CHARACTERIZATION AND PROPERTIES OF CONDUCTIVE POLYMER COMPOSITES POLYCAPROLACTONE/POLYANILINE

by

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In the name of Allah the Most Gracious and The Most Merciful.

With the Selawat and Salam to Prophet Mahammad SAW.

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LIST OF SYMBOLS, ABBREVIATIONS OR NOMENCLATURE

PANI	Polyaniline
CPC	Conductive polymer composites
PPY	Polypyrrole
EMI	Electromagnetic interference
DSEA	Dodecyblenzene sulfonic
PVP	Polyvinyl Pyrrolidone
PCL	Polycaprolactone
ICPs	Intrinsically conducting polymers
ASTM	American standard Tensile Machine
SEM	Scanning Electron Microscopy
TGA	Termogravimetric analysis
°C	Degree Celsius
DP	Dispersion polymerization
DOP	Dioctye phthalate
CNSL	Cashes nut shell liguid
Tg	Glass transition temperatures
Tm	Melting temperature
G/ml	Gram/Milliter
µm	Micrometer
S/cm	Siemens/Centimeter
CB	Carbon Black
3-APE	3-aminopropyltriethoxysilane
min	Minute
rpm	Rotations per minute
TCB	Treated Carbon Black
phr	Part per hundred resins
N_2SA $m^{2/}g$	Nitrogen Specific Surface Area

mm	Millimeter
°C/min	Degree Celsius/Minute
ml/min	Milliter/Minute
SR	Surface Resistivity
php	per part hundred polymer
%	Percentage
Ohm/mm^2	Ohm/Millimeter Square
log	Logarithm
MPa	Mega Pascal
FTIR	Fourier Transform Infrared Spectroscopy
Silane A-174	α- methacryloxypropyltrimethoxysilane
DSC	Differential scanning calorimetry
DMA	Dynamical mechanical analysis
g	Gram
SA	Salt Films
CV	Cyclic Voltammetry
OR	Group of coupling agent
OH	Hydroxyl Group
DC	Dependent Conductivity
SPAN	Sulfonated Polyaniline
PMCs	Polymer Matrix Composites
PET	Polyethylene terephthalate
THF	Tetrahydrofuran

Pencirian dan Sifat-Sifat Konduktif Polimer Komposit Polikaprolakton/Polianilin

ABSTRAK

Penyelidikan ini telah dilakukaan untuk menentukan sifat-sifat komposit polikaprolakton (PCL)/Polianilin (PANI). Kesan kandungan hitam karbon (CB) dan agen pengkupel silana, 3-aminopropiltrietoksilana (3-APE) ke atas sifat-sifat mekanikal, sifat-sifat terma dan morfologi juga telah dikaji. Komposit PCL/PANI telah disediakan menggunakan pencampur Brabender Plastograf EC-PLUS pada suhu 60 °C dan halaju rotor 50 rpm selama lima minit. Keputusan-keputusan menunjukkan bahawa dengan meningkatnya kandungan PANI kekuatan tensil dan pemanjangan pada takat putus berkurang, tetapi modulus elastisiti dan ketahanan terma di dapati meningkat. Keberintangan isipadu yang rendah dan konduktifiti yang tinggi ditunjukkan pada kandungan PANI 3 php. Kecenderungan yang sama seperti komposit PCL/PANI, dimana kekuatan tensil dan pemanjangan pada takat putus di dapati berkurang tetapi modulus elastisiti meningkat. Sifat-sifat terma menunjukkan kencederungan bahawa dengan meningkat kandungan CB ketahanan terma meningkat. Bagaimanapun, rawatan CB dengan 3-APE telah member kesan yang nyata, dimana komposit PCL/PANI/CB yang dirawat mempunyai kekuatan tensil dan pemanjangan pada takat putus yang lebih tinggi, tetapi rendah pada modulus elastisiti dibandingkan komposit tanpa rawatan. Keputusan ini disokong dengan kajian SEM, dimana agen pengkupel silana telah meningklatkan pelekatan antaramuka diantara CB dan komposit PCL/PANI.

