SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF LOW DENSITY POLYETHYLENE FILLED WITH REDUCED GRAPHITE OXIDE

by

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LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
ASTM	American standard testing method
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
C_2F	Graphite fluoride
CNT	Carbon nanotube
DA	Dodecyl amide
DI	Deionized
DMF	Dimethylformamide
DSC	Differential scanning calorimetric
EVA	Ethylene vinyl acetate
FDA	Food and drug administration
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transmission infrared spectroscopy
FWO	Flynn-Wall-Ozawa
GC	Gas chromatography
GO	Graphene oxide
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
HDPE	High density polyethylene
HMWHDPE	High molecular weight high density polyethylene
HNO_3	Nitric acid
IR	Infrared
K	Kissinger
KBr	Potassium bromide
$KClO_3$	Potassium chlorate
$KMnO_4$	Potassium permanganate
LDPE	Low density polyethylene
LLDPE	Linear low-density polyethylene
MS	Mass spectroscopy
MSD	Mass selective detector

MWNT	Multi-walled nanotubes
MWS	Maxwell-Wagner-Sillars
$NaBH_4$	Sodium borohydride
$NaNO_3$	Sodium nitrate
NMR	Nuclear magnetic resonance
OIT	Oxidative induction time
OTR	Oxygen transmission rate
PB-1	Polybutene-1
PC	Polycarbonate
PE	Polyethylene
PMMA	Poly(methyl methacrylate)
PMP	Polymethylpentene
PP	Polypropylene
PPC	Poly(propylene carbonate)
PPMS	Physical property measurement system
PS	Polystyrene
rGO	Reduced graphite oxide
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
UHMWPE	Ultra high molecular weight polyethylene
UV	Ultraviolet
VLDPE	Very low density polyethylene
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffractometer

LIST OF SYMBOLS

λ	Wavelength
d	d-spacing
θ	Angle
n	Integral
Δc	Difference in gas concentration
l	Length
J	Diffusion flux
D	Diffusivity
C_p	Parallel capacitance
ε_0	Permittivity of free space
ε_r	Relative dielectric constant
t	Thickness
W_b	Weight of the initial thin film
W_a	Weight of the thin film after extraction
k	Rate constant
A	Pre-exponential factor
E_a	Activation energy
R	Universal gas constant
T	Thermodynamic temperature
β	Heating rate
ΔH_f	Enthalpy of melting
ΔH_c	Enthalpy of crystallization
$\Delta H_{f100\%}$	Enthalpy of the melting for fully crystalline material

