



Conductive polypyrrole and acrylate nanocomposite coatings: Mechanistic study on simultaneous photopolymerization



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ABSTRACT

Facile preparation of conductive polypyrrole coatings with optimized binding and conductive properties for various electronic applications such as printing circuit boards and conductive inks using simultaneous photopolymerization method was investigated in this article. This method involves independent polymerization processes of pyrrole and acrylate monomers occurring simultaneously to produce conductive coating. While AgNO_3 was used as oxidizing agent for photopolymerization of pyrrole, Irgacure 907 was used as the photoinitiator for the acrylate monomer, 1,6-hexanediol diacrylate. Based on Real-time Fourier Transform Infrared (RT-FTIR) spectroscopy characterization on polymerization rates and mechanisms, it was deduced that the selection of proper initial concentrations of monomers and their corresponding photoinitiators was essential to obtain optimized conductive and binding properties of the final coating. In addition, microscopic techniques such as TEM and SEM revealed that the size, morphology and dispersion of polypyrrole were also affected by the initial concentrations. Finally, conductivity measurements obtained via four-point probe method and conductive AFM were correlated with the spectroscopic and microscopic characterization to determine the optimal conditions for the preparation of conductive polypyrrole/acrylate coatings via this method.

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1. Introduction

Intrinsically electronic conductive polymers have attracted great attention for their potential applications in printed circuit boards, flexible electronics, organic thin film transistors (OTFTs), sensors and various electronic devices due to their lower weight than metals, ease of preparation, and a wide range of controllable properties [1–5]. The past few decades have seen significant development in this field in terms of fundamental scientific research and many industrial applications. Several attempts have been made to fabricate micro-patterns, structures of conductive polymers, and their coatings on various substrates via chemical oxidation and electropolymerization processes [6–9]. While some of the advantages that electropolymerization method offers are controllability on thickness of coatings and conductivity; the advantages of chemical oxidation method are feasibility of large-scale production and variability of precursors [10]. However, solubility of conductive polymers has been a major issue in both these methods in order to obtain thin films with improved adherence to various substrates.

The field of photo-induced chemistry offers a wide variety of tools that are useful in obtaining desired chemical transformations with an application of light for a broad range of applications. Among the photo-induced chemical reactions, photodoping and photopolymerization are notable techniques for the deposition of metals into polymers [11,12]. Photodoping involves the incorporation of metals such as silver into various materials such as glass and polymer upon illumination of light. During the process, the charged metallic species migrate into the materials under the influence of intrinsic electric fields caused by the exposure of light. Photopolymerization is a process in which a liquid transforms into solid by the irradiation of generally UV light or electron beam. This phenomenon causes significant changes to physical properties of material such as viscosity, solubility, adhesion, color, and electrical conductivity. This technique for material synthesis has been found highly useful in obtaining microfabrication and coatings directly onto the substrate where there are limitations such as temperature and solubility. Complex nano- and micro-sized patterns and structures have been fabricated using photopolymerization onto printed circuit boards, miniature wiring boards, and biomaterial scaffolds [13,14].

Recent studies on photopolymerization of pyrrole in the presence of electron acceptors, for example silver salts, excited by UV light have shown interesting results for the incorporation of metal

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nanoparticles into polypyrrole [15–17]. Previously, some reports on multiphoton-sensitized polymerization of pyrrole, self-sensitized photopolymerization of pyrrole, and photopolymerization of pyrrole using ruthenium, cobalt, ferrocene and copper complexes as electron acceptors were published [18–21]. The photopolymerization method has been successfully used to manufacture composites of polypyrrole/metal nanoparticles for applications such as gas sensors and humidity sensors [22,23]. However, so far very few reports have been published on the use of photopolymerization because of lower yields and inferior conductivity of polypyrrole obtained in this method as compared to chemical and electrochemical methods. One of the major advantages of photopolymerization is that it can be readily applied with the ease of design and control to make polymer coatings directly onto conducting and non-conducting substrates.

In this paper, the preparation of conductive polymer coatings of polypyrrole and acrylate via simultaneous photopolymerization was reported. This method facilitates the fabrication of conductive polymer coatings for various applications such as printing conductive inks and semiconductor devices. In this method, the reaction mixture contains pyrrole with its corresponding photo-activated oxidant and acrylate monomer with its corresponding photo-initiator. This reaction mixture will be converted into a hybrid coating through photopolymerization processes of both pyrrole and acrylate occurring simultaneously. While polypyrrole serves as conductive path link, acrylate polymer acts as binder to bind polypyrrole particles as well as strongly adhere to the substrate. Due to the fact that it is a single step process, it minimizes total preparation time and eliminates the processibility of conductive polymer. In this work, Real-time Fourier Transform Infrared (RT-FTIR) spectroscopy was used to investigate polymerization conversion of pyrrole to polypyrrole in the presence of UV activator, AgNO_3 . Subsequently simultaneous photopolymerization, which is the combination of polypyrrole formation and acrylate polymer formation occurring together in a reaction mixture, was also studied using RT-FTIR. Finally, coatings were made on aluminum substrate and characterized using four-point probe method and conductive AFM in order to measure conductivity and surface roughness of coatings. Further, coatings prepared on epoxy substrate were analyzed using transmission electron microscope (TEM) and scanning electron microscope (SEM).

