TENSILE, BARRIER, AND DEGRADATION PROPERTIES OF LOW DENSITY POLYETHYLENE/EPOXIDIZED NATURAL RUBBER NANOCOMPOSITE FILMS

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To my beloved father, mother, sister, and brother
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ABSTRACT

The demand for the development of high-performance packaging films and the equally growing environmental awareness have called for intensive research in the field of eco-friendly films with good mechanical and barrier properties. The present study investigates the use of epoxidized natural rubber (ENR) and organo modified montmorillonite (OMMT) in the development of low density polyethylene (LDPE) nanocomposites films. The films were successfully prepared by first melt blending at 190 °C in a twin-screw extruder and then blown via single screw machine. Linear low density polyethylene-grafted-maleic anhydride (LLDPE-g-MA), was used as compatibilizer to obtain better dispersion of nanoclay in the system. The nanocomposite films were prepared at different amounts of rubber from 2.5-10 wt%. The obtained nanocomposites were analyzed for tensile, thermal, morphology, gas permeability and degradation properties. The study of tensile properties of films was done via Lloyd 2.5 kN according to ASTM D882 in machine direction. Thermal analysis was carried out via differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). Atomic force microscope (AFM) was used to probe the morphology of phases, and X-ray diffraction (XRD) was applied to examine the interlayer distance of OMMT. Chemical characterization and interaction between materials were studied by Fourier transform infrared spectroscopy (FTIR). The barrier property of films was determined by constant pressure/variable volume type permeation cell. Degradation and biodegradation were studied via Q-SUN Xenon test chamber and soil burial test, respectively. The study has shown the presence of OMMT enhanced the tensile modulus and barrier property of LDPE film by 46% and 80%, respectively. In addition, incorporation of ENR improved the Young’s modulus and barrier properties of compatibilized nanocomposite films. Improvement in the degradation onset temperature (T. 10%) of nanocomposite films was observed with addition of 6wt% OMMT and ENR contents. The intercalation of OMMT regarding addition of LLDPE-g-MA into nanocomposites was confirmed by XRD. FTIR analysis has shown a formation of (C-O) ester bond; the driving force for intercalation between MA group of LLDPE-g-MA and epoxy group of ENR. Significant degradation took place through addition of OMMT and ENR as samples were highly fragile and broken. Biodegradation of films increased through addition of ENR. The most significant finding from this research is the development of eco-friendly nanocomposite film formulation with enhanced barrier properties. Based on tensile modulus, barrier and biodegradation properties, compatibilized nanocomposites film containing 7.5 wt% ENR (LDPE/OMMT/LLDPE-g-MA/ENR7.5) was the optimum formulation. The unique combination of tensile modulus, barrier and biodegradation properties for nanocomposite films has shown that this nanocomposite is a potential candidate for a variety of food packaging applications.
ABSTRAK

Permintaan yang sentiasa meningkat terhadap pembangunan filem pembungkusan yang berprestasi tinggi di samping perkembangan tentang kesedaran alam sekitar yang setara telah menarik perhatian untuk menggiatkan penyelidikan dalam pengeluaran filem yang bersifat mesra alam dengan sifat-sifat mekanikal dan rintangan yang baik. Penyelidikan ini mengkaji kemungkinan untuk menggunakan getah asli terepoksi (ENR) dan organo montmorilonit yang diubahsuai (OMMT) secara bersama dalam membangunkan filem berasaskan polietilena berketumpatan rendah (LDPE). Filem telah berjaya disediakan melalui pengadunan leburan pada suhu 190 °C dengan menggunakan penyemperitan skru berkembar diikuti oleh peniupan filem melalui mesin skru tunggal. Polietilena linear berketumpatan rendah tercantum malik anhidrida (LLDPE-g-MA) digunakan sebagai penserasi untuk mendapatkan penyertaan tanah liat bersaiz nano yang lebih baik di dalam sistem. Filem komposit nano telah disediakan dengan kandungan getah yang berbeza (2.5-10) peratus berat. Komposit nano yang diperolehi dianalisis untuk sifat-sifat regangan, terma, morfologi, kebolehtelapan gas dan penguraian. Kajian regangan filem dilakukan menggunakan Lloyd 2.5 kN mengikut ASTM D882 di dalam arah mesin (MD). Sifat-sifat terma dan kestabilan telah dilakukan melalui analisa kalorimetri pengimbasan pembezaan (DSC) dan analisa termogravimetri (TGA). Mikroskop daya atom (AFM) telah digunakan untuk menyiapai fasa morfologi dan pembelauan sinar-X (XRD) telah digunakan untuk memeriksa jarak di antara lapisan OMMT. Ciri-ciri kimia dan interaksi di antara bahan-bahan dikaji menggunakan Fourier infra merah (FTIR). Sifat rintangan filem ditentukan melalui system tekanan malar dan ketelapan sel jenis isipadu bolehubah. Penguraian dan bio-penguraian masing-masing telah diperiksa melalui ujian kebuk Q-SUN Xenon dan ujian penanaman dalam tanah. Kajian menunjukkan kehadiran OMMT meningkatkan modulus regangan dan sifat rintangan filem LDPE sebanyak 46.25% dan 80%. Masing-masing tambahan pula, penambahan ENR meningkatkan modulus Young serta sifat rintangan filem komposit nano berpenserasi. Peningkatan dalam suhu pemulakan degradasi (T$_{10\%}$) filem komposit nano telah diperhatikan dengan penambahan 6 peratus berat OMMT dan kandungan ENR. Interkalasi OMMT disebabkan penambahan LLDPE-g-MA dalam filem komposit nano telah disahkan oleh XRD. Analisis FTIR menunjukkan pembentukan ikatan C-O ester, daya penggerak untuk interkalasi antara kumpulan MA daripada LLDPE-g-MA dan kumpulan epoksi daripada ENR. Penguraian telah berlaku secara ketara melalui penambahan OMMT dan ENR dengan sampel menjadi terlalu rapuh dan mudah patah. Bio-penguraian filem telah meningkat dengan penambahan ENR. Penemuan yang terpenting dalam kajian ini ialah pembangunan filem komposit nano yang mesra alam dengan sifat rintangan yang dipertingkatkan. Berdasarkan sifat modulus regangan, rintangan dan bio-penguraian, filem komposit nano yang mengandungi 7.5 peratus berat ENR (LDPE/OMMT/LLDPE-g-MA/ENR$_{7.5}$) merupakan formulasi yang optimum. Gabungan unik sifat modulus regangan, rintangan dan bio-penguraian untuk filem komposit nano telah menunjukkan komposit nano ini merupakan pilihan untuk pelbagai pembungkusan makanan.
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| 4.92 | Effect of OMMT on biodegradation of LDPE/ENR\textsubscript{10} blend |
| 4.93 | Effect of LLDPE-g-MA on biodegradation of LDPE/OMMNT |
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<td>ASTM</td>
<td>American society for testing and materials</td>
</tr>
<tr>
<td>ATM</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>BUR</td>
<td>Blow up ratio</td>
</tr>
<tr>
<td>CEC</td>
<td>Cation exchange capacity</td>
</tr>
<tr>
<td>CI</td>
<td>Carbonyl index</td>
</tr>
<tr>
<td>CPE</td>
<td>Chlorinated polyethylene</td>
</tr>
<tr>
<td>CPP</td>
<td>Chlorinated polypropylene</td>
</tr>
<tr>
<td>DCP</td>
<td>Dicumyl peroxide</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimeter</td>
</tr>
<tr>
<td>EB</td>
<td>Elongation at break</td>
</tr>
<tr>
<td>EMA</td>
<td>Ethylene-co-methyl acrylate</td>
</tr>
<tr>
<td>ENR</td>
<td>Epoxidized natural rubber</td>
</tr>
<tr>
<td>EUV</td>
<td>Extreme ultraviolet</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>FUV</td>
<td>Far ultraviolet</td>
</tr>
<tr>
<td>GDI</td>
<td>Gasoline direct injection</td>
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<tr>
<td>HDPE</td>
<td>High density polyethylene</td>
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<tr>
<td>ICI</td>
<td>Imperial chemical industries</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>IIR</td>
<td>Butyl rubber</td>
</tr>
<tr>
<td>iPP</td>
<td>Isotactic polypropylene</td>
</tr>
<tr>
<td>IR</td>
<td>Ionizing radical</td>
</tr>
<tr>
<td>ISO</td>
<td>International organization for standardization</td>
</tr>
<tr>
<td>KH-MT</td>
<td>Alkylamine modified MMT</td>
</tr>
<tr>
<td>LCPs</td>
<td>Liquid crystal polymers</td>
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<tr>
<td>LDPE</td>
<td>Low density polyethylene</td>
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<tr>
<td>LDPE-g-MA</td>
<td>Low density polyethylene grafted maleic anhydride</td>
</tr>
<tr>
<td>LLDPE</td>
<td>Linear low density polyethylene</td>
</tr>
<tr>
<td>LLDPE-g-MA</td>
<td>Linear low density polyethylene grafted maleic anhydride</td>
</tr>
<tr>
<td>LUV</td>
<td>Low ultraviolet</td>
</tr>
<tr>
<td>MD</td>
<td>Machine direction</td>
</tr>
<tr>
<td>mEPDM</td>
<td>Maleated Ethylene-propylene-diene Rubber</td>
</tr>
<tr>
<td>mEPR</td>
<td>Ethylene–propylene random copolymer grafted with maleic anhydride</td>
</tr>
