PROPERTIES OF EGGSHELL POWDER FILLED LOW DENSITY POLYETHYLENE/ ACRYLONITRILE BUTADIENE STYRENE COMPOSITES

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by

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بسم الله الرحمن الرحيم

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

With the Selawat and Salam to Prophet Mohammad SAW.

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Sifat-Sifat Serbuk Kulit Telur Diisikan Dalam Komposit Polietilena Ketumpatan Rendah/Akrilonitril Butadiena Stirena

Abstrak

Serbuk kulit telur merupakan salah satu bahan yang banyak terdapat di bumi kita dan ianya digunakan dalam bentuk kisaran untuk menghasilkan komposit polimer sejak awal lagi. Serbuk kulit telur yang tidak diubahsuai dan telah diubahsuai dengan bahan kimia telah diisikan dengan komposit polietilena ketumpatan rendah dan akrilonitril butadiena stirena telah dipelajari. Komposisi LDPE/ABS/ESP dengan agen pengganding dan tanpa agen pengganding telah ditetapkan di mana jumlah berat ialah 120g per formulasi. Komposit tersebut dileburkan dan dicampurkan pada suhu 200^{o}C dengan kelajuan rotor 50rpm. Selepas itu, komposit tersebut dimampatkan dalam acuan dengan tekanan hidraulik secara pemanasan elektrik dan pemanasan awal dijalankan pada suhu selama 7 minit dan suhu pemanasan selama 4 minit dan penyejukan selama 4 minit. Ini telah didapati bahawa komposit LDPE/ABS/ESP dengan N-asetil N,N,N-trimetil ammonium bromide sebagai agen pengganding menunjukkan sifat mekanikal yang lebih baik; kekuatan tensil bertambah sementara pemanjangan pada takat putus telah berkurang. Analisis kelakuan pembengkakan menunjukkan komposit dengan agen pengganding menyerap lebih banyak air. Analisis Pengimbasan pembezaan kalorimetri menunjukkan suhu peralihan kaca, T_g dan suhu peleburan, T_m komposit LDPE/ABS/ESP yang diubahsuai telah meningkat. Analisis termogravimetri menunjukkan $T_{-50\%wt}$, suhu penguraian akhir dan jisim baki untuk komposisi yang diubahsuai meningkat dengan peningkatan suhu. Analisis mikroskop pengimbas elektron (SEM) menunjukkan komposit LDPE/ABS/ESP yang diubahsuai mempunyai banyak garis-garis menyiat and kasar pada permukaan patah kekuatan tensil berbanding dengan komposit LDPE/ABS/ESP tanpa diubahsuai. Analisis pembelauan sinar-x (XRD) menunjukkan d-ruangan dalam komposit LDPE/ABS/ESP adalah lebih tinggi berbanding dengan komposit LDPE/ABS/ESP tanpa diubahsuai.

Properties of Eggshell Powder Filled Low Density Polyethylene/Acrylonitrile Butadiene Styrene Composites

ABSTRACT

Eggshell powder is one of the most abundant materials on our planet and has been quite early used in ground form to produce polymer composites. Chemical unmodified and modified eggshells powder filled low density polyethylene and acrylonitrile butadiene styrene composites were studied. The compositions of LDPE/ABS/ESP with and without coupling agent were fixed which is the total weight are 120g per formulations. The composite was melt mixed at temperature of 200℃ and rotor speed of 50 rpm. Afterwards, the blend was compression molded in an electrically heated hydraulic press and was preheat at temperature for about 7 minutes and heated temperature about 4 minutes and cooled for 4 minutes. It was found those LDPE/ABS/ESP composites with N-acetyl N,N,N-trimethyl Ammonium Bromide as a coupling agent exhibit higher mechanical properties; tensile strength increased while elongation at break were decreased. Swelling behavior analysis shows that the composites with coupling agent had more water absorption. The differential scanning calorimetry analysis shows that the glass transition temperature, Tg and melting temperature, Tm of the modified LDPE/ABS/ESP composites increased. The Thermogravimetry analysis shows that the T-50% wt, final decomposition temperature and residual mass for modified compositions increased with increasing filler loading. The scanning electron microscopy (SEM) analysis shows that the modified LDPE/ABS/ESP composites has more tear line and rough tensile fracture surface than unmodified LDPE/ABS/ESP composites. The X-ray diffraction (XRD) analysis exhibited the d-spacing in the modified LDPE/ABS/ESP composites have higher than the unmodified LDPE/ABS/ESP composites, the interlayer distance decreased with increasing the filler loading.

