



**INTERLAYER DESTABILIZATION PROCESS OF
NATURAL AND COMMERCIAL BENTONITE
INCORPORATED ETHYLENE VINYL ACETATE
(EVA) NANOCOMPOSITE WITH HYBRID
SILICATE NANOFILLERS**

by

**ASFA AMALIA BINTI AHMAD FAUZI
(1630412153)**

A thesis submitted in fulfillment of the requirements for the degree of
Master of Science (Materials Engineering)

**School of Materials Engineering
UNIVERSITI MALAYSIA PERLIS**

2018

UNIVERSITI MALAYSIA PERLIS

DECLARATION OF THESIS

Author's Full Name : ASFA AMALIA BINTI AHMAD FAUZI
Title : INTERLAYER DESTABILIZATION PROCESS OF NATURAL AND COMMERCIAL BENTONITE INCORPORATED ETHYLENE VINYL ACETATE (EVA) NANOCOMPOSITE WITH HYBRID SILICATE NANOFILLERS
Date of Birth : 18 February 1993
Academic Session : 2016/2017

I hereby declare that this thesis. becomes the property of Universiti Malaysia Perlis (UniMAP) and to be placed at the library of UniMAP. This thesis is classified as:

- CONFIDENTIAL (Contains confidential information under the Official Secret Act 1997)*
RESTRICTED (Contains restricted information as specified by the organization where research was done)*
OPEN ACCESS I agree that my Thesis. to be published as online open access (Full Text)

I, the author, give permission to reproduce this Thesis in whole or in part for the purpose of research or academic exchange only (except during the period of ___1___ years, if so requested above)

Certified by:

SIGNATURE

SIGNATURE OF SUPERVISOR

930218145140

Dr. Azlin Fazlina Osman

(NEW IC NO. /PASSPORT NO.)

NAME OF SUPERVISOR

Date: 24 May 2018

Date: 24 May 2018

NOTES : * If the thesis is CONFIDENTIAL or RESTRICTED, please attach with the letter from the organization with the period and reasons for confidentiality or restriction.

ACKNOWLEDGMENT

Alhamdulillah. Praise to Allah for giving me this opportunity and spirit in finishing my study. First of all, I would like to express my gratitude to my main supervisor Dr Azlin Fazlina Bt Osman for her support, advise and continuous guidance while I'm trying to finish this study. Next, I would like to thanks to my co supervisor Dr. Mohd Aidil Adhha b. Abdullah for all the support and advice he gave me during the journey of this study. Thanks to all lecturers that are directly or indirectly involve in helping me finishing this study. My sincere thanks to all science officers, laboratory technical staff and laboratory assistant from PPK Bahan and UMT as they always give their best in teaching and guidance me while handling the instrument and completing the test.

I'm very thankful to my dearest friend whom always together throughout the course of the project. Last but not least, I would like to thanks to my parents and my siblings for always understanding and supporting me mentally and financially as I'm trying to finish this study. Many thanks to all of you.

©This item is protected by original copyright

TABLE OF CONTENTS

	PAGE
DECLARATION OF THESIS	i
ACKNOWLEDGMENT	ii
TABLE OF CONTENTS	vi
LIST OF TABLES	vii
LIST OF FIGURES	x
LIST OF ABBREVIATIONS	xii
LIST OF SYMBOLS	xiii
ABSTRAK	xiv
ABSTRACT	xv
CHAPTER 1 : INTRODUCTION	1
1.1 Research Background	4
1.2 Problem Statement	5
1.3 Research Question/Hypothesis	7
1.4 Objectives Study	8
1.5 Scopes of Study	9
CHAPTER 2 : LITERATURE REVIEW	10
2.1 Copolymer	12
2.1.1 Ethylene Vinyl Acetate (EVA)	13
2.2 Polymer Nanocomposite	17

