CHARACTERIZATION OF IRRADIATION MODIFICATION OF ETHYLENE VINYL ACETATE/ EPOXIDIZED NATURAL RUBBER/ HALLOYSITE NANOTUBES NANOCOMPOSITES

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I dedicated this entire work to my beloved family especially my father Kamal Rudin Mohd and mother Saharah Mohamad, husband Ahmad Shamizan and beloved son Ahmad Harith Danial for their support and encouragement throughout this project….

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ABSTRACT

Ethylene vinyl acetate (EVA)/ Epoxidised natural rubber (ENR50)/ Halloysite nanotubes (HNTs) nanocomposite were prepared using twin screw extruder at temperature profile of 120-150˚C and rotor speed of 70 rpm. The compounds were injection molded to produce test specimens and exposed to electron beam (EB) radiation at 50-200 kGy dose range to induce crosslinking. EB radiation was perform under the acceleration energy, beam current, and dose rate of 2MeV, 2 mA, and 20kGy/pass, respectively. The effects of HNTs loading on the tensile, gel content, thermal and morphological properties of the EVA/ENR50/HNT nanocomposite were investigated before and after irradiation. The effects of crosslinking agents, N, N-m-phenylenedimaleimide (HVA-2) and trimethylolpropane triacrylate (TMPTA) on nanocomposites were also examined. Prior to irradiation, no significant changes in tensile properties of the EVA/ENR50/HNT nanocomposite were observed upon addition of HNT. However, at 4 php HNT content, a good dispersion of HNT in EVA/ENR50 matrix was observed while agglomeration found to occur at 8 php HNT content. The thermal stability of the EVA/ENR50/HNT nanocomposite was increased as the HNT content increased. Upon irradiation, the gel content, tensile strength and thermal properties of the EVA/ENR50/HNT nanocomposites were increased with the increase of HNT content and irradiation dose due to the formation radiation induced crosslinking. The tensile strength of the EVA/ENR50/4HNT nanocomposites was improved with the addition of TMPTA and HVA-2 due to crosslinking. It can be proven from Scanning Electron Micrographs that the compatibility of EVA/ENR50/4HNT nanocomposites improved upon irradiation. The incorporation of HVA-2 and TMPTA found to play major role in EVA/ENR50/4HNT nanocomposite compatibilization upon irradiation.

ABSTRAK

Etilena vinil asetat (EVA)/ getah asli terepoksida (ENR50)/ tiub nano hallosit (HNT) disediakan dengan menggunakan penyemperit skru berkembar pada profil suhu 120-150 °C dan kelajuan rotor 70 rpm. Adunan tersebut telah diacuan suntikan untuk menghasilkan spesimen ujian dan didedahkan kepada radiasi elektron (EB) pada julat dos 50-200 kGy untuk mengaruhkan paut silang. Radiasi EB telah dilakukan di bawah tenaga pecutan, alur arus, dan kadar dos masing-masing pada 2MeV, 2 mA dos, dan 20kGy/laluan. Kesan kandungan HNT pada kekuatan tegangan, kandungan gel, kestabilatan terma dan morfologi dikaji untuk kedua-dua nanokomposit sebelum dan selepas radiasi. Kesan agen silang, N, N m-phenylenedimaleimida (HVA-2) dan trimethylolpropana triakrilat (TMPTA) pada nanokomposit juga dikaji. Sebelum radiasi, tiada sebarang perubahan ketara dalam sifat-sifat tegangan yang nanokomposit EVA/ENR50/HNT diperhatikan dengan penambahan HNT. Namun, pada komposisi 4php HNT, penyebaran HNT kelihatan lebih baik berbanding penumpuan/longgokan pada sampel yang mengandungi 8php HNT. Kestabilan terma untuk nanokomposit EVA/ENR50/HNT yang tidak diradiasikan meningkat apabila kandungan HNT meningkat. Selepas radiasi, kandungan gel, kekuatan tegangan dan kestabilan termal nanokomposit EVA/ENR50/HNT telah meningkat dengan peningkatan kandungan HNT dan dos radiasi kerana pembentukan paut silang disebabkan oleh radiasi. Kekuatan tegangan EVA/ENR50/4HNT telah bertambah baik dengan penambahan TMPTA dan HVA-2 disebabkan oleh paut silang. Ia boleh dibuktikan dari imbasan mikrograf elektron yang menunjukkan keserasian nanocomposit EVA/ENR50/4HNT diperbaiki selepas radiasi. Penggunaan HVA-2 dan TMPTA didapati memainkan peranan utama dalam keserasian EVA/ENR50/4HNT nanokomposit selepas radiasi.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

