 1992
- Technical Report Writing, The Institution of Electrical Engineers, Jan 1993
- Proceedings of the 3rd Nordic Symposium on Insect Pest Control in Museums, Sept 1998
- How to write effective reports, John E Sussams, 1983
- Report Writing, Gordon Wainwright, 1984
- How to write and publish a scientific paper, Robert A Day, 1989
- Writing for Science, Heather Silyn-Roberts, 1996
- Adhesives and Coatings, Science for conservators, 1992
- Research in Conservation; Inert Gases in the Control of Museum Insect Pests
- Engineer in Industry, Materials 2002-3, Dr Christopher Stoney, The Management School
- Plastic Films; Technology and Packaging Applications, Kenton R Osborn and Wilmer A Jenkins, 1992
- Polymers in Conservation, Ed by N.S. Allen, M. Edge and C.V. Horie, 1992
- Handbook of Polymer Degradation, S. Halim Hamid, 2000
- Materials Science and Engineering; An Introduction, William D. Callister, 2000
- An Introduction to Polymers, Young and Lovell, 1991

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- Mitsubishi Gas Chemicals Ltd. Inc.
- Electron Microscopy and Mineral Analysis Labs, Natural History Museum
- Honeywell

Conservation Difference

- Conservation ethic
- Material Science
- Data
- Future Developments

Short Term

- For short term treatments e.g. Pest Control
- Standard EVOH barrier film is more than adequate
 - Oxygen and water vapour migration rates
 - Relatively stable in the long-term
 - Low cost
 - Minimal pollution problems

Long-Term storage

- Control
 - Oxygen
 - Relative Humidity
 - Pollution
 - Light
- Minimal Intervention with Object
- Stability of barrier

Benchmark Standards

- Low oxygen migration
- Low water vapour migration
- Stability in range of humidities
- Stability in contact with high pollutant concentrations
- Good tear strength
- Good tensile strength
- Clear
- Easy to seal with good seal properties

- Known composition
- Flexible
- Low cost

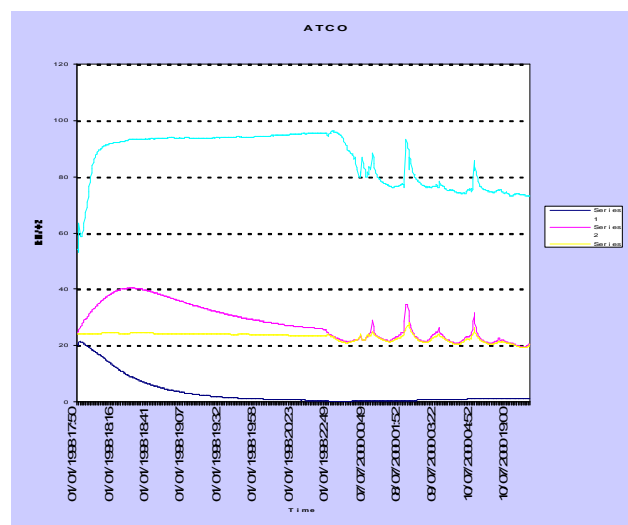
Benchmark Material

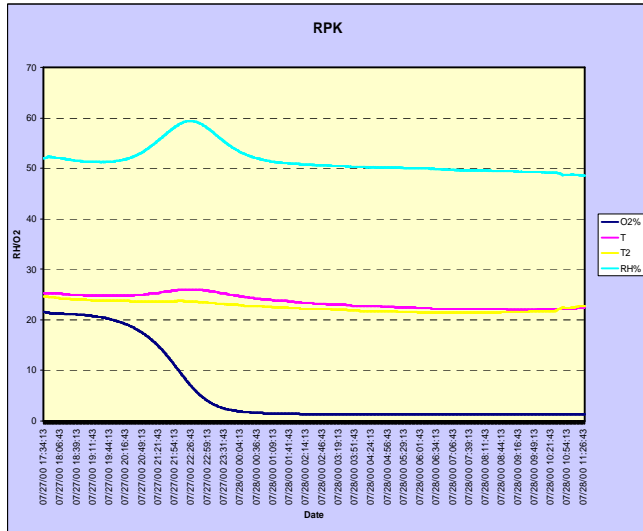
Escal®

Areas of Research

- Barrier Films
 - Surface
 - Construction
 - Materials

Oxygen, RH and Temperature Levels





Range of barrier films reviewed

