Effect of Cleaning Conditions on Heat Seal Strength between 1N30-H18 Aluminium Foil and Polyvinyl Chloride Plastic Sheet

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In recent years press through packaging has become more popular in the pharmaceutical packaging industry because of its remarkable advantages over traditional packaging. To sustain the practicality of press through packaging, high heat seal strength is one of the most important requirements. To obtain high heat seal strength, 1N30-H18 aluminium foil was washed with different alkaline detergents. The results showed that the heat seal strength increased with temperature in alkaline washing. In alkaline washing conditions, the heat seal strength increased in the order of alkaline detergent D, alkaline detergent C, alkaline detergent B and alkaline detergent A in the first one week but began to seriously deteriorate under washing with alkaline detergent D in the ageing test due to pitting. To obtain high and stable heat seal strength, the use of alkaline detergent should be carefully observed. The improved heat seal strength under high temperature washing, which forms hydrated pseudoboehmite, can be a result of stronger acid-base interaction between adhesive and pseudoboehmite.

Keywords: Aluminium foil, Heat sealing strength, Press through package

1. INTRODUCTION

Packaging is one of the largest industry sectors in the world. Pharmaceutical packaging represents about 5% of the overall packing industry. The global pharmaceutical packaging market was valued at US$47.8 billion in 2010. The market is forecast to grow at a Compound Annual Growth Rate (CAGR) of 7.3% from 2010 to 2017, to reach a value of US$78 billion by 2017(1). Pharmaceutical blister packaging, also called press through packaging, is one of the main forms of pharmaceutical packaging. Press through packaging is becoming more popular in pharmaceutical packaging because of its remarkable advantages over conventional packaging including product integrity, product protection, tamper evidence, reduced possibility of accidental misuse and patient compliance. Moreover press through packaging possesses many functions such as identification and counter forgery, etc. There are four basic components of press through packaging which consist of a forming film, lidding material, heat seal adhesive, and printing ink. The forming film receives the product in a deep-drawn pocket. PVC is the most common forming film material because it exhibits excellent thermoformability, high flexural strength, good chemical resistance, low permeability to oils, fat and flavoring ingredients, easy tintability and low cost. The lidding material provides the base or main structure component upon which the final press through packaging is built. Aluminium is the most widely used push-through lidding material because it has a low water-vapor transmission rate. The heat seal adhesive provides a bond between the plastic blister and the printed lidding material and it is predominantly solvent-based vinyls (because of its superior gloss). The printing inks provides graphics and aesthetic appeal to the whole package(2).

Since the components of the press through packaging would be in contact with the pharmaceuticals directly, the material testing should be especially noticed. The testing items include appearance, barrier property, heat seal strength, impact resistance strength, thermal tensile strength ratio and other mechanical properties. Among them, heat seal strength is an important testing item because sealing performance is a vital index for the practicality of press through packages. To reach high heat seal strength, it is necessary either to modify the heat seal adhesive or the aluminium surface. Since the heat seal adhesive needs to meet the FDA's regulation and is confidential to the pharmaceutical packaging industry, therefore this study only focuses on modifying the aluminium foil surface to attain the highest heat seal strength possible.

After rolling, a continuous amorphous oxide layer is immediately formed due to the reaction between oxygen and humidity in the environment and the newly produced metal surface. This is a so-called room-temperature oxide(3). Oxide layers formed on aluminium at room temperature are generally considered to be non-crystalline, although short-range cubic ordered structure has been reported(4). There are a number of aluminium oxide, oxyhydroxide and hydroxide crystal structures. Common oxides include α-Al_2O_3 and γ-Al_2O_3, oxyhydroxides including α-AlO(OH) (diaspore) and γ-AlO(OH) (boehmite) and bayerite, gibbsite and nordstrandite are all three-forms of the hydroxide, $Al(OH)_3$. In the presence of water, hydroxyl functionalities form at the alumina surface. It has been shown that hydroxyl ions may be present either at tetrahedra or octahedrally coordinated sites at the surface of crystalline alumina(5). The hydroxyl functionality at the surface of aluminium has been implicated in the formation of interfacial carboxylate functionalities with carboxylic acids and is likely to play an important role in the interaction with other organic functionalities(6). As a result, different treatments of aluminium will result in the growth of different types of oxides on the aluminium surface and hence the performance of bounded aluminium relies on its surface chemical characteristics.

