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Ionic conductivity and related studies of polymer electrolytes based on poly(ε-caprolactone)

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ABSTRACT

Poly(ε-caprolactone) (PCL)-based polymer electrolytes (PE) were prepared by solution casting. PCL has excellent properties of biocompatibility and biodegradability leading to wide applications in the biomedical field. In this work, PCL was used as a polymer host to reduce environmental impact. Ammonium thiocyanate (NH_4SCN) salt was incorporated as the source of charge carriers. Ethylene carbonate (EC) was added as the chain lubricant to enhance ionic conductivity of the PE system. Two systems (PCL-NH_4SCN and PCL-NH_4SCN-EC) were prepared and characterized by using differential scanning calorimetry (DSC), scanning electron microscope (SEM), x-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and electrochemical impedance spectroscopy (EIS). The pure PCL exhibited ionic conductivity of 1.86×10^{-10} S cm^{-1} at room temperature. The highest conductivity of PCL-NH_4SCN system was 3.94×10^{-7} Scm^{-1} with addition of 26 wt.% NH_4SCN. A further conductivity enhancement was observed with addition of EC to the highest conducting PCL-NH_4SCN sample. The highest conductivity of PCL-NH_4SCN-EC system was 3.82×10^{-5} S cm^{-1} at 50 wt.% EC concentration. Vogel-Tamman-Fulcher (VTF) fitting of the temperature dependent conductivity showed that the ionic motion was coupled with polymer segmental motion. The addition of EC had improved the dissociation rate of free ions and also made the polymer chain more flexible to facilitate ionic motion. Deconvolution of the SCN^- stretching mode of the FTIR spectrum reveals that the increase in salt concentration results in the increase in number density of free ions. On the other hand, the incorporation of EC was observed to dissociate contact ion pairs and ion aggregates contributing to more free ions. FTIR analysis also demonstrated interactions between PCL and NH_4SCN, PCL and EC and between EC and NH_4SCN through appearance of new shoulder, changes in peak intensities and shifts in peak position. Incorpoaration of

EC has introduced new pathways with shorter jump distance for the cation to move from one complex site to another. VTF fitting showed that the calculated pseudo energy of PCL-NH_4SCN-EC system was one order lower than PCL-NH_4SCN system. The complexation in the PCL-NH_4SCN and PCL-NH_4SCN-EC systems were supported by DSC studies. The melting enthalpy calculation shows an increase in amorphousness in the two systems. However, the glass transition temperature, T_g was found to increase gradually in the PCL-NH_4SCN system but decreased drastically in the PCL-NH_4SCN-EC system. The semi-crystalline nature of the PE films was revealed by XRD. When the sharp crystalline peaks were decomposed from the broad amorphous spectrum, the relative degree of crystallinity was estimated and the values obtained were in agreement with DSC results. EC molecules were trapped into the polymer matrix and disrupting some regions of the crystalline phase. From morphology studies using SEM, large spherulites were observed for pure PCL film. As more salt was incorporated to PCL until 26 wt.%, the number of spherulite was observed to increase with a reduction in their size. Upon addition of EC, the clear spherulite boundaries faded away and eventually showed a homogeneous smooth surface.

