The Malaysian Journal of ANALYTICAL SCIENCES ISSN 1394-2506

CARBOXYMETHYL CELLULOSE FROM KENAF REINFORCED COMPOSITE POLYMER ELECTROLYTES BASED 49% POLY(METHYL METHACRYLATE)-GRAFTED NATURAL RUBBER

(Komposit Polimer Elektrolit Berasaskan 49% Poli(metil metakrilat)-cangkukan Getah Asli Diperkuat Karboksimetil Selulosa Daripada Kenaf)

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Abstract

Composite polymer electrolytes based 49% poly(methyl methacrylate)-grafted natural rubber (MG49) incorporating lithium triflate ($LiCF_3SO_3$) were prepared. The study mainly focuses on the ionic conductivity performances and mechanical properties. Prior to that, carboxymethyl cellulose was synthesized from kenaf fiber. The films were characterized by electrochemical impedance (EIS) spectroscopy, linear sweep voltammetry (LSV), universal testing machine and scanning electron microscopy (SEM). The conductivity was found to increase with carboxymethyl cellulose loading. The highest conductivity value achieved was 6.5×10^{-6} Scm^{-1} upon addition of 6 wt% carboxymethyl cellulose. LSV graph shows the stability of this film was extended to 2.7 V at room temperature. The composition with 6 wt% carboxymethyl cellulose composition showed the highest tensile strength value of 7.9 MPa and 273 MPa of Young's modulus. The morphology of the electrolytes showed a smooth surface of films after addition of salt and filler indicating amorphous phase in electrolytes system. Excellent mechanical properties and good ionic conductivity are obtained, enlightening that the film is suitable for future applications as thin solid polymer electrolytes in lithium batteries.

Keywords: carboxymethyl cellulose, ionic conductivity, mechanical properties, polymer electrolytes

Abstrak

Komposit polimer elekrolit berasaskan 49% poli(metil metakrilat)-cangkukan getah asli (MG49) dengan penambahan garam triflat ($LiCF_3SO_3$) telah disediakan. Kajian ini lebih menumpukan kepada ciri-ciri kekonduksian ion dan kekuaan sifat mekanik sistem elektolit yang dihasilkan. Sebelum itu, karboksimetil selulosa daripada kenaf disediakan terlebih dahulu. Filem yang dihasilkan dicirikan menggunakan spekroskopi impedans (EIS), voltametri sapuan linear (LSV), mesin pengujian universal dan mikroskopi imbasan elektron (SEM). Nilai kekonduksian ion didapati meningkat dengan penambahan karboksimetil selulosa. Kekonduksian ion tertinggi diperolehi dengan nilai 6×10^{-6} Scm^{-1} pada penambahan 6 bt% karboksimetil selulosa. Graf LSV menunjukkan kestabilan filem yang dihasilkan mencapai sehingga 2.7 V pada suhu bilik. 6 bt.% karboksimetil selulosa menunjukkan 7.9 MPa kekuatan regangan dan 273 MPa modulus young. Morpologi permukaan elektrolit mempamerkan permukaan lebih licin selepas penambahan garam dan pengisi yang menunjukkan kawasan amorfus pada sistem elektrolit. Kekuatan regangan dan kekonduksian ion memberansangkan yang diperolehi menunjukkan filem yang dihasilkan sesuai digunakan sebagai filem pepejal elektrolit polimer dalam bateri litium.

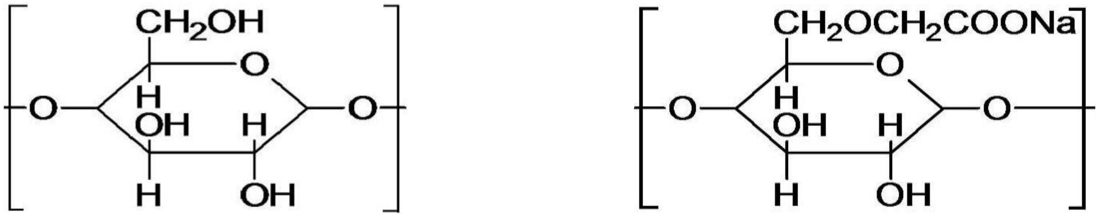
Kata kunci: karboksimetil selulosa, kekonduksian ion, sifat mekanik, polimer elektrolit

Introduction

Nowadays, composite polymer electrolytes have attracted much attention due to potential applications in electrochemical devices especially in lithium batteries. Polymer electrolytes have the potential to be used as rechargeable batteries, fuel cells, and light-emitting fuels, and in many other applications in electrochemistry [1].

