J Mater Sci (2010) 45:1280–1283
DOI 10.1007/s10853-009-4079-2

Mechanical studies on poly(vinyl chloride)–poly(methyl methacrylate)-based polymer electrolytes

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Received: 5 October 2009 / Accepted: 24 November 2009 / Published online: 3 December 2009
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Abstract The aim of the present work is to study the mechanical properties of poly(vinyl chloride) (PVC)/poly(methyl methacrylate) (PMMA) blends based polymer electrolytes for lithium ion batteries. The introduction of PVC into PMMA is found to increase the Young's modulus value from 5.19 MPa (in pure PMMA) to 6.05 MPa (in PVC:PMMA = 70:30). The different Young's modulus values in PVC blends is due to the difference in the cross-linking density provided by PVC with different weight fraction values. The stress–strain analysis reveals that the mechanical strength of the polymer electrolyte system deteriorated with the incorporation of $LiCF_3SO_3$. The results show that the introduction of salt decreases the Young's modulus and stress at peak values along with higher elongation at peak value. The addition of low molecular weight plasticizers to PVC–PMMA–$LiCF_3SO_3$ decreases the modulus and stress at peak of the complexes. To be applicable in practical applications, the mechanical strength of the plasticized films is found to improve with the addition of silica as nanocomposite filler.

Introduction

Polymer electrolytes have emerged as the key object of academic and industrial interest. These materials have vast potential application in solid-state batteries, fuel cells, and electrochromic devices. The solid polymer electrolytes (SPEs) display many advantages, such as satisfactory mechanical properties, ease of fabrication as thin-films of desirable sizes, and good contact with electrode materials. A major drawback of these SPEs, however, is the low ionic conductivity at ambient temperature.

Various approaches to enhance the ionic conductivity in a polymer matrix are suggested in the literature [1–5], among which the addition of plasticizer assumes importance. However, one of the important drawbacks in plasticized electrolytes is poor mechanical properties at high degree of plasticization [6]. Incorporation of fillers into a polymer matrix is a good approach to improve conductivity and mechanical properties [7].

This paper reports the studies on the mechanical properties of poly(vinyl chloride) (PVC)/poly(methyl methacrylate) PMMA blend-based polymer electrolytes with various $LiCF_3SO_3$, plasticizers, and silica contents. The obtained values of Young's modulus, stress at peak, and elongation at peak were compared.

Experimental

The host materials, PVC was obtained from Fluka, while PMMA was obtained from Aldrich. The required amounts of PVC and PMMA were dissolved in tetrahydrofuran (THF) that was obtained from J.T. Baker. Lithium triflate ($LiCF_3SO_3$), obtained from Aldrich, was used as the doping salt. The plasticizers, dibutyl phthalate (DBP), and ethylene

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carbonate (EC) were both procured from Aldrich and Fluka, respectively. Fumed silica (SiO_2) which was kindly supplied by Wacker Chemie was used as the nanocomposite filler. The particle size of SiO_2 is 10–30 nm.

The first step to preparation of the polymer electrolytes is to dry the $LiCF_3SO_3$ at 100 °C for an hour. Subsequently, desired amounts of PVC/PMMA blends and $LiCF_3SO_3$ were dissolved separately in THF and then mixed together and stirred. After incorporating the required amounts of plasticizers (DBP and EC), inorganic filler SiO_2 powder was suspended in the solution and stirred for 24 h in order to achieve a homogeneous mixture. The solutions thus obtained were cast on a glass plate and allowed to evaporate slowly inside a desiccator.

An Instron Corporation Series 1X automated Materials Testing System 7.51.00 was used to measure the mechanical properties. The test pieces are designed according to the ASTM designation JIS K 6900. The thickness of the test pieces were between 1 and 3 mm. The crosshead speed for these test pieces was controlled to be 10 mm/min.

Results and discussion

Figure 1 shows the typical stress versus strain curve for pure PVC, pure PMMA, and PVC:PMMA (30:70) blend. It is observed for all the plots that, at low strain, there exists a so-called elastic energy in the materials. This energy is stored in the chemical bonds in the form of strain energy prior to break. For greater strain, the stored energy is termed plastic energy and is used to describe the amount of energy residually stored in the material as internal and free (orientation) energy after break. There are two basic processes assumed to occur during material rupture. First, unstable fissures or microcracks begin to appear as a result of the intermolecular forces being overcome at the weakest sites. Once the crack exists, fracture occurs when the energy stored in the part above the crack surpasses the energy stored for chemical bond strain, together with the energy stored for molecular orientation around the microcrack, for example macroscopic cracks [8].