$CaCO_3$	-	Calcium carbonate
$CaCl_2$	-	Calcium chloride
CB	-	Carbon black
CNTs	-	Carbon nanotubes
CO_2	-	Carbon dioxide
DMA	-	Dynamic mechanical analysis
DMTA	-	1, 6-hexanediol dimethylacrylate
DSC	-	Differential scanning calorimetry
EEA	-	Poly(ethylene-co-acrylate)
EVA	-	Poly(ethylene vinyl acetate)
ENR	-	Epoxidized natural rubber
EPDM	-	Ethylene propylene diene monomer
FTIR	-	Fourier transform infrared
H_2O	-	Water
HCl	-	Hydrochloric acid
HDPE	-	High density Polyethylene
HVA-2	-	N,N-mpehylenebismaleimide
IR	-	Infrared spectroscopy
KBr	-	Potassium bromide
KOH	-	Sodium hydroxide
LDPE	-	Low density polyethylene
MEK	-	Methyl ethyl ketone
MMT	-	Montmorillonite
Na-MMT	-	Sodium-montmorillonite

NaOH	-	Sodium hydroxide
Na+	-	Sodium
NBR	-	Acrylonitrile butadiene rubber
NR	-	Natural rubber
O	-	Octahedral
OH^-	-	Hydroxide ion
PE	-	Polyethylene
PA6	-	Polyamide 6
PP	-	Polypropylene
PS	-	Polystyrene
PTFE	-	Polytetrafluoroethylene
PVC	-	Poly(vinylchloride)
QM-HNTs	-	Quartenary modified halloysite nanotubes
rpm	-	Revolution per minute
SBR	-	Styrene butadiene rubber
SEM	-	Scanning electron microscopy
Si	-	Silicon
TEM	-	Transmission electron microscopy
T_g	-	Glass transition temperature
TGA	-	Thermogravimetry analysis
TMPTA	-	Trimethylolpropane triacrylate
T	-	Tetrahedral
Tm	-	Melting temperature
XRD	-	X-ray diffraction

LIST OF SYMBOLS

%	-	Percentage
°C	-	Degree Celsius
°	-	Degree
λ	-	Wavelength
A	-	Area
L	-	Length
n	-	Integer
t	-	Time
W	-	Width
Wf	-	Final weight
Wi	-	Initial weight
wt%	-	Weight percentage
v/v	-	Volume/volume

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Thermoplastic elastomer (TPEs) has been commercialised in industry decade ago. TPE can be prepared by mixing a thermoplastic and elastomer under high shearing action using standard plastic machinery above melting temperature of thermoplastic. Interestingly, it can be processed in molten state as a thermoplastic and has many of the performance characteristic of a thermoset rubber. The great properties of TPE extended the diversity of product in industry such as cable and insulator.

There are many variety type of elastomer and thermoplastic combination that has been reported involves the natural and synthetic rubber. Among them are PVC/ENR blend (Nasir and Ratnam, 1989), EVA/NR (Koshi *et al.,* 1992), EVA/PA6 (Arup *et al.*, 2001), ENR/PMMA (Nakason *et al.*, 2004), EVA/ENR50 (Zurina *et al.*, 2006, Ratnam *et al.*, 2006), NR/EVA (Sharif *et. al.*, 2006), SMR/EVA (Yong *et al.*, 2007). However the existence of elastomer had reduced the strength and thermal properties due to compatibility of both elastomer and thermoplastic depending on type of polymer itself.