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LIST OF SYMBOLS, ABBREVIATIONS OR NUMENCLATURE

LDPE	Low density polyethylene
ABS	Acrylonitrile–butadiene–styrene
CRA	Calcium reserve assembly
CRB sac	Calcium reserve body sac
SEM	Scanning electron microscopy
ES	Eggshell
PP	polypropylene
XRD	X-ray diffraction
TGA	Thermal gravity analysis
PE	Polyethylene
ICI	Imperial chemical industries
MW	Molecular weight
MWD	Molecular weight distribution
HDPE	High-density polyethylene
LLDPE	Linear low density polyethylene
VLDPE	very-low density polyethylene
HMWHDPE	High molecular weight HDPE
UHMWPE	Ultra high molecular weight polyethylene
ULDPE	Ultra low density polyethylene
g	Gram
PEMAH	Polyethylene graft maleic anhydride
PEAA	Poly(ethylene-co-acrylic acid)
PS	Polystyrene

PVC	Poly (vinyl chloride)
LCP	Liquid crystalline polymer
SAN	Styrene acrylonitrile
GCC	Ground calcium carbonate
PCC	Precipitated calcium carbonate
phr	Per hundred resin
pH	Power of hydrogen
J	Joule
PEG	Polyethylene glycol
DSC	Differential scanning calorimetry
ESP	Eggshell powder
°C	Degree Celsius
wt %	Weight percent
μm	Micrometer
min	Minute
mm	Millimeter
ASTM	American standard testing material
Q_t	Molar absorption,
Tg	Glass transition temperatures
Tm	Melting temperature
$\Delta H^{o}f$	Enthalpy of fusion
FTIR	Fourier transform infrared spectroscopy
XRF	X-ray fluorescence spectrometer

CHAPTER 1

INTRODUCTION

1.1 Background

Over the past few years the development of new materials has been orientated towards polymer composites in other to obtain materials, which are characterized by specific properties and low manufacturing costs Suwanprateeb et al., (2000). LDPE are among the most common used plastics and often used as blends for balanced mechanical properties and processability, Maurer et al., (1985). Filling or reinforcement of polymers to enhance some properties of the material is one of the most important and popular methods of production of plastics, rubbers, coatings, adhesives, etc., which must possess the necessary mechanical and physical properties for any given practical application. Polymer filled with solid particulate or fibrous fillers of organic and inorganic nature are classified as polymeric composite materials. A variety of inorganic and organic reinforcing fillers may be incorporated into LDPE in order to improve specific properties or reduces cost, Maged et al., (2004). Nanoclay is one of the inorganic materials that can be used as filler in the polymer composites. Thermal properties of materials were study to know the thermal responses of material. Thermal analysis includes a group of analytical methods in which the properties of a substance or a polymeric material are measured as a function of temperature. Thus, dynamic thermogravimetry involves a physical measurement in which the weight loss is recorded as a function of the temperature while the substance is subjected to a controlled temperature programmer.

In polymer production, it is very important to determine the thermal stability of the polymeric material because this gives the temperature range over which the material can be used without degradation. The degradation of condensation polymers can occur by random decomposition or at reactive sites in the polymeric chain, depending on the nature of the polymeric material, while depolymerization reactions with monomer formation are characteristic of vinylic polymer structure. Thus, the principal degradation reactions will depend on the polymer structure and the heating condition, Maurer et al., (1985).