Many studies have focused on the enhancement of ionic conductivity at ambient temperature, excellent mechanical properties, and stable performances of polymer electrolytes since various finding about practical applications as electrolytes in high energy density, thin, and lightweight secondary Li-ion batteries [2].

Moreover, the need of low cost, ecologically friendly, and safe becomes fundamental for the sustainable mass production of the next generation energy storage systems. The introduction of carboxymethyl cellulose from kenaf in polymer electrolytes as an alternative to traditional glass fibres such as Al_2O_3 and TiO_2 in commercial composite materials has drawn much attention [3]. The impressive mechanical properties and reinforcing capability, abundance, low weight, and biodegradability of cellulose make them ideal candidates for the processing of polymer composites [2]. Futhermore, the preparation process is easy, low cost and does not involve chemical reactions. Various sources of cellulose such as cavendish banana pseudo stem [4], chitosan [5], sago starch [6], etc have been used to synthesize carboxymethyl cellulose by different method depend on its application.



a) b)

Figure 1. Structure of a) cellulose and b) carboxymethyl cellulose

In this work, polymer electrolyte from 49% poly(methyl methacrylate)-grafted natural rubber and cellulose or cellulose derivative which is carboxymethyl cellulose was chosen due to the naturally occurring polysaccharide and the most abundant organic sub- stance on the earth. Carboxymethyl cellulose was synthesized from extracted cellulose and using as fillers in polymer electrolytes system. The incorporation of carboxymethyl cellulose as filler in MG49 composite polymer doped with lithium triflate was prepared via solution casting. Polymer electrolytes films were characterized by using electrochemical impedances spectroscopy (EIS) and electrochemical stability window (ESW) by linear sweep voltametry (LSV). The evaluation of the mechanical performances of the films was obtained via tensile strength and Young's modulus.

Materials and Methods

Materials

Kenaf fibres were supplied by Kenaf Fibres Industry Sdn. Bhd. (Malaysia). Chemical used during this study were sulphuric acid (98%), sodium chlorite, sodium hydroxide (99%) and acetic acid glacial 99.5%, isopropanol, ethanol, methanol, sodium chloroacetate (SCA) were purchased from SYSTERM-chemAR (Malaysia) and Sigma-Aldrich (Germany). Tetrahydrofuran (THF) was purchased from JT Baker. MG49 rubber was commercially obtained from Green HPSP (M) Sdn. Bhd. Lithium triflate ($LiCF_3SO_3$) salt was supplied by Fluka. All chemicals were used without further purification.

Synthesis of Carboxymethyl Cellulose

Prior to that, cellulose powder from kenaf was extracted according to [7]. Preparation of cellulose consisting two steps, alkali treatment and bleaching process. The carboxymethylation reaction consist two steps, alkalization and etherification of cellulose under heterogeneous condition [8]. For alkalization, 5% cellulose was suspended in isopropyl alcohol, and 20% NaOH was added to the mixture under mechanical stirring at room temperature for 1 hour to yield alkali cellulose. Etherification reaction was continued by the addition of SCA to the mixture for 30 min. It was left to stir and heated up to reaction temperature of 50°C for 4 hours. The mixture was terminated by adding alcohol. Carboxymethyl cellulose was then recovered by filtration and washed three times with methanol. Finally, the product was dried at 50°C in cabinet drier.