Characterization and Properties of Conductive Polymer Composites Polycaprolactone/Polyaniline

ABSTRACT

This research was done to determine the properties of polycaprolactone (PCL) Polyaniline (PANI) composites. The effect of carbon black (CB) content and silane coupling agent, 3-aminopropyltriethoxysilane (3-APE) on mechanical properties, thermal properties and morphology were also studied. The PCL/PANI composites were prepared by using Brabender Plastograph mixer EC-PLUS at temperature 60 °C and rotor speed 50 rpm for five minutes. Results showed that the increasing of PANI content have decreased the tensile strength and elongation at break, but increased the modulus elasticity and thermal stability of PCL/PANI composites. The lower volume resistivity and higher conductivity is shown at 3 Php of PANI content. The addition of carbon black (CB) into PCL/PANI composites exhibited similar tendency as neat PCL/PANI composites, where tensile strength and elongation at break decreased but modulus of elasticity increased. The thermal properties indicate that the increasing of CB content increased the thermal stability of PCL/PANI/CB composites. However, treatment of CB with 3-APE has significant effect in composites. The treated PCL/PANI/CB composites have higher tensile strength, elongation at break and thermal stability but lower modulus of elasticity compared untreated composites. This result was supported by SEM study, where the silane coupling agent has enhanced interfacial adhesion between CB and PCL/PANI composites.

CHAPTER 1

INTRODUCTION

1.1 Research Background

One of the major objectives in conducting polymer research is production of materials that combine and ready processing properties of common thermoplastic polymers with significant electrical of conductivity (Davies et al. 1995; Xie et al. 1999). Generally, polymers are known as insulator in nature due to non polarity character; however latter discoveries observed that the presence π – conjugation in the backbone of main chain imparts conductive properties for some polymers.

Conductive polymers are a suitable replacement for inorganic materials since exhibit extraordinary electrical properties and a wide variety in which due to their conjugated double bond chain structure, which derives from their conducting or neutral (non-conducting) forms. However, their properties such as insoluble in common organic solvent, inflexible and non-processable due to strong intermolecular interaction become drawback and far from satisfactory for many applications (Luo et al. 2007).

Owing to this problem, many attempts have been developed such as blends with conventional polymers by melt mixing (Basheer et al. 1999; Hosier et al. 2001; Omastova et al. 1996; Reghu et al. 1993; Yang & Rannou, 1998; Zilberman, 1997), or by solution casting (Cao et al. 1995; Gettinger et al. 1995; Reghu et al. 1993; Titelman et al. 1997; Yin & Yoshino, 1997).

Polycaprolactone (PCL) is known as linear hydrophobic and partially crystalline polyester which produced from renewable resources. It makes PLC as a biodegradable polymer that can be slowly consumed by microorganisms. PCL as a high physical strength polymer has received much attention in the research of alternative biodegradable and biocompatible polymers. This fact is responsible for growing interest in PCL for many applications, as it expected to reduce an impact on the environment caused by the production and utilization of petrochemical polymers (Souza et al. 2007). These properties make PCL as a good candidate for blend with conductive polymers in order to obtain conductive properties (Jang et al. 2000).

Among the conjugated conducting polymers, Polyaniline (PANI)) has attracted much interest worldwide because of high environmental thermal and chemical stability and high conductivities. The electrical conductivity of this polymer is between 10^{-5} S/cm and 10^{2} S/cm which being doped, whereas common insulator exhibit conductivities below 10^{-12} S/cm. Currently, Polyaniline (PANI) is one of the most extensively studied conductive polymers. Potential applications include uses in rechargeable batteries, sensors (Dispenza et al. 2006), switchable membranes (Souza et al. 2007), anticorrosive coatings, and electronic devices (Cho et al. 2004).

Polyaniline (PANI) is commercially attractive owing to its easy synthesis either through chemical or electrochemical methods, good environmental stability, ease of conductivity control, and inexpensive production in large quantities. However, like other conductive polymers, polyaniline by itself cannot be easily fabricated as a thin film form with good mechanical properties. Thus, its practical use has been limited (Gamgopadhyay et al. 2001).

As reported previously, polyaniline (PANI) blends can be prepared by blending polyaniline with other polymers in solution or in the melt state. Alternatively, aniline can be polymerized chemically or electrochemically in a solution of a matrix polymer. Polymers that have been used to prepare conductive polyaniline blends include epoxy resin polyethylene (Gamgopadhyay & De, 2002), poly(vinyl alcohol), polystyrene and poly(acrylic acid).

Except blend with conductive polymers, conductive materials can also improve conductive properties of the conventional polymer as reinforced fillers. Many materials have been used as reinforced fillers, such as metal particles, carbon black, graphite or carbon nanotubes (Bellingen et al. 2002; Feller et al. 2002; Tan & Zhang, 2001).

Carbon black (CB) is known as reinforcing filler for some polymers. At the same time, the electrical conductivity of polymer/CB composites increases sharply at a critical filler concentration, because of the formation of a three-dimensional conductive network throughout the polymer matrix (Zhijun & Xingxiang, 2009). The conductive polymer composites can be obtained, which have a wide variety of potential application such as self-regulated heating, positive temperature coefficient materials, antistatic plastics, electromagnetic shielding, and environmentally sensitive membranes because of their resistivity change with mechanical, thermal, electrical, or chemical solicitations.