LIST OF EQUATIONS

SINTESIS, PENCIRIAN DAN SIFAT-SIFAT KOMPOSIT NANO POLIETILENA BERKETUMPATAN RENDAH TERISI GRAFIT TERKURANG

ABSTRAK

Bahan berasaskan grafit telah menjadi calon yang menjanjikan dalam nanokomposit poliolefin dalam aplikasi luas seperti bahan pembungkusan. Walau bagaimanapun, penggunaan gabungan ini menimbulkan keraguan tentang kesan haba yang digunakan pada nanokomposit. Di sini, kajian sistematik telah dijalankan untuk menyiasat kesan penurunan oksida grafit (rGO) ke arah bahan poliolefin. Kaedah pengecoran hijau dan mudah diperkenalkan dalam fabrikasi polietilena berketumpatan rendah / pengurangan grafit oksida (LDPE / rGO) nanokomposit dengan kandungan pengisi 0.05 - 1 wt%. Tanpa sebarang pengubahsuaian antara polietilena dan oksida grafit yang diturun, beberapa pencirian telah dilaksanakan ke arah nanokomposit. Sifat optik melalui spektroskopi yang kelihatan UV secara berkesan mengenal pasti ketelusan nanokomposit, di mana ketelusan berkurangan dengan penambahan rGO. Ujian ketegangan juga dilakukan untuk menentukan sifat ketegangan filem yang direka. Filem yang berkandungan 0.3 wt% rGO menunjukkan kekuatan ketegangan tertinggi secara keseluruhan. Halangan gas bersama-sama dengan sifat-sifat dielektrik dari nanokomposit dikaji secara mendalam. Mikroskop elektron penghantaran (TEM) digunakan untuk memerhatikan penyebaran dan morfologi grafit oksida yang dikurangkan dalam polietilena. Selanjutnya, penguraian haba nanocomposites diselidiki melalui analisis termogravimetrik (TGA). Kajian kinetik terhadap nanokomposit yang berdegradasi telah menunjulkan bahawa model Flynn-Wall-Ozawa (FWO) adalah satu langkah lebih tinggi berbanding dengan model Kissinger (K). Walaupun hanya terdapat satu langkah kemerosotan terma yang muncul namun unsur-unsur yang terurai masih tidak diketahui. Oleh itu, kromatografi gas (GC) dan spektroskopi jisim (MS) ditambah dengan TGA digunakan untuk memisahkan sebatian yang berkembang ke dalam alkana, alkena dan kumpulan aromatik masing-masing. Gas yang beracun hanya akan dikeluarkan apabila nanokomposit dipanaskan hingga 460 °C. Dengan penambahan rGO dalam matrik LDPE, tingkah laku degradasi nanocomposites mengenal pasti melalui sinaran UV. Terdapat hanya sedikit atau tidak ada perbezaan pada sifat-sifat filem nipis selepas 360 jam radiasi UV-B. Berdasarkan analisis, kajian menunjukkan bahawa penambahan rGO ke atas LDPE akan meningkatkan sifat optik, mekanik, termal dan dielektrik. Ini telah meluaskan aplikasi LDPE/rGO yang berpotensi berfungsi sebagai bahan pembungkus.

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ABSTRACT

Graphite based materials have become promising candidates in polyolefin nanocomposites in widening the application such as a packaging material. However, the utilization of these combination exhibits a doubt on how was the effect once heat is applied onto the nanocomposites. Herein, a systematic study has been carried out to investigate the effect of reduced graphite oxide (rGO) towards low density polyethylene (LDPE). A simple solvent casting method was carried out in fabricating low density polyethylene / reduced graphite oxide (LDPE/rGO) nanocomposites with the filler contents of 0.05 – 1 wt%. Without any modification between LDPE and rGO, several characterizations have been implemented towards the nanocomposites. Optical properties through UV-visible spectroscopy were effectively identifying the transparency of the nanocomposites, where the transparency decreased with the increased of rGO. The tensile test was also carried out in order to determine the tensile properties of the fabricated film. Thin film with 0.3 wt% of rGO content has showed highest tensile strength compared to the rest of the nanocomposites film. Gas barrier together with the dielectrical properties of the nanocomposites were studied in depth. Transmission electron microscopy (TEM) was employed to observe the dispersion and morphology of the rGO in LDPE. Further, thermal decomposition of the nanocomposites was investigated through thermogravimetric analysis (TGA). Kinetic studies on the degradation nanocomposites had concluded that Flynn-Wall-Ozawa (FWO) model is one step higher compared to Kissinger (K) model. In order to identify the elements that decomposed, gas chromatography (GC) and mass spectroscopy (MS) coupled with TGA were used to separate the evolved compounds into alkane, alkene and aromatic groups, respectively. Where, toxic gaseous will only being released out when the nanocomposites was heated up to 460 °C. With the addition of rGO in the LDPE matrix, the degradation behaviour of the nanocomposites was identifying through UV radiation. There is only slight difference on the thin film's properties after 360 hours of UV-B radiation. Based on the analysis, the studies clearly indicated that the feasibility of incorporating rGO into the LDPE matrix had improved the optical, mechanical, thermal and dielectric properties. This has widened the application of LDPE/rGO nanocomposites in serving as a packaging material.

