



Simultaneous improvement in ionic conductivity and mechanical properties of multi-functional block-copolymer modified solid polymer electrolytes for lithium ion batteries

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ABSTRACT

Solid polymer electrolytes (SPEs) with high ionic conductivity and acceptable mechanical properties are of particular interest for increasing the performance of batteries. Our previous studies indicated that copolymers could be good candidates for SPE materials due to the variable properties contributed by each block. A series of copolymers applied in this research was poly(ethylene oxide)-*block*-polyethylene, PEO-*b*-PE, which contains a conductive block (PEO block) and a reinforcement block (PE block). This study examines the effects of composition and molecular weight of the copolymers on performance of the resulting SPEs. The ternary SPEs were prepared by addition of copolymers into PEO/LiClO₄. It was found that increasing the PE block percentage in the copolymer resulted in a significant increase in both ionic conductivity and mechanical properties. The SPEs that contained the highest percentage of PE block, 80 wt%, exhibits the best performances. The results showed an increase of more than two orders in ionic conductivity, about 350% increase in tensile modulus, and about 97% increase in ultimate tensile strength when the PE block increased from 50 wt% to 80 wt%. It was also observed that increasing the molecular weight of the copolymer resulted in better mechanical properties, and an identical ionic conductivity.

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1. Introduction

Lithium ion batteries are used overwhelmingly for various applications and are expected to expand the usage in the future. An ideal way to obtain a light-weight, leak proof and flexible lithium ion battery is to utilize solid polymer as a separator as well as an electrolyte. Solid polymer electrolytes (SPEs) are a kind of solid-state coordination compounds, consisting of a polymer host and a complexing lithium salt [1]. Therefore, SPEs combine the properties of polymers, such as easy processability, design flexibility, light weight, shape versatility, safety and nontoxicity, with the electrical properties of the traditional liquid electrolytes. Ion transport occurs mainly through an association–disassociation between the ions and the polymer hosts and coupling with segmental movement [2,3]. However, existing SPEs have inherently lower conductivities due to the more restricted motion of the polymer molecules [4], and thus, make them unacceptable for practical use. Many efforts have been made to increase the ionic conductivity of polymers, such as blending, plasticization, blocking, cross-linking, and inorganic composite [5–9]. Some of these methods have improved the ionic conductivity

to some extent. However, the mechanical strength is often sacrificed in order to increase ionic conductivity so that the SPE film preparation can become more difficult.

Enhancements in both ionic conductivity and mechanical properties are usually in conflict because both these two types of properties are contrary with respect to the movements of the polymer chains. The high chain mobility can lead to high ion conductivity but at the same time can lead to lower mechanical properties [10,11]. Many researchers have attempted to find an optimized balance between the ionic conductivity and mechanical properties, but the outcomes are not yet satisfactory. Our previous work revealed that poly(ethylene oxide)-*block*-polyethylene (PEO-*b*-PE) possesses a capability for enhancing the multiple performances of poly(ethylene oxide) (PEO)-based polymer electrolyte, in which the conducting pathways, provided by polar groups contained within PEO parts (PEO parts include PEO matrix and PEO block in the copolymer), are called conductivity parts; while a non-conducting block (PE-*b*, PE block in the copolymer) imparting the desired mechanical properties, is called a reinforcement block [12,13]. In this paper, a series of diblock copolymer with different composition and molecular weight are studied. The effects of the composition and molecular weight of the copolymer on both ionic conductivity and mechanical properties of the resulting SPEs are examined.

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Table 1
Compositions of the PEO-based SPE samples.

Sample	Multi-functional filler	PE percent (wt%)	Number average molecular weight
SPE-0	PEG	0	800–1000
SPE _h -50	PEO- <i>b</i> -50 wt% PE	50	1400
SPE _l -50	PEO- <i>b</i> -50 wt% PE	50	920
SPE-80	PEO- <i>b</i> -80 wt% PE	80	875

For all the samples, the concentration of the LiClO₄ is 15 wt%.

