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CHARACTERIZATION AND PROPERTIES OF CALCIUM CARBONATE FILLED POLYPROPYLENE (PP) / ETHYLENE PROPYLENE DIENE TERPOLYMER (EPDM) COMPOSITES

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Characterization and Properties of Calcium Carbonate Filled Polypropylene (PP) / Ethylene Propylene Diene Terpolymer (EPDM) Composites

by

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- Siti Rohana Binti Ahmad -

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LIST OF ABBREVIATIONS, SYMBOLS, SPECIALIZED NOMENCLATURES

µ	Micron
µm	Micron meter
3-APE	3-Aminopropyltriethoxysilane
AA	Acrylic acid
ABS	Acrylonitrile-butadiene-styrene copolymer
AFM	Atomic Force Microscope
ASTM	American Society for Testing and Material
BA	Butyl acrylate
BPO	Benzoyl peroxide
$CaCO_3$	Calcium carbonate
COPEs	Thermoplastic copolyester elastomers
CPP	Nanocomposites chlorinated polypropylene
DCPD	Dicyclopentadine
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
DV	Dynamic Vulcanization
EAA	Ethylene-acrylic acid
E_b	Elongation at break
EEA	Ethylacrylate
ENB	5-ethylidene norbornene
EMA	Ethylene methyl acrylate
EPDM	Ethylene propylene diene terpolymer

EPM	Ethylene propylene copolymer
EVA	Ethylene vinyl acetate
EWF	Essential wok of fracture
FTIR	Fourier transform infrared spectroscopy
G_{Ic}	Strain energy release rate
HDPE	High density polyethylene
HPC:poly(AA)	Hydroxypropyl cellulose: poly(acrylic acid)
K_{Ic}	Critical stress intensity factor
LDPE	Low density polyethylene
MAA	Methacrylic acid
MAPP	Maleic anhydride grafted polypropylene
MMA	Methyl methacrylate
NR	Natural rubber
NBR	Acrylonitrile-butadiene rubbers
OMMT	Organophilic montmorillonite
Pd	Palladium
PE	Polyethylene
PET	Polyethylene terephthalete
PLLA	Amorphous poly(L-lactide)
PMMA	Polymethyl Methacrylate
PP	Polypropylene
PVC	Polyvinyl chloride
SBS	Styrene block copolymers
SEBS	Styrene-ethylene-butylene block copolymer
SEM	Scanning electron microscope
T	Temperature
T_c	Crystallization temperature
TEM	Transmission electron microscope

TGA	Thermogravimetric analysis
TPEs	Thermoplastic elastomers
TPOs	Thermoplastic olefinics
TPR	Thermoplastic rubber
TPUs	Thermoplastic polyurethanes
TPVs	Thermoplastic vulcanisates
VI	Vinylimidazole
W_d	Original dry weights
W_N	After exposure weights
WRHA	White rice hush ash
WFC	Wood flour composite
X_{com}	Crystallinity of composites
X_{pp}	Crystallinity of PP
1,4 HD	4 hexadiene
3-APE	3-aminopropyltriethoxysilane
$\Delta H^0_{f\,(com)}$	Heat of fusion of composites

PENCIRIAN DAN SIFAT-SIFAT KOMPOSIT POLIPROPILENA (PP)/ ETILENA PROPILENA DIENA MONOMER (EPDM) TERISI KALSIUM KARBONAT

ABSTRAK

Komposit elastomer termoplastik bagi adunan polypropilena (PP) dan etilena propilena diena monomer (EPDM) yang diperkuat kalsium karbonat telah dikaji. Kesemua komposit disediakan menggunakan pencampur bilah-Z pada 180^{o}C dan kelajuan rotor 50 rpm. Kesan pembebanan pengisi kalsium karbonat terisi komposit PP/EPDM keatas sifat-sifat mekanikal, penyerapan air, morfologi dan sifat-sifat terma telah dikaji. Secara umumnya, didapati pembebanan kalsium karbonat yang semakin meningkat telah meningkatkan modulus elastisiti, penyerapan air, kestabilan terma dan penghabluran komposit didapati berkurang. Manakala kekuatan tensil dan pemanjangan pada takat putus didapati berkurang. Agen pengserasi, MAPP atau agen pengkupel 3-APE digunakan untuk meningkatkan sifat-sifat mekanikal komposit. Kehadiran MAPP atau 3-APE telah meningkatkan kekuatan tensil, modulus elastisiti, kestabilan terma, penghabluran komposit kecuali pemanjangan pada takat putus dan penyerapan air yang didapati semakin berkurang. Kajian mikroskop electron penskanan (SEM) menunjukkan bahawa kehadiran MAPP atau 3-APE telah meningkatkan interaksi antara muka pengisi-matrik. Kesan modifikasi kimia kalsium karbonat dengan asid akrilik (AA) untuk komposit PP/EPDM telah meningkatkan kekuatan tensil, modulus elastisiti, kestabilan terma dan penghabluran komposit tetapi penyerapan air didapati berkurang. Morfologi SEM menunjukkan komposit rawatan dengan asid akrilik menghasilkan penyebaran pengisi di dalam matrik yang lebih baik. Kesan pemvulkanan dinamik bagi komposit PP/EPDM/$CaCO_3$ menunjukkan kekuatan tensil, pemanjangan pada takat putus dan modulus elastisiti yang lebih tinggi tetapi penyerapan air yang rendah. Kajian SEM pada permukaan patahan tensil komposit pemvulkanan dinamik menunjukkan peningkatan interaksi antara muka di antara kalsium karbonat dan matrik PP/EPDM. Komposit pemvulkanan dinamik mununjukkan kestabilan terma yang lebih baik dan penghabluran yang lebih tinggi.

CHARACTERIZATION AND PROPERTIES OF CALCIUM CARBONATE FILLED POLYPROPYLENE (PP) / ETHYLENE PROPYLENE DIENE TERPOLYMER (EPDM) COMPOSITES

ABSTRACT

Composites of thermoplastic elastomer blend of polypropylene (PP) and ethylene propylene diene terpolymer (EPDM) reinforced calcium carbonate ($CaCO_3$) was investigated. All the composites were prepared by using Z-blade mixer at 180^oC and rotor speed 50 rpm. The effect of filler loading of calcium carbonate filled PP/EPDM composites on mechanical properties, water absorption, morphology and thermal properties were studied. In general, increased of calcium carbonate loading have increased the value of modulus of elasticity, water absorption, thermal stability, whereas tensile strength, elongation at break and crystallinity of composites reduced. A compatibilizer, (MAPP) or coupling agent, (3-APE) was used to improve the mechanical properties of composites. The presence of MAPP or 3-APE improved the tensile strength, modulus of elasticity, thermal stability and crystallinity composites, whereas elongation at break and water absorption reduced. Results from scanning electron microscope (SEM) show that filler-matrix interaction was improved with incorporation of MAPP or 3-APE. The effect chemical modification of calcium carbonate with acrylic acid (AA) in PP/EPDM composites increased the tensile strength, elongation at break, modulus of elasticity, thermal stability and crystallinity composite but water absorption reduced. The micrograph SEM showed the treated composites with acrylic acid has better dispersion in PP/EPDM matrix. Effects of dynamic vulcanization on the properties of PP/EPDM/$CaCO_3$ composites exhibit higher tensile strength, elongation at break and modulus of elasticity but lower water absorption. The SEM study of tensile fracture surface of dynamic vulcanized composites show interfacial interaction between calcium carbonate and PP/EPDM matrix has been improved. The dynamic vulcanized composites also exhibit better thermal stability and higher crystallinity.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Nowadays in new era of technologies, the improvement of material becomes an important in industries. Many researchers has come out with several ideas in order to meet the material properties requirement for most modern applications includes automotive, aerospace, underwater and etc. Besides, needs of sophisticated materials that friendly environment playing an important role due to ecological reasons.

