SURFACE MODIFICATION OF WASTE TIRE DUST UNDER PRE-IRRADIATION EMULSION GRAFTING TECHNIQUES

by

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LIST OF ABBREVIATIONS

H_s	Height of the aqueous layer at the bottom
H_t	Height of the emulsion
W_o	Initial weight
W_f	Final weight
4-VP	4-vinylpyridine
AA	Acrylic acid
AgNPs	Silver nanoparticles
AM	Acrylamide
AMP	Ammonium 12-molybdophosphate
AN	Acrylonitrile
ARP	Activated rubber powder
ATR-FTIR	Attenuated total reflectance-Fourier transformed infrared spectroscopy
BA	Butyl acrylate
CFF	Chicken feather fibre
CI	Creaming index
CMS	4-chloromethylstyrene
DCP	Dicumyl peroxide
DG	Degree grafting
DMAEMA	N,N-dimethylaminoethyl methacrylate
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
DOG	Degree of grafting
DPEHA	Di- pentaerythritol hexaacrylate
DPNR	Deproteinized natural rubber
DR	Devulcanized rubber
DTG	Differential thermogravimetry
DWR	Devulcanized waste rubber
EB	Electron beam
EB	Elongation at break
EBPFOA	Pentadecafluoro-octanoic acid 1-(4-benzoyl-phenoxymethyl)-2-hydroxy-ethyl ester

EGDMA	Ethylene glycol dimethacrylate
ENR	Epoxidized natural rubber
EPDM	Ethylene-propylene-diene monomer rubber
EVA	Ethylene vinyl acetate
FA	Fly ash
FESEM	Field emission scanning electron microscopy
FF	Flax fibres
FTIR	Fourier transform infrared spectroscopy
GMA	Glycidyl methacrylate
GTR	Ground tire rubber
G-WTD	Grafted WTD
G-WTD10	10 wt% grafted WTD
G-WTD20	20 wt% grafted WTD
G-WTD30	30 wt% grafted WTD
GY	Grafting yield
HDPE	High-density polyethylene
HEMA	Hydroxyethyl methacrylate
HNT	Halloysite nanotube
LDPE	Low-density polyethylene
MA	Maleic anhydride
MAH	Maleic anhydride
MFA	Multifunctional acrylate
MMA	Methyl methacrylate
NR	Natural rubber
NVF	N-vinylformamide
NWF	Nonwoven fabric
OCA	Optical contact angle
OEGMA	Oligo(ethylene glycol) methyl ether methacrylate
OEGMA300	Oligo(ethylene glycol) methyl ether methacrylate
PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile
PBL	Polybutadiene rubber latex
PCL	Poly (ε-caprolactone)
PDMAEMA	Poly2-(dimethyl amino) ethyl methacrylate

PE	Polyethylene
PEI	Polyetherimide
PET	Poly(ethylene terephthalate)
PETA	Pentaerythritol triacrylate
PGMA	Polyglycidyl methacrylate
PHEMA	Poly(2-Hydroxy ethyl methacrylate)
PMMA	Poly(methyl methacrylate)
pNaSS	Poly (sodium4- styrenesulfonate)
PP	Polypropylene
PSA	Particle size analyzer
PU	Polyurethane
PVA	Polyvinyl alcohol
RIG	Radiation-induced grafting
RR	Recycled rubber
SBR	Styrene-butadiene rubber
SBS	Styrene-butadiene-styrene
SEM	Scanning electron microscope
SiO_2NPs	Silica nanoparticles
SR	Silicone rubber
SSS	P-sodium styrene sulphonate
TAIC	Triallyl isocyanurate
TDI	Toluene-2,4-diisocyanate
TGA	Thermogravimetry analyzer
TGME	Triethylene glycol methyl ether
TiO_2	Titanium dioxide
TMPTA	Trihydroxy methyl propane triacrylate
TMPTMA	Trimethylolpropane trimethacrylate
tPA	Ternary copolyamide
TPGDA	Tripropylene glycol diacrylate
TS	Tensile strength
Tw-20	Tween 20
UV	Ultraviolet
VBC	Vinylbenzyl chloride
VTMS	Vinyltrimetoxysilan

w-HDPE	Waste high-density polyethylene
WTD	Waste tire dust
WTD10	10 wt% non-grafted WTD
WTD20	20 wt% non-grafted WTD
WTD30	30 wt% non-grafted WTD
WTR	Waste tire rubber