<tr>
<td>MFI</td>
<td>Melt flow index</td>
</tr>
<tr>
<td>MMT</td>
<td>Montmorillonite</td>
</tr>
<tr>
<td>mPOE</td>
<td>Maleated ethylene-octene copolymer</td>
</tr>
<tr>
<td>MRB</td>
<td>Malaysian Rubber Board</td>
</tr>
<tr>
<td>mSEBS</td>
<td>Ethene-co-butene-styrene grafted with maleic anhydride</td>
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<tr>
<td>MUV</td>
<td>Middle ultraviolet</td>
</tr>
<tr>
<td>NOX</td>
<td>Oxides of nitrogen</td>
</tr>
<tr>
<td>NR</td>
<td>Natural rubber</td>
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<tr>
<td>NBR</td>
<td>Acrylonitrile butadiene rubber</td>
</tr>
<tr>
<td>Acronym</td>
<td>Full Form</td>
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<tr>
<td>NUV</td>
<td>Near ultraviolet</td>
</tr>
<tr>
<td>OMMT</td>
<td>Organo modified montmorillonite</td>
</tr>
<tr>
<td>OTR</td>
<td>Oxygen transmission rate</td>
</tr>
<tr>
<td>PA</td>
<td>Polyamide</td>
</tr>
<tr>
<td>PA6</td>
<td>Polyamide 6</td>
</tr>
<tr>
<td>PA12</td>
<td>Polyamide 12</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>PCL</td>
<td>Poly caprolactone</td>
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<tr>
<td>PCNs</td>
<td>Polymer/clay nanocomposites</td>
</tr>
<tr>
<td>PDMS</td>
<td>Poly (dimethyl siloxane) rubber</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PEA</td>
<td>Poly(ethylene coacrylic acid)</td>
</tr>
<tr>
<td>PE-g-MA</td>
<td>Polyethylene grafted maleic anhydride</td>
</tr>
<tr>
<td>Pema-Zn</td>
<td>Poly(ethylene-co-methacrylic acid)</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>PETG</td>
<td>Polyethylene terephthalate glycol</td>
</tr>
<tr>
<td>PEU</td>
<td>Poly(ester-urethane)</td>
</tr>
<tr>
<td>PHAs</td>
<td>Poly(hydroxy alkanoates)</td>
</tr>
<tr>
<td>PHBV</td>
<td>Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with 12% mole of hydroxyvalerate content</td>
</tr>
<tr>
<td>Ph-PP</td>
<td>Phenolic modified PP</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly(lactic acid)</td>
</tr>
<tr>
<td>PLLA</td>
<td>Poly(L-lactic acid)</td>
</tr>
<tr>
<td>PLSNs</td>
<td>Polymer layered silicate nanocomposite</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>PLST</td>
<td>Plasticized starch</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>POO</td>
<td>Peroxide</td>
</tr>
<tr>
<td>POOH</td>
<td>Hydro peroxide</td>
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<tr>
<td>PP-b-PPG</td>
<td>Polypropylene monobutyl ether</td>
</tr>
<tr>
<td>PPC</td>
<td>Poly(propylene carbonate)</td>
</tr>
<tr>
<td>PPCH</td>
<td>Polypropylene-clay hybrid</td>
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<tr>
<td>PS</td>
<td>Polystyrene</td>
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<tr>
<td>Psi</td>
<td>Pound per square inch</td>
</tr>
<tr>
<td>PU</td>
<td>Polyurethane</td>
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<tr>
<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
</tr>
<tr>
<td>PVDC</td>
<td>Poly(vinylidene chloride)</td>
</tr>
<tr>
<td>RR</td>
<td>Reclaimed rubber</td>
</tr>
<tr>
<td>SBR</td>
<td>Styrene butadiene rubber</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>Si-69</td>
<td>Silane coupling agent</td>
</tr>
<tr>
<td>SOX</td>
<td>Oxides of sulphur</td>
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<tr>
<td>SR</td>
<td>Silicone rubber</td>
</tr>
<tr>
<td>SUV</td>
<td>Supper ultraviolet</td>
</tr>
<tr>
<td>T-10</td>
<td>Onset temperature, evaluated as 10% weight loss temperature</td>
</tr>
<tr>
<td>T-5</td>
<td>The 5% weight loss temperature</td>
</tr>
<tr>
<td>TC</td>
<td>Crystallization temperature</td>
</tr>
<tr>
<td>TD</td>
<td>Transverse direction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transition electron microscopy</td>
</tr>
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<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Glass transition temperature</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>T&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Melting temperature</td>
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<tr>
<td>TPOs</td>
<td>Thermoplastic olefins</td>
</tr>
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<td>TPU</td>
<td>Thermoplastic polyurethane</td>
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<tr>
<td>TPVs</td>
<td>Thermoplastic vulcanizates</td>
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<tr>
<td>UFNBRP</td>
<td>Ultra-fine fully-vulcanized acrylonitrile butadiene rubber powder</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>Ultra high molecular weight polyethylene</td>
</tr>
<tr>
<td>ULDPE</td>
<td>Ultra low density polyethylene</td>
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<tr>
<td>UP</td>
<td>Unsaturated polyester</td>
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<tr>
<td>USCC</td>
<td>U.S. composting council</td>
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<td>UTS</td>
<td>Ultimate tensile strength</td>
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<td>Ultraviolet</td>
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<td>Ultraviolet B</td>
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<td>Ultraviolet C</td>
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<tr>
<td>VOC</td>
<td>Volatile organic compounds</td>
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<tr>
<td>VUV</td>
<td>Vacuum ultraviolet</td>
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<tr>
<td>X&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Degree of crystallinity</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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# LIST OF SYMBOLS

