RADIATION VULCANIZATION OF RUBBER COMPOSITES

547.8426 H. A.

SUBMITTED TO

FACULTY OF SCIENCE

AIN SHAMS UNIVERSITY

in the fulfillment

of the requirements for

THE DEGREE OF DOCTOR OF PHILOSOPHY

IN CHEMISTRY

57422



HUSSEIN AMER ALI YOUSSEF

(B.Sc. 1977, M.Sc. 1991)

NATIONAL CENTER FOR RADIATION RESEARCH

AND TECHNOLOGY

ATOMIC ENERGY AUTHORITY

1996





THESIS

ENTITLED

RADIATION VULCANIZATION OF RUBBER COMPOSITES

Approved

Prof. Dr. K . Makuuchi
Takaski Radiation Chemistry Research Establishment.
Japan Atomic Energy Research Institute
Pro. Dr. A. M. Rabie ————————————————————————————————————
Prof. Dr. A . A . El Miligy

Thesis Supervisors

NCRRT, AEA

NCRRT, AEA

Assist. Prof. Dr. M. M. Abdel Aziz

HEAD OF CHEMISTRY DEPARTMENT

PROF. DR. F. A. FAHMY

ACKNOWLEDGMENT

This work was carried in the Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy research Institute (JAERI) and the National Center for Radiation research and Technology, Atomic Energy of Egypt.

The author wishes gratefully to thank Prof. Dr. Abdel Gwad Rabie Chemistry Department, Faculty of Science Ain Shams University and Prof. Dr. K. Makuuchi ,Takasaki Radiation Chemistry Research Establishment (TRCRE), Japan Atomic Energy research Institute for their supervision, continuous guidance and helpful discussion throughout this work.

The author wishes to express his deepest thanks and gratitude to Prof. Dr. Ahmed. A. El Miligy, National Center for Radiation research and Technology (NCRRT) for supervision, continuous guidance and helpful discussion throughout this work.

The author wishes to express his deepest thanks and gratitude to Assist. Prof. Dr. Mohamed M. Abdel Aziz (NCRRT) for supervision, valuable discussion, help and continuous guidance throughout this work.

The author wishes to express his deepest thanks and gratitude to Prof. Dr. F. Yoshii (TRCRE) for help, valuable discussion and continuous guidance. Also, the author wishes to thanks Dr. T. Sasaki and Dr. T. Sasuga (TRCRE) for their help and valuable discussion. Also, thanks to Mr. H. Hyakutake, Chemical Inspection and Testing Institute, Japan for his valuable favor in doing DSC measurements.

The author wishes to express his appreciation to the Head of Radiation Chemistry Department, NCRRT, AEA for his continuos encourage. Also, many thanks are due to my colleagues in the department.

CONTENTS

I. INTRODUCTION	1
1. 1. CROSSLINKING REACTIONS	2
I. 2. CHEMICAL VULCANIZATION OF RUBBER	2
I. 3. 1. RUBBER VULCANIZATION BY RADIATION	4
I. 3. 2. TYPES AND SOURCES OF RADIATION	5
i. 3. 3. MECHANISM OF RADIATION REACTION	6
I. 3. 4. RADIATION EFFECTS ON POLYMERS IN ABSENCE OF ADDITIVES	9
A. CROSSLINKING AND DEGRADATION ASPECTS	9
I. 3. 5. RADIATION EFFECTS ON POLYMERS IN PRESENCE OF ADDITIVES	12
A. RADIATION PROMOTERS	12
B. FILLERS	13
C. ANTIOXIDANTS	14
II. LITERATURE REVIEW	17
II. 1. THE EFFECT OF RADIATION PROMOTERS (COAGENTS)	
ON THE CROSSLINKING OF POLYMERS	17
II. 2. EFFECT OF STYRENE CONTENT ON THE PROPERTIES OF SBR	20
II. 3. CARBON BLACK ROLE IN ELASTOMERS	22
II. 4. SHORT FIBERS REINFORCED ELASTOMERS	27
II. 5. STABILIZATION OF SBR AGAINST DEGRADATION	32
III. MATERIALS AND TECHNIQUES	41
III. 1. MATERIALS	41
A. STYRENE-BUTADIENE RUBBER (SBR)	41
B. FUNCTIONAL MONOMERS	42
C. ANTIOXIDANTS	43
D. CARBON TYPE FILLERS	44
1. CARBON BLACK	44
2. SHORT CARBON FIBERS	44
E. ZINC OXIDE	44
F. STEARIC ACID	44
III. 2. TECHNIQUES	40

II. 2. 1. PREPARATION OF THE SAMPLES AND IRRADIATION PROCESS	45
PART 1	45
PART 2	46
PART 3	46
PART 4 (A) & (B)	46
PART 5	47
III. 2. 2. MECHANICAL PROPERTIES	47
1. TENSILE STRENGTH ANT ULTIMATE ELONGATION	47
2. TEAR STRENGTH	48
3. HARDNESS	48
4. ABRASION	48
5. DYNAMIC MECHANICAL PROPERTIES	49
III. 2. 3. PHYSICO-CHEMICAL PROPERTIES	49
A. GEL FRACTION	49
B. SWELLING	49
C. SWELLING ANISOTROPY	50
D. CROSSLINKING DENSITY	50
E. AGING ACCELERATION	51
, F. DIFFERENTIAL SCANNING CALORIMETER (DSC) MEASUREMENTS	52
G. SCANNING ELECTRON MICROSCOPY (SEM)	52
H. ASPECT RATIO	52
I. ELECTRICAL CONDUCTIVITY	53
IV. RESULTS AND DISCUSSION	54
IV. 1. EFFECT OF FUNCTIONAL MONOMERS ON THE DIFFERENT	
PROPERTIES OF ELECTRON BEAM VULCANIZED STYRENE-BUTADIENE	54
RUBBER	
IV. 1 . 1 . EFFECT OF DIETHYLENE GLYCOL DIMETHACRYLATE	
MONOMER ON RADIATION VULCANIZATION OF SBR	55
IV. 1. 2 . EFFECT OF POLYFUNCTIONAL MONOMERS ON	
RADIATION VULCANIZATION OF SBR	65
IV. 2. MECHANICAL PROPERTIES AND PHYSICO-CHEMICAL PROPERTIES OF	
FLECTRON BEAM VULCANIZED SBR ^{-S}	7:

IV . 2. 1. MECHANICAL PROPERTIES	73
A - TENSILE, ELONGATION AT BREAK AND HARDNESS	73
B - TEAR AND ABRASION RESISTANCE	75
IV. 2. 2. PHYSICO-CHEMICAL PROPERTIES	80
A - SWELLING NUMBER	80
B - EVALUATION OF CROSSLINKING DENSITY	80
IV. 3 .DYNAMIC MECHANICAL PROPERTIES OF ELECTRON BEAM ELECTRON	
BEAM VULCANIZED SBR ^{-S}	85
IV.3. 1. EFFECT OF ADDITIVES ON THE SHEAR MODULUS OF SBR (23.5%)	85
IV. 3. 2. EFFECT OF ADDITIVES ON THE DAMPING OF SBR (23.5%)	88
IV. 3 . 3. EFFECT OF ADDITIVES ON THE SHEAR MODULUS OF SBR (46%)	92
IV. 3. 4. EFFECT OF ADDITIVES ON THE DAMPING OF SBR (46%)	94
IV. 4 . EFFECT OF DIFFERENT CLASSES OF ANTIOXIDANTS ON THE THERMO-	
OXIDATIVE DEGRADATION OF LOADED SBR	97
IV. 4 . 1 . AGING TECHNIQUE	97
A - THE EFFECT OF DIFFERENT CLASSES OF ANTIOXIDANTS	98
B - EFFECT OF COMBINATION OF TWO DIFFERENT CLASSES OF	
ANTIOXIDANTS	107
IV.4.2. DIFFERENTIAL SCANNING CALORIMETER TECHNIQUE (DSC)	112
A. DSC MEASUREMENTS	
IV . 5 . EFFECT OF SHORT CARBON FIBERS ON SBR VULCANIZATE	124
IV.5.1.SWELLING MEASUREMENTS	124
IV . 5 . 2 . MECHANICAL PROPERTIES	129
TV . 5 . 3 . SCANNING ELECTRON MICROSCOPY STUDIES	137
V . 5 . 4 . ELECTRICAL PROPERTIES	142
DEDUCTIONS	145
SUMMARY	153
REFERENCES	159
ARABIC SUMMARY	171

List of figures

Figure 1	Effect of the different concentrations of DEGDM on the tensile strength of SBR.	56
Figure 2	Effect of the different concentrations of DEGDM on the elongation at break of SBR.	58
Figure 3	Relation between the hardness, the different concentrations of DEGDM and irradiation doses.	60
Figure 4	Gel fraction at different concentrations of DEGDM Vs. irradiation doses.	61
Figure 5	Effect of irradiation doses on the crosslinking density of SBR enhanced with DEGDM at different concentrations.	62
Figure 6	Effect of irradiation doses on the tensile strength of SBR enhanced with different acrylate monomers.	66
Figure 7	Effect of irradiation doses on crosslinking density of SBR enhanced with acrylate monomers.	67
Figure 8	Effect of irradiation doses on the tensile strength of SBR enhanced with cyanate and cyanurate monomers.	70
Figure 9	Effect of irradiation doses on crosslinking density of SBR enhanced with cyanate and cyanurate monomers.	71
Figure 10	Effect of irradiation doses on the tensile strength of SBR with different styrene contents and loaded with different additives.	74
Figure 11	Effect of irradiation doses on the elongation at break of SBR with different styrene contents and loaded with different additives.	76
Figure 12	Shore hardness A as a function of irradiation doses for SBR with different styrene contents and loaded with different additives.	78
Figure 13	Effect of irradiation doses on tear strength and abrasion resistant for both types of loaded SBR samples.	79

Figure 14	Effect of irradiation doses on swelling ratio of both types loaded SBR samples in toluene at 30°C.	81
Figure 15	Effect of irradiation doses on the degree of crosslinking in terms of 1/Mc for both types of loaded SBR samples.	83
Figure 16	Effect of temperature on the elastic shear modulus of loaded SBR (23.5%) samples.	86
Figure 17	Effect of temperature on the damping of loaded SBR (23.5%) samples.	89
Figure 18	Effect of temperature on the elastic shear modulus of loaded SBR (46%) samples.	93
Figure 19	Effect of temperature on the damping of loaded SBR (46%) samples	95
Figure 20	Effect of the different types of antioxidants on the retained tensile strength of loaded SBR (23.5%) after thermal aging.	102
Figure 21	Effect of the different types of antioxidants on the $\%$ elongation at break of loaded SBR (23.5%) after thermal aging .	103
Figure 22	Effect of mixed antioxidants (1phr each) on the retained tensile strength of SBR (23.5%) after thermal aging .	108
Figure 23	Effect of mixed antioxidants (1phr each) on the retained elongation at break of SBR (23.5%) after thermal aging .	109
Figure 24	Thermogram of irradiated loaded SBR (23.5%) samples in presence of different concentrations of Nocrac 6C	112
Figure 25	Thermogram of irradiated loaded SBR (23.5%) samples in presence of different concentrations of Nonflex MB	113
Figure 26	Thermogram of irradiated loaded SBR (23.5%) samples in presence of different concentrations of Antigene NBC	114

Figure 27	Thermogram of irradiated loaded SBR (23.5%) samples in presence of different concentrations of Antage crystal	115
Figure 28	Thermogram of irradiated loaded SBR (23.5%) samples in presence of different concentrations of Nonflex TNP	116
Figure 29	Effect of the antioxidants on the first temperature peak of loaded SBR samples.	121
Figure 30	Effect of irradiation doses on the crosslinking density for loaded SBR with carbon fibers (1mm length)	127
Figure 31	Effect of irradiation doses on the crosslinking density for loaded SBR with carbon fibers (6 mm length)	128
Figure 32	Histogram showing the distribution of carbon fibers (1 mm) at different concentration after mixing.	130
Figure 33	Histogram showing the distribution of carbon fibers (6mm) at different concentration after mixing.	131
Figure 34	Effect of irradiation doses on the tensile strength of SBR loaded with carbon fibers (1 mm) at different concentrations.	132
Figure 35	Effect of irradiation doses on the tensile strength of SBR loaded with carbon fibers (6 mm) at different concentrations.	133
Figure 36	Effect of irradiation doses on the elongation at break of SBR loaded with carbon fibers (1 mm) at different concentrations.	135
Figure 37	Effect of irradiation doses on the elongation at break of SBR loaded with carbon fibers (6 mm) at different concentrations.	136