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Ultrasonic Devulcanization of Sulfur Vulcanized Natural Rubber

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by

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This thesis was submitted to the Department of Chemical and Process Engineering of the University of Moratuwa in partial fulfillment of the requirements for the Degree of Master of Philosophy

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Declaration

I hereby declare that this submission is my own work and that, to the best of my knowledge and behalf, it contains no material previously published or written by another person nor material which to substantial extent, has been accepted for the award of any other academic qualification of a university or other institute of higher learning except where an acknowledgment is made in the text.

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December, 2002

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Abstract

The high-energy ultrasound could be used to devulcanize rubber as it can focus energy into localized sites for selective bond rupture. The research work reported to-date suggests that the ultrasonic technology is more suited to convert rubber waste to a usable material efficiently, effectively and environmental friendly.

The ultrasonic devulcanization reactor consisted of three main sections, namely a power source, ultrasonic transducer with sample holding unit, and a monitoring system to measure the amplitude, frequency and power. N-cyclohexyl-2-benzthiazyl sulfenamide (CBS) accelerated unfilled natural rubber vulcanized with conventional sulfur vulcanizing system and with efficient sulfur vulcanizing system were used as the model rubber compounds in these experiments. 2 mm thick vulcanized rubber sheets were directly kept on the vibrating diaphragm of the ultrasonic transducer. The frequency of ultrasonic wave was varied in a range of 20 to 50 kHz and the power level was varied up to 800 watt. The treatment time was limited to 10 minutes when treated at high power levels. The vibrating amplitudes were measured at different power levels with the variation of ultrasonic frequency.

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Curing behaviour, gel content and cross-link density were studied for rubber samples devulcanized at different process conditions. The increase in cross-link density and gel content of the samples treated at lower amplitudes indicated the formation of additional cross-links. However, the higher vibrational energies associated with high amplitudes resulted in lower cross-link densities and gel contents indicating a breakdown of bonds. Cure curves of virgin and devulcanized NR samples suggested that the fast initial curing of devulcanized NR was due to the presence of active sufidized rubber molecules formed due to break down of some cross-links during devulcanization. The lower maximum torque values observed in the devulcanized samples were due to the partial breakdown of C-C bonds in the main chain. The tensile properties of the revulcanized samples gave comparable results with that of virgin rubber.

A theoretical process model was developed to express the extent of devulcanization in terms of cross-link density. It was based on the vibrational energy transfer mechanism. The model treated the vulcanized rubber as a pure elastic solid containing void regions. Experimental and theoretical values lied within ± 10% error limits. The model showed that the media effect on the nature of void excitation was significant and the viscoelasticity was also considerable. However, the effect due to surface tension was negligible.

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Nomenclature

$\overline{\nabla}\bar{r}_0$	A deformation gradient
$\hat{s}$	Deviatoric part of the stress tensor
$\bar{r}_0(\xi)$	Radius vector of a point in the initial configuration
G'	Storage modulus
$\overline{\nabla}_s\bar{r}(t)$	A relative deformation gradient
$\overline{\nabla}_t\bar{r}(s)$	A relative deformation gradient
G''	Loss modulus
$\overline{\nabla}_0\bar{r}$	A deformation gradient
$\hat{\sigma}$	Cauchy stress tensor
$\bar{g}_0^i(\xi)$	Dual vector in the initial configuration
$\hat{E}_{F*}$	Finger strain tensor
$\bar{r}(t,\xi)$	Radius vector of a point in the actual configurations
$\bar{g}^i(t,\xi)$	Dual vector in the actual configuration
$\%E_b$	Percentage elongation at break
χ	Huggins interaction constant
ρ	Density of the material
μ	Poisson's ratio
φ	Void fraction
$\sigma(\tau)$	Stress history
$\sigma(t)$	Longitudinal stress
$\epsilon(t)$	Strain at instant t
ζ_0	Friction coefficient per monomer unit
ΔH	Enthalpy difference
ΔL_a	Active volume thickness
ρ_r	Dry density of rubber
τ_{Rp}	Relaxation time for Rouse model
η_s	Viscosity of solvent
ρ_s	Density of solvent

