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Effect of surface pre-treatment on the hydrophilicity and adhesive properties of multilayered laminate used for lithium battery packaging

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ABSTRACT

The surface of aluminum foil was treated using silane coupling agent and chromate–phosphate conversion solution respectively, then a flexible laminate consisting of five layers was prepared using polypropylene film as inner sealant layer and epoxy resin as adhesive between polypropylene film and aluminum foil. The surface morphology and composition of the foil after treatment were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), and the hydrophilicity of the foil was evaluated by contact angle measurement (CAM). The adhesive strength between the aluminum foil and polypropylene film, and the heat sealing strength of polypropylene film were measured by tensile tester, their dependences on the surface treatments were further investigated. It can be concluded that the adhesive strength and heat sealing strength depend on not only the hydrophilicity, but also the morphology of the foil surface. The rough and porous surface of the treated foil can enhance both the adhesive strength and heat sealing strength.

1. Introduction

It is well known that aluminum and its alloys are widely used in aerospace industry owing to its light weight, high strength, high formability and good plasticity, especially aluminum foil has a wide range of applications in packaging industry including foods and medicines because it possesses excellent barrier properties to moisture and air [1–4]. However, aluminum foil is rarely used alone because it is easy to tear; therefore it is usually applied in the form of multilayered laminates [5]. The multilayered laminates generally consist of aluminum foil with a protective polymer film (outer layer) on one side for scratch protection and a heat-sealable polymer film (inner layer) on the other side [6,7]. Epoxy and polyurethane are usually used as adhesives between aluminum foil and polymer film [5,7]. In order to enhance the adhesive strength between aluminum foil and epoxy resin, special surface pre-treatment processes are usually employed and they can also make up for the disadvantages of adhesive property and corrosion resistance of aluminum foil [8,9].

There are plenty of aluminum pre-treatment methods to enhance adhesion. Mechanical methods such as abrasion using abrasive paper and cloth or abrasive blasting are based on physical mechanism, the purpose is to remove loose contaminated layers and provide rough surface for mechanical interlocking with the adhesive [10]. Another pre-treatment method is solution degreasing or alkali eclipse, however, there is no stable chemical layer newly formed during the process, which results in poor durability of joints between the aluminum and adhesive. Therefore, more efficient chemical methods are developed to generate a suitable layer to meet the application requirement.

Anodic oxidization treatment such as chromic acid anodizing (CAA) is a procedure using electrochemical process to form a relatively thin and ductile oxide layer, which can provide a good bonding with adhesive [11]. Chromic etching is conducted by immersion of the substrate in a solution containing chromate and other acid such as sulphuric acid or phosphoric acid, the porous and amorphous chemical conversion layer with good stability and paint adhesion is formed on the substrate surface [12]. Besides, trivalent chromium or chrome-free solutions can also produce new surface with excellent corrosion resistance [13,14]. Silane coupling agent treatment is a relatively fresh technique to improve surface properties by forming an organic layer on aluminum surface, supplying coupling function with coatings [15]. The effects of surface pre-treatments on the interface and properties of aluminum have been extensively studied; especially the corrosion stability has been paid much attention in many reports [16–18]. Prolongo and Ureña [19] made comparisons for the adhesive properties between epoxy and aluminum alloys with different surface treatments.

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The lithium battery has been used in a large scale in many fields. In the past, the electrolyte was sealed in metal container, which has many limitations in packaging situations where the form of the battery is important, such as in hand-held electronics. In recent ten years, the soft packaging material used for lithium battery has been greatly developed [20–22]. The soft packaging material is generally multilayered laminate composed of aluminum foil and polymer films. However, the research on the relationship between the structure and the property of the multilayered laminate has not been reported.

In this paper, silane solution and chromate–phosphate conversion treatment were applied to treat aluminum foil, then a multilayered laminate was prepared, which consisted of five layers from the outer to inner, i.e., nylon/polyurethane/foil/epoxy/polypropylene. The surface morphology of the treated foil was observed by scanning electron microscopy (SEM), and the chemical composition was characterized by energy dispersive spectroscopy (EDS) and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). Besides, the hydrophilicity of the treated foil was evaluated by contact angle measurement (CAM). Then the effects of the morphology and the hydrophilicity of the foil on the adhesive strength and heat sealing strength of the inner layer of laminate were explored.

