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Polyester/aluminium adhesion: improvement by heat treatments

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Because of its industrial importance, poly(ethylene terephthalate) (PET) has been the subject of numerous studies concerning surface modifications in order to improve its bonding ability. Most of the previously reported surface treatments performed before the metallization provide good dry adhesion of vapour deposited metallic layers. However, food packaging applications also require good wet adhesion and strong oxygen barrier properties. Heat treatments have been found to improve these properties. Hence, the aim of this study was to isolate an efficient heat treatment for the metallized PET films suitable for industrial application. The adhesive performance of aluminized polyester films has been assessed by use of an ultrasonic vibration test.

1. Introduction

Due to a high mechanical strength, toughness and durability, biaxially oriented and heat stabilized poly(ethylene terephthalate) (PET) films find use in a wide variety of industrial applications. These include the insulation for electric motors, capacitors, wires and cables as well as being the base material for audio, video and computer tapes. Due to its high resistance to most chemicals and solvents, PET films are used in many composite structures for packaging, especially food packaging. Most of these applications require a metallization of the polymer film, this is particularly true for thin films used as dielectrics in capacitors, high barrier performance packaging films and base films for the new generation of magnetic recording media. The suitability of PET films for vacuum metallization is related to its moisture retention which is below 0.5 % at 25 °C and a 50% relative humidity [1]. Packaging films are nearly always metallized with aluminium in a thermal evaporation process. The typical Al thicknesses in this case are 30–50 nm on a 12 μm thick PET film. The desired properties are a good adhesive behaviour of the metal layer on the polymer film in both dry and wet atmospheres and also a low oxygen permeation.

The influence of the metallization parameters on the composition, microstructure and morphology of the evaporated aluminium layers and their correlation with the adhesive performance of the final joints has been the subject of numerous studies [2–4]. These results must be compared carefully, taking into account the differences in (i) the nature of the studied films, (ii) the experimental equipment and (iii) the characterization methods. However some constant trends can be observed in that it appears that the oxygen content at the Al–PET interface plays a critical role in the microstructure due to its influence on the nucleation and growth of the aluminium layers. It can be concluded that the aluminium mean grain size, as determined from transmission electron microscopy micrographs, increases when the degree of oxidation of the interfacial aluminium decreases, i.e., when the Al:O ratio, as determined by Secondary Ion Mass Spectrometry (SIMS) profiling, increases. This degree of oxidation mainly depends on two related parameters: the residual pressure in the metallization chamber and the deposition rate of the aluminium adatoms. For a given deposition rate, the oxygen content at the interface increases with the residual pressure and hence the aluminium grain size decreases. When the deposition rate is higher at constant residual pressure, a lower degree of interfacial oxidation is reached and larger aluminium grains are obtained.

Depending on the adhesion test used the influence of this degree of oxidation can be somewhat different. From peel and scratch tests [3] it seems that an optimum oxygen content is required in order to obtain the best adhesive behaviour. Whilst an ultrasonic vibration test [2] suggests that the higher the oxygen content the better the adherence. These different behaviours can be related to residual stresses in the metallic layer and to interfacial stresses [5, 6]. Moreover, in order to be able to peel the aluminium layer, a polymer film must be bonded under pressure at

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a high temperature for short times and it should be noted that this step may also influence the adhesive behaviour.

The oxygen barrier performances of metallized polyester films is also strongly related to the structure of the aluminium layer. In particular, they seem to be primarily affected by the appearence of various sized and shaped pinholes under all metallizing conditions [7].

A third important metallization parameter is the temperature and especially the substrate temperature during processing. It has been shown that the adherence of different metal/PET systems can be improved by increasing the film temperature [8]. Some attempts have been made to find a correlation between the substrate temperature, the internal stresses and the adherence for different metal/substrate systems [9]. It appears that substrate heating causes the relief of the internal stress and hence an increase in adhesion. Otherwise, it has been shown that annealing and taut-annealing treatments of virgin PET films lead to a decrease of the oxygen permeation as the temperature of the treatment increases [10, 11].

