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DEVELOPMENT OF IRRADIATED NATURAL RUBBER(NR)/ETHYLENE-PROPYLENE-DIENE TERPOLYMER(EPDM) BASED COMPOSITE MATERIALS FOR OUTDOOR APPLICATIONS

by

GAMAETHIGE DON DINESH KRISHANTHA

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DECLARATION BY THE CANDIDATE

The work described in this thesis was carried out by me under the supervision of Dr. Laleen Karunanayake, Senior Lecturer, Department of Chemistry, Faculty of Applied Science, University of Sri Jayewardenepura, and a report on this has not been submitted in whole or in part to any other university or institution for another Degree/Diploma.

....
Signature of the candidate

G. D. D. Krishantha
Name with initials

DECLARATION BY THE SUPERVISOR/S

I/We certify that the above statement made by the candidate is true and that this thesis is suitable for submission to the University for the purpose of evaluation.

....
Signature of the supervisor

Dr. L. Karunanayake
Name with initials

Name and address
Dr. L. Karunanayake
Dept. of Chemistry
University of Sri Jayewardenepura
....
....

DECLARATION FOR THE SUBMISSION OF THE FINAL COPY

This is to certify that all the corrections, additions and amendments suggested by the examiners have been done accordingly.

…………………………………
Signature of the supervisor

Dr. L. Karunanayake
…………………………………
Name with initials

Head / Dept. of Chemistry

Prof. S.I. Samarasinghe
Associate Professor in Chemistry
University of Sri Jayewardenepura
Nugegoda, Sri Lanka.

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LIST OF ABBREVIATIONS

R	Retention percentage
%wt	Weight percentage
γ-irradiation	Gamma-irradiation
1, 4 HD	1, 4 hexadiene
6PPD	N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine
A	Accelerator
A/S	Accelerator to Sulphur ratio
A-400	Poly(ethylene glycol) 400 diacrylate
A-600	Poly(ethylene glycol) 600 diacrylate
ABS	Acrylonitrile butadiene styrene terpolymer
ASTM	American standard test method
ATR	Attenuated total reflectance
BR	Butyl rubber
CB	Carbon black
CBS	N-cyclohexyl-2-benzothiazole sulphenamide
Co-60	Cobalt-60
CON	Control
conc.	Concentration
CR	Polychloropene (neoprene)
Cs	Cesium
CV	Conventional vulcanization
CV 60	Constant viscosity-60
DBP	n-Dibutyl phthalate
DCP	Dicumyl peroxide
DCPD	Dicyclopentadiene
DIPDIS	Bis(diisopropyl)thiophosphoryl disulphide
DIPTOS	Diisopropyl thiophosphoryl-N-oxydiethylene sulfonamide
DMA	Dynamic mechanical analysis
dNm	Deci newton meter
Eb	Elongation at break
EB	Electron beam

EBM	Electron beam machine
EHA	2-Ethylhexyl acrylate
ENB	Ethyledene norbornene
ENR	Epoxidized natural rubber
EP	Engineering polymer
EPB	Engineering polymer blend
EPDM	Ethylene propylene diene terpolymer
EPDMSH	Mercapto-modified EPDM
EPDMTA	Thioacetate-modified EPDM
EPM	Ethylene propylene monomer
EPR	Ethylene propylene rubber
EPS1	NORDEL IP4640
EPS2	KELTAN 314
EPS3	KELTAN 512X50 (oil extended)
EV	Efficient vulcanization
EVA	Ethylene vinyl acetate
FBL	Full loading of CB into NR/EPDM blend
FEF	Fast extrusion furnace black
FEP	Full loading of CB into EPDM phase
Fig.	Figure
FNR	Full loading into NR phase
FTIR	Fourier transform infrared
GPF	General purpose furnace
Gy	Gray
HAF	High-abrasion furnace black
HNE	Half CB loading into NR phase and half CB loading into EPDM phase
IIR	Butyl rubber
IPN	Inter penetrating network
IRG	Irganox 1520 (4,6-bis (octylthiomethyl)-o-cresol)
ISAF	Intermediate super abrasion furnace
ISO	International standard organization

J/kg	Joule per kilogram
kGy	Kilogray
kGy/h	Kilogray per hour
LCST	Lower critical solution temperature
m	Meter
M 100	Modulus at 100% elongation
M 300	Modulus at 300% elongation
Max	Maximum
MeV	Mega electron volt
Min	Minimum
min	Minute
ML	Mooney unit (large rotor type)
MPa	Megapascal
MPB	Miscible polymer blend
MPR	Melt processable rubbers
NBR	Acrylonitrile-butadiene rubber
Ni-60	Nickel-60
nm	Nano meter
NR	Natural rubber
ODR	Oscillating disc rheometer
p MSAN	Poly (p-methylstyrene-co-acrylonitrile)
PA	Poly amide
PAs	Polymer alloys
PB	Polymer blend
PBEMA	Poly (2-bromoethyl methacrylate)
PBT	Poly (butylene terephthalate)
PC	Polycarbonate
PCL	Poly (ϵ-caprolactone)
PE	Polyethylene
PECH	Poly (epichlorohydrin)
PET	Poly (ethylene terephthalate)
phr	Parts per hundred parts of rubber

