Fabrication of metal/polymer layer structure composites by demulsification-induced fast solidification

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Abstract. In this study, a simple and convenient method of demulsification-induced fast solidification was demonstrated to in situ prepare Zn/RE-906 polyurethane acrylate (906) polymer film layer structure composites. The mechanical connection strength between 906 polymer films and Zn, that is, adhesive strength, was characterized via lap shear testing. The adhesive strength between the 906 polymer films and Zn is adjustable by adjusting the adhesive time and adhesive temperature. The 906 polymer films exhibited an outstanding adhesive performance within the temperature range from room temperature to 175 °C. The 906 polymer films exhibited excellent adhesion capacity with Zn, making them attractive for applications in the automotive and aeronautic.

1. Introduction

Metal/polymer layer structure composites play an essential role in a wide variety of applications, such as aeronautic, automotive, building panels, and boats.[1–4] Metal/polymer layer structure composites have been used as a protective coating to reduce the corrosion of metal as well as for purely cosmetic,[1,5] and are used as passive dampers to reduce vibration and noise.[6,7] The combination between metals and polymers was complicated and difficult because of their different mechanical and physical properties, such as the difference of surface energy between metals and polymers, the viscoelastic behavior of polymers and the plastic behavior of metals, and the structural differences between them that metals have crystal structures and most of the polymers are amorphous in nature.[4] The different methods of indirect adhesion such as adhesive bonding, hot-pressing, mechanical joining, and roll bonding, or a combination of these methods has been applied to establish a connection between metal and polymer.[4,6,8] In the case of indirect adhesion, long processing time, adhesive cost, emissions of volatile organic compounds, and complex processing process and conditions have led to the development of direct adhesion between metal and polymer. The development of the adhesive polymer films in situ formed on the metal surface that is capable of rapid and facile preparation could attract further interest in metal/polymer layer structure composites and foster their extension to practical applications.
Demulsification-induced fast solidification (DIFS) method has been proposed to *in situ* prepare the polymer films on the conductive substrate surface based on the thermodynamic instability of emulsion, which has been demonstrated to be well suited to prepare adhesive films on the metal substrate.\[9\]

Here, we demonstrated a facile method of DIFS to prepare a metal of Zn/polymer film of RE-906 polyurethane acrylate (906) layer structure composite, achieving direct adhesion of 906 polymer films and Zn. The 906 polymer films were *in situ* prepared on the Zn metal. Lap shear testing was used to characterize the adhesive strength between 906 polymer films and Zn. Results indicated that 906 polymer films and Zn exhibited an excellent and stable mechanical connection. The adhesive strength was adjustable by adjusting the adhesive time and adhesive temperature. Furthermore, excellent adhesive performance can be observed within the temperature range from room temperature to 175°C. Therefore, we used an *in situ* adhesive 906 polymer film formation method of DIFS with controllable adhesive strength to prepare Zn/906 polymer film layer structure composites.

### 2. Materials and Methods

#### 2.1. Materials

RE-906 polyurethane acrylate emulsion (906, solid content 52.0±2.0, pH 4.0–7.0, viscous 300–1000 cps) was purchased from Bondly Chemical Co., Ltd. The metal alloy wire (Al alloy) with a diameter of 750 μm and the Zn sheet with a thickness of 100 μm were purchased from Changchun Metal Materials Corporation.

#### 2.2. Fabrication of 906 polymer films via the DIFS method with the electrochemical method

The metal alloy wire used as cathode and the Zn sheet used as anode were dipped in a 906 emulsion at room temperature, and a voltage was applied to the working electrode. The distance between the cathode and anode was set as 1 cm. Then the 906 polymer films were formed on the Zn sheet. The 906 polymer films were dried in a vacuum oven for 12 h.

#### 2.3. Adhesion of 906 polymer films

The emulsion was dropped on the surface of 906 polymer films prepared on one end of the two Zn sheets for 3 min. The 906 polymer films were bonded face to face with a contact area of 5 mm × 5 mm. A pressure of 1 MPa was applied for stable adhesion for 1 min. The bonded samples are then put into a vacuum oven for a different time and at different temperatures.

#### 2.4. Characterization

The thickness of the 906 polymer films was measured *via* a Vernier caliper. The lap shear strength of the samples was measured on an electronic universal testing machine (PT14-014, 1 kN). And the load change rate and displacement rate are 50 N s⁻¹ and 200 mm min⁻¹, respectively. At least five samples were used for lap shear testing under each condition. The results were shown in terms of the mean ± standard deviation.