2. Experimental

2.1. Materials

Poly(ethylene oxide) (PEO) (Mw = 4,000,000 g mol⁻¹), pure polyethylene glycol (PEG, low molecular weight of PEO), poly(ethylene oxide)-*block*-polyethylene (PEO-*b*-PE) (875 with 80 wt% PE, 920 with 50 wt% PE, and 1400 with 50 wt% PE) and lithium perchlorate (LiClO₄) were obtained from Aldrich. The LiClO₄ was dried in a vacuum oven at 70 °C for 24 h.

2.2. SPE preparation

Polymer electrolyte films were made by dissolving pure PEG or copolymer and LiClO₄ in a 50 ml glass bottle with 15 ml of acetonitrile. Then, 0.2 g of PEO (4,000,000 g mol⁻¹) was added to the solution and dissolved by magnetic stirring at room temperature. The bottled solution was then run through an ultrasonic bath for 3 h to remove any air bubbles. Ice was added to the ultrasonic bath to prevent excess heating of the solution. The entire solution was cast on a glass substrate in a 2.5" × 2.5" stainless steel mold at room temperature and left in a hood until the solvent was evaporated. Mold release wax was applied to the glass substrate for films used for mechanical testing in order to prevent any deformation during film removal. The films were removed from the glass and dried in an oven at 40 °C for 24 h to ensure that the solvent was completely evaporated from the system. The detailed information and abbreviation are shown in Table 1.

2.3. Characterizations

Dielectric tests were run on each type of film using a Universal Dielectric Spectrometer (UDS) BDS 20. Two 25 mm² squares were cut from each of the films and the thickness of each film was measured using a digital caliper. Each 25 mm² film was individually placed between the electrodes of the UDS. Each film was test over

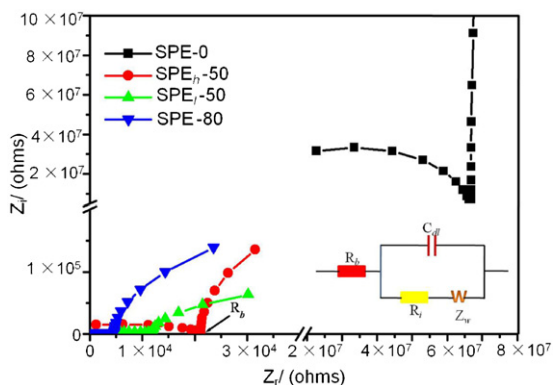


Fig. 1. Comparison of impedance spectra for four kinds of solid polymer electrolytes at room temperature: SPE-0 (with pure PEG; without copolymer), SPE_h-50 (with high molecular weight PEO-*b*-50 wt% PE), SPE_l-50 (with low molecular weight PEO-*b*-50 wt% PE), and SPE-80 (with PEO-*b*-80 wt% PE).

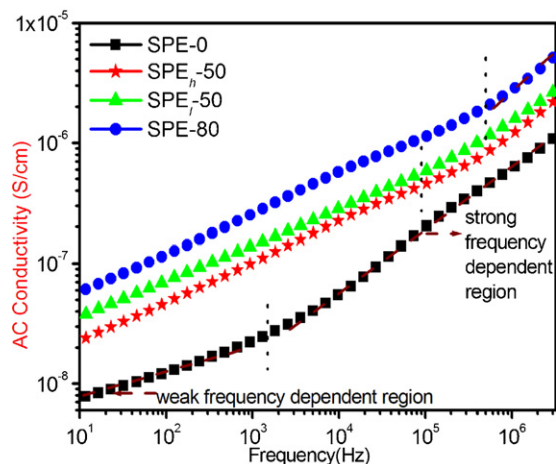


Fig. 2. Frequency dependence of AC conductivity of the SPE films.

the frequency range of 10 Hz to 10⁶ Hz at room temperature. Several properties were recorded during these tests; of interest are ionic conductivity and impedance.

The ionic conductivity (σ) was calculated from the bulk electrolyte resistance value (R_b) found in the complex impedance diagram according to the following equation:

$$\sigma = \frac{L}{RS} \quad (1)$$

where L is the thickness of the polymer electrolyte film and S is the area of the polymer electrolyte film.

