

Investigation on the effect of nanosilica towards corn starch–lithium perchlorate-based polymer electrolytes

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Abstract Biodegradable corn starch–lithium perchlorate (LiClO_4)-based solid polymer electrolytes with addition of nano-sized fumed silica (SiO_2) were prepared by solution casting technique. Ionic conductivity at ambient temperature was measured by AC impedance spectroscopy. Upon addition of nano-sized SiO_2 , the ionic conductivity at room temperature is increased. The optimum ionic conductivity value obtained was $1.23 \times 10^{-4} \text{ S cm}^{-1}$ at 4 wt% SiO_2 . This may be attributed to the low crystallinity of the polymer electrolytes resulting from the dispersed nanosilica particles. Fourier–transform infrared spectroscopy studies confirmed the complexation between corn starch, lithium perchlorate, and silica. The thermal properties of the prepared samples were investigated with differential scanning calorimetry and thermogravimetric analysis. The surface morphology of the polymer electrolytes confirmed the agglomeration of particles after excess dispersion of inorganic filler. This was proven in the scanning electron microscopy studies.

Keywords Corn starch · DSC · TGA · SEM · FTIR · Silica

Introduction

In the last decade, environmental friendly materials from natural and renewable sources have greatly captured much of the scientists' attention [1–4]. Corn starch caught the most

attention among carbohydrate present in the nature owing to its widely availability, low cost, and biodegradability [5]. It is a semi-crystalline polymer composed of a mixture of linear amylase and branched amylopectin polysaccharide chain [3]. However, corn starch depicts poor mechanical stability and semi-crystalline properties. In view of this, various method have been developed to reduce crystallinity and improve mechanical properties of corn starch [6]. Incorporation of inorganic oxide filler into polymer electrolyte has become an alternative approach which attracted considerable attention due to their improved mechanical stability and enhanced ionic conductivity [7].

Nano-sized silica is of great interest due to its small size and large specific area which enable it to penetrate into polymer matrix easily. Xiong et al. [8] reported that, the addition of nano-sized silica into starch-based polymer electrolyte matrix reduces the crystallinity of the polymer matrix and increased the mechanical properties such as water resistance, tensile strength, and breaking elongation. Composite polymer electrolyte based on fumed silica was shown to be highly transparent in the visible region and to have a wide electrochemically stable potential window. Nano-sized silica is found to improve the interfacial stability of polymer electrolytes film by reducing the passivation layer formed with electrodes [9].

Lithium perchlorate (LiClO_4) is comprised of a small-sized cation and a large-sized anion. The ionic conductivity is affected by the diffusion rate of ions which depends on the size of the ion. LiClO_4 is chosen due to its good conductivity and ease of complex formation in the preparation of solid polymer electrolytes [10]. Hence, LiClO_4 is more favorable compared to other lithium salts due to the low interfacial resistance when lithium metal was used as anode. Moreover, LiClO_4 has high dissociation energy, thus it is readily soluble in most solvents. The utilization of distilled water as solvent functions as a plasticizer as well. Water is crucial in the gelatinization process as it disrupts the granular structure

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causing starch molecules to dissolve [8]. These interactions are Van der Waals forces which make water functions as agent of polymer network formation [3]. Furthermore, water is chosen due to its non-toxicity and excellent compatibility which also promotes green energy to the world.

In this work, studies have been carried out to investigate the composition effect of nanosilica towards biodegradable solid polymer electrolytes. The SPEs were characterized by AC impedance spectroscopic studies to study the conductivity and dielectric properties. The complex interaction between the corn starch, LiClO_4 , and nanosilica was studied by Fourier transform infrared spectroscopy (FTIR). Additionally, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) studies were conducted to elucidate the interactions of fillers with lithium-polymer chains.

Experimental

Corn starch with a linear formula of $\text{C}_6\text{H}_{10}\text{O}_5$ was obtained from Sigma–Aldrich. Lithium perchlorate salt, LiClO_4 , with 99.99 % purity and less than 100 ppm total metallic purities was obtained from Aldrich. Fumed silica (SiO_2) with 7-nm particle size was obtained from J.T. Baker. The nanocomposite polymer electrolyte films were prepared by solution casting technique with distilled water as the solvent. The solution was stirred for 24 h to ensure homogeneity and complete dissolution of the polymer complexes. The mixture was cast in Petri dish and allowed to evaporate slowly inside an oven at 40 °C to produce free standing and mechanically stable nanocomposite polymer electrolyte films. The designation of the prepared polymer electrolytes is shown in Table 1.