In recent years, researchers and chemist are looking forward for a new technology in enhancing material properties. New class of composite material, nanocomposite is composed of organic and inorganic particles in nanometer dimension scale such as nanofiller (Alexander and Dubois, 2000). Nanocomposites have held much in academic and industrial interest. Currently, polymer/clays are successfully developed with diversity of application in the industry and dominated by montmorillonite (MMT). At lower filler loading level, the nanocomposites show improved properties due to high aspect ratio of the nanoscale filler by reinforcing the polymer matrix. Experimental investigation indicates that nanoparticles can improve stiffness, dimensional stability, improved flame retardancy and reduce gas permeability (Alender and Dubois, 2000; Zanetti *et al.,* 2000; Sharif *et al.,* 2008, Khalid *et al.,* 2010; Rawtani and Agrawal, 2012).

Usually, elastomeric materials are reinforced by carbon black, silica, other microscopic filler to achieve the desired properties (Li *et al.,* 2008). Composites filled with nanofillers such as metallic nanoparticles, montmorillonite, carbon nanotubes (CNT) and halloysite nanotube (HNT) have been used to have superior physical and mechanical properties such as tensile strength, modulus, and thermal properties compared to the conventional fiber or particle reinforced composites (Oya, 2000). Nanotube nanofiller such as CNT and HNT has been widely used with different kind of polymers for advance of high performance composite materials (Du *et al.,* 2008; Ismail *et al.,* 2009; Hedicke-Hochstotter *et al.,* 2009). In nanocomposite, there are binary and ternary system that has been carried out currently include of thermoplastic and rubber. However, TPE/HNT or CNT are still in involving field and not much work was documented.

Ethylene Vinyl Acetate (EVA) is a modification of polyethylene (PE) with vinyl acetate as comonomer which reduces the crystalline of PE. Thus, the characteristic of EVA is depends on the vinyl acetate content. This polymer provides a good mechanical properties, excellent ozone resistance, good weather resistance and relatively lower material cost (Henderson, 1993; Doak, 2004; Yong *et al.,* 2007). EVA co-polymer has been under extensive expansion of product that can be found in flexible shrink wrap (Bai *et al.,* 2007), adhesive, paper coating, foam and mainly in wire and cable insulation.

Epoxidised Natural Rubber (ENR50) is a modified natural rubber having properties resembling those of synthetic rubber rather than natural rubber (Gelling, 1999). ENR has unique properties such as good oil resistance, low gas permeability, improved wet grip and rolling resistance, coupled with high strength epoxy group contains in the rubber make the rubber increased in the polarity as the epoxidation level increased (Baker and Gelling 1987). Ethylene vinyl acetate/ epoxidised natural rubber blend is a novel blend material recently found by researcher (Zurina *et al.,* 2006; Zurina *et al.,* 2008). These blend materials consist of thermoplastic elastomer of epoxidised natural rubber which is a local Malaysian product and versatile thermoplastic ethylene vinyl acetate. The major application of this blend material is as an insulator.

A new type of nanofiller, Halloysite nanotubes (HNTs) recently been used in polymers such as epoxy, polypropylene and polyvinyl alcohol in order to improve the mechanical and thermal properties of the nanocomposites (Du *et al.,* 2008; Hedicke-Hochstotter *et al.,* 2009; Pasbaksh *et al.,* 2010; Sharif *et al.,* 2012). HNT can be classified as well-crystallized kaolin naturally occurring aluminosilicate ($Al_2Si_2O_5(OH)_4 \cdot H_2O$ 1:1) type which in built up in a dioctahedral 1 : 1 clay mineral chemically similar to kaolinite group (Ismail *et al.,* 2009; Ruiz-Hitzky and Van Meerbeek, 2006.

Electron beam (EB) irradiation recently received a great deal of attention, primarily because of its ability to produce crosslinked networks with a wide range of polymers. In irradiation, crosslinking agent such as TMPTA and HVA-2 was used as another method for extending the properties of polymers. It is used as additive to hold the free radical faster and produce more irradiation induced crosslinking. The low operation cost, additive-free technique and room temperature operations are among the added advantages of radiation vulcanization over the existing vulcanizing techniques (Chaudry *et al.,* 2005; Dubey *et al.,* 2006)]. Significant work on EB also has been reported much especially in EVA, ENR50 and nancomposite area (Varghese and tripathy, 1992, Sen and Guven, 1995; Ratnam *et al.,* 2006; Sharif *et al.,* 2008; Noori and Ziaie, 2010; Wang *et al.,* 2011).