CHAPTER 1 : INTRODUCTION

1.1 Nanocomposites: Current Status, Challenges and Future

Nanocomposites briefly defined as nanofillers bonded to a matrix, which have been reported since past decades has increased an interested for commercial use. Fillers play an important role in modifying the desirable properties in composites and can adversely affect some properties of the neat matrix with the main aim to reduce the cost of the composites. In conventional composites, fillers are usually added into matrix as reinforcement to rebuild the properties of the composites. The most widely employed composites nowadays in industrial sectors are those with micron-sized particles or fibers as reinforcement. In fact, traditional micro composites might have achieved the optimizing properties in terms of physical and mechanical properties (Pezzin, Amico, Coelho, & de Andrade, 2011). Therefore, about twenty years ago, researchers proved that novel materials could be produced with tailored properties using nanofillers. Current trend of fillers used is available on nanoparticles, nanoplatelets, nanofibers, carbon nanotubes, and more recently on graphite (Pezzin et al., 2011).

Substitution of the traditional micro-reinforced materials using polymer nanocomposites has attracted most of the researchers nowadays. Indeed, the combination of nanomaterials with thermoplastic or thermoset polymers lead to very interesting mechanical or physical properties. According to Mohammed (2016) different particle size of titanium dioxide has been implemented into thermoset materials such as epoxy with the purpose to study its physical properties. Wear rate and hardness test on the polymer nanocomposite has showed better properties compared to composites filled with micron size filler. Besides, comparison has been made between nano and sub-micrometer zinc oxide with an organophilic surface layer as fillers in poly(methyl methacrylate) based on its UV absorber and thermal stabilizer. Nano sized zinc oxide showed effective UV absorber than submicrometer zinc oxide. Therefore, Anžlovar, Crnjak Orel, and Žigon (2008) concluded that the average particle size is an important parameter for optimizing the composites properties.

Although nanotechnology is now revolutionizing the world of materials and has very high impact in developing a new generation of composites with enhanced functionality and wide range of applications. But investment in state of the equipment and the enlargement of core research team's is another bottleneck to bring out innovative technologies on nanocomposites. A part of that, nano fillers selection based on the requirement needed such as an interfacial interaction or compatibility with the polymer matrix and the processing technique which aimed for the proper uniform dispersion and distribution of nano-particles or nano-particles aggregates within the polymer matrix is another problem should be considered too (Müller et al., 2017) .

Thus, extension of this nanotechnology using additional types of polymer system would likely to be a prerequisite aim as the future trends for nanocomposites materials. New compatibility strategies between nano fillers and polymer matrix are also one of the interests in the development of properties enhancement for polymer nanocomposites.

1.2 Graphite Oxide based Thermoplastic Nanocomposites

Graphite oxide based fillers in polymer nanocomposites has hold potential for various application. Thermoplastic polymer as matrix with graphite based filler include polypropylene (PP), polymethylpentene (PMP), polybutene-1 (PB-1), polystyrene (PS), poly(methyl methacrylate) (PMMA) and polycarbonate (PC) (Ma, Siddiqui, Marom, & Kim, 2010). To achieve large property of enhancements in polymer nanocomposites, it is important to focus on the preparation method. Layered structure graphite oxide must be exfoliated and well dispersed in the polymer matrix. Upon achieving this criterion, ultrasonication have been wisely use extensively to produce highly exfoliated nanoplatelets for nanocomposites. However, it is proved that graphite oxide can be easily dissolved in a variety of solvent such as dimethylformamide (DMF) and tetrahydrofuran (THF), which will further help to improve interfacial interaction with polymer matrix.

