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**CLAY POLYMER NANOCOMPOSITES: INVESTIGATION OF THEIR
ELECTRICAL PROPERTIES FOR INDUSTRIAL AND TECHNOLOGICAL
APPLICATIONS**

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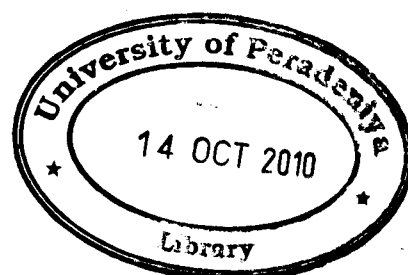
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**CLAY POLYMER NANOCOMPOSITES: INVESTIGATION OF THEIR
ELECTRICAL PROPERTIES FOR INDUSTRIAL AND TECHNOLOGICAL
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Pioneering researches on hosts that can hold vast number of inorganic and organic materials have opened a new era on development of composite materials over the past years. Among them clay minerals belong to the smectite group have shown ample range of distinct properties such as hosting capabilities for numerous cations and layer expansion abilities upon guest intercalations. Montmorillonite (MMT) and Fuller's Earth (FE) are insulating smectite hosts that can be transferred into highly conducting polymer nanocomposites upon spontaneous polymerization of conducting polymers within their nanometer level interlayer spaces by pre-exchanged oxidizing agents. Clay conducting polymer nanocomposites made by this phenomenon showed remarkable electronic, ionic or even mixed conducting properties over their un-modified pure forms.

This research was mainly focused to improve the conductivity of the low cost conducting polypyrrole (PPY) nanocomposites prepared by solution-phase ion-exchange process with the use of Ce^{4+} , Cu^{2+} modified MMT and FE hosts. The resulted clay-conducting polypyrrole nanocomposites with the reduced form of the oxidizing agents have been extensively characterized by X-ray diffraction (XRD) technique for interlayer spacing variations and by Fourier Transform Infra Red (FT-IR) spectroscopy to study the interactions between the clay and polymer functional groups. Thermal gravimetric analysis (TGA) and differential scanning calorimetric (DSC) techniques were used to determine the thermal behavior of those. DC

polarization technique with both blocking and non-blocking electrodes was used to distinguish the ionic and electronic transport numbers and recognize the type of mobile ion species. AC impedance analysis further resolved the electrical conduction of these materials while electrochemical performance and application prospects were determined by cyclic voltametry.

The XRD analyses for MMT, FE and Cu^{2+} ion intercalated smectites show similar d spacing of $\sim 15 \text{ \AA}$ suggesting that they contain two water layers within interlayers. However, for Ce^{4+} modified smectites it gives the d spacing of $\sim 18 \text{ \AA}$, suggesting higher interlayers water capacity. Heat treatments for the above reduce the d spacing to a value of $\sim 10 \text{ \AA}$ due to the removal of all interlayer water. As the monomer pyrrole is introduced to the modified smectites, the enhancement of the d spacing by $\sim 7 \text{ \AA}$ is observed. These layer expansions due to the ion induced in situ polymerization of pyrrole do not change upon heat treatments revealing the thermal stability of formed PPY within smectite interlayers. Further, it is revealed that for a desired amount of modified clay, interlayer polymer saturation can be achieved by gradual loading of PPY with increasing the monomer concentration. For [Cu(I)-PPY-MMT], (the interlayer saturation) the optimum layer expansion is $\sim 17 \text{ \AA}$ that dose not change upon further loading.

FTIR analyses observed for raw and ion-modified clays clearly coincide with the typical bands observed for natural MMT whereas for polymerised clay the bands ($\nu = 1198 \text{ cm}^{-1}, 1304 \text{ cm}^{-1}, 1460 \text{ cm}^{-1}$ and 1550 cm^{-1}) suggest the formation of PPY. Further, the band intensity variations of ($1638 \text{ cm}^{-1}, 3200\text{-}3400 \text{ cm}^{-1}$) prior and following the PPY formation is a clear suggestion for the transformation of hydrophilic ion-modified clays into hydrophobic clay PPY nanocomposites.

TGA and DSC data overlap with the XRD and FTIR data suggesting raw and ion-modified clays contain interlayers water that can be overcome upon heating to $200 \text{ }^\circ\text{C}$. These analyses justified that polymerized clays are hydrophobic and PPY within the clay is stable at even $\sim 350 \text{ }^\circ\text{C}$, where polymer begins decomposition.

Bulk conductivity analyses carried out for the copper ion intercalated PPY smectites suggest mixed conducting nature as observed by preliminary analyses (DC polarization tests) whereas cerium ion intercalated PPY nanocomposites show almost electronic conducting nature. The optimum electronic conductivity observed upon PPY saturation within clay interlayers is 0.53 S m^{-1} for [Cu(I)-PPY-MMT]. Dual transmission model facilitates the necessary theoretical background to explain AC impedance results on mixed conducting clay PPY nanocomposites while a theory proposed by Hsu et al assists to identify the behavior of [Ce(III)-PPY-MMT] [110].

Cyclic voltametry analyses undoubtedly show the electrochemical behavior of ion-modified and polymerised clays. Peaks obtained for Cu^{2+} and Ce^{4+} intercalated smectites almost coincide with copper and cerium redox potentials. The well-defined nature of the CV's for PPY nanocomposites precisely unveil the overcoming of non conducting environment of the hosts while further analyses on [Ce(III)-PPY-MMT] reveal its oxygen reduction ability suggesting promising, cheap, ease of fabrication and environment friendly alternative for high cost cathode materials in fuel cells.