2.2.1	Copolymer Based Nanocomposite	19
2.2.2	EVA Nanocomposite	21
2.3	Clay as Nanofiller in Polymer Nanocomposite	23
2.3.1	Bentonite	24
2.3.1.1	Properties of Bentonite	27
2.3.2	Montmorillonite	27
2.3.2.1	Oragnomontmorillonite (OMMT)	28
2.4	Strategies to Improve Dispersion of Clay Polymer Matrices	36
2.5	Hybrid Filler	38
2.6	Gap in Existing Knowledge on Processing and Properties Aspects of EVA Nanocomposite with Hybrid Bentonite/OMMT Nanofillers	41
CHAPTER 3 : METHODOLOGY		42
3.1	Overview of Research Methodology	42
3.1.1	Materials	43
3.1.1.1	Ethyl Vinyl Acetate (EVA)	43
3.1.1.2	Natural Bentonite	43
3.1.1.3	Commercial Bentonite(Nanoclay, Nanomer PGV)	44
3.1.1.4	Organo Modified Montmorilonite (OMMT)	44
3.1.1.5	Nitric Acid (HNO ₃)	44
3.1.1.6	Sodium Chloride (NaCl)	45
3.2	Destabilization of the Natural and Commercial Bentonites	45
3.2.1	Destabilization by pH Control	46
3.2.2	Destabilization by Salt Addition	46
3.2.3	Destabilization by Combination of pH Control and Salt Addition	47
3.3	Preparation of Polymer Nanomposites	50
3.4	EVA/Bentonite Nanocomposite Sheet Preparation	50

3.5	Characterization, Mechanical and Thermal Testing	51
3.5.1	Fourier Transform Infrared Spectroscopy (FTIR)	51
3.5.2	X-Ray Diffraction (XRD)	52
3.5.3	Field Emission Scanning Electron Microscope (FESEM))	52
3.5.4	Transmission Electron Microscopy (TEM)	52
3.5.5	Thermogravimetric Analysis (TGA)	53
3.5.6	Differential Scanning Calorimetry (DSC)	54
3.5.7	Tensile Test	56
3.6	Flow Chart	57
CHAPTER 4 : RESULT & DISCUSSION		58
4.1	Characterization of Destabilized Natural and Commercial Bentonite	59
4.1.1	X-Ray Fluorescence Analysis (XRF)	60
4.1.2	X-Ray Diffraction Analysis (XRD)	68
4.1.3	Field Emission Scanning Electron Microscope Analysis (FESEM)	71
4.1.4	Fourier Transform Infrared Analysis (FTIR)	74
4.2	Mechanical Properties of the EVA Nanocomposites Incorporating Pristine and Destabilized Natural and Commercial Bentonites in Single and Hybrid Form: Correlations with Structure and Morphology	75
4.2.1	Mechanical Analysis	83
4.2.2	Structure and Morphology Analysis	83
4.2.2.1	X-ray Diffraction Analysis (XRD)	85
4.2.2.2	Transmission Electron Microscopy Analysis (TEM)	89
4.2.2.3	Fourier Transform Infrared Analysis (FTIR)	91
4.3	Thermal Properties of the EVA Nanocomposites Incorporating the Destabilized Natural and Commercial Bentonites in Single and Hybrid Form.	92
4.3.1	Thermogravimetry Analysis (TGA)	95
4.3.2	Differential Scanning Calorimetry Analysis (DSC)	99

CHAPTER 5 : CONCLUSION	100
5.1 Conclusion	102
5.2 Recommendations for Future Studies	103
REFERENCES	120
APPENDIX A PUBLICATIONS	123

©This item is protected by original copyright

LIST OF TABLES

NO.		PAGE
Table 3.1:	The Formulation of EVA Nanocomposites	48
Table 3.2:	Acronym of the Composite Samples	50
Table 4.1:	Chemical Component Present in Pristine Natural and Commercial Bentonite.	60
Table 4.2:	d_{001} Value of XRD Pattern of Pristine Natural and Commercial Bentonite, Destabilized Natural and Commercial Bentonite	62
Table 4.3:	Comparison on Tensile properties of Neat EVA and EVA nanocomposite	78
Table 4.4:	Comparison on T_{dmax} and Weight loss (%) in First Step and Second Step of Neat EVA and EVA Nanocomposite	93
Table 4.5:	Summary of DSC heating and cooling curves of Neat EVA and EVA Nanocomposite	97