The maximum break strength value obtained for the PVC:PMMA (30:70) blend is lower than the value of the pure PVC. The experimental and theoretical values of Young's modulus are presented in Table 1. There are many theories proposed in the literature for predicting the theoretical values of the mechanical properties of polymer blends. A simple "rule of mixture" gives a straight-line relationship with composition [9].

$$P_b = P_1X_1 + P_2X_2,$$

where P_b is the value of the property of the blend; P_1 and P_2 are values of the property of the pure components 1 and 2; and X_1 and X_2 are weight fractions of the pure components 1 and 2. The margin of error between the experimental value and the theoretical value is less than 9%.

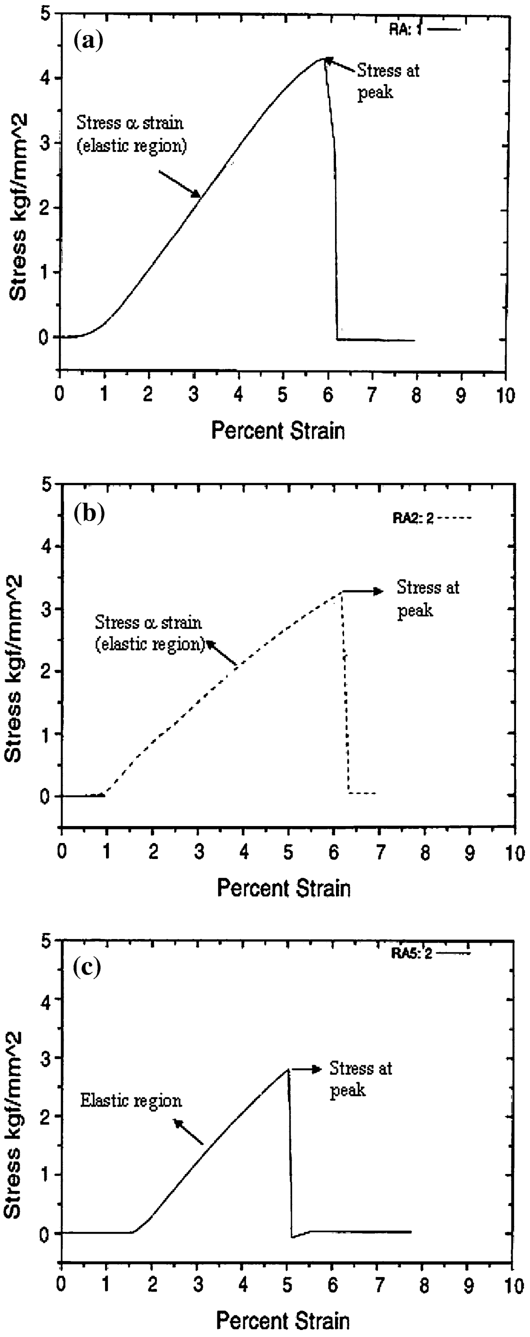

Fig. 1 Stress versus strain curve for **a** pure PVC, **b** pure PMMA, and **c** PVC:PMMA (30:70)

Results show that pure PVC, pure PMMA, and PVC–PMMA blends exhibit high Young's modulus value (ca. MPa), high stress at peak (ca. MPa), and short elongation at peak. These results are typical for hard and brittle materials. PVC, having a higher Young's modulus and lower elongation at peak values is harder and more brittle than

Table 1 The experimental and theoretical values of Young's modulus in PVC/PMMA blend

% of PVC	Young's modulus (MPa)	
	Experimental value	Theoretical value
0	5.19	5.19
30	5.45	5.79
50	5.85	6.19
70	6.05	6.59
100	7.19	7.19

PMMA. The introduction of PVC into PMMA increases the Young's modulus value from 5.19 MPa (in pure PMMA) to 6.05 MPa (in PVC:PMMA = 70:30). This results in harder and more brittle blends. The different Young's modulus values in PVC blends is due to the difference in the cross-linking density provided by PVC with different weight fraction values [10].