Preparation of Film

Composite polymer electrolytes were prepared by dissolving MG49 in conical flasks containing THF for 24 hours. The solution was then stirred with efficient magnetic stirring for the next 24 hours until complete dissolution of MG49. Salt solution with 25% $LiCF_3SO_3$ salt was stirred in THF solution and added to the MG49 solutions for the next 24 hours with continuous stirring. THF suspension of carboyxmethyl cellulose was added to the MG49/salt in conical flask with continuous stirring for 24 hours to obtain a homogeneous solution. The electrolyte solutions were cast onto a glass petri dish and the solvent was allowed to slowly evaporate at room temperature for 24 hours. Resulting films were dried under vacuum oven for 24 hours at 40^oC to remove remaining solvents. The films were then kept in desiccators for further use.

Sample Characterization

Ac impedance measurement was carried out using a high frequency resonance analyzer (HFRA): Solartron model 1260 with applied frequencies from 1 MHz to 0.1 Hz at a perturbation voltage of 1000 mV. The samples were placed between two stainless-steel blocking electrodes. The bulk impedance (R_b) value was obtained from the plot of negative imaginary impedance (*Zi*) versus real part (*Zr*) of impedance. The conductivity of electrolytes was calculated from the equation 1,

$$\sigma = \frac{l}{R_b A} \tag{1}$$

where; A = Area of film-electrode contact and l = thickness of the film (in cm) [1]. Electrochemical stability window also carried out to complete the electrochemical testing. It was evaluated by linear sweep voltametry. Mechanical performance of the films was evaluated tensile strength and Young's modulus with universal testing machine (Instron model 5566, USA) at room temperature according to ASTM D882. A crosshead speed of 50 mm/min, initial grip distance of 40 mm and load cell of 50 N were used to perform this test. The samples were cut into a dumbbell shape and average value of 5 replicates for each sample was taken. Morphological characterization of the samples was performed by Zeiss Supra 55VP scanning electron microscope (SEM).

Results and Discussion

Ionic Conductivity Study

Table 1 shows the variation of conductivity values of polymer electrolytes at room temperature. The conductivity of the carboxymethyl cellulose polymer electrolytes systems at room temperature is illustrated in Fig. 2. The conductivity of polymer electrolytes is expected to increase after addition of carboxymethyl cellulose. This is due to the modification of cellulose will enhance the amorphous phase of systems. Thus, polymeric chains in the amorphous phase become more flexible which results in the enhancement of segmental motion of the polymer [5].

It can be seen in Fig. 2 that ionic conductivity increases with the amount of carboxymethyl cellulose up to a maximum of 6.5×10^{-6} Scm^{-1} for the sample containing 6 wt% of carboxymethyl cellulose. The increase in ionic conductivity is strongly ascribed to the effective interaction between oxygen atoms and lithium ions in the electrolytes [1]. Mobarak et al. [5] reported that the amount of oxygen was increase after modification of cellulose with sodium chloroacetate. By increasing the amount of oxygen, the conductivity value of samples also will increase accordingly. The ionic conductivity value is comparable with the previous studies that using synthetic filler. Low et al. [9] produced nanocomposite polymer electrolyte with the titanium dioxide (TiO_2) as inert ceramic filler and the highest conductivity achieved was 1.4×10^{-5} $Scm^{-1}$with 6 wt.% filler. It is found that ionic conductivity achieved maximum value (1.0×10^{-7} Scm^{-1}) at 12 wt.% Al_2O_3 as reported by [10].

However the addition of carboxymethyl cellulose higher than 6 wt% shows the reduction of the ionic conductivity. The conductivity rapidly reduced with high percentage of carboxymethyl cellulose loading due to fibre agglomeration, which reduced the Li^+ ion mobility and thus the bulk conductivity [11].