LIST OF SYMBOLS

%	Percentage
ΔL	Final length
µm	Micronmetre
A	Absorbance
A	Cross section
C	Concentration
℃	Degree Celcius
E	Young’s modulus
F	Maximum test force
h	Hour
kGy	KiloGray
l	Pathlength
L	Initial length
MeV	Mega Electronvolt
mm	Millimetre
MPa	Megapascal
w/v%	Weight per volume percent
wt%	Weight percent
ε	Absorptivity
ε	Elongation, strain
σ	Tensile strength, stress

Pengubahsuaian Permukaan Serbuk Sisa Getah Menggunakan Teknik Pra-Penyinaran Cangkukan Emulsi

ABSTRAK

Kebelakangan ini, kadar pembuangan tayar terpakai telah meningkat secara mendadak, sehingga menjejaskan keseimbangan ekologi dunia. Penggunaan sisa ini di dalam polimer komposit sebagai pengisi kos rendah yang lestari merupakan salah satu jalan penyelesaian. Walau bagaimanapun, keserasian sisa debu tayar (WTD) dengan kebanyakan matriks adalah terhad yang mengakibatkan penurunan sifat mekanik komposit. Tujuan kajian ini adalah untuk meningkatkan ikatan antara muka pada getah-matrik. Proses ini dilakukan dengan menggunakan kumpulan karbonil dari tripropylene glycol diacrylate (TPGDA) dengan teknik cangkukan emulsi pra-penyinaran bagi menghasilkan WTD dicangkuk (G-WTD) yang akan menghasilkan ikatan kimia yang kuat antara getah dan polimer matriks. WTD pada mulanya diubah suai melalui cangkukan aruhan sinaran (RIG) dengan TPGDA emulsi. Kesan parameter cangkukan diukur terhadap hasil cangkukan (GY) dan sifat fizikokimia WTD disahkan. Akhirnya, keserasian etilena vinil asetat (EVA) teriiradiasi dengan WTD tidak dicangkuk dan WTD dicangkuk ditentukan dan dibandingkan. Dos penyinaran alur elektron (EB) pada 100 kGy dan ke bawah dipilih dalam kajian ini kerana ia memberi kesan minimum pada WTD dan dapat mengekalkan kestabilannya semasa penyinaran. Di samping itu, 0.4 wt% surfaktan Tween 20 (Tw-20) dipilih sebagai parameter optimum kerana jumlahnya mencukupi untuk mengekalkan kestabilan emulsi TPGDA dalam tempoh 24 jam proses cantuman. Di dalam eksperimen ini, teknik RIG berjaya, dengan GY maksimum iaitu 930 % pada parameter cangkukan ideal dengan 5 w/v % kepekatan monomer, 60 kGy dos penyinaran, 3 jam masa tindak balas, dan 60 ºC suhu tindak balas. Menurut identifikasi kumpulan berfungsi dan kebolehbasahan, kaedah RIG ini berjaya memperkenalkan sebilangan besar kumpulan karbonil ke permukaan WTD, seperti yang ditunjukkan oleh kewujudan puncak baru pada 1720 cm^{-1} dan pengurangan sudut kontak antara permukaan getah dan air. Morfologi permukaan WTD dicangkuk, menebal, membengkak, dan dilapisi jika dibandingkan dengan WTD. Selain itu, dapat ditunjukkan bahawa dengan integrasi monomer TPGDA ke tulang belakang WTD, purata diameter WTD dicangkuk diperluas sekitar 111.5 %. Penambahan WTD tidak dicangkuk ke dalam adunan EVA mengurangkan kekuatan tegangan dan kekerasan adunan. Walaubagaimanapun, bagi adunan yang mengandungi WTD dicangkuk menunjukkan kekuatan tegangan dan kekerasan yang lebih tinggi berbanding adunan EVA yang diadun dengan WTD tidak dicangkuk. Bagi adunan teriradiasi yang mengandungi WTD dicangkuk menunjukkan peningkatan di dalam kekuatan tegangan dan kekerasan. Peningkatan tersebut adalah dipengaruhi oleh proses pertautan silang oleh sinaran teraruh dan seterusnya meningkatkan keserasian diantara WTD dicangkuk bersama matriks EVA. Ia dapat juga dilihat di dalam kandungan gel yang meningkat dengan peningkatan dos sinaran yang turut membuktikan peningkatan ketumpatan pertautan silang di dalam adunan. Hasil kajian menunjukkan bahawa modifikasi permukaan WTD menggunakan teknik RIG ini telah berjaya dan menghasilkan peningkatan sifat mekanik akibat ikatan antara muka yang lebih baik antara WTD dicangkuk dengan adunan EVA.

