Effect of Graphene Oxide on Poly (Methyl Methacrylate)-Grafted Natural Rubber Polymer Electrolytes

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ABSTRACT

Polymer electrolytes (PE) are presently the subject of the majority of research due to their capacity to replace liquid electrolyte that suffer from high flammability and electrolyte leakage and also as a new forms of electrical power production and storage systems. Solid polymer electrolytes (SPE) typically have low ionic conductivity at room temperature because of the high crystallinity of the polymers. Methyl-grafted natural rubber has been studied extensively by a number of researchers due to its advantageous properties such as high flexibility, and ability to solvate inorganic salts to form a polymer-salt complex. Graphene oxide (GO) was used as a nanofiller, ammonium triflate ($NH_4CF_3SO_3$) served as a dopant salt, and 30 % polymethyl methacrylate grafted natural rubber (MG30) served as the polymer host in the preparation of the nanocomposite polymer electrolyte (CPE) using the solution casting-method. Electrochemical impedance spectroscopy (EIS) was used to analyse the ionic conductivity of the samples, and Fourier-transform infrared spectroscopy (FTIR) was used to analyse the complexation between salt, polymer host and filler while Optical microscope was used to study the surface morphology of the prepared CPE samples. The decrease in peak strength for C=O in the FTIR spectra indicates the interaction between the polymer host and salt.

The sample containing 15 weight percent $NH_4CF_3SO_3$ had the highest conductivity, which was 2.05×10^{-5} S cm^{-1}. This substance has the potential to be used in energy storage devices like batteries and supercapacitors as an alternative to commercial liquid electrolyte.

Keywords: Composite Polymer Electrolyte; GO; MG30; $NH_4CF_3SO_3$

INTRODUCTION

Energy storage and devices such as batteries, supercapacitors, solar cells, sensors, and electrochromic windows have been developed in response to the rising demand for high-tech electronics such as tablets, smartphones, laptops, and electric vehicles [1–4]. Polymer electrolytes (PE) are under study as a potential replacement for liquid electrolytes (LE) due to the problems they solve, such as excessive flammability and electrolyte leakage [5]. When compared to other types of PE such as solid polymer electrolyte and gel polymer electrolyte, composite polymer electrolyte (CPE) excels in both mechanical strength and ionic conductivity at room temperature [6, 7]. 30 % polymethyl methacrylate grafted natural rubber (MG30) is such an excellent candidate as polymer host due to its characteristic of low glass transition temperature (Tg), good flexibility and ionic conduction capability [8]. Previously MG30 was selected to prepare gel polymer electrolyte though peroxidization and blended with lithium triflate and ethylene carbonate and the highest ionic conductivity obtained was approximately 2.9×10^{-3} Scm^{-1} [9]. For this study MG30 is chosen as polymer host, graphene oxide (GO) selected as nanofiller and ammonium triflate ($NH_4CF_3SO_3$) as dopant salt. The resulting CPE thin film undergoes Fourier-transform Infrared spectroscopy (FTIR) to study the interaction between polymer, nanofiller and salt. Meanwhile, Electrochemical Impedance Spectroscopy (EIS) and optical microscope (OM) were used to study the CPE thin film ionic conductivity and surface morphology, respectively.

MATERIALS

MG30 was obtained from Rubber Research Institute of Malaysia, GO nanosheets were purchased from Sigma Aldrich, tetrahydrofuran (THF)

was purchased from Merck and $NH_4CF_3SO_3$ was purchased from Aldrich Chemistry.

METHODOLOGY

The CPE systems were prepared via solution casting technique where 10 wt.% of GO nanosheets were homogenized in 50 mL THF dispersed using sonicator at ultrasonic frequency (20 000 Hz) from a total of 1 g of polymer blend dissolved in 40 ml THF. The GO dispersion was added to the 90 wt.% of MG30 solutions and stirred until a homogeneous solution was obtained. Before the preparation of the polymer-salt system, $NH_4CF_3SO_3$ was dried at 100 °C for 1 hour to remove any remaining presence of water. Different amount of $NH_4CF_3SO_3$ as listed in Table 1 were then added to the MG30-GO homogenized polymer blend and stirred until complete dissolution. The homogenized blend was casted onto petri and left to dry at room temperature. The sample was peeled and stored for further characterizations. EIS was performed on the sample at room temperature with the frequency range of 50 to 5 MHz. OM was performed with the magnification of 4 and lastly FTIR was performed in wavenumber range of 600-4000 cm^{-1} with the resolution of 2 cm^{-1}

Table 1: Composition of $NH_4CF_3SO_3$ added into the polymer blend

Polymer blend	$NH_4CF_3SO_3$ (wt%)	$NH_4CF_3SO_3$ (g)	Designation
	0	0	A0
	5	0.0526	A5
90 % MG30: 10% GO of 1 g	15	0.1765	A15
	25	0.3333	A25
	35	0.5385	A35
	45	0.8182	A45

