Study of Chemical Absorption and Swelling Kinetics at 50°C for Polyurethane/ Montmorillonite Clay Nanocomposites

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***Abstract*– Layered silicate composites having polyurethane matrix were prepared by in situ polymerization. Montmorillonite clay was pretreated with centyl tri-methyl ammonium bromide (CTAB) to convert hydrophilic clay into organophilic MMT so that it is compatible with hydrophobic polyurethane matrix. The composites so prepared were characterized for their morphology using SEM and chemical absorption in various chemicals like toluene, ethyl acetate, xylene, hexane, methanol, DMF, tetrahydrofuran, acetone, petroleum ether, distilled water, saline water, and ethanol with varying solubility parameters. The absorption study revealed that depending upon the absorption the solvent can be divided into three categories, high absorbing, medium absorbing and low absorbing depending upon their solubility parameters vis-a-vis polyurethane resin. Two high absorbing solvents i.e. ethyl acetate and xylene, one medium absorbing i.e. ethanol and one low absorbing i.e. saline water were taken to further study the swelling kinetics at 50oC to establish its barrier properties and diffusivity. For all the solvents, the presence of montmorillonite layers caused a decrease in permeability due to more tortuous path for diffusing molecules that must bypass impermeable platelets.**

***Keywords*– Chemical absorption, Montmorillonite clay, Polyurethane, nanocomposite, swelling kinetics.**

I. INTRODUCTION

Nanocomposites are new class of materials with improved physical, thermal, mechanical and barrier properties than those of conventional composites due to the much stronger interfacial forces between the dispersed nanometer-sized domains and the matrices. Clay/polymer nanocomposites offer tremendous improvement in a wide range of physical and engineering properties for polymers with low filler loading. The major development in this field has been carried out over the last one and half decades. The significant progress has been made in the development of synthetic methods, applications to engineering polymers, and the investigation of major engineering properties.

Natural clays are composed of oxide layers with cations in between layers. These layered materials are present in the form of the aggregate with a size of about 0.1–10 mm consisting of several primary particles with a height of about 8–10 nm. The primary particles are composed of a number of layers, and the thickness of the layers is about 0.96– 1.0 nm .

Nanoscale layered clays with very high aspect ratios and high strength can play an important role in forming effective polymer nanocomposites owing to their intercalation chemistry. Montmorillonite has been particularly important in polymer nanocomposites. Montmorillonite is a crystalline, 2:1 layered clay mineral in which a central alumina octahedral sheet is sandwiched between two silica tetrahedral sheets.

Due to the poor compatibility of MMT with organic monomers and polymer matrices, it is necessary to modify MMT in the preparation of polymer–MMT nanocomposites for high performance. An effective way to modify the nature of MMT is to substitute the cations in the interlayer galleries of layers with cationic-organic surfactants. On one hand, organic modifiers can impart hydrophilic properties to the MMT, which can improve the compatibility of MMT with polymers. On the other hand, the gallery spacing of the modified MMT becomes larger than that of MMT. Organically modified clays play an important role in the formation of the structure and morphology of polymer/clay nanocomposites, and thus significantly influences material properties. Therefore, the choice of modifiers used to treat clay is crucial to prepare polymer/clay nanocomposites with enhanced properties. At present, alkylammonium and alkylphosphonium are used widely to treat MMT . In the present study we have used centyl tri-methyl ammonium bromide (CTAB) for converting the hydrophilic clay into hydrophobic form.

Tien and Wei synthesized PU/MMT nanocomposites from PPG, MDI and DMF in order to induce efficient exfoliation and dispersion of MMT layers in the PU matrix. It has been reported that nanoclay can increase the hardness and scratch resistance. Nanosilica has enhanced the tensile strength and elongation of polyurethane elastomers, however the modulus and hardness are lower than those of the corresponding micro size filled polyurethane, because the surface properties, particle size, and dispersion of nano particles are diversified. However, studies on swelling kinetics for these composites in the solvents like ethanol, methanol, saline water, petroleum ether, ethyl acetate and hexane has not been reported anywhere.

The interaction between the organic solvents and polymer membranes have been studied for almost half a century; nevertheless a complete understanding of the transport mechanism, namely, sorption, diffusion, and permeation, at the molecular level is still not well understood. The interest in the accumulation of a large body of coherent and accurate experimental data on diffusion coefficient (D), permeability coefficient (P), and sorption coefficient (S), of solvents molecules through polymer membranes is attributed to a number of important engineering applications that depend wholly or partly on such phenomena. These include protective coatings, paints, and varnishes, electronic devices and cable sheathing materials, packaging goods for food and beverages, selective barriers for the separation of liquid mixtures, biomedical devices etc.