In recent years, polymers become an important engineering materials and the number of applications is increasing steadily. Polymers have increasingly replaced metallic components in an amazing array of applications, including automobiles, microelectronics, composites, civilian and military aircraft, sporting goods, toys, appliances, and office equipment, due to their many unique and diverse properties. Humans have taken advantage of the versatility of polymers for many centuries in the form of naturally occurring polymers (those derive from plants and animals) include tars, gums, resins, oils, wood, rubber, cotton, wool, leather, and silk. The introduction of these revolutionary materials began an explosion in polymer research that is still going on today.

"Polymer" word literally means "many units". In other words, repeating many structural unit of a plastics chain is termed as 'mers'. Also, polymer is a branch of carbon chains from petrol-chemical industry. According to the ASTM, the definition of a plastic is; *"A material that contains as an essential ingredient an organic substance of* *large molecular weight, is solid in its finished state, and at some stage in its manufacture or in its processing into finished can be shaped by flow".* Polymers are generally classified into three main groups according to their structure, properties and use as thermoplastics, thermosetting plastic and elastomers. The advantages of polymers are low density, corrosion resistance and resistance to chemical, high strength-to-weight ratio, particularly when reinforced, low electrical and thermal conductivity, noise reduction, relatively low cost, ease if manufacturing and complexity of design possibilities etc. The modification of polymer molecular architecture either during or post polymerization includes (i) copolymerization of more than one polymer (ii) control of monomer architecture (iii) post polymerization polymer reactions (iv) introduction of functional groups (Ebewele, 2000).

Polymer composites receive increasingly interest because it is a relatively easy way to obtain new materials with balanced properties. The name polyolefinic thermoplastic elastomer (TPE) has been coined to refer to a specific family of thermoplastic alloys that offers the main advantages of two types of polymeric materials: elastomeric behavior at room temperature and thermoplastic behavior at processing temperatures. This dual behavior is obtained because the morphology consists of small rubber particles dispersed in a continuous thermoplastic matrix.

To date, thermoplastic elastomer compositions based on polypropylene (PP)/ ethylene polypropylene diene terpolymer (EPDM) composites have increased tremendously in popularity. These composites are used for a wide range of products including automotive parts such as rub strips, sight shields, bumper covers, side claddings and etc. PP/EPDM composites also excellent weatheability, low density and relatively low cost make them a common component in a number of exterior and interior automotive applications (De and Bhowmick, 1990).

Polypropylene is an economical material that offers a combination of outstanding physical, chemical, mechanical, thermal and electrical properties not found in any other thermoplastic. In addition, toward the comparison with low or high density polyethylene, it has a lower impact strength, but superior working temperature and tensile strength. Polypropylene (PP) is one of the important commodity polymers. It is widely used in automobile, household appliance and construction industry due to its balanced mechanical properties. The application of PP, however, is limited by its brittleness, especially at low temperature, as well as low stiffness at elevated temperature.

Most commercial elastomer are based on ethylene propylene diene terpolymers (EPDM), because of its stability against high temperatures, oxygen and ozone, thus giving to the corresponding good heat, oxidation and ozone resistance. Ethylene propylene diene terpolymer (EPDM) is an unsaturated polyolefin rubber with wide applications, it has become extensively used in making automotive tire sidewalls, cover stripes, wires, cables, hoses, belting, footwear, roofing barriers and sporting goods.

In the past decade, the use of inorganic filler to improve the physical properties of polymer composites has become widespread in the production of high-performance materials. Adding inorganic filler can enhance the stiffness but result in a decrease of toughness. To overcome the drawback resulted by only adding elastomer or filler, a lot of work has been done on polymer/elastomer/filler ternary system, where both elastomer and filler were used to enhance the toughness and stiffness simultaneously (Zhang *et al*., 2000; Jancar & Dibenedetto, 1995).

Fillers are essential components of multiphase composite structures. The use of fillers in the preparation of polymeric compositions increases every year, because of the advantages which can be obtained, such as reduction in the final price of the product, improvement in process ability and achievement of specific. Usually, fillers form the minor dispersed phase in a polymeric matrix. Various fillers have been employed in ternary phase polymer composites. These include talc, calcium carbonate (Kolarik *et al*., 1990) and kaolin. In particular, the fillers can improve the toughness, processibility, heat distortion temperature of polymer blends, and conductive fillers can even make the insulative polymer blend to become a conductive one.

