Novel Approach for the Synthesis of Natural Rubber-Montmorillonite Clay Nanocomposites

by

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DECLARATION

The work described in this thesis was carried out by me, under the supervision of Dr. Upul N Ratnayake, General Manager Technical of Dipped Products Lanka PLC and Prof. Nilwala Kottegoda, Senior Lecturer, Department of Chemistry, University of Sri Jayewardenepura, Sri Lanka. I also certify that, this thesis has not been submitted in whole or in part to any university or any other institute for another Degree/Diploma.

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbols

d	Interlayer spacing for XRD
dNm	Deci-Newton meters
MH	Highest measured torque during rheometry
MH-ML	Torque rise upon vulcanization
ML	Lowest measured torque during rheometry
n	Integer representing the order of the diffraction peak for XRD
T_{90}	Time taken to reach 90% curing during rheometry
Tan δ	Loss tangent
T_g	Glass transition temperature
TS_2	Time taken for torque to reach ML + 2dNm during rheometry
Wt %	Quantity of ingredient as a percentage of the total weight of a second ingredient
γ_0	Maximum shear strain during dynamic testing
δ	Loss angle
θ	Scattering angle for XRD
λ	X-ray wavelength for XRD
τ_0	Maximum shear stress during dynamic testing

G^*	Dynamic shear modulus
$G^{/}$	Shear storage modulus
$G^{//}$	Shear loss modulus
$\tau^{/}_{0}$	In-phase components of the shear stress
$\tau^{//}_{0}$	Out of phase components of the shear stress

Abbreviations

CEC	Cation exchange capacity
CIM	Charge inversion method
CRI	Cure rate index
CTAB	n-hexadecyl trimethyl ammonium bromide
CV	Conventional vulcanization
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
EB	Elongation at break
EV	Efficient vulcanization
IPPD	N-isopropyl-N'-phenyl-P-phenylenediamine
IRHD	International rubber hardness degrees
ISO	International Organization for Standardization
LCM	Latex compounding method
M300	300 % modulus
MCM	Melt compounding method
MMT	Montmorillonite
NR	Natural rubber (cis-1,4-polyisoprene)

NRCNC	Natural rubber clay nanocomposites
OMMT	Organo modified montmorillonite
PCN	Polymer/clay nanocomposite
phr	parts per hundred parts of rubber
RCN	Rubber clay nanocomposites
SEM	Scanning electron microscopy
SEV	Semi efficient vulcanization
TBBS	Nt-butylbenzothiozole-2-sulphanamide
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TS	Tensile strength
XRD	X-ray diffraction

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Novel Approach for the Synthesis of Natural rubber-Montmorillonite Clay Nanocomposites

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ABSTRACT

A new preparation technique has been studied based on charge inversion approach for developing natural rubber (NR)-clay nanocomposites using nano scale montmorillonite (MMT) clay platelets in order to improve the reinforcement properties of the NR compounds. Anionic NR latex particles are converted into positively charged particles (cationic latex) by treating with a quaternary ammonium surface active substance (n-hexadecyltrimethylammonium bromide) to achieve a better compatibility with MMT layers and subsequent coagulation of the positively charged NR latex is carried out using the negatively charged aqueous MMT clay dispersion where clay platelets are fully exfoliated with in the medium. This method allows the MMT clay platelets to be remained exfoliated within the NR latex leading to favorable electro static interactions between the NR latex particles and MMT clay platelets. As a result, NR-MMT clay nanocomposite is formed with improved interfacial interactions between the two phases resulting in higher physico-mechanical performances.

Powder X-ray Diffraction (PXRD) and Transmission Electron Microscopic (TEM) imaging suggest that the clay platelets are exfoliated within the rubber matrix offering a higher surface area for interactions between the NR latex particles and inorganic matrixes in rubber clay nanocomposite. Low shear strain rate flow property characterization, with Mooney Viscometer, of un-vulcanized Natural Rubber Clay Nanocomposites (NRCNC) prepared via Charged Inversion Method (CIM) shows a

significant enhancement in interfacial strength between NR and MMT clay platelets whilst tensile green strength and tensile modulus results of the un-vulcanized nanocomposite further proved the enhanced interfacial interactions, enhanced thermal stability and improved thermo-oxidative stability of the NRCNC in comparison to conventional NRCNC prepared by Latex Compounding Method (LCM) further demonstrate the higher interfacial strength.

Dynamic Mechanical Thermal Analysis (DMTA) results of the vulcanized NRCNC containing 10 phr of MMT clay showed higher dynamic mechanical properties, indicating the presence of higher percentage of interface and a higher interfacial strength of the nanocomposite prepared by the new methodology. Therefore, interfacial interactions in the novel nanocomposite are very strong thus eliminating the challenges faced due to re-aggregation of the clay platelets in the conventional NRCN composites prepared by latex compounding technique.

Based on the new preparation technique developed, NRCN vulcanisates with different MMT clay loadings were evaluated for the reinforcement. Significant enhancement in strength characteristics and stiffness is achieved while maintaining a good elasticity of the vuclanisates. Therefore, this preparation technique opens up new opportunities in developing rubber nanocomposites based on clays.