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$\hat{\epsilon}(t)$	Infinitesimal strain tensor
ΔV_a	Active volume around a single excited region
$\tau_{z,}$	Relaxation time for Zener model
$\Omega(t)$	A domain in the actual configuration at instant t
Ω_0	A domain in the initial configuration
A	Initial cross-section area
	Vibrating amplitude
a	Root-mean-square end-to-end distance
$\hat{F}_*(t,s)$	Finger deformation tensor
A_1S-	A sulfidic group
A_2S-	A sulfidic group
ω	Angular frequency
ASTM	American Society of Testing and Materials
B_1S-	A sulfidic group
B_2S-	A sulfidic group
c	Velocity of sound in rubber
C=C	Carbon-carbon double bond
C_1	A Mooney-Rivlin constant
C_2	A Mooney-Rivlin constant
CBS	N-cyclohexyl-2-benzthiazyl sulfenamide
C-C	Carbon-carbon bond
C-H	Carbon-hydrogen bond
c_M	Velocity defined by Mallock's formula.
c_s	Modified velocity of sound in rubber with voids
C-S	Carbon-sulfur bond
CV	Conventional sulfur vulcanizing system
E	Young's modulus
$E(t)$	Elastic modulus
E_0	Reference bond strength
E_c	Carbon-carbon bond strength
E_i	Bond strength of specific type of the bond
EPDM	Ethylene propylene diene terpolymer
E_s	Bond strength of monosulfidic cross-links

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E_{sx}	Bond strength of polysulfidic cross-links
EV	Efficient sulfur vulcanizing system
EVA	Ethylene vinyl acetate
f	Force at the required elongation
	Ultrasonic frequency
F	Breaking force
$G,G(t)$	Shear modulus
G_r	Relaxed shear modulus
GTR	Ground tyre rubber
G_u	Unrelaxed modulus
	Shear modulus of rubber in glassy state
H	Allylic hydrogen atom
Hz	Herts
i	Specific bond
I_1	First strain invariant
I_2	Second strain invariant
IPPD	N-isopropyl-N'-phenyl-p-phenylene diamine
k	Boltzmann constant
	An integer
K_i	A fitting parameter
k_i	Rate constant of the breakage of specific molecular bonds
K_r	A fitting parameter
k_r	Rate constant of the reaction of destruction of rubber bound intermediates
k_{s1}	Rate constant of reaction of breakage of monosulfidic cross-links
K_{s1}	A fitting parameter
K_{sc}	A fitting parameter
k_{sc}	Rate constant of reaction of conversion of polysulfidic cross-links to monosulfidic cross-links
k_{sx}	Rate constant of reaction of breakage of polysulfidic cross-links
K_{sx}	A fitting parameter
K_{sxf}	A fitting parameter
k_{sxf}	Rate constant of the reaction of formation of additional cross-links by reacting rubber bound intermediates with zinc complexes

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L	Length between gauge marks at break
L	Large rotor
L_0	Initial length between gauge marks
ξ	Lagrangain curvilinear coordinates .
M	Mooney viscosity number
M_0	Molecular weight of initial network chain
	Molecular weight of monomer unit
M_c	Molecular weight between cross-links
MHz	Megahertz
mm	millimeter
MPa	Megapascal
N	Newton
n	Number of moles of the ideal network chains
	Number of molecules per unit volume of solution
N_0	Initial void concentration
N_A	Avogadro's number
NBR	Nitrile rubber
N_c	Number of network chains per unit volume
n_c	Cross-link density
$N_c(t)$	Total concentration of cross-links remain at time t
$N_{cs}(t)$	Concentration of monosulfidic cross-links formed by conversion of polysulfidic cross-links to monosulfidic cross-links at time t
$N_i(t)$, N_i	Number of specific molecular bonds per unit volume at time t
$N_{ia}(t)$	Active molecular bonds per unit volume at time t
$N_{ia.}$	Number of active molecular bonds per unit volume
NMR	Nuclear magnetic resonance
NR	Natural rubber
$N_r(t)$	Concentration of rubber intermediates remaining at time t
$N_s(0)$	Initial concentration of monosulfidic cross-links
$N_s(t)$	Concentration of monosulfidic cross-links remaining at time t
$N_{sx}(0)$	Initial concentration of polysulfidic cross-links
$N_{sx}(t)$	Concentration of polysulfidic cross-links remaining at time t

