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Introduction

To start let us explain what is meant when we refer to a barrier material and then go on to describe where these barrier materials might be used. A barrier is something that provides a resistance against something else so that in packaging or encapsulation terms the meaning of barrier tends to mean as resistance to the ingress of something that might degrade the product being packaged or encapsulated.

Everyone has their own idea of what is meant by a barrier material depending on what is most detrimental to their product. For some people barrier only refers to protection against water vapour whereas for others it is more important to protect the goods against oxygen. So barrier is a generic term that needs to be elaborated as a good barrier material against water vapour may have little barrier performance against oxygen and vice versa.

As will be shown there is a growing market for these existing barrier materials. There is also an, as yet, unexploited market for barrier materials with a much better barrier performance. As the performance requirements increase the difficulty in producing the barrier materials also increases, as does the cost.

The barrier performance starts with the choice of materials and includes the whole manufacturing process. Glass bottles and tin cans are long established barrier materials for food packaging. It was believed that to improve the barrier performance of polymers it was simply a matter of adding a thin enough glass or metal layer that would not impair the flexibility but, it was thought, would match the performance of the bottles or cans. The standard method of applying a glass or metal coating to polymer substrates is by vacuum deposition. In roll-to-roll vacuum deposition the quality of the supply rolls is a critical factor as too is any pre-treatment or cleaning process. Subsequent chapters will follow the process through from the polymer web production and any cleaning or pre-treatment through to the nucleation and growth of coatings deposited by various vacuum deposition techniques. In order to be able to compare the performance of different barrier coatings it is necessary to be able to measure the performance and so there is also a chapter that describes the most common methods of measuring the barrier performance. In this way it is hoped that it can be shown how the ultimate performance of the barrier materials can be affected throughout the whole manufacturing process.

A barrier is anything that keeps things apart and we can see examples of barrier materials everyday in food packaging where food products are protected from a variety of different elements be they gases, liquids or solids. Depending on the food and the sensitivity of the foods to degradation they may need protecting from moisture, oxygen, light as well as bacteria, moulds, aromas and taint (1). As might be expected different materials will perform differently as a barrier to liquids or gases and so there is not any one material used as a universal barrier. There are many possible solutions to providing a suitable barrier in fact one of the problems we now have is the vast choice of materials that in combination could provide the necessary barrier performance.

It is not just food that requires barrier materials but anything that has some sensitivity to the ingress or egress of some other material, be it a gas or moisture, will require a barrier to protect it. Thermal insulation panels, used to improve the insulation performance of buildings, are designed to have a working lifetime of 50–100 years. Throughout this time these panels are expected to maintain their insulation performance which is, in part, dependent upon the evacuated panel remaining under vacuum and hence air and moisture have to be kept out for all this time. The reality is that this is not achieved by the barrier material performance alone but by a combination of the barrier material and scavenger materials incorporated into the product that getter what little amount of gas or moisture that is passed through the barrier material. Once the scavenger material is saturated there will be a build up of gas or moisture and the performance of the insulation will then begin to decline.

In the area of electronics there are the organic light emitting devices (OLEDs) that are degraded by moisture ingress and are so sensitive to attack that the barrier requirements are six orders of magnitude higher than those used in most food packaging applications. These very high performance barrier materials are often referred to as ultra-barrier materials.

It is interesting to note that often the same materials are used for both the food packaging and for the ultra-barrier applications. There can be a huge performance difference for exactly the same materials that is dependent upon the quality of how the materials are supplied, handled and used to make the final barrier material. Polymer webs have a certain amount of barrier performance that is inherent but it is often not enough to meet the customer specifications and so is coated with something to improve the barrier performance. The two materials that have been used for food packaging for decades are metal and glass. The expectation being that adding a very thin glass or metal layer would change the polymer barrier performance into the same perfect performance exhibited by the glass or metal. The metal and glass or glass-like very thin layers, sometimes as thin as a few nanometers, can be deposited using vacuum deposition techniques. The question that has taken time to answer is what happens to these materials when they are deposited as very thin coatings that they no longer perform as well as when they are in the more rigid thick form.