Tensile tests were performed using an Instron 4466 with a 500 N load cell and a laser extensometer. For these tests, films were cut into five 0.9 cm wide strips each. A digital caliper was used to measure the thickness of each film strip. The cross-sectional area of the film is needed to calculate the strain. Two pieces of reflective silver tape were placed 0.25 in. (0.635 cm) apart across the width of film. The distance between the two pieces of tape is the original length of the test film. Rectangular rubber pieces were used to sandwich the long ends of the test film. This was necessary to provide a way to mount the test film into the Instron grips. The ends of the film were taped to the rubber to ensure that the film would not be pulled out of the grips during testing. The speed for these tests was set to 10 cm min⁻¹.

The microstructures of the films were analyzed using a polarized optical light microscope (Olympus BX51). Differential Scanning Calorimetry (DSC) analysis was performed using a TA Instruments DSC822 Mettler Toledo DSC in a nitrogen atmosphere. The specimens were heated at a rate of 10 °C min⁻¹ from 25 °C to 130 °C to erase the heat history, then quenched to -100 °C at a rate of 300 °C min⁻¹. The specimens were maintained at -100 °C for 5 min and then heated to 130 °C at a rate of 10 °C min⁻¹. The specimens were weighed about 5 mg.

Table 2
Stress–strain results of polymer electrolyte films.

Samples	Tensile modulus (MPa)	Ultimate tensile stress (MPa)	Breaking strain (%)
SPE-0	–	–	–
SPE _h -50	882.4 ± 16.2	7.0 ± 0.7	3936.7 ± 164.8
SPE _l -50	197.3 ± 11.8	3.0 ± 0.8	4754.4 ± 230.4
SPE-80	905.7 ± 15.3	5.9 ± 0.6	3196.7 ± 74.7

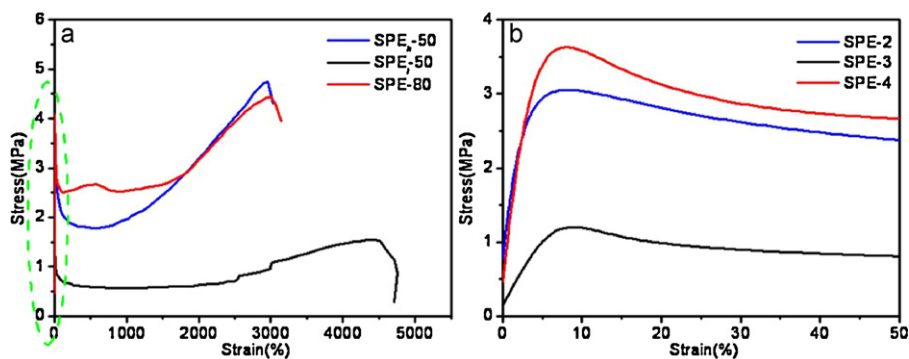


Fig. 3. Stress–strain curves for the block copolymer contained SPE films: (a) complete curves and (b) enlarged portion of plot (a) within dotted ellipse.