ABSTRAK

Polimer elektrolit yang berasaskan poli(ε-kaprolakton) (PCL) telah disediakan melalui kaedah acuan larutan. PCL mempunyai ciri-ciri yang cemerlang dalam biokompatibiliti dan biodegradabiliti. Ini membawa aplikasi yang luas dalam bidang bioperubatan. Dalam karya ini, PCL telah digunakan sebagai matriks polimer untuk mengurangkan kesan buruk terhadap alam sekitar. Garam ammonium tiosianat (NH_4SCN) digunakan sebagai sumber cas. Etilena karbonat (EC) pula ditambah sebagai pelincir rantai untuk meningkatkan kekonduksian ionik. Dua sistem (PCL-NH4SCN dan PCL-NH4SCN-EC) telah disediakan dan dicirikan dengan kalorimetri imbasan pembezaan (DSC), mikroskopi elektron (SEM), pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR) dan spektroskopi impedans electrokimia (EIS). Nilai kekonduksian PCL tulen pada suhu bilik ialah 1.86×10^{-10} S cm^{-1}. Nilai ini telah meningkat kepada 3.94×10^{-7} S cm^{-1} dengan penambahan 26 wt.% NH_4SCN. Peningkatan yang berikutan berlaku dengan penambahan EC pada sampel sistem PCL-NH_4SCN yang berkekonduksian tertinggi. Nilai kekonduksian yang tertinggi untuk sistem PCL-NH_4SCN-EC adalah 3.82×10^{-5} S cm^{-1} dengan penambahan EC 50 wt.%. Pemadanan Vogel-Tamman-Fulcher (VTF) ke atas pergantungan kekonduksian terhadap suhu menunjukkan bahawa pergerakan ion seiring dengan pergerakan segmen polimer. Penambahan EC telah meningkatkan kadar penceraian ion bebas dan juga menjadikan rantai polimer lebih fleksibel bagi membantu pergerakan ion. Dekonvolusi mod regangan SCN^- menunjukkan bahawa penambahan garam telah meningkatkan bilangan ion bebas. Manakala penambahan EC dapat menceraikan lebih banyak ion pasangan dan ion agregat, menyumbang kepada lebih banyak ion bebas. FTIR analisis juga menunjukkan interaksi di antara PCL dan NH_4SCN, PCL dan EC , EC dan NH_4SCN melalui penampilan bahu baru, perubahan ketinggian dan kedudukan

puncak. Penambahan EC telah memperkenalkan laluan baru untuk ion melompat dengan jarak lebih pendek. Pemadanan VTF menunjukkan bahawa tenaga pseudo untuk sistem PCL-NH_4SCN-EC adalah sepuluh kali lebih rendah daripada sistem PCL-NH_4SCN. Kompleksasi kedua-dua sistems PCL-NH_4SCN dan PCL-NH_4SCN-EC juga disokong oleh DSC analisis. Pengiraan entalpi perleburan menunjukkan sifat amorfus sampel untuk kedua-dua sistem meningkat. Walau bagaimanapun, suhu transisi kaca, T_g untuk sistem PCL-NH_4SCN didapati meningkat secara beransur-ansur tetapi T_g untuk sistem PCL-NH_4SCN-EC menurun secara drastik. Sifat separuh-hablur boleh ditunjukan melalui XRD. Apabila puncak-puncak tajam hablur diasingkan daripada spectrum amorfus yang luas, nilai-nilai peratusan penghabluran relative boleh dianggarkan. Nilainya setuju dengan keputusan DSC. Molekul-molekul EC yang tersekat di dalam matriks polimer telah mengganggu sebahagian fasa habluran. Dari kajian morfologi SEM, sferulit-sferulit besar dan jelas telah diperhatikan dalam sampel PCL tulen. Apabila PCL ditambahkan dengan 26 wt.% garam, bilangan sferulit bertambah sementara saiznya berkurang. Kesan penambahan EC telah menghilangkan sempadan sferulit dan akhirnya memberikan permukaan yang licin sekata.

PUBLICATIONS

Articles published in ISI-cited journals:

- Woo, H.J., Majid, S.R., Arof, A.K., Conduction and thermal properties of a proton conducting polymer electrolyte based on poly (ε-caprolactone), Solid State Ionics 199-200 (2011) 14-20.

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- Woo, H.J., Majid, S.R., Arof, A.K., Proton conducting polymer electrolyte based on poly (ε-caprolactone), 3^{rd} International Conference on Functional Materials & Devices 2010 (ICFMD-2010), Permai Inn Hotel, Kuala Terengganu, Malaysia, 14^{th} – 17^{th} June 2010.

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- Woo, H.J., Majid, S.R., Arof, A.K., Ionic conductivity and related studies of polymer electrolytes based on poly(ε-caprolactone), Physics Colloquium 2013, Physics Department, University Malaya, Malaysia, 4^{th} – 5^{th} June 2013.

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