The adverse effect of water on the durability of metallized flexible films

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ABSTRACT

Vacuum web metallizing is widely used in the packaging, holographic, electronic, solar window film and other industries for barrier, optical and electronic effects. However, there is a continuous demand in the market for further improvements in quality to extend the lifetime of the metallised products. Water vapour (moisture) is considered to be an important factor that can have extreme adverse effect on the quality and durability of the metallizing process and the metallised product. Due to its polarity, water can be adsorbed or absorbed on vacuum chamber walls, parts and polymeric film. Most polymers absorb water vapour to a greater or lesser extent. Although some water moisture can be removed from vacuum chamber before metallizing, adsorbed and absorbed moisture in the polymeric matrix penetrates deep and is very difficult to remove. This could have a long term effect on the product. Moisture trapped in the metal-polymer interface can result in the formation of interstitial oxidation due to slow reaction of moisture with the metallized layer. This may tarnish the metallised layer and result in a subsequent failure as in the case of capacitors made from metallized BOPP films. The slow oxidation of the metallized layer due to trapped moisture may also increase metallized film temperature after the removal of the film roll from the vacuum chamber. This results in the blockage and damage of film layers during slitting.

The present article evaluates the adverse effect of water moisture during vacuum metallization and the long term impact of moisture trapped in the metal-interface on the durability of the product.

1- INTRODUCTION

Vacuum web metallizing is a very important process for various metallized products in the market. In recent years, metallized films have become increasingly more popular over metal foil or paper mainly due to their cost, flexibility, durability and improved technical performance. Vacuum metallizing is currently used for food and pharmaceutical packaging, holographic, solar window films and electronic. In the electronic industry, vacuum metallizing is used for the production of flexible printed circuit boards and capacitors. Metallized films usually consist of a polymeric flexible film and a metallic single or multi nano-layers covering the polymer surface to achieve the required properties. The Roll-to-Roll metallization process is performed under vacuum using physical vapour deposition technique (PVD) to metallize the surface of the polymer film. Polyester and Polypropylene films, such as Biaxially- Oriented Polypropylene (BOPP), represents the main choice in many packaged products due to their cost, mechanical strength, durability and good dielectric properties. However, continuous demand to improve durability and to extend the life time of products resulted in further investigations to improve adhesion, structure and to minimize high temperature and high humidity effects on the product. Water vapour is considered as important factor in the vacuum system, metallizing process and the metallized products. Water is highly polar and can stick on various surfaces in the metallizing chamber and the polymeric surface. This is done via adsorption and absorption processes.

The present article evaluates the adverse effect of water vapour / moisture during vacuum metallization and the long term impact of moisture trapped in the metal-interface on the durability of products.

In addition, some practical examples of such effects will be presented to understand the nature of water vapour problems.

2- Adsorption and Absorption Processes

Water molecules have high polarity and can preferentially adsorb or absorb on any surfaces particularly on clean and activated ones (Figure 1).

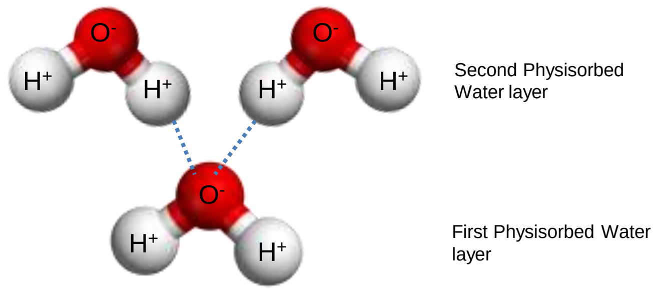

Figure 1. Adsorption of Water Molecules

Adsorption is defined as the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid onto a surface. This process can create a layer of water molecules on the surface of the metallizer parts and polymeric film.

Absorption is a process in which a fluid, such as water, permeates a surface of a material.

Therefore, adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of it.

Adsorption is a consequence of surface energy and is a characteristic of weak van der Waals forces or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction.

The distinction between adsorption and absorption vanishes as the material change from perfectly crystalline macroscopic materials to porous/structured materials with smaller grains. In structures such as the metallized layer or the polymeric films the internal surface area of particulate matter is very large. Thus adsorption on internal surfaces simply becomes absorption. As an example, during early stage of manufacturing, polymeric materials have large internal surface area which can adsorb water molecules on its surface. Eventually this will change to internal absorbed water inside the bulk of the polymeric film.

Therefore, absorption distributes the water vapour/moisture it captures throughout the bulk of the polymeric film, while adsorption distributes water molecules on the surface.