In the present study, the effect of cleaning conditions (alkaline detergents and cleaning temperature) on heat seal strength between aluminium foil and PVC sheet were investigated. 1N-30-H18 aluminium foil was washed with different alkaline detergents at different temperatures. The chemical and topographic changes of the aluminium foil surface after different washing conditions were characterized by Scanning Electron Microscope/Energy Dispersive Spectrometer (SEM/EDS), X-ray Photoelectron Spectroscope (XPS), and Confocal Laser Scanning Microscope (CLSM). The changes to the aluminium foil surface resulted in different heat seal strengths and the mechanisms of improved heat seal strength were discussed.

2. EXPERIMENTAL METHOD

2.1 Materials

The 20-μm-thick aluminium foil (JIS 1N30-H18) for press through packaging was supplied by China Steel. Aluminium Corporation. The chemical composition of the 1H30-H18 aluminium foil is as follows: Al $\geqq$ 99.3%, Si + Fe $\leqq$ 0.7%, Cu $\leqq$ 0.1%, Mn $\leqq$0.05%, Mg $\leqq$ 0.05%, and Zn $\leqq$ 0.05%. The tensile strength of the 20-μm-thick 1H30-H18 aluminium foil is $\geqq$ 130 (N/mm^2).

The heat sealing adhesive used here is a polyester/vinyl chloride-vinyl acetate copolymer and complies with FDA 21 CFR 173.300 (resinous and polymeric coatings). The nonvolatile content of the heat sealing adhesive is 28$\pm$2% and its viscosity at 25℃ is 130$\pm$15 seconds as measured by Ford Viscosity Cup# 4.

To obtain high heat seal strength, cleanliness of substrate surface is always one of the universal requirements. Hence foreign materials such as dirt, residual rolling oils, moisture, and weak oxide layers must be removed from the aluminium foil. Alkaline washing (also referred to as degreasing) is commonly used to clean the aluminium alloy. In this study, the aluminium foil was washed by different alkaline detergents. Commercial alkaline detergent A, B, C, and D, which contains KOH, Ethylenediaminetetraacetic Acid (EDTA), and detergent were used in the alkaline washing.

2.2 Heat seal strength test

First, the aluminium foil was resized to a 12×10 cm sheet for the subsequent coating process. To coat about 3 μm-thick adhesive on the aluminium foil, a #7 coating rod was applied for this purpose. The cross-section view of the aluminium foil by SEM confirms the thickness of the adhesive on the aluminium foil, as shown in Fig.1. The aluminium foil with adhesive coating was then resized to a 60×15 mm sheet which is an identical dimension to the PVC sheet tested. The PVC laminated aluminium sheets were prepared by pressing the aluminium foil and the PVC sheet at 141℃ for 1 second under 0.3 MPa using a heat seal tester (HST-H3, Labthink, China). The heat-sealed area was 10×15 mm on top of the PVC laminated aluminium sheets. Lastly, the heat seal strength of the PVC laminated aluminium sheets were measured using 180° peeling test by an auto tensile tester (XLW, Labthink, China). The peeling speed was set at 100 mm/min for the whole experiments.

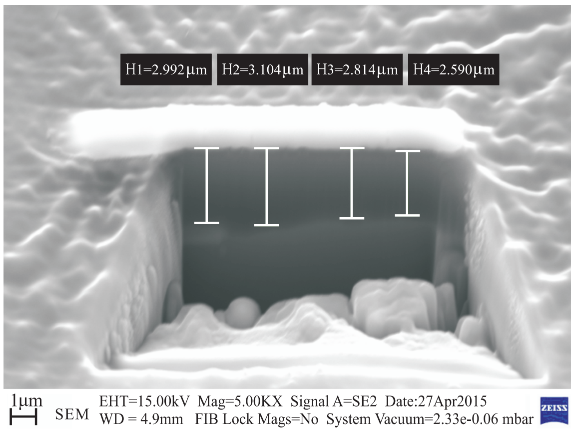

Fig.1. Cross-section of the aluminium foil coated with adhesive by using #7 coating rod.

