POLYMERIZATION AND CHARACTERIZATION OF HIGH CONDUCTIVITY AND GOOD ADHESION POLYPYRROLE FILMS FOR ELECTROMAGNETIC INTERFERENCE SHIELDING*

Yong-sheng Qiao a, b, La-zhen Shen b ** and Tao Dou a

a Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan 030024, China
b School of Chemistry and Chemical Engineering, Shanxi Datong University, Datong 037009, China

Abstract  Polypyrrole (PPy) shows a favorable application in the electromagnetic interference (EMI) shielding due to its good electrical conductivity and outstanding air stability. Conducting PPy films with high conductivity and good adhesion were successfully polymerized on the surface of insulating epoxy resin substrates using chemical polymerization. The factors affecting the properties of PPy films, such as the surface morphology, adhesion between PPy film and substrate, electrical conductivity, EMI shielding effectiveness (SE), were investigated. The adhesion was improved significantly through a three-step surface pretreatment of epoxy resin substrates including removing impurities, roughening, and surface modification with silane coupling agent. An enhancement in the conductivity of PPy films of about one order of magnitude was achieved by adding dopant in FeCl 3 solution. The higher the conductivity, the better the shielding effectiveness. Taking sodium p-toluenesulfonate doped PPy film as example, EMI SE was in the practically useful range of about 30 dB over a wide frequency range from 30 MHz to 1500 MHz. The PPy film samples were characterized by scanning electron microscopy (SEM), infrared spectra (IR), X-ray photoelectron spectroscopy (XPS) and the flange coaxial transmission device. The four-point probe method was used to measure conductivity of PPy films.

Keywords: Polypyrrole film; EMI; Conductivity; Adhesion.

INTRODUCTION

Polypyrrole (PPy) is considered one of the most investigated conducting polymers and also is the focus in many studies with various practical applications because of its high conductivity, outstanding air stability and special physical, chemical properties compared with other conducting polymers [1-4]. PPy film is widely used in electronic device [5], semiconductor apparatus [6], biosensor [7], polymeric battery [8] and electromagnetic interference shielding (EMI) [9]. Three methods of preparing conducting polypyrrole films were previously reported [10, 11]: chemical polymerization, electrochemical polymerization and chemical vapor deposition (CVD). In recent years, most of this research focused on electrochemical polymerization, but the dimension of electrode restricted the area of PPy film [12-15]. Chemical polymerization has an advantage over electrochemical method because it is suitable for both conducting and non-conducting substrates and is not restricted by area and surface shape of substrates. Furthermore, chemical method is convenient and rapid.

In this paper, a three-step pretreatment including removing impurities, roughening and silane coupling agent modification of the surface of insulating epoxy resin substrates was carried out first. The pretreatment has
great influence on the morphology and continuity of PPy films as well as the adhesion between the PPy film and epoxy resin surface. Then, PPy film was chemically polymerized on the surface of epoxy resin in FeCl₃ oxidant solution. The conductivity of PPy films was increased by the addition of dopants, such as I₂, HClO₄, sodium dodecyl benzenesulfonate (SDBS), sodium p-toluenesulfonate (STS), etc. Doped PPy films obtained in this paper have the ability to shield electromagnetic interference.

EXPERIMENTAL

Materials
The pyrrole monomer (Aldrich, 99%) was distilled prior to use. FeCl₃·6H₂O (Alfa, reagent grade) was used as the oxidant. All other reagents are analytically pure reagent. The insulating reinforced epoxy resin sheet (7 mm × 7 mm × 1 mm) was used as substrate in this study. The epoxy resin sheet is the epoxy molding compound (EMC) used in integrated circuit chip, which is provided by Motorola.

Pretreatments on Epoxy Resin Substrate Surface
The epoxy resin substrate was pretreated with three steps. First, the substrate was treated with mixed base solution (mass ratio of NaOH:Na₃PO₄:Na₂CO₃ = 5:2:1) to remove surface impurities at 70°C for 30 min with gently stirring, and then was washed with distilled water. After drying, the substrate was put in the strong acid roughening solution (the concentration ratio of concentrated H₂SO₄:CrO₃ = 1:1) at 85°C for 25 min. Then the substrate was rinsed repeatedly with dilute alkali (10% NaOH), distilled water and absolute alcohol in turn several times, and dried at 60°C. Finally, the substrate was dipped in silane coupling agent aqueous solution (1% V/V vinyltriethoxysilane) for 10 min. Subsequently the substrate modified by silane coupling agent was obtained after drying in the air at room temperature.

Polymerization of Polypyrrole Film
Pyrrole monomer (98%, Aldrich) was purified by distillation under reduced pressure prior to use. The pretreated epoxy resin substrate was first dipped in the solution of pyrrole monomer with absolute alcohol as solvent (30% V/V). Then, the substrate was immersed into oxidant solution (10% FeCl₃), in which dopant was added. Subsequently, polypyrrole was in situ polymerized on the substrate surface to form a PPy film in the above ferric chloride solution. Meanwhile, the color of reaction solution was changed from rust orange to green and finally changed to black. After 30 min, the PPy film was washed with distilled water and absolute alcohol in turn. Finally the resultant film was dried by air at room temperature and the conducting PPy film was obtained.

Measurements
The morphology of the surface of substrate and PPy film was carried out by a Philips XL30 scanning electron microscope (SEM) to obtain SEM images. Infrared spectrum (IR) was taken on a BIO-RAD3000 IR spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurement was made on a PHI-1600 spectrometer with a Mg Kα X-ray source. The electrical conductivity of polypyrrole films was measured using a four-point probe instrument (SDY-5). The flange coaxial transmission device (ROHDE & SCHWARZ) was used to measure the shielding effectiveness of critical frequency points as well as the amplitude-frequency curve of PPy film samples in the frequency range of 30 MHz–1.5 GHz.

RESULTS AND DISCUSSION
The surface of epoxy resin attached with impurities is unclean and has less reactive site, thereby it is difficult for polypyrrole to deposit on the substrate surface. As mentioned above three important factors, such as removing impurities, roughening and surface modification with silane coupling agent, etc., can affect the morphology and adhesion of PPy. These factors were studied and discussed carefully in this paper. The electromagnetic interference shielding effectiveness (SE) is proportional to electrical conductivity according to Schelkunoff theory[16, 17]. In order to obtain PPy films with high SE value, the factors improving the conductivity of PPy films were investigated.