UNIVERSITI PUTRA MALAYSIA

PERFORMANCE OF IRRADIATED AND CROSSLINKED ETHYLENE VINYL ACETATE-WASTE TIRE DUST BLEND

ANIS SAKINAH BINTI ZAINAL ABIDIN

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By

ANIS SAKINAH BINTI ZAINAL ABIDIN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Science

April 2009

DEDICATION

This work is dedicated to my beloved parents and family for their endless love, patience and support.

My Parents and family

SADIAH BAHAROM, ZAINAL ABIDIN, SUMAIYA, IRFAN, ZUHAIR, ATIFA

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Supervisor : Luqman Chuah Abdullah, PhD
Faculty : Engineering

The influences of electron beam irradiation, addition of crosslinking agents and the combination of irradiation and crosslinking agents on the properties of Ethylene Vinyl Acetate/Waste Tire Dust (EVA/WTD) blends were investigated. Trimethylolpropane triacrylate (TMPTA) and tripropyleneglycol diacrylate (TPGDA) were chosen as crosslinking agents. Blends were prepared by melt mixing in an internal mixer, Haake Rheomix Polydrive R600/610 at temperature and rotor speed of 140^{o}C and 50 rpm, respectively. Studies in processing conditions were carried out in order to ensure the enhancement of EVA/WTD blend properties through irradiation. Results revealed that the optimum processing conditions were at 140^{o}C mixing temperature, with 10 min of blending time and at 90/10 (EVA/WTD) blend ratio. The dynamic mechanical properties showed two glass transition temperatures that indicates

incompatible blends. The introduction of electron beam irradiation on EVA/WTD at different doses, 50, 100, 150 and 200 kGy has enhanced the irradiation-induced crosslinking. Irradiation-induced crosslinking has increased with the increase in irradiation dose and lead to the improvement in tensile properties, compatibility, dynamic and thermal mechanical properties of the blends. The incorporation of TMPTA and TPGDA as crosslinking agents lead to the improvement of tensile strength, thermal and dynamic mechanical properties. A decline in tensile strength and dynamic properties of the EVA/WTD blend at above 50 kGy irradiation dose in the presence of TMPTA was observed. Such a decrease attributed to the embrittlement of the blend due to high extent of irradiation-induced crosslinking. TPGDA was found to serve the optimum tensile and dynamic mechanical properties upon EB irradiation of EVA/WTD blends.

Abstrak tesis ini dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi syarat-syarat untuk memperolehi Ijazah Sarjana Sains

PRESTASI ADUNAN ETILINA VINIL ACETAT-SERBUK TAYAR TERBUANG TERSINAR DAN BERANGKAI SILANG

Oleh

ANIS SAKINAH BINTI ZAINAL ABIDIN

April 2009

Penyelia : Luqman Chuah Abdullah, PhD
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Kesan radiasi alur elektron dan agen sambung silang serta gabungan kedua-duanya ke atas sifat-sifat adunan etilina vinil acetat/serbuk tayar terbuang (EVA/WTD) telah dikaji. Trimethylolpropane triacrylate (TMPTA) dan tripropyleneglcol diacrylate (TPGDA) telah dipilih sebagai agen sambung silang. Adunan disediakan dengan menggunakan pencampur dalaman Haake Rheomix Polydrive R600/610 pada suhu 140^{o}C dan kelajuan rotor 50 rpm. Kajian terhadap proses pembuatan adunan telah dijalankan bagi memastikan sifat-sifat adunan EVA/WTD akan lebih baik apabila menjalani radiasi. Keputusan menunjukkan bahawa proses pembuatan adunan EVA/WTD yang optimum perlu dijalankan pada suhu 140^{o}C bagi suhu pengadunan dan 10 min bagi masa pengadunan serta berkomposisi 90/10 EVA/WTD. Sifat-sifat mekanik dinamik menunjukkan adunan adalah tidak serasi kerana terdapat dua

suhu peralihan kaca. Dengan mengenakan radiasi alur elektron ke atas adunan EVA/WTD pada dos yang berbeza iaitu 50, 100, 150 and 200 kGy, telah meningkatkan sambung silang adunan. Sambung silang yang dipengaruhi oleh radiasi meningkat dengan peningkatan dos radiasi dan menyebabkan peningkatan pada sifat-sifat tensil, keserasian, sifat-sifat mekanikal dinamik, dan sifat-sifat terma adunan. Penggunaan agen sambung silang seperi TMPTA dan TPGDA telah meningkatkan lagi sambung silang ini dalam kekuatan tensil, sifat-sifat terma dan sifat-sifat mekanikal dinamik. Pada dos radiasi 50 kGy, dengan kehadiran agen sambung silang, penurunan pada kekuatan tensil dan mekanikal dinamik berlaku. Ini adalah kerana peningkatan sambung silang yang berlebihan telah menyebabkan adunan menjadi rapuh. TPGDA didapati paling berkesan dalam meningkatkan sambung silang yang dipengaruhi oleh radiasi.

