PRE-DISPERSING PROCESS OF ORGANO-MONTMORILLONITE NANOFILLER: INFLUENCE TO THE TOUGHNESS, FLEXIBILITY AND THERMAL STABILITY OF ETHYLENE VINYL ACETATE (EVA) NANOCOMPOSITES

by

TUTY FAREYHYNN BINTI MOHAMMED FITRI

(1531621603)

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School of Materials Engineering
UNIVERSITI MALAYSIA PERLIS

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TUTY FAREYHYNN BINTI MOHAMMED FITRI

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LIST OF ABBREVIATIONS

Ag	Silver
Al	Aluminium
Al_2O_3	Aluminium oxide
Au	Gold
BTHC	Butyryl trihexyl citrate
$CaCo_3$	Calcium Carbonate
CEC	Cation exchange capacity
CNTs	Carbon nanotubes
DEHA	di (2-ethylhexyl) adipate
DEHP	di-(2-ethylhexyl)-phthalate
DIDP	di-iso-decyl phthalate
DINCH	di (isononyl) cyclohexane-1,2-dicarboxylate
DINP	di-iso-nonyl phthalate
DMTA	Dynamic thermal mechanical analysis
DSC	Differential scanning calorimetry
EB	Elongation at break
EVA	Ethyl vinyl acetate
Fe	Ferrum
FTIR	Fourier transform infrared
H_2O	Water
Mg	Magnesium
MMT	Montmorillonite
MS	Magnetic stirrer
Na	Sodium
O	Oxygen

OH	Hydroxyl groups
Organo-MMT	Organically modified montmorillonite
PDMS	Polydimethylsiloxane
PE	Polyethylene
PP	Polypropylene
PVA	Polyvinyl alcohol
PVC	Polyvinyl Chloride
rpm	Revolutions per minutes
SEM	Scanning electron microscope
Si	Silicon
SiC	Silicon carbide
SiO_2	Silicon dioxide
SWNT	Single wall carbon nanotubes
Tg	Glass transition temperature
TGA	Thermogravimetric analysis
TiO_2	Titanium dioxide
TL	Toluene
TOTM	Trioctyl trimellitate
TPU	Thermoplastic polyurethane
US	Ultrasonication
UV	Ultraviolet
VA	Vinyl acetate
W	Water
ZnO	Zinc oxide

LIST OF SYMBOLS

%	Percentage
wt%	Weight percentage
°C	Degree Celsius
°	Degree
T_{dmax}	Temperature maximum degradation
g	Gram
J	Joule
Kg	Kilograms
m^3	Cubic metre
mm	Millimeter
min	Minute
mg	Milligram
Hz	Hertz
K	Kelvin
MPa	Megapascals
cm^3	Cubic centimeter
<	Less than
>	More than
ΔH_m	Enthalpy of fusion of PE melting endotherms
ΔH_c	Enthalpy of crystallization of PE

Proses Pra-penyebaran untuk Pengisi-nano Organo-Montmorilonit: Pengaruh ke atas Keliatan, Fleksibiliti dan Kestabilan Haba untuk Etilena Vinil Asetat (EVA) Nanokomposit