Acrylonitrile–butadiene–styrene ABS can be processed by standard mechanical tools as used for machining of metals and wood. The cutting speed need to be high and the cutting tools has to be sharp. Cooling is recommended to avoid melting of the material. If the surface finish is importance for the product, the ABS can be treated with varnish, chromium plated or doubled by a layer of acrylic or polyester. ABS can be glued to itself by use of a glue containing dissolvent. Polyurethane based or epoxy based glue can be used for gluing to other materials. Acrylonitrile–butadiene–styrene (ABS) is an important engineering copolymer widely used in industry due to superior mechanical properties, chemical resistance, and eases of processing and recycles ability.

The chicken eggshell is a composite bioceramic containing organic and inorganic phases. The organic phase contains, among other constituents, type X collagen and proteoglycans a keratan sulfate proteoglycan, and ovoglycan, a dermatan sulfateproteoglycan., whose localization depends on a topographically defined and temporally regulated deposition.

Although the distribution of these macromolecules in the eggshell has been well established, little is known about their precise localization within eggshell substructures and oviduct cells or their pattern of production and function during eggshell formation, Maria et al., (2001). The avian eggshell is a composite bioceramic containing organic (3.5%) and inorganic (95%) phases, Heuer et al., (1992). It is composed of a bilayered membrane and calcified extracellularmatrix which are sequentially assembled during the 22-h the egg moves along the oviduct, Fernandez et al., (1997). Ultra structurally, eggshells are composed of shell membranes, mammillary knobs, palisades and a cuticle, Arias et al., (1993).

The shell membranes are two nets of fibrils in which each fibril is composed of core surrounded by a fuzzy material referred to as a mantle, (Simons, 1971). Sparsely deposited on the outer side of the shell membranes are the mammillary knobs, which are the sites where crystal nucleation and the initial phases of calcium deposition take place, Stemberger et al., (1977). Mamillary knobs consist of the calcium reserve assembly (CRA). And crown region. The CRA consists of a dense, flocculent material partially embedded within the outer shell membrane. The CRA is capped by a centrally locate calcium reserve body sac (CRB sac) containing numerous 100-300-nm, electron-dense, spherical vesicles Dennis et al., (1996). The proper calcified layer, or palisade region, is formed by calcite columns beginning above each mammilla and ending below the cuticle, Dieckert et al., (1989).

Maged et al., (2004) reported the influence of excessive filler coating on the tensile properties of LDPE-calcium carbonate composites. It was found that the calcium carbonate increase the stiffness and yield stress of the polymer but reduce all it is other tensile properties. A Scanning electron microscopy (SEM) micrograph of fracture surface of the composite that indicate that the adhesion between the two phases is weak. In the other hand, Patricio et al., (2007) reported eggshell, a new bio-filler for polypropylene composite investigate that the scanning electron microscopy SEM showed an improved interfacial bonding on the tensile fractured surface. The improvement in the mechanical properties was attributed a better ES/matrix interface related to the geometric ratio of the ES particles similar to talc particles. The mechanical behavior of PP-ES composite shows a higher tensile modulus. Eggshells obtained from aviculture waste can easily be used as filler for PP composites, which show better reinforcement properties than the composites, made with traditional calcium carbonate filler, and also can replace talc to great extent without decreasing the mechanical properties of the composites.

Otherwise, Ziku et al., (2009) reported the application of waste eggshell as low-cost solid catalyst for biodiesel production. Waste eggshell was investigated in triglyceride transesterification with a view to determine it is viability as a solid catalyst for use in biodiesel synthesis. A use of eggshell as a catalyst for biodiesel production not only provides a cost-effective and environmental effect, but also reduces the price of biodiesel to make biodiesel competitive with petroleum diesel.

In this study the reporter detected that the waste eggshell enhance the thermal properties by the change occur in the X-ray diffraction (XRD) caused by the removal of CO_2 from the starting material and also investigate the homogeneous structure of eggshell because of the change of composition. In this study also investigated that the eggshells enhance the thermal properties of the composites. The calcinations of eggshell with thermal gravity analysis (TGA) technology. TGA showed the temperature at which the eggshell precursors decomposed when heated in a controlled environment. However the studies on the influence of chemical unmodified and modified eggshell to the polymer composites on molecular dynamics and structure in filled system of low density polyethylene (LDPE) and Acrylonitrile butadiene styrene (ABS) are limited. Polyethylene is a hydrophobic and Acrylonitrile–butadiene–styrene is a semi hydrophobic while calcium carbonate is hydrophilic filler. I decided to study about the effect of filler loading of eggshell powder filled acrylonitrile butadiene styrene and low density polyethylene composites. The samples were analyzed with several testing method such as tensile test, swelling behavior test, scanning electron microscopy analysis, thermogravimetry analysis, X-ray diffraction and thermal properties by using differential scanning calorimetry.

