EFFECT OF POLYANILINE LOADING, TYPES OF SURFACE MODIFIERS AND SECONDARY DOPING PROCESS ON THE PROPERTIES OF POLY (VINYL CHLORIDE) / POLY (ETHYLENE OXIDE) / POLYANILINE CONDUCTIVE FILMS

by

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LIST OF ABBREVIATIONS

1D	One dimension
2D	Two dimension
3D	Three dimension
ABS	Acrylonitrile-butadiene-styrene
AFM	Atomic force microscopy
APS	Ammonium persulfate
ASTM	American Society for Testing and Materials
CB	Carbon black
CPC	Conductive polymer composites
DBP	Dibutyl phthalate
DDS	Drug delivery systems
DOA	Dioctyl adipate
DOTP	Dioctyl terephthalate
DSC	Differential scanning calorimetry
E^0	Oxidation potential
EB	Emeraldine base
EC	Ethylene carbonate
EDMA	Ethylene dimethacrylate
EGDMA	Ethyleneglycol dimethacrylate
EMI	Electromagnetic interference
ER	Electrorheological
ES	Emeraldine salt
ESCR	Environmental stress cracking resistance

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eV	Electron volt
EVA	Ethylene vinyl acetate
FIT	Fluctuation induced tunneling
FTIR	Spectroscopy infrared analysis
HCSA	*d,l*-camphorsulfonic acid
HDPE	High density polyethylene
HIPS	High-impact polystyrene
ICPs	Intrinsically conducting polymers
IUPAC	Council of the International Union of Pure and Applied Chemistry
$KMnO_4$	Potassium permanganate
LDPE	Low density polyethylene
LEDs	Light emitting diodes
M_W	Molecular weight
MWCNT	Multiwall carbon nanotubes
N66	Nylon66
NaDDBS	Sodium dodecylbenzene sulfonate
OLEDs	Organic light emitting diodes
OM	Optical microscopy
PA	Polyamide
PAni	Polyaniline
PC	Polycarbonate
Pc	Percolation threshold
PE	Polyethylene
PEDOT	Poly 3, 4-ethylenedioxythiophene
PEGDCE	Poly (ethylene glycol) diglycidyl ether

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PEGDE	Poly (ethylene glycol) digycidyl ether
PEGME	Polyethylene glycol methyl ether
PEO	Poly (ethylene oxide)
pH	Potential of hydrogen
Phr	Part per hundred resins
PMMA	Poly (methyl methacrylate)
PP	Polypropylene
PPO	Poly (phenylene oxide)
PPy	Polypyrrole
PS	Polystyrene
PSf	Polysulfone
PTh	Polythiophene
PVC	Poly (vinyl chloride)
SAN	Styrene-acrylonitrile
S/cm	Siemens per centimeter
S/m	Siemens per meter
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
SPM	Scanning probe microscopy
TEM	Transmission electron microscopy
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
T_m	Melting temperature
TP	Thermoplastic

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TS	Thermoset
V	Volt
VRH	Variable range hopping
WAXD	Wide angle X-ray diffraction
Wt.%	Weight percentage
XRD	X-ray diffraction

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LIST OF SYMBOLS

π	Pi
σ	Conductivity
ρ	Resistivity
λ	Wavelength

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Kesan Penambahan Polianilina, Bahan Modifikasi Permukaan dan Proses Doping Sekunder kepada Sifat-Sifat Filem Konduktif Polivinil klorida / Polietilena Oksida / Polianilina.