ABSTRAK

Di alaf baru ini, kemajuan lebih mapan di dalam peranti perubatan generasi baru agak terbatas disebabkan oleh keperluan yang lebih ketat terhadap bahan bio-perubatan untuk kegunaan rawatan dan prosedur bio-perubatan yang semakin canggih dan menyeluruh. Ahli-ahli sains oleh itu, mengekalkan usaha untuk membangunkan bahan-bahan baru dan lebih baik untuk pertumbuhan industri bio-perubatan ini. Penyelidikan ini bertujuan untuk menghasilkan bahan keserasian-bio yang baru dengan fleksibiliti, kekuatan dan kestabilan haba yang sangat baik sebagai calon masa depan untuk aplikasi bio-perubatan. Nanokomposit Etilena Vinil Asetat mengandungi 5wt% organo-montmorilonit telah dihasilkan degan menggunakan kaedah pensebatian leburan supaya relevan dengan proses pembuatan industri. Prosedur pemprosesan baru, yang dikenali sebagai proses 'pra-penyebaran' telah diperkenalkan untuk memudahkan penyebaran pengisi-nano organo-MMT di dalam matriks, dan pada masa yang sama memberikan kesan pemplastikan untuk perumah EVA kopolimer. Cecair toluene dan air telah digunakan sebagai medium pra-penyebaran dan keberkesanan mereka untuk meningkatkan prestasi mekanikal dan haba nanokomposit EVA telah dikaji. Sebagai tambahan, beberapa parameter pra-penyebaran turut digunakan di mana ianya melibatkan jenis kaedah dan tempoh penyebaran yang berbeza. Hubungan di antara struktur-sifat-pemprosesan nanokomposit EVA telah dikaji dan medium dan parameter pra-penyebaran terbaik telah ditentukan. Berdasarkan kajian morfologi, mekanikal dan haba oleh FTIR, SEM, ujian tensil, DMTA, DSC dan TGA, pengisi-nano organo-MMT yang telah disebarkan melalui pengultrasonikan dalm medium medium air selama 2 minit (MMT(W)2m_u) memberikan kesan pemplastikan yang paling ketara untuk kopolimer EVA. Analisis FTIR telah membuktikan 'kesan ketidakstabilan' oleh proses pra-penyebaran terhadap tenaga pengikat di dalam antara-galeri organo-MMT. Kesan ketidakstabilan ini memudahkan pengelupasan organo-MMT dan penyebarannya di dalam EVA, meningkatkan pengedaran ion onium pada antara-muka nanoplatelet-polimer, dan kemudiannya menyebabkan kelonggaran rantai kopolimer EVA semasa pembentukan dan prosess mengubah bentuk. Hasilnya, EVA nanokomposit yang terplastik telah diperlolehi. Apabila dikenakan ubah bentuk tensile, penurunan keelastikan modulus diiringi juga oleh peningkatan pemanjangan ketika putus dan keliatan. Analisis DMTA telah membuktikan lagi kesan pemplastikan ini apabila modulus simpanan EVA dilihat telah berkurangan di dalam lingkungan suhu -40 °C hingga 45°C apabila diisikan dengan pengisi-nano MMT(W)2m_u. Berdasarkan sifat redaman, seseorang boleh mencadangkan bahawa keserasian di antara rantaian Polietilena (PE) dan Poli Vinil Asetat (PVC) di dalam kopolimer EVA telah ditambah apabila ditambah nanofiller. Semua faktor-faktor ini membawa kepada peningkatan dalam kestabilan haba EVA nanokomposit seperti yang dapat diperhatikan dalam TGA. Kesimpulannya, proses pra-penyebaran pengisi-nano organo-MMT nanofiller boleh membawa kesan-kesan yang baik kepada prestasi keseluruhan EVA nanokomposit, sebagai calon untuk bahan bio-perubatan.

Pre-dispersing Process of Organo-Montmorillonite Nanofiller: Influence to the Toughness, Flexibility and Thermal Stability of Ethylene Vinyl Acetate (EVA) Nanocomposites

