

**EVALUATION OF THE APPLICABILITY OF
NATURAL POLYMERS AS COUPLING AGENTS IN
IMPARTING REINFORCEMENT ACTION OF SILICA
FILLERS IN NR LATEX FILMS**

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DECLARATION

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Signature of the supervisor:

Date:

Name of the supervisor: Dr. (Mrs). N.M.V.K. Liyanage

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Gnanaratna W.D.S.N

ABSTRACT

The results of an evaluation of the applicability of natural polymers (NPs) as coupling agents in imparting reinforcement action of silica fillers in natural rubber (NR) latex films are described in this research investigation.

Three types of NPs namely; chitin, chitosan and cellulose were used for this investigation. Standard extraction processes were used for the extraction of chitin and chitosan. A commercially available grade of cellulose was used for this investigation without purification. Modification of surface of silica particles with NPs was affected by two techniques; in-situ surface modification, and surface modification through a sol-gel process. Coupling action of these NPs was compared with that of the most widely used commercially available coupling agent silane, Si₆₉.

A range of stable aqueous colloidal dispersions of precipitated silica were prepared with the use of NPs and Si₆₉. In-situ surface modification performed with NPs and Si₆₉. With NPs, the surface modification was done at four different proportions as 2.5%, 5%, 7.5% and 10% by weight of silica. With Si₆₉, the modification was done at two different proportions as 5% and 10% by weight of silica.

Sol-gel surface modification performed with chitosan was done at two different proportions as 5% and 10% by weight of silica.

Interactions between polar groups of silica and functional groups of the NP which hinder aggregation of silica particles were confirmed by FTIR spectroscopy. The dispersion stability of the unmodified/modified filler (UMF/MF) dispersions was assessed by observing the phase separation upon standing. Dispersion stability of MF dispersions prepared using both surface modification method is much better than that of UMF dispersions. The particle size distribution of unmodified/ modified filler dispersions was measured by using "Fritsch" particle size analyzer. The particle size of the modified filler with cellulose was found to be lower than that of UMF dispersion.

Effectiveness of NPs in enhancing reinforcing action of silica in NR latex was evaluated through investigation of mechanical properties of vulcanized films cast from NR latex compounds containing modified/unmodified fillers in different proportions. Distribution of unmodified/modified fillers within the rubber matrix was investigated through metallurgical microscope and scanning electron microscope by examining micrographs of surfaces of dipped NR latex films and micrographs of cross sections of cast NR latex films containing modified/unmodified fillers respectively.

High colloidal stability of modified fillers with NPs indicates that are capable of acting as colloidal stabilizers for silica dispersions.

Some of the NPs tested were found to be capable of conferring an appreciable enhancement in reinforcing action of silica in NR latex films. Micrographs of the filled NR latex films revealed that same NPs have conferred uniform distribution of filler particles within the rubber matrix.

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LIST OF ABBREVIATIONS

APS	Amino propyltriethoxysilane
BR	Butadiene rubber
CTAB	Cetyltrimethylammonium Bromide
d	Particle diameter
DD	Degree of deacetylation
DMAc	Dimethylacetamide
DOTG	Diorthotolylguanidine
DPG	Diphenylguanidine
DRC	Dry rubber content
EB	Elongation at break
EPDM	Ethylene propylene diene monomer
FTIR	Fourier transforms infrared
GCC	Ground natural calcium carbonate
HA	High ammonia
HCl	Hydrochloric acid
IGC	Inverse gas chromatography
IIR	Isobutylene Isoprene Rubber
KN	Kilo Newton
KOH No.	Potassium hydroxide number
KOH	Potassium hydroxide
LA	Low ammonia
LiCl	Lithium chloride
LLDPE	Linear low density polyethylene
LS	Layered silica

M400	Modulus at 400% elongation
MF	Modified filler through in – situ surface modification
MF _{10Ce}	Modified filler with 10% cellulose by weight of silica
MF _{10Ch}	Modified filler with 10% chitin by weight of silica
MF _{10Cs}	Modified filler with 10% chitosan by weight of silica
MF _{10Sil}	Modified filler with 10% silane69 by weight of silica
MF _{2.5Ce}	Modified filler with 2.5% cellulose by weight of silica
MF _{2.5Ch}	Modified filler with 2.5% chitin by weight of silica
MF _{2.5Cs}	Modified filler with 2.5% chitosan by weight of silica
MF _{5Ce}	Modified filler with 5% cellulose by weight of silica
MF _{5Ch}	Modified filler with 5% chitin by weight of silica
MF _{5Cs}	Modified filler with 5% chitosan by weight of silica
MF _{5Sil}	Modified filler with 5% silane69 by weight of silica
MF _{7.5Ce}	Modified filler with 7.5% cellulose by weight of silica
MF _{7.5Ch}	Modified filler with 7.5% chitin by weight of silica
MF _{7.5Cs}	Modified filler with 7.5% chitosan by weight of silica
MFH	Modified filler through sol – gel reaction
MFH _{10Cs7}	Modified filler with 10% chitosan/silica hybrid at pH7
MFH _{10Cs9}	Modified filler with 10% chitosan/silica hybrid at pH9
MFH _{5Cs7}	Modified filler with 5% chitosan/silica hybrid at pH7
MFH _{5Cs9}	Modified filler with 5% chitosan/silica hybrid at pH9
MST	Mechanical stability time
NaOH	Sodium hydroxide
NBR	Acrylo Nitrile butadiene rubber
NMR	Nuclear magnetic resonance



NPs	Natural polymers
NR	Natural rubber
PCC	precipitated calcium carbonate
phr	Parts per hundred parts of rubber
PU	Polyurethane
RI400	Reinforcing index at 400% elongation
rpm	revolutions per minute
RSS	Ribbed smoked sheets
SBR	Styrene butadiene rubber
SEM	Scanning Electron Microscopy
SP	Styrenated phenol
TCPTS	3 – Thiocyanatopropyltriethoxy silane
TESPT	Bis(Triethoxysilylpropyl)tertrasulphide
TR	Tear strength
TS	Tensile strength
TSC	Total solid content
UMF	Unmodified filler
VFA No.	Volatile fatty acid number
w/v	weight/volume
w/w	weight/weight
ZDBC	Zinc dibutyldithiocarbamate
ZDEC	Zinc diethyldithiocarbamate
ZMBT	Zinc mercaptobenzothiazole
ZnO	Zinc oxide
ρ	Specific gravity