In view of the importance of polyurethane nanocomposite as a membrane in engineering applications, we found it necessary to explore the interactions with several organic solvents. In this, we will present some useful engineering data on sorption, diffusivity, and permeability of a number of organic and inorganic solvents, which have some relevance in industry and engineering.

II EXPERIMENTATION

A. Materials

Polypropylene glycol (PPG), Montmorillonite K-10 was supplied by Fluka. Centyl tri-methyl ammonium bromide (CTAB) was supplied by National Chemicals, India. Dimethyl formamide (DMF) was procured from E-Merck, xylene, ethyl acetate were procured from Qualigens, India.

B. Modification of Montmorillonite K10

To disperse montmorillonite in a polyurethane matrix, it was necessary to first replace the hydrophilic inorganic exchange cations with more alkyl ammonium ions. To achieve this, 12.04 gram of Na montmorillonite was added to 500 ml of the aqueous solution of CTAB (0.5 wt %). The suspension was vigorously stirred for 4 hours at 60°C. A white solid product formed after filtration was collected and repeatedly washed by distilled water and acetone. After removal of the solvent by evaporation under reduced pressure, the solid product was dried in a vacuum oven at 70°C for 10 hrs. The obtained organophilic montmorillonite was ground and screened with sieve.

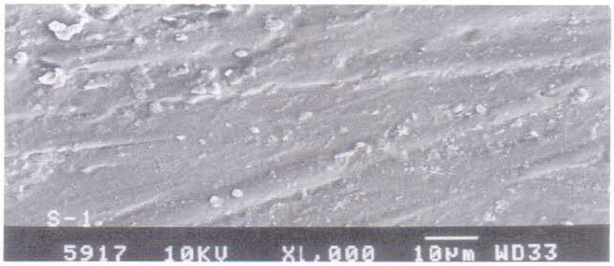

Fig. 1 SEM of polyurethane nanocomposite samples containing 2 wt% of nanoclay

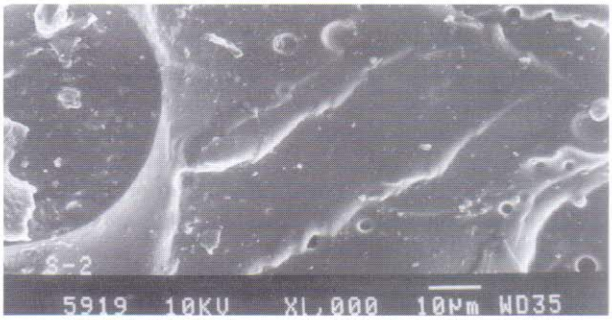

Fig. 2 SEM of polyurethane nanocomposite samples containing 1 wt% nanoclay

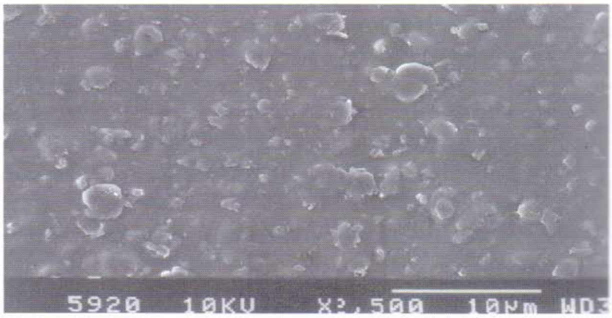

Fig. 3 SEM of polyurethane nanocomposite samples containing 10 wt% nanoclay

C. *Synthesis of polyurethane resin*

PU was prepared using dehydrated PPG, MDI and DMF solvent. The reaction was carried out in a well agitated reaction vessel maintained at a constant temperature of 80°C. When the reaction mass become very viscous but had flow characteristics, the reaction mass was poured into the mold and the necessary pressure was applied for sheet forming. Nanocomposite of polyurethane/montmorillonite was prepared by in-situ polymerization using same method in presence treated organoclay. The percentage of clay was varied by weight of the total mixture i.e.1%,2%,4%,6%,8% and 10%. Continuous stirring and mixing under nitrogen atmosphere led to increase in viscosity of the reaction mixture which when had appropriate flow was poured on