ABSTRACT

In these new millennia, further advances in new generation medical devices are restricted due to more stringent requirements of biomedical materials for use in more sophisticated and comprehensive biomedical treatment and procedures. Scientists are therefore, keeping an effort to develop new and improved materials for the growth of this biomedical industry.This research intends to develop a new biocompatible material with excellent flexibility, toughness and thermal stability as future candidate for biomedical applications. Ethylene Vinyl Acetate nanocomposites containing 5wt% organo-MMT were produced by melt compounding method, to be relevant with the industrial manufacturing process. A new processing procedure, the so called 'pre-dispersing' process was introduced in order to facilitate the organo-montmorillonite nanofiller dispersion in the matrix, and at the same time provide the plasticizing effect to the host EVA copolymer. Toluene and water liquids were used as pre-dispersing medium and their efficiency to enhance the mechanical and thermal performance of the EVA nanocomposites was investigated. Furthermore, several pre-dispersing parameters were employed involving different types of dispersing method and time. The structure-property-processing relationships of the EVA nanocomposites were studied and the best pre-dispersing medium and parameters were determined. Based on the morphological, mechanical and thermal studies by FTIR, SEM, tensile test, DMTA, DSC and TGA, the organo-MMT nanofiller pre-dispersed by ultrasonication in water medium for 2 minutes (MMT(W)2m_u) gives the most significant plasticizing effect to the EVA copolymer. The FTIR analysis evidenced the 'destabilizing effect' of the pre-dispersing process to the binding energy within the organo-MMT inter-galleries. This destabilization effect facilitated the organo-MMT exfoliation and dispersion inside the EVA, enhanced the distribution of onium ions at the nanoplatelet-polymer interfaces, and subsequently promoted relaxation of EVA copolymer chains during conformation and deformation process. As a result, plasticized EVA nanocomposite was obtained. When subjected to tensile deformation, the lowering of modulus of elasticity was accompanied by an increased in elongation at break and toughness. DMTA analysis has further proved this plasticizing effect as the storage modulus of the EVA was seen to reduce in the region of -40° to 45°C when incorporated with the MMT(W)2m_u nanofiller. Based on the damping behaviour, one could suggest that the compatibility of the polyethylene (PE) and polyvinyl acetate (PVA) of the EVA copolymer was enhanced when the MMT(W)2m_u nanofiller was added. All these factors led to the enhancement in thermal stability of the EVA nanocomposite as can be observed in TGA. In conclusion, the pre-dispersing process of organo-MMT nanofiller can bring beneficial effects to the overall performance of the EVA nanocomposite, as a candidate for biomedical material.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The medical uses of polymeric materials have grows rapidly, during the last decades in conjunction with the advancements in polymer technology. The growth in human populations and the needs to extend an average individual health-span led to the development of new generation medical devices, medical diagnostic technologies and drug delivery systems. In the production of the components for medical equipments, the variation of materials used has also expanded. Many devices for use in medicine such as tubing, catheters, probes, packaging for drugs and ointments, nursing aids, and also surgical instruments are now being made from polymeric materials (Tuzhilkin & Rylov, 1974; Lloyd, 2004). This is due to the flexibility, ease of shaping and processing of the polymeric materials as compared to metal and ceramic materials. However, as new medical device designs continue to reduce in size and thickness, new materials that exhibits improved strength and toughness, while maintaining their flexibility and biocompatibility are also required. The medical industries are still keeping an effort to develop these new, sophisticated and ideal biomedical plastics which are having the above mentioned characteristics. Ongoing research and invention are needed in order to overcome the limited number of existing biostable, biocompatible, flexible and tough materials that offer versatility, exceptional performance, and meet industrially relevant manufacturing process.

The biocompatibility and flexibility of the biomedical plastics are much more in concern if the materials are to be used for the implantable device. Biocompatible, soft and flexible materials are needed for close contact with human tissue in order to avoid irritation and tissue damage. For more than 30 years, crosslinked silicone elastomers have been used extensively in implantable devices (Ward, 2000; Osman, 2013). This is due to their biostability and biocompatibility combined with a low hardness and modulus making them useful for many devices applications (Lamba et al., 1998; Ratner, 2004; Osman, 2013). The use of silicone materials in medical implantable devices can be seen for example in facial, breast, pacemaker and cochlear implants (Agrawal, 1998). However, the applications of silicone elastomer are often limited due to the inherently poor mechanical properties of these materials, particularly in relation to tensile and tear strength. In many long-term implantable medical device applications where silicones are currently used, the poor tear strength, toughness and high surface tack of these silicone elastomers are restricting further advances in the new generation of devices (Szycher, 2012; Osman et al., 2014).