The samples were cut and sandwiched between two stainless-steel blocking electrodes. A HIOKI 3532–50 LCR Hi-Tester connected to a computer for data acquisition over the frequency range of 50 Hz to 5 MHz at room

temperature, 25 °C. The thickness of the film was measured by means of a micrometer screw gauge. The FTIR studies were performed with a Thermo Scientific Nicolet IS 10 in the wave region between 4,000 and 600 cm^{-1} . The resolution of the spectra obtained at room temperature was 1 cm^{-1} . Thermal analyses were carried out in a DSC TA Q200 differential calorimeter with a heating rate of 30 °C/min and over the temperature range –50 to 200 C under nitrogen atmosphere. Prior to DSC analyses, the samples were heated up to 100 °C for 5 min to eliminate trace amount of water molecules. TGAs were conducted with TA Q500 thermogravimeter under nitrogen atmosphere at a heating rate of 50 °C/min. A 50×50-mm polymer sheet film was soaked in distilled water for 5 min. The weights of the dried samples (W_0) were measured prior to water absorption test. After drying, the swollen samples were placed in desiccators for 24 h until a constant weight were obtained (W_1) and the water solubilities (W_s) were calculated using following equation:

$$W_s = \frac{W_0 - W_1}{W_0} \times 100\%$$

Surface morphology of polymer electrolytes was recorded by Leica's scanning electron microscopy (SEM) instrument model S440 and examined at 10 kV at room temperature.

Results and discussion

Alternating current impedance studies

The ionic conductivity for various compositions of nano-sized fumed silica incorporated in corn starch- LiClO_4 polymer electrolyte films were studied using impedance spectra. Impedance spectroscopy provides a better understanding in the conduction mechanism, mobility, and carrier generation

Table 1 Designation, ionic conductivity, DSC profiles, decomposition temperature, and water solubilities of (corn starch- LiClO_4)/ SiO_2 nanocomposite polymer electrolyte films

Designation	Composition of corn starch- LiClO_4 - SiO_2					Ionic conductivity, S/cm	T_g , °C	Decomposition temperature, °C	Water solubilities, W_s (%)
	Weight (g)		Weight percentage (wt%)	Weight (g)	Weight percentage (wt%)				
	Corn starch	LiClO_4							
Si-0	0.600	0.400	100	0.000	0	1.55×10^{-5}	65.2	237.8	50.44
Si-2	0.588	0.392	98	0.020	2	5.29×10^{-5}	73.0	240.9	45.29
Si-4	0.576	0.384	96	0.040	4	1.23×10^{-4}	87.1	244.4	43.31
Si-6	0.564	0.376	94	0.060	6	8.01×10^{-5}	87.5	259.8	40.19
Si-8	0.552	0.368	92	0.080	8	5.64×10^{-5}	106.4	261.4	39.59
Si-10	0.540	0.360	90	0.100	10	5.58×10^{-5}	128.9	257.7	29.57

processes. In order to calculate the ionic conductivity of a thin film sample, the following relationship is used:

$$\sigma = \left(\frac{l}{R_b A} \right)$$

Where σ is the conductivity in Siemens per centimeter, l is the thickness of thin film sample in centimeter, R_b is the bulk resistance in Ω obtained from the Cole–Cole impedance plot, and A is the surface area of the stainless-steel blocking electrodes in square centimeter.

Figure 1 depicts the variation of log ionic conductivity values as a function of nano-sized silica concentration. The ionic conductivity increases upon addition of nano-sized silica in Corn starch–LiClO₄ polymer electrolytes. As can be seen, Si-4 exhibits highest ionic conductivity which is 1.23×10^{-4} S cm⁻¹ at ambient temperature. The increase in the ionic conductivity with increasing nano-sized silica can be related to the weakening of the polyether-cation association induced by the nano-sized silica particles, the high interface area between the matrix and the dispersion of nano-sized silica particles [5]. It is believed that the charged nature of the surface of fumed silica promotes dissociation of aggregate ion and undissociated salt into free-moving ions which increase the conductivity of polymer films [11]. Consequently, ionic conductivity increases due to formation of highly conducting interfacial layer between the particles of nanosilica and bulk electrolytes. This increase can be attributed to the conducting pathways that repeatedly keep forming [12].

