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Synthesis and Characterization of Polymer Nano-Composite Materials

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Abstract— **The synthesis of polymer-nano composite materials is a vital facet of polymer-nanotechnology. By incorporation of suitable inorganic nano-materials, the properties of polymers are improved and hence these have a lot of applications depending upon the types of inorganic materials present in the polymer. Solvent casting is one of the effective and less time consuming methods for the synthesis of polymer nano-composites. In this work, different types of polymer nano-composites, methods of synthesis, characterization techniques and different applications of composite materials have been presented. Layered silicate polymer-nano-composites exhibit superior mechanical characteristics (i.e. 40% increases in tensile strength at room temperature), heat resistance (i.e. 100% increase in the heat modification temperature) and chemical resistance (i.e. approx 10 fold decrease in O_2 and H_2O permeability) compared to the neat or traditionally filled resins. These improvements in properties have been archived by addition of 0.1-5% by volume of the dispersed nano-particles.**

Index Terms— **Layered silicate polymer, polymer nano-composite materials.**

I. INTRODUCTION

Polymer nano-composites (PNC) consist of a polymer or copolymers having nanoparticles or nano-fillers dispersed in the polymer matrix in order to significantly improve the performances of the polymer [1, 2]. These may be of different shapes (e.g., platelets, fibers, rods, spheroids etc), but at least one dimension must be in the range of 1–100 nm [2, 3]. Polymer nano-composites represent a new alternative to conventionally filled polymers [4, 5]. Because of their dispersion in nano-size, nano-composites exhibit distinctly improved properties when compared to the pure polymers or their traditional composites [5, 6]. Systems in which the inorganic particles are the individual layers of a lamellar compound; most typically a clay or nano-composites of a polymer (such as nylon) embedded among layers of silicates exhibit significantly changed physical properties related to the pristine polymer [7, 8]. An example of the layer orientation, polymer silicate nano-composite exhibits stiffness, strength and stability in two dimensions rather than one. Due to nanometer scale, it minimizes scattering of light, nano-materials seem to be usually transparent [8,9].

PNC represent a new alternative to conventionally filled polymer. These include increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability [10,11]. Polymers that contain transition metal complexes either attached to a conjugated backbone are an exciting and a promising class of modern materials. These macromolecules are hybrid of conjugated organic and transition metal-containing polymers [12-14].

Conjugated organic polymers, such as poly acetylene, -poly-thiophene, and polypyrrole, as well as oligomers and derivatives of these materials have been extensively explored. These materials are endowed with many important properties such as nonlinear optical properties, electronic conductivity and luminescence, and have been proposed for their use in various applications including chemical sensors, electroluminescent devices, electro catalysis, batteries, smart windows and memory devices [9,10]. The addition of reinforcing agents is widely used in the production of commodities (e.g. packaging films and tyres etc). It is expected that the reduction of the added particles size down to nano-metric scale could enhance the performance of these materials, even though not to the extent as layer addition. These new materials are aimed at being a substitute for more expensive technical parts (gear systems in wood drilling machines, wear resistance materials etc) and in the production of barrier plastic film for food industry [10,11].

Besides structural applications, polymer nano-particle compounds have very interesting functional applications [4,10,11]. For instance, R-Fe_2O_3-polymer nano-composites are used as advanced toner materials for high quality colour copiers and printers and as contrast agents in NMR analysis, memory devices. The means to manufacturing such novel materials are being understood and manipulated the chemistry occurring between the polymer and the layered compounds or the nanoparticles, in order to obtain a homogenous dispersion and a good contact between polymer matrix and added particle's surface. There have been major advances in solid state and materials chemistry in the last two decades and the subject is growing rapