Preparation of Nanocomposite Polymer Latex

A Thesis
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DEDICATION

To my Parents

I have to thank Allah for choosing both of you to be my parents.

To my Dear Fiancée

Thank you for supporting me.

To my Family, and my Friends

Thank you for helping me.

Ahmed Elkady

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LIST OF ABRIVATIONS

APHA	American Public Health Association
BA	Butyl Acrylate
CIE	Commission internationale de l'éclairage
CMC	Critical Micelle Concentration
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infra Red Spectroscopy
GPC	Gel Permeation Chromatography
HD	Hexadecane
HLB	Hydrophilic Lipophilic Balance
KPS	Potassium Persulfate
KU	Krebs Unit
MEHQ	Mequinol, or 4-Methoxyphenol
OA	Oleic Acid
O/W	Oil / Water
P(St-BA)	Poly (Styrene-Co-Butyl acrylate)
PVC	Pigment Volume Concentration
SDS	Sodium Dodecyl Sulfate
St	Styrene
TBC	4-tert-Butylcatechol
TEM	Transmission Electron Microscopy
T_g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran

AIM OF THE WORK

The main objective of this work is to prepare TiO_2 / Poly(styrene-co-butyl acrylate) nanocomposite latex via in situ miniemulsion polymerization technique.

To make the encapsulation process, the surfaces of TiO_2 nanoparticles will modified with a proper coupling agent to convert the nanoparticles into a more hydrophobic one.

The nanocomposite latexes will characterize by: Transmission Electron Microscopy (TEM), Fourier Transform Infra Red Spectroscopy (FTIR), Gel Permeation Chromatography (GPC), Thermo-Gravimetric Analysis (TGA), Differential Scanning Calorimeter (DSC), and Pendulum Hardness.

The nanocomposite latex will evaluate as binder in the waterborne paint comparing to neat latex and sample filled with unmodified TiO_2 nanoparticles that will prepare under the similar polymerization conditions.

ABSTRACT

Nanocomposite latexes of encapsulated TiO_2 nanoparticles with core-shell morphology were successfully prepared through in situ miniemulsion polymerization of styrene / butylacrylate monomers onto the modified surface of TiO_2 in a semi-continuous operation. Oleic acid was used to act as a coupling agent between TiO_2 surface and polymer. Neat latex and latex filled with unmodified TiO_2 nanoparticles were also prepared under the similar polymerization conditions as a control samples to have a worthwhile comparison.

Results of TEM revealed that; the TiO_2 nanoparticles are coated with the polymer nanolayer in a core-shell structure and uniform distribution of the nanoparticles in size of about 55 - 65 nm without any agglomerations, while latex filled with unmodified TiO_2 nanoparticles showed the nanoparticles placed on the surface of the polymer particles. Thermal analysis including DSC and TGA was used to investigate T_g and thermal stability of the samples. DSC analysis demonstrated that T_g of the nanocomposites was increased as the content of the modified TiO_2 nanoparticles was increased in compare with the neat polymer and that filled with unmodified TiO_2 nanoparticles, while TGA results showed remarkably improved thermal stability due to the uniform dispersion of the non-agglomerated nanoparticles within the matrix of the polymer. Furthermore, the nanocomposite latexes showed improved hardness as the content of the encapsulated TiO_2 nanoparticles increased in compare with the neat polymer and that filled with unmodified TiO_2 nanoparticles indicating their superior mechanical properties.

The prepared nanocomposite latexes were evaluated as binder in the waterborne paint. The paint films of the nanocomposite latexes showed a good opacity and have superior scrub resistance comparing to the control samples prepared under the similar polymerization conditions.

Keywords:

Latex; Nanocomposite; TiO_2 nanoparticles; Oleic acid; Miniemulsion polymerization.

SUMMARY

In recent years, significant efforts have been devoted to elaboration of organic-inorganic nanocomposite particles due to their superior properties compared with conventional composite materials and their potential applications in the areas of plastics and rubber reinforcement, coatings, electronics, catalysis, and diagnostics.

One of the organic-inorganic hybrid nanomaterials is inorganic core - polymer shell hybrid microspheres where encapsulation of inorganic nanoparticles in polymer shell provides better mechanical properties, thermal stability and chemical resistance. The properties of nanocomposites are greatly influenced by both the dispersing degree of nanoparticles in the base polymers and the interfacial adhesion between the inorganic and organic components.

Miniemulsion polymerization is a powerful technique to encapsulate inorganic nanoparticles into a polymer shell. In this method, the submicron-size monomer droplets ranging from 50 to 500 nm are formed by shearing - using high shear generator devices such as a sonicator - premixed system containing water, monomer, surfactant, hydrophobe (costabilizer). Surfactant is used to

provide the droplets with colloidal stability against coalescence by collisions. A hydrophobic costabilizer retards the degradation by Ostwald ripening of the miniemulsion droplets and makes the subsequent propagation reaction occur primarily in sub-micrometer monomer droplets. Since each of those droplets can be regarded as an individual nanoreactor. Polymerization reaction results in latex particles of size similar to the initial size of the monomer droplets.

According to the mechanism of miniemulsion, the key problem involved in preparing inorganic core - organic shell hybrid microspheres is how to introduce the interaction between polymer and inorganic component. Selecting the proper agent to modify the surface properties of inorganic nanoparticles is very effective route.

In the present work Nanocomposite latexes of encapsulated TiO_2 nanoparticles with core-shell morphology were prepared through in situ miniemulsion polymerization of styrene / butylacrylate monomers onto the modified surface of TiO_2 in a semi-continuous operation. Oleic acid was used to act as a coupling agent between TiO_2 surface and polymer. The presence of oleic acid was confirmed by FTIR which reveal the