Recently, ternary nanocomposite using various type of nanofiller with and without EB irradiation was reported by researcher (Sharif *et al.,* 2006; Norazlina *et al.,* 2012; Lu *et al.,* 2005). However, there are no works reported in development of EVA/ENR50/HNT nanocomposite with and without EB irradiation. The objective of the present work was to analyze the effect of HNT addition on on EVA/ENR50/HNT nanocomposite with the irradiation induced crosslinking behavior of EVA/ENR50/HNT nanocomposites. An attempt has also been made to find an effective of different crossliniking agent towards EVA/ENR50/HNT nanocomposite.

1.2 Problem Statement

Ethylene vinyl acetate/ epoxidised natural rubber blend is a novel blend recently found by researchers. This blend consists of elastomer ENR50 which is a local Malaysian product and versatile non halogen thermoplastic ethylene vinyl acetate. However, the properties such as mechanical properties and thermal stability of this blend reduced due to the existence of elastomer component.

The introduction of a third component, nanofiller in the EVA/ENR-50 blend is expected to enhance the properties of nanocomposites. Recently, a new type of Halloysite nanotube (HNTs) nanofiller has been used in polymers such as epoxy, polypropylene and polyvinyl alcohol in order to improve the mechanical and thermal properties of the nanocomposites (Pasbakhsh et al., 2010, Sharif et al., 2012). The abundance and availability of HNTs mineral reserves as raw material sources and the relatively low cost of HNTs compared to other organoclay such as montmorillonite (MMT) and carbon nanotube (CNTs), promising the utilization of HNTs in future.

Electron beam irradiation is well-known tool for the modification of polymers. Radiation-modified blends of polyolefins have become commercially important, with the properties of the blends better than those of the parent homopolymers. It is well known that the effects of high-energy irradiation on polymers are mainly degradation or crosslinking; with the latter effect leads to an improvement in the thermal resistance and mechanical properties.

In previous works, only research on EVA/NR/MMT nanocomposites was carried out in the nanocomposites area and their properties were significantly improved. Irradiation modification of EVA/ENR-50/HNTs nanocomposite system with and without the presence of crosslinking agent has not yet been investigated. The approach of radiation-modification of polymer nanocomposites was utilized in this study.

In this project several questions need to be answered

i) What is the effect of HNTs loading on the properties of irradiated and unradiated EVA/ENR-50/HNTs nanocomposite?

ii) What is the effect of different irradiation dose on the properties of EVA/ENR-50/HNTs nanocomposite?

iii) What is the effect of crosslinking agent (HVA-2, and TMPTA) on the properties of EVA/ENR-50/HNTs nanocomposite?

1.3 Objectives of Study

The project aim is to produce the irradiated EVA/ENR-50/HNTs nanocomposites. The objectives of this works are:

i) To investigate the effects of halloysite nanotube loading on the mechanical properties, thermal properties, and morphology of EVA/ENR-50/HNTs nanocomposites.

ii) To examine the effect of different irradiation dose on the percentage of gel content, mechanical properties, thermal properties and morphology of EVA/ENR-50/HNTs nanocomposites.

iii) To investigate the effect of crosslinking agents (HVA-2 and TMPTA) on the properties of irradiated and unirradiated EVA/ENR-50/HNTs nanocomposites

1.4 Scope of Study

The scope involved the preparation of EVA/ENR-50/HNTs nanocomposites using the melt mixing method in a twin screw extruder and then the nanocomposite sample were prepared by using injection moulding process. In order to achieve the objectives, the scopes covered are as follows:

i) Preparation of sample by using twin screw extruder and injection moulding.

ii) The sample were subjected to electron beam irradiation at different dosage (50, 100, 150, 200 kGy)

iii) The samples were subjected to several testing and characterization in order to access the perfomance of the produced samples.

- The mechanical properties were evaluated by tensile test. The strength of the nanocomposites is determined.
- SEM and TEM were used to examine the morphology of the nanocomposites.

- Differential scanning calorimeter (DSC) to examine the T_g and T_m of nanocomposites and thermo gravimetric analysis (TGA) were used to access the decomposition temperature of the samples.
- The interactions between the components in nanocomposites were determined by Fourier Transform Infrared (FTIR) analysis.
- The crosslinking percentage were determined using gel content test

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