Vacuum deposition onto flexible webs is where a roll of material is loaded onto a winding mechanism that is enclosed in a vacuum vessel that can be evacuated to remove the air. Different materials can be evaporated, or deposited by a variety of means onto the web as it is wound between unwind and rewind rolls. The lack of air enables metals to be deposited with minimal oxidation or for controlled stoichiometry compounds to be deposited. Glass as used in packaging is very rigid but if the glass is thinned down it shows increasing flexibility. The very thin glass used for displays that is less than 500 microns thick can be flexed and bent without breaking. If this same glass is vacuum deposited onto a flexible polymer web at a thickness of less than 15 nm the glass becomes even more flexible making it suitable for use in flexible packaging applications.

Similarly metals are also much more flexible when vacuum deposited as thin films than when produced as a rolled thin foil. Aluminium foil has in some countries been banned from being used in packaging as it is deemed to have too high an environmental cost. As the vacuum deposited aluminium coatings are often around one hundredth of the thickness of the rolled foils these have been targeted at replacing many of the packaging foil products (1). This foil replacement application is one of the highest growth markets.

When these coatings are examined in detail it becomes apparent that they are not perfect but contain a large number of defects. A detailed examination of the supply materials, previous processing and the vacuum deposition process show that there are many factors that can affect the integrity of the coatings which in turn affect the resultant barrier performance.

Even with these less than perfect coatings the market for the vacuum deposited barrier films is huge with approximately 550,000 tonnes of vacuum coated products being sold into the packaging industry annually and a predicted growth of ~5% per annum. This represents the coating of approximately 22,000 million square metres of material. Of these packaging materials metallised polypropylene takes the largest share at over 50% with metallised PET being the second most widely used substrate. The market continues to grow partly encouraged by environmental pressures with metallised polymers being used to replace aluminium foil and also replace tin cans. Within the area of vacuum deposited coatings there is a difference in market growth expectation for different materials. The deposition of metals, primarily aluminium, has been done for more than 50 years whereas the deposition of the transparent barrier materials is relatively new. It is only relatively recently that the costs have reduced enough, as well as the banning of a chlorine containing coating, to make the transparent barrier vacuum deposited coatings attractive to the packaging industry. This market sector of transparent barrier coatings has been growing at in excess of 20% although from such a small volume this still makes the volumes small by comparison to the metallised films.

When we look at different barrier coatings we can group them into specific types such as packaging, intermediate and ultra-barrier coatings and then subdivide these into opaque or transparent barrier materials.

1.1 Packaging

Packaging has to achieve a number of different functions. Ideally it provides containment to keep the product secure. It has to be convenient to use providing an opportunity for communication, have suitable aesthetics, be non-toxic, tamper-resistant (or tamper-evident), be functional in size & shape and compatible with the production process and the product it contains, low cost, recyclable, reusable or disposed of easily. In addition it has to preserve the product by providing protection against environmental (oxygen, water/moisture, light, chemical attack, contamination from micro organisms), physical attack (such as rodents, and insects), and mechanical hazards (handling damage) during storage and distribution. So when incorporating a barrier coating it needs to be complimentary to the existing substrate properties.

The largest volume of vacuum deposited packaging materials is used for the packaging of food. Often this market segment is driven by minimising cost and as vacuum coating adds cost over the basic flexible webs there has to be a cost benefit to justify using this coating process.

Extending the shelf-life of products is one of the most easily proven cost benefits that can used to justify the addition of vacuum deposited coatings. If we take an example of potato crisps/chips if we open the pack and the crisps are left in the open then moisture will be absorbed and the crisps become soft and soggy. If they were left out in the air and in daylight over a period of time the taste of the crisps would decline as the fats turn rancid because of degradation by oxidation by the oxygen in air or photo-oxidation by daylight. The same pack of crisps can be left for weeks on the shelf and when opened will still be crisp and with the same taste as when first made because the vacuum deposited coating has provided a barrier to the oxygen, moisture and light keeping the crisps dry and fresh. Providing this superior barrier performance means that the bags of crisps do not have to be sold within a few days of manufacture but can still be safely sold weeks later and so the waste and loss of profit is reduced.

The manufacturer of any food product will know what quantity of moisture, or oxygen or light will cause the product to degrade. The manufacturer will also choose a shelf-life that they wish to achieve and this information can be used to calculate how good the barrier performance of the packaging has to be to achieve these goals.

Most of the time we think of the barrier being to prevent things getting into the food but the reality is that it also prevents things escaping from the food too. If we think of water vapour it can turn food soggy but if lost from food it can allow the food to dry out too much. The drying out of food can be a problem for foods such as breads and cakes. A less obvious problem is in frozen food where the loss of moisture through the sublimation of ice can lead to freezer burns of the food.