With regards to the above mentioned problems, this project intends to develop a new biocompatible material with excellent flexibility, toughness and thermal stability as future candidate for biomedical applications. Previous researches proved that polymeric materials can be tailored to meet specific property requirements by the incorporation of organically modified nanoclays such as montmorillonite (MMT), fluoromica and hectorite. This combination of polymers and organoclays resulted in new form of materials called polymer nanocomposites, which possess various advantages over the neat polymer such as the improvement in mechanical and barrier properties, biocompatibility, biostability, flame retardancy and also thermal stability (Osman et. al.,

2012a; Osman et al., 2012b; Andriani, 2013; Osman et. al., 2016). While a large body of research concerning polymer-organoclay nanocomposites exists, the number of studies specifically devoted to ethyl vinyl acetate (EVA) nanocomposite is relatively small. The use of EVA as the nanocomposite matrix presents some interesting challenges to understand the complex morphology of the EVA, due to existence of amorphous, crystalline, polar and non-polar structure. EVA is a type of copolymer which is composed from long chains of ethylene (non-polar) and randomly distributed vinyl acetate (polar) monomers (Fink, 2010; Merinska et al., 2013). Recently, the number of researches on EVA copolymer has kept increasing, further revealing its potential for various applications (Merinska et al., 2013). EVA possess thermoplastic characteristics, which means it can be easily moulded and processed by conventional industrial method such as calendaring, injection, extrusion, blow moulding and rotational moulding. The main advantage of this copolymer is the possibility to obtain a wide range of properties by varying the VA content in its composition. Therefore, it is possible to broaden their applications from rigid plastic to the rubber like/ elastic products (Fink, 2010; Peacock, 2000). Recent works proved that EVA copolymers have potential to be developed as biomedical materials as their mechanical and thermal properties, biostability and biocompatibility can be further enhanced by the incorporation of organically modified montmorillonite (organo-MMT) nanofiller (Osman et al., 2015a; Osman et al., 2016).

Montmorillonite (MMT) nanoclay is regularly used nanofiller, due to its high aspect ratio and a large surface area; hence its incorporation into the polymer matrix generates a large surface area for the polymer/filler interaction to provide the required reinforcement and barrier effects (Agubra, 2013). A MMT comprises of one nanometer

thick aluminosilicate layers surface which substituted with metal cations and stacked in 10 micro size multilayer stacks. In the original state, nanoclays are hydrophilic in nature; hence, the interaction with most polymers is not favoured (Osman et al., 2016). By introducing a suitable surfactant or compatibilizer, the compatibility between the MMT and the host polymer can be achieved. MMT in stacking (tactoids) form can be exfoliated or delaminated into individual nanometer thick layers to form plate like nanoparticles with very high aspect ratio inside the polymer matrix. With regard to this, compatibility of MMT-polymer can be optimized with different types of surface modifications (Barick & Tripathy, 2010). The most widely applied was the surface modification of natural MMT via the ion-exchange reactions, in which the interlayer cations are replaced with quaternary alkyl ammonium or alkyl phosphonium cations (Lee & Tiwari, 2012). Organic cations from long-chain alkyl ammonium salts have been widely used for exchanging the inorganic cations from the MMT because of their ability to increase the basal spacing of the nanoplatelets, therefore facilitate their dispersion inside the polymer matrix. The exfoliation and dispersion of the organo-MMT nanofiller are vital to ensure the improvement in thermal, mechanical and barrier properties of the end nanocomposite product (Osman et al., 2016). It has been reported by many researchers that poorly dispersed nanoparticles could degrade the mechanical properties of host polymers (Agubra et al., 2013; Andriani, 2013a; Osman et al., 2015a). For example, Osman et al. (2015a) demonstrate that the incorporation of 5 wt% organo-MMT into the EVA resulted in reduced mechanical properties of the host TPU when exposed to oxidative and hydrolytic conditions, due to poor dispersion of the nanofiller. Furthermore, the previous research by Andriani et al. (2013b) also suggested that the organoclays which are poorly dispersed in the host polymer are nearly to leach out and leads to safety risk as a contrast to the well-dispersed organoclays. This was due to their