2. Experimental

2.1. Materials

KH-560 (3-Glycidoxypropyltrimethoxy silane) with the purity of 97∼99%, diglycidyl ether of bisphenol A (DGEBA) with epoxy equivalent weight of 185–210 and methyl tetrahydrophthalic anhydride (METHPA) were purchased from Shanghai Resin Co., Ltd.. Methanol, chromium trioxide and phosphoric acid were from Ling Feng Chemical Reagent Co., Ltd.. Aluminum foil (AA 8021), from Henan Mingtai Al. Industrial Co., Ltd., was used as the substrate. Cast polypropylene film (CPP), supplied by Gloport Plastic Industries Co., Ltd., was used as the sealant layer.

2.2. Preparation of pre-treatment solutions

The equal volume of deionized water and methanol were mixed under stirring, and then KH-560 was slowly dropped into the mixture until the 5 vol.% silane solution was formed. The solution was stirred at room temperature for 24 h so that KH-560 hydrolyzed completely.

The chromium trioxide, phosphoric acid, and film-forming agent in proportion were dissolved in deionized water, and then stirred at room temperature to form a chromate–phosphate conversion solution.

2.3. Surface pre-treatments

Silane coupling agent treatment: aluminum foil was first treated with chemical polishing, and then immersed in the prepared silane solution at room temperature for 2 min. After that, the foil was rinsed in tap water, and finally dried in oven at 80 °C for 1 h.

Chromate–phosphate conversion treatment: aluminum foil was first immersed in the prepared solution at room temperature for 5 min, then rinsed in tap water, and finally dried in oven at 80 °C for 1 h.

2.4. Analysis of aluminum foil surface

Scanning electron microscope (SEM, JSM-6360LV) with an accelerating voltage of 15 KV was used to observe surface morphology of aluminum foil. Energy dispersive spectrometer (EDS, Falcon, 15 KV) and attenuated total reflection FTIR (ATR, Nicolet 6700) were used to explore the composition changes on the aluminum surface. The wettability of aluminum surface after pre-treatment was characterized by contact angle measurement (CAM, JC2000D3), when liquid drop contacted with the interface of the foil, timing started and the image was collected, the contact angle was measured at 15 s. The measurement was conducted at room temperature (11 °C) and humidity of 40%, five different zones on the surface were measured for every sample, and the average value was calculated and reported.

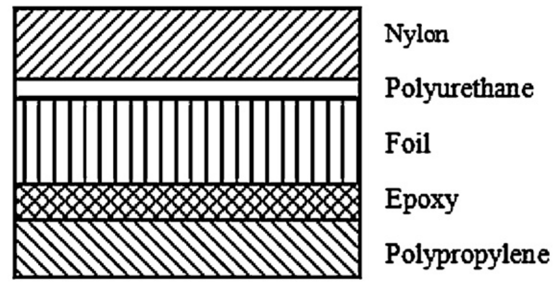

Fig. 1. Structure of prepared multilayered laminate.

2.5. Preparation of multilayered laminate

First the nylon film and the aluminum foil were laminated with polyurethane as adhesive, then CPP film was laminated using DGEBA as the inner adhesive with METHPA as curing agent. The final multilayered laminate consists of five layers from the outer to inner, i.e., nylon/polyurethane/foil/epoxy/polypropylene, and its structure is shown in Fig. 1.

2.6. Measurement of adhesive and heat-sealing strength

The adhesive properties of the prepared multilayered laminate, including peeling strength and heat-sealing strength, were measured by tensile tester (CMT 2203), according to GB 8808-88 and QB/T2358-98 standards.

3. Results and discussion

3.1. Surface morphology observation

Fig. 2 shows the SEM micrographs of untreated and treated aluminum foil surfaces, which were subjected to different pretreatments. The surface morphology of the untreated aluminum foil at different magnification is shown in Fig. 2(A) and (a), it can be seen that the surface is rough with plenty of granular materials and holes, besides, regular scratches with rolling lines can be observed on the surface, possibly from fracture of brittle particles or embedding of debris [23], all of these local damages should be produced in the processing of aluminum foil. The SEM photographs of the aluminum surface treated by KH-560 are shown in Fig. 2(B) (low magnification) and (b) (high magnification). It seems that the topology of the foil surface is almost unchanged compared with Fig. 2(A) and (a), however, the surface of the aluminum becomes smoother after being treated by silane solution, which is more obvious at high magnification (Fig. 2(a) and (b)). This is because chemical polishing removed loose contaminated layers on aluminum foil before silane treatment. Fig. 2(C) and (c) show the surface morphology of aluminum foil treated by chromate–phosphate conversion solution, it can be seen that the natural film has been corroded fully, and a rugged and porous surface was newly formed, which implies that the oxide layer formed through chemical etching is more porous