Oxygen from the air can oxidize some materials such as fats turning them rancid but also can oxidize vitamins such as vitamin C, causing it to lose potency. However oxygen is not the only gas that can be controlled by barrier coatings and this is used to advantage in controlled or modified atmosphere packaging (MAP). In modified atmosphere packaging the package is flushed out using a gas, such as dry nitrogen, and then the package is filled with a specific gas or mixture of gases. In this case the barrier is designed not only to keep the air out but also to keep the modified gas composition inside the package. The gas being used to fill the package might be used to slow down the ripening of fruit and so extending the shelf-life or it may be used to maintain the colour of the food which can be more about aesthetics than food safety.

Light can be quite detrimental to food with photocatalytic reactions causing the degradation of fats, flavours, vitamins, such as vitamins A, B12, D, E, K, etc and changes of colour. So one early choice is to decide if the product needs to be protected from light and so have a metal coating deposited as the barrier or if light is not a problem then it may be preferable for the foods to be visible to the customer and these would have a transparent barrier coating deposited.

The packaging also needs to be benign and not interact with the product either. The polymer may absorb aromas from the foodstuffs and this may reduce the aroma detected by the consumer. This process of aroma absorption is known as scalping. The packaging also should not taint the foodstuffs by losing anything from the polymer into the foodstuffs known as migration.

1.1.1 Opaque Barrier

Opaque light barrier vacuum deposited coatings are achieved primarily by aluminium metallization. The opacity of the very thin metal coating is usually quoted as the optical density of the coating. Opacity is a measure of light incident on the coating divided by the amount of light transmitted through the coating. The optical density (OD) of a coating is the opacity expressed as a logarithm to base ten. This measurement uses a white light source and detector. The transmitted light value can be obtained before deposition starts each time to establish the 100% value and so the substrate is eliminated from the measurement.

$$\text{Opacity} = \frac{\text{Incident light}}{\text{Transmitted light}}$$

$$\text{Transmittance} = \frac{\text{Transmitted light}}{\text{Incident light}}$$

$$\text{Opacity} = \frac{1}{T}$$

$$\text{Opacity Density} = \log_{10}\text{Opacity} = \log_{10}\frac{1}{T}$$

One packaging company has a requirement of a shelf life of 49 days for packaging their potato chips. Light will turn the chips rancid in only 3 days and so they require an opaque thin metal coating for which they have assessed that an OD of 1.7 will achieve the 49 days. Another customer requiring a 90 day shelf life needs a thicker coating to block out more light and an OD of more than 2.2 is necessary (2,3). At the same time as the light needs to be blocked the moisture ingress needs to be limited too. The moisture content of the chips after processing is between 1.3%–1.8% and the acceptable limit at the end of the 49 day shelf life is 2.5%. This means that an increase of only 0.7% can be allowed in 49 Days. This increase can be converted into a weight increase and can provide the target for the acceptable water vapour barrier performance. We can look at this type of calculation in Chapter 4 on materials. In their case the metallized oriented polyester met their requirements but was too expensive and polypropylene met most of their requirements. It was found that improving the surface smoothness of the polypropylene film improved the performance enough to achieve all their requirements and at a lower cost than metallized polyester.

Examination of the metallized film has shown that not only do defects affect the barrier performance of the metallized polymer film but also that the handling of the film in the downstream processes, such as laminating or filling, will increase the number of defects and further degrade the barrier performance. Hence when designing and calculating the barrier packaging there needs to be some allowance for this reduction in performance during packaging processing (4,5).

The opaque packaging is primarily done using aluminium metal and the cheapest metallization process for this is by resistance heated evaporation sources. This technology is mature and the vacuum metallizers have been developed over the years such they can now be built to 4.45m width and with a maximum winding speed of 1250 m/min.