3- Water Vapour In Vacuum Systems

Water is a highly polar molecule, therefore it sticks tenaciously by both chemical and physical forces to any solid surface. When a vacuum chamber is opened to air for loading, unloading or maintenance, the chamber will be exposed to water vapour/moisture in the atmosphere. Water adsorbs on the walls at a rate of 10^{15}molecules/cm^2 of real surface area. This water then diffuses into the passivation oxide layer of the chamber's wall. The amount of water trapped inside the walls depends on the surface condition and the humidity of atmosphere. The longer the system is left opened to air the more water vapour will enter and adsorb on the inner walls.

The first monolayer (a single, closely packed layer of atoms or molecules) of water adsorbing on the walls will attract other water molecules until a thick layer of water molecules is formed. At this stage the bond strength between deposited water layers will become weaker as the layer thickness increases. When pumping down a chamber from atmosphere, most of the air and trace gases are removed relatively quickly (depending on chamber and vacuum system design). At a pressure of about 10-20 mb, water vapour becomes almost invariably the dominant remaining gas species since it sticks to any surface it encounters. At this stage, the layer of adsorbed water may be as much as 100 monolayers. This is difficult to remove, and limits the ultimate attainable pressure. The desorption rate of water is very slow during the roughing process but increases greatly as the pressure drops to values allowing the molecular flow of gas. In this range, the amount of water is the predominant gas species. Increasing pumping speed does not remove water from the walls faster, since adsorbed water desorbs slowly.

The amount of free water vapour in a vacuum chamber can be calculated as follows:

On a humid summer day at 20^{o}C, 100% relative humidity (RH) means that one out of every 45 molecules of air is a water molecule, or that water has a partial pressure of 17 torr (760torr x 1/45).

Assume a chamber with 1000 atmospheric litre volume. At a pressure of 17 torr (partial pressure of water), the chamber would contain:

1000 lit x 17torr (H_2O)/760 torr = 22.4 atmospheric liter of water vapour.

At RH=100%, there are 18g of liquid water in the free water vapour state per 1000 litre of void volume. Controlling the RH to 45% reduces the partial pressure of water to about 8 torr.

When water is pumped down with mechanical pump, water vapour condenses and adsorbed in the oil, changing it to a milky condition. This limits the minimum pressure that can be achieved. Water usually condenses on cold surfaces inside the vacuum system. Condensation requires a particular combination of humid atmosphere and a cold surface. When the amount of water is large compared to the evaporation surface area, energy required to evaporate the water is large. Therefore, for evaporation during pump down, water molecules absorb the energy from the bulk of water leading to a drop in its surface temperature. For a large amount of free water, ice can be formed and the ice takes a very long time to sublime. Adsorb water is difficult to remove than atmospheric free water.

The other source of water vapour that can affect the overall vacuum level during metallizing is virtual and real leaks in the vacuum system. Real leaks are caused by holes, O- rings and other seals in the system. Virtual leaks are caused by cracks in the chamber welds and other mechanical parts. In order to speed up the removal of water vapour from the system four basic methods can be employed. These are:

1. Time

2. Temperature

3. UV radiation

4. Momentum energy transfer exchange.

Pumping the vacuum system for a long time will eventually remove water but this may take days or weeks. Naturally, this is not acceptable in industrial production. The rate of water removal can be enhanced by heating, thereby making the molecules more energetic to leave the surface. However, temperature in the range of 200-300^oC have to be used for a quick drying. The heating should be uniform otherwise the water will simply transferees to any cold surface and remains adsorbed. In some applications where the chamber is water cooled, a hot water is circulated around the chamber during pumping down to release trapped water. Hot water is also used during venting, loading and reloading to minimize water adsorption on the chamber walls. In other methods, the chamber is pumped down to about 133mb then backfilled with dry nitrogen at atmospheric pressure for a few minutes before roughing again. Adsorbed water can also be removed by using ultra-violet radiation at a pressure of 0.1 mb and power density of 0.4-8mW/cm^2. Water absorbs UV radiation at λ=190-200nm and the absorbed energy provides thermal energy to the water layer. However, UV lights should be shielded very well during coating cycle to allow for the continuous utilization of the UV. Glow discharge can be used for the removal of water from vacuum system. In this case anodes are used inside the grounded chamber in the presence of some gases such as Ar/O_2 mixture at a pressure of $7.5x10^{-3}$ mb. Ions generated in the plasma accelerate toward the chamber walls and the continuous bombardment releases water molecules and carries it to the pump. The problem with this approach is the possible contamination of the substrate due to the continuous sputtering of contaminants on the chamber walls.

