MECHANICAL AND THERMAL PROPERTIES OF CHITOSAN FILLED RECYCLED POLYETHYLENE BIOCOMPOSITES

AZIEYANTI NURAIN BT AZMIN

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Mechanical and Thermal Properties of Chitosan Filled Recycled Polyethylene Biocomposites

by

AZIEYANTI NURAIN BT AZMIN
0830410245

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LIST OF SYMBOLS, ABBREVIATIONS OR NOMENCLATURES

AM	Alkaline method
ASM	Alkaline followed by silane method
ASTM	American Society for Testing and Materials
CAPE	Carboxylated polyethylene
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetric
EBAGMA	Ethylene-butyl acrylate-glycidyl methacrylate
EFB	Empty fruit bunch
EWR	Eucalyptus wood residue
FA	Fly ash
FS	Film solubility
FTIR	Fourier transform infrared spectroscopy
GTR	Ground tyre rubber
HDPE	High density polyethylene
HDS	hexadecyltrimethoxy-silanes
ISRI	Institute of Scrap Recycling Industries
LA	Lactic acid
LDPE	Low density polyethylene
LLDPE	Linear low-density polyethylene
MA	Maleic anhydride
MAPE	Maleated polyethylene
MAPP	Maleated polypropylene
MDPE	Medium density polyethylene
MPS	γ-methacryloxypropyltrimethoxy
MRPS	γ-mercaptopropyltrimethoxy
OHP	Olive husk flour
PAE	Polyaminoamide-epichlorohydrin
PALF	Pineapple-leaf fiber

PCL	Polycaprolactone
PCW	Post-consumer waste
PE	Polyethylene
PE-g-MA	Maleic anhydride-grafted polyethylene
PET	Poly(ethylene terephthalate)
PP	Polypropylene
PS	Polystyrene
PVA	Poly(vinyl alcohol)
PVC	Polyvinyl chloride
rHDPE	Recycled high density polyethylene
rONP	Recycled old newspaper
RPE	Recycled polyethylene
rPP	Recycled polypropylene
SEM	Scanning electron microscope
SM	Silane method
T_c	Crystallization
TDM	Titanium-derived mixture
T_g	Glass transition temperature
TGA	Thermogravimetry analysis
T_m	Melting temperature
TS	Tensile strength
UPR	Unsaturated polyester resin
WRPC	Wood/recycled plastic composite
WVP	Water vapor permeability
X_{com}	Crystallinity of composite
XRD	X-ray diffraction

Sifat-Sifat Mekanikal dan Terma Biokomposit Polietilena Kitar Semula Terisi Kitosan

ABSTRAK

Kajian ini difokuskan untuk menyelidiki penggunaan kitosan biopolimer ke atas sifat-sifat polietilena kitar semula. Kesan kandungan kitosan biokomposit polietilena kitar semula ke atas sifat-sifat mekanikal, terma, penyerapan air dan morfologi telah dikaji. Kitosan dicampurkan dengan polietilena kitar semula menggunakan pencampur bilah-Z pada suhu 180°C dan kelajuan rotor 50 rpm. Keputusan menunjukkan dengan peningkatan pembebanan kitosan, kekuatan tensil, modulus Young dan penyerapan air meningkat tetapi pemanjangan pada takat putus bagi biokomposit polietilena kitar semula terisi kitosan berkurang. Kajian morfologi menunjukkan bahawa pembebanan pengisi yang lebih tinggi menghasilkan penyebaran kitosan lebih baik pada matrik. Penghabluran biokomposit meningkat dengan semakin meningkatnya pembebanan kitosan. Kehadiran α-metakrilosipropiltrimetoksilana (Silana A-174) telah meningkatkan kekuatan tensil, modulus Young, penghabluran dan mengurangkan pemanjangan pada takat putus dan penyerapan air biokomposit polietilena kitar semula/kitosan. Mikrograf SEM menunjukkan interaksi antaramuka yang lebih baik antara kitosan dan polietilena kitar semula. Kesan maleik anhidrida-cantuman-polietilena (MAPE) sebagai agen pengserasi meningkatkan kekuatan tensil dan modulus Young tetapi pemanjangan pada takat putus dan penyerapan air berkurang. Biokomposit dengan agen pengserasi menunjukkan penghabluran yang tinggi dan meningkatkan pelekatan pengisi dan matrik. Biokomposit dengan MAPE dan silana menunjukkan kekuatan tensil, modulus Young dan penghabluran yang lebih tinggi berbanding biokomposit tanpa MAPE dan silana di mana pemanjangan pada takat putus dan penyerapan air lebih rendah. Peningkatan sifat-sifat tensil disokong oleh kajian morfologi. Penambahan eko-rosotan PD 04 yang dikomersialkan sebagai bahan penambah dalam biokomposit polietilena kitar semula/kitosan telah meningkatkan kekuatan tensil dan modulus Young dan mengurangkan pemanjangan pada takat putus.