The manufacturing process of the polyester film includes bi-axial stretching of the cast film in both the machine and transverse directions at different stretching factors. The polymer is at this stage oriented and partially crystallized. The stretched film is then stabilized by heat-setting at a specific temperature for a short time. This process is complex. Moreover, the metallization conditions involve an increase of the temperature of the polymer. Therefore, it appears to be important to study the influence of further heat treatments on the adhesive properties to see if it is possible to improve this behaviour under certain heat treatment conditions. We present laboratory experimental results and propose a possible way of transferring these procedures to an industrial level. In comparison with other available treatments such as plasma or corona treatments usually used to improve interfacial properties, the advantage of the proposed procedure mainly lies in the fact that the treatment of the metallized film is efficient.

2. Experimental procedures

2.1. Heat treatments

Two bi-axially oriented PET films from DuPont de Nemours (Mylar® 12 and 23 μm thick) aluminized by vapour deposition under vacuum have been investigated. Two heat treatments have been performed on these films. During these treatments the films are held under a stress in an aluminium frame. The first treatment, called taut-annealing, consists of placing the samples in an air forced oven in different temperature and time of exposure conditions. In the second treatment, the metal side of the sample is heated using an air flow produced by a hot air gun. The quoted temperature corresponds to that of the air at the surface of the sample. The temperature reached by the film surface is unknown and other conditions being constant depends on two parameters: (i) the distance between the output of the gun and the surface and (ii) the translation rate through the air flow. The experimental equipment and the modifications induced by this treatment on a virgin PET film have been published elsewhere [12].

2.2. Adhesion measurements

Although various tests have been described in the literature [13, 14], the determination of the experimental work of adhesion in the case of metallic layers (30–50 nm) on thin polymer films (12 μm) is extremely difficult. The measurement of the adhesive behaviour of thin granular layers by means of the destructive ultrasonic vibration technique is not widely used [15, 16]. This test has been adapted in our laboratory for application to the specific problem of the characterization of thin granular metallic layers deposited onto a polymer [17]. The metallized polymer film is attached to the free end of a metallic rod which amplifies the longitudinal vibrations produced by means of a piezo-electric transducer. The sample is then submitted to mechanical vibrations until partial or complete ejection of the metallic particles is achieved. If the adhesive strength is too high for the ejection to occur then the strength can be decreased by performing the test in a liquid medium [18]. Water was used in our experiments. The adhesive strength is expressed in terms of either the duration of the exposure to the vibrations required to break the interface *i.e.*, the ejection of the complete aluminium layer or in terms of a practical adhesion energy. In this paper, the duration of the exposure to the vibrations will be used with a typical standard deviation of between 5–10 s. Both optical microscopy and Scanning Electron Microscope (SEM) images are used to monitor the surfaces after complete ejection of the aluminium particles.

3. Results and discussion

3.1. Taut-annealing

Figs 1 and 2 show the relationship between the duration of the exposure to the vibrations required to totally separate the aluminium layer from the PET film as a function of time of residence in the oven for temperatures ranging between 40–230 °C and for both taut-annealed films after metallization. For the 12 μm thick film, all annealing temperatures resulted in an increase in the duration of the exposure to the vibrations and hence to a better adhesive performance of the treated samples: the higher the annealing temperature the more important the modifications. The plateau value observed for each temperature after about a 10 min treatment shows that the temperature and time of exposure do not affect the adhesive properties to similar extents in that a longer treatment at a lower temperature does not correspond to a short time at a higher temperature. For the 23 μm thick film, the adhesive strength is improved only by temperatures above 140 °C. Moreover, the adhesive strength goes through a maximum as a function of time for a treatment at 230 °C. This observation has to be correlated with the heat setting step of the manufacturing process of the PET film. Indeed, the orientations of the polymer molecules induced by the bi-axial stretching need

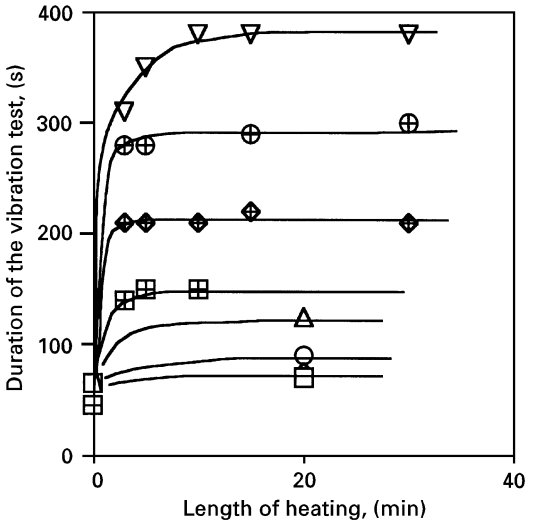

Figure 1 Duration of the vibration test as a function of the heating time during taut-annealing of the 12 μm thick film (control value = 65s). The temperatures investigated were (□) 40 °C, (◇) 80 °C, (○) 100 °C, (△) 140 °C, (■) 160 °C, (◆) 185 °C, (⊕) 210 °C and (▽) 230 °C.

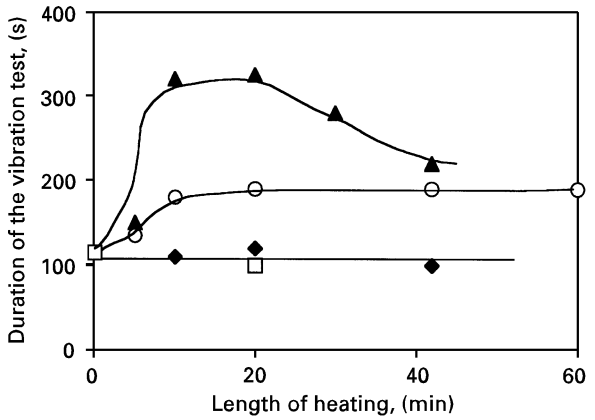

Figure 2 Duration of the vibration test as a function of the heating time during taut-annealing of the 23 μm thick film (control value = 115s). The temperatures investigated were (□) 100 °C, (◆) 140 °C, (○) 185 °C and (▲) 230 °C.

to be stabilized at higher temperatures. Depending on the required properties for the PET application, the temperature of the heat setting may vary over a large domain (180–230 °C). The subsequent mechanical properties of the final PET are determined by this treatment. Although we do not accurately know the manufacturing conditions of the films, we may assume in agreement with the shrinkage behaviour of both films that they are quite different. In the case of the thinner film, the temperature of the heat setting would be higher or at least equal to 230 °C. On the other hand, due to the fact that the adhesive properties of the thicker film are improved only for annealing times shorter than about 25 min, the heat setting temperature would be lower.

The maximum duration of exposure to the vibrations obtained after taut-annealing as a function of the treatment temperature for the 12 μm thick film is presented in Fig. 3. It is clearly apparent that the adherence improves for temperatures as low as 80 °C.

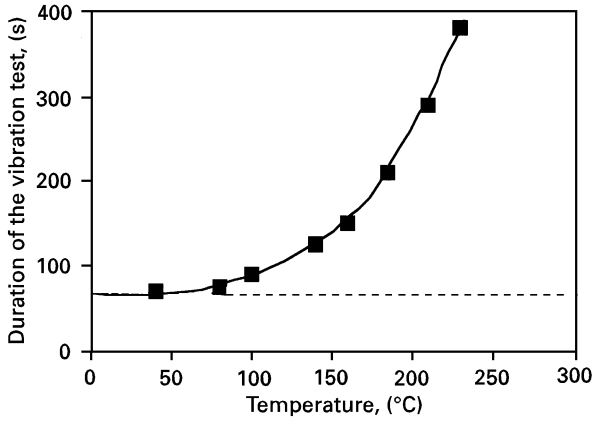

Figure 3 Maximum duration of vibration test as a function of the treatment temperature (12 μm thick film). The dotted line is the control measurement.

This value corresponds to the glass transition temperature of amorphous PET. However, the observation does not hold for the thicker sample as is shown in Fig. 4 Indeed, no variation is observed for temperatures below 150 °C. Again, the manufacturing conditions may explain these differences. The higher stability of the thinnest film leads to the improved effect of the taut-annealing treatment.