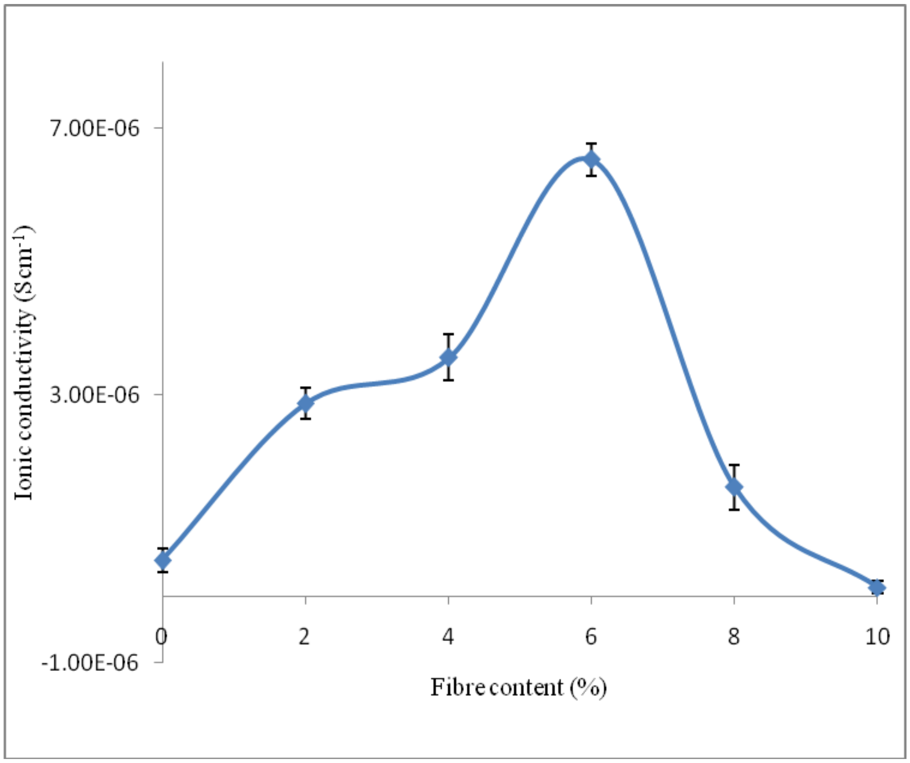


Figure 2. Ionic conductivity of composite polymer electrolytes at the variation of fibre content

Table 1. The ionic conductivity of composite polymer electrolyte MG49-$LiCF_3SO_3$-Carboxymethyl cellulose

Carboxymethyl Cellulose content, wt%	**Conductivity, σ [Scm^{-1}]**
0	5.3×10^{-7}
2	2.9×10^{-6}
4	3.6×10^{-6}
6	6.5×10^{-6}
8	1.6×10^{-6}
10	1.3×10^{-7}

Linear Sweep Voltammetry

Electrochemical stability window was carried out by choosing the sample at the highest ionic conductivity which is 6 wt% of carboxymethyl cellulose. For lithium battery, the anodic reaction occurs in the vicinity of 0 V (vs. Li), while the cathode potentials can be approached as high as 4.5 V (vs. Li) [12]. MG49/carboxymethyl cellulose/$LiCF_3SO_3$ film shows an appreciably high anode breakdown voltage which makes it suitable in battery application. From the current-voltage obtained in the voltage range 0 and 5.0 V (vs. Li) at room temperature by linear sweep voltametry can be seen in Figure 3. The plateau is flat and straight with wide ESW which no electrochemical reactions occurs at positive potentials ranging from the lithium plating to above 2.7 V (vs. Li) at 25°C. Composite polymer electrolytes system is sensitive to oxygen, water and other impurities [13]. Therefore, this system can be categorized as pure system because it gives very low residual current level prior to breakdown voltages, which no peaks at the lower voltage ranges. The increase of current during anodic scan was taken in correspondence to the onset of a low current peak at ~2.7 V related the decomposition of the electrolytes [2].

