CHARACTERIZATION OF IRRADIATED EPOXIDIZED NATURAL RUBBER/POLYVINYL CHLORIDE/CARBON NANOTUBES NANOCOMPOSITES

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I dedicate this dissertation to my family…

Dad and Mom,

Ahmad Bin Kadir for opening my eyes to the World;

Khalijah Binti Siolin for instilling the importance of hard work and higher education

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ABSTRACT

The effects of carbon nanotubes addition and irradiation modification on the characterization and properties of epoxidized natural rubber (ENR-50)/poly(vinyl chloride) (PVC)/multi-walled carbon nanotubes (MWNTs) nanocomposites were investigated. ENR-50/PVC/MWNTs nanocomposites were prepared by melt mixing in a Brabender Plastigraph at 150 °C with a rotor speed of 50 rpm followed by compression molding at 160 °C. The samples were irradiated in a 2 MeV electron beam machine in a dose range from 50 to 200 kGy. The functional groups, gel content, morphology, dynamic mechanical properties, volume resistivity and tensile properties of the resulting composites were investigated as a function of MWNTs contents, functionalized MWNTs and irradiation dose. Gel content confirmed the existence of irradiation-induced crosslinking. The highest gel content value was recorded at 8 phr of MWNTs content in nanocomposites. At 0 kGy (up to 6 phr), the MWNTs-COOH had higher gel content value. However, after irradiation (150 kGy), MWNTs nanocomposites recorded the highest gel content value. The x-ray diffraction pattern showed that 2 phr MWNTs content nanocomposites had a better degree of crystallinity than 8 phr MWNTs content and the degree of crystallinity was enhanced after irradiation. The addition of 8 phr of all MWNTs led to the increase of storage modulus and glass transition temperature, and was further enhanced after irradiation (200 kGy). Based on dynamic mechanical analysis results, 8 phr of functionalized MWNTs had better crosslinking as compared with unfunctionalized MWNTs. Volume resistivity increased with increasing MWNTs contents and irradiation dosage. The functionalized MWNTs showed higher resistivity at 0 and 150 kGy of irradiation doses. The tensile strengths of the irradiated nanocomposites increased up to 8 phr of unfunctionalized MWNTs, 6 phr of MWNTs-COOH and 10 phr of MWNTs-OH above 50 kGy. The modulus 100 (M100) increased and elongation at break (Eb) decreased with increasing of MWNTs content and irradiation doses. Functionalized MWNTs showed higher M100 and lower Eb at 0 kGy. However at 200 kGy of irradiation dose, the M100 was lowered and Eb was higher for functionalized MWNTs nanocomposites.