high tendency of forming large tactoids, which can easily phase separated from the host polymer (Osman et al., 2015a). Even though it is highly importance to produce well dispersed and exfoliated layered nanofiller in the host polymer, several researches proved that fully exfoliated nanoclay structure is difficult to achieve, even when surface modified (Osman et al., 2012b; Osman et al., 2015b; Osman et al., 2016). In previous research by Osman et al. (2015b) state that the large organo-MMT stacking platelets (tactoids) with limited mobility and high spatial restrictions were believed to experience frustrated orientational freedom in the matrix. Consequently, making it more difficult for intercalated polymer to deliminate them into single layers (Osman et al., 2015b). Therefore, there is an urgent need for further improving the processing method towards optimization of nanoclay delamination (exfoliation) and dispersion in the host material. Vigorous stirring and adequate shear energy might needed in order to break the tactoids and fully exfoliate this particular nanofiller for better dispersing ability inside the polymer matrix. One possible way is to create loosely packed nanoplatelets or swell nanoclay layers prior to melt compounding with the polymer. Previous researches proved that the swelling of the organoclays can be achieved by dispersing them in both types of ancillary molecules (Jones 1983; Volzone et al., 2000; Pereira et al., 2005). Therefore, it was postulated that pre-dispersing of the nanoclay in liquid medium prior to melt compounding with polymers may weaken the tactoid bonding and further facilitate the exfoliation and dispersion of the nanoclay during the melt compounding process.

In this project, ethyl vinyl acetate (EVA) nanocomposites incorporating organically modified montmorillonite (organo-MMT) have been produced using melt compounding method prior various pre-dispersing parameters. This pre-dispersing

procedure was done to enhance nanofiller dispersion in the host EVA and also being investigated as a new approach to plasticize this biomedical plastic, while improving its toughness and thermal stability. The scientific concept used to tailor the EVA properties was based on the manipulation of the nanoscale interactions between the EVA (host polymer) and the organo-MMT (nanofiller). Two types of liquid were used as pre-dispersing medium; which are toluene (non-polar) and distilled water (polar). The pre-dispersing procedure was applied prior to melt compounding process between the EVA and organo-MMT to form the nanocomposites and the purpose was to further facilitate the exfoliation and dispersion efficiency of the organo-MMT nanofiller, so that improvements in performance of the EVA can be assured. The structure-processing-property relationships of the neat EVA and EVA nanocomposites were studied and reported in this work to provide better understanding on the EVA nanocomposite system for future improvement and development of this new biomedical candidate material.

1.2 Problem Statement

Nowadays, there are constant demand for cost-effective and innovative biomedical materials for both medical devices and packaging purposes. As fluid delivery and medical treatments became more sophisticated, the need for newer and better materials also grew. However, a problematic issue in the medical field is the limited number of existing flexible, biocompatible, durable and tough materials that offer versatility, exceptional performance, and meet industrially relevant manufacturing process. The above mentioned desired properties are highly needed especially if the material is to be used as the implantable medical devices. Flexibility of biomedical

material can be of great importance for certain non-implantable medical device applications. Some medical procedures need flexible medical equipment such as haemodialysis, blood transfusion and tubing. There are also medical devices and packaging containing specimens and vaccines that need to be stored in freezer. Therefore, materials with low temperature flexibility, toughness and stress-crack resistance are needed to avoid functional failure upon low temperature storage (Centers for Disease Control and Prevention, 2015).