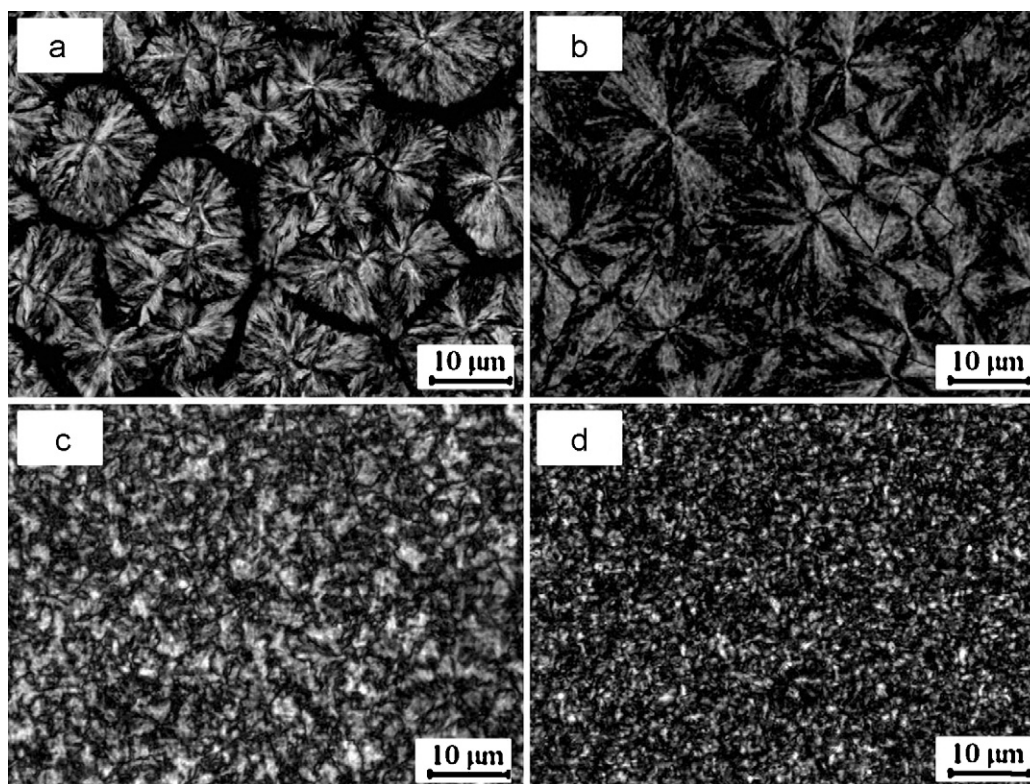


Fig. 4. Optical micrograph of (a) SPE-0 (pure PEG contained), (b) SPE_h-50 (high molecular weight PEO-b-50 wt% PE contained), (c) SPE_l-50 (low molecular weight PEO-b-50 wt% PE contained) and (d) SPE-80 (PEO-b-80 wt% PE contained) films at the magnification of 50×.

3. Results and discussion

3.1. Ionic conductivity

Ionic conductivity of an electrolyte functioning between the anode and cathode is its most important property. In order to test it, the polymer electrolyte films were cut into disks of 20 mm in

diameter sandwiched between golden coated copper electrodes and subjected to the dielectric analyzer at room temperature.

Fig. 1 shows the impedance spectra for the four kinds of SPE films prepared in this study. The insert is the equivalent circuit. The meanings of the elements in this assumed equivalent circuit are as follows: R_b represents the bulk resistance; R_i and C_{dl} represent the resistance and the double layer capacitance

Table 3
Thermal properties for various polymer electrolyte samples obtained from Fig. 5b.

Samples	T_g (°C)	T_{m1} (°C)	ΔH_{m1} (J g ⁻¹)	X_{EO} (%)	T_{m2} (°C)	ΔH_{m2} (J g ⁻¹)	X_E (%)
SPE-0	-47.14	54.67	83.57	43.3			
SPE _h -50	-60.39	56.67	54.82	37.9	105.33	39.36	54.5
SPE _l -50	-59.35	57.33	43.02	29.7	88.33	21.74	30.1
SPE-80	-62.28	56.67	33.77	25.0	106.67	74.49	85.9