Surface Modification of Waste Tire Dust Under Pre-Irradiation Emulsion Grafting Techniques

ABSTRACT

In recent years, the rate of waste tire disposal has increased dramatically, jeopardizing world ecological equilibrium. The utilization of this waste in polymer composite as a sustainable and low-cost filler is one of the possible solutions. However, the compatibility of waste tire dust (WTD) with most matrices is limited which results in the degradation of the composite's mechanical properties. The goal of this study was to enhance the interfacial bonding at the rubber-matrix interface. This was done by utilizing the carbonyl group of tripropylene glycol diacrylate (TPGDA) using pre-irradiation emulsion grafting techniques to develop grafted WTD (G-WTD) which can generate a strong chemical bond between the rubber and the polymer matrix. The WTD was initially modified via radiation-induced grafting (RIG) techniques with a TPGDA emulsion. The effect of grafting parameters on the grafting yield (GY) was calculated and grafted WTD's physicochemical properties were confirmed. Finally, the compatibility of irradiated ethylene vinyl acetate (EVA) with the integration of un-grafted WTD and grafted WTD were determined and compared. Electron beam (EB) irradiation dose at 100 kGy and lower is preferred in this study for WTD, as it has minimal effect on the WTD and maintains the WTD stability upon irradiation. In addition, the 0.4 wt% of Tween 20 (Tw-20) surfactant was chosen as the optimal amount needed as the amount is sufficient to maintain the stability of the TPGDA emulsion during the grafting process for 24 hours. The RIG technique was successful in this experiment, with a maximum GY of 930 % obtained at an ideal grafting parameter of 5 w/v % monomer concentration, 60 kGy absorbed radiation dosage, 3 h reaction time, and 60 ºC reaction temperature. According to the chemical identification and wettability analysis, the RIG method successfully introduced a large number of carbonyl groups into the WTD surface, as demonstrated by the creation of a new peak at 1720 cm^{-1} and a reduction in the angle of contact between the rubber surface and the water. The grafted WTD surface morphology has thickened, swelled, and coated in comparison to WTD. Additionally, it can be shown that by integrating the TPGDA monomer into the backbone of the WTD, the grafted WTD's average diameter was expanded by approximately 111.5 %. The incorporation of non-grafted WTD in the EVA blend decreased the tensile strength and hardness of the blend. However, the EVA blend containing grafted WTD has higher tensile strength and hardness compared to EVA blend with non-grafted WTD. An irradiated blend containing grafted WTD has shown an increase in tensile strength as well as hardness. The increment is due to the radiation-induced crosslinking process and improved compatibility between the grafted WTD and EVA matrix in the blend. It can also be seen that the gel content increase as the irradiation dose increases which further prove the increase in crosslinking density in the blend. The findings indicate that surface modification of WTD using the RIG technique is successful, resulting in an improvement in mechanical properties as a result of better interfacial bonding between the grafted WTD and the EVA blend.

