Emulsion Prepared Vinyl Acetate Based Ter Polymer/Kaolin Clay Composites And Their Characterizations

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By

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Under the supervision of

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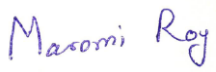
Dedicated to my parents

and teachers

Declaration

I, Maromi Roy, hereby declare that the thesis entitled "*Emulsion Prepared Vinyl Acetate Based Ter Polymer/Kaolin Clay Composites And Their Characterizations*" submitted in the fulfilment of the requirements for the degree of Doctor of Philosophy (PhD) at Bodoland University is my original work. I confirm that the thesis is based on my own research and it hasn't been submitted for consideration for any other degree before. This work includes precise citations and acknowledgments for all sources and references used. Additionally, I affirm that I have not participated in any type of academic dishonesty, such as plagiarism. In the relevant area, any support obtained during the production of this thesis has been acknowledged. I am concerned that making any false claims in this declaration or disobeying the rules of academic integrity could have severe consequences.



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CERTIFICATE

This is to certify that the thesis entitled "***Emulsion Prepared Vinyl Acetate Based Ter Polymer/Kaolin Clay Composites And Their Characterizations***" submitted by ***Miss. Maromi Roy*** to Bodoland University was carried out under my supervision and is worthy of consideration for the award of the degree of Doctor of Philosophy of the University.

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Maromi Roy

Miss Maromi Roy

List of Abbreviations

AA	Acrylic acid
ATESPC	Allyl 3-(triethoxysilyl) propyl carbamate
AMPS	2-Acrylamido-2-methylpropane sulfonic acid
AM	Acrylamide
APS	Ammonium persulfate
ATRP	Atom transfer radical polymerization
BA	Butyl acrylate
RB	Bottom flask
CTA	Chain transfer agent
CRP	Controlled radical polymerization
CTAB	Cetyltrimethylammonium bromide
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetry
2EHA	2-Ethylhexyl acrylate
EI	Electronic india
EVA	Polyethylene-*co*-vinyl acetate
FTIR	Fourier transform infrared spectroscopy
FESEM	Field emission scanning electron microscopy
FRP	Free radical polymerization
GPC	Gel permeation chromatography
HEA	2-Hydroxyethyl acrylate
KPS	Potassium persulfate
MA	Methyl acrylate
MMA	Methyl methacrylate
NMP	Nitroxide-mediated polymerization
NMR	Nuclear magnetic resonance
PDI	Polydispersity index
PVAc	Polyvinyl acetate
PU	Polyurethane
PLA	Poly-lactic acid
PXRD	Powder X-ray diffraction
RAFT	Reversible addition fragmentation transfer polymerization

RB	Round bottom flask
RI	Refractive index
RDRP	Reversible-deactivation radical polymerization
RPA	Rubber process analyzer
rpm	Revolutions per minute
SDS	Sodium dodecyl sulfate
SEC	Size exclusion chromatography
Sty	Styrene
SVS	Slovasol 2510
TBA	Tributyl amine
TEM	Transmission electron microscopy
THF	Tetrahydrofuran
TGA	Thermogravimetric analysis
UTM	Universal testing machine
UV-visible	Ultraviolet-visible spectroscopy
VAc	Vinyl acetate
VAcM	Vinyl acetate monomer
VeoVa10	Vinyl ester of neodecanoic acid
VEVA	Vinyl ester of versatic acid
VDF	Vinylidene fluoride
VOH	Vinyl alcohol
VOC	Volatile organic content
VV	Vinyl versatate
XRD	X-ray diffraction

List of symbols

°C	Degree Celsius
g	Gram
G*	Complex modulus
G″	Loss modulus
η*	Complex viscosity
Hz	Hertz
kPa	Kilo pascal
kV	Kilo volt

mol	Mole
mm	Milli meter
mL	Milli litre
mmol	Milli mole
Mn	Number average molecular weight
MHz	Megahertz
mg	Milli gram
MPa	Mega Pascal
µL	Micro liter
N	Newton
nm	Nanometer
ppm	Parts per million
η'	Storage viscosity
T_g	Glass transition temperature
tan δ	loss factor
%wt	Weight percentage
λ_{max}	Wavelength of maximum absorption.
δ	Chemical shift value

ABSTRACT

Vinyl acetate (VAc) is an important monomer used in paint, coating and adhesive industries. VAc based polymers have good film-formation property and for which they have wide range of applications. This thesis reports the synthesis and characterization of VAc-based copolymer, terpolymers, and their composites with Kaolin clay. The copolymer of VAc with butyl acrylate (BA) was synthesized via emulsion polymerization at 70°C using two different thermal initiators, ammonium persulfate (APS) and potassium persulfate (KPS). Sodium dodecyl sulfate (SDS) was used as an emulsifier, The terpolymer of VAc, poly(VAc-*t*-BA-*t*-AA), and poly(VAc-*t*- BA-*t*-Sty) with butyl acrylate (BA) and acrylic acid (AA) / Styrene (Sty) were also prepared using all the optimized polymerization parameters of the copolymerization. The latexes obtained from these polymerizations were coagulated to obtain the pure co- and terpolymers. The prepared co- and terpolymers were characterized by GPC, FT-IR, and NMR analyses. Transparent characteristics of the latexes were evaluated by UV-Vis analyses. GPC analysis of the co- and terpolymers showed unimodal GPC traces indicating successful preparation of the co- and terpolymers that were free from homopolymers of individual monomers. Furthermore, the incorporation of monomers in the co- and terpolymers was confirmed by FT-IR and ^{1}H NMR analyses. The molar compositions in the prepared copolymers were determined by ^{1}H NMR analysis. Morphological analysis of the prepared latexes was carried out via TEM analysis. The prepared terpolymer latexes were used for the preparation of composites with kaolin clay at different clay loadings. The prepared poly(VAc-*t*-BA-*t*-AA)/kaolin clay and poly(VAc-*t*- BA-*t*-Sty)/kaolin clay composites were characterized by FT-IR, TGA, DSC, SEM, PXRD, and RPA analyses. The effect of the amount of kaolin on the properties of the terpolymer/clay composites were studied. FT-IR studies revealed the distinct interaction between the >Al=O groups of the clay with that of the carbonyl group in the terpolymer. The bonding of clay to the terpolymer chain was confirmed by DSC analysis by noting the increase in T_g of the composites with the clay loading. TGA analysis showed that the thermal stability of the composites was improved with clay loadings.

Keywords: Vinyl acetate, styrene, butyl acrylate, acrylic acid, emulsion, kaolin clay, terpolymer, composite.