LIST OF FIGURES

NO.		PAGE
Figure 2.1:	Ethylene Vinyl Acetate (EVA) (Barnes, Brown, Sibley, Edwards & Coates, 2005)	12
Figure 2.2:	Structure of Bentonite (Ray and Okamoto, 2003).	26
Figure 2.3:	Tetrahedral and Octahedral shape of Bentonite (Grim, 1968)	26
Figure 2.4:	Size of Bentonite (Ray and Okamoto, 2003)	26
Figure 2.5:	Schematic Illustration of a Cation Exchange Reaction Between the Layered Silicate and an Alkylammonium Salt (Osman, 2013)	30
Figure 2.6:	Structure of Clay After Treated with Acid and Salt (Kelessidis, 2007; Tombacs and Szekeres, 2004)	34
Figure 2.7:	Type of Nanocomposites (Alexandre and Dubois , 2000)	35
Figure 2.8:	Illustration of Hybrid filler (bentonite and OMMT) with EVA polymer (Osman et al., 2016b)	38
Figure 3.1:	Stress-strain Curve Showing Toughness of a Material Obtained Through the Determination of Area Under the Curve	55
Figure 3.2:	A Stress-Strain Curve Showing the Initial Section Slope is the Young Modulus.	56
Figure 3.3:	Flow Chart of Research Methodology	57
Figure 4.1:	Basal Spacing Obtained from the XRD Analysis of the NB dDestabilized with pH values: a) 4 b) 5 and c) 6 and Ultrasonication Time of 5, 10 and 15 minutes	64

Figure 4.2:	Basal Spacing Obtained from the XRD Analysis of the CB Destabilized with pH values: a) 4 b) 5 and c) 6 and Ultrasonication Time of 5, 10 and 15 minutes	65
Figure 4.3:	Basal Spacing Obtained from the XRD analysis of the NB Destabilized with Salt Concentration of: a) 0.01M b) 0.1M and c) 1M and Ultrasonication Time of 5, 10 and 15 min	66
Figure 4.4:	Basal Spacing Obtained from the XRD Analysis of the CB Destabilized with Salt Concentration of: a) 0.01M b) 0.1M and c) 1M and Ultrasonication Time of 5, 10 and 15 min	67
Figure 4.5:	Comparison on Basal Spacings of the a) Natural Bentonite b) Commercial Bentonite Upon Destabilization Process Through pH Control(pH), Salt Addition(s) and combination of pH Control and Salt Addition (pHs)	68
Figure 4.6:	FESEM Images of a) NB b) CB c) NB_pH d) CB_pH e) NB_s f) CB_s g) NB_pHs and h) CB_pHs	71
Figure 4.7:	FTIR Spectra for Pristine and Destabilized Natural and Commercial Bentonites in Scan Range of a) 4000 cm^{-1} to 450 cm^{-1} b) 1000 cm^{-1} to 700 cm^{-1} c) 3750 cm^{-1} -3000 cm^{-1}	73
Figure 4.8:	Tensile Strength of Neat EVA and EVA Nanocomposite Incorporating with Destabilized Natural and Commercial Bentonite	76
Figure 4.9:	Elongation at Break of Neat EVA and EVA Nanocomposite Incorporating with Destabilized Natural and Commercial Bentonite	76
Figure 4.10:	Tensile Toughness of Neat EVA and EVA Nanocomposite Incorporating with Destabilized Natural and Commercial Bentonite	77

Figure 4.11: Modulus of Elasticity of Neat EVA and EVA Nanocomposite Incorporating with Destabilized Natural and Commercial Bentonite	81
Figure 4.12: Tensile Stress-Strain Curve of Neat EVA and EVA Nanocomposite with Natural Bentonite	83
Figure 4.13: XRD Pattern of Destabilized Natural, Commercial Bentonite, OMMT, Neat EVA and EVA Nanocomposite	84
Figure 4.14: TEM Images of EVA Nanocomposites: a) EVA/NB b) EVA/NB_pH c)EVA/O/NB d)EVA/OMMT and e) EVA/O/NB_pHs	88
Figure 4.15 Comparison on Morphology of the EVA Nanocomposite with Pristine and Destabilized Bentonite	89
Figure 4.16: FTIR Spectra of Neat EVA and EVA Nanocomposite with Pristine Natural and Commercial Bentonite, Destabilized Pristine Natural and Commercial Bentonite, and Hybrid Filler in the Scan Range of a) 4000 cm^{-1} to 650 cm^{-1} and b) 1200 cm^{-1} to 900 cm^{-1} .	91
Figure 4.17: Thermogram of Neat EVA and EVA Nanocomposite	92
Figure 4.18: Derivative Curve of Neat EVA and EVA Nanocomposite	93
Figure 4.19: DSC Heating Curve of Neat EVA and EVA Nanocomposite	96
Figure 4.20: DSC Cooling Curve of Neat EVA and EVA Nanocomposite	97

