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Low-voltage electrophoretic deposition of polyetherimide through quarternization and re-imidization reactions

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The electrophoretic deposition (EPD) process successfully applied for the deposition of quarternized polyetherimide (q-PEI) emulsion on the Cu surface in the relatively low voltage range of 2~7 V. Allowing the rheological movement of q-PEI suspension drops to move to the cathode, this voltage level allowed q-PEI (or PEI) coating to be in the thickness range in a few micrometers within 300 sec. The coating thickness increased with the applied voltages and seemed to reach a plateau with time seemingly allowing a stable control of EPD operating conditions. The low-voltage in EPD minimized the violent water electrolysis or gas evolution, and subsequently the quality of the deposited PEI layer was excellent with the RMS roughness in 15~35 nm. The thermally transformation of q-PEI to PEI was confirmed using FT-IR. Based on the electro-rheological theory of suspension drops under electrical potential, the key operation parameters of EPD, i.e., deposition time and applied voltage, were thoroughly investigated by measuring the thickness, surface roughness, and cross-section images of specimens. This work demonstrated that the low-voltage EPD could minimize the gas evolution rates and, thus, provide a high-quality PEI coating on metal surfaces without pinholes, voids, or delaminated areas within a reasonable span of EPD processing time.

Keywords: electrophoretic deposition, re-imidization, polyetherimide, quarternization

1. Introduction

Electrodeposition (EPD) has many advantages over other coating or painting methods because water is used as a carrier and, thus, fire/health hazard or environmental pollution issues are eliminated, which subsequently reduces the operation cost. Thus, it has been used for various parts in construction, automobile, applied appliance industry (Neirinck *et al*., 2009; Besra and Liu, 2007; Sarkar *et al*., 2005). Since EPD is suited for coating large-area and 3D-geometry structure, it may well be extended to other emerging applications, *e.g.*, electronic and display packaging (Jeong *et al*., 2013). Polymer coating on metal is intensively used in electronic-device packaging industry as an insulation or solder resist layer, which is usually applied to the copper traces of a printed circuit board (PCB) for protection against oxidation and to prevent solder bridges from forming between closely spaced solder pads (Eom *et al*., 2010; Baek *et al*., 2010; Noh *et al*., 2006).

Various water-dispersed emulsion polymer systems have been used for EPD including epoxies, acrylics, polyesters, polyimides, *etc* (Buchwalter *et al*., 1989; Allen and Craig, 1973; Schafheutle *et al*., 1995; Zlata, 1973; Qariouh *et al*., 1999). Although there are several exceptions, most EPD coating takes place at the anode, where oxidation and dissolution of the metal substrate could occur (Sarkar *et al*., 2005; Qariouh *et al*., 1999). Particularly in PCB packaging application, it could raise critical problems because the dissolved and/or migrated metal may smear into the insulating polymer materials, which could cause serious circuit failure particularly in long-term utilization. In this sense, EPD of polyetherimide (PEI) is considered quite desirable (Qariouh *et al*., 1999). Using quarternized PEI (q-PEI) emulsion, the polymer film can be formed in the cathode and, the q-PEI can be converted subsequently to PEI in a facile manner. It should also be mentioned that PEI is an excellent electronic packaging material due to its excellent properties of high Tg (215~217°C), excellent thermal stability, low relative permittivity (3.14), low CTE (47~56 μm/m°C), and excellent mechanical properties (3.13 GPa of flexural modulus) (Krevelen, 1972).

EPD of PEI has been well investigated in previous literature (Qariouh *et al*., 1999). However, applied voltage for EPD is high in the range of ca. 40 V~180 V, which is

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considered too high to be applied for the emerging field of electronic packaging because it may very well cause serious damage in the electronic parts as well as circuits in PCB. In addition, this high voltage causes violent electrolysis of water and discharges various ionic species (Ferrari and Moreno, 2010), which results in violent bubble formation during EPD. Subsequently, the trapped gas bubbles or dissolved hydrogen gas could cause pinholes or rough surface in the electrodeposited PEI films. Accordingly, the critical issue of EPD with PEI is lowering electrophoresis voltage in order to minimize the gas evolution rates and side reactions, which could ensure circuit protection and smooth deposition surface. We believe that it could lead an important technical breakthrough in electronic packing industry.

In this study, the EPD process was applied for the deposition of PEI on Cu metal surfaces at a low voltage level, < 10 V, where the rheological dialysis is dominant while minimizing the violent electrolysis reactions. Although the electrolysis water occurs in > 1.23 V, the hydrogen evolution may well be substantially decreased in this voltage level. The EPD time, deposition thickness, and surface smoothness of the deposited PEI were thoroughly investigated identifying the processing window in a practical sense.