ABSTRAK

Kesan penambahan tiub nano karbon dan pengubahsuaian penyinaran ke atas ciri-ciri dan sifat getah asli terepoksida (ENR-50)/poli(vinil klorida) (PVC)/tiub nano karbon pelbagai dinding (MWNTs) komposit nano telah dikaji. ENR-50/PVC/MWNTs komposit nano telah disediakan melalui campuran leburan menggunakan Brabender Plastigraph pada suhu 150 °C dengan kelajuan rotor 50 rpm diikuti dengan pengacuan mampatan pada suhu 160 °C. Seterusnya, sampel disinarkan di dalam mesin alur elektron 2 MeV dalam julat dos di antara 50-200 kGy. Kumpulan berfungsi, kandungan gel, morfologi, sifat mekanikal dinamik, isipadu kerintangan dan sifat regangan bagi komposit yang terhasil telah dikaji sebagai fungsi kepada kandungan MWNTs, MWNTs berfungsi dan dos penyinaran. Kandungan gel telah mengesahkan kehadiran sambung silang teraruh-penyinaran. Nilai kandungan gel pada 8 phr kandungan MWNTs adalah tertinggi. Pada 0 kGy (sehingga 6 phr), MWNTs-COOH mempunyai nilai kandungan gel yang paling tinggi. Walau bagaimanapun, selepas penyinaran (150 kGy), komposit nano MWNTs merekodkan nilai kandungan gel yang paling tinggi. Analisis pembelauan sinar-x menunjukkan komposit nano dengan kandungan MWNTs 2 phr mempunyai tahap penghabluran yang lebih baik berbanding 8 phr kandungan MWNTs dan struktur penghabluran dipertingkatkan selepas penyinaran. Penambahan 8 phr pada kesemua MWNTs membawa kepada peningkatan modulus simpanan dan suhu peralihan kaca dan dipertingkatkan lagi selepas penyinaran (200 kGy). Berdasarkan keputusan analisa mekanikal dinamil, untuk 8 phr MWNTs berfungsi, komposit nano mempunyai sambung silang yang lebih baik daripada MWNTs tanpa fungsi. Isipadu kerintangan meningkat dengan penambahan MWNTs dan dos penyinaran. Selain itu, MWNTs berfungsi mempunyai isipadu kerintangan yang tinggi pada dos penyinaran 0 dan 150 kGy. Sifat regangan komposit nano yang disinarkan telah meningkat pada 8 phr MWNTs, 6 phr MWNTs-COOH dan 10 phr MWNTs-OH selepas 50 kGy penyinaran. Modulus 100 (M100) meningkat dan pemanjangan pada takat putus (Eb) menurun dengan kenaikan kandungan MWNTs dan dos penyinaran. MWNTs berfungsi merekodkan M100 yang tinggi dan Eb yang rendah pada 0 kGy. Walau bagaimanapun, pada dos penyinaran 200 kGy, M100 menjadi rendah dan Eb menjadi tinggi untuk komposit nano MWNTs yang berfungsi.

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LIST OF ABBREVIATIONS

ASTM	-	American Standard Test Method
BS	-	British Standard
CNT	-	Carbon nanotubes
DMA	-	Dynamic mechanical analysis
DMTA	-	Dynamic mechanical thermal analysis
DSC	-	Differential scanning calorimetry
DTG	-	Derivative thermograms
DWNTs	-	Double – walled carbon nanotubes
Eb	-	Elongation at break
EB	-	Electron – beam
ECO	-	Polyepicchlorohydrin-*co*-ethylene
EDX	-	Electron dispersion X – ray analyzer
ENR	-	Epoxidized natural rubber
EVA	-	Ethylene vinyl acetate
FTIR	-	Fourier transform infrared spectroscopy
GNP	-	Graphite Nanoplatelets
LDPE	-	Low density polyethylene
LLDPE	-	Liner low density polyethylene
LNR	-	Liquid natural rubber
M100	-	Modulus at 100% elongation
MAH	-	Maleic anhydride
MMR	-	Montmorillonite
MPa	-	Megapascal
MWNTs	-	Multi – walled carbon nanotubes
MMR	-	Montmorillonite

MWNTs	-	Multi – walled carbon nanotubes
NBR	-	Acrylnonitrile butadiene – rubber
PA6	-	Polyamide 6
PE	-	Polyethylene
PEI	-	Polyetherimide
PI	-	Polyimide
PP	-	Polypropylene
PU	-	Polyurethane
PVC	-	Polyvinyl chloride
PVCw	-	Waste poly(vinylchloride)
SEM	-	Scanning electron microscopy
SMR	-	Standard Malaysia Rubber
SWNTs	-	Single-walled carbon nanotubes
TEM	-	Transmission electron microscopy
TGA	-	Thermo gravimetric analysis
TPE	-	Thermoplastic elastomer
UV	-	Ultraviolet
XRD	-	X-ray diffraction

LIST OF SYMBOLS

°C	-	Temperature in degree Celsius
GPa	-	Gigapascal
Hz	-	Hertz
kN	-	Kilonewton
kGy	-	KiloGray (radiation unit of measure)
mA	-	Milliampere
MeV	-	Megaelectron volt
MPa	-	Megapascal
nm	-	Nanometer
rpm	-	Revolution per minute
TPa	-	Terapascal
T_g	-	Glass transition temperature

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Polymer blending is a common technology, frequently applied in order to produce a product with superior mechanical properties of inexpensive polymer material and small amounts of compatibilizers. The large diversity of commercially available elastomers and thermoplastics offers huge opportunities for blending of thermoplastic elastomers (TPEs).