Mineral filler such as calcium carbonate ($CaCO_3$) used in the PP/EPDM composites to reduce cost and improve the properties of the composites. Besides, this type of filler has a primary function as a mechanical property improver likes slightly increased of modulus of elasticity (Zuiderduin *et al*., 2003; Xanthos, 2005). It is available in different grades: dry processed, wet or water ground and can be easily surface treated (Lazzeri *et al*., 2005) and usually micron-sized (easier to disperse) with a broad size distribution and irregular shape (Osman *et al*., 2004).

Gonzalez *et al*., (2002) used $CaCO_3$ particles treated by different coupling agents to modify the mechanical properties of PP/HDPE blends. They found that, due to the particular characteristics of the coupling agents, each treated $CaCO_3$ particles gave rise to increase in a specific mechanical property. The main problem of preparation of $CaCO_3$ thermoplastic elastomer composite is the incompatibility of hydrophilic $CaCO_3$ and hydrophobic thermoplastic elastomer matrix.

Maleic anhydride grafted polypropylene (MAPP) was used as a compatibilizer in order to improve the properties of PP/EPDM/$CaCO_3$ composites. MAPP has been used as a coupling agent to promote the filler-matrix adhesive strength. Furthermore, the PP part of MAPP adheres to the long hydrophobic chains of the PP virgin matrix and lowers the surface tension of the fibres and form a strong interface (Mohanty and Nayak, 2007). MAPP have been widely used to improve the interfacial interaction between the components in polymer blends and polymer composites to maximize the physical properties (Moad, 1999). Qui *et al.*, (2005) reported that the novel technique for preparing maleic anhydride grafted polypropylene offers new opportunities in modification of polyolefins, which has also the advantages of solventless, lower process temperature, energy efficient, low cost, and simple running process.

Since 1950's, silanes have been used, whereby it had been instrumental in producing successful fibreglass reinforced thermoset polyester composite applied on automotive industry. The incorporation of coupling agents onto the filler surface is an obvious solution in order to modify interaction or increased the bonding of filler to polymer by either altering the strength or changing the size of the interaction. Liang and Li, (2000) reported that the treatment of glass beads with silane coupling agents have successfully improved the tensile strength and modulus of elasticity of PP. Demjen, (1997) on studied of the treatment of calcium carbonate using eight types of silane coupling agents to determine their effect on PP/$CaCO_3$ composite. The incorporation of aminofuctional silane coupling agents was carried out in the reactive coupling of PP and $CaCO_3$, in which both are inactive components, leading to increased strength and decreased deformability. Bezerdi *et al*., (1998) concluded that the reactive (aminosilane) coupling agent lead to an increase in composite strength in their research used linear elastic fracture mechanics to characterize fracture resistance of PP/$CaCO_3$ composites with aminosilane coupling agent.

Some of academicians, researchers or industrial scientists have a significant interest in developing techniques for modifying the surfaces of solid substrates without altering the bulk properties (Ma *et al*., 2001). Acrylic acid was classified as surface modifiers in polymer composites industry. Some of the method used for rubber surfaces is surface modification using acrylic acid. According to Kaynak *et al*., (2001), the interface between an epoxy resin matrix and recycled scrap car tire rubber particles can be improved by the modification of the surfaces of rubber particles. Okrasa et al., (2001) reported that the larger modification of the molecular relaxation processes is observed in the hydroxypropyl cellulose: poly (Acrylic acid), (HPC:poly(AA)) composites, where the stronger intermolecular interactions are present.

Vulcanization or cross-linking is the process in which mainly polymer is converted from a plastic state to an elastic state or a hard rubber state. The process is brought about by linking of macromolecules at their reactive sites (Ismail *et al*., 2004). Dynamic vulcanization (DV) is a process of cross-linking the elastomer during its melt mixing with molten plastic. It can improve properties such as mechanical properties (Mehrabzadeh and Delfan, 2000), resistance to heat and resistance to attack by fluid (Ismail *et al*., 2001). It is quite obvious that the cross-link density of the dispersed