2. Experimental

2.1. Materials

N-methylpyrrolidone (NMP), acetophenone, 1-methylpiperazine, lactic acid (50%) were purchased from Sigma-Aldrich. Poly-(etherimide) (PEI, ULTEM 1000) was purchased from Quadrant Co., Ltd (Korea).

2.2. Preparation of q-PEI emulsion

PEI pallets (80 g) were added to a mixture of acetophenone (20.6 g) and NMP (165.3 g), and, then, mixed for 4 hours at temperature of 90°C with gentle stirring in N_2 condition. After the PEI pallets are completely dissolved in solvent the mixture of acetopheone (62 g) and 1-methylpiperazine (18.9 g) was added slowly within 2 hours to the PEI solution with vigorous stirring. When the addition is completed, the solution was heated to 110°C and this quarternization reaction was carried out for 2 h 30 min. Afterward the mixture of acetophenone (5.96 g) and lactic acid (1.48 g) was added to the quarternized PEI (q-PEI) solution, and then DI-water (80 ml) was slowly added to the solution using dropping funnel to give a milky emulsion.

2.3. Characterization

The infrared spectra of PEI, q-PEI, and re-imidized PEI were analyzed using a Fourier transform infrared (FTIR) spectroscopy (Bruker IFS-66/S). The cross-sectional morphology of PEI coated on metal electrode was observed by FE-SEM (SUPRA 55VP, Germany).

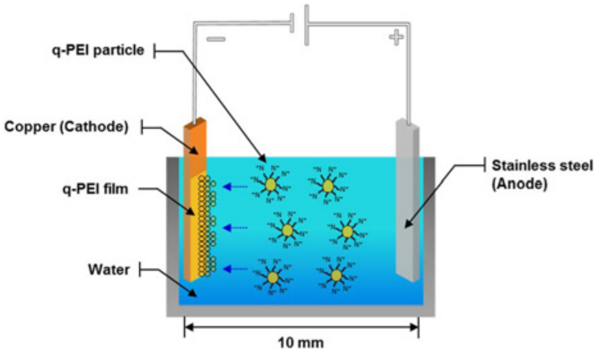

Fig. 1. Schematic of EPD process exhibiting that the positively-charged q-PEI oil drops are deposited on the cathode plates (stainless steel).

2.4. EPD of q-PEI films and its re-imidization

The stainless steel and Cu plates were used EPD electrodes. As schematically shown in Fig. 1, the Cu electrodes were immersed in the q-PEI emulsion with an interval distance of 1 cm from the counter electrode (anode, stainless steel). Applying negative (-) potential on the metal electrode, the deposition time and voltage were varied 0~300 min and 2~7 V. After EPD, the q-PEI coated metal plate was immediately withdrawn from the q-PEI emulsion and washed with DI-water and dried in air at room temperature for 1 hour. Afterward the film was placed in a vacuum oven annealing over 250°C for 3 hours in order to remove remaining solvents, where re-imidization of the q-PEI film simultaneously occurred resulting in the PEI film.

3. Results and Discussion

Fig. 2 shows the closed cycle of q-PEI and PEI through the reactions of quarternization and re-imidization. As can be seen, N-methylpiperazine, a secondary-tertiary amine, is attached to the polymer main chain via breakage of imide rings ("step 1"). Then, the tertiary amine group is protonated with acid to become the positively-charged q-PEI ("step 2"), which can be dispersed as positive oil drops in water. The positively-charged q-PEI oil drops allow cathodic electrophoretic deposition. Subsequently, the deposited q-PEI film can be re-imidized to PEI through heat treatment ("step 3").

The FT-IR spectra of three materials, PEI, q-PEI, and re-imidized PEI, are compared in Fig. 3. Two major peaks of imide I appear at 1,779 cm^{-1} and 1,720 cm^{-1} corresponding to the symmetrical and asymmetrical stretching vibrations of the imide carbonyl absorptions. Vibration of N-C=O appears at 1,680 cm^{-1} and 1,548 cm^{-1}

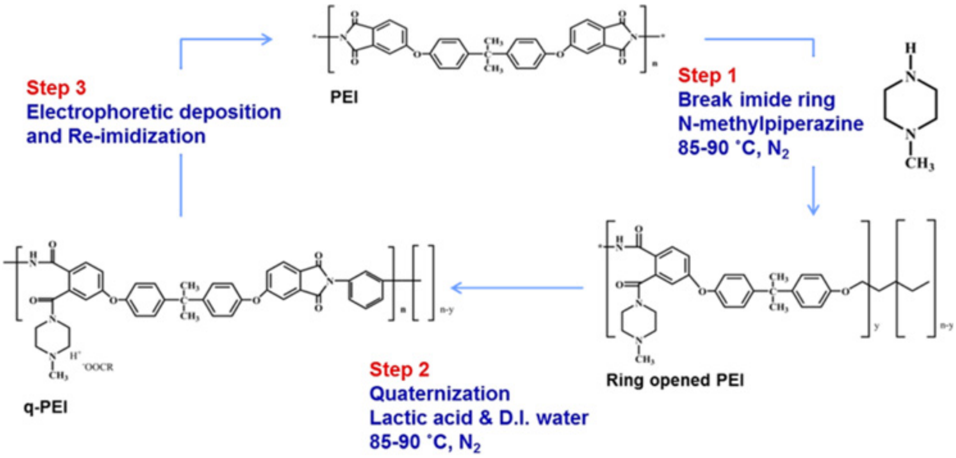

Fig. 2. Schematic of reaction cycle of PEI quarternization of PEI and re-imidization of q-PEI.

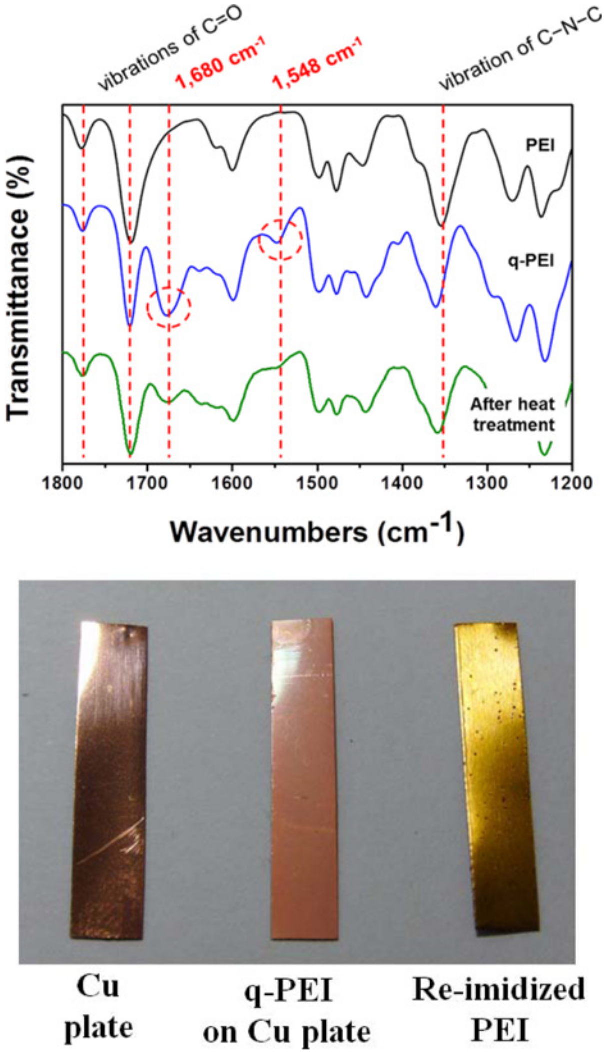

Fig. 3. FT-IR comparison of PEI, q-PEI, and re-imidized PEI after the heat treatment. Camera pictures exhibiting pristine Cu plate, q-PEI deposited on Cu plate, and re-imidized PEI on Cu plate.

in q-PEI, demonstrating that the imide rings are open and q-PEI is successfully prepared. These peaks of N-C=O disappears (or substantially decreases) after heat treatment (250°C for 3 hrs), which confirms that the q-PEI is re-imidized to PEI. The appearance of q-PEI and PEI is clearly different as seen in Fig. 3. The q-PEI coated on the Cu plate exhibits a pastel Cu color, which turns yellow after being re-imidized. The q-PEI layer is likely to contain voids that could be included in the deposition process as water/solvent evaporation, which is eliminated during re-imidization. The re-imidized PEI coating becomes shiny and light yellow demonstrating the coating quality is excellent.

In the EPD process, which is based on the suspension rheology and electrochemical dialysis, the deposited mass per unit area m (g cm^{-2}) has been expressed as follows: (Besra and Liu, 2007; Ferrari and Moreno, 2010; Omer *et al.*, 1999)

$$m = \frac{aC_s\varepsilon_0\varepsilon_r\xi SEt}{\eta} \tag{1}$$

where a is the adhesion factor, C_s is the suspension concentration (g cm^{-3}), ε_0 and ε_r are the permittivity of the free space and the suspension medium, respectively, ξ is the zeta potential of colloidal particles, S is the deposition area (cm^2), E is the electric field (V cm^{-1}), t is time (s), and η is the viscosity of the suspension medium. It indicates that the EPD membrane thickness can be changed by changing the deposition conditions of concentration of q-PEI drops, pH of the dispersion (or zeta potential), applied voltage, and deposition time. In this study, we focused on the processing conditions of applied voltage and deposition time. The other deposition conditions should be investigated further in the future.

Fig. 4 and Table 1 represent thickness variation of PEI films deposited by the EPD process using relatively low

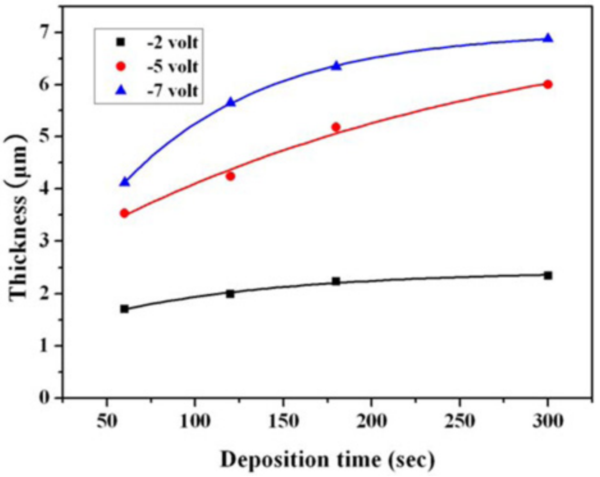

Fig. 4. EPD coating thickness of re-imidized PEI films plotted as a function of deposition time at different voltages at 2, 5 and 7 V.

Table 1. Coating thickness of re-imidized PEI films as a function of deposition time at different voltages (thickness unit in μm)

Deposition Time (sec)	-2 Volt	-5 Volt	-7 Volt
60	1.71	3.53	4.12
120	2.00	4.24	5.65
180	2.24	5.18	6.35
300	2.35	6.00	6.88

voltages in 2~7 V, which is substantially lower than the previous works or commercial operating conditions, say, ~ 100 volts (Qariouh *et al*., 1999). As can be seen, the deposited thickness of PEI increases with time seemingly giving a limiting thickness as a plateau. The thickness increases very fast within 60 seconds, which seems to comply with Faraday's law. However, the deposition rate decelerates with time over ca. 60 seconds. The deposited PEI is an insulating material and, thus, the deposition potential may well decrease as the PEI layer thickness is increased with time. As a result of this insulating q-PEI layer, the EPD deposition decrease as the deposited-layer thickness increases. As also can be seen in Fig. 5, the limiting thickness depends on the applied voltage. For example, 2 V gives 2.35 μm, and 7 V 6,88 μm after 300 sec of our experimental conditions, which is considered significant in practical application of EPD coating especially when EPD is carried out at low voltages. It is quite advantageous because the low-voltage EPD process may be controlled by the equilibrium operating conditions, which could give a stable and repeatable thickness of PEI coating.

The SEM images of the PEI layer deposited on the Cu plate are shown in Fig. 5. Complying with the quantitative values in Fig. 4 and Table 1, it can be clearly seen that the PEI thickness increases with EPD time at different voltages. There are no voids or cracks observed within the PEI coating layer demonstrating the low-voltage EPD process could give high-quality coating. It should also be mentioned that the coating surface is extremely smooth without pinholes or craters, which are usually observed in high-voltage EPD process. The interface between the Cu plate and PEI deposition looks also excellent without any voids or delaminated region. Overall, the low-voltage EPD demonstrates that an excellent-quality coating can be achieved on the metal surface, which is due to the fact that the gas evolution is minimized. In addition, it should be mentioned that the deposition time is not substantially long even in this low-voltage EPD process from an industrial point of view.

Finally, the surface roughness of the EPD coating is shown in Fig. 6. The root-mean-square (RMS) roughness