<table>
<thead>
<tr>
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<tr>
<td>Al</td>
<td>Aluminum</td>
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<td>$\text{AL}^{3+}$</td>
<td>Aluminum cation</td>
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<td>Å</td>
<td>Angstrom</td>
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<td>CC</td>
<td>Cubic centimeter</td>
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<td>CH$_4$</td>
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<td>CO$_2$</td>
<td>Carbon dioxide</td>
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<td>°C</td>
<td>Degree of centigrade</td>
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<td>d</td>
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<td>kg</td>
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<td>kN</td>
<td>Kilo Newton</td>
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<td>L</td>
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<td>Meter</td>
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<td>m$^2$</td>
<td>Square meter</td>
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<td>Milliampere</td>
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<td>Symbol</td>
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<td>Mg</td>
<td>Magnesium</td>
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<tr>
<td>mm</td>
<td>Millimeter</td>
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<td>min</td>
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<tr>
<td>MPa</td>
<td>Mega Pascal</td>
</tr>
<tr>
<td>nm</td>
<td>Nano meter</td>
</tr>
<tr>
<td>rpm</td>
<td>Revolution per minute</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>Si$^{+4}$</td>
<td>Silica cation</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
</tr>
<tr>
<td>P</td>
<td>Permeability</td>
</tr>
<tr>
<td>$\Delta H_f$</td>
<td>Enthalpy of fusion for 100% crystalline</td>
</tr>
<tr>
<td>$\Delta H_m$</td>
<td>Melting enthalpy</td>
</tr>
<tr>
<td>$\Delta m$</td>
<td>Flow of a gas</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>Pressure difference</td>
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<tr>
<td>$\tan \delta$</td>
<td>Mechanical loss factor</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Degree</td>
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<tr>
<td>$\mu$</td>
<td>Micron</td>
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<tr>
<td>$\mu m$</td>
<td>Micro meter</td>
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# LIST OF APPENDICES