### 3. Results & Discussion

#### 3.1. Preparation of 906 polymer films based on the DIFS method

Metallic zinc is widely used because of its excellent flexibility and machinability. Thus, the 906 polymer films were prepared on the Zn sheet *via* the DIFS method with an electrochemical method based on the thermodynamical instability of 906 emulsion. The preparation process was shown in Figure 1a. The metal alloy wire used as cathode and the Zn sheet used as anode were dipped in a 906 emulsion at room temperature, and a voltage of 1.5 V was applied to the working electrode. The Zn²⁺ produced on the surface of the Zn sheet was used as a demulsifier to induce the demulsification of 906 emulsion. Then the 906 polymer films were formed on the Zn sheet to prepare metal/polymer layer structure composites. The variation in the 906 polymer film thickness was shown in Figure 1b with respect to conduction time.
We note that the thickness of the 906 polymer films increases rapidly and subsequently there was steady increases. The minimum thickness of 153.6±2.07 μm of the 906 polymer films was obtained at 5 min.

Figure 1 (a) Schematic illustration for the preparation process of the DIFS method via electrochemical deposition. (b) Thickness of 906 polymer films as a function of conductive time.

3.2. Adhesion of 906 polymer films
Lap shear testing was conducted to evaluate the mechanical connection strength, that is, adhesive strength, between the 906 polymer films and Zn. The bonding process was shown in Figure 2a. The 906 polymer films prepared on the Zn sheet were dried in a vacuum oven for 12 h before bonding to improve the modulus of compression of 906 polymer films, which is beneficial to the adhesion. The emulsion was then dropped on the surface of the 906 polymer films prepared on one end of the two Zn sheets. The 906 polymer films were bonded face to face with a contact area of 5 mm × 5 mm and a pressure of 1 MPa. The emulsion was employed to facilitate the intermixing and bonding at the interface of the two overlying 906 polymer films by reducing the surface compression modulus and the improved mobility of the polymer chains. The bonded samples were then put into a vacuum oven for 2 d at 65 °C to evaluate the relationship of the 906 polymer film thickness and adhesive strength, as shown in Figure 2b. The adhesive strength of the 906 polymer films decreased with increasing thickness because a threshold thickness is important for stable and efficient adhesion. The defects such as voids and microcracks could appear with increasing adhesive 906 polymer film thickness, which was according to the previous work.[10–13] Thus, a thickness of 153.6±2.07 μm was enough to obtain stable adhesion.

Figure 2 (a) Schematic illustrating the bonding and lap shear testing processes. (b) Relationship between the 906 polymer film thickness and adhesive strength.

The 906 polymer film with a thickness of 153.6±2.07 μm was adopted to investigate the relationship of the adhesive time, adhesive temperature, and adhesive strength, as shown in Figure 3. The variation of adhesive strength has resulted from the evaporation of water when the adhesive temperature was less than 100 °C. When the adhesive temperature was more than 100 °C, the variation of adhesive strength
can be attributed to the fluidity of the molecular chain which was increased at the melting state at high temperature and thus improved the adhesive strength. These results also indicated that the adhesive 906 polymer films possessed an excellent adhesive performance within the temperature range from room temperature to 175°C. The maximum adhesive strength of 2.03±0.29 MPa between 906 polymer films and Zn was obtained at 175°C for 4 d. The excellent adhesive strength demonstrated the stable mechanical connection between the 906 polymer film and Zn. These results also strongly demonstrated that the 906 polymer films and Zn can be bonded together tightly to prepare Zn/906 polymer films layer structure composites based on the DIFS method. This is significant for industries’ application.

Figure 3 Relationship between the adhesive time, adhesive temperature, and adhesive strength.

4. Conclusions
In summary, a simple and convenient DIFS method was demonstrated for fabricating Zn/906 polymer film layer structure composites. The stable mechanical connections with the maximum adhesive strength of 2.03±0.29 MPa between the 906 polymer films and Zn are obtained at 175°C for 4 d, and the adhesive strength is controllable by adjusting the adhesive time and adhesive temperature. This work demonstrated a facile DIFS method for designing metal/polymer layer structure composites and hence, opened a new avenue for bonding applications.

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