CHAPTER 1 : INTRODUCTION

1.1 Overview

This chapter describes the background study of this research, the problem statement, the objectives of the research, the scope of the study and the thesis outline.

1.2 Research Background

In recent years, the management of discarded tires has been a major issue. In order to handle discarded tires at the end of their useful lives, many strategies are advised, including dumping, retreading and reusing, fuel for combustion, recycling to get raw materials, and so on. The estimated data show that about 1.2 billion tires would be discarded yearly worldwide by the end of the year 2030 (Bala & Gupta, 2021) and each year, approximately 1 billion tires are deemed unfit for further use or retreading (Formela, 2021). Improper management and improper burning of waste tires will harm the air, human health, and the environment (Idris et al., 2019). To achieve sustainability, these scrap tires can be regulated by using the principle of 4R's which are reuse, reduce, recycle, and recovery (Malijonyte et al., 2016).

Nowadays, many researchers have been working with waste tires as a modifier for insulation, construction, thermoplastic, and road pavement (Celauro et al., 2019; Fathy et al., 2019; Hwang et al., 2018; Simon-Stőger & Varga, 2021). Grinding, devulcanization, and pyrolysis of the waste tire are three common recycling methods used before further use for any specific applications (Jiang et al., 2018; Z. Wang & Zeng, 2021). Researchers have discovered various findings to improve the behaviour of rubberbased materials before they can be recycled for new products by reflecting the effect of (a) the size of rubber particles, (b) the amount of rubber, and (c) types of treatments for rubber particles (Adesina et al., 2020; Bala & Gupta, 2021; Zhang et al., 2020). The surface of rubber particles can be modified in various ways such as pre-reaction which involves pre-swelling and pre-degradation, polymer coating, solution soaking as well as grafting with chemical or radiation onto the waste tire surface (Chen et al., 2019; Dong & Zhao, 2018; Lim & Shin, 2020; Mousavi et al., 2019; Xiang et al., 2020).

Among the modification technique used, grafting induced by radiation such as microwave, plasma, gamma and electron beam is well known as a clean method that is possible to modify polymer matrix with improved material properties. This technique provides a homogeneous reaction and high diffusion nature without chemical by-products. A powerful energy of electron beam radiation can be used to generate active sites (free radicals) and react with vinyl monomers or functional groups to create tremendous graft modification in the polymer matrix (Hosseinnezhad et al., 2019; Kabir et al., 2020; J. Li et al., 2021; Lim & Shin, 2020). This versatile method can expose newly grafted moiety to the surface or bulk reinforced materials such as fibres or waste tire rubber and endowed tuneable grafting yield to meet specific applications. In addition, no residues from the chemical initiator will remain in the modified polymer matrix (Moawia et al., 2016). There are two methods for radiation-induced grafting (RIG) which are mutual and pre-irradiation steps. These steps for grafting can be in a solution or an emulsion.

Emulsion grafting is an efficient, environmentally friendly, and economical approach to grafting, which applies to insoluble monomers in an aqueous solution (Akkaş

Kavakli et al., 2016). While tripropylene glycol diacrylate (TPGDA) is a widely used monomer due to its ease of preparation, low cost, and effectiveness in terms of dielectric, structural properties, thermal stability and crosslinking rate (Y. He et al., 2017; R. Liu et al., 2020). However, TPGDA is an insoluble monomer in water and can be used in an emulsion state which will reduce the consumption of chemicals. The use of TPGDA has been found to improve the activity by crosslinking which results in higher stability and can be reusable (Jamwal et al., 2020). Another study reported by Ahmed et al., (2020) mentioned that TPGDA is the best crosslinking agent among the four tested crosslink agents. They stated that TPGDA provides a high-performance blend due to a three-dimensional crosslinking network which improved the tensile strength.