2.3 Characterization of the aluminium foil surface

A FIB (Focused Ion Beam) -SEM equipped with EDS (1540 XB Crossbeam, Zeiss, Germany) was used to observe the thickness of the coated adhesive, the topography and the chemical composition of the aluminium foil. The oxide surface of the aluminium foil was characterized by XPS (JPS-9010 MX, JEOL, Japan). The monochromated Mg Kα source was operated at 10 kV and 5 mA. The aluminium foil samples were analyzed at a take off angle normal to the surface. Charge correction was compensated by setting the C-C/C-H components of the C 1 s core level peak at a binding energy of 285 eV. Due to the softness of the aluminium foil, the surface roughness was measured by CLSM (TCS SL, Leica, Germany). The measured area of each sample for determining surface roughness was controlled at 0.09 mm^2 with total magnification of 100× (ocular 10×, objective 10×). The wettability of the aluminium foil was determined by FTA 1000 B contact angle goniometer (First Ten Angstroms, USA). Each experiment was run quadruplicate for the contact angle measurement.

3. RESULTS AND DISCUSSION

3.1 Effect of washing temperature on heat seal strength

Figure 2 illustrates the heat seal strength between 1N30-H18 aluminium foil and PVC sheet when the foil was washed with alkaline detergent C at different temperatures. As can be seen, the heat seal strength increased with the washing temperature. The highest heat seal strength was obtained when washing at the highest temperature and the lowest heal seal strength was obtained when washing at 60℃. The results implied that the under high temperature washing the aluminium surface would form a oxide layer which can increase the heat seal strength. In contrast, when washing at 60℃ the oxide layer that formed on the aluminium surface was found to easily to flake off[7]. As a result, washing conditions in terms of temperature played an import role on the heat seal strength. The possible mechanisms of the improved heat seal strength under high temperature washing will be discussed in more detail in the following sections.

3.2 The heat seal strength under different types of alkaline washing

Figure 3 shows the heat seal strength under different types of alkaline washing. After the aluminium foil was washed, the heat seal strength tests were performed in one week (refer to 1st in Fig.3). To test the stability of the seat seal strength (ageing test) under different washing conditions, the heat seal strength was repeatedly performed after the aluminium foil was washed for 1 month (refer to 2nd in Fig.3). As can be seen in Fig.3, the heat seal strength increased in the order of alkaline detergent D, alkaline detergent C, alkaline detergent B and alkaline detergent A in the 1st test. This can be explained by the cleanliness of the aluminium foil surface[8] since alkaline detergent D has the best cleaning efficiency (data not shown here). As the cleaning efficiency of alkaline detergent was increased, the unwanted or weak boundary layers such as residual rolling oil and dirt were further removed. Nevertheless, in the ageing test serious deterioration of the heat seal strength was observed in the alkaline detergent D. The aluminium foil washed with alkaline detergent B possesses the highest heat seal strength and the values are the closest between the 1st and 2nd tests. The reason is that the oxide film on aluminium became unstable and was prone to flake off with time when using alkaline detergent D. As shown in Fig.4, pitting can be found on the

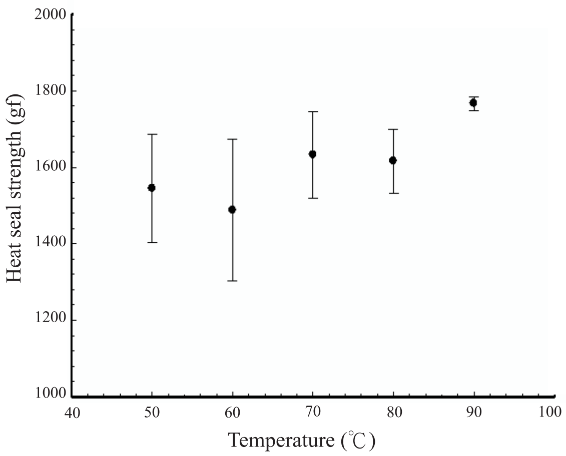

Fig.2. Heat seal strength under different washing temperatures. The aluminium foil was washed with alkaline detergent C for 20 s and then the foil was washed with pure water for 10 s to remove the residual alkaline detergent.