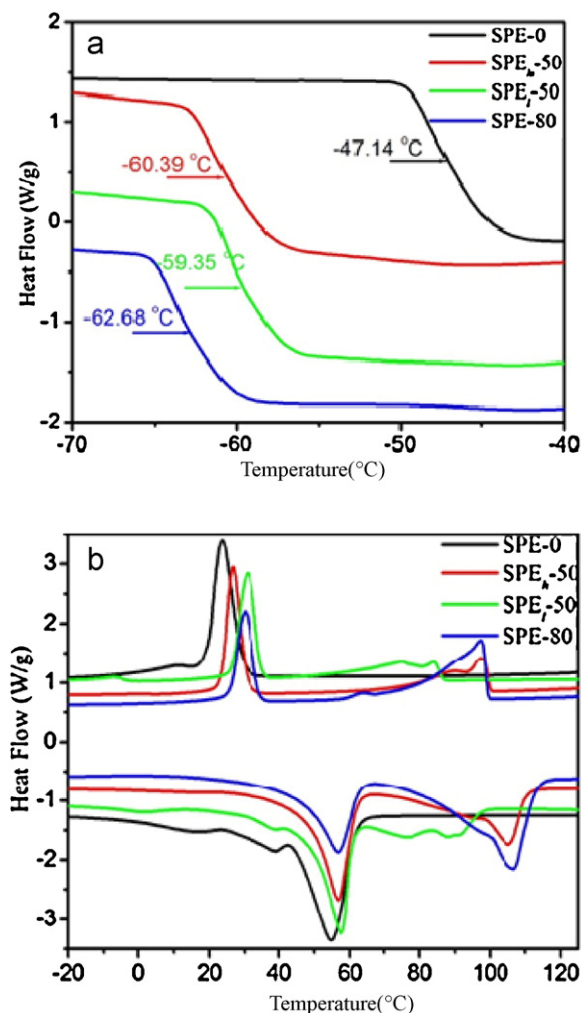


Fig. 5. DSC curves for SPEs.

of the interface between electrode and the electrolyte; and Z_w represents the Warburg impedance. The complex impedance spectrum consists of a distorted semicircular arc in the high frequency region followed by a spike in the low frequency region. The intercept of the semicircle with the real axis in the high frequency region gives rise to the bulk resistance (R_b) of the polymer electrolyte [14], as shown in Fig. 1. According to Eq. (1), the calculated ionic conductivities of SPE-0, SPE_h-50, SPE_l-50 and SPE-80 are $1.9 \times 10^{-9} \text{ S cm}^{-1}$, $6.0 \times 10^{-6} \text{ S cm}^{-1}$, $1.1 \times 10^{-5} \text{ S cm}^{-1}$, and $3.2 \times 10^{-4} \text{ S cm}^{-1}$, respectively. Comparing the ionic conductivity of the pure PEG loaded electrolyte, SPE-0, with those of the block copolymer loaded electrolytes, SPE_h-50, SPE_l-50 and SPE-80, it can be deduced that the presence of the PE-*b* may help increase the ion flow through the films. The ionic conductivity of the polymer electrolytes increased more than four and five orders due to the additions of the copolymer containing 50 wt% and 80 wt% PE-*b*, respectively. Moreover, the more PE-*b* is contained, the higher ionic conductivity is obtained. When it comes to the same PE-*b* percentage (SPE_h-50 and SPE_l-50), the influence of molecular weight on the bulk resistance is minor. The ionic conductivity values obtained from the SPE_h-50 and SPE_l-50 electrolyte films were compared, and it was found that they were almost identical. This result implies that decreasing the molecular weight of the block copolymer results in only small increases in ionic conductivity. However, increasing the PE-*b* percentage resulted in a large increase in ionic conduc-

tivity. This was an unexpected result because the electrolyte film with 80 wt% PE-*b* has a much smaller amount of the conductive PEO parts. It is possible that higher ionic conductivity was found in this electrolyte film because the larger amount of PE-*b* from this block copolymer allows the tunnels to induce ion transport without obstruction by decreasing the entanglement of the PEO chains. Another possible reason is the confinement of the pre-existing PE crystalline parts; the orders of the PEO structure are disrupted [15], which resulted in an increase in the polymer chain flexibility and boosting the motion of ion transport. This can be confirmed by the following DSC results.

