

STATIC DISSIPATIVE BIOPOLYMER COMPOSITES FOR ELECTRONIC PACKAGING

W. Prissanaroon-Ouajai*, S. Ouajai and A. Reung-u-rai,
Department of Industrial Chemistry, Faculty of Applied Science,
King Mongkut's University of Technology North Bangkok,
1518 Piboonsongkarm Road, Bangsue, Bangkok, 10800 THAILAND
*Email Address: pwalaip@hotmail.com

SUMMARY

Static dissipative biopolymer composites have been prepared by adding conducting polypyrrole nanoparticles into poly(lactic acid) (PLA). Poly(ethylene glycol) has been added to the composites in order to improve the dispersion of polypyrrole nanoparticles in PLA matrix. Resistivity of the composites is in the electrostatic discharge (ESD) protection range, offering potential in electronic packaging applications where ESD is a major concern.

Keywords: Poly(lactic acid), Polypyrrole, Static dissipative, ESD

INTRODUCTION

Electrostatic discharge (ESD) is considered as a major problem in electronic industry since it can either degrade or destroy the electrical characteristics of semiconductor devices. It has been estimated the actual cost of ESD damage to the electronic industry as running into billions of dollars annually [1]. Static dissipative materials, having surface resistivity between 10^6 and 10^{12} ohms/square, are required for electronic packaging in order to minimize the effects of ESD of the sensitive electronic devices during handling and transportation. Unfortunately, plastics used for packaging are well known as insulator. Therefore, a degree of static dissipation needs to be imparted to the plastic part by adding conductive fillers such as metal particles, metal fibers, carbon black, and intrinsically conducting polymers.

Poly(lactic acid) (PLA) has received much attention in the research due to its biodegradability and biocompatibility. PLA has been considered as a major alternative to petroleum-based plastics for disposable items, such as packaging [2], as it is expected to reduce an impact on the environment caused by the production and utilization of petrochemical polymers. The combination of insulating PLA with intrinsically conducting polymer such as polypyrrole (PPy) allows us to create new biopolymer composites with unique electrical properties, applying in ESD protection [3]. However,

the polymer composites prepared as a mixture of PPy phase and PLA phase show a static dissipative property for ESD applications at a relatively high content of PPy due to aggregations of PPy particles.

This research project aims to prepare static dissipative biopolymer composites from PLA and conducting PPy nanoparticles prepared via a micro-emulsion polymerization. Poly(ethylene glycol) (PEG) has been added to the composites to play a dual function of a plasticizer and a dispersing agent. Conductivity, mechanical properties and morphology of the composites have been investigated. The proposed biopolymer composites offer potentials in electronic packaging applications since they achieve the dissipative range, exhibiting good ESD protection without the requirement of large amount of PPy, as well as they are largely biodegradable.

EXPERIMENTAL

Materials

Pyrrole (Fluka) was purified by double distillation under reduced pressure and stored in a refrigerator before use. Ammonium peroxydisulfate (APS, Sigma-Aldrich), sodium dodecylsulfonate (SDS, Ajax Finechem) and poly(ethylene glycol) (PEG10000, Merck) were used as received. PLA (Grade 4042D) was supplied by Nature Work[®]. Distilled water was used as solvent for all solutions.

Synthesis and Characterization of PPy Nanoparticles

PPy nanoparticles were synthesized via a micro-emulsion polymerization. A typical method was done as follows: an aqueous solution of dopant (0.08 M) was stirred vigorously for 20 min at approximately 0°C. Pyrrole was subsequently added into the above solution and further stirred for 30 min, followed by adding of APS solution. The initial molar ratio of monomer/oxidant/dopant was kept at 1:1:1. The mixture was kept at 0°C for 24 h. Excessive methanol was poured into the solution to terminate the reaction. The resulting PPy precipitate was centrifuged, washed with methanol, distilled water and acetone for several times. Finally, the PPy precipitate was vacuum-filtered, dried and kept in a desiccator. Surface composition of the PPy was investigated by XPS using a Kratos Axis Ultra DLD spectrometer with a monochromatised Al K α radiation source ($h\nu = 1486.6$ eV) operating at 150 W. UV-Vis absorption spectra were measured in transmission mode by a Lambda 2S UV-Vis spectrometer. Scanning electron microscopy (SEM) of PPy nanoparticles covered with a thin layer of sputtered gold, was conducted using a JEOL-JSM-6480LV instrument. Electrical conductivity of the compressed pellets of PPy was measured by a four-point probe method with a 2400 Keithley source-meter under laboratory condition.