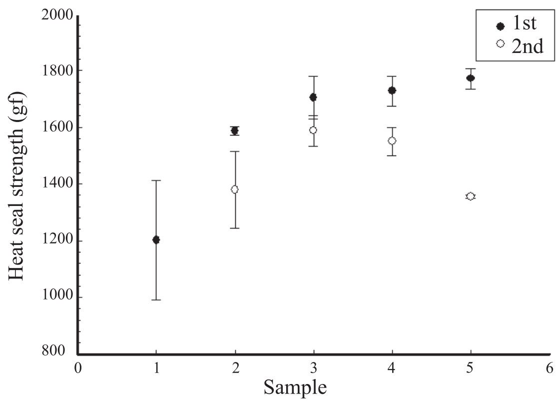

Fig.3. Heat seal strength after washing with different types of alkaline detergents. Sample 1: aluminium foil without any treatment (blank); Sample 2: aluminium foil washed with alkaline detergent A at 90℃; Sample 3: aluminium foil washed with alkaline detergent B at 90℃; Sample 4: aluminium foil washed with alkaline detergent C at 90℃; Sample 5: aluminium foil washed with alkaline detergent D at 90℃.

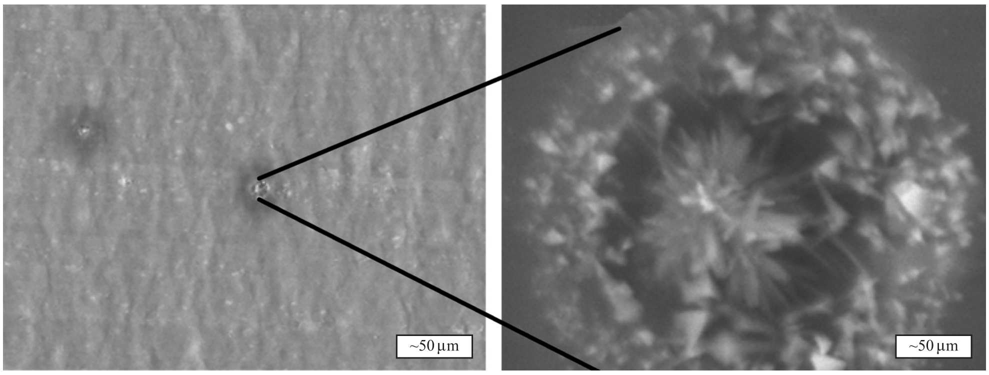

Fig.4. SEM images of the aluminium foil surface after washing with alkaline detergent D.

aluminium foil washed with alkaline detergent D. According to EDS, Al, Si, and Fe are the main elements in the pitting. Because the precipitations like Al-Si-Fe is more noble than the surrounding metal matrix in the presence of electrolyte, the aluminium itself can act as a sacrificial anode to be the locally electrochemically converted to oxide(9). As a result, the pitting acting as a weak boundary layer will deteriorate the heat seal strength in the ageing test. To obtain high and stable heat seal strength, the use of alkaline detergent should be carefully noticed.

3.3 Impact of aluminium surface topography and wettability on heat seal strength

According to the adsorption theory of adhesion, good wetting results when the adhesive flows into the valleys and crevices on the substrate surface; poor wetting results when the adhesive bridges over the valleys formed by these crevices(10). Poor wetting causes less actual area of contact between the adhesive and adherend, and stress regions develop at the small air pockets along the interface. This results in lower heat seal strength. However, as shown in Fig.5, there is no obvious tendency showing that the better wettability of the aluminium foil obtained, the higher heat seal strength. It does not follow the adsorption theory of adhesion mentioned above. Therefore, there are some other important mechanisms affecting the heat seal strength in this case.

The surface of a solid material is not truly smooth but consists of a maze of peaks and valleys. According to the mechanical theory of adhesion, the adhesive must penetrate the cavities on the surface, displace the trapped air at the surface, and lock-on mechanically to the substrate. The increase of surface roughness will aid in adhesion by mechanical keying or increasing the total contact area between the adhesive and the adherend(11). The relationship between aluminium foil surface roughness and heat seal strength is shown in Fig.6. The results reveal that increasing aluminium foil surface roughness would not increase the heat seal strength in return. Therefore, the mechanical theory of adhesion cannot properly explain this result. Both adsorption and mechanical theories are not able to fully explain the adhesion in this study and therefore chemical interaction between aluminium foil and adhesive seems to be the key mechanism of adhesion governing in this case.