1.1.2 Transparent barrier

Transparent barrier packaging becomes essential where it is desired that the product being packaged is seen by the consumer or user (6,7). Transparent barrier has the added benefit that it makes online metal detection easier. Also electronic devices such as OLEDs where there is a display that needs to be read by the consumer or a photovoltaic device where the light needs to pass through the barrier material to reach the photovoltaic device to be converted into electricity the barrier materials also need to be transparent. The most widely used transparent materials have been alumina and silica (8,9). Both of these materials have been deposited by a variety of different means all aimed at trying to reduce the costs. Over the last ten years the costs have fallen considerably but the production of the transparent barrier materials still remains at a cost of at least twice that of aluminium metallization. Silica has been deposited by thermal evaporation, electron beam evaporation, induction heating evaporation and chemical vapour deposition. Alumina has been deposited by electron beam reactive evaporation until recently when a number of companies have produced material using modified resistance heated evaporation metallizers (10–13). The aim of this work was to take a standard metallizer and with a slight modification convert the opaque aluminium into a transparent alumina whilst maintaining as much of the original winding speed as possible. In this way it was hoped to bring the costs down to a similar level of aluminium metallizing.

There have been occasional other coatings developed (14,15) that have been championed by the company or institute that developed them but as yet none have shown either sufficient cost or technical advantage to make the technology be taken up very widely. An example of this would be the evaporation of melamine barrier coatings (16,17).

The need for transparent ultra barrier coatings has caused the whole barrier technology to be reviewed and developed in order to improve the standard packaging grade barrier coatings by several orders of magnitude. Not only was the quality of the substrate surface improved but also different inorganic coatings were investigated. Until the problem with pinholes was understood and improved there was no need to test if the inorganic coatings were the best for the job. Once improved surfaces had been produced, enabling more defect free vacuum deposited coatings to be deposited (18–20), different inorganic coatings such as indium tin oxide, silicon nitride and carbon or hydrogenated versions of silicon nitride were used to produce ultra barrier materials for evaluation (21–26). This area of development has not yet been completed and I would expect that there will be many more inorganic materials evaluated either as individual layers or in combination with other inorganic layers either as discrete or merged layers. There is the thought that to improve the water barrier performance modifying the chemical composition to make the coating hydrophobic might have some advantages and might be achieved by adding fluorine (27,28). The concern over making the surface hydrophobic is that it would also make the surface harder on which to stick other layers, either as additional vacuum deposited layers or by lamination.

The evaporation process tends to be very fast but the structure of the coating can contain defects relating to the nucleation and growth. The electronics market can, at least in the development phase, withstand a higher price for producing the ultra barrier materials. A number of groups have used sputtering as the deposition process even though these sources may deposit coatings much more slowly, even as much as three orders of magnitude more slowly. The advantage of the sputtered coatings can be the production of higher density coatings with fewer morphological defects. Work is being done to use additional plasma along with evaporation sources to match this densification but with the higher deposition rates.

One additional difficulty in the deposition of some of these ultra barrier coatings for electronic applications, that is not present for the food packaging applications, is the need to deposit the coatings over surface features. In photovoltaic cells there are several laser cut trenches made through various layers to connect or separate individual cells. Thus the polymer layers that are used as separation layers in multilayer transparent barrier coatings have to be conformal. It is possible to smooth out some of these features by depositing a thicker initial polymer layer first (29).

1.2 Markets

The information on markets can appear misleading because some of it is described in area of coated material others quote weight of material coated and still others will quote value. As the price of aluminium coated material for packaging can be a hundred times cheaper than a transparent ultra barrier material and the substrate thickness of the ultra barrier may be ten times as thick for the electronics applications compared to the packaging barrier materials the proportions can be skewed in different ways.

The largest area of material to be coated is for the opaque packaging market and is from simple aluminium metallizing machines. This market is mature and still growing at around 5% per annum. The amount of growth depends on where in the world you are with India and China growing substantially more than the more mature European and USA markets. The Asia pacific region has grown very rapidly and from supplying <20% capacity of metallized films in 2002 it now is the largest supplier with >33% world capacity.

The markets that are currently grabbing the headlines are the transparent barrier packaging markets as these are growing at between 10%–15% per annum worldwide and more than 20% in Europe which is considered a mature packaging market and so for most barrier materials is lower than average. Of these the largest growth is in the retortable transparent barrier materials.

With the interest in reducing energy use there is renewed interest in reducing materials use and energy used in materials production and energy used in transportation. Tin cans are steadily being replaced by stand-up pouches. This segment of the market for metallized film has been growing quickly but the growth of the transparent barrier retortable materials for this market is growing at more than double the rate of the metallized materials. Again there is different interest in the different world regions with approximately half of the vacuum coated films in Japan being transparent barrier films. This transparent market got a boost when Japan banned polyvinyl dichloride (PVdC) and the vacuum coated transparent barrier was one of the few materials able to replace it. Since then Europe has followed this course of action and growth of transparent vacuum deposited barrier coatings has increased similarly.

