Vacuum Metallization of Polyethylene Films

Problems and Solutions

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Abstract

Synthetic polyolefins materials such as polyethylene (PE) are characterized by very poor wetting properties. Following vacuum metallizing, this will result in poor adhesive properties due to the low surface energy values. For non-polar polymeric films such as polyethylene (PE) a specific additional surface treatment is required to increase surface energy, enhance wettability and, consequently, increase the adhesive properties.

This article will discuss the structure of the non-polar polyethylene film material and describe the most convenient surface treatment method to enhance the adhesion of the PE metallized films.

1- Introduction

Polyethylene (PE) material is one of the most widespread polymers used for different industrial and medical applications due to its favourable properties. Polyethylene properties include low density, flexibility, and high chemical resistance. Polyethylene is the most common plastic used in packaging industry for products such as food packaging, containers, etc. The annual global production in 2008 was around 80 million tonnes. However, the low surface energy of the polymer and in particular, the low proportion of polar regions, as well as the lack of functional groups on its surface, results in poor adhesion and poor reactivity with metallized materials. Metallized packaging films made from polyethylene (PE) usually face issues of poor metal adhesion and bond strengths limiting their end use application. These metalized PE films have PE in the skin layer(s) which may contain low molecular weight fractions of PE and low molecular weight high comonomer fractions of linear low density polyethylene (LLDPE). Such PE- based metallized films typically exhibit very poor bond strength due to poor metal adhesion to the metalized skin layer leading to challenges during lamination as well as poor barrier properties due to metal transfer. It would be therefore, desirable to produce metallized PE films having the desired metal adhesion properties.

The aging effect of treated polyethylene over time is another problem to be solved in order to extend the durability of such polymer for packaging and other applications.

In order to improve the functionality of the surface, various methods have been used to modify the surface properties of PE films including chemical, thermal, mechanical and electrical (plasma) treatments. At present, plasma treatment is one of the most important methods used since it is a dry process, environmentally friendly, very efficient and allow a uniform treatment of the film surface. With plasma treatment it is possible to activate the polymeric surface by introducing active polar groups or to produce surface abrasion or etching. The combined effects including plasma enhanced cross linking would increase surface energy and improve adhesion.

2- The Chemical Structure of Polyethylene Films

Polyethylene has the chemical formula $(C_2H_4)_n$ and it is a mixture of polymers of ethylene with various values of n (Figure 1).

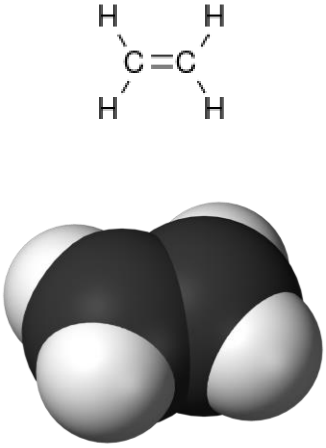

Figure 1. The Chemical Structure of Polyethylene

Polyethylene has low strength, hardness and rigidity properties, but it has a high ductility and impact strength as well as low friction. It shows strong creep under persistent force and feels waxy when touched.

The melting point of common commercial grades of low-density polyethylene (LDP) is typically 105 to 115 °C. These temperatures vary strongly with the type of polyethylene.

Polyethylene consists of nonpolar, saturated, high molecular weight hydrocarbons (CH group). The individual macromolecules are not covalently linked. Because of their symmetric molecular structure, they tend to crystallize. Overall, polyethylene is partially crystalline. Higher crystallinity increase density, mechanical and chemical stability.

Polyethylene absorbs almost no water. The gas and water vapour permeability (only polar gases) is lower than for most plastics. On the other hand, oxygen, carbon dioxide and flavouring can pass through it easily.

Due to low surface energy, Polyethylene cannot be imprinted or stuck together without pretreatment..

3- Types of Polyethylene Films

In commercial production, Polyethylene is classified by its density and branching. Its mechanical properties depend significantly on variables such as the extent and type of branching, the crystal structure, and the molecular weight. There are several types of polyethylene films available in the market. However, this article will discuss the production and treatment of two polyethylene grades:

a- Low density Polyethylene (LDPE)

b- High density Polyethylene (HDPE)

a- Low density Polyethylene (LDPE)

LDPE is defined by a density range of 0.910–0.940 g/cm^3. LDPE has a high degree of short- and long-chain branching, which means that the chains do not pack into the crystal structure as well. It has, therefore, less strong intermolecular forces as the instantaneous-dipole induced attraction. This results in a lower tensile strength and increased ductility. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap. In 2013, the global LDPE market had a volume of almost US$33 billion.

b- High density Polyethylene (HDPE)

HDPE is known for its large strength-to-density ratio. The density of HDPE can range from 0.93 to 0.97 g/cm^3 or 970 kg/m^3. Although the density of HDPE is only marginally higher than that of low-density polyethylene, HDPE has little branching, giving it stronger intermolecular forces and tensile strength than LDPE. The difference in strength exceeds the difference in density, giving HDPE a higher specific strength. It is also harder and more opaque and can withstand somewhat higher temperatures (120 °C for short periods, 110 °C continuously). High-density polyethylene is used for food storage containers and other applications.