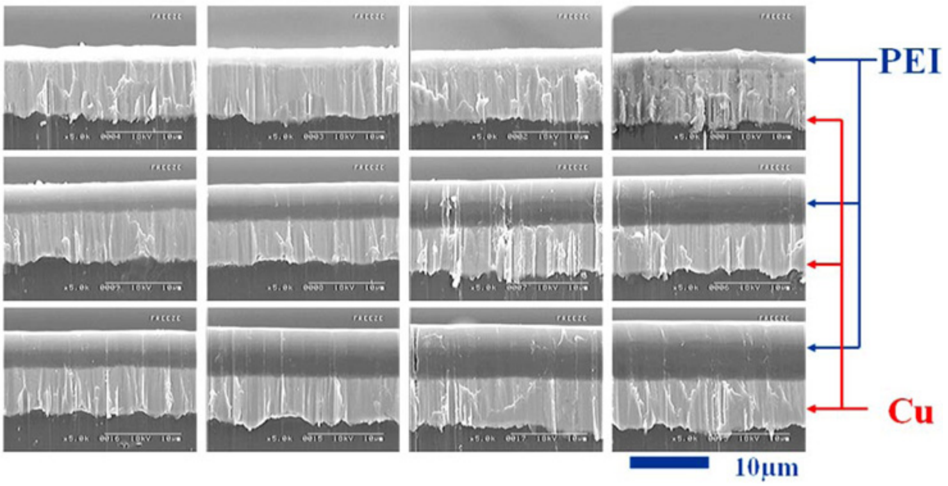

Fig. 5. SEM images of PEI coating on Cu plate under the same EPD conditions as Fig. 4 and Table 1.

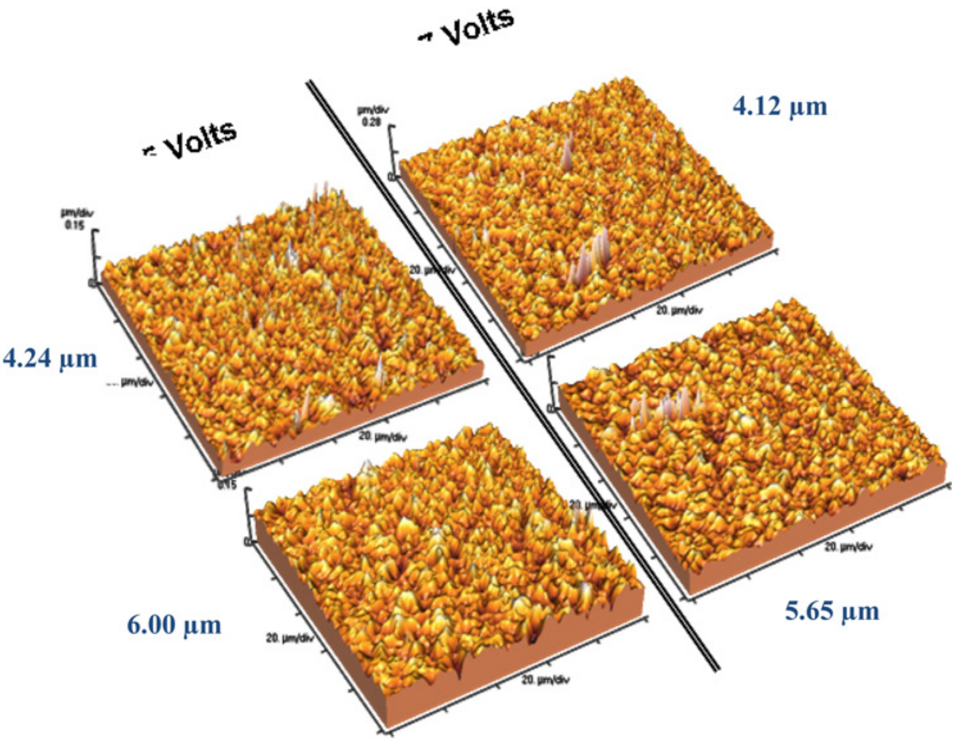

Fig. 6. Surface roughness (RMS, root-mean-square) of PEI coating measured by AFM for the specimens at different EPD voltages: 5 V giving 18.9 and 23.2 nm of RMS roughness for 4.24 and 6.00 μm of thickness, respectively, and 7 V giving 34.0 and 28.3 nm of roughness for 4.12, and 5.65 μm of thickness, respectively.

is 21 ± 2 nm at 5 V, and 31 ± 3 nm for the PEI surfaces fabricated by EPD. Regardless of the EPD processing conditions or the resulting thicknesses, the RMS roughness is considered excellent. Although further experiments are needed, one of the major factors affecting the surface roughness seems to be the applied voltage seemingly because the deposition speed and the gas evolution rate are proportional to the applied voltage.

4. Conclusions

Using a low voltage in 2~7 V, the EPD process successfully applied for the deposition of q-PEI emulsion on metal surfaces. This voltage level ensured q-PEI (or PEI) coating with a thickness in a few micrometers within 300 sec. Thermally converting q-PEI to PEI, this work demonstrated that the low-voltage EPD could provide a high-quality PEI coating layer on metal surfaces without pinholes or voids.

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