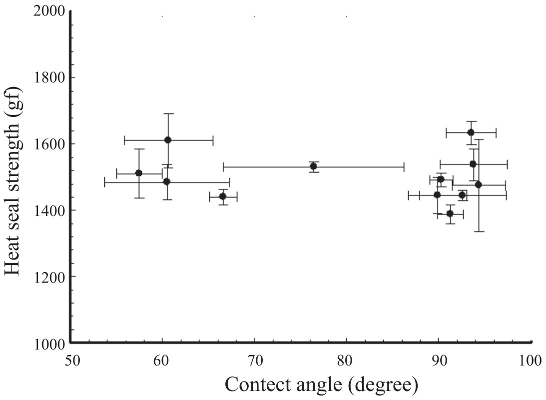

Fig.5. The relationship between contact angle and heat seal strength.

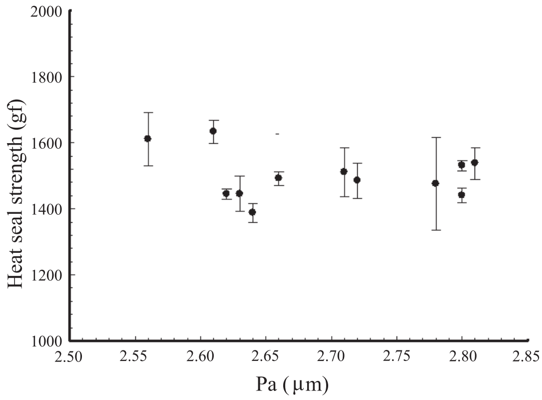

Fig.6. The relationship between aluminium foil surface roughness and heat seal strength. Pa: arithmetic average of the unfiltered raw profile.

Table 1 The elemental composition and oxide/hydroxide composition of the aluminium foil samples determined by XPS

	$^{a}Al_{ox}/Al_{met}+Al_{ox}$	$^{b}O_{OH}^{-}/O_{OH}^{-}+O_{O}^{2-}$
Aluminium foil washed with alkaline detergent A at 50℃	69.18%	34.97%
Aluminium foil washed with alkaline detergent A at 80℃	75.42%	37.22%
Aluminium foil washed with alkaline detergent A at 98℃	94.16%	56.34%

$^{a}Al_{ox}$: oxide aluminium; Al_{met}: metallic aluminium.

$^{b}O_{OH}^{-}/O_{OH}^{-}+O_{O}^{2-}$ represents the proportion of hydroxide or oxyhydroxide in the aluminium oxide layer.

3.4 Impact of aluminium oxide layer on heat seal strength

After washing at different temperatures, the aluminium foil was analyzed by XPS to investigate the characteristics of the oxide layer that had grown on the surface. As shown in Table 1, it could be found that $Al_{ox}/Al_{met}+Al_{ox}$ increased with temperature. This represents that oxide grown on the aluminium foil surface was more abundant at higher temperatures than the ones at lower temperatures. Moreover, $O_{OH}^{-}/O_{OH}^{-}+O_{O}^{2-}$ was also found to increase as temperature increased, which means that the aluminium oxide layer was hydrated at a high temperature. When the amphoteric aluminium oxide surface is hydrated into pseudoboehmite, it becomes more acidic, which allows a stronger acid-base interaction to the electron donating carbonyl oxygen in the adhesive(9). As can be seen in Fig.2, our results are in agreement with this elucidation. As a result, the modification of the chemical structure on the aluminium foil surface has a great impact on the heat seal strength.

In brief, the improved heat seal strength under high temperature washing, which forms hydrated pseudoboehmite, can be a result of stronger acid-base interaction between adhesive and pseudoboehmite.

4. CONCLUSION

The heat seal strength of 1N30-H18 aluminium foil/PVC laminates was found to increase with temperature in alkaline washing. In alkaline washing conditions, the heat seal strength of the aluminium foil/PVC laminates increased in the order of alkaline detergent D, alkaline detergent C, alkaline detergent B, and alkaline detergent A in the first one week but began to seriously deteriorate under washing with alkaline detergent D in the ageing test. Pitting causing a weak boundary layer on the aluminium foil can be explained for this deterioration of heat seal strength. As a result, to obtain high and stable heat seal strength, the use of alkaline detergent should be carefully observed. Traditional adsorption and mechanical theories of adhesion cannot properly explain the mechanism of adhesion in this study. The higher heat seal strength obtained under high temperature washing was found to relate to the growth of a hydrated pseudoboehmite layer on the aluminium foil surface. The acidic pseudoboehmite layer on the aluminium foil surface enhances the acid-base interaction with the adhesive improving the heat seal strength.

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