1.2 Objective

- To study the effect of modified eggshell powder on mechanical and tensile fracture surface properties of LDPE/ABS composite.

- To study water absorption of LDPE/ABS composite with and without modification by using swelling behavior test.

- To study the effect of modified eggshell powder on thermal properties and thermal degradation of LDPE/ABS composite by using differential scanning calormetry (DSC) and thermogravimetry analysis (TGA).

- To analyze the d-spacing of eggshell powder filled LDPE/ABS composite by using X-ray diffraction (XRD).

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Polyethylene

Polyethylene (PE) was discovering in 1933 by Eric Fawcett and Reginald Gibson at the British industrial giant, Imperial Chemical industries (ICI). Although it is more than 70 years since it was produced, it is still a very promising material. It is produced at high pressures and temperatures in the presence of any one of several catalysts, depending on the desired properties of the end-use product. Other structure (leading to long and short branches) may be present, depending on the producer used in the synthesis. PE is the largest volume polymer consumed in the world. It is versatile material that offers high performance compared to other polymers and alternative materials such as glass, metal or paper, Cornelia et al., (2005).

Polyethylene plastics have the largest volume use of any plastics. They are prepared by the catalytic polymerization of ethylene at high pressure and temperature. Depending on the mode of polymerization or the desired properties of the end-use product, molecular weight (MW), molecular weight distribution (MWD), as well as on the degree and type pf branching there can be three basic types of polyethylene: high-density (HDPE), low-density polyethylene (LDPE) polymers, and linear low-density (LLDPE). LDPE is prepared under more vigorous conditions, which result in short-chain branching. LLDPE is prepared by introducing short branching via copolymerization with a small amount of long-chain olefin. Other types of PE product are such as very-low density polyethylene (VLDPE), high molecular weight HDPE (HMWHDPE), ultra high molecular weight polyethylene (UHMWPE) and ultra low-density polyethylene (ULDPE), Cornelia et al., (2005).

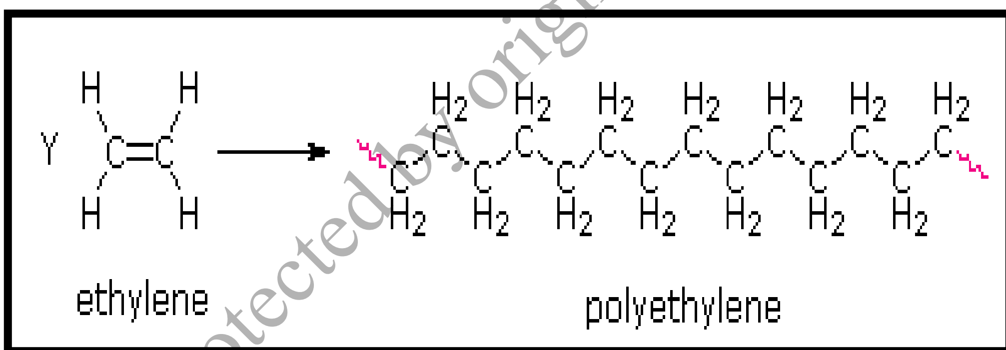

Figure 2.1.1: Low density polyethylene (LDPE), Cornelia et al., (2005).

2.1.1 Properties of Polyethylene

LDPE is defined by a density range of 0.910 - 0.940 g/cm³. It is unreactive at room temperatures, except by strong oxidizing agents, and some solvents cause swelling. It can withstand temperatures of 80 °C continuously and 95 °C for a short time. Made in translucent or opaque variations, it is quite flexible, and tough to the degree of being almost unbreakable. LDPE has more branching (on about 2% of the carbon atoms) than HDPE, so its intermolecular forces (instantaneous-dipole induced-dipole attraction) are weaker, its tensile strength is lower, and its resilience is higher. Also, since its molecules are less tightly packed and less crystalline because of the side branches, its density is lower. It has important properties which include good flexibility over a wide range of temperature even down to -73℃, toughness at room temperature and low temperatures with sufficient for many product applications, excellent corrosion resistance, excellent insulating properties, odorlessness and tastelessness, and low water-vapor transmission.