However, it should be noted that no comparison of the absolute values of the duration of the exposure to the vibrations for the two metallized samples is possible. Indeed, the ultrasonic vibrations are partially absorbed by the polymer film before reaching the polyester/metal interface. The damping of the vibrations in the bulk of the polymer is influenced by both the thickness and also the structure of the PET. Nevertheless, it is interesting to note that, for the thin sample, the duration of the exposure to the vibrations has increased from 65 to 380s for a taut-annealing treatment at 230 °C whereas it has only increased from 110 to 325s for the thicker film. This again highlights the influence of the initial properties of the polymer film.

In order to study the relative importance of each kind of modification, the effect of taut-annealing on a virgin film has been checked on the 23 μm thick PET film. This pretreatment of the polymer film was eventually followed by a retreatment of the metallized film at a higher temperature. The results are presented in Table I. A 20 min of treatment was chosen because this time corresponds to that leading to the maximum modifications of the metallized films.

The treatment performed before the metallization at temperatures lower than 230 °C has disastrous effects on the adhesive strength as is shown by the results presented in this table. However, if a new treatment is performed on these metallized samples, the duration of the exposure to the vibrations again increases. The films recover the same high adhesive strength of non pretreated samples before the metallization. In this way, the term taut-"annealing" is fully justified.

These results reveal two important facts. Firstly, the treatment of the virgin film influences in some instances the behaviour of the subsequent metallized film, at

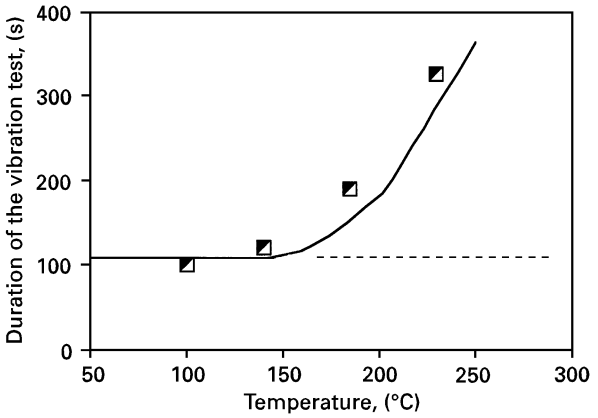

Figure 4 Maximum duration of the vibration test as a function of the treatment temperature (23 μm thick film). The dotted line is the control measurement.

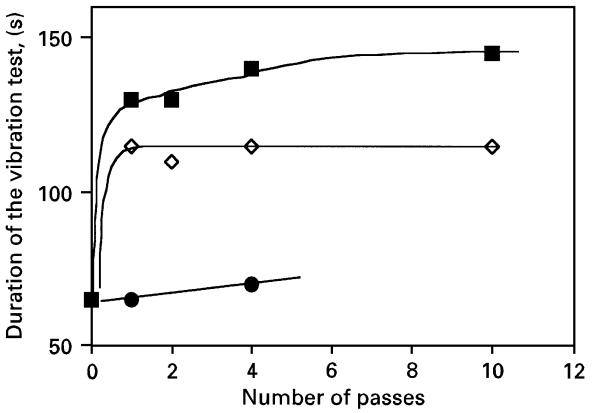

Figure 5 Duration of the vibration test as a function of the number of passes at 200 °C at rates of (■) 3 cm s^{-1}, (◇) 15 cm s^{-1} and (●) 30 cm s^{-1} (12 μm thick film).