ABSTRAK

Objektif utama bagi kajian ini adalah untuk menganalisa fungsi polianilina (PAni) sebagai pengisi pengaliran di dalam matriks, polivinil klorida (PVC) / polietilena oksida (PEO). Filem konduktif PVC/PEO/PAni telah dihasilkan melalui kaedah penuangan larutan. Berdasarkan ujian pengaliran elektrik, penelusan ambang bagi filem konduktif ditemui pada pembebanan PAni sebanyak 10 wt.%. Dua pendekatan berbeza telah digunakan bagi menambah baik interaksi PAni / matriks, seterusnya sifat-sifat elektrik, tensil dan termal filem-filem yang dihasilkan. Pendekatan pertama digunakan adalah dengan memperkenalkan bahan modifikasi permukaan di mana keberkesanan dua jenis bahan modifikasi permukaan; etilena dimetakrilat (EDMA) dan naftalena, terhadap peningkatan penyebaran PAni dan juga interaksi PAni / matriks, telah dikaji. Kedua-dua bahan modifikasi permukaan ini telah berjaya menaikkan sifat-sifat tensil, pengaliran elektrik, kestabilan termal dan penyebaran bahan pengisi bagi filem konduktif. Mikrograf SEM juga menunjukkan bahawa penyebaran bahan pengisi menjadi lebih baik dengan adanya bahan modifikasi permukaan. Bagi kaedah yang ke dua, PAni telah melalui proses doping sekunder menggunakan ferik klorida, $FeCl_3$, supaya pengaliran elektrik di dalam filem konduktif bertambah. Malangnya, sifat-sifat tensil dan termal bagi filem konduktif ini telah merosot dengan ketara, akibat pengurangan kualiti penyebaran PAni di dalam PVC/PEO matriks. Polietilena glikol diglicidil (PEGDE) sebagai agen taut silang, ditambah kepada filem konduktif PVC/PEO/PAni-$FeCl_3$ untuk menambahbaik penyebaran PAni dan juga interaksi PAni / matriks. Kesannya, sifat-sifat tensile dan termal telah ditambahbaik, tetapi pengaliran elektrik pula sedikit menurun. Selain daripada faktor penyebaran PAni, faktor kehabluran juga telah dikaji untuk mengaitkan hubungan di antara struktur dan pengaliran elektrik filem-filem dengan pembebanan PAni yang berlainan, penambahan bahan modifikasi permukaan, agen pengoksida dan agen taut silang. Hasil keputusan XRD menunjukkan bahawa kehabluran untuk matriks telah berkurang apabila beban PAni meningkat (sama ada menggunakan bahan modifikasi permukaan atau tidak). Peningkatan fasa amorfus kepada struktur matriks telah menyumbang kepada peningkatan pengaliran elektrik filem konduktif dengan membolehkan lebih banyak pergerakan ion. Akhir sekali, filem konduktif PVC/PEO/PAni, PVC/PEO/PAni/EDMA, PVC/PEO/PAni/naftalena, PVC/PEO/PAni-$FeCl_3$ dan PVC/PEO/PAni-$FeCl_3$/PEGDE pada bebanan PAni sebanyak 10 wt.% telah dibandingkan. Kekuatan tegangan yang paling tinggi dapat dilihat pada filem konduktif PVC/PEO/PAni/naftalena. Tambahan pula, filem konduktif PVC/PEO/PAni/naftalena juga mempamerkan pengaliran konduktif dan kestabilan termal yang paling baik. Naftalena merupakan bahan modifikasi permukaan yang paling mampan bagi membantu penyebaran bahan pengisi PAni di dalam matriks PVC/PEO, dan ini merupakan penyumbang terbesar di dalam penambahbaikan sifat-sifat filem konduktif tersebut. Naftalena juga menunjukkan penurunan kehabluran terhadap matriks. Bahagian amorfus pada filem konduktif PVC/PEO/PAni/naftalena-10 adalah lebih tinggi berbanding filem konduktif yang lain, yang mana menyumbang kepada peningkatan pergerakan ion.

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Effect of Polyaniline Loading, Types of Surface Modifiers and Secondary Doping Process on The Properties of Poly (Vinyl Chloride) / Poly (Ethylene Oxide) / Polyaniline Conductive Films.

ABSTRACT

The main objective of this research was to analyse the role of polyaniline (PAni) as conductive filler in the poly (vinyl chloride)(PVC) / poly (ethylene oxide)(PEO) matrix. The PVC/PEO/PAni conductive composite films were prepared via solution casting method. Based on the electrical conductivity test, the percolation threshold of the conductive films was obtained when 10wt% of PAni was used. Two different approaches were employed to enhance the PAni / matrix interactions in the conductive composite structure, thereby the electrical conductivity, tensile and thermal properties of the produced films. The first approach was to introduce surface modifiers where the efficiency of two types of surface modifiers; ethylene dimethacrylate (EDMA) and naphthalene in enhancing the PAni dispersion and PAni/matrix interactions was studied. Both surface modifiers have successfully increased the mechanical properties, electrical conductivity, thermal stability and filler dispersion of the conductive films. The SEM micrograph also indicated better filler dispersion with the addition of these surface modifiers. In the second approach, PAni was doped using ferric chloride, $FeCl_3$ in order to raise the electrical conductivity of the conductive films. Unfortunately, the tensile and thermal properties of the resultant conductive composite films dropped significantly due to reduced quality of PAni dispersion inside the PVC/PEO matrix. Polyethylene glycol diglycidyl, (PEGDE) was then added into the PVC/PEO/PAni-$FeCl_3$ conductive film as crosslinking agent to improve the PAni dispersion, and also the PAni/matrix interactions. As a result, the tensile and thermal properties were improved, but the electrical conductivity was seen to slightly decreased. Other than the PAni dispersion factor, the crystallinity factor also being examined to correlate between the structure and the electrical conductivity of all the conductive films containing different PAni content, surface modifiers, oxidant and crosslinking agent. The XRD results show that the crystallinity of the matrix reduced when greater amount of PAni was incorporated into the conductive films (with and without surface modifiers). Increased portion of amorphous phase in the matrix structure could also contribute to enhanced electrical conductivity of the conductive film by allowing higher mobility of ions. Lastly, PVC/PEO/PAni, PVC/PEO/PAni/EDMA, PVC/PEO/PAni/naphthalene, PVC/PEO/PAni-$FeCl_3$ and PVC/PEO/PAni-$FeCl_3$/PEGDE conductive films at 10 wt. % PAni loading were compared. The highest tensile properties were displayed by PVC/PEO/PAni/naphthalene conductive film. Moreover, PVC/PEO/PAni/naphthalene conductive film also exhibits the greatest electrical conductivity and thermal stability among all the conductive films. The capability of naphthalene in assisting dispersion of PAni filler inside the PVC/PEO matrix was the best among those surface modifiers, and this was thought to be the main cause of such properties enhancement. Furthermore, the naphthalene was seen to induce the greatest reduction in the matrix's crystallinity. The amorphous portion in the PVC/PEO/PAni-10/naphthalene conductive film was higher as compared to other conductive films, which is beneficial in inducing higher mobility of ions.

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CHAPTER 1: INTRODUCTION

1.1 Research Background

One of the most fascinating and explored areas in materials science and engineering is polymer composite. The recognition comes as no surprise as polymer composites showed promising potential as multifunctional and high performance materials. Polymer composites can be produced via the mixture of polymer matrix with filler which subsequently combines the polymer matrix's characteristics, such as flexibility and low density, with the filler's properties such as mechanical strength, thermal stability and electrical conductivities (Byrne & Gun'ko, 2010; Chou, Gao, Thostenson, Zhang, & Byun, 2010; Sengupta, Bhattacharya, Bandyopadhyay, & Bhowmick, 2011; Winey, Kashiwagi, & Mu, 2007).

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Tremendous efforts have been devoted to the research of polymer composites to improve their mechanical, electrical, thermal, gas barrier and other properties (Ahir, Huang, & Terentjev, 2008; Bauhofer & Kovacs, 2009; Chunyu Li, Thostenson, & Chou, 2008; P.-C. Ma, Siddiqui, Marom, & Kim, 2010; Spitalsky, Tasis, Papagelis, & Galiotis, 2010). In the 1930s, the first conductive polymer composites were claimed to be applied in hindering corona discharge, a form of electrostatic discharge (Goldman, Goldman, & Sigmond, 1985). Conductive fillers such as metal particles, graphite fiber and carbon black are loaded in polymer to produce conductive filled polymers, which also known as, conductive polymer composites (CPCs).

Due to their wide range of applications, tunable properties and ease of processing, conductive polymer composites (CPCs) has remained active for several decades and are

known as one of the most fascinating and significant areas in polymer composite research (Ingo Alig, Pötschke, Lellinger, Skipa, Pegel, Kasaliwal et al., 2012; Bauhofer & Kovacs, 2009; Winey, Kashiwagi, & Mu, 2007). Besides their use in electronic applications (including antistatic, electrostatic painting and electromagnetic interference (EMI) shielding), CPCs have been investigated for many potential electroactive functionalities, including strain/damage, vapour/liquid and temperature sensors, stretchable conductors, shape memory materials and thermoelectric materials (Deng, Lin, Ji, Zhang, Yang, & Fu, 2014). To fabricate CPCs, conductive fillers are incorporated into insulating polymers. With high conductive filler loading, critical filler content in the polymer matrix is achieved, which will subsequently cause a jump in conductivity. The circumstance is referred as the electrical percolation threshold (Pc).