However, the ionic conductivity does not continue to rise indefinitely with increasing concentration of nano-sized silica. The ionic conductivity falls once the concentration of nano-sized silica is over an optimal value. Further increase in filler content results in the blocking of existing conducting pathways and the possible of conglomeration of the excess silica. This will reduce the polymer-filler interface and hence reduces the conducting pathways which hinder the motion

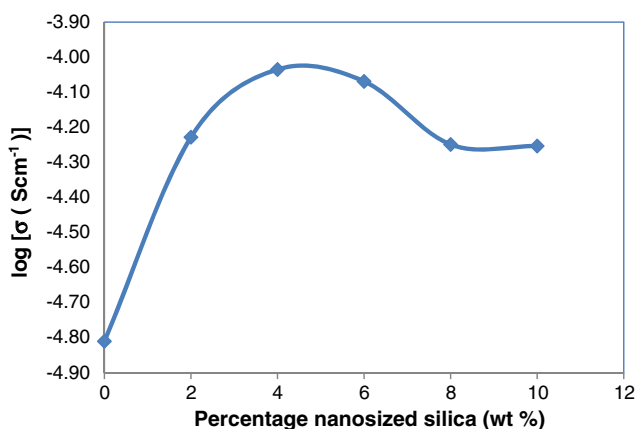


Fig. 1 Variation of log ionic conductivity as a function of weight percentage of nano-sized silica added in (corn starch–LiClO₄)/SiO₂ complexes

of mobile ions [11]. Other than that, nano-sized silica forms C–O–Si bond with corn starch reducing the bonding sites for the movement of mobile ions [4]. Thus, excessive nano-sized silica eventually reduce the bonding sites for Li⁺ and constraint the movement of mobile ion which leads to decrease in ionic conductivity. The above findings are in agreement with those described in the literature, where it has been observed that a rise in conductivity occurs as the concentration of inorganic filler increases followed by a decrease in conductivity values for higher concentration [13–15].