LIST OF ABBREVIATIONS

ABS	Acrylonitrile Butadiene Styrene
Al	Aluminium
Al ₂ O ₃	Aluminium Oxide
Al ₂ SO ₃	Aluminium Sulfite
BR	Polybutadiene rubber
CaCO ₃	Calcium Carbonate
CaO	Calcium Oxide
CB	Commercial Bentonite
CEC	Cation Exchange Capacity
CNFs	Carbon Nanofibre
CNTs	Carbon Nanotube
CuO	Copper Oxide
DSC	Differential Scanning Calorimetry
EFG	Exfoliated Graphite
EP	Poly (ethylene-co-propylene)
EVA	Ethyl Vinyl Acetate
EVAO	Ethyl Vinyl Alcohol
Fe	Iron
Fe ₂ O ₃	Iron(III) Oxide
FTIR	Fourier Transform Infrared
FESEM	Field Emission Scanning Electron Microscope
GNP	Graphite Nanoplatelet
HNO ₃	Nitric Acid
KCl	Pottasium Chloride
K ₂ O	Potassium Oxide
LDPE	Lower Density Polyethylene
Mg	Magnesium
MgO	Magnesium Oxide
MMT	Montmorillonite
MnO	Manganese (II) Oxide
MRI	Magnetic Resonance Imaging
MWCN	Mutliwalled Carbon Nanotube
Na	Sodium
NaCl	Sodium Chloride
NB	Natural Bentonite

NIR	Near Infrared
O	Oxygen
ODA	Octadecylamine
OH	Hydroxyl Groups
OMMT	Organomontmorillonite
PBT	Polybutylene Terephthalate
PE	Polyethylene
PEG	Polyethylene Glycol
pH	Potential Hydrogen
PMMA	Polymethamethyl acrylate
PP	Polypropylene
PSPEB	polystyrene-block-poly(ethylene-ran-butylene)- block- polystyrene
PU	Polyurethane
PVA	Polyvinyl Acetate
PVC	Polyvinyl Chloride
rpm	Revolutions per minute
SBR	Poly (styrene-co-butadiene) (SBR) copolymer
SEM	Scanning Electron Microscope
Si	Silicon
SiO ₂	Silicon Dioxide
SWNT	Single Wall Carbon Nanotube
T _g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
TiO ₂	Titanium Dioxide
Tm	Melting Temperature
VA	Vinyl Acetate
V ₂ O ₅	Vanadium (V) Oxide
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
ZnO	Zinc Oxide

LIST OF SYMBOLS

%	Percentage
wt%	Weight Percentage
°C	Degree celcius
°	Degree
d_{001}	d-spacing
T_{dmax}	Temperature Maximun Degradation
g	Gram
J	Joule
Kg	Kilogram
M	Molar
m^3	Cubic Meter
mm	Milimeter
min	Minutes
mg	Miligram
Mpa	Megapascals
cm^3	Cubic Centimeter
%	Percentage
wt%	Weight Percentage
°C	Degree celcius
°	Degree
d_{001}	d-spacing

Proses Penyahstabilan Antara-lapis Bentonit Semulajadi dan Komersil Yang Dimasukkan ke Dalam Nanokomposit Etilena Vinil Asetat (EVA) Yang Berpengisi-Nano Silikat Hibrid