Typical stress–strain curves for the PVC:PMMA (30:70) blend having $LiCF_3SO_3$ concentration of 10% and 40% are presented in Fig. 2. The stress–strain analysis reveals that the mechanical strength of the polymer electrolyte system deteriorated with the incorporation of $LiCF_3SO_3$. The decreased mechanical strength of PVC–PMMA blends with the addition of $LiCF_3SO_3$ may be due to the mode of interaction of the Li-ions with the polymer matrix, which is predominantly intramolecular rather than intermolecular [11]. The mechanical properties of PVC–PMMA blends change from hard and brittle to soft and tough, depending on the percentage of $LiCF_3SO_3$ added.

The variation of Young's modulus, stress at peak and elongation at peak values in PVC–PMMA blend with respect to $LiCF_3SO_3$ content are presented in Figs. 3, 4, and 5. Results show that the introduction of salt decreases the Young's modulus and stress at peak values along with higher elongation at peak value. These indicate that PVC–PMMA blends become more amorphous with the addition of $LiCF_3SO_3$.

Table 2 shows the stress–strain measurements for the PVC–PMMA–$LiCF_3SO_3$ blend plasticized with DBP and EC. The addition of single plasticizer, DBP to PVC–PMMA–$LiCF_3SO_3$ decreases the modulus and stress at peak of the complexes. In a double plasticizer system (DBP and EC), there is an obvious decrease in modulus and stress at peak for the complexes. The influence of plasticizers on the mechanical properties of polymer electrolyte films resembles the plasticization effect. The dipole–dipole type attractions between the chlorine atom of one chain and hydrogen of another in PVC are weakened by the presence of plasticizers. This will increase its flexibility and reduce the viscosity of the molten material. The decrease in viscosity improves the flow rate. Subsequently, this improved flow rate increases the energy at break and the plastic strain of the system. Hence, the polymer system is able to stretch further and become more plastic in nature [11].

It is also found that the elongation at peak value is higher in PVC–PMMA–$LiCF_3SO_3$–DBP–EC system compared to PVC–PMMA–$LiCF_3SO_3$–DBP system. This further indicates that the elasticity of the double plasticized

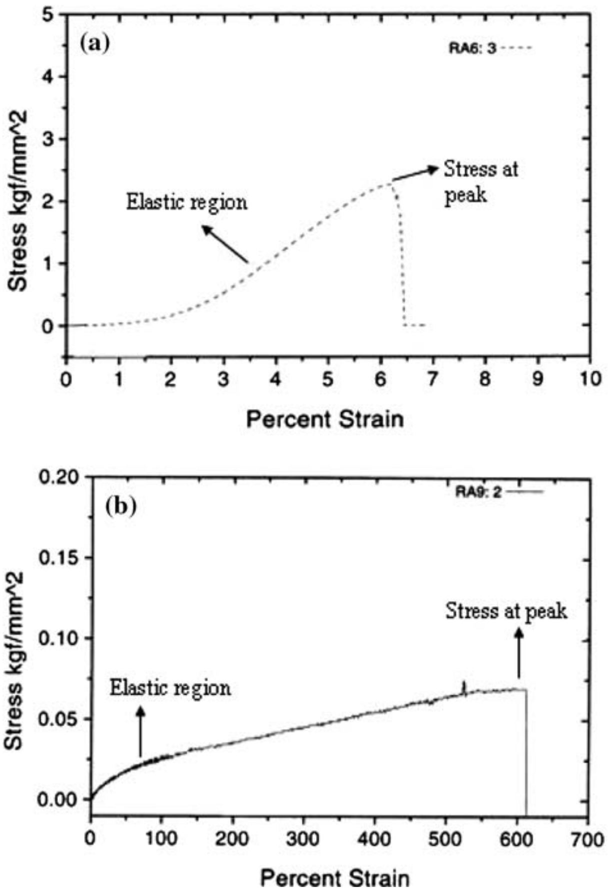

Fig. 2 Stress–strain curve for **a** PVC–PMMA: $LiCF_3SO_3$ (90:10) and **b** PVC–PMMA: $LiCF_3SO_3$ (60:40) systems

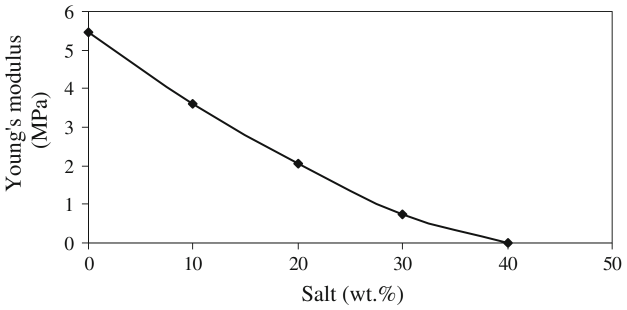

Fig. 3 The variation of Young's modulus in PVC–PMMA blend with respect to $LiCF_3SO_3$