In order to understand the ion dynamics in the polymer electrolytes, the frequency dependence of the AC conductivity has been analyzed for all samples [16]. Fig. 2 shows the AC conductivities acquired from all four electrolyte films, SPE-0 (only with pure PEG), SPE_h-50 (with high molecular weight PEO-*b*-50 wt% PE), SPE_l-50 (with low molecular weight PEO-*b*-50 wt% PE), and SPE-80 (with PEO-*b*-80 wt% PE), over the frequency range of 10^1 – 10^6 Hz. The plots consist of two distinct regions: a weak frequency-dependent region in the low frequency range and a strong frequency-dependent region in the high frequency range where AC conductivity varies significantly with frequency. It is believed that the variation of AC conductivity is reflected in the mechanism of charge transport and interactions among charge carriers. According to the jump relaxation model [16,17], at low frequencies, an ion can jump from one site to its neighboring vacant site successfully. While at higher frequencies, due to the short time periods, the probability for the ions to go back to their original sites increases. This high probability is responsible for the higher conductivity in higher frequencies. With the copolymer addition, the switchover (the vertical dotted line) from the frequency independent to frequency dependent region that shifts to higher frequencies, which indicates a higher probability for the ions to return to their original sites. This increased probability contributes to the improvement in ion conductivity.

3.2. Mechanical properties

Fig. 3a shows the stress–strain curves of the SPE films. The elastic region of the stress strain plots are magnified in Fig. 3b and the modulus was calculated by the slope of the curves in linear portion of Fig. 3b. The mechanical properties obtained from this stress–strain plot, tensile modulus, ultimate tensile stress and the breaking strain can be seen in Table 2.

As seen in Fig. 3, the mechanical properties of these films depend on the composition and the molecular weight of the copolymer added in the SPE. The mechanical property of the SPE-0 is too weak to be tested, and failed to obtain mechanical property values. It can be seen that the presence of PE-*b* in the copolymers helps enhance the mechanical properties that can be observed in the stress–strain behavior of the films. The SPE films show higher ultimate stress when the PE-*b* weight percent is higher. When the weight percent of the PE-*b* in copolymer increased from 50 wt% to 80 wt%, the ultimate tensile strength and modulus increased $\sim 97\%$ and $\sim 359\%$, respectively.

It is apparent from Fig. 3 and Table 2 that molecular weight also plays a big role with respect to the mechanical properties. Comparing the SPE_h-50 and SPE_l-50, $\sim 350\%$ increase in tensile modulus and $\sim 130\%$ increase in ultimate tensile strength is found when the molecular weight of the copolymer increased from 920 to 1400. This is possibly due to the fact that the structural block formed from PE chains in the lower molecular weight copolymers are shorter and are not able to rearrange and organize into an ordered crystal structure, which is confirmed by the following DSC results.

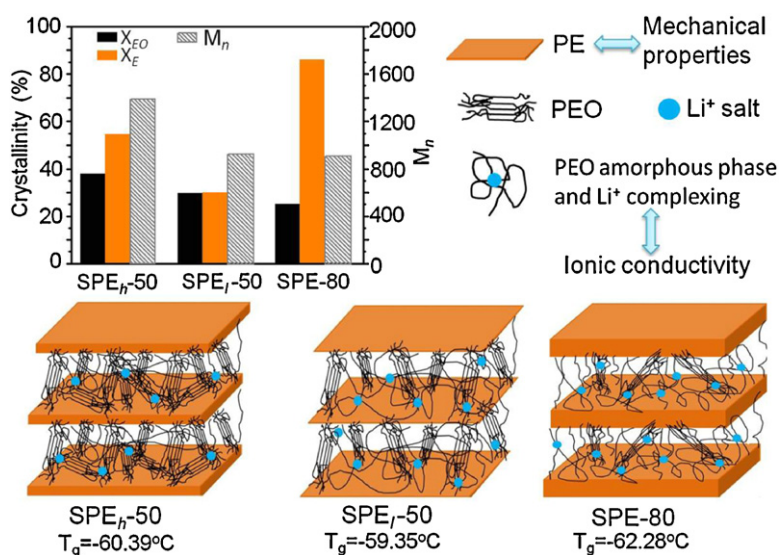


Fig. 6. Schematic representation of copolymer contained PEO-based SPEs.