Preparation and Testing of PLA-PPy Composites

PLA-PPy composites were obtained by compounding PLA granulate, PEG (20% wt.) and a certain amount of PPy nanoparticles. All compositions were initially mixed in a closed container and then shook the content for a minute. The compounding was carried out by feeding either the virgin PLA or PLA-PEG-PPy mixture into a twin screw extruder (Model TSE 16 TC, PRISM) with three heating zones. The zone temperatures were set at 160, 170, 175 °C from feed to die and the screw speed was fixed at 20 rpm. The extrudate was palletized and vacuum-dried at 60 °C for at least 3 hours before molding. Surface resistivity of the PLA and PLA-PPy composites was examined using a 8009 test figure in conjunction with a Keithley 6517 electrometer, according to ASTM test method D-257. Tensile tests of the compression-molded specimens were performed with a Universal testing machine (Model 100 RC, Hounsfield) with a crosshead speed of 25 mm/min and a gauge length of 25 mm. To observe the phase of PPy particles in the composite, a thin film of the composite obtained from the compression molding was observed using an optical microscope (Model Olympus BH2) equipped with a digital camera (Olympus E-330).

RESULTS

Characteristics of PPy nanoparticles

PPy nanoparticles were obtained at a yield greater than 100 % due to incorporation of dodecylsulfonate ions into the PPy backbones. SEM image (Figure 1) shows that PPy particles had a packed spherical morphology with 60-100 nm in average diameter. The conductivity of the PPy pellet was found to be 47.2 ± 8.5 S/cm.

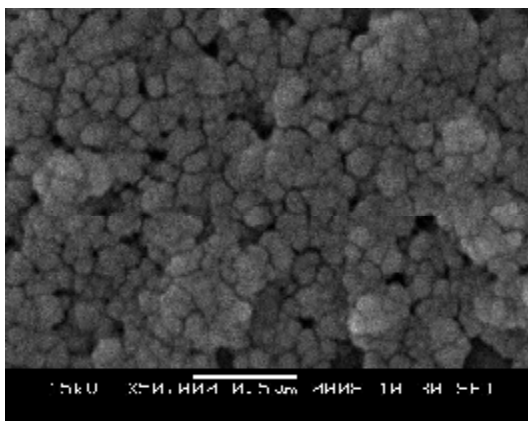


Figure 1 Typical SEM image of PPy particles.

Survey XPS spectrum, shown in Figure 2a, indicates the expected elemental composition of PPy-doped with SDS including carbon, oxygen, nitrogen and sulfur. The N 1s photoelectron spectrum together with the fitted peak components is illustrated in Figure 2b. A major component at 399.5 eV is attributed to the -NH- whereas two components at the higher binding energy tail are associated with N^+ (400.5 eV) and N^{2+}

(401.6 eV). The positively charged nitrogen species indicate that the PPy prepared via the micro-emulsion polymerization is in the conducting state [4]. The doping level of PPy doped with SDS, calculated from the ratio of total positively charged nitrogen to total nitrogen [4], $(N^+ + N^{2+})/N_{\text{total}}$, was 35%. The possible chemical structure of the PPy doped with SDS is presented in Figure 3.