However, the most efficient method for the removal of water from the vacuum system is the utilization of refrigeration cooled panels or pipes (Cryopanels). A typical panel with a surface area of one square meter at a temperature of -100^oC will provide approximately 100,000 litres/second for the removal of water vapour at a chamber pressure of greater than $5x10^{-5}$ mb. Another method of removing moisture from film is the employment of a plasma treater.

4- **Moisture content in Flexible Films**

Water moisture can be adsorbed or absorbed inside Polymeric films during manufacturing. Certain polymer materials can absorb large amount of moisture, especially if they are stored in humid areas prior to metallizing (Figure 2).

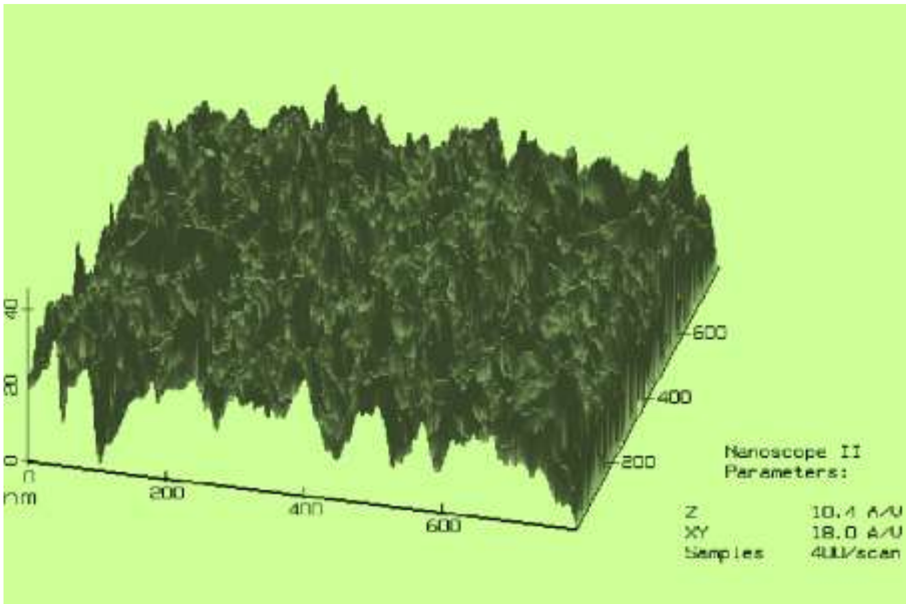

Figure 2. Surface Roughness of 20 micron BOPP Film

Nylon is an example of such a material. When a Polymeric film is metallized at high speeds the film releases a large amount of air which contain trapped water moisture. As an example, a 5% of the total volume of a 12.7 micron thick polyester film is a trapped air. Therefore, a large film web could contain more than 13 standard litres of trapped air and moisture. This large amount of trapped water vapour should be pumped out in a separate zone (such as the unwind zone in the metallizer) to minimise contaminating the coating in the metallizing zone. BOPP films usually have higher moisture levels than PET.

5- Problems related to water vapour (moisture)

Water or moisture content adsorbed or trapped inside Polymeric films can chemically react with the metallized surface thus affecting the structure of coating and causing bad adhesion, dis-colouration, poor barrier performance and other undesirable effects. There are numerous reports in the literature on the effect of water on the performance of metallized films. The followings are some examples:

a- ***Temperature rise in BOPP films after metallization***

Unlike Polyester (PET), metallized Polyproylene (BOPP) films can exhibit a temperature rise after removal from the vacuum metallizer. Temperature rises of 5°C or more above the initial temperature following metallization have been reported. The temperature peaks at the centre of the web and gradually decreases toward the edges of the roll. This process can take a few hours to stabilise and often carries the risk of permanent damage to the roll of film. Temperatures as high as 35°C have been observed and this has often resulted in the film losing its surface tension level making it unsuitable for printing and lamination. In extreme cases the roll can “block” and become scrap..

Figure 3 shows evidence of the correlation between water content and temperature rise in various types of BOPP films.