TABLE I Duration of the vibration (s) test as a function of the temperature of pretreatment for the 23 μm thick virgin and metallized films

Temperature of treatment for the Virgin film	Temperature of treatment for the metallized film			
	none	140 °C	185 °C	230 °C
none	115	115	180	325
140 °C	35	105	145	325
185 °C	65		150	325
230 °C	110			325

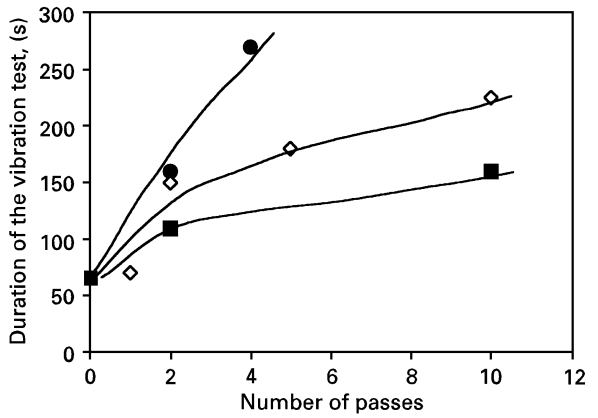

Figure 6 Duration of the vibration test as a function of the number of passes for temperatures of (■) 200 °C, (◇) 230 °C and (●) 250 °C. (V = 3 cm s^{-1}, 12 μm thick film).

least for temperatures below 230 °C. This effect can be related to modifications of the polymer surface, that have been revealed through wettability measurements. These modifications affect the amount, nature and accessibility of nucleation sites, the mobility of the functional groups and the oxidation of the evaporated metal. Secondly, the efficiency of the taut-annealing occurs mainly in the case of the treatment of a metallized film. Therefore, it is the role played by the PET/Al interface and by the aluminium layer which is predominant. In other words, although the modifications induced in the film cannot be neglected, the influence of the treatment on the metal/polyester interface predominates.

3.2. Hot-air

Although highly efficient, the previously described treatment cannot be directly transferred in to industrial usage. Considering the two important characteristics of the taut-annealing namely the temperature and the stress, we have developed a taut-hot-air treatment suitable for industrial processes. The results obtained with the 12 μm thick film will now be presented. In Fig. 5, the distance between the sample and the output of the gun has been chosen so as to produce an air temperature at the surface of the metallized film of 200 °C. The number of passes and also the rate of translation through the air flow have been varied. It can be observed that the slower the translation rate and/or the higher the number of passes, the more efficient the treatment. Fig. 6 shows the results obtained at a constant rate of translation (3cm s^{-1}) with the temperature of the air flow having values of 200, 230 and 250 °C.

From Figs 5 and 6 it is clear that the trends first observed in the taut-annealing experiments are reproduced in this case namely that an improved adhesive behaviour is obtained when the temperature is higher for a given rate or when the rate is slower for a given temperature. As previously, the temperature and time do not affect the adhesive properties to similar extents. However, over the studied range, the enhancement of the properties does not reach a plateau for treatment temperatures above 230 °C. For more passes or higher temperatures, the treated samples become torn in the frame.

Nevertheless, these results confirm the positive effects on the adhesive strength of aluminized PET heat treated under strain in a manner compatible with industrial application. Moreover, it has been shown that a hot-air treatment, performed without any strain i.e., without placing the film in a frame, lead to a quite different effect. Although this experiment has been performed on a very different sample (100 μm in thickness and metallized in our laboratory equipment), it is very instructive. The use of a thicker film is necessary in order to obtain some degree of rigidity. This sample

has been treated under the following conditions: 2 successive passes in the air flow at 160 °C at 5.6 cm s^{-1}. No significant variation is observed after this treatment is applied to the metallized film as compared to the non treated one. A slight but significant decrease in the duration of the variation when the virgin film is treated before metallization corresponds to changes in the surface properties that were observed in a previous publication [17]. This result shows the influence of the strain during the heat treatment, and leads to an assumption of a reorganization in the bulk polymer, and a stress relaxation phenomena at the interface and also possibly in the aluminium layer.

4. Conclusion

In this work, we have proposed an experimental procedure to improved adhesion of metallized PET films during heat treatments. The adhesive characteristics were determined using an ultrasonic vibration test which is highly suitable for the study of granular metallic layers. It has been shown that a heat treatment can be highly advantageous when applied to strained metallized films, although the same treatment performed on a virgin polymer film led to opposite behaviour. The results obtained in this study clearly highlight the important role of the metal and the metal/polyester interface in such treatments.

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