3.3. Morphology

Fig. 4 shows optical micrographs of four kinds of polymer electrolyte films. Distinct spherulites are visualized in the micrographs of the pure PEG included film (Fig. 4a). The boundary between the spherulites shows the existence of an amorphous phase. After addition of the copolymer, the microstructure of the electrolyte film was dramatically changed as shown in Fig. 4(b–d). It indicates the addition of the copolymers indeed changed the structure of the electrolytes that are believed to be related to conductivity properties for the materials. The characteristic morphology of the SPE materials is controlled by the composition and molecular weight of the block copolymer chains. Comparing the morphology of SPE_l-50 and SPE-80 (Fig. 4c and d), the size of the crystals in SPE_l-50 is larger than in SPE-80. In SPE-80, due to the high disturbance of the pre-existing PE crystal parts, the crystal structure of PEO block is not visible. While in SPE_l-50, the crystallinity of the PE-*b* is much lower (shown in the following DSC results), and the imperfect crystallization of PE-*b* cannot disturb the order of the PEO as much as the PE-*b* did in SPE-80. As for the molecular weight, for example in SPE_h-50 and SPE_l-50 (Fig. 4b and c), the higher molecular weight resulted in more well-shaped crystal structure.

3.4. Thermal properties

Thermal performance is an important property for electrolytes composed of polymers and lithium salts for application in lithium ion polymer batteries. The thermal properties were evaluated by DSC. Typical DSC thermograms of the electrolytes are shown in Fig. 5. Various parameters related to thermal properties such as glass transition temperature (T_g), melting temperature (T_m) and heat of fusion (ΔH_m) of crystalline phase of the polymer electrolytes and degree of crystallinity (X_c) can be evaluated from the DSC data and are summarized in Table 3. ΔH_m can be calculated from the integral area of the baseline and of each melting curve [18]. The degree of crystallinity (X_c) can be calculated from the ratio of the melting heat of fusion (ΔH_m) of polymer electrolytes to the melting heat of 100% crystalline PEO or PE phase [15], which are denoted as X_{EO} and X_E , respectively.

Polymer chain mobility in the amorphous phase can be reflected from the glass transition temperature (T_g). In this study, T_g is mainly correlated with flexibility of EO chains, i.e., T_g is correlated with segmental motion of EO chains. Numerous experiments have shown

that ionic conductivity occurs in an amorphous phase and it is coupled with the segmental motion of polymeric chains [2–4,19–21]. Hence, mobility of carrier ions in polymer electrolytes is corrected with T_g . The lower T_g indicates a higher mobility of the segmental motion of polymeric chains or a better mobility of carrier ions when considering at room temperature. From Fig. 5a, the T_g values of the electrolytes containing block copolymer decreased $\sim 12^\circ\text{C}$ compared with that of electrolyte with only PEG. That would in turn imply that the ionic conductivity could be enhanced by introducing PE block. The electrolytes with the highest PE-*b* concentration (SPE-80) showed the lowest T_g , which indicated the ion mobility in SPE-80 is better than the other two copolymer addition systems (SPE_h-50 and SPE_l-50). This agrees well with the ionic conductivity results (shown in Fig. 2). The SPE-80 system possesses the highest ionic conductivity, and SPE_h-50 and SPE_l-50 shows similar ionic conductivity values.

The thermogram of (Fig. 5b) shows the presence of two sharp endothermic peaks at $\sim 56^\circ\text{C}$ and $\sim 105^\circ\text{C}$ corresponding to the crystalline melting temperature (T_m) of PEO and PE parts, respectively. The decrease in both melting heat and crystallinity of PEO parts as the weight percent of PE-*b* increases has been observed. The crystallinity of the PEO parts decreased by 42% (from 43.3% to 25.0%) when the PE-*b* percentage in the block increased from 0 to 80 wt%, which implies the involvement of the PE-*b* highly disturbed the order of the PEO chains. As for SPE_l-50 and SPE-80 (the molecular weights of the copolymer are very close), both the melting temperature and crystallinity of the PEO parts decreased slightly. A remarkable change happened in the PE-*b*. The melting temperature increased 18.34°C , while the crystallinity increased 185%, which indicates a more highly ordered PE crystal phase is formed in SPE-80 than in SPE_l-50. As shown in Fig. 5b, a well-defined endothermic peak exists in SPE-80. Comparing the SPE_h-50 with SPE_l-50, as evident from Fig. 5b, the solid polymer electrolyte with higher molecular weight copolymer shows more ordered PE phase than the lower molecular weight system when the PE-*b* percentage is the same. That is the reason that the mechanical properties of the high percentage PE-*b* contained systems is better.