RESULTS AND DISCUSSIONS

The ionic conductivity studies were performed using EIS and the values of ionic conductivity are shown in Figure 1. As indicated in Figure 1(a), the addition of GO in the MG30 polymer matrix has successfully enhance the base ionic conductivity. Furthermore, it can be confirmed that the ionic

conductivity improves when the total amount of $NH_4CF_3SO_3$ in the polymer blend rises to 15 wt.%, the ionic conductivity improves but decrease drastically at higher salt loading. The increase in ionic conductivity can be attributed to the increase of free mobile ions in the CPE and successful complexation between the polymer host and the dopant salt. Meanwhile the decrease in ionic conductivity at higher salt content can be attributed to the recombination of cation and anion of the dopant salt during evaporation of the solvent resulting in ion agglomeration as shown in Figure 3(b) [10 –12].
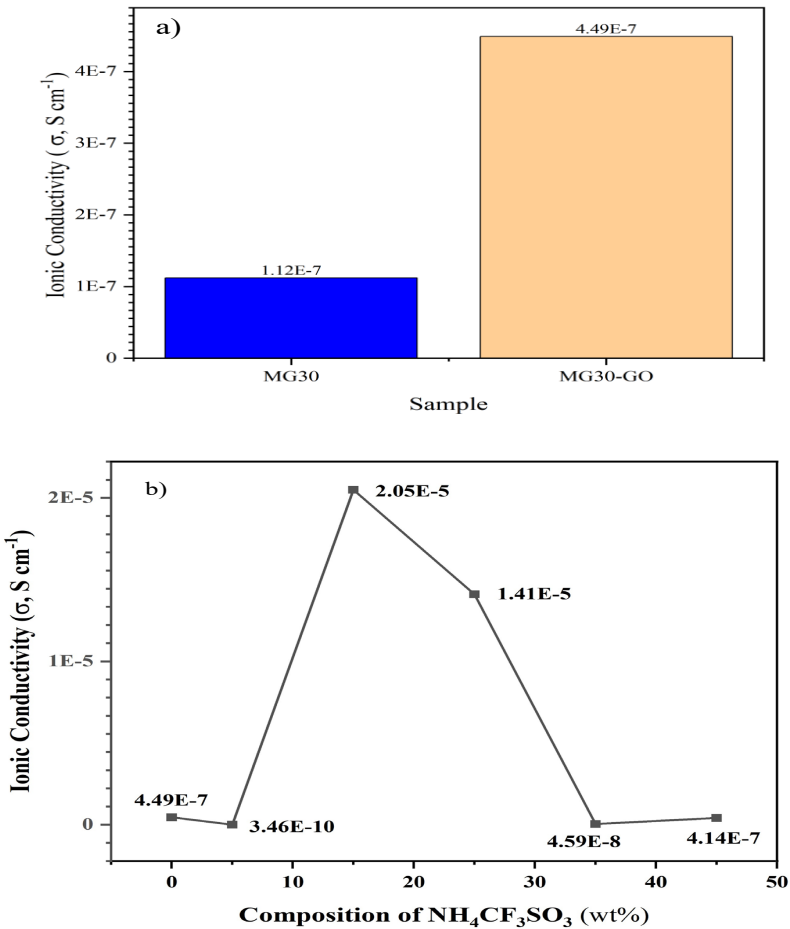

Figure 1: Conductivity comparison of a) MG30 and MG30-GO thin films and b) CPE with different composition of $NH_4CF_3SO_3$