4- **Plasma Surface Modification of Polyethylene**

For various applications of polyethylene (PE) films it is desirable to modify its surface properties because of the low surface energy. There are many ways to modify polymer surfaces, such as wet chemical etching, mechanical treatments, exposure to flames, ions, plasma, corona discharge, ultraviolet (UV) radiation, and UV ozone. However, atmospheric and low-pressure plasmas offer several advantages over other techniques with the most important being the modification of only the top surface layer of the polymer. Treatment in plasma often leads to modification of polymeric chains, chemical bond cleavage, creation of free radicals and release of gaseous degradation products. Furthermore, subsequent chemical reactions of transient, highly reactive species result in the creation of excessive double bonds, production of low mass stable degradation products, large crosslinked structures and eventually oxidized structures. Plasma treatment of non-polar polyolefins such as PE leads to the creation of polar groups on the polymer surface and in this way it enhances printability, wettability and adhesion with inorganic materials such as metallized aluminium. The degree of modification and character of induced changes depend on the composition of plasma gases, energy of plasma ions, temperature during the treatment and plasma power density.

In order to improve PE surface energy (wettability), RF, AC and Pulsed DC Plasma treatment methods have been employed to change the morphology of surface without changing the bulk properties.

Various gases can be employed in the plasma treatment to induce structural and compositional changes in HDPE, LLDPE and LDPE films. This includes Ar, O_2, N, He, Ne, CO_2 or mixtures of gases such as (He / 5%CO_2) and (He/ 10% C_2 H_2). Plasma treatments with such gases have been found to improve the surface energy and wettability of PE Films to certain levels. For example, the surface energy of PE film can be increased from about 31 dyne/cm to about 47 dyne/cm. However, this also depends on plasma power and exposure time in plasma.

During plasma treatment of PE film, polymer degradation may take place due to the interaction of plasma constituents with the polymeric chains on the surface. Low molecular mass gaseous products are created and, at the same time, crosslinking processes may occur. As a result of these complex processes an ablation of the polymer surface and changes in polymer mechanical and chemical properties can be induced. Changes in the chemical structure result in further oxidation of the surface and formation of carboxyl, carbonyl and hydroxyl groups.

5- Aging Effect

Following plasma treatment it is important to study the Aging effects over a 30-day period or more to determine the stability of the chemically modified PE film surface and to optimise the treatment parameters. Depending on the treatment conditions, hydrophobic recovery may appear in the first couple of days after the treatment. Then, the PE surface reach equilibrium and the surface energy remain stable with time. The aging effect can be due to re-arrangement of degraded structures. Research works have indicated that plasma treated PE film surface usually exhibit a surface rich in oxygen-containing groups. It has been suggested that plasma treatment can result in the formation of carboxyl, hydroxyl, and carbonyl groups on the surface, thereby enhancing the hydrophilicity (wettability) of the polymer surface and the adhesion with the metallized aluminium. It must be mentioned at this point that during plasma exposure hydrophilic groups (most of them with low stability) are formed. However, during aging most of these polar groups change their orientation towards the bulk thus reducing the hydrophilic nature of the treated surface. It is also important to note that not all the hydrophilic nature achieved by the plasma treatment is lost during the aging process. This is because the plasma treatment not only promotes the formation of polar groups but also increases surface roughness which improves wettability and, what is more important, this component remains constant during aging. The aging process can be observed by the evolution of the contact angles with the storage time.

It is also possible that other external factors such as contamination may contribute to the aging process which occurs in an exponential form over time.

It has also been suggested that short-time plasma treatment does not lead to significant increases in surface roughness since its main effect is the formation of polar species on the film surface. Many of these polar species are re-arranged during aging thus reducing surface wettability. On the other hand, long-time plasma treatments are more aggressive, causing some changes in surface morphology by slightly increasing surface roughness and softening or reducing surface aging. Therefore, the selection of the most suitable plasma treatment parameters is required to reduce aging and degradation of the PE film surface.

6- Conclusions

The effects of plasma treatment of LDPE and HDPE have been studied by many workers using different techniques. It has been found that plasma treated HDPE films exhibits pronounced increase of surface roughness in contrast to LDPE. In general, plasma treatment leads to the production of oxidized structures in PE surface layer. Plasma treatment of PE films can improve wettability by increasing the surface free energies. It can also increase adhesion by increasing surface roughness.

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8- Further Readings

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