Mechanical and Thermal Properties of Chitosan Filled Recycled Polyethylene Biocomposites

ABSTRACT

The research was focused to investigate the utilization of chitosan biopolymer on properties of recycled polyethylene (RPE). The effect of chitosan loading of RPE biocomposites on mechanical properties, thermal properties, water absorption and morphology were studied. Chitosan was compounded with RPE using Z-blade mixer at processing temperature 180°C and rotor speed 50 rpm. The results show that the increasing chitosan loading increased the tensile strength, Young's modulus and water absorption but decreased the elongation at break of RPE/chitosan biocomposites. The morphology study show the higher filler loading exhibit better dispersion of chitosan in matrix. The crystallinity of the biocomposites increased with increasing chitosan loading. The presence of α-methacryloxypropyltrimethoxysilane (Silane A-174) have increase the tensile strength, Young's modulus, crystallinity and decreased the elongation at break and water absorption of RPE/chitosan biocomposites. The SEM micrograph show the better interfacial interaction between chitosan and RPE. The effect maleic anhydride-grafted-polyethylene (MAPE) as compatibilizer improved the tensile strength and Young's modulus but elongation at break and water absorption decrease. The compatibilized biocomposites indicates higher crystallinity and enhanced the adhesion of filler and matrix. The biocomposites with MAPE and silane show higher tensile strength, Young's modulus and crystallinity compared to the biocomposites without MAPE and silane, whereas lower elongation at break and water absorption. The improvement of tensile properties was supported by morphology studied. The addition of commercialized eco-degradant PD 04 as additive in RPE/chitosan biocomposites was increased the tensile strength, Young's modulus and reduced the elongation at break.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Polymer composites have been subjected to increase interest, study, and utilization for some decades. The interest arose toward polymer composites filled with natural organic fillers, especially in conjunction with recycled and/or recyclable polymer matrices. These class of composites (sometimes indicated as "green composites") shows other interesting features, certainly concerns the costs issues, which are quite reduced since natural organic fillers are usually extracted from wastes (La Mantia & Morreale, 2006). Currently, there is considerable concern about materials 'running out', and a renewed intent in conserving natural resources and increasing recycling. Also as landfill space runs out, recycling becomes increasingly attractive.

The amount of plastic waste increases as the production of polymeric materials grows dynamically and their application is wider. Managing the plastic waste is one of the challenges faced by today's world. It is stimulated by two basic factors:

1) Unconditional need to protect the natural environment being more and more contaminated, with plastics constituting over 10% of total waste and
2) Inevitable running out of natural resources of our planet which include the primary source for plastics (La Mantia, 2002).

There are numerous applications for blown film but a very high percentage of film is used in commodity applications packaging and bags. These products require a combination of performance, processing and cost that make polyethylene and ideal polymer for most application. Polyethylene is lightweight, water resistant, has a good balance of strength and flexibility and can provide some clarity, easy to extrude and heat-seal.

Synthetic plastics such as polystyrene, polypropylene, polyurethane, polyethylene and polylactides are used in daily life in food industry, biomedical field and agriculture. However, some of these polymers have disadvantages in such applications, i.e. poor biocompatibility and release of acidic degradation products. A heavy environmental pollution accompanies their uses, because they need hundreds of years to degrade, and the disposal of waste plastics has become a serious problem. Biodegradable materials used as alternative to the petroleum-derived plastics. The natural polymers have undergone reevaluation regarding their ability to biodegrade. Natural biopolymers including starch, cellulose and chitosan were tested, alone or combined with synthetic polymers, for the possibility to form a fully or partially biodegradable film. Most of the naturally occurring polysaccharide, e.g. cellulose, dextran, pectin, alginic acid, agar, agarose and carragenans, are neutral or acidic in nature, whereas chitin and chitosan are examples of highly basic polysaccharide (Guohua et al., 2006; Eldin et al., 2008; Sakurai et al., 2000; Majeti & Kumar, 2000).