In summary, the DSC results show that for T_g and degree of crystallinity, both decreased with increase in PE-*b* percentage. The reduction in T_g indicates a weakening of the dipole–dipole interactions between the PEO chains, which facilitates the motion of charge carrier transport through the polymer backbone. The drop in crystallinity of PEO block (X_{EO}) values of the polymer electrolytes

reveals the disruption of crystalline to amorphous phase, which indicates the number of free charge carriers is increased. Both the increased free charge number and the ion mobility resulted in the enhancement in the ionic conductivity. The crystal structure of the PE parts is highly related with the mechanical properties. It is clearly seen that the non-polar PE-*b* shows a prominent effect on the properties of both the ionic conductivity and mechanical properties.

3.5. Mechanism

Combining the conductivity, mechanical and structure information presented above, a quite complex situation for these materials emerges. The most astonishing result is the fact that the ionic conductivity of polymer electrolytes increases upon the introduction of non-polar PE-*b* weight percent in copolymer. While the higher the percentage of PE-*b* in copolymer is, the higher the ionic conductivity is. Moreover, the mechanical properties increased with the percentage of PE-*b* in the copolymer and the molecular weight of the copolymer also play an important role in increasing mechanical properties. As shown in above DSC results, the structure of crystal phases of the both blocks are highly influenced by the intrinsic properties of the copolymer and the final properties, i.e. ionic conductivity and mechanical properties, are significantly dependent on the crystalline structure. To illustrate this fact a simple diagram (Fig. 6) is proposed. The PEO matrix is compatible with the copolymer through the miscible PEO block, and the lithium ions are transported in the amorphous PEO phase. According to literature [12,13,22,23], due to the slight solubility of PE block in solvent acetonitrile, the PEO block in the copolymer PEO-*b*-PE are always confined by the pre-existing crystal phase of PE block. Finally, the crystalline lamellae of PE and PEO blocks are alternately stacked. Therefore, a kind of PE crystal phase-layered-continuous PEO amorphous structure is formed, in which PEO parts (PEO parts include PEO matrix and PEO block in the copolymer) are responsible for the conduction process, and the PE parts are responsible for the mechanical integrity. The ion-transporting domain is formed by doping PEO with lithium salts. PE-*b* are not compatible with ions, thus, ion transport is restricted to the microphase of the PEO parts. In a situation of SPE_h-50 and SPE-80, as shown in DSC results (Fig. 5), the crystallinity of the PE block is much higher than in the situation of SPE_l-50 and the perfect crystal structure is beneficial to the mechanical enhancement. Though the copolymer composition in SPE_h-50 and SPE_l-50 is the same, the PE-*b* chains are shorter in SPE_l-50 and the strong interaction between PEO block and PE block decreased the thickness of the PE crystal plate resulted in a lower mechanical properties.

4. Conclusions

From this study we can conclude that the composition and molecular weight of the multi-functional copolymer, PEO-*b*-PE, have significant effects on the properties of PEO-based SPE films. The best ionic conductivity and mechanical properties are obtained in 80 wt% PE-*b* solid polymer electrolytes (SPE-80) by comparing the properties with the pure PEG (SPE-0) and 50 wt% PE-*b* (SPE_l-50) contained electrolytes. Molecular weight did not seem to have much effect on the ionic conductivity. However, for the mechanical properties, tensile tests showed that increasing the molecular weight of the block copolymer resulted in ~350% increase in tensile modulus and ~130% increase in ultimate tensile stress. According to the optical micrograph and DSC results, the crystal structure is highly changed due to the introduction of the different amount of PE-*b*, which is responsible for the resulting properties. The lower the crystallinity of the PEO parts, the higher is the resultant ionic conductivity, while the higher the crystallinity of the PE-*b* the better mechanical properties are obtained.

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