UNIVERSITI TEKNOLOGI MARA

THERMAL PROPERTIES AND DIELECTRIC BEHAVIOUR OF POLY(ETHYLENE OXIDE)/POLYACRYLATE WITH AND WITHOUT SALT

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ABSTRACT

Immiscible blends of poly(ethylene oxide) (PEO)/polyacrylate (PAc) were reported on enhancement of conductivity but silent on the mechanical properties of the materials. Hence, in this study, by simple melt mixing of PEO/PAc, miscible blends can be prepared. Mechanical properties of the miscible blends are normally additives to the parent polymers. Blends of salt-free PEO/PAc, PEO/PAc 100/0, 85/15, 75/25, 50/50, 25/75 and 0/100 added with lithium perchlorate (LiClO₄) of concentrations (Y_S) from 0.005-0.30 (w/w) were prepared via solution casting method. Thermal properties of the salt-free and salt-added of the PEO/PAc blends were characterised by differential scanning calorimetry (DSC) and polarized optical microscope (POM). The impedance spectroscopy (IS) and dynamic mechanical analysis (DMA) used to study the dielectric behaviour of the blends. Miscibility of the salt-free PEO/PAc blend is marked by the presence of a single composition dependent glass transition temperature (T_g) and the continual suppression of the melting temperature (T_m) , equilibrium melting temperature (T_m^0) and degree of crystallinity (X^*) of PEO with ascending PAc content. A reduction in the rate constant (K_A) with increasing PAc content evaluated using Avrami equation indicates restricted crystallization of PEO in the homogeneous PEO/PAc blend. Meanwhile, miscibility of the PEO/PAc/LiClO₄ blend is evident in the presence of a single T_g and a decrease in the radial spherulite growth rate of PEO. Morphology result shows that the as-prepared blend with 15 wt% PAc displays co-continuous amorphous region transverse through the entire PEO matrix. No crystal is observed when PAc content is > 30 wt%. Coarsening of PEO lamellae and distorted morphology of PEO spherulites spotted with dark regions are observed in the neat PEO and the PEO/PAc 85/15 blend when $Y_s = 0.02$ of LiClO₄ is added. PEO/PAc 85/15 blend doped with Y_s =0.12 of LiClO₄ exhibits the highest DC conductivity (σ_{DC}) of 2.9 x 10⁻⁵ S cm⁻¹ suggesting firstly the preferential coordination of the salt to PEO as compared to PAc and secondly the amorphous phase of PEO forms the percolation pathway for ion-transport in the blend. A relaxation peak is observed at the high frequency of the plot between the imaginary dielectric modulus (M'') and frequency. Shifting of the relaxation peak towards higher frequency with increasing salt content reflects the shortening of the relaxation time of PEO leading to an increase in the ionic charge carrier. DMA analysis shows a high E' value (in the range of $10^8 - 10^9$ Pa) for neat PEO impling that it has a high density of chain alignment. All the compositions of both the salt-free and the salt-added blends behave dominantly elastic or solid-like as evident from the higher value of E' as compared to E''. However, the elastic characteristic of the salt-added blend becomes more viscous liquid-like as the concentration of salt is increased.

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CHAPTER ONE INTRODUCTION

1.1 GENERAL

Polymer is formed by connecting repeating structural units called monomers via covalent bonds. The unique properties of polymer which include food packaging, clothing, transportation, medical devices and so forth are extremely useful to mankind. Polymer can be classified as thermoplastic, thermoset and elastomer. Above a specific temperature, thermoplastic becomes pliable or mouldable but returns to its original solid state upon cooling without any significant degradation. The macromolecular chains of thermoplastic are associated through intermolecular interactions which strengthened upon cooling, thus bringing about remoulding in thermoplastic and restoring its bulk properties. High impact polystyrene is one of the commercial thermoplastics commonly used as vacuum-formed packaging and casing. On the contrary, thermoset cannot be remoulded or recycled and may be degraded in the reheating process. Meanwhile, elastomer is a polymer with good viscoelasticity, generally low Young modulus and high failure strain compared with other materials. Elastomers such as natural rubber are amorphous polymers that exist only above their glass transition temperature (T_g).

Polymers can be categorized into natural and synthetic polymers. Natural polymers like fibre, wool, cotton and natural rubber have been used in the manufacturing of textile and many domestic materials such as gloves, bags etc. In the 19th century, some natural polymers were chemically modified to produce materials of improved and varied properties so as to widen the applications of natural polymer. Epoxidized natural rubber (ENR) is an example of a chemically modified natural rubber. After World War II, owing to the shortage of natural resources and the great demand of materials to cater for industrial development, synthetic polymers begin to gain popularity especially in the construction and automobile sectors. In fact, extensive research has been done in an attempt to replace natural polymer with synthetic polymer because of low cost in production and the possibility of tailoring the properties of synthetic polymers for specific applications.