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List of Abbreviations

AA	Acrylic Acid
Al-alloy	Aluminum alloy
AC-AMC	Acrylic acid-CTAB Adduct Modified Clay
AC-AMC0.5x	Acrylic acid-CTAB Adduct Modified Clay at 0.5 meq
AC-AMC1x	Acrylic acid-CTAB Adduct Modified Clay at 1 meq
AC-AMC1.5x	Acrylic acid-CTAB Adduct Modified Clay at 1.5 meq
AC-AMC2x	Acrylic acid-CTAB Adduct Modified Clay at 2 meq
AMC	Adduct Modified Clay
ANS	8-Anilinonaphthalene-1-Sulfonic acid
BPO	Benzoyl Peroxide
CC-AMC	Cinammic acid-CTAB Adduct Modified Clay
CEC	Cation Exchange Capacity
CRS	Cold Rolled Steel
CTAB	Cetyl Trimethyl Ammonium Bromide
CTAB-MC	CTAB Modified Clay
DSC	Differential scanning calorimetry
E_{corr}	Corrosion Potential
FRS	Frequency response analyser software

FT-IR	Fourier Transform Infrared
GPC	Gel permeation chromatography.
I_{corr}	Corrosion Current
meq	Milliequivalent
MMT	Montmorillonite
Na^+ -MMt	Sodium Montmorillonite
NMP	N-Methyl pyrrolidone
OC-AMC	Oleic acid-CTAB Adduct Modified Clay
OCP	Open Circuit Potential
OM	Optical Microscopy
PANI	Polyaniline
PCN	Polymer Clay Nanocomposite
PMMA	Polymethymethacrylate
PS	Polystyrene
PSC	Polystyrene Clay Nanocomposite
PSC-AC	Polystyrene Clay Nanocomposite using Acrylic acid-CTAB Adduct Modified Clay
PSC-AC20	Polystyrene Clay Nanocomposite using Acrylic acid-CTAB Adduct Modified Clay at 20 wt.% clay loading
PSC-AC10	Polystyrene Clay Nanocomposite using Acrylic acid-CTAB Adduct Modified Clay at 10 wt.% clay loading

PSC-AC5	Polystyrene Clay Nanocomposite using Acrylic acid-CTAB Adduct Modified Clay at 5 wt.% clay loading
PSC-AC3	Polystyrene Clay Nanocomposite using Acrylic acid-CTAB Adduct Modified Clay at 3wt.% clay loading
PSC-AC1	Polystyrene Clay Nanocomposite using Acrylic acid-CTAB Adduct Modified Clay at 1wt.% clay loading
PSC-AC0.5x	Polystyrene Clay Nanocomposite using Acrylic acid-CTAB Adduct Modified Clay at 0.5 meq concentration
PSC-AC1x	Polystyrene Clay Nanocomposite using Acrylic acid-CTAB Adduct Modified Clay at 0.5 meq concentration
PSC-AC1.5x	Polystyrene Clay Nanocomposite using Acrylic acid-CTAB Adduct Modified Clay at 0.5 meq concentration
PSC-AC2x	Polystyrene Clay Nanocomposite using Acrylic acid-CTAB Adduct Modified Clay at 0.5 meq concentration
PSC-AC	Polystyrene Clay Nanocomposite using Acrylic acid-CTAB Adduct Modified Clay at 10 wt.% clay loading
PSC-CC	Polystyrene Clay Nanocomposite using Cinnamic acid-CTAB Adduct Modified Clay at 10 wt.% clay loading
PSC-OC	Polystyrene Clay Nanocomposite using Oleic acid-CTAB Adduct Modified Clay at 10 wt.% clay loading
R_{ct}	Charge Transfer Resistance
R-6G	Rhodamine-6G
SAXS	Small-angle powder X-ray diffraction

SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscope
T _d	Degradation Temperature
T _g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
WAXS	Wide-angle powder X-ray diffraction
XRD	X-Ray Diffraction

PREFACE

Polymer-clay nanocomposites are a new class of materials which have attracted much attention from both scientists and engineers in recent years due to their excellent properties such as high dimensional stability, heat deflection temperature, gas barrier performance, reduced gas permeability, optical clarity, flame retardancy, and enhanced mechanical properties when compared with the pure polymer or conventional composites (micro- and macrocomposites). These unique properties resulted from the combining characteristics of components at nanoscale level and make them competitive with other materials for a wide range of applications. Recently, polymer clay nanocomposites became commercially available, and were applied to the automotive and food packaging industries. Biodegradable polymer based nanocomposites appear to have a very bright future for a wide range of applications as high performance biodegradable materials. Although significant amount of work has already been done on various aspects of polymer clay nanocomposites, much research still remains in order to understand the complex structure–property relationships in various nanocomposites. Organomodification of clay and its dispersion in polymers is one of the potential areas for research. Hence the thesis aims in synthesis of polymer clay nanocomposite using adduct modified clays and evaluation of its self-assembling and anticorrosive characteristics.

