

## Preparation and characterization of poly(ethylene-oxide)/clay-silica nanocomposites

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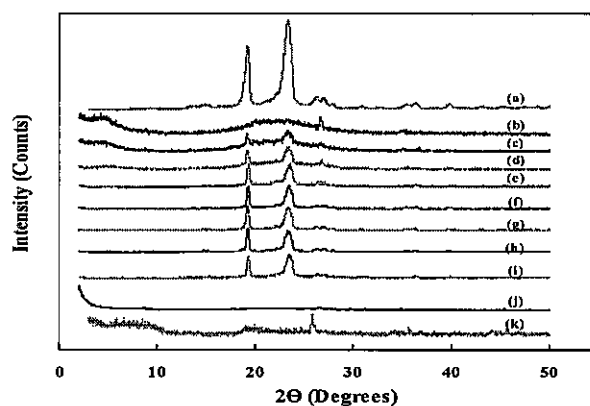
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**Abstract**— We have aimed the preparation of the montmorillonite-silica nanocomposites by a sol-gel technic involving hydrolysis reaction of alkoxysilanes (TEOS) and subsequent condensation reaction with hydroxyl groups of the clay. The modified clay minerals are prepared by adding different amounts of TEOS in both the cases of acid- and non-catalyzed procedures. The characterization of the organo clay minerals are made by XRD and FTIR spectroscopy. XRD and FTIR results indicated that the structure and surface properties of the sol-gel-modified clay can be controlled by varying the TEOS/clay mass ratio and/or adding trace amounts of acid as catalyst. Organic-inorganic hybrid materials, incorporating nanostructured silica lattice within a poly (ethylene oxide) matrix (PEO), were produced via the sol-gel process from aqueous solution mixtures of poly(ethylene oxide) and prehydrolyzed tetraethylorthosilicate (TEOS).

Hybrid organic-inorganic materials have been developed during the past two decades or so[1] as intimate combinations of these dissimilar materials not constrained by classical material compromises. The sol gel process under mild conditions offers an efficient and convenient approach to the synthesis of organic inorganic composite material nanoscales in domain sizes[2] or approaching molecular level[3]. Originally, the sol-gel reaction is usually in two steps: hydrolysis of metal alkoxides to produce hydroxyl groups, followed by polycondensation of the hydroxyl groups, and residual alkoxyl groups, to form a three dimensional lattice.

The inorganic clay, used in this study, was K-10 grade montmorillonite purchased from Sigma-Aldrich Co. (USA) with a surface area 220–270 m<sup>2</sup>/g. The chemical composition (wt%) of the clay (main elements) was SiO<sub>2</sub>:67.6, Al<sub>2</sub>O<sub>3</sub>: 14.6, Fe<sub>2</sub>O<sub>3</sub>:2.9, MgO: 1.8 and others. Cation exchange capacity of the clay was 60 meq/100g. Firstly, the clay sample was modified. The modification process involves hydrolysis reaction of alkoxysilanes and subsequent condensation reaction with hydroxyl groups on the clay surfaces, resulting in the formation of mesoporous silica lattice or silica nanoparticles combined on the clay surfaces. Surface properties and structures of these sol-gel-modified clays were tunable by varying the initial TEOS/clay ratio and by adding trace amounts of acid as catalyst. The samples were characterized by X-ray diffraction analysis (XRD) and Fourier Transform Infrared Spectrum (FTIR). In the case of acid-catalyzed procedures, the intensity of diffraction peaks of MMT decreases steadily as the initial TEOS/clay ratio increases. At high TEOS/clay ratio, such as 20/3 and 10/3, their diffraction peaks are vanished, suggesting that clay platelets are delaminated during the sol-gel process. At low TEOS/clay ratio, however, the diffraction peaks are still detectable at an unchanged position, suggesting that the clay tactoids are disturbed or partially delaminated during sol-gel process but unable to be fully delaminated. In the case of non-catalyzed procedure, the intensity of diffraction peak decrease with varying TEOS/clay ratios, but not disappeared in all cases compared with the pristine clay. This result indicates that the loss of diffraction peaks in the case of high TEOS/clay ratio was not due to dilution by TEOS, but due to the influence of the acid-catalyzed procedure. FTIR results revealed that the TEOS was covalently bonded on clay surface and can further react with other hydrolyzed TEOS molecules, in the case of acid-catalyzed procedures. As a result, the clay surfaces were attached by silica lattices or nanoparticles, depending on the TEOS/clay ratio and acidic catalysis. Sol-gel nanocomposites

(PEO/silica nanocomposites) are prepared by in situ acid catalyzed hydrolysis and condensation of mononuclear precursors such as tetraethoxysilane (TEOS) in organic polymer matrices. This procedure was used to prepare the hybrids with TEOS/clay =20/3(w/w) and the varying ratios of PEO / MMT. The samples were characterized by X-ray diffraction analysis (XRD), Fourier Transform Infrared Spectrum (FTIR). XRD results are given in Fig.1.



**Figure-1:** XRD diffractograms for PEO, acid catalyzed modified MMT(20/3) and PEO/clay-silica nanocomposites containing various clay amounts (a) PEO, (b) 25%, (c) 20%, (d) 15%, (e) 10%, (f) 5%, (g) 2%, (h) 1%, (i) 0.5%, (j) acid catalyzed (20/3), (k) Montmorillonite.

This figure clearly shows that a decrease in the number of tactoidal structures and consequent increase in the proportion of the exfoliated silicate layers dispersed in the polymer matrix, provided by possible bonding mechanisms such as the H-bonding between the hydrated exchangeable cations in the interlayer region of the clay and the oxy-groups of PEO chains and directly the ion-dipole interactions[3] between the oxy-groups of PEO chains and the exchangeable cations, as clay loading was increased up to wt.15%. In the Na<sup>+</sup>-PEO coordination, the polymer backbone adopts a trans-gauche-trans conformation, 'crown ether type' that deviates from the helical conformation typically found in PEO crystal [4]. The conformational changes occurred in PEO chains depending on the better dispersion of clay platelets in the polymeric matrix may lead to a decrease in the degree of polymer crystallization.

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