1.2 Problem Statement

It is been described that the main problem associated with the effective utilization of all conductive polymers including polyaniline (PANI) is poor mechanical performance and difficult to process. In order to overcome this problem, conductive polymer composites (CPC) have been developed by blending conductive polymer and/or reinforcing filler with conventional polymer. Polymer composites containing polyaniline and/or carbon black, where they are used as conducting filler in other polymers (matrixes), have received much attention because of the combination of improved processability and fairly good mechanical properties with good conductivity.

1.3 Objectives

The objectives of research are to investigate the conductive polymer composites from PCL/PANI and PCL/PANI/CB composites.

1. To study the effect of polyaniline (PANI) in polycaprolactone (PCL) conductive polymer composites on mechanical, electrical, thermal properties and morphology.
2. To study the effect of carbon black (CB) in properties of PCL/PANI conductive polymer composites.
3. To study the effect of coupling agent on properties of PCL/PANI/CB composites.

1.4 Scope

The scope of this project is to prepare the samples of polymer (PCL /PANI) blend with different formulation of polyaniline (PANI), carbon black (CB), and chemical treated carbon black. All formulated PCL composites was prepared through melt compounding by using Brabender Plastograph mixer. The all compounded sample was compressed into tensile bar regarding to ASTM D638 by compression molding. Furthermore, the mechanical properties (e.g., tensile strength, modulus of elastic, and elongation at break) of PCL/PANI composites were study through Instron universe tensile machine. The morphology studies on filler distribution and fracture properties can conduct thought the scanning electron microscopy (SEM). Besides, electric properties of the composites were studied by using resistivity meter, where the surface of resistivity can be measured. The thermal properties of PCL composites were carry out by using Thermogravimetry analyzer (TGA).

CHAPTER 2

LITERATURE REVIEW

2.1 Composites

Composite material are materials that are mixtures of two or more micro or macro constituent with and interface separating them that differ in form and chemical composition and are essentially insoluble in each other (William & Callister, 2007; William & Javad, 2006). Besides, composite materials or composites for short are engineered materials made from two or more constituent materials with significantly different physical or chemical properties and which remain separate and distinct on a macroscopic level within the finished structure (Khashaba & Seif, 2006). Fiberglass reinforced material in polyester or epoxy is one of the familiar examples. A composite is design to display a combination of the best characteristics of each of the component materials (William & Javad, 2006).

Figure 2.1 show the classification of composite materials, which consist of three main division: particle-reinforced, fiber-reinforced and structural composites; also, at least two subdivision exits for each. The dispersed phase for particle-reinforced composite is equaled (i.e., particle dimensions are approximately the same in all directions); for fiber-reinforced composites, the dispersed phase has the geometry of a fiber (i.e., a large length-to-diameter ratio). Structural composites are combination of composites and homogeneous materials (William & Callister, 2007).

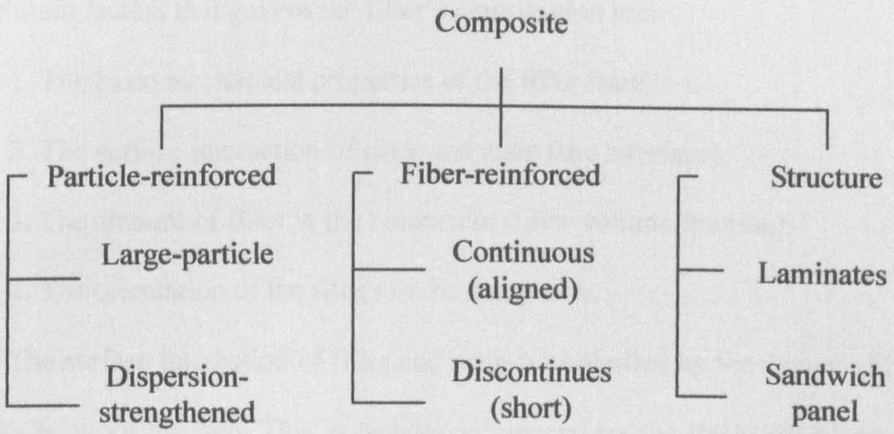


Figure 2.1 : A classification scheme for the various type of composite (William & Callister, 2007)

2.1.1 Reinforcement in Composite Material

The role of the reinforcement in a composite material is fundamentally one of increasing the mechanical properties of the neat resin system. All of the different fibers used in composites have different properties and so affect the properties of the composite in different ways. However, individual fibers or fiber bundles can only be used on their own in a few processes such as filament winding. For most other applications, the fibers need to be arranged into some form of sheet, known as a fabric, to make handling possible. Different ways for assembling fibers into sheets and the variety of fiber orientations possible lead to there being many different types of fabrics, each of which has its own characteristics (Attia, 2001).