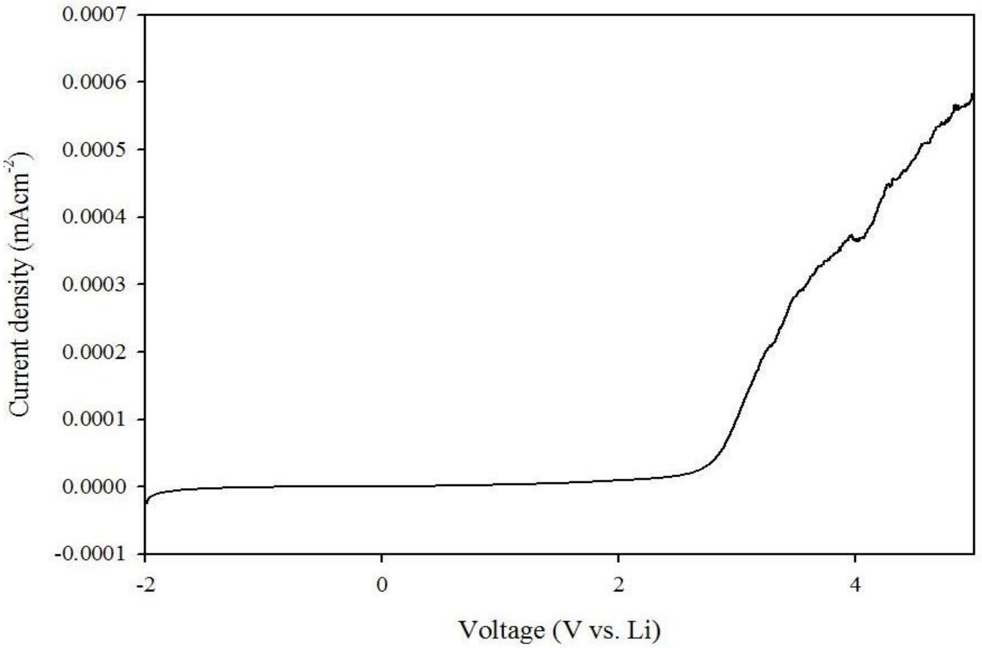


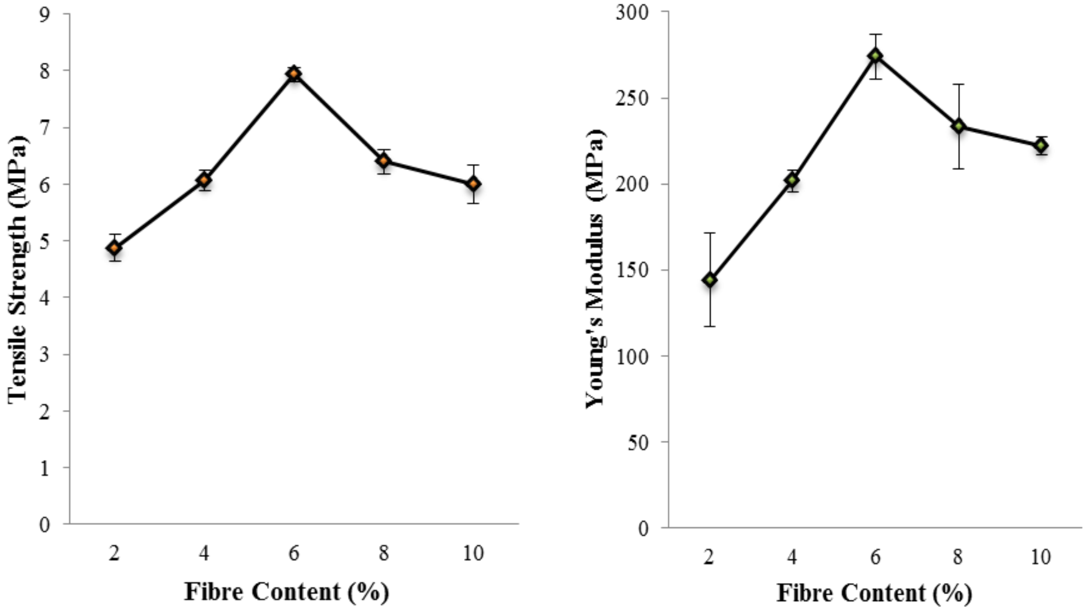
Figure 3. Current vs voltage curves in the anodic voltage range

Mechanical Properties

Figure 4 shows the effect of the carboxymethyl cellulose loading on the tensile strength and Young's modulus of the composite polymer electrolytes. The result showed the increase of tensile strength with filler loading. It is noted that 2 wt% of carboxymethyl cellulose show the lowest tensile strength value at 4.9 MPa. The optimum value for the composite polymer electrolytes films is 7.9 MPa obtained at 6 wt% carboxymethyl cellulose loading. The increase is due to effective interaction between carboxymethyl cellulose and MG49 or salt. This is explained by the increase of uniformity that contributes to the increase in strength. The formation of a rigid percolating cellulose fiber network also assumed to be formed through strong hydrogen bonds interactions in carboyxmethyl cellulose fiber [11].