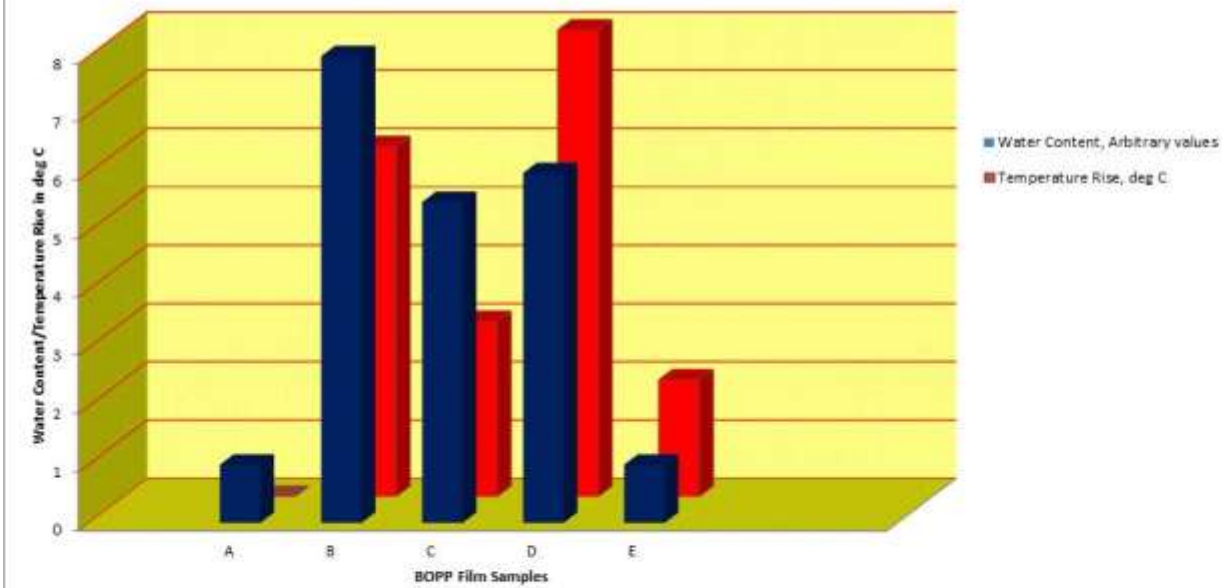

Figure 3. The Co-relation between Moisture Content and Temperature Rise in BOPP Films

There have also been some reports indicating a correlation between temperature rise and surface roughness in BOPP films. Rough wettable surfaces can trap more water moisture than smooth un-wettable surfaces (Figure 2). The increase in surface roughness and water content in BOPP may well be due to variations of manufacturing procedures such as anti-block additions which can be hygroscopic, corona treatment and storage conditions.

The temperature rise in BOPP films following metallization maybe due to an exothermic reaction between aluminium and the water trapped in the film after metallization due to diffusion from the bulk (Figure 4).

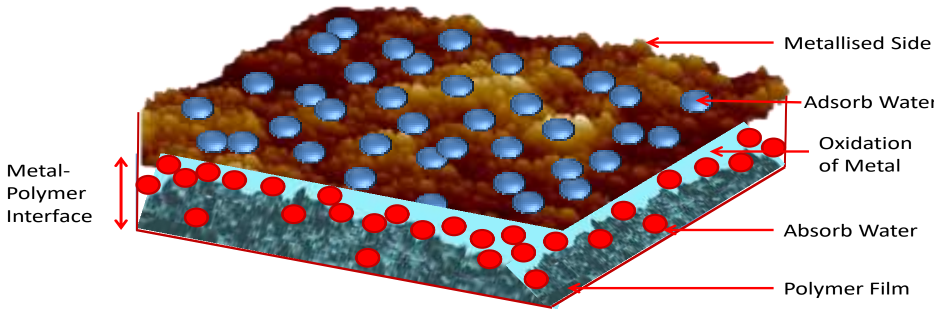

Figure 4. Possible Effect of absorbed and adsorbed moisture on temperature rise in BOPP Film

b- Water effect in metallized Capacitor films

Metallized film capacitors are more popular over the paper-foil or plastic film foil capacitors mainly due to their reduced size and improved technical performance. In particular, the self-healing characteristics of these capacitors represent a highlighted advantage that extends the lifetime of these devices. Metallized film capacitors are constituted by a polymeric thin film such as BOPP and a metallic nano-layer covering the polymer surface.

Metallized film capacitors are susceptible to atmospheric corrosion which may strongly decrease their electrical performance and tarnish the metallized layers.

In some studies, the metal /polymer interface was analysed using dynamic secondary ion mass spectrometry (d-SIMS) for depth profiling and the interstitial oxidation of the Al in the metallized layer. The results indicated a close relationship between the oxidation of the metallized layer and the moisture content within the metal–polymer interface. The moisture content modified the metallized layer morphology and the capacitor performance. It also led to the dis-colouration of the metallized layer. The results also found a larger presence of AlO+ and

AlOH+ in the metal–polymer interface of samples with high moisture content within the polymer film.

Conclusions

Water vapour (moisture) is considered to be an important factor that can have extreme adverse effect on the quality and durability of the metallizing process and the metallized product. It is difficult to completely eliminate the amount of water content in the polymer film. However, high quality metallized products can be produced by selecting films with lower water content, controlling the humidity level in the work place and by improving vacuum pumping and the use of high performance plasma treaters.

Further Readings

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