2.1.2 Properties of Reinforcing Filler in Composite Materials

The mechanical properties of most reinforcing fibers are considerably higher than those of un-reinforced resin systems. The mechanical properties of the filler/resin composite are therefore dominated by the contribution of the fiber to the composite. The four main factors that govern the filler's contribution are:

1. The basic mechanical properties of the filler itself.
2. The surface interaction of filler and resin (the interface).
3. The amount of filler in the composite (filler volume fraction).
4. The orientation of the fillers in the composite.

The surface interaction of filler and resin is controlled by the degree of bonding that exists between the two. This is heavily influenced by the treatment given to the filler surface (Wang, et al., 1996).

2.2 Polymer Matrix Composite (PMCs)

Polymer-matrix composites (PMCs) consist of glass, carbon, or other high strength fibers in a thermoset or thermoplastic resin. The resulting materials are strong, stiff, and corrosion resistant. PMCs adopt flat, gently curved, or sharply sculpted contours with ease, providing manufacturers with design flexibility. In addition, composites offer the opportunity for parts consolidation and lower assembly costs.

Polymer-matrix composites provide a stiff, lightweight alternative to steel, aluminum, and traditional materials such as wood. Currently, composites find use in a broad range of applications. In the aerospace, automotive, rail, and bus sectors, their light weight leads to lower fuel consumption. Their resistance to corrosion enables their use in marine, construction, and infrastructure applications, including piping and storage tanks. Composites' lightweight strength and vibration-damping properties protect athletes from tennis elbow and allow fisherman to cast with increased accuracy. In addition, polymer-matrix composites are the materials of choice for wind-turbine blades (John et al. 2002).

Composites continue to make steady progress in existing as well as established applications. In the aerospace industry, the current emphasis on fuel efficiency favors the use of PMCs instead of aluminum; in addition, a new class of aircraft, micro jets, makes extensive use of lightweight composites. In the automotive industry, manufacturers are recognizing the advantages of weight reduction, parts consolidation, and design freedom that PMCs afford. In the energy sector, the growing use of wind energy has led to increased demand for PMC turbine blades. Despite lingering concerns about the materials' recyclability (an important factor in automotive markets), the outlook for PMCs is bright (Zhang et al. 2010).

2.3 Conductive Polymer Composites (CPC)

For the past few decades, composite materials has shown great increasingly remarked interest and set it apart in its own class due to its distinct properties. Among these materials, one subgroup was conductive polymer composites (Wang et al. 2007). Nowadays, the investigation of the Conductive Polymer Composites (CPC) was shown a great interest among the researcher due to their wide range of conductivity and large technology applications, such as catalysis, chemical sensors, antistatic products and electronic devices (Heinig et al. 2008; Kimura & Horikoshi, 2005; Lin et al. 1998).

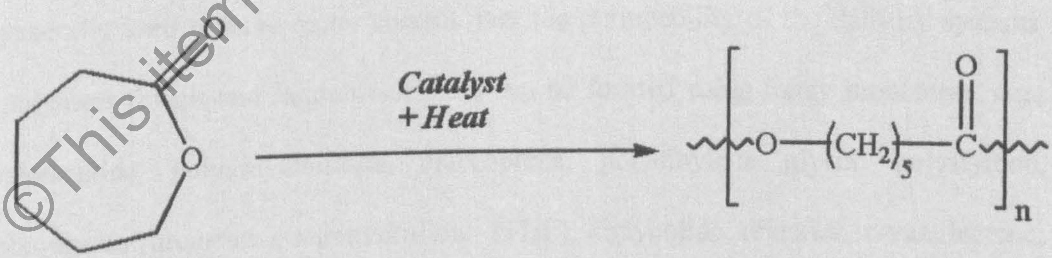
In electronic industry, antistatic polymer can be conductive polymer, conductive polymer composites, and antistatic agent modified polymer, which surface resistivity between 10^{12}-10^{10} Ω/square. The classical antistatic agent was chemical compound like fatty acid ester, ethoxylated amines, and phosphate ester, which will migrate to the surface providing conductive surface by attracting layer of water molecule (Dudler et al. 2000). However, antistatic effect of antistatic agent modified polymer was no permanently and limited by humidity (Chen et al. 2009).