Moreover, Young's Modulus also can be considered high for small amount fiber upon addition of $LiCF_3SO_3$. Polymer electrolytes films with 6 wt% carboxymethyl cellulose showed the optimum value of the modulus which is 273 MPa. This due to a stabilizing effect of the salt which may lead to better dispersion cellulose on the polymer matrix [14].

However, when the percentage of fibre further increased up to 8-10 wt% the tensile strength and Young's Modulus was decreased. The reduction is due to non-uniform distribution of carboxymethyl cellulose in the matrix. The increasing of the cellulose concentration cause the rigidity of network is increase and agglomeration occurred. So, the mechanical behaviour of polymer electrolytes will decrease for 8-10 wt% of fibres. These results reveal that the incorporation of carboxymethyl cellulose into MG49 matrix is quite effective reinforcement.



(a) (b)

Figure 4. Graph of the a) tensile strength, b) Young's Modulus of composite polymer electrolytes

Morphological Investigation

The morphology of the films was characterized by SEM analysis. SEM micrographs were obtained from cross-section on the polymer electrolytes based MG49, carboxymethyl cellulose and $LiCF_3SO_3$ salt. SEM micrographs for (a) pure MG49, (b) 0 wt% carboxymethyl cellulose, (c) 6 wt% carboxymethyl cellulose and (d) 10 wt% carboxymethyl cellulose are shown in Figure 5. It can be seen from that a pure MG49 film shows a rough morphology with some rumples. Differences in the phase structure can be observed due to the existence of dark and bright areas on the surface that represent the crystalline and the amorphous phase fraction, respectively. From Fig. 5b, the white dots can be interpreted as carboxymethyl cellulose fibres in MG49 composite polymer electrolytes with no apparent aggregates [3]. A homogeneous distribution of white dots was observed due to the good dispersion of carboxymethyl cellulose in MG49.

The blending of MG49 with salt and carboxymethyl cellulose, improved surface morphology to be smoother compared to the pure MG49. The addition of 6 wt% of carboxymethyl cellulose seems to be optimum percentage of fibre as shows in Fig. 5c with smoother surface compare to 10 wt% carboxymethyl cellulose. Therefore, the highest conductivity obtained with the addition of 6 wt% carboxymethyl cellulose is represented by overall mobility of ion in polymer matrix which leads to the increase in ionic and segmental mobility. The smoother surface morphology may associate with a reduction in the degree of crystallinity of the polymer matrix after the addition of salt and fibres. This was due to the formation of coordinate bonds of lone pair electrons of oxygen atoms from MMA with Li^+ ions from the salt to form polymer complexes [1].

From Figure 5 (e), we can see some agglomeration occurred for the sample with higher amount of carboxymethyl cellulose which resulted in the reduction of mechanical properties of SPEs. These observation support the conductivity result that shows the ionic conductivity of polymer electrolytes decreased after addition more than 6 wt% of carboxymethyl cellulose.