The basis of epoxidized natural rubber (ENR) is from the chemical alteration of natural rubber (NR). In obtaining ENR, carbon-carbon double bond on the NR molecular chains being converted into the polar epoxy group, when the free volumes of chain phases is decreased and the density and polarity of the derivates are increased, which can provide the ENR with excellent impermeability of air, oil and organics solvent proofness and performance of wet road grip (Yu *et al.*, 2008).

Characteristics of polyvinyl chloride (PVC) can improve ozone and resistance of mechanical in some applications such as conveyor, fuel hose, belt covers and printing roll covers (Ismail and Supri., 2004). Ratnam *et al.* (2001) reported that ENR forms miscible blends with PVC in which PVC is expected to impart high tensile strength and good chemical resistance whereas ENR acts as a permanent plasticizer to PVC, induces good tear strength and enhances the resistance against hydrocarbon oils.

Studies on the blends between ENR-50/PVC had been reported (Ratnam, 2002). Various researchers have reported on the attainment of miscible, well – fused and homogenous ENR-50/PVC blends in relation to the improvement in mechanical and physical properties of the blend. Properties of ENR-50/PVC blends can be improved by electron beam irradiation. The studies revealed by Ratnam *et al.* (2006) that they can be crosslinked by irradiation.

ENR-50/PVC blends were found to be miscible over the entire composition ranges. ENR-50/PVC blends have many potential areas of usage such as cable jackets, conveyer belt covers, hose linings and covers, cellular sporting surfaces and footwear. High energy irradiation (gamma and electron beam) is a well-known technique for polymer modification (Ratnam and Zaman, 1999). Electron beam processing needs high energy electrons from an accelerator for crosslink reactions and initiate polymerization in suitable matrices, thus improving their specific physical and also chemical properties.

Nanocomposites exhibit important enhancement in mechanical and physical properties in relation to the polymer host. The stiffness and strength with a minimal loss in ductility and impact resistance can be enhanced by adding of the minimum percentage of nanofiller. Other than that, it also can help in increasing of permeability and swelling in solvents, abrasion improvement, flame resistance and thermal endurance, with an improvement optical properties and electrical conductivity (Arroyo *et al.,* 2007).

There are many uses of carbon nanotubes in engineering application and electronics such as photovoltaic devices, nanoelectronic, superconductors, electrochemical actuators, nanowires and electrochemical capacitors. This nanotube can be divided into several types such as single-walled carbon nanotubes (SWNTs), double-walled carbon nanotubes (DWNTs) and multi-walled carbon nanotubes (MWNTs). Sahoo *et al.* (2010) reported that the presence of carbon nanotubes can enhance the properties of polymer composites including tensile strength, tensile modulus, toughness, glass transition temperature, electrical conductivity, thermal conductivity, optical properties, solvent resistance, etc.

SWNTs and DWNTs compose cylinders of one or two (concentric), respectively, graphene sheets, whereas MWNTs consists several concentric cylindrical shells of graphene sheets (Sahoo *et al.*, 2010). Sahoo *et al.* (2010) also reported that production of CNTs has variety of methods such as laser ablation, arc discharge, high pressure carbon monoxide (HiPCO) and chemical vapor deposition (CVD).

Irradiation can be utilized to strengthen the characteristics of polymer blends and composites. Irradiation also can help to induce crosslinking like those obtained by sulphur curing, but the net effects, while similar, are not identical. The type of carbon-carbon crosslink formed in this method enhances the mechanical properties at higher temperature. Also, it can lead to greater resistance of abrasion and superior ozone resistance (Khalid *et al.*, 2010).

In this study the irradiation effect on the properties of ENR-50/PVC blends filled with functionalized and unfuntionalized MWNTs will be investigated.