Studies on poly(propylene carbonate) (PPC) reinforced graphite oxide was reported by J. Gao et al. (2011) using solvent mixing method during preparation. As expected, the mechanical properties of PPC/GO nanocomposites have been highly improved together with tensile strength and Young's modulus by adding of only 1wt% graphene oxide. These properties are comparable to those of polyethylene and poly (L-lactic) acid as matrix (Chaudhry & Mittal, 2013; Pinto, Cabral, Tanaka, Mendes, & Magalhães, 2013). Other than that, Kuila et al. (2012) claims that linear low density polyethylene filled modified graphene oxide using dodecyl amide (DA) with the purpose to achieve better dispersion in the polymer matrix due to the nucleophilic addition of organic molecules to the surface of graphene is an effective way to the bulk production of surface modified graphene (Bourlinos et al., 2003; Stankovich et al., 2010) were also made some improvement in the storage moduli and thermal stability than the neat LLDPE. In addition, graphene and silica hybrid fillers to PP-based nanocomposites has increased the tensile strength by 13.8% when the filler content was fixed at 0.25 wt% (Kamal, Khan, Haider, Alghamdi, & Asiri, 2017). A previous study used octadecylamine-modified graphene oxide into PP and found that the layered morphology exhibited better thermal stability and mechanical properties compared to the neat PP (H. X. Zhang et al., 2017). However, the incorporation of carbonaceous materials into LDPE has received less attention. Bu, Huang, Li, and Jiang (2016) have filled the antioxidant functionalized reduced graphene oxide (rGO) to LDPE and found that functionalized rGO could enhance the dielectric constant as well as improve the dielectric loss tangent of nanocomposites. An improvement in the thermal behavior of the composites was noticeable when 3 wt% functionalized graphene filler content was loaded to the linear LDPE matrix (Kuila et al., 2011). However, the physicochemical properties of incorporation of rGO into the LDPE matrix with respect to the packing materials including optical, tensile, thermal and dielectrical properties are yet to be well understood. In addition, the surface modification of fillers shoots up the cost of nanocomposites and longer time is needed during fabrication process, which may hamper the industrial adaption (Tanahashi, 2010).

With these, studies on graphite oxide based thermoplastic are piling up highly desirable demand to develop novel LDPE/rGO nanocomposites without any surface modification for multifaceted applications.

1.3 Problem Statement

The current trend of packaging materials use biopolymer as matrix in packaging application has become potentially renewable alternative to petroleum-based plastics due to the long term benefits of reducing global warming pollution and the dependence on fossil fuels. Although bio-based polymer matrix sounds "green" but according to the Life Cycle Analysis of biopolymer, bioplastic has resulted in more pollution or energy consumption imposing higher costs to the society than the conventional petroleum based polymer matrix. Bioplastic that designed to be composted, not recycle has become one of the issues that concern nowadays (S. Lee & Xu, 2005).

Among the list of the polyolefin materials that is being used in the packaging application such as high density polyethylene (HDPE), linear low density polyethylene (LLDPE) and low density polyethylene (LDPE), the LDPE is chosen as the polymer matrix for packaging application. By comparing the characteristics between these polyolefin materials, low density polyethylene (LDPE) with its unique properties such as having the most excessive branching in its structural has provided a good flow properties that can make it particularly for plastic film applications, high ductility, good chemical resistance and excellent water resistance has also become the reason why LDPE is the most outstanding characteristics among the polyolefin materials (Fayyaz, Muhamad, & Sulong, 2018). Unfortunately, LDPE is poor in both gas barrier and less tensile strength. In order to overcome the above mentioned drawback, incorporating layered structure graphite oxide into the LDPE matrix, which served as packaging material was studied.

To overwhelm gas barrier of the selected polymer matrix, two dimensional carbon based filler was selected as it contains unique characteristics. Besides, sheets structure filler was highly introduced in the nanocomposites system. Although there are various types of two dimensional carbon based materials, such as graphene, graphene oxide, graphite oxide, etc. And, graphene oxide can be exfoliating well if the polymer matrix used is hydrophilic in nature. But, along with the study, hydrophobic polyethylene which has totally opposite nature with graphene oxide is being selected as the matrix used. Thus, reduction process was applied onto the graphene oxide so that reduced graphite oxide can be used as the filler in the nanocomposites. Although there are numbers of researchers have been studying on the characteristics between carbon based filler and polymer matrix, yet limited amount towards the unmodified filler filled polymer matrix and its degradation behaviour of the composites materials is still remain unknown.

Aside from examine the effect of reduced graphite oxide that incorporated into LDPE matrix that focus as packaging material, the degradation behaviour of the nanocomposites was taken into account in order to obtain a reliable material in packaging application. With these, two different degradation aspects were observed from thermal and ultraviolet light at wavelength 305 nm.

1.4 Objectives of study

The aim of this work focuses on preparation and characterization of graphite oxide nanoplatelet as filler that incorporate into the low density polyethylene thin film nanocomposite. Emphasis is given on the synthesis of the graphite oxide and reduced