

**Biopolymer Congress 2018: Electro-responsive material based on plasticized poly (lactic acid) and graphene nanoplatelets as a fillers****Natlita Thummarungsan***Chulalongkorn University, Thailand*

Poly(lactic acid) (PLA) is an attractive candidate to replace petrochemical polymers because it is biodegradable and can be derived from renewable resources. The main problems with PLA have been its fragility and toughness that limit many commercial applications. Using a plasticizer is one way to improve the flexibility and ductility of the PLA matrix. Furthermore, combining PLA with nano-sized particles, such as carbon-based nanoparticles, can be expected to improve the properties of PLA. In this work, poly(lactic acid) (PLA) films were prepared, incorporated with graphene nanoplates as fillers, and dibutyl phthalate (DBP) as plasticizer by the solvent molding method. All compounds possessed good electromechanical recovery capacity during time response experiments under the applied electric field. The 0.1% v / v MG / PLA / DBP compound showed the highest storage modulus sensitivity to electrical field resistance of 1.5 kV / mm. At a graphene concentration of 1.0% v / v, the response of the storage modulus ( $\Delta G'$ ) became defined negative, where the storage modulus under the electric field ( $G'$ ) was less than the value of  $G'_0$ . Negative  $\Delta G'$  under electric field at room temperature has not been previously reported for any electrostatic material. In addition, the pristine PLA / DBP showed the greatest deflection distance with respect to composite materials with an electrical resistance of 550 V / mm; The deviation distance of the compounds decreased with the graphene concentration.

The next major breakthrough in EAP took place in the late 1960s. In 1969 Kawai demonstrated that poly(vinylidene fluoride) (PVDF) exhibits great piezoelectric effect. This sparked research interest in developing other polymer systems that would show a similar effect. In 1977 Hideki Shirakawa et al. They discovered the first

electrically conductive polymers. Shirakawa along with Alan MacDiarmid and Alan Heeger demonstrated that polyacetylene was an electrical conductor and that, by doping it with iodine vapor, they could improve its conductivity by 8 orders of magnitude. Thus, the conductance was close to that of a metal. In the late 1980s, other polymers were shown to exhibit a piezoelectric effect or to be shown to be conductive. Ionic polymer-metal compounds consist of a thin ionomeric membrane with noble metal electrodes plated on its surface. It also has cations to balance the charge of the anions attached to the polymer backbone. These types of polymers show the greatest promise for biomimetic uses, since collagen fibers are essentially made up of naturally charged ionic polymers. Nafion and Flemion are commonly used ionic polymer metal compounds. In this work, PANI nanoparticles were synthesized following the procedure of Kim et al.<sup>12,13</sup> using aniline monomer, ammonium persulfate and SDS. The reaction was carried out in an Erlenmeyer flask connected with a mechanical stirrer. The 0.1M HCl solution was prepared from 10M HCl (grade AR). After 30 minutes, 5.5 g of the aniline monomer in ecotism mix solution was added. 0.98 g of ammonium persulfate was dissolved with 10 ml of 0.1 MHC solution and added dropwise at a rate of 1 ml / min into the previously obtained mixture solution. The reaction was performed at  $20 \pm 1^\circ \text{C}$  with mechanical agitation at 500 rpm for 12 h. After 12 hr, an excess amount of methanol was added to the mixture to precipitate the PAN nanoparticles breaking the SDS micelles and to stop the reaction.<sup>12</sup> The precipitated powder was collected on a glass filter and washed twice with methanol, acetone and pure water until the washing solution became colorless.<sup>12,13</sup> The PANI particles were then dried in a vacuum oven

for 48 hr at 60 ° C. The chemical structures of PANI are shown in the Scheme 1. Large PANI particles were synthesized following the procedures of Hiamtup et al. 7 and Cao et al. 19 using aniline as monomer and ammonium sulfate as initiator. 0.98 g of ammonium persulfate was dissolved in 10 ml of 0.1 MHC solution, and 5.5 g of heaniline monomer were added dropwise at a rate of 1 ml / min into the mixing solution. 100 ml of 0.1 M HCl. The reaction was carried out at 0 ° C with mechanical stirring. SCHEME 1. Chemical structure of PANI undoped and doped with HCl. 500 rpm for 12 h. The PANI powder was then collected on a glass filter and washed twice with methanol, acetone, and pure water until the wash solution became colorless. The PANI particles were then dried in the vacuum oven for 48 h at 60 ° C. In this work, the specific electrical conductivities of the conductive particles added to the chloroprene matrix remained the same. Large PANI particles were required to be manipulated with NH<sub>4</sub>OH and then doped again with HCl to adjust the electrical conductivity. Large dried PANI particles were finger painted by suspending them in 100 ml of 0.1 M NH<sub>4</sub>OH at room temperature for 4 hr. After 4 hr, the discarded powders were filtered using a funnel and dried at 27 ° C at empty for 24 h.

### CHARACTERIZATION AND TESTING

The large PANI particles fingering and the nano / large particles PANI doped were characterized by an FT-IR spectrometer and a UV-vis spectrometer to identify their functional groups. The FT-IR spectrometer (Thermo Nicolet, Nexus 670; Thermo Scienti fi c, USA) was operated in absorption mode with 32 scans and with a resolution of  $\pm 4 \text{ cm}^{-1}$ , covering a range of wave numbers between 400 and 4000  $\text{cm}^{-1}$ , using a deuterated triglycine sulfate detector. Optical grade KBr (Carlo Erba reagent) was used in the background material. The PANI powder was intimately mixed with dry KBr in a ratio of PANI: KBr = 1: 20. UV-vis spectra of nano / large PANI particles were recorded with a UV-vis absorption spectrometer (Perkin-Elmer

Lambda 10; Perkin-Elmer, Waltham, MA). Measurements were taken in the absorbance mode in the 200–700 nm wavelength range. The synthesized PANI particles were ground into a fine powder and dissolved in 1-methyl-2-pyriridone. The transfer rate was 50 mm / min, using a deuterium lamp as the light source. The specific density ( $\rho_p$ ) of the nano and large PANI particles was measured using a 25 ml glass pycnometer (Labor- und Messgerate GmbH Stutzerbach, Jena, Germany). The specific density ( $\rho_p$ ) of chloroprene W, given on the Dupont Co. Ltd. product technical information sheet, is 1.23 g /  $\text{cm}^3$ . PANI morphologies and mixtures were observed with a scanning electron microscope (SEM; Hitachi, S-4800). Scanning electron micrographs were obtained using an accelerating voltage of 5-10 kV at various magnifications between 40,000  $\times$  and 100,000  $\times$ . The samples were stacked on pieces using carbon adhesive papers and platinum coated using an ion coating machine (Hitachi, E-1010; Hitachi High-Technologies Corporation, Tokyo, Japan) at 90 s, to improve electronic conductivity. Photographs at 100,000  $\times$  magnification were captured to measure the particle size of PANI nanoparticles in W: PANI nano mixtures using Scion Image software (version 4.0.3). The particle sizes of the large doped PANI particles were determined using a particle size analyzer (Malvern Instruments, Masterizer X version 2.15; MalvernInstruments Ltd., Malvern, UK).