1.2 Problem Statement

The use of ENR/PVC blends is commonly used in conveyer belt covers, hose linings and covers, cable jackets, cellular sporting surfaces and footwear (Ratnam and Zaman, 1999). From these applications, this blend is also expected very suitable to use in interior part of car such as gasket and o-ring which are exposed to the higher temperature and dynamic movement. Otherwise, work on ENR/PVC blend might be has some weaknesses such as low in mechanical strength, electrical conductivity and also thermal properties as compared with addition of nanofiller and irradiation modification. Moreover, the ENR/PVC blend had found its commercial applications, work on the improvement of its properties still become the subject of interest. Broza *et al.* (2007) reported that in the presence of MWNTs the electrical conductivity had increased with increasing of MWNTs in the PVC matrix. This was due to MWNTs are homogenously distributed in the PVC matrix. Study on polyurethane (PU)/CNTs nanocomposites that had done by Sahoo *et al.* (2006) reported that adding of CNTs into PU had drastically increased the tensile strength and also modulus. So *et al.* (2007) also reported that in-situ polymerized PI containing MWNTs-COOH showed increment in tensile strength and modulus as compared to that of the neat PI. Hence, the modification of this blend is needed in order to enhance its overall properties. The main aim of this research is to enhance the current properties of ENR/PVC blends with incorporation of multi-walled carbon nanotubes (MWNTs) and functionalized MWNTs. This is due to the superior properties of MWNTs are not limited to electrical and thermal conductivities, and also included mechanical properties (Sahoo *et al.*, 2010). Furthermore, enhancement is expected when the use of MWNTs is along with irradiation. This is because ionising irradiation can induce crosslinks of the blends.

1.3 Objective of the Study

In this research, the main objective is to characterize ENR-50/PVC/MWNTs nanocomposites. This can be further divided into:

(i) To investigate the effect of MWNTs loading on the properties of the ENR-50/PVC/MWNTs nanocomposites.
(ii) To investigate the effect of functionalized MWNTs (MWNTs-COOH and MWNTs-OH) on the properties of the ENR-50/PVC/MWNTs nanocomposites.
(iii) To investigate the effect of irradiation dose on the properties of the functionalized and unfunctionalized ENR-50/PVC/MWNTs nanocomposites.

1.4 Scope of the Study

In this research, the materials required are epoxidized natural rubber, ENR-50 (rubber), polyvinyl chloride, PVC (thermoplastic), multi-walled carbon nanotubes, MWNTs (nanofiller). Equipments used are Brabender Plastigraph W 50 E-3 Zones, Hot and Cold Press Machine Scientific Laboratory Hydraulic Press Type LP-S-50 and 2 MeV electron beam accelerator Model EPS 3000 (Cockroft Walton). Moreover, compounding of ENR-50/PVC/CNT by using Brabender Plastigraph and the compound subjected to Hot Press Machine in order to produce samples 1-, 2-, and 2.5- mm thick sheet form. In this research, there are a few aspects of testing involved such as physical, mechanical, thermal, electrical and also morphological tests. Firstly, Fourier transform infrared spectroscopy (FTIR) is to determine the interaction between the components in nanocomposites. In aspect of physical properties, gel content is to measure the crosslinking percentage of nanocomposites. Other than that, there are a few of morphological which are scanning electron microscopy (SEM), to observe the morphology behavior of polymer phase in nanocomposites, transmission electron microscope (TEM), to observe the dispersion of MWNTs filler and its functionalized in polymer matrix and characterization on XRD-pattern, to investigate the interaction between MWNTs filler and ENR-50/PVC matrix and to access the effect of MWNTs content on the crystallinity of polymer matrix. Dynamic mechanical analysis (DMA), the parameters that measured is glass transition temperature (T_g), storage modulus and loss modulus.in order to investigate thermal properties of nanocomposites. For electrical properties, volume resistivity is to quantify how strongly a given material opposes the flow of electric current. Lastly, the measurement of tensile properties included in calculation of tensile strength (Ts), modulus 100 (M100) and elongation at break (Eb).

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