PMMA	Poly(methyl methacrylate)
P_o	Plasticity
PP	Polypropylene
PPO	Poly (2,6-dimethyl-1,4-phenylene ether)
PRI	Plasticity retention index
PS	Polystyrene
PVAc	Poly (vinyl acetate)
PVC	Poly(vinyl chloride)
PVME	Poly (vinyl methyl ether)
PαMS	Poly (pα-methyl styrene)
R-H	Rubber hydrocarbon
RLC	Ralox LC
RSS	Ribbed smoke sheet
R-Sx-R	Initial polysulphidic crosslinks
R-Sy-X	Rubber–bound intermediate
RVNRL	Radiation vulcanized natural rubber latex
S	Sulphur
S_2Cl_2	Sulphur chloride
SAN	Poly (styrene-co-acrylonitrile)
SBR	Styrene butadiene rubber
SEV	Semi-efficient vulcanization
SI	Standard international
SO_2	Sulphur dioxide
St. acid	Stearic acid
T6P	Blend of TMQ/6PPD(50/50)
t_{90}	The time to achieve 90% cure
TETD	Tetraethylthiuram disulfide
TMM	Pentaerythritol triacrylate
TMPT	Trimethylolpropane triacrylate
TMQ	2,2,4-Trimethyl-1,2-dihydroquinoline
TMTD	Tetramethylthiuram disulfide
TOR	Trans-polyoctylene

TPE	Thermoplastic elastomers
TPV	Thermoplastic vulcanisates
Ts	Tensile strength
TSR	Technically specified rubber
TZM	Blend of TMQ/ZMTI(50/50)
UCST	Upper critical solution temperature
UV	Ultra-violet
Vanox ZMTI	2H-Benzimidazole-2-thione,1,3-dihydro-4(or 5)-methyl-zinc salt
wt.	Weight
ZnO	Zinc oxide

LIST OF SYMBOLS

%	Percentage
μm	Micrometer
^{o}C	Degree centigrade
T	Temperature in Kelvin
T_g	Glass transition temperature
γ	Gamma
ΔG_{mix}	Gibbs free energy of mixing
ΔH_{mix}	Enthalpy of mixing
ΔS_{mix}	Entropy of mixing
Φ_1	Volume or weight fraction of relevant polymer
χ_{12}	Interaction coefficient

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Gamaethige Don Dinesh Krishantha

ABSTRACT

The effect of γ-irradiation on the natural rubber (NR)/ethylene propylene diene terpolymer (EPDM)/carbon black (CB) ternary composites was investigated. The effects of compounding conditions such as mixing sequence of component materials and compositional variables such as filler type and filler loading in preparation of NR/EPDM/CB ternary composites were studied first. The best conditions to develop materials for outdoor applications among the investigated conditions were established. NR:EPDM ratio was maintained at 70:30. These composites were then partially cured using sulphur as the crosslinking agent. Partially cured composites were subjected to irradiation using a γ-irradiation source. The effects of radiation dose on the mechanical properties of the composites were evaluated. The effectiveness of five different sensitizers (radiation crosslink promoters) on the irradiation crosslinking process of the composites was compared. The optimum concentration of the best sensitizer among the candidate sensitizers was also identified. The performance of five different antioxidant systems against the thermal degradation of these composites was also studied. This work was followed by the preparation of NR/EPDM/CB composites using three different grades of EPDM rubber and the evaluation of their mechanical properties upon irradiation. Based on the results, processing, compounding and irradiation conditions

were proposed to produce a new material for outdoor applications. Attempts were made to develop a hypothetical model to explain the vulcanizate structure of the composite.

Of the four mixing sequences studied, the Full loading of CB into the NR/EPDM preblend yielded reasonably good mechanical properties before ageing and the highest retention percentage of some important mechanical properties after ageing. As such this mixing sequence was selected for the preparation of composites. The experimental results also showed that CB N220 at 30 phr loading offered the overall best properties. It was found that efficient crosslinking of the composites was possible in the presence of polyethylene glycol 400 diacrylate, (A-400) at an optimum radiation dose of 80 kGy whereas an optimum dose of 100 kGy was required to get the equivalent improvement in properties of sensitizer free composites. It was also found that variation of tensile properties, tear strength and abrasion loss showed a linear relationship with the radiation dose up to the optimum dose and hence mathematical models were developed and validated within a 4% error. The optimum dose of the selected sensitizer was found to be 1phr

The composites containing a blend of TMQ:Vanox ZMTI possessed optimum mechanical properties when compared with the other antioxidant systems investigated. Among the EPDM grades used the composite prepared with oil extended grade exhibited the best long term ageing property. Finally, considering the effect of various ingredients on the performance of mechanical properties, a hypothetical model showing possible crosslinks that could have formed was proposed and presented at the end of this study.