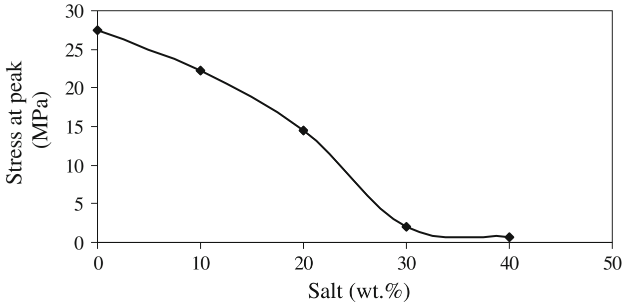

Fig. 4 The variation of stress at peak in PVC–PMMA blend with respect to $LiCF_3SO_3$

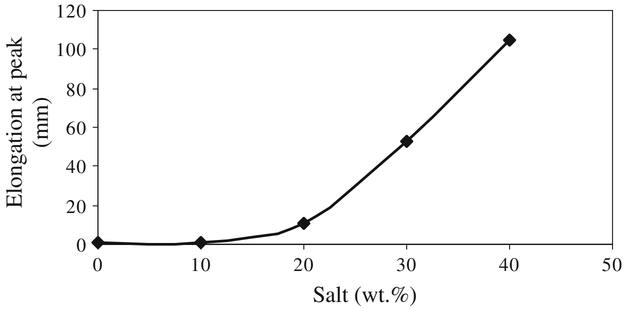

Fig. 5 The variation of elongation at peak in PVC–PMMA blend with respect to $LiCF_3SO_3$

Table 2 Stress–strain results of plasticized PVC blends

	Young's modulus (MPa)	Stress at peak (MPa)	Elongation at peak (mm)
PVC–PMMA–$LiCF_3SO_3$–DBP	1.18×10^{-3}	0.112	18.990
PVC–PMMA–$LiCF_3SO_3$–DBP–EC	1.12×10^{-4}	0.082	146.300

system increases and behaves more like a gel-type polymer complex compared to single plasticized system.

Although many polymer electrolytes are fabricated as free-standing films, their mechanical strength needs further enhancement when it comes to practical applications. In practical Li polymer cells, inorganic fillers are frequently added to improve the mechanical strength of the electrolyte films [12].

Figure 6 shows the variation of Young's modulus values for PVC–PMMA–$LiCF_3SO_3$–DBP–EC system with respect to SiO_2 content. The mechanical strength of the plasticized films is found to improve with the addition of silica as nanocomposite filler. The nanosized silica particles lodge themselves at the interface between the phases and enhance the stress transfer, which results in enhancement of mechanical properties, particularly the Young's modulus value [13]. The polymer chains become stiffened and rigid, making the nanocomposite polymer electrolytes less susceptible to stretching [14, 15].

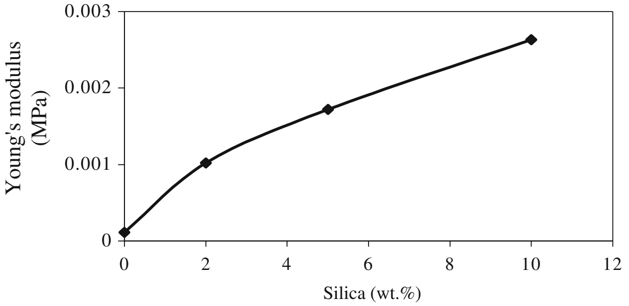

Fig. 6 The variation of Young's modulus with respect to silica content in PVC–PMMA complexes

Conclusion

PVC/PMMA blend films with high Young's modulus, high stress at peak, and low elongation at peak behave like hard and brittle material. The incorporation of $LiCF_3SO_3$ in the PVC–PMMA blends deteriorated the mechanical strength of the polymeric electrolytes. The addition of plasticizers (DBP and EC) decreases the Young's modulus value and improves the flexibility of the system. In order to be applicable in practical applications, the mechanical strength of the plasticized films was improved with the addition of nanosized silica.

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