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CHAPTER 1

INTRODUCTION

1.1 Background

Environmental concerns and petroleum resource limitations have drawn ever increasing attention over the past two decades to the development of polymers from renewable resources, particularly in the field of plastic industries. Characteristic features of petroleum-produced plastics such as light weight, high strength, chemical inertness, and low cost have led to their replacement of normal packaging plastics which include glass, metals, and ceramics. However, despite their versatilities and performances, their uses in the food packaging industry, in particular, are limited due to inherent permeability to gases and non-degradability that lead to many environmental problems due to their disposal including harm to the environment ecosystem, water supplies and sewer systems as well as to rivers and streams.

Food packaging is one of the largest growing sectors within the plastic packaging market domain. Food needs to be packaged with a strong material that can keep it safe from contamination from the environment as well as be durable enough to keep the food safe from the time of packaging up to delivery to the consumer. The primary function of food packaging is to preserve the food from penetration by harmful or dangerous substances (oxygen, moisture, light, microbes, etc.) during storage and distribution.
Traditional disposal methods include recycling, incineration and burying in landfills. Recycling has remained the most viable method of waste disposal mainly since it reduces pollution and damage to the environment. However, recycling of waste into new products after processing requires prior collection and segregation, which increases the cost of processing and thus the price of recycled products (Roy et al., 2011). In addition, these products tend to have inferior long-term properties even after proper stabilization, thereby limiting their market ability.

Non-renewability, instability and rising prices due to depletion of petroleum resources, and inherent permeability of product are among the main reasons that motivate researchers to seek alternative packaging materials in place of fossil fuels to overcome the drawbacks associated with conventional plastics. Drawbacks include renewability and/or biodegradability (Gross and Kalra, 2002, Imam et al., 2008), and permeability (Arora and Padua, 2010).

Organo modified layered silicate clay such as montmorillonite (OMMT) has received much attention due to low cost, availability and eco-friendly substance. Polymer/OMMT offers enormous improvement in the range of physical and engineering properties at low filler loading. Modifying the properties of various composites is greatly contributed to some characteristic parameters such as filler loading, size and shape and affinity towards matrix material. Nanosized layered structure has a large surface area providing sufficient interfacial regions in polymer nanocomposites for enhancement in mechanical and barrier properties of polymer matrix (Durmus et al., 2007, Gatos and Karger-Kocsis, 2007, Goettler et al., 2007, Khalili et al., 2013). In addition, OMMT as nano-particles in packaging industry has been focused recently due to low cost, attainability and availability, process ability and good performance (Majeed et al., 2013).

Bio-polymers are potential materials for packaging applications as they have many advantages over synthetic polymers including renewability, recyclability and cost effectiveness (Okhamafe, 2009). Regarding advancement in nanocomposite science and technology, compounding of polymers with bio-polymer/nanoclay is a technique that can complement the drawbacks of conventional polymers and provide
promise of a new product featuring stronger, higher barrier, short life, disposal, and environmentally compatible packaging materials (Yu et al., 2006). It is intended that the use of bio-polymer/nano clay based materials will contribute to sustainability through a reduction in environmental hazards and a reduction in the accumulation associated with disposal of synthetic polymer-based packaging materials and plastic litter, both in the sea and on land.

It is discovered that incorporation of OMMT caused to increase and accelerate the degradation of polymer (Qin et al., 2003, Shah and Paul, 2006, Kumanayaka et al., 2010, Ammala et al., 2011). The experiment result indicates that the photo-oxidative degradation of PE/OMMT nanocomposite is faster than that of pure PE upon UV exposure due to the effect of OMMT and ammonium ion, in which the effect of ammonium ion is primary. Azlina et al. (2011) investigated the permeability of TPNR nanocomposite using OMMT nanoclay and the result indicated that oxygen barrier property of TPNR increased two-fold by adding only 2 wt% OMMT. Moreover, preparation of LDPE/OMMT nanocomposite by Arunvisut et al. (2007) shows gas permeability of LDPE film for O₂ gas decreased when clay contents were increased in PE/clay nanocomposites. From neat PE to 7 wt % of clay, oxygen permeability slightly decreased by 24%; from $3.8 \times 10^{-6}$ cc.m/s.atm.m² for neat LDPE to $2.9 \times 3 \times 10^{-6}$ cc.m/s.atm.m² for 7 wt % of clay in PE/clay nanocomposites.

