PREPARATION AND CHARACTERIZATION OF NATURAL RUBBER-MONTMORILLONITE CLAY NANOCOMPOSITES AND THEIR VULCANIZATES

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DECLARATION

I declare that this is my own work and this dissertation does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any other university or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

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Signature of the Supervisor Date

Signature of the Supervisor Date

DEDICATION

To,

My ever loving...

Parents,

Wife

&

Son

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ABSTRACT

Preparation and characterization of Natural rubber-montmorillonite clay nanocomposites and their vulcanizates

Rubber-clay nanocomposites at low nanoclay loadings are generally prepared using mechanical mixing method as similar to mixing of conventional fillers with rubber. However, the resultant properties prepared with mixing method were reported as not high as expected and the main challenge was the retaining of exfoliated clay structures in the final product after vulcanization. This study focuses on the development of nanocomposites with superior properties from Natural rubber (NR) and Montmorillonite clay (MMT), through development of suitable clay structures, by incorporating of nanoclay into rubber at the latex stage. Twelve series of nanocomposites were prepared to study the effect of processing method (acid co-coagulation named ACC method and acid free co-coagulation named AFCC method using latex, and mechanical mixing method with pale crepe); gelling agents (sodium silicofluoride-G1, cetyl trimethyl ammonium bromide (CTAB)-G2 and combination of CTAB and sodium dodycyl sulphate (SDS)-G3); type of natural rubber latex (field NRL and centrifuged NRL); modifications of MMT and NRL. MMT was organically modified with a cationic surfactant of CTAB to enhance interactions with NR. The modified MMT (OMMT) was further treated with bis(triethoxysilylpropyl) tetrasulfide to facilitate separation of clay layers in the clay stacks, and the treated clay was designated as OMMT-S. The NRL was grafted with succinimide to enhance the compatibility with OMMT-S. The incorporation of OMMT-S into Succinimide grafted NRL was the novelty of the study. These nanocomposites prepared were compounded with the curing and other compounding ingredients to prepare nanocomposite vulcanizates. The clay dispersions, nanocomposites, nanocomposite compounds were characterized by XRD, SEM, FTIR, TGA and the mechanical and thermal properties of the nanocomposite vulcanizates were determined as per the international standards.

Tensile strength, elongation at break, mod 300% and hardness of the nanocomposite vulcanizates prepared using AFCC and ACC methods initially increased and then decreased with the increase of MMT loading while tear strength remained unchanged. The nanocomposite vulcanizates prepared using AFCC method showed higher mechanical properties compared to the nanocomposite vulcanizates prepared using ACC method. However, AFCC method exhibited slow drying characteristics. The optimum MMT loadings for nanocomposites prepared using AFCC method and ACC method were recorded at 8 phr and 12 phr, respectively, due to formation of aggregated clay structures at higher loadings, as evident by SEM images. Addition of a gelling agent successfully solved the slow drying problem associated with the AFCC method, however, G1 and G2 gelling agents exhibited significant changes to the properties of the vulcanizates. G3 gelling agent functioned effectively by facilitating quick gel formation, and by exhibiting better mechanical properties of the nanocomposite vulcanizates.

Replacement of MMT by OMMT in nanocomposite vulcanizates prepared using AFCC method without a gelling agent showed enhanced mechanical properties at a lower loading of 2 phr. The mechanical properties were further enhanced with the addition of the G3 gelling agent to the nanocomposites with OMMT and is associated with greater interactions between OMMT and NR. The optimum loading was recorded at 5 phr. Replacement of OMMT by OMMT-S in nanocomposite vulcanizate prepared with G3 gelling agent exhibited greater tensile strength and elongation at break at 2 phr loading, and greater mod 300%, tear strength and hardness at 5 phr. XRD analysis and SEM images of nanocomposite vulcanizates revealed that the addition of OMMT-S promotes existences of separated clay layers and fine morphology in the vulcanizates. The nanocomposite vulcanizates prepared using mechanical mixing method incorporating OMMT and OMMT-S into pale crepe gave comparatively lower mechanical properties due to presence of clay aggregates.

The novel nanocomposite vulcanizates prepared with grafted NRL and OMMT-S with the G3 gelling agent showed overall remarkable mechanical properties at 5 phr. The X-ray diffractograms of the nanocomposite vulcanizates showed exfoliated clay structures and fine morphology. The remarkable properties obtained due to fine morphology developed through exfoliated clay structures as a result of rubber filler interactions are tensile strength of 41 MPa, mod 300% of 6 MPa, elongation at break of 620%, tear strength of 49 N/mm, hardness of 55 IRHD, and abrasion loss of 190 mm^3.

Keywords

Nanocomposite, Organoclay, Acid-free Co-coagulation, Modified natural rubber, Exfoliated clay

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

ACC	-	Acid Co-Coagulation
AFCC	-	Acid Free Co-Coagulation
AFCC-G1	-	AFCC used with gelling agent SSF
AFCC-G2	-	AFCC used with gelling agent CTAB
AFCC-G3	-	AFCC used with gelling agent CTAB and SDS
CEC	-	Cation Exchange Capasity
CRI	-	Cure Rate Index
CTAB	-	Cetyl Trimethyl Ammonium bromide
DMTA	-	Dynamic Mechanical Thermal Analysis
DRC	-	Dry Rubber Content
DSC	-	Differential Scanning Calorimetry
FTIR	-	Fourier Transform Infrared
HCl	-	Hydrochloric Acid
IRHD	-	International Rubber Hardness Degrees
KOH	-	Potassium Hydroxide
NR	-	Natural Rubber
NRL	-	Natural Rubber Latex
MA	-	Maleamic Acid
MAH	-	Maleic Anhydride
MBTS	-	Mercaptobenzothiazole Sulphanamide
M_H	-	Maximum Torque
M_L	-	Minimum Torque
MMT	-	Montmorillonite
mod 300%	-	Modulus at 300% elongation
OMMT	-	MMT Clay modified by CTAB
OMMT-S	-	OMMT clay modified by TESPT
PRV	-	Property retention value

RSS	-	Ribbed Smoke Sheet
SA	-	Succinamic acid
SBR	-	Styrene Buitadiene Rubber
SDS	-	Sodium Dodecyl Sulfate
SEM	-	Scanning Electron Microscopy
SI	-	Succinimide
SSF	-	Sodium Silicofluoride
TEPA	-	Tetraethylenepentamine
TESPT	-	Bis(Triethoxysilylpropyl) Tetrasulfide
T_g	-	Glass Transition Temperature
TMTD	-	Tetramethyl Thiurium Disulfide
XRD	-	X-ray Diffraction
ZnO	-	Zinc Oxide

LIST OF APPENDICES