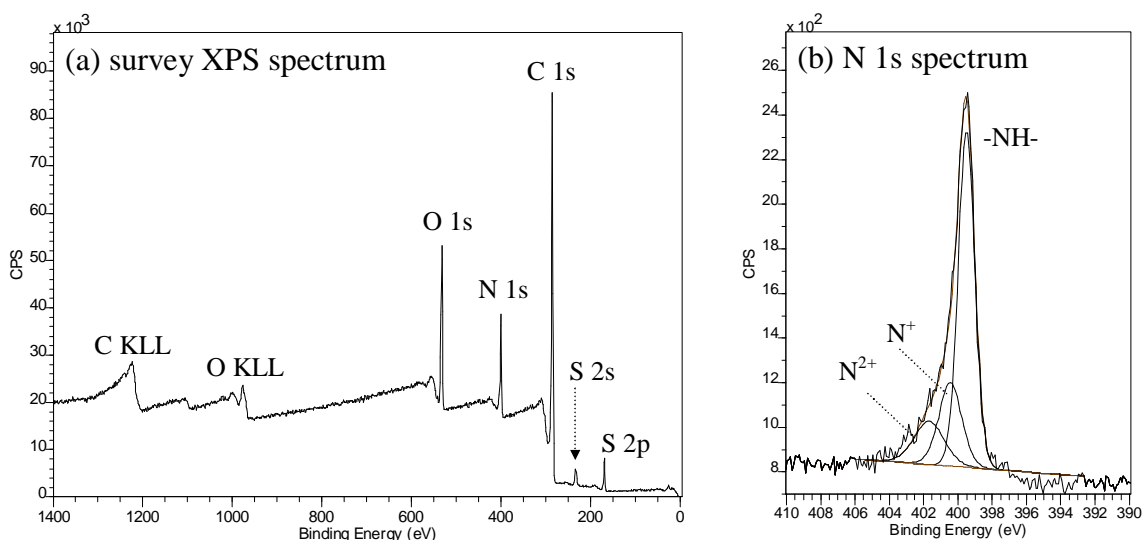


Figure 2 XPS spectra of PPy doped with SDS.

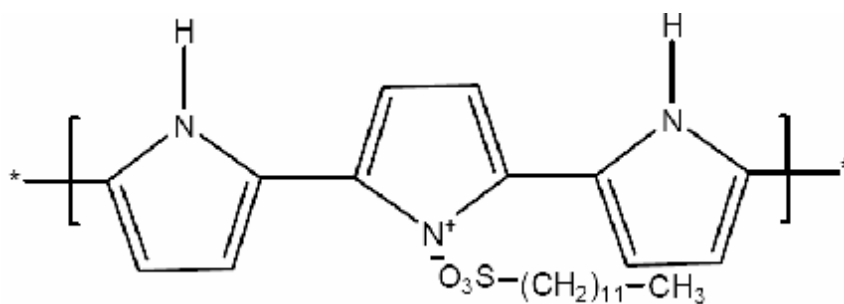


Figure 3 Possible structure of PPy doped with SDS.

UV-Visible spectrum of the PPy, as seen in Figure 4, corresponds well with the XPS result. A weaker absorption at around 460 nm (2.7 eV) is associated with the $\pi-\pi^*$ transition while a stronger absorption at around 900 nm (1.4 eV) is assigned to the bipolaron state of PPy, respectively [5].

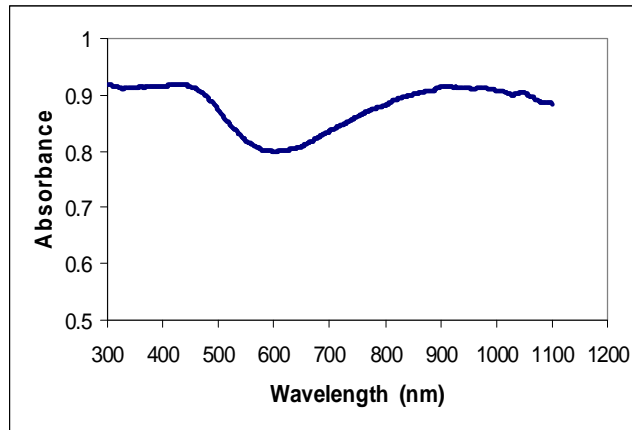


Figure 4 UV-VIS spectrum of PPy particles.

Conductivity and Mechanical Properties of PLA-PPy Biopolymer Composites

The influence of PPy content in the PLA-PPy composites on their surface resistivity is investigated and shown in Figure 5. Surface resistivity of virgin PLA was found to be about 10^{15} ohms/square. Even 1%wt. PPy nanoparticles incorporated, the composites exhibit a significant decrease (by three orders of magnitude) in surface resistivity. Further increase in the PPy content up to 5 %wt appears to slightly increase surface resistivity of the composites. This may be due to aggregation of the PPy nanoparticles in the PLA matrix at high level of PPy content, as seen in Figure 6. However, the PLA-PPy composite with 1 %wt PPy content shows a surface resistivity as $4.7 (\pm 1.4) \times 10^{11}$ ohms/square indicating a static dissipative property which is suitable for ESD protection. This offers a potential in electronic packaging applications where ESD is a major concern. Through the compounding process, the static dissipative becomes inherent in the moulded materials, thus eliminating costly, time-consuming secondary operations required for conventional coating process.