The plasticized PVCs have been widely used to produce non-implantable medical devices due to their appreciable flexibility, versatility and ease of processing. However, there has been increasing environmental concern in recent years, over the use of PVC materials in the manufacture of medical devices, such as blood bag and extracorporeal tubing. DEHP is the most commonly used as plasticizer is compounded with the PVC to produce flexible PVC. However, this substance may leach out during use and lead to diminish biocompatibility and bring probable complications to the patient's health. As suggested by recent reports by Rhodes et al. (2010) these effects can be associated with estrogenic-like properties of the plasticizer and other added additive chemicals. In addition, a migration of plasticizer and additives may occur when plasticized PVC packagings are put into contact with liquids such as blood and food, resulting in the contamination of the liquid and reduction of mechanical properties of the polymer. The amount of DEHP (plasticizer) that will leach out rely on the lipid content of the liquid, temperature and the duration of contact with the plastic. More than one medical treatment procedures often required by the seriously ill individuals, hence higher levels of DEHP can be exposed to them. Besides, over the increasing in the level of dioxins in the atmosphere because of the incineration of PVC products, concern has

been expressed (Taverdet & Vergnaud, 1984; Lloyd, 2004; U.S Food and Drug Administration, 2015).

The above issues highlight the need for innovation and research on new and improved biomedical materials for both implantable and non-implantable devices. In this project, EVA nanocomposites incorporating organo-MMT were produced and investigated as new candidate for biomedical material. The improvements in flexibility, toughness and thermal properties were targeted by adding the EVA copolymer with 5wt% of organo-MMT nanofiller. However, the critical issue in producing EVA nanocomposite containing organo-MMT filler is to breakdown/exfoliates the MMT tactoids to the scale of individual particles and disperse them well inside the EVA matrix to form a "true nanocomposite". Previous research on the same EVA nanocomposite system shows the reduction of tensile and toughness of the EVA when the nanofiller loading were increased from 3wt% to 5wt%. These were due to the reduced quality of organo-MMT exfoliation and dispersion in the host EVA (Osman et al., 2015a). While high loading of nanofiller (5wt%) is expected to provide better improvement in thermal stability and biostability of the EVA, this current research aims to improve the quality of organo-MMT dispersion in the EVA containing 5wt% organo-MMT. Therefore, a pre-dispersing procedure was introduced, in which the organo-MMT nanofiller was pre-dispersed in liquid medium prior to melt compounding process with the EVA matrix. The main aim was to obtain the destabilized structure of the organo-MMT before being incorporated in the EVA, so that the exfoliation and dispersion of the organo-MMT can be further facilitated during the melt compounding process. In parallel, this pre-dispersing technique also was studied as a new processing approach to plasticize the EVA copolymer, in order to enhance its flexibility and

toughness. Two types of pre-dispersing medium switch different polarity were used; they were toluene (hydrophobic) and water (hydrophilic). The effects of pre-dispersing medium and parameters on the morphology, mechanical and thermal properties of the EVA nanocomposites were studied.

1.3 Objectives

The main objective of this study was to produce flexible and tough EVA nanocomposite by incorporating pre-dispersed organically modified montmorillonite (organo-MMT) for use in biomedical applications. The three specific objectives were:

1) To investigate the efficiency of toluene and water as pre-dispersing medium of organo-MMT nanofiller in order to enhance toughness, flexibility and thermal stability of EVA nanocomposite
2) To compare two types of pre-dispersing methods which were; magnetic stirring and ultrasonication to the chemistry of the organo-MMT nanofiller and subsequent EVA nanocomposite toughness, flexibility and thermal stability.
3) To compare the effects of pre-dispersing time (2 and 5 minutes) to the toughness, flexibility and thermal stability of the EVA nanocomposite.

1.4 Scope of study

The materials used in this study were, ethylene vinyl acetate copolymer (EVA) which acts as a matrix and organo-MMT as nanofiller. The pre-dispersing process of