The increasing demand for plastic or polymer products nowadays, a substantial growing percentage of municipal waste streams and poses environmental challenges to our country. While finding substitution material for plastic, this could involve a great cost and effort as it is much anticipated that used plastic can be recycled again and reused as their original product to prevent the waste of potentially useful materials, reduces the consumption of raw materials and reduces energy usage. Therefore studies on recycled plastic are very important because it will help to decrease the amount of waste. Thermoplastics are polymers that soften upon exposure to heat and return to their original condition at room temperature. Because thermoplastics can easily be shaped and molded into various products such as bottles, jugs, and plastic films, they are ideal for packaging. Moreover, virtually all thermoplastics are recyclable (melted and reused as raw materials for production of new products), although separation poses some practical limitations for certain products.

A number of technologies are available for recovering and recycling plastics. Some are currently in use by industry and capable of processing large quantities of material in a cost-effective manner, whilst others currently exist only in laboratories. Plastic recycling is an area that is constantly developing to try to meet the often competing demands of legislation, market forces and environmental pressure. The inter-relationship is complex and is illustrated in Figure 1.1. Recycled plastics are used in the same market in which they originated. They replace and compete against virgin materials. The price recyclate can command will depend on both the price of the virgin materials and the quality of the recyclate. The price of virgin materials can vary greatly as it is linked to both oil prices and supply and demand within the market. This in turn means that the price that recyclate can command varies greatly.

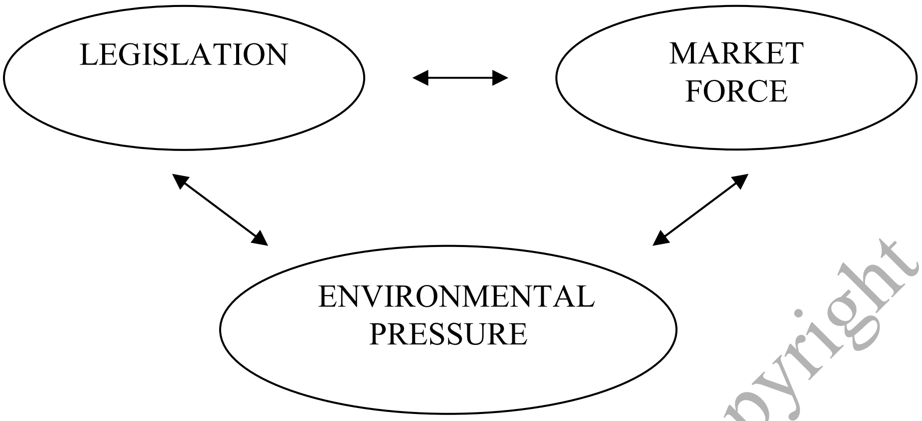

Figure 1.1: Interrelationships affecting recycling activity

Environmental pressure may create a demand from the consumer for recycled goods. By creating such a market, a manufacturer can see a profit to be made, and will therefore begin to produce and sell recycled goods. Environmental pressure may also result in legislation forcing manufacturers to use recycled materials. In this case, a market may not exist already and this legislation will impact upon the 'natural' market force. The result may less be profitable and require subsidies to kick-start such activity. For long-term growth however, the activity must be self-supporting.

A fully sustainable infrastructure for the recycling and recovery of plastics is required if the vast quantities of plastic material available are to be diverted from landfill. However, this will occur only when the demand is created for the end product materials and it is economically viable to recycle them. Currently, this has meant that recycling activities need to be subsidized if they are not commercially profitable. Therefore it is paramount that the plastic industry continues to educate the public and potential recyclate users in order to create and develop the supply and demand for these materials (Goodship, 2001).

Chitosan is biopolymers derived from chitin and cellulose, respectively, which are very common natural polysaccharides present in the environment. Chitosan is natural family biopolymer, biodegradable, non toxic as well as low-cost materials. Therefore, these biopolymers are extensively used in many scientific and technological applications such as medicine, pharmacology, biotechnology textile and food industry, photographic films, as well as fiber and plastic applications. A tremendous awareness of the suitability of using natural biopolymers for diversified applications in life science is increasing. Biopolymers are polymers that are biodegradable. The input materials for the production of these polymers may be either renewable (based on agricultural plant or animal products) or synthetic. Natural biopolymers have several advantages, such as availability from replenishable agricultural or marine food resources, biocompatibility, biodegradability, therefore leading to ecological safety and the possibility of preparing a variety of chemically or enzymatically modified derivatives for specific end uses. Polysaccharides, as a class of natural macromolecules, have the tendency to be extremely bioactive and are generally derived from agricultural feedstock or crustacean shell wastes. Cellulose, starch, pectin, etc. are the biopolymers derived from the former, while chitin and chitosan are derived from the latter (Prashanth & Tharanathan, 2007).