Low density polyethylene (LDPE) polymers are crystalline thermoplastic that exhibit toughness, near-zero moisture absorption, excellent chemical resistance, excellent electrical insulating properties, low coefficients of friction, and ease of processing. Their heat deflection temperatures are reasonable but not high. The branching in LDPE decreases the crystallinity. LDPE is also semi-rigid, translucent material, and primarily used at normal temperature. It is easily processed by most methods and has low cost. LDPE is lightweight and formable, has a high impact resistance and machinable and weldable. LDPE can be processed by all conventional methods: hot gases welded, fusion and butt welded, ultrasonically sealed, die cut, machined with wood- or metal- working tool, vacuum formed and thermoformed, the long side-chain branching of the LDPE molecules produces a more amorphous polymer having a lower melting point and higher clarity compare to LLDPE. LDPE also differentiated from LLDPE by poorer physical properties as regards tensile strength, puncture, test resistance and elongation, Cornelia et al., (2005). It is also resist to chemical substances:

1. Excellent resistance (no attack) to dilute and concentrated acids, alcohols, bases and esters.
2. Good resistance (minor attack) to aldehydes, ketones and vegetable oil.
3. Limited resistance (moderate attack suitable for short-term use only) to aliphatic and aromatic hydrocarbons, mineral oils, and oxidizing agents.
4. Poor resistance, and not recommended for use with Halogenated hydrocarbons.

2.1.2 Application of Polyethylene

Polyethylene is a very versatile polymer and is used a wide variety of applications. The most common is in flexible packaging particularly foodstuffs. This application requires the combinations of easy processing into a flexible film, excellent toughness, chemical inertness and the ability to form strong heat seals quickly. Typical flexible packaging examples for low density polyethylene include bread, frozen food the sealant layer in a laminated structure for confectionery and pet food packaging, the internal/external coating of fiberboard for packaging milk and fruit juices, shrink warpping and the stretch/cling collation wrapping of pallets. Other applications include rotomoulded toys, playground/recreational equipment and a range of tanks as well as the insulation and/or jacketing of telecommunications cable, power cable and related network system. Polyethylene is also used to provide corrosion protection of steel pipe for water distribution and a variety of injection moulded lids for a wide range of containers. High density polyethylene is most commonly used in blow moulded milk bottles, pressurized thick wall water pipe and very thin carry bags such as supermarket check-out bags.

2.1.3 Blend of Polyethylene

There were many studies have been carried out polyethylene, Suwanprateeb et al., (2000). It is possible to obtain polymer blends with more desirable properties by mixing miscible polymers, and thus it is very important to examine the factors affecting the miscibility of polymers mixtures. It was found that exfoliated/intercalated dispersion of the clay layers in the polymer matrix could be achieved in certain polymers with polar functional groups that make the polymer more compatible with the polar groups on the silicate clay layers. Polyolefins have been an attractive choice for polymer composites because of it is wide use and low cost, but as non-polar polymers it is very difficult to disperse the nanoclay into the polyolefin matrix to achieve a nanostructure. Due to this challenge, much work has been done in the area of compatibilization of these systems. Wang and Coworkers reported in intercalated structure of aspect ratio of clay on melt extensional process of maleated polyethylene/clay nanocomposites, Ki Hyun et al., (2001). In other study, Seno and Coworkers reported about thermal degradation and crystallization studies of reactively compatibilised polymer blend, Seno Jose et al., (2008). Otherwise, Pietrasanta et al., (1998) reported in Mechanical Performance Improvement of Low-Density Polyethylene Blends, Mechanical properties of recycled low-density polyethylene have been improved by using calcium carbonate as filler. Compatibility of the filler with a