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I certify that the Examination Committee has met on 16 April 2009 to conduct the final examination of Anis Sakinah binti Zainal Abidin on her thesis entitled "Performance of Irradiated and Crosslinked Ethylene Vinyl Acetate-Waste Tire Dust Blend" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

ANIS SAKINAH ZAINAL ABIDIN
Date:

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

T_g	Glass transition temperature
T_m	Melting temperature
ΔH_f	Heat of fusion
X_c	Degree of crystallinity
^oC	Degree Celsius
kGy	Kilo Gray

LIST OF ABBREVIATION

phr	Part per hundred rubber
rpm	Revolution per minutes
wt%	Weight percentage
ABS	Acrylonitrile butadiene styrene
ASTM	American Society for Testing and Material
BrTFF	2-bromotetraflouroethyl trifluorovinyl ether
cPTFE	poly(tetrafluoroethylene)
DCP	dicumyl peroxide
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
EB	Electron beam
ENR	Epoxidized natural rubber
EPDM	Ethylene propylene diene terpolymer
EVA	Ethylene vinyl acetate
HDPE	High-density polyethylene
HIPS	High impact polystyrene
HVA-2	N,N-m phenylene dimaleimide
LDPE	Low-density polyethylene
MFI	Melt flow index
MIDA	Malaysia Industrial Development Authority
NBR	Nitrile rubber
NR	Natural rubber

PC	Polycarbonate
PE	Polyethylene
PP	Polypropylene
PU	polyurethane
PVC	Polyvinyl chloride
RMA	Rubber modified asphalt
RPE	recycle polyethylene
SBR	Styrene butadiene rubber
SEM	Scanning electron microscope
TMPTA	Trimethylolpropane triacrylate
TPE	Thermoplastic elastomer
TPGDA	Tripropyleneglycol diacrylate
UV	Ultra violet
VA	Vinyl acetate
VPFESEM	Variable pressure field emission scanning electron microscope
WTD	Waste tire dust
XBR	Carboxylated nitrile rubber

CHAPTER 1

INTRODUCTION

1.1 Background of study

The production of tire is increasing every year due to the increase of vehicle sales, where tire is an integral part of vehicle. The generation and disposal of waste are inherent to life itself and have presented problems to the human community. Data from the Malaysia Industrial Development Authority (MIDA) shows that Malaysia generates about 150,000 tons of scrap tires every year. Although there are low performance uses for granulated scrap tire rubber, and small amounts of powder are used in the production of new tires, demand has been limited because the relatively large particle sizes produced commercially are expensive and do not compound well (Wendy, 2008). Waste tire rubber can be blended with thermoplastics to produce thermoplastic elastomers with a range of properties. Thermoplastic elastomers (TPE) have physical properties of both thermoplastic and elastomer as well as similar processability to that of thermoplastics. TPE provides better material utilization, as scrap and rejects can be recycled.

These materials can be used in conventional thermoplastics processing equipment. The unique characteristics of thermoplastic elastomer make them an attractive alternative to conventional elastomers in a variety of markets such as

the automotive industry. The potential to convert a conventional elastomer (thermoset) into thermoplastic elastomer through blending offers the potential for new market applications for waste tire dust (WTD). Several studies have been done by blending WTD with polypropylene (PP) (Ismail *et al*., 2006), high density polyethylene (HDPE) and low density polyethylene (LDPE) (Sonnier *et al*., 2007), recycle polyethylene (RPE) (Scaffaro *et al*., 2005) and natural rubber (NR) (Ismail *et al*., 2002). In their work, they found that recycle tires behave as filler with relatively low interaction with the matrix without any additives. Therefore, a study of the influence of electron beam irradiation and crosslinking agent were done in attempt to improve the compatibility and enhance the properties of the ethylene vinyl acetate (EVA)/WTD blend. High energy irradiation (gamma and electron beam) is a well known technique for the modification of polymers (Makhlis, 1972). It causes molecular changes in polymer resulting chain crosslinking, chain scission, grafting and curing. As the irradiation doses increase, chains in the polymer network will undergo further crosslink until it produce high crosslink density. Chain crosslink may enhance the tensile strength, elongation, modulus and hardness, while chain scission decreases these properties (Scaffaro *et al*., 2005).

EVA are random structured polymers which offer excellent ozone resistance, weather resistance and mechanical properties (Sujit, 1996). EVA also is a halogen free thermoplastic which may suit many applications that are currently

dominated by plasticized poly(vinyl chloride) (PVC) (Zurina *et al*., 2008). It has good clarity and gloss, barrier properties, low-temperature toughness, stress-crack resistance, hot-melt adhesive and heat sealing properties and resistance to ultra violate (UV) radiation. EVA is used as wire and cable coating, flexible tubing, shoe soles, food packaging and impact modifier (Zurina, 2007). Thus, making it suitable in formulation of thermoplastic elastomer (Zurina *et al*., 2006a)

1.2 Problems Statement

The problems associated with disposal of the vast number of scrap tires produced annually worldwide are very clear. The durability of tires and the time it takes them to degrade makes them suitable for long term applications (Al-Tabbaa *et al*., 2001). A potential re-use of waste tire dust, which has received a lot of attention, can be use as filler in polymer compound. However, waste tire dust has low properties, as it is a used material which causes weak interaction between the ethylene vinyl acetate and waste tires dust component. Thus, variety of modification techniques has been done to improve the compatibility between the immiscible blend components. The modification technique that have been chosen are radiation induce using electron beam accelerator and adding crosslinking agent in the blend. Radiation and crosslinking agent effect for EVA/WTD blend in researching for compatibility and improving properties of the blend are the principle problems that paving the track of this thesis work.