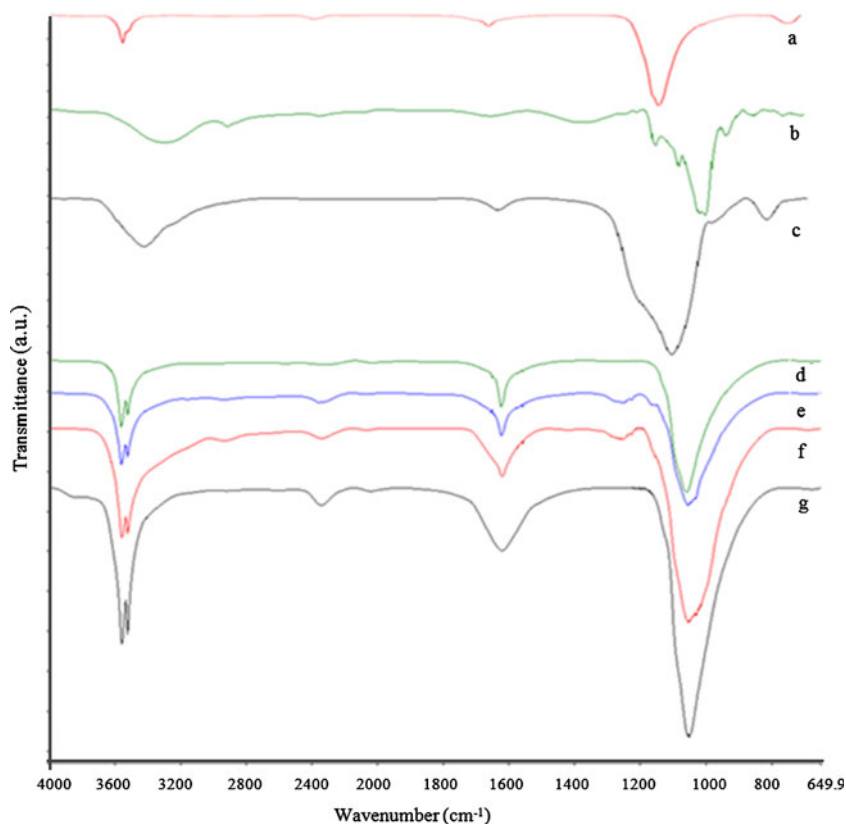
FTIR studies

The infrared spectra depict the occurrence, complexation, and interactions between various constitutions which vary according to the compositions of polymer electrolytes. Figure 2 shows the FTIR spectra for pure corn starch, silica, and lithium perchlorate. Some band assignments for corn starch, silica, and LiClO₄ have already been reported and listed in Table 2 [16–20]. The strong and wide absorption at 3,309 cm⁻¹ of the pure corn starch samples indicated that there was plenty of –OH on the surface of the corn starch. The absorption at 1,374, 1,148 cm, and 1,077 cm⁻¹ were attributed to CH₃ symmetry deformation, C–O stretching vibration, and C–O–H stretching vibration respectively. Meanwhile, the characteristic absorption of starch also appeared at 1,008 and 995 cm⁻¹ which attributed to the stretching vibration of C–O in C–O–C groups.

From the spectra of LiClO₄, the bands at 698 cm⁻¹ were assigned to the internal vibration modes of ClO₄⁻. The absorption peak at 1,097 cm⁻¹ was associated with the ClO₄⁻ asymmetrical stretching. The sharp absorption peak at 1,628 cm⁻¹ is ascribed to pure LiClO₄ [20]. The characteristic peaks of nanosilica are observed at 809, 1,103, 1,636, and 3,423 cm⁻¹. However, after the addition of silica into the polymer electrolyte complex, characteristic bands of silica disappeared or become less intense. This may be due to the nanoparticle size (7 nm) and thus might have just disrupted the initial order of the polymer electrolyte complex [21]. Upon addition of LiClO₄ into polymer electrolyte films, the characteristic peak of corn starch shows a decrease in intensity. The strong absorption band at around 1,628 cm⁻¹ rise accordingly to the amount of silica added into the polymer matrix. In addition, there is a distinctive change of characteristic absorption region. The absorption peaks at 1,148, 1,077, 1,008, and 995 cm⁻¹ which belongs to C–O stretching vibration of corn starch shifted towards 1,060 cm⁻¹, while the absorption peak for asymmetrical stretching vibration of ClO₄⁻ shifted to 1,060 cm⁻¹ when LiClO₄ is added into corn starch polymer matrix.

Formations of new peaks are observed at wavenumber around 1,250 cm⁻¹ in Si-2 and Si-4. This could be the new bond formation of Si–O–Li owing to the ferromagnetism of

Fig. 2 The FTIR spectra of (a) pure LiClO₄, (b) pure corn starch, (c) nano-sized silica, (d) Si-0, (e) Si-2, (f) Si-4, and (g) Si-6



SiO₂. This promotes a new ion migration pathway and thus enhances the Li⁺ ion transport in the polymer electrolyte matrix. However this characteristic peak disappeared in Si-6 spectrum rationalizing the blocking of new ion migrating sites which results in a drop in conductivity.

Thermal analysis

The glass transition temperature (T_g) of solid polymer electrolytes is determined by using DSC analysis. Table 1 shows the T_g of undoped and nanosilica-doped polymer

electrolytes. The T_g does show an increasing trend with increase in nanosilica content. The complexation of silica with corn starch polymer matrix showed an increase in T_g . The increase in T_g is attributed to the formation of transient cross link between silica and corn starch–LiClO₄ polymer matrix which restricts the segmental motion of the polymer chain, leading to an increase in T_g [22]. Based on Table 1, one can easily find that T_g increases remarkably with nanosilica content. This will reduce the chain segment and consequently reduce the resistance to transport electroactive substance, hence a drop in ionic conductivity.

Table 2 Peak description for corn starch, LiClO₄, and silica

Sample	Wavenumber (cm ⁻¹)	Description of vibrations	References
Corn starch	3,309	–OH stretching	[18]
	1,374	CH ₃ symmetry deformation	[20]
	1,148	C–O stretching	[16–18]
	1,077	C–O–H stretching	[16–18]
	1,008	C–O in C–O–C	[16–18]
	995	C–O in C–O–C	[18]
	LiClO ₄	1,628	Pure liclo4
LiClO ₄	1,097	ClO ₄ ⁻ asymmetrical stretching	[19]
	698	ClO ₄ ⁻ stretching	[19]
SiO ₂	809, 1,636	Characteristic peaks of silica	[11]
	1,103	Si–O–Si in silica	[11]
	3,423	Si–OH of surface hydroxyl group in fumed silica	[11]

Thermal stability can be determined by using TGA where the weight loss of the sample will be observed over the temperature range of 20–500 °C. TGA thermograms of Si-0, Si-4, and Si-10 are shown in Fig. 3. All the degradation temperature were measured and listed in Table 1. The initial weight loss for Si-0 up to 118 °C is around 14 %. However the intensity of weight loss increases sharply up to 66 % at a higher temperature of 237 °C. The first degradation step is attributed to the loss of water molecules. The prolonged weight loss due to solvent evaporation is most likely due to some of the water molecule becomes entrapped in small cavities formed in corn starch polymer matrix upon gelatinization, where it is hard for them to diffuse out from the sample. The decomposition of corn starch polymer contributes to the second weight loss.