In addition, CPC can be produced by blending the insulating polymer with the conductive fillers. According to the literature studies, the CPC can classify based of the filler as carbon black particles, carbon fibers, metal particles, and intrinsically conductive polymer (example, Polyaniline (PAN)) (Feller et al. 2003; Rybak et al. 2010). Nowadays, carbon black particles was commonly used conductive components to incorporate conduction to polymer composites due to the chain like aggregate structure, which shown high tendency to provide a conductive network (Zhang et al. 2007). In certain application such as current limiting devices, metal particle filled CPC as metallic filler exhibit high thermal conductivity, therefore heat dissipation problem occurs in carbon based CPC was no appeared (Rybak et al. 2010). Nevertheless, metal particle based CPC cannot be obtain with high filler loading, as the metallic filler was easily to form agglomeration compare to conductive network at high filler loading (Rybak et al. 2010). However, Chen et al. (2009) using Zinc Oxide whisker (ZnOw) as conductive filler in PET, and with the Silane coupling agent the ZnOw shown uniform and random dispersion with continuous conductive networking, which providing the conductivity to PET.

The CPC have several advantages compared to metallic conductor as easily process, low density, corrosion resistance, and wide range of electrical conductivities (Zhang et al. 2007). In the near future, CPC was produced from the mixing of conductive filler and conventional polymer, such as Poly (Ethylene Terephthalate) (Chen et al. 2009), high density Polyethylene (Rybak et al. 2010), Polycarbonate, and Polystyrene.

2.4 Polycaprolactone

Polycaprolactone (PCL) was one of the earliest polymers synthesized by the Carothers group in the early 1930s (Hill et al. 1934). It became commercially available following efforts to identify synthetic polymers that could be degraded by microorganisms (Huang, 1985). PCL can be prepared by either ring opening polymerization of ε-caprolactone using a variety of anionic, cationic and co-ordination catalysts or via free radical ring-opening polymerization of 2-methylene-1-3-dioxepane (as shown in Figure 2.2). Polycaprolactone is biodegradable polyester and it is a crystalline, tough and flexible polymer (Brode & Koleske, 1972), since its low glass transition temperature (Tg) - 60 to -70 °C and an ability to increase molecular mobility of the polymer chains, PCL resin has been used as a polymeric plasticizer (Hammer, 1978). PCL is difficult to melt-process by itself, because of its low melting temperature (Tm) of 60 °C. The number average molecular weight of PCL samples may generally vary from 3000 to 80,000 g/mol and can be graded according to the molecular weight (Hayashi, 1994).



ε-Caprolactone

PolyCaprolactone

Figure 2.2: Process of ring opening polymerization of ε-caprolactone to produce Polycaprolactone

Catalysts such as stannous octoate are used to catalyze the polymerization and low molecular weight alcohols can be used to control the molecular weight of the polymer (Storey & Taylor, 1996). PCL is soluble in chloroform, dichloromethane, carbon tetrachloride, benzene, toluene, cyclohexanone and 2-nitropropane at room temperature. It has a low solubility in acetone, 2-butanone, ethyl acetate, dimethylformamide and acetonitrile and is insoluble in alcohol, petroleum ether and diethyl ether (Coulembier et al. 2006). PCL can be blended with other polymers to improve stress crack resistance, dyeability and adhesion and has used in combination with polymers such as cellulose propionate, cellulose acetate butyrate, polylactic acid and polylactic acid-co-glycolic acid for manipulating the rate of drug release from microcapsules (Chandra & Rustgi, 1998).

In the 1970s it had already been recognized that PCL is particularly amenable to blending and polymer blends based on PCL were thus categorized with three types of compatibility; firstly exhibiting only a single Tg, secondly as mechanically compatible, exhibiting the Tg values of each as component but with superior mechanical properties and thirdly as incompatible, exhibiting the enhanced properties of phase-separated material Compatibility of PCL with other polymers depends on the ratios employed and is generally used to have better control over the permeability of the delivery systems. Copolymers (block and random) of PCL can be formed using many monomers, e.g., ethyleneoxide, polyvinylchloride, chloroprene, polyethylene glycol, polystyrene, diisocyanates (urethanes), tetrahydrofuran (THF), diglycolide, dilactide, ε-valerlactone, substituted caprolactones, 4-vinyl anisole, styrene, methyl methacrylate and vinyl acetate (Okada, 2002). Physico-mechanical properties of several degradable polymers, amongst them PCL, have been investigated and compared by Engelberg and Kohn who investigated thermal properties (Tg, crystallization, melting and decomposition points)