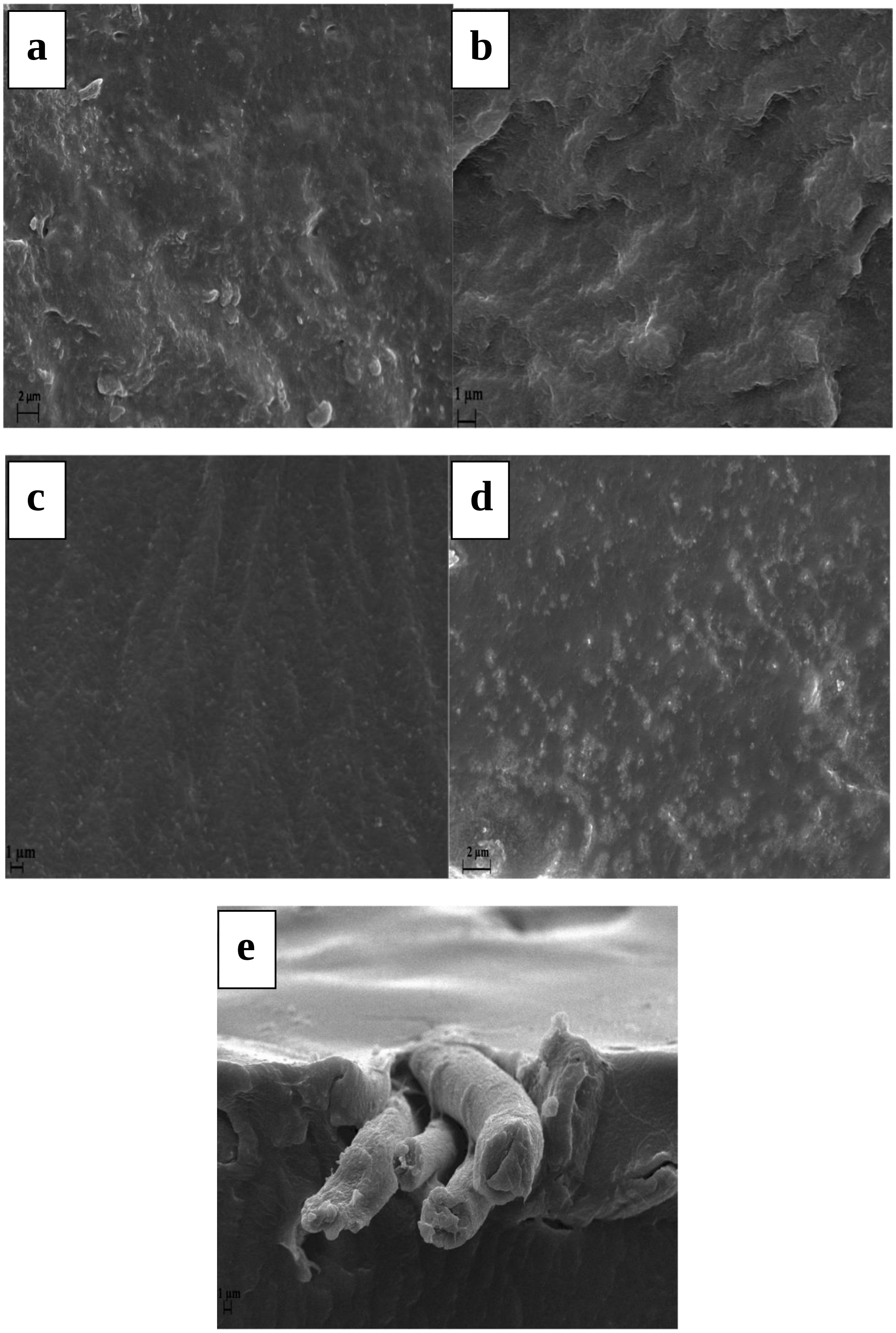


Figure 5. SEM micrographs of composite polymer electrolytes a) pure MG49; b) 0 wt% c) 6 wt%; d) 10 wt% of carboxymethyl cellulose with 1.0 Kx magnification; e) 10 wt% of carboxymethyl cellulose with 2.5 kx magnification

Conclusion

The development of modified natural rubber incorporating carboxymethyl cellulose has potential in composite polymer electrolytes system. The highest conductivity achieved was 6.5×10^{-6} Scm^{-1}. The electrochemical stability window (~2.7 V (vs.Li)) evidenced a wide window and interesting performed in real battery application. The incorporation of carboxymethyl cellulose in lithium polymer electrolytes leads to high-performance composite electrolytes with 6 wt% carboxymethyl cellulose loading showed the optimum tensile strength and Young's modulus with the of values of 7.9 MPa and 273 MPa respectively. From these results, we summarized that the promising reinforced with natural fibre polymer electrolytes could be used in various electrochemical energy sources which demonstrate both high ionic conductivities and good mechanical characteristics.

Acknowledgement

The authors would like to thank Universiti Kebangsaan Malaysia for the permission for this research to be carried out within the university premises. Financial support was received from the Ministry of Higher Education under research grant numbers ERGS/1/2012/STG01/UKM/02/4 and UKM-DLP-2012-02.

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