Many studies have already been carried out to recycle waste tires by blending them with other polymeric materials to obtain composite displaying both thermoplastic and elastomeric properties (Danielli & Sousa, 2018; Luna et al., 2020; Zedler et al., 2020). However, most of the cases led to the conclusion that the addition of waste tires would also decrease drastically the mechanical properties such as tensile strength, Young's modulus and elongation at break (Bee et al., 2018; Fathy et al., 2019; Luna et al., 2020; Martínez-Hernández et al., 2003; Yu et al., 2016). The reason is the lack of interfacial interaction between waste tires and the thermoplastic matrix. A study reported by Zhong & Zhang, (2020) has shown that the incorporation of the waste tire has decreased the tensile strength, elongation at break and Young's modulus of the blend. The decline in mechanical properties of the blend could be attributed to agglomeration and particle-particle interaction of the waste tire rather than the interaction between the rubber and matrix. Therefore, the treatment of the surface properties of a waste tire is needed with the employment of a new crosslink bond that can improve the compatibility between them.

Radiation processing of polymeric materials involves the treatment of polymeric materials with ionizing radiation to modify their physical and chemical properties. The properties of polymeric materials can be modified by irradiation as it is bound to crosslink, degrade, grafted or be cured when subjected to ionizing radiation (Ramarad et al., 2017). In this study, three steps have been employed and it involved; surface modification of waste tire dust (WTD), blending and electron beam irradiation has been used on the ethylene vinyl acetate (EVA), ethylene vinyl acetate/waste tire dust (EVA/WTD) and ethylene vinyl acetate/grafted waste tire dust (EVA/G-WTD) blend. The grafted WTD has been confirmed and studied the newly properties developed. Besides, the performance of the grafted blends and the efficiency of electron beam irradiation in improving the properties of EVA/G-WTD blends has been reported.

1.3 Problem Statement

The recyclability of a waste tire is difficult due to the matrix phase in tires being a vulcanized rubber that cannot be dissolved which makes it incompatible with most polymeric matrices. The crosslinked structure may hinder molecular interaction and interfacial adhesion (Simon-Stőger & Varga, 2021) which results in deterioration in both mechanical and physical characteristics (Montoya-Villegas et al., 2020; Phiri et al., 2021). To date, a lot of research has been done to treat the WTD surface before and after the blending process such as in-situ polymerisation, sintering the WTD, as well as using irradiation (Molanorouzi & Mohaved, 2016; Zhang et al., 2021; Zhang et al., 2020). High energy irradiation via an electron beam is a clean method with less use of chemical usage.

A study by (Tian et al., 2017), it was found that the use of pre-irradiation emulsion grafting techniques onto polybutadiene rubber latex (PBL) with polyvinyl alcohol (PVA) has successfully improved the surface free energy and hydrophilic properties of PBL. However, none have been done by using the pre-irradiation emulsion grafting techniques to graft a new functional group onto WTD to improve its surface properties of it, for further uses in blending with other polymeric materials.

For WTD to be used in practical applications, good adhesion between WTD and the polymer matrix is important (Xu et al., 2018). The highly cross-linked network of sulfur in a waste tire is insoluble and infusible, which makes it very difficult to recycle in other polymeric materials (Adesina et al., 2020; Saputra et al., 2021; Zhang et al., 2020). Therefore, improving the physicochemical properties of WTD with a new monomer will enhance the interaction of WTD and another polymer. According to a study done by Deng et al., (2020), it was found that TPGDA has a high efficiency in the conversion band to form a graft copolymer. The fact that TPGDA has four free radical sites will act as a crosslinker that generates macroradicals. These sites will react with the polymer backbone and result in a well-defined three-dimensional network. Furthermore, the properties of TPGDA have a high conversion double bond will increase the number of possibilities for TPGDA attachment sites. This situation is favourable towards WTD with a newly grafted monomer. Previous research has studied the effect of TPGDA on various polymer materials (Kessler et al., 2020; Onn et al., 2018; Shahriari et al., 2019; Wang et al., 2020). However, none has been used to graft TPGDA onto WTD via radiation-induced graft copolymerization technique to improve the physicochemical properties of WTD. Thus, in this work, TPGDA is used to graft onto the WTD rubber backbone, before it can be used in other polymeric blends.