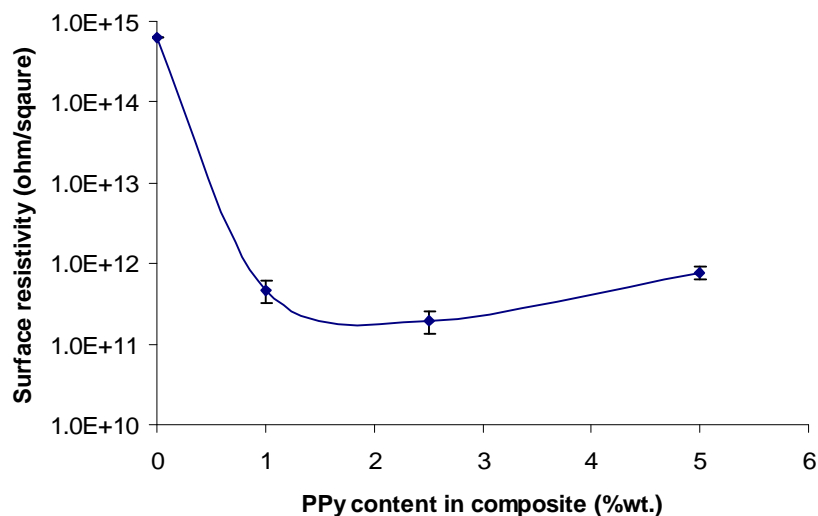


Figure 5 Dependence of surface resistivity of PLA-PPy composites on the PPy content.

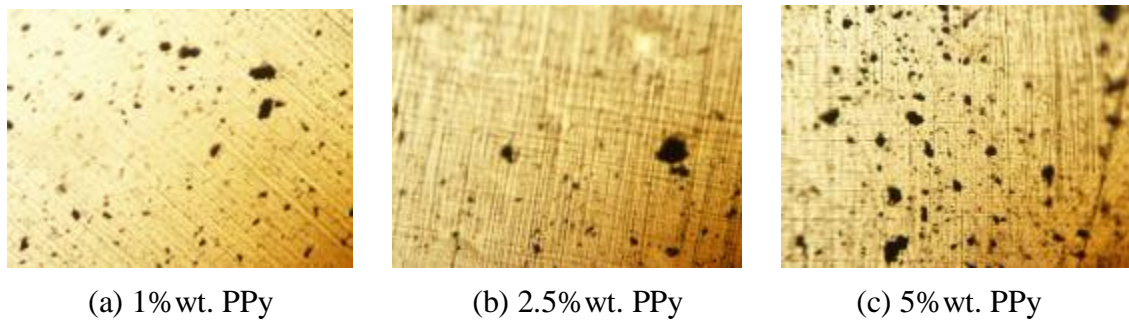


Figure 6 Optical images at 100x magnification of PLA-PPy composites contained different PPy content.

Stress-strain test of the PLA-PPy composites were performed with the compression molded specimens. Tensile strength and elongation of the composites as a function of PPy content are presented in Figure 7 and Figure 8, respectively. The tensile strength decreases whereas the elongation increases with increasing PPy content. It can be seen that the steep drop in tensile strength and rapid increase in elongation occur at the PPy content of 1% wt. which was considered as a conductivity percolation threshold. Beyond this point, the formation of conductive network leading to a substantial decrease in resistivity has a pronounced effect on the mechanical properties via a formation more or less continuous filler phase. The critical crack formation and unstable crack growth in such a system are expected to be much easier and faster than the virgin PLA matrix or in the composite where the PPy particles are incorporated but the continuous network has not yet be formed.