The surface morphology analyses of the thin films obtained were performed using OM. Based on Figure 2(a), it can be observed that for the pure MG30 thin film is semi-transparent and has non-uniform pores distributed throughout the thin film. Meanwhile in the morphology presented in Figure 2(b) it can be observed that GO is distributed over the entire thin film. In Figure 2(c) and 2(d), the sample with the highest ionic conductivity, it can be observed that there are small gaps in the distribution of GO in the CPE thin films after the addition of $NH_4CF_3SO_3$. The incorporation of GO into MG30 matrix has enhanced the ionic conductivity of mentioned polymer as shown in Figure 1(a) and the interaction between GO and MG30 was further explained based on Figure 3(b) in later section [13].
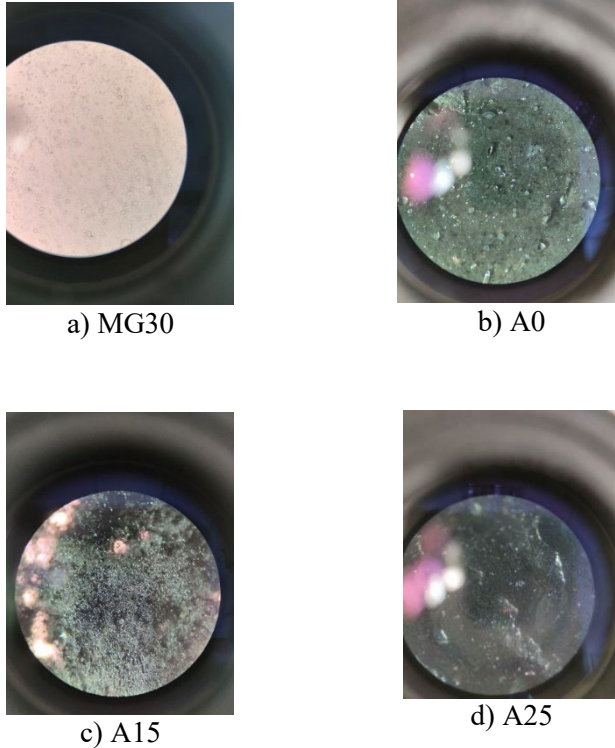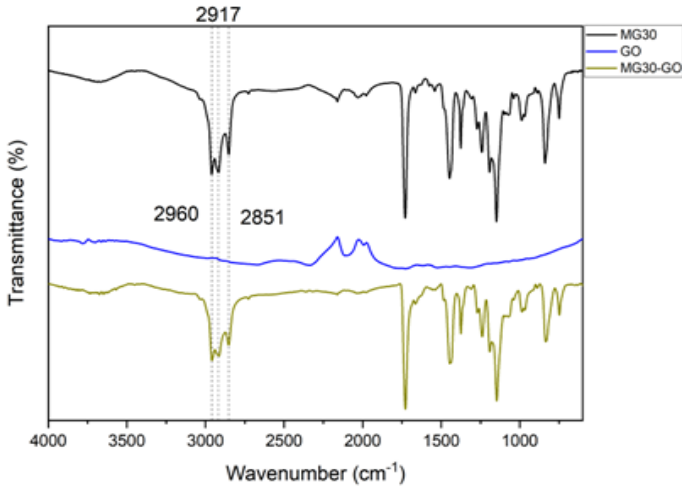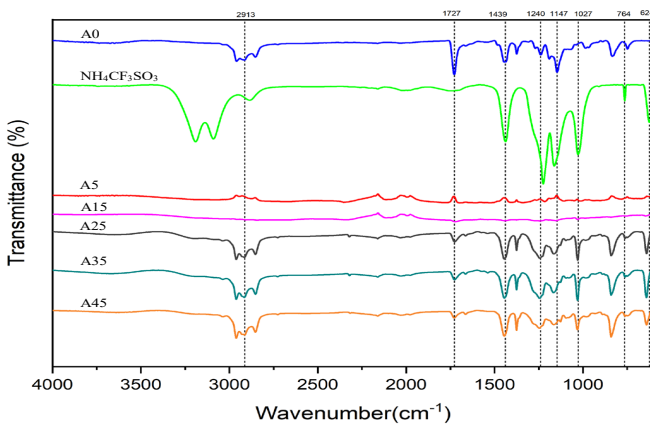
a) MG30

b) A0

c) A15

d) A25

Figure 2: OM images for a) pure MG30 thin film, b) A0, c) A15 and d) A25

The characterization of the prepared samples was observed using FTIR instruments. Figure 3(a) shows that the interaction between GO and the polymer was shifted to a lower wave number 2913 cm^{-1}, which represents the C-H stretching mode, shifted to a lower wave number at 2913 cm^{-1}. A similar finding was mentioned in previous study [14] where GO was used as a filler in a potato starch polymer blend.

(a)

(b)

Figure 3: The FTIR spectra for a) MG30, GO and MG30-GO while b) different amount of added NH₄CF₃SO₃

In Figure 3(b), the carbonyl group on the side chain of the grafted polymethyl methacrylate that caused the C=O stretching frequency peak in MG30 at 1727 cm^{-1} acted as an indicator for the analysis of complexation between the polymer and the salt. In the structure of the polymer host, the oxygen atom of the carbonyl group (C=O) functions as an electron donor atom and this functional group later forms a coordination bond with an ion of the dopant salt to form the polymer-salt complex. The ammonium cation and the carbonyl functional group coordinate at the bond NH^{4+}→O=C thus increasing the ionic conductivity. However, as the dopant salt loading increases from 25 wt.% to 45 wt.%, the ionic conductivity decreases due to ion agglomeration as indicated by the shifting of the symmetric deformation mode of the triflate anion (CF$_3\delta_s$) at 764 cm^{-1} to 761 cm^{-1}. No further shift was observed after the addition of 45 wt.% NH$_4$CF$_3$SO$_3$ [15–17].

CONCLUSION

The CPE thin films of MG30-GO-NH$_4$CF$_3$SO$_3$ were successfully prepared using the solution casting technique. The interaction between MG30, GO and NH$_4$CF$_3$SO$_3$ can be observed from the FTIR spectra. The highest ionic conductivity was obtained at 2.05×10^{-5} Scm^{-1} with the addition amount of 15 wt% NH$_4$CF$_3$SO$_3$. The surface morphology of the thin films shows that GO is distributed as a nanofiller in the CPE thin film and reinforces the sample. The CPE thin film has shown that it has the potential to be applied in various energy storage devices such as solid-state batteries and supercapacitors.

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