The markets that are quoted as having the largest potential growth are the ultra barrier materials as these are linked to two huge markets, the display industry with the OLEDs and the flexible photovoltaic market. To realise this potential market the performance, reliability and reproducibility of these ultra barrier coatings has to be proven. Also there is an expectation that as the deposition process is developed and production scaled up the price will decline. Currently, although there have been announcements of material becoming available it is hard to get rolls of material, many offering only A4 sheets for evaluation.

To put some numbers on these markets is difficult. The world market for vacuum deposited products is estimated to be of the order of 800 kT for 2009 which is approximately 32,000 Million sq.m. of coated area. However this figure tends to neglect the specialist coatings markets as they are fragmented and small by comparison to the packaging markets that dominate because of the quantity of materials coated and as the substrates tend to be thin with much of the materials coated being around 12 microns thickness this results in the area coated being similarly huge.

If we look at the photovoltaic market for barrier coatings it is currently negligible but once products are widely available this will grow very rapidly. What this means in terms of tonnes of material or area of material coated is more of an unknown. Photovoltaics are predicted to grow at more than 20% per annum for some time to come. Flexible photovoltaics are predicted to grow faster than this as they take some market share. The growth is often quoted as an increase in gigawatts of installed conversion capacity such as growth from approximately 6GW in 2008 to 35GW by 2015. The area of this increase in installations will depend on the efficiency conversion of the type of cells used. This can vary from less than 5% to close to 20% for standard cells or arrays. So calculating the area from the energy can vary widely. As flexible cells can be deposited on metal foil substrates or polymer substrates the need for barrier coatings can either be for one side barrier only in the case of metal foils or both sides for the polymer substrate materials. This again potentially adds a large error to any estimates of the requirements barrier coatings. In reality it probably does not matter what the numbers are other than it is likely to be growing to require several million square meters over the next few years. As the profit margins for the ultra barrier materials are expected to be larger than for food packaging applications this makes this type of barrier coating a very attractive target.

A similarly humungous market growth is forecast for OLEDs by the likes of IDTechEx and Pira International with an estimated 35% per annum growth over the next five years taking the market from an estimated $615Million to a more than ten fold increase. This could represent 500–750 million display devices per year. Again the guess of the required area of protective barrier materials is difficult as this type of figure can include devices that have more than 100 small displays per square meter to much larger displays for computer screens, etc. However it is probably safe to believe that this too will require a few million square meters of ultra barrier coatings. This requirement for ultra barrier coatings looks to be required for many different technologies as a number of the newer photovoltaic and display devices are all sensitive to moisture or oxygen or both. Thus even if the preferred product technology changes the ultra barrier for encapsulation will still be required.

Between the packaging barrier products and the ultra barrier materials for the electronics markets is the market for materials with intermediate barrier performance needed by the vacuum insulation panel markets (30–32). This is where an insulation material is encapsulated by a vacuum coated barrier material. The insulation material is evacuated before sealing and the panel acts something like a vacuum flask and can be used in white goods or buildings as an insulation material. The requirement for the materials to be included in buildings is that the performance will still be good in anything from 50 years to 100 years time. This is usually achieved by having a barrier performance half way between food packaging barrier and the ultra barriers needed for the sensitive electronic materials and then assisting the barrier by adding a scavenger material embedded in the insulation to absorb a quantity of gas or moisture that does pass through during the 50 or more years. An alternative design has used a gas filled insulation panel with the barrier preventing the exchange of gas from the inside and being replaced by gas from the outside (33).

Although this market is growing there are few predictions about how big it will become. The rate of building varies enormously and there are many other competing materials that can be used to deliver an equivalent performance and it is not clear which materials will become favoured. These materials are not required to be transparent and so laminated metallized materials can be used. Using double side and laminations of multiple metallized films can be used to achieve the desired level of permeability. Thus the growth of this market is probably hidden within the continued growth of metallized films.

Of all these dispirit markets the need for barrier for electronic applications would appear to have a difficult technical specification but the market looks to be stable and growing well for some time to come.

At the other end of the spectrum the packaging market that is currently by far the largest market in general has the lowest margins with a more easily achieved technical target but is also the most fickle of the markets. There are the conflicting requirements of preserving food for longer but also reducing the quantity of packaging and the need to increase re-cycling. This, in many respects, makes this the harder market to participate in.

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