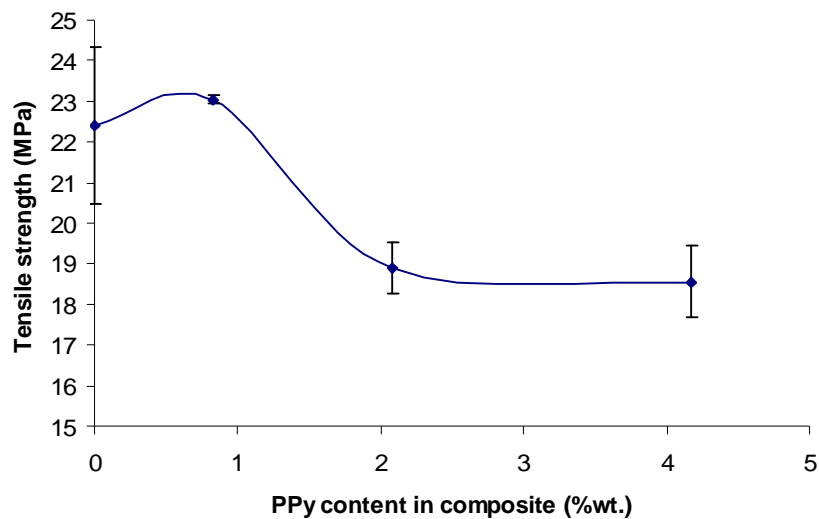


Figure 7 Tensile strength of the PLA-PPy composites as a function of PPy content.

It is important to note that PEG incorporated in the PLA-PPy composites effectively perform the plasticizing behavior beyond the conductivity percolation as well. At low PPy loading, well dispersion of PPy nanoparticles in the polymer blend (PLA-PEG) matrix was observed, probably leading to the decrease in plasticizing performance of PEG. At high PPy loading, on the other hand, the aggregation of PPy nanoparticles resulted in phase separation hence lowering the tensile strength accompanied with increasing elongation.

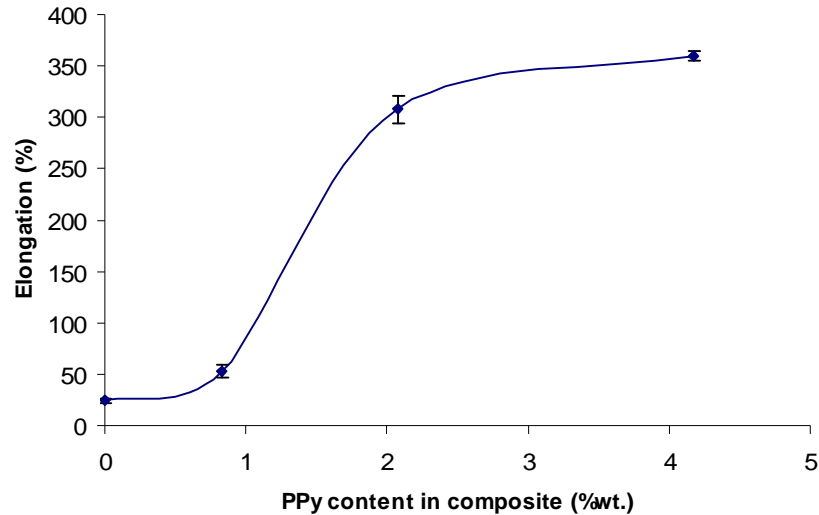


Figure 8 Elongation of the PLA-PPy composites as a function of PPy content.

CONCLUSION

Biopolymer composites have been prepared by mechanical melt mixing of conducting PPy nanoparticles, synthesized via a micro-emulsion polymerization, and PLA. The electrical property of the biopolymer composites was in static dissipative range. Presence of PPy nanoparticles in the composites influenced the mechanical properties of the biopolymer composites. The content of about 1% wt. PPy loading in the composites is the threshold concentration at which the conducting network is sufficient to enable their application as an ESD protection. Further work has been focused on the development of PPy distribution in the composites in order to obtain the biopolymer composites having surface resistivity in the optimal ESD protection range ($10^6 - 10^9$ ohms/square) without adding high content of PPy.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial supports of the Faculty of Applied Science, King Mongkut's University of Technology North Bangkok (KMUTNB) and Thailand Toray Science Foundation (TTSF). The authors also would like to thank Assoc. Prof. Paul J. Pigram, Centre for Materials and Surface Science (CMSS) and Department of Physics, La Trobe University for the use of XPS.

References

1. L. Brown and D. Burns, *The ESD control Process is a tool of managing quality*, "Electronic Package and Production, 50-53 (1990)
2. G. Shi, *et.al.*, *Biomaterials*, 25, 2477 (2004)
3. M. Angelopoulos, *IBM J. Res. & Dev.*, 45, 57 (2001)
4. W. Prissanaroon, *et. al.*, *Surf. Interface Anal.* 33, 653 (2002)
5. K.S Jang, *et.al. Synth. Met.* 143, 289 (2009)