

Chapter 6

Summary

Polymer-clay nanocomposites (PCN) have attracted the attention of several researchers, primarily because significant improvements in physical properties can be achieved at low clay concentrations. The dispersion of nanolayers of clay mineral in the polymer matrices, providing a large surface area due to high aspect ratio of the clay platelets is considered to be responsible for such an improvement in properties. Depending on the interaction between clay layers and polymer chains intercalated and exfoliated type of nanocomposites are formed.

It was reported that nanocomposites with various applications can be tailor made by tuning the polymer-clay interactions. The use of reactive organo-modifiers with unsaturated bonds or other reactive functional groups for clay is a good strategy to improve the strength of the interface between the inorganic and the polymer matrix. These groups are expected to react with the growing polymer chains so that the polymer chains remain attached to the clay surface.

In this respect, Adduct-modified organoclays (AMC) with reactive functional groups will be particularly attractive for Polystyrene Clay nanocomposites (PSCs) preparation. Adducts were prepared by treating CTAB (Quaternary ammonium salt) with unsaturated organic acids like Acrylic acid (AA), Cinnamic acid (CA) and Oleic acid (OA). The AMCs (AC-AMC, CC-AMC and OC-AMC) were prepared via cation exchange of Na^+ with adduct. Hydroxyl group of unsaturated acid react with CTAB to form adduct, were as its

olefinic part polymerize with styrene monomer during polymerization reaction.

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. Hence, the AMC with reactive functionality was used for the preparation of polystyrene clay nanocomposite (PSC).

A series of exfoliated PSCs using 10 wt.% AMCs 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 particles (PSC-AC, PSC-CC and PSC-OC) were characterized by FT-IR spectroscopy, XRD, TGA and DSC. From XRD, the absence of the 001 reflection for all the three PSCs suggests that the d_{001} value between the layered silicates is intercalated to spacing greater than the measurable range, or clay layers are disorderly dispersed in the polystyrene matrix. Also by the addition of AMC, the onset thermal decomposition and glass transition temperature (T_g) of all the PSC materials were shifted significantly towards the higher temperature range than that of pristine PS and was maximum for PSC-AC. The improvement in the thermal stability of clay composites has been attributed to the restricted thermal motion polymer chain within and close to the silicate layer, providing greater resistance to thermal degradation for different clay-polymer system. From these results, mainly PSC-AC is used for further self-assembling studies and also for anticorrosion coating studies.

Concentration dependent self-assembling properties and the morphology of the PSC-AC were studied in THF solvent by microscopic techniques such as optical microscopy, SEM, and fluorescence microscopy. PSC-AC particle exhibited solvent assisted self assembly in highly volatile THF solvent by varying the solution concentration from range (1-50 mg/mL). Uniform vesicles of 2-3 μm are produced by lateral association of PSC-AC particle through H-bonding interactions between edge hydroxyls of the silicate layers on drop casting and drying of the PSC-AC solution on glass slide. The potential use of these vesicles could be microstorage system and drug delivery vehicles. And relatively uniform two dimensional microporous film of long range order were produced at solution concentration of 20mg/mL. The mechanism for the formation of two dimensional microporous film was breath figure mechanism in which the extended bilayers formed closely packed lamellar arrangement. Above 50 mg/mL concentration formation of a solid film or a non patterned PSC-AC film was obtained due to high viscosity of PSC-AC solution which prevents the sinking of water droplets on to the polymer surface and restricts the formation of concavities.

For corrosion studies, a series of polystyrene clay nanocomposites with different clay loading (1, 3, 5, 10 and 20 wt.%) of AMCs were successfully synthesized via *in situ* thermal polymerization. The PS and PSC coatings were prepared by dissolving 6 wt.% of the PS and PSC fine powder in NMP solvent. Drops of corresponding solutions were subsequently spread onto the Aluminum 6061 alloy coupons and cured in an oven at 40°C for 2 h. Then the coated coupons were allowed to completely dry for 24 h at 100°C.

The thickness of the coatings was measured by a digimatic micrometer (Mitutoyo) and the film thickness of all the coatings was about $20 \pm 2 \mu\text{m}$. The potentiodynamic and electrochemical impedance spectroscopic measurement results showed that the resistance to corrosion of Al alloy was significantly improved by PSC coatings and provided an efficient barrier against aggressive attacking species. Comparatively the PSC-AC10 coatings showed better adherence and stability on Al alloys and the from the tafel plots it's clear that 10 wt % AMC loaded PSC coated Al alloy offers high protection because of high E_{corr} and large impedance value (R_{ct}). The UV- visible transmission spectra of PSC films even at 5 wt % clay loading (e.g. PSC-AC5) showed that the visible region (400 –700 nm) was almost unaffected by the presence of the clay and retained the high transparency of the PS. However, dispersion of nanolayers of MMT clay in PS-clay nanocomposite materials led to a significant increase in thermal decomposition temperature and also crystalline temperature than that of neat PS based as observed in TGA and DSC studies. Electrical conductivity of all the PSC (1-10 wt.%) materials was slightly smaller than that of the pristine PS as measured using four-point probe technique.

Similarly, Corrosion studies were also carried out by varying modifier concentrations of clay during organo-modifications on cold rolled steel (CRS) using same procedure. The PSC materials (PSC-AC0.5x, PSC-1x, PSC-AC1.5x, PSC-AC2x) were coated on CRS and they found to possess superior anticorrosion performance over those of bulk PS based on a series of electrochemical measurements and impedance spectroscopy in 3.5 wt % aqueous NaCl electrolyte. The corrosion protection efficiency was increased with increase

in modifier concentration. PSC coatings with high modifier concentration (PSC-AC2x) on CRS were found to exhibit higher anticorrosion properties. Similarly, from electrochemical measurement it was found that as the PSC coatings on CRS with high clay loading (e.g. 10 wt.% - PSC-AC10) exhibited superior corrosion protection over those of bulk PS. Also the effects of modifier composition on thermal stability of PS and PSC materials, in the form of fine powders, were studied by DSC and TGA. This enhanced anticorrosion property of PS–clay nanocomposite materials compared to pristine PS results from dispersing silicate nanolayers