With the addition of fumed silica as in Si-4, the sample has a larger initial weight loss approximately up to 20 % compared to Si-0. The Hydroxyl group on the surface of nanosilica increased the moisture absorption where the initial weight loss can be due to evaporation of water molecule. The second weight loss begins at a temperature of 244 °C which is the maximum weight loss reflecting the decomposition of polymer main chain. Si-10 shows similar properties as Si-4 with around 20 % initial weight loss which is suspected from the contribution of hydrophilicity of SiO₂ particles. However the decomposition temperature increases with higher content of nanosilica in the polymer matrix. Si-10 decomposes at 257.7 °C which indicates that Si-0 has better thermal stability than Si-4. This behavior can be explained on the basis of strengthening of the C–O bond, caused by the transient crosslink of silica with the oxygen atom [23]. This is in good agreement with DSC results showing that higher T_g and higher decomposition temperature can be obtained by higher content of nanosilica. The above analysis reveals that, the addition of nanosilica restricts the segmental motion of the polymer chain and thus

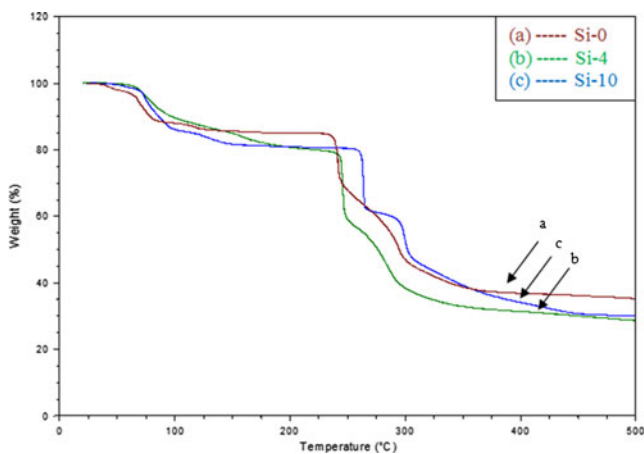


Fig. 3 TGA curves of Si-0, Si-4, and Si-10

increased the T_g and decomposition temperature of the polymer electrolyte system.

