Synthesis of New Polymeric Nanolattices Via Emulsion Polymerization And Their Applications In Petroleum Industries

AThesis

Submitted for the requirement of
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Approval Sheet

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بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

﴿ أَمَّنْ هُوَ قَانِتٌ آنَاءَ اللَّيْلِ سَاجِدًا وَقَائِمًا يَحْذَرُ الْآخِرَةَ وَيَرْجُو رَحْمَةَ رَبِّهِ ۗ قُلْ هَلْ يَسْتَوِي الَّذِينَ يَعْلَمُونَ وَالَّذِينَ لَا يَعْلَمُونَ ۗ إِنَّمَا يَتَذَكَّرُ أُولُو الْأَلْبَابِ ﴾

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ABSTRACT

Abstract

Corrosion is first and foremost a safety risk which has to be understood and managed.

In this study, copolymers based on styrene / vinyl acetate at different proportions were synthesized. The copolymers were utilized with SiO_2 nanoparticles for the preparation of superhydrophobic nanocomposites coating films.

The effect of the modified SiO_2-NPs concentration, the efficiency of the prepared material on the hydrophobicity of the coating films were studied as corrosion resistant materials. Different factors affecting the efficiency of prepared materials in corrosion inhibition e.g. i) concentration of the coating solution, ii) temperature, iii) activation energy and iv) contact angle; were studied.

Keywords: superhydrophobic, copolymer, nanocomposite, corrosion, inhibitor.

SUMMARY

Summary

Corrosion management is a key concern in all oil and gas assets due to the nature of fluids produced and injected throughout their life cycle. This is applicable for all asset types, regardless of their age and the level of corrosive agents' present in the flow stream, such as CO_2, H_2S, water or chlorides. Accordingly, application of effective corrosion management concerning different types of mitigations like application of coating, chemical treatment and material selection are important elements. The main object of this work is to synthesize a highly water-repellent film (superhydrophobic coated film) to be used for corrosion protection of carbon steel pipelines. To achieve this purpose, polystyrene, styrene / vinyl acetate copolymer using emulsion polymerization technique, SiO_2 nanoparticles and nanocomposites were prepared and evaluated as corrosion inhibitors of carbon steel.

The prepared polymers and their composites were characterized using a variety of techniques, namely: (i) FT-IR, (ii) ^{1}H-NMR spectroscopy, (iii) Gel permeation chromatography (GPC) (for molecular weight determination), (iv) Thermogravimetric analysis (TGA), (v) differential scanning calorimetry (DSC), (vi) dynamic light scattering (DLS), (vii) transmission electron microscopy (TEM), (viii) energy dispersive X-ray spectroscopy (EDX), (ix) X-ray diffraction (XRD), (x) scanning electron microscopy (SEM), (xi) contact angle measurements, (xii) atomic force microscopy (AFM).

The prepared polymers and their composites were evaluated as superhydrophobic coating films to be used as corrosion resistant materials for carbon steel.

Generally, the results obtained from the present investigation reveal the following:-

1) Effect of emulsifier concentration on emulsion stability

Particle size growing, polydispersion index (PDI), and ζ- potential, using four emulsifiers blends (EB) concentrations as 1, 0.75, 0.5 and 0.25 wt., % showed that the optimum concentration of EB (Emulsifier Blend), which gives the highest emulsion stability and the lowest P(St-VAc) particle size was 0.50 wt., % at monomer ratio of 1:1 for styrene:vinyl acetate monomers, respectively

2) Effect of styrene:vinyl acetate (St:VAc) monomer molar ratio on emulsion stability

Particle size, film sheet morphology, the resultant molecular weights and the contact angle revealed that the best initial monomer ratio (St:VAc) was 75:25 (E3); that produce a copolymer with smallest droplet size (89.01 nm), highest morphology properties (adhesion and transparency on glass surface), and highest molecular weight (MW=13.75 x 10^4).

3) Corrosion inhibition test

a) Evaluation of the coated surface as corrosion resistance material

It was evident that the corrosion rate decreased from 1.5 to 0.3 mpy as the concentration of the coating solution increased from 100 to 300 ppm, respectively. This may be attributed to the formation of compacted inhibiting superhydrophobic film on metal surface.

b) Effect of temperature and activation energy (Ea) on the corrosion rate

Increasing the temperature leads to activate the coupons surface; thereby, the corrosion rate increases. Higher activation energy (Ea) indicates to higher resistance of the coated metal to corrosion.

c) Effect of contact angle on the corrosion performance

It is obvious that the tendency of the coated film to roll-off the water droplets from the coated film has a direct impact on the corrosion resistance efficiency of the coated coupons. As the water contact angles of the coated coupons increased from 65.01° to 163.77°, the inhibition efficiency of the coated film by PSt-polymer and Z- composite increased from 90.66 % to 98.1 %.

LIST OF ABBREVIATIONS

Abbreviation	Item
^{1}H-NMR	Proton Nuclear Magnetic Resonance
AFM	Atomic force microscopy
AKD	Alkyl Ketene Dimers
AOT	Anionic Emulsifier
CA	Contact angle measurement
CMC	Critical micelle concentration
DIW	Deionized water
DLS	Dynamic light scattering
DM	Diiodomethane
DRIE-chamber	Deep Reactive Ion Etching chamber
DSC	Differential scanning calorimeter
E1	(Styrene : Vinyl Acetate) copolymer in monomer ratio percentage of 50:50, respectively
E2	(Styrene : Vinyl Acetate) copolymer in monomer ratio percentage of 25:75, respectively
E3	(Styrene : Vinyl Acetate) copolymer in monomer ratio percentage of 75:25, respectively
Ea	Energy of activation
EB	Emulsifier Blend (Mixed surfactant)
EC	(E3-SiO_2 NPs) composites
EDX	Energy Dispersive X-ray Spectroscopy
EPIC	Emulsion Phase Inversion Concentration

List of Abbreviations

FT-IR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
HLB	Hydrophilic-lipophilic balance
IE	Inhibition efficiency
INISURFS	Surface-active initiators
L- Composite	MC with dodecyl triethoxysilane coupling agent
mils	In the U.S. the thickness of paint is expressed in mils (one mil equals 1/1000 of inch).
MPY	Mils Per Year
O- Composite	MC with tetraethyl-orthosilicatesilane coupling agent
OT	Optical Transmission
P(St-VAc)	(Styrene : Vinyl Acetate) copolymer
PC	Polycarbonate
PDI	Polydispersion index
PE	Polyethylene
PMMA	Polymethyl Methacrylate
PSt	Polystyrene
PTFE	Polytetra fluro ethylene
Ra	arithmetic mean roughness
RC	Rotating Cage
RHLB	The required hydrophilic-lipophilic balance
RMS	Root Mean Square
SAED	Selected Area Electron Diffraction
SEM	Scanning electron microscopy
SFE	Surface free energy

SiO_2-NPs	SiO_2 Nanoparticles
SRB	Sulphate Reducing Bacteria
St	Styrene
St-VAc	Styrene : Vinyl Acetate
TEM	Transmission electron microscopy
TEOS	Tetraethylorthosilicate
TGA	Thermo-gravimetric analysis
VAc	Vinyl acetate
WCA	Water Contact Angle
XRD	X-Ray Diffraction
Z- Composite	MC with hexadecyl trimethoxysilane coupling agent

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