The thesis is divided into six chapters, of which the first chapter gives an overview on polymer clay nanocomposites including structure and characteristics of clays, organic modification of clays, structural characterization of

nanocomposite, preparative methods and morphological study, nanocomposite properties, advantages and applications like self assembly and corrosion resistant coatings and finally the scope and objectives of the present research work.

The second chapter deals with the synthesis of adduct modified clay (AMC) having different reactive acid group like acrylic acid, cinammic acid and oleic acid. A facile method is adopted for the modification of Na^+ -MMT using Cetyl Trimethyl Ammonium Bromide (CTAB)- Acid adducts. The successful clay modification via cation exchange was confirmed by FT-IR spectroscopy and X-ray diffraction (XRD). In the second part, these AMC with reactive functionality was used for the preparation of polystyrene clay nanocomposite (PSC). A series of exfoliated PSC using 10 wt.% AMC were prepared by effectively dispersing the inorganic MMT clay platelets in organic polystyrene (PS) matrix via in situ intercalative polymerisation. The as-synthesized neat PSC materials were characterized by FT-IR spectroscopy, XRD, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). FT-IR spectrum supports the successful intercalation of adducts into the interlayer space of MMT. This was further confirmed by XRD analysis, in which the (001) reflection of all the AMC appeared at smaller angles (2θ) as compared to the pristine clay- indicating the successful ion exchange. Further the PSC-AC prepared using AC-AMC showed a higher thermal stability and higher glass transition temperature (T_g) compared to other Adduct modified PSC. The molecular weight distribution studies were carried out using Gel permeation chromatography.

The third chapter deals with the morphology and self-assembling properties of a series of Polystyrene (PS)-clay nanocomposites are investigated via in-situ free radical polymerization using adduct modified montmorillonite (MMT) clay. Adducts are synthesised by reacting quaternary ammonium salt with unsaturated organic acid like Acrylic acid, Cinnamic acid and Oleic acid. The resulting reactive cation is used to organo-modify the Na⁺-MMT clay. Polystyrene clay nanocomposites (PSC) prepared by effectively dispersing styrene monomers into the interlayer regions of organophilic clay hosts are used for studying solvent assisted Self-assembling property in THF. Among the three polystyrene clay nanocomposites, PSC-AC was found to exhibit better self-assembling properties than PSC-CC and PSC-OC. Microvesicles of uniform size were produced from solution concentration of 2.5 mg/mL. Micropatterned PSC film with concavity size of 1 to 1.5 μm was obtained by drop-casting PSC solution (20 mg/mL) under relative humidity of 70-80% and a uniform film of PSC was obtained at a solution concentration of 50 mg/mL and above. Solvent-assisted self-assembling studies are characterized using Optical microscope (OM), and Scanning electron microscope (SEM). The Guest-encapsulation of PSC vesicles are gained by encapsulating with fluorescent dyes and oil by Fluorescent microscope.

The fourth chapter, deals with the investigation on processing of a series of clay polystyrene nanocomposite (PSC) coatings containing different adduct modified montmorillonite (AMC) for corrosion resistance coating applications and also by varying the clay loading from 1- 20 wt.%.. The corrosion properties were studied using potentiodynamic and electrochemical impedance spectroscopy measurements in 3.5 wt.%

aqueous NaCl electrolyte. The PSC coatings offered enhanced corrosion protection for Aluminum 6061 alloy even at high clay loading (20 wt.%). The order of their protection efficiency was PSC-AMC > Pristine PS > Pristine Na⁺-MMT. Dispersion of clay in the polystyrene matrix resulted in significant improvement of properties such as corrosion protection and thermal stability.

Chapter five describes the synthesis of a series of polystyrene clay nanocomposite (PSC) coatings containing different concentration of adduct modified clay (AMC). These AMCs were designed to investigate the impact of their chemical structure on the corrosion protection efficiency. PSC coatings with high modifier concentration on cold rolled steel were found to exhibit much better in corrosion protection over those of pristine PS based on a series of electrochemical measurements including corrosion potential, polarization resistance, and corrosion current in 3.5 wt % aqueous NaCl electrolyte. Also the PSC with high clay loading (10 wt.%) showed higher protection efficiency than one with low clay loading. Finally, chapter six summarises the major conclusions of the thesis.