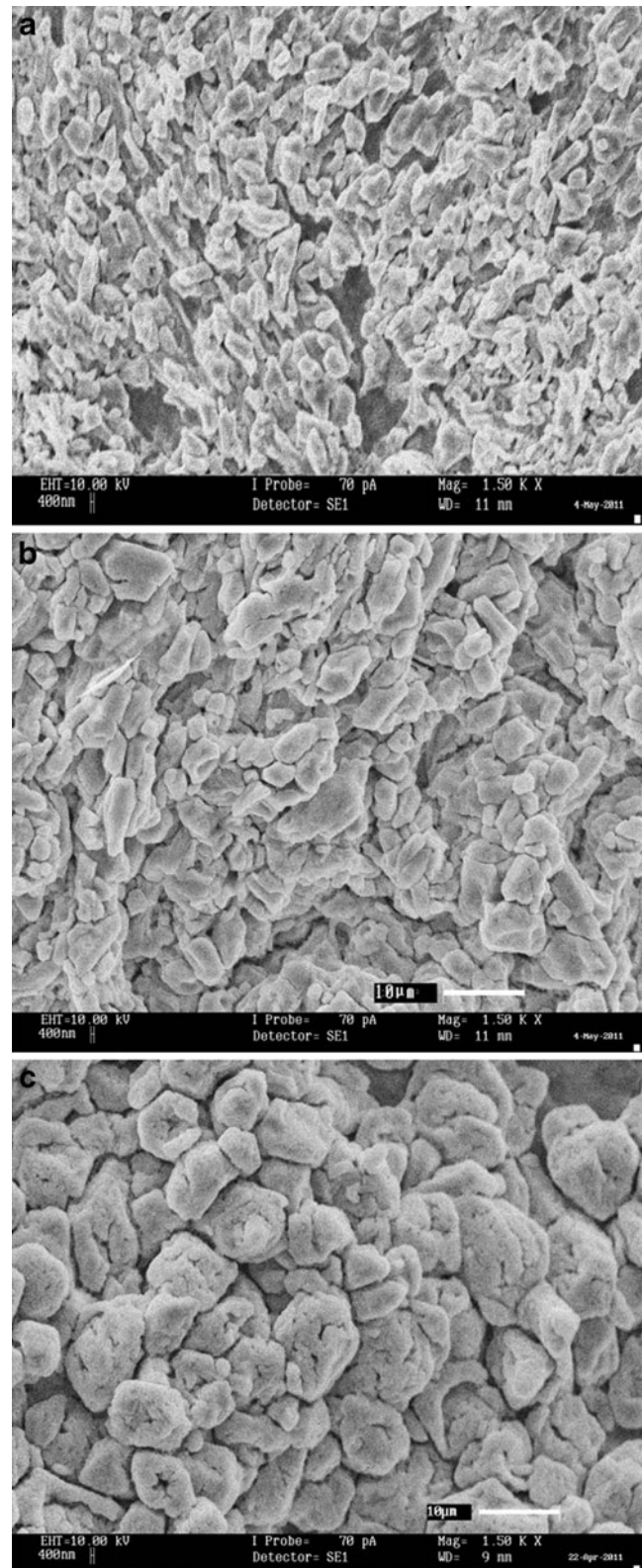


Fig. 4 SEM images of Si-0 (a), Si-4 (b), and Si-10 (c)

Degree of swelling

The hydrophilic nature of the hydroxyl group in amylose and amylopectin allows water absorption, results in swelling, and assists permeation in transporting through membrane. However, if too much water absorption occurs, then it may result in excessive mechanical fragility and morphological instability of membrane. The addition of nanosilica into the system reduced the total weight loss percentage of the polymer from 50.44 to 29.57 % for Si-0 and Si-10, respectively. This can be explained by the cross-linking between corn starch and nanosilica. Meanwhile, as the cross-linking density increases, it limits the polymer chain mobility and leads towards a denser membrane structure as well as a smaller free volume, which results in a smaller hydrophilic channel. The network structure formed by combining nanosilica with starch prevented the water molecules from dissolving, improved the water resistance of the film. This is in good agreement as describe in thermal analysis, when more nanosilica is added into the system the silica will restrict the segmental mobility of the main chain polymer and thus leading to higher decomposition temperature and T_g value.

Scanning electron microscopy

The grain morphology and microstructure of the samples were investigated using SEM. Figure 4 shows the morphology (SEM) of the prepared films for Si-0 (Fig. 4a), Si-4 (Fig. 4b), and Si-10 (Fig. 4c) at magnification of $\times 1,500$. From the results, we can observe that when excessive nanosilica is added into the system, they tend to aggregate to form larger grain. Si-0 shows a uniform distribution of crystalline LiClO_4 salt on the surface. On the other hand, upon addition of nanosilica into the system, the particles grow as platelet-like to form a grain size between 1 and 5 μm . A different morphology is observed in Si-10 with interconnected sphere particles as a result of agglomeration with grain size about 5–8 μm . The larger grain size reduced the number density of ions and reduced the ionic mobility that could be due to ions trap in the polymer electrolytes. From the SEM morphology, we can observe that the presence of SiO_2 will induce larger grain size. As suggested earlier in conductivity measurement, the ionic conductivity drops when excess nanosilica is added.

Conclusion

In this present work, the amount of nanosilica has been found to affect the ionic conductivity of corn starch-based polymer electrolytes. A series of nanocomposite polymer electrolytes have been successfully prepared by dispersing

up to 10 wt% of nano-sized silica in the matrix formed by corn starch and LiClO_4 . Polymer electrolyte consisting of 4 wt% nano-sized silica shows the highest ionic conductivity which is $1.23 \times 10^{-4} \text{ S cm}^{-1}$ at ambient temperature. The FTIR spectra show some complexation between corn starch, LiClO_4 , and silica. Excessive nano-sized silica content decreases the ionic conductivity by means of agglomeration of particles and cross-linking in the polymer which is verified by DSC, TGA, and SEM studies.

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