The most important issue associated with these composites is the interfacial adhesion between the natural reinforcing fillers and matrix polymers. In order to obtain good properties by improving the compatibility between two materials having different properties, reinforcing fillers are used after chemical modification. In other words, chemical modification is performed to overcome the incompatibility between the hydrophilic lignocellulosic material and the hydrophobic matrix polymer. This results in poor adhesion and prevents the reinforcing filler from acting effectively within the composite. In order to solve these problems, studies have been performed on surface modification or treatment using a compatibilizing agent for the purpose of making the polyolefin chain hydrophilic. The strong interfacial bonding strength obtained by improving the compatibility between the hydrophilic filler and hydrophobic matrix polymer can improve the physical, mechanical and thermal properties of the composite system (Yang et al., 2007a).

1.2 Objectives of Study

The research is emphasized the utilization of chitosan as biopolymer in recycled polyethylene (RPE) biocomposites on properties. The objectives of study include:

1) To determine the effect of chitosan loading on mechanical properties, thermal properties, water absorption and morphology of recycled polyethylene biocomposites.
2) To investigate the effect of coupling agent, compatibilizer and both on properties of RPE/chitosan biocomposites.
3) To assess the effect of eco-degradant on properties of RPE/chitosan biocomposites.

Several testing had been done to investigate the properties of the biocomposites such as tensile test, water absorption, morphology studies and thermal properties. Tensile test was performed to measure tensile strength, elongation at break and Young's modulus for each composition of the biocomposites. Water absorption was determined does it is necessary for end use applications of biocomposites in surrounding. Studies of the morphology of the tensile fracture surface of the biocomposites were carried out by using a scanning electron microscope (SEM). The thermal properties of biocomposites were investigated by differential scanning calorimetric (DSC).

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer Composites

A composite material is a materials system composed of a suitably arranged mixture or combination of two or more micro- or macroconstituents with an interface separating them that differ in form and chemical composition and are essentially insoluble in each other. The engineering importance of a composite material is that two or more distinctly different materials combine to form a composite material that possesses properties that are superior, or important in some other manner, to the properties of the individual components. The incorporation of these materials results in improved, but possibly anistropic, mechanical and thermal properties. Newer materials or composites are being developed to reduce the stress to the environment (Smith & Hashemi, 2006; Jacobson et al., 1995).

Thus composites are those materials formed by aligning extremely strong and stiff constituents such as fibers and particulates in a binder called matrix. The materials in this class have exceptional mechanical properties. One of the components is that accommodate stress to incorporate component called reinforcing phase and provide a strong bond called matrix. The matrix or binder (organic or inorganic) maintains the position and orientation of the reinforcement. Polymers, ceramic and metals have found application as matrix materials. The matrix is responsible for transferring the load from the matrix to the reinforcement, for distributing the stress among the reinforcement elements and for protecting the reinforcement from the environmental attack. The reinforcing phase is other component and is called reinforcement and can be fiber, particulate or laminar. Reinforcement provides strength and rigidity, helping to support structural load. Significantly, constituents of the composites retain their individual, physical and chemical properties; yet together they produce a combination of qualities which individual constituents would be incapable of producing alone (Gupta & Gupta, 2005; Taj et al., 2007; Paul & Bucknall, 2000).

The interface between filler and matrix is crucial in terms of composite performance. The interface serves to transfer externally applied loads to the reinforcement via shear stresses over the interface. Controlling the 'strength' of the interface is imperative. Clearly, good bonding is essential if stresses are to be adequately transferred to the reinforcement and hence provide a true reinforcing function (Fowler et al., 2006). The properties of polymer blends depend on the physical and chemical properties of the participating polymers and on the state of the phase (homogeneous or heterogeneous blends). Phase morphology (particle shape and size as well as size distribution) and the interfacial bonding between the phases (also named partial compatibility or partial miscibility) are additional parameters for heterogeneous blends (Braun et al., 2001).

Polymers are natural man-made molecules, frequently called macromolecules. Macromolecules or polymers consist of at least one hundred atoms linked in a chain-like order. Accordingly, the lower limit for the molecular weight of macromolecular substances is around 10^3 g/mol. Because of this high molecular weight macromolecules have properties quite different from those of low molecular weight substances. The influence of molecular weight or, respectively, the length of the polymer chain can be seen very impressively in the case of polyethylene. While polyethylene waxes