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Many studies have been conducted to decrease Pc, such as through the morphological control of the conductive networks in the polymer matrix. It is believed that the electrical conductivity can be improved through the addition of a small quantity of filler and by altering the filler network formation and filler distribution in the matrix. CPCs' electrical properties arise from their conductive networks and it is regarded that the distance between conductive fillers are in the range of a few nm which were separated by a thin layer of polymer matrix (Ingo Alig, Pötschke, Lellinger, Skipa, Pegel, Kasaliwal et al., 2012; Bauhofer & Kovacs, 2009; Johner, Grimaldi, Maeder, & Ryser, 2009). It is understandable that tunnelling between neighbouring conductive fillers is what has caused most of the overall conductivity in the CPCs.

Intrinsically conducting polymers (ICPs) are organic polymers with electrical, optical and magnetic properties commonly related with metals (MacDiarmid, 2001). ICPs can conduct electricity, owing to their ordered and continuous π-conjugated backbone. The degree of the ICP conductivity relies on its mobility and density of electrons which

functioned as charge carriers (Skotheim & Reynolds, 2006). At the point when ICPs are oxidized, electrons are removed along the backbone which consequently created 'holes'. This phenomenon allowed neighbouring electrons to freely fill the holes, permitting the movement of charge along the polymer. This principle explains why the ICPs' value of conductivity can extend to some orders of magnitude. The application of ICPs has covered numerous areas due to its versatility. ICPs are used in sensing devices, field effect transistors, corrosion inhibitors, light emitting diodes (LEDs), electroluminescent displays, integrated circuits, antistatic coatings and as electromagnetic shielding. In addition, ICPs have also been utilized in biomedical field such as in drug delivery systems (DDS), biosensing and also for nerve regeneration (Svirskis, Travas-Sejdic, Rodgers, & Garg, 2010). There are several polymers which fall under the ICPs category. Among them, polyaniline (PAni) has stood out amongst the most promising ICPs attributable to its ease of synthesis, low production cost, environmentally stable and of course, good electrical properties (S. Bhadra, Khastgir, Singha, & Lee, 2009; C.-H. Chen, 2002). Therefore, PAni is viewed as a solid choice for numerous applications such as actuators, corrosion protection, electromagnetic shielding (EMI), and sensors to name a few (S. Bhadra, Khastgir, Singha, & Lee, 2009; C.-H. Chen, 2002; Mattoso, Medeiros, Baker, Avloni, Wood, & Orts, 2009). Instead of using metal particles as filler, PAni was used in particulate form as filler in this research to produce the conductive polymer composites.

Despites all of the potentials, the poor mechanical and thermal properties of PAni has restricted its viability for high performance applications (S. Bhadra, Khastgir, Singha, & Lee, 2009). This limitation can be overcame through the blending of PAni with a polymer matrix to produce blends or composites (Fattoum, Othman, & Arous, 2012; Han, Cho, Oh, & Im, 2002; John, Joseph, & Mathew, 2007; Yong & Saad, 2009). Various polymer matrices can be utilized in this system, such as rubbers, poly vinyl chloride (PVC), poly

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(methyl methacrylate) (PMMA), epoxy resin, polyurethane and cellulose nanofiber (M. J. d. Silva, Sanches, Malmonge, & Malmonge, 2014).

Although the improvement in electrical conductivity of the polymer matrix is obtained through the incorporation of conductive filler, reduction in mechanical properties and poor processability of the CPC could be induced when high filler loadings is used. This is because, the mechanical properties of particulate-polymer composites depend strongly on the particle-matrix interface adhesion and particle loading. For example, the tensile strength of glass bead filled polystyrene (PS) composites depends on the glass bead particle - PS matrix adhesion and therefore can be improved if the interface adhesion between both constituents is greater (Kojima, Usuki, Kawasumi, Okada, Kurauchi, & Kamigaito, 1993). The addition of coupling agents to the composite systems can assist in the enhancement of the particle-matrix adhesion, and hence improving the tensile strength of the material.

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With regard to the above matter, filler-matrix adhesion is much related to the level of filler dispersion and distribution in the polymer matrix, the aspect which determines the properties of the resultant composites. With poor filler distribution, the composites are expected to have poor mechanical properties. Several researchers have suggested that the conductivity of CPCs is highly affected by the dispersion state of the conductive fillers (Antunes, De Oliveira, Ett, & Ett, 2011; Király & Ronkay, 2013; Pan, Li, Chan, & Zhao, 2010). Carmona and Ravier (2002) illustrates the percolation threshold of polymers filled with carbon black by outlining the significance of the carbon black morphology. They have claimed that the processing conditions influences the filler dispersion in the polymer matrix, thereby the interaction of macromolecular chains with the conductive particles. This in turn, influences the electrical conductivity of the polymer composite. In this study,