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$N_{sxf}(t)$	Concentration of polysulfidic cross-links formed due to reaction of rubber bound intermediates with zinc complexes during time t
$N_{sxr}(t)$	Concentration of polysulfidic cross-links remains at time t, after breaking into non cross-links
N_{vk}	Number of k^{th} cross-links per unit volume
ODCB	Dissolution by o-dichlorobenzene
P	Power level
p	Sound pressure
	An integer
P_∞, $P_\infty(t)$	Pressure at infinity in rubber
P, $P(r,t)$	Local pressure in rubber
P_0	Ambient pressure
P_A	Ultrasonic pressure amplitude
P_c	Critical value of the pressure difference
P_g	Gas pressure
phr	Parts per hundreds rubber
P_i, $P_i(t)$	Pressure in rubber at the wall.
P_m	Inflation pressure
$P_m(elastic)$	Critical pressure for elastic model
$P_m(viscoelastic)$	Critical pressure for viscoelastic model
q	Number of monomeric units between cross-links
$Q(t,\tau)$	Relaxation measure
r	Radial distance from center
R	Universal gas constant
$\dot{R}$	Velocity
$\ddot{R}$	Rate of change of velocity
$R(t,\tau)$	Relaxation kernal.
R, $R(t)$	Radius of a void region at time t
R_0	Initial radius of a void region
γ	Ratio of the specific heats of gas
RCOOH	An organic activator
RH	Rubber hydrocarbon
R_{max}	Radius of a void region at peak excitation

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$R\text{-}S_{2z}\text{-}R$	Initial polysulfide cross-links
RSR	Monosulfidic cross-link
RSS	Ribbed smoke sheet
RS_xR	Polysulfidic cross-link
s	Actual configuration
S_8	Elementary sulfur
SBR	Styrene butadiene rubber
β	Sensitivity of void region formation
Si-C	Silicon-carbon bond
Si-O	Silicon oxygen bond
S-S	Sulfur-sulfur bond
STP	Standard test procedure
σ	Surface tension
S_x	Polysulfides
t	Treatment time
T	Temperature.
T/S	Tensile strength at break
T_g	Glass transition temperature
$T_{r,i}$	Radial stress on the wall due to motion
U	Velocity of the wall
u	Radial velocity in rubber relative to center
v	Total number of moles of various cross-links per unit volume
V_l	Molecular volume of the solvent
η	Viscosity of the dash pot
v_k	k^{th} type sulfur cross-link
	Number of moles of k^{th} cross-link per unit volume
V_r	Volume fraction of rubber in the swollen vulcanizate
W	Stored-energy function
W	Watt
λ	Wave length
W_r	Weight of dry rubber
W_s	Weight of solvent
x	An integer

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X	Accelerator residue
$x(t)$	Relative radius of a void region
	Extension ratio
$x_3(t)$	An auxiliary function
$x_4(t)$	An auxiliary function
X_{max}	Relative void radius at peak excitation
XSS_xZnS_xSX	Zinc per-thio-salt
	Active sulfurating agent
XS_xSR	Rubber bound intermediate
	Accelerator-terminated polysulfidic groups
	Initial cross-link precursors
XSZnSX	Zinc accelerator complexes (zinc complexes)
y	An integer
z	An integer
ZnO	Zinc oxide
ZnS	Zinc sulfide
δp	Pressure difference
ϕ	Velocity potential
μm	microns

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