2. Experimental section

2.1. Materials

Pyrrole was purchased from Sigma Aldrich, distilled under vacuum, and stored in refrigerator around 0°C prior to use. AgNO_3 and methanol were also purchased from Sigma Aldrich. 1,6-hexanedioldiacrylate (SR238) and Irgacure 907 were obtained from Sartomer. EPO-TEK[®] 377 purchased from Epoxy Technology, Inc., (USA) of the dimensions of 1×1 inch was used to prepare epoxy substrates for the coating applications.

2.2. Investigation of polymerization conversions using real-time FTIR

Real-time FTIR (RT-FTIR) technique was used to determine the polymerization conversion mechanisms and rates of polypyrrole and acrylate polymer. Initially the conversion mechanisms and rates of these polymers were studied separately. This information helped us to find out the optimum conditions, for example monomer to initiator ratio, in order to match the conversion rates of these polymers in simultaneous photopolymerization process.

RT-FTIR experiments were performed using Nicolet Magna-IR 850 Spectrometer Series II with detector type DTGS KBr, with a UV DC mercury vapor lamp. A 100-W compact arc DC mercury vapor lamp from AUV/LESCO Co. was used as the UV light source for all RT-FTIR experiments. A germanium pellet from Sigma Aldrich was used as the substrate for all experiments. A spin coater was used to spread the reaction mixture uniformly over the substrate.

2.3. Preparation and characterization of conductive polypyrrole/acrylate coatings

Conductive polypyrrole/acrylate coatings were prepared on substrates such as aluminum, glass and epoxy. While AgNO_3 was used as electron acceptor for photopolymerization of pyrrole, Irgacure 907 was used as the photoinitiator for photopolymerization of acrylate. A Dymax 2000-EC flood curing equipment with a mercury vapor lamp having the UV-light intensity of 35 mW/cm^2 was used as the light source. Prior to the application of the coatings, the substrates were degreased with hexane and dried for few minutes. Each coating was made by spreading the reaction mixture onto the substrate using spin coater and irradiated under UV light for 20 min. After the preparation of coating, the panel was wiped off with hexane to remove any unreacted contents and placed in oven at 60°C for 30 min. A Veeco Dimension 3100 atomic force microscope with contact mode and current sensing probe was used as C-AFM to characterize the coatings prepared on aluminum substrate for surface morphology and current density. The platinum-iridium (Pt/Ir) coated cantilevers (Model: SCM-PIC, 0.01–0.025 ohm-cm Antimony (n) doped Si, spring constant 0.25 N/m) were purchased from Veeco Instruments. A 100 mV DC bias voltage was applied between the substrate and the coatings in all experiments. Four-point probe technique assembled from Signatone probe, Keithley 2000 multimeter and Keithley 220 programmable current source was used to measure the conductivity of the coatings. Using the four-point probe technique a current of $4.5 \mu\text{A}$ was applied and the voltage was measured. The morphology of coatings prepared on epoxy substrate cured from the material, EPO-TEK[®] 377, was investigated with JEOL JEM-100CX II tungsten-filament transmission electron microscope (TEM) and a JEOL JSM-6300 scanning electron microscope (SEM). For SEM, the magnification ($\times 5,000$), accelerating voltage (5 kV), and the scale ($1 \mu\text{m}$) were specified on each image.

3. Results and discussion

3.1. Photopolymerization of pyrrole

Real-time Fourier Transform Infrared (RT-FTIR) spectroscopy is one of the most valuable techniques in measuring the polymerization rates qualitatively by monitoring the changes in the IR absorption characteristics of the reactive groups such as acrylates, methacrylates, epoxies, double bonds and thiol groups. In addition, it can further be used to calculate the degree of conversion at any time during the polymerization process. It has often been effectively used to investigate the kinetics of polymerization reactions depending on the reaction conditions such as irradiation, type of monomers and initiators, and their concentrations. One of the major advantages of RT-FTIR is that it provides the information about the amount of residual unreacted groups in the reactive ingredients at any point during the course of polymerization process [24,25].

In this work, the photopolymerization of pyrrole with AgNO_3 as oxidizing agent was initially studied using RT-FTIR to understand the effect of AgNO_3 concentration on the rate and mechanism of photopolymerization. Four different molar ratios of pyrrole to

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