ABSTRAK

Bentonit semulajadi dan komersil boleh bertindak sebagai pengisi yang efisien untuk mengukuhkan matriks polimer sekiranya daya pengikat antara-lapis yang kuat menjadi lemah untuk mengurangkan pembentukan taktoid. Dalam penyelidikan ini, proses menyahstabilkan antara-lapis dilakukan bagi mendapatkan struktur tanah liat berlapis yang longgar, mengembang dan tidak teratur untuk penyelitan polimer dan penyerakan pengisi yang lebih baik semasa fabrikasi komposit polimer/tanah liat. Tiga kaedah ketidakstabilan yang berbeza digunakan untuk bentonit semulajadi dan komersil dan kesannya terhadap kembangan dan susunan platlet tanah liat diperhatikan. Bentonit semula jadi asli dan yang telah dinyahstabilkan telah dicirikan dan dibandingkan berdasarkan komponen kimia mereka (XRF), struktur kimia (XRD dan FTIR) dan morfologi (FESEM). Analisis kimia mendedahkan bahawa komposisi mineralogi dan kimia kedua-dua jenis bentonit mempengaruhi struktur dan keupayaan pengembangan semasa proses penyahstabilan. Keputusan XRD menunjukkan bahawa jarak asas (d_{001}) bentonit semulajadi dan komersil berkurangan apabila proses ketidakstabilan tunggal (dengan tambahan garam) telah digunakan tetapi meningkat apabila ketidakstabilan dilakukan dengan gabungan kawalan pH dan proses penambahan garam. Peningkatan jarak asas berlaku dari 1.55 nm ke 1.59 nm bagi bentonit semulajadi dan dari 1.42 nm ke 1.46 nm bagi bentonit komersial. Ini menunjukkan bahawa proses penyahstabilan melalui gabungan kawalan pH dan penambahan garam adalah lebih cekap dalam mengembangkan bentonit semulajadi dan komersil. Ini disokong oleh analisis FESEM di mana platlet yang lebih kecil, lebih tersusun longgar dan seragam diperhatikan kerana pegubahsuaian dan kelemahan daya pengikat antara-lapis dari bentonit semula jadi dan komersil. Bentonit 'tidak stabil' digunakan sebagai pengisi-nano-bersama dengan montmorillonite yang telah diubah suai (OMMT) untuk membentuk pengisi-nano silikat hibrid pada matriks kopolimer EVA. Keputusan menunjukkan bahawa bentonit 'tidak stabil' yang disediakan oleh gabungan kawalan pH dan penambahan garam adalah lebih berkesan dalam menguatkan matriks EVA apabila digabungkan dengan OMMT dengan memberi kesan pencapaian tertinggi sebanyak 124.9% terhadap kekuatan tegangan, 13.5% terhadap pemanjangan pada takat putus dan 190.8% terhadap ketahanan tegangan. Tambahan lagi, kestabilan terma nanokomposit EVA juga bertambah baik. Ini boleh dikaitkan dengan penyebaran bentonit yang lebih baik ketika proses penyahstabilan yang membolehkan interaksi pengisi matriks yang lebih baik dalam sistem nanokomposit. Secara ringkas, proses penyahstabilan melalui kawalan pH dan penambahan garam adalah teknik yang berkemampuan dan praktikal untuk meningkatkan penyebaran bentonit di seluruh matriks polimer. Tanpa menggunakan bahan kimia yang mahal dan beracun, ia boleh diguna pakai sebagai pendekatan baru untuk mengembangkan bentonit untuk teknologi nanokomposit mesra alam sekitar.

Interlayer Destabilization Process of Natural and Commercial Bentonite Incorporated Ethylene Vinyl Acetate (EVA) Nanocomposite with Hybrid Silicate Nanofillers

ABSTRACT

Natural and commercial bentonites can act as efficient fillers to reinforce a polymer matrix if their strong interlayer binding forces are weakened to reduce tactoid formation. In this research, interlayers destabilization process was applied to gain a loosely packed, swelled and disorganized clay layered structure for better polymer intercalation and filler dispersion during the polymer/clay composite fabrication. Three different destabilization methods were applied to the natural and commercial bentonites and their effects on swelling and platelets ordering/stacking of the clays were observed. The pristine and destabilized natural and commercial bentonites were characterized and compared based on their chemical component (XRF), chemical structure (XRD and FTIR) and morphology (FESEM). Chemical analysis revealed that mineralogical and chemical compositions of both types of bentonite affect their structure and swelling capability during the destabilization process. XRD results suggest that basal spacing (d_{001}) of both natural and commercial bentonites reduced when single destabilization process (by salt addition) was applied but increased when destabilization was done by the combination of pH control and salt addition processes. The increment of basal spacing was seen to be ~ 0.04 nm for both natural and commercial bentonites showing that the destabilization process through combination of pH control and salt addition is more efficient in swelling both natural and commercial bentonite clays. This is supported by FESEM analysis where smaller, more loosely packed and uniform platelets were observed due to swelling and weakening of the interlayer binding forces of both natural and commercial bentonite clays. The 'destabilized' bentonites were used as co-nanofiller with the organically modified montmorillonite (OMMT) to form hybrid silicate nanofillers for EVA copolymer matrix reinforcement. Results show that the 'destabilized' bentonite prepared by the combination of pH control and salt addition is most efficient in reinforcing the EVA matrix when combined with the OMMT by allowing 124.9% increment in tensile strength, 13.5% in elongation at break and 190.8% in toughness values. Furthermore, thermal stability of the EVA nanocomposite was also improved. This could be related to the improved dispersion of bentonite upon the destabilization process that allows greater matrix-filler interactions in the nanocomposite system. In summary, destabilization process through pH control and salt addition is the promising and practical technique to improve the dispersion of bentonite throughout the polymer matrix. Without the use of expensive and toxic chemicals, it can be adopted as a new approach to swell bentonite for more environmental friendly nanocomposite technology.