Epoxidized natural rubber (ENR) is a modified NR formed typically from poly(cis-1,4-isoprene), employing peracetic acid (Baker and Gelling, 1987) with an estimated annual world production of 12.5 million metric tons. ENR is one of the most promising resources and plays an important role in fulfilling the specific requirements of the composites as engineered materials. ENR has received attention from scientists and researchers owing to its advantages over most other polymers. Effective properties included bio-based material, susceptibility for living organisms, nontoxic, low cost, and biocompatibility which enabled ENR to be utilized for producing heat resistance, impact resistance, chemical resistance, tear resistance, eco-friendly and naturally degradable composite blends (Linos et
This research presents a novel nanocomposite film, which is partially biodegradable, based on LDPE/OMMT nanocomposite modified with ENR, an environmentally friendly biobased polymer. The physicochemical characterizations of films are analyzed by Fourier transform infrared (FTIR) spectrum, X-ray diffraction (XRD) and atomic force microscope (AFM). Furthermore, thermal stability and behavior of films are studied by thermogravimetric analysis (TGA), and differential scanning calorimeter (DSC), respectively. Permeability, mechanical property, degradation and biodegradation behavior of films are also studied using constant pressure and a soap bubble flow meter, tensile testing machine, Q-SUN Xenon test chamber, and soil burial test, respectively.

1.2 Problem Statements

In recent years, there is an increased requirement in the plastic industry for producing packaging films with high barrier and great mechanical properties compared with those already on the market (Lange and Wyser, 2003). The latest researches on the properties of an inventive class of composite material investigated as polymer/clay nanocomposite (PCN) indicate that it provides the answer to improve the properties (Xie et al., 2012, Khalili et al., 2013). Properties such as super mechanical strength (Santamaria and Eguiazaabal, 2012) as well as improved barrier properties against oxygen (Zhong et al., 2007, Dadbin et al., 2008, Dadfar et al., 2011) are achievable with this process.

Currently, polyolefins especially LDPE is the largest market section and is used widely in packaging industry due to flexibility, low cost, and good processing property; as a result, improvements in both the mechanical and barrier properties seem important. Nevertheless, LDPE as one of hydrophobic polymers is resistant to biodegradation, which is another main attribute in packaging.
Environmental problems caused by disposal films including harm to the environment eco-system, water supplies and sewer systems as well as to rivers, and streams have drawn considerable attention of scientists to produce and utilize alternative material with environmentally friendly property. Recently, most scientists and researchers have focused their studies on the production of biodegradable films in addition to meeting the desired purpose in improving mechanical and barrier properties (Henriette, 2009, Cho and Kim, 2011).

In order to reduce the waste pollution as a result of packaging production attempt has been done to improve the biodegradability of film. ENR known as bio-based polymer with characteristic property has been blended to nanocomposites. Due to existence of ether group in ENR’s backbone, it has enhanced and accelerated the rate of degradation mechanism that can promote degradability. Moreover, respect to biodegradability characteristic and susceptibility for living organisms, the biodegradability of film has been improved.

Furthermore, despite low barrier property of LDPE, incorporation of ENR has been enhanced the barrier property of film due to impermeability characteristic feature during stretching process and its polarity, which promises to expand the production of high barrier film in addition to biodegradable and environmentally friendly material.

In present study, novel LDPE/OMMT/ENR nanocomposites are developed. The nanocomposites with various ENR contents (0-10 wt%) are melt-compounded and blown to films. OMMT nanoclay has been used as impermeable layers and high aspect ratio to promote the barrier property and improve tensile properties. ENR as one of the environmental friendly bio-based polymers and barrier modifier has been blended with LDPE/OMMT nanocomposite to produce biodegradable nanocomposite packaging films alongside desired barrier property. Compatibilizer known as linear low-density polyethylene grafted maleic anhydride has been employed to improve the clay distribution and reduce the interfacial tension between phases.
1.3 Objectives of Research

The present study investigates the effect of ENR concentration on barrier and biodegradation of films. The knowledge obtained from this investigation will be useful in designation of film with improved barrier property and environmentally friendly degradable films. The overall main aims of the present study are to make environmentally compatible packaging film based on LDPE by enhancing its rate of biodegradation without scarifying its barrier.

The specific objectives of this research are:

i) To examine the effect of 6 wt% of OMMT on tensile, thermal, morphology, barrier properties of neat LDPE, and LDPE/ENR nanocomposites films

ii) To study the effect of LLDPE-g-MA as compatibilizer on the tensile, thermal, morphology, barrier and biodegradation properties of neat LDPE and LDPE/ENR nanocomposites films

iii) To carry out the effect of ENR content on the tensile, thermal, morphology, barrier, and biodegradation properties of neat LDPE, un-compatibilized and compatibilized LDPE nanocomposites films

1.4 Scopes of Research

In this project, LDPE, OMMT, ENR and LLDPE-g-MA have been used as raw materials to produce nanocomposite films. ENR as one of environmental friendly bio-based polymers and barrier modifier has been blended with LDPE/OMMT nanocomposites to produce biodegradable nanocomposites packaging film alongside desired barrier property. OMMT has been used as nanofiller, and
LLDPE-g-MA has been applied with reference to compatibilizer because of chemical interaction between the polar groups of ENR and OMMT and miscibility with LDPE.

To obtain LDPE nanocomposite the twin screws extruder has been used for compounding the raw materials, and single screw blown film machine has been applied to produce nanocomposite film. In addition, following tests are carried out:

i) The tensile properties of LDPE blend and nanocomposite films are determined by tensile test

ii) The influence of nanoclay on film characterization is examined by using X-ray diffraction (XRD)

iii) The chemical interactions of blends and nanocomposites are determined by Fourier transform infrared spectroscopy (FTIR)

iv) Thermal behavior properties of blends and nanocomposite films are studied by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA)

v) Permeability of the films through O$_2$ is examined via constant-pressure system and a soap bubble flow meter

vi) Morphology and distribution of ENR and OMMT is observed by using atomic force microscope (AFM)

vii) Degradation progress of different films is analyzed via Q-SUN Xenon test chamber

viii) Biodegradability of films is examined through soil burial test

The study is highly relevant from applied viewpoint of nanotechnology and sustainability for development of advanced and environmental friendly packaging material having higher performance properties and enhanced biodegradability. It is expected this study will serve as millstone in achieving our goals toward development of environmentally friendly product without scarifying barrier property.
1.5 Thesis Outline

Chapter 1 presents background of the study supported with an overview of discovering previous research have been conducted to packaging, nanotechnology and nanocomposites. In addition, problem statements, objectives and scope of study have been reported.

Chapter 2 begins with some general characteristic of polyolefin being used in food packaging in particular LDPE, along with its particular applications. Properties of compatibilizer, nanoclay, epoxidized natural rubber, in general, and discussion regarding their potential to develop high performance nanocomposites are presented as well. In the literature survey, some information regarding degradation and classification of degradable polymer also is reported. The key finding of previous studies done by other researchers for barrier property of film and parameters affecting the property is described as well.

Chapter 3 describes the properties of material used in present study. A detailed formulation of all prepared samples and experimental procedure to prepare film is also reported. Different utilized techniques and their operating conditions are also reported.

Chapter 4 reports the influence of OMMT which is being used frequently in nanocomposite on tensile, thermal, morphology and barrier properties. This chapter also discusses the role of LLDPE-g-MA on the properties of LDPE/ENR blends and LDPE/OMMT/ENR nanocomposites. Influence of adding ENR also on properties of un-compatibilized and compatibilized nanocomposites are discussed. Result and discussion about varying contents of ENR and influence on tensile, thermal, morphology, barrier and biodegradation is presented in details.

Chapter 5 concludes the results presented in chapter 4. In addition, suggestions for future work are also included.
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