CHAPTER 1

INTRODUCTION

1.1 Research Background

It is widely known that polymeric materials can be tailored to meet specific property requirements by the incorporation of nanosize clays (nanoclays) such as bentonite, montmorillonite (MMT), fluoromica and hectorite (Kotal and Bhowmick, 2015; Osman et al., 2012a). This combination of polymers and nanoclays 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., 2015; Alosime, Edward, & Martin et al., 2015; Andriani et al., 2013). While a large body of research concerning polymer-organoclay nanocomposites exists, the number of studies specifically devoted to ethylene vinyl acetate (EVA) nanocomposite is relatively small (Merinska, Kalendova, Dujkove, Slouf & Simonik, 2013; Feldman, 2016a). The use of EVA copolymer as the nanocomposite matrix presents some interesting challenges to understand the complex morphology of the EVA, due to existence of semicrystalline, non-polar polyethylene (PE) and amorphous, polar poly(vinyl acetate) (PVA) structure (Merinska et al., 2013; Fink, 2010). Silicate material like bentonite is one of the best nanofiller candidates for EVA as it is abundant, low cost, having high aspect ratio and tailorable surface chemistry (Osman et al., 2012a, Ray & Okanamoto, 2003). Bentonite is a naturally-occurring material with clay mineral smectite as its predominant composition. Its layered structure

comprises of high aspect ratio platelets, suitable for reinforcing polymers. However, its hydrophilic characteristic may hinder efficient reinforcing effect of the hydrophobic polymers. Therefore, the semi-synthetic silicates such as the surface modified montmorillonites are commercially available as the more compatible fillers used to reinforce the hydrophobic polymers. The addition of small amount of organically modified montmorillonite (OMMT) as nanofiller has been proved to provide enhancement in tensile strength, toughness and thermal stability to the host EVA, without reducing its flexibility (Osman, Kalo, Hassan, Hong & Azmi, 2016; Osman et al., 2017a). However, it was also been demonstrated that the use of hydrophobic OMMT alone as nanofiller could not optimize the mechanical and thermal properties of the copolymer (Osman et al., 2016; 2017a). This is because; the EVA copolymer comprises of both hydrophobic and hydrophilic phases of PE and PVA, respectively.

As continuation of these previous studies (Osman et al., 2016; Osman et al., 2017a), this project was conducted to investigate the effect of using more than one type of silicate material as nanofiller in EVA, to further upgrade the properties and viability of EVA for advanced applications, such as biomedical. The combination of both hydrophobic and hydrophilic nanoclays as hybrid nanofillers can ensure greater nanofiller interactions with both monomers in the EVA copolymer system. This benefit in more efficient stress transfer mechanism and greater shielding of the more susceptible-to-degrade PVA chains. The use of bentonite as co-filler with OMMT was thought can reduce the 'catalytic' effect as less amount of organic surfactant is used and stronger PVA-Bentonite interface bonding can be developed due to polar-polar interactions established between both constituents. Subsequently, more stable PVA chains can be produced to resist thermal degradation. In previous preliminary work, the

combination of unmodified bentonite (Bent) and organically modified montmorillonite (OMMT) as nanofiller which is known as ‘hybrid nanofillers’ was proved to provide synergistic effects to morphology and properties of the EVA (Osman et al., 2017a). Their incorporation into the EVA structure has provided nanofiller interactions with both co-monomers exist in the EVA copolymer, which are PE and PVA. The use of small portion of unmodified bentonite clay (Bent) has successfully enhanced the nanofiller-PVA interaction as both are hydrophilic. However, due to poor Bent dispersion, they have observed only small improvement in the EVA/OMMT/Bent hybrid nanocomposite properties when benchmark with EVA/OMMT nanocomposite system (Osman et al., 2017b). To achieve the optimum ‘interaction’ and ‘shielding effect’, the bentonite needs to be well exfoliated and dispersed throughout the host polymer structure. An efficient dispersing technique needs to be applied to exfoliate the highly stacked platelets (tactoids) in the pristine bentonite, prior to melt compounding with the EVA copolymer. This is because; this ‘filler pre-dispersing technique’ can ensure greater nanoclay dispersion during the melt compounding process (Osman et al., 2017a). Previous work indicates that ultra-sonication is an efficient pre-dispersing technique for OMMT (Osman et al., 2017b). However, this method is not efficient to be applied for bentonite because this unmodified clay has much greater stacked platelets (tactoids) due to the absence of organic surfactant on the silicate surface. In this project, a new, simple, safe and economic destabilization technique was proposed to produce well exfoliated bentonite nanofiller. Without the use of any toxic and costly surfactants, this method involves the use of salt concentration and pH control during the bentonite suspension preparation to destabilize the bentonite interlayers cohesive energy. The efficiency of this technique to enhance the bentonite dispersion and subsequent EVA nanocomposite properties (mechanical and thermal properties) was studied.

Furthermore, the morphology and exfoliation behaviour of the destabilized natural bentonite were compared with the commercial bentonite. The purpose was to observe the exfoliation degree and efficiency between the natural and commercial bentonite towards the applied destabilization process. Both natural and commercial bentonites (pristine and destabilized state) were characterized using XRF, XRD, FTIR, and FESEM and the structure and properties of the resultant nanocomposites were evaluated by tensile test, XRD, FTIR, TEM, TGA and DSC.

1.2 Problem Statement

Ethyl vinyl acetate copolymer has potential to be applied for various applications because of its versatility, tailorable chemical composition (by varying the proportion of vinyl acetate (VA) and ethylene monomers) and wide range of mechanical properties (depending on the ethylene and VA composition)(Fink, 2010). The EVA mechanical and thermal properties can be greatly improved with the incorporation of OMMT nanofiller without sacrificing its intrinsic property (flexibility). The flexible, tough and thermally stable EVA plastic is beneficial for biomedical application, for instance as insulation material for electrically active implantable device. However, the incorporation of OMMT alone has resulted in insignificant mechanical and thermal property enhancement. The imbalance OMMT nanofiller interactions with PE and PVA phases of the copolymer may resist optimum reinforcing and toughening effects of the nanofiller. Furthermore, the hydrophilic, amorphous and flexible component in the EVA the (PVA chains) has tendency to degrade due to lack of nanofiller-PVA interactions. The OMMT, which possess hydrophobic characteristic, has more affinity towards the hydrophobic polyethylene (PE) chains. As a result, these

non-optimized nanofiller-PVA-PE interactions will prevent greater property enhancement in the EVA copolymer system. The incorporation of the hydrophilic bentonite nanofiller can overcome this problem, as these polar nanofiller can interact with the PVA chains of the EVA. However, bentonite has close packed tactoid that can prevent polymer intercalation between the clay interlayers. Bentonite is commonly modified via cation exchange method using alkyl ammonium or alkyl phosphonium surfactant to expand the interlayer spacing and subsequently facilitate polymer chain intercalation. However, this surface modification method has some drawbacks such as the high cost of the organic surfactant, its toxicity effect and tendency of surfactant to degrade upon high temperature melt compounding process (Andriani et al., 2013). In this work, an alternative method; the so called ‘destabilization process’ of bentonite by pH control and salt addition was applied. This more environmental friendly technique does not involve the use of costly and toxic surfactants to reduce the binding energy of clay interlayers, thus the tactoids formation.

1.3 Research Question/Hypothesis

It is widely known that in the conventional production of polymer nanocomposite using melt compounding process, the nanoclay exfoliation process will take place during the compounding of both nanoclay and polymer mixture. This is due to melt shear viscosity and shearing effect from the screw/mixing blade. However, most of the cases, the intercalated nanocomposite structure were obtained rather than fully exfoliated structure. This is because, the polymer viscosity and screw shearing effect are not sufficient to assist in complete exfoliation of nanoclay into individual layer, especially if the nanoclay is used in its original form (unmodified). The question is, is

the nanoclay ‘destabilizing’ approach through salt and pH control that applied prior to melt compounding can assist in greater degree of clay exfoliation before and after being incorporated into the polymer matrix and subsequently enhance the nanocomposite mechanical and thermal performance.

The study was conducted based on two main hypotheses:

1) Dispersion of the ‘destabilized’ Bentonite :

Bentonite has pH dependant charges on the edge of the clay and permanent charges on the clay surface. The edge sited of clay is positive at low pH and negatively charged at higher pH. The changes in the pH will influence the cohesive strength between the silicate interlayer, thereby the stability of the tactoid formed. The electrical double layer form as salt was added and the positive charge spills to the edge site. The closely packed tactoids can be opened up as the negative surface charge interacts with positive edge charge as lower pH and salt was added. Consequently, loosely packed clay tactoids can be obtained to allow better platelet exfoliation and dispersion within the polymer matrix, during the melt compounding process. In this project, well dispersed and exfoliated Bent nanofiller was targeted to produce an optimize EVA copolymer/Bent/OMMT hybrid nanocomposite system for biomedical application.

2) Hybrid exfoliated Bent/OMMT nanofillers to improve EVA-nanofiller molecular interactions:

Hybrid silicate nanofillers with different polarity (OMMT: hydrophobic; Bentonite: hydrophilic) was hypothesized to result in more optimum EVA-nanofiller interactions, as the EVA copolymer contains the hydrophobic PE chains and hydrophilic PVA chains in its structure. Enhancement in nanofiller-EVA interactions will also lead to improvement in overall EVA nanocomposite performance (mechanical & thermal properties). Furthermore, the use of the 'exfoliated' bentonite as co-nanofiller with the OMMT can reduce the production cost of the nanocomposite as it is cheaper and naturally available.

1.4 Objective Study

In this research, the main objectives of study were to apply a new method called 'destabilization process' to exfoliate nanoclay (bentonite) and investigate its effectiveness in optimizing the mechanical and thermal properties of the EVA/hybrid-filler nanocomposite. The three specific objectives were;

1. To characterize and compare the morphology and exfoliation behavior of bentonite clay nanofiller upon the application of a new destabilizing technique with varying pH condition, salt concentration and ultra-sonication time.
2. To evaluate the mechanical properties, structure and morphology of the EVA nanocomposites incorporating the pristine and destabilized natural and commercial bentonites, in single and hybrid form.

3. To evaluate the thermal properties of the EVA nanocomposites incorporating the destabilized natural and commercial bentonites, in single and hybrid form.

1.5 Scope of Study

In this study, destabilization technique was the method used to disorganize the clay layer silicates. Destabilization method is a process to ensure that the clay can be more efficiently exfoliate within the polymer matrix. The polymer used as matrix was ethylene vinyl acetate 40% (EVA). For nanocomposite comprising single nanofiller, the clays used were natural bentonite, commercial bentonite and OMMT. On the other hand, for nanocomposite comprising hybrid nanofillers, the OMMT was used as main nanofiller while commercial or natural bentonite was employed as co-nanofiller. As both bentonites existed in pristine state (without surface modification), destabilization process was done to ensure good dispersion of the bentonite platelets throughout the EVA matrix. There were three different type of destabilization process involved; first method was destabilization of both types of bentonite with nitric acid (HNO_3) at different pH value (pH4, 5 and 6) and various time (5, 10 and 15 minutes). HNO_3 was used as destabilizing agent because it has a medium strength of acid concentration, suitable for industrial use. Second destabilization method involved the addition of sodium chloride (NaCl) with different concentrations of; 0.01M, 0.1M and 1M as well as various time (5, 10 and 15 minutes). NaCl was used over other salt because it contains Na^+ ion with larger atomic size than other types of salt such KCl and KNO_3 , thus swelling of tactoid layer can be more efficient. The third destabilization process involve destabilization of both bentonite with HNO_3 (pH4) and addition of 0.01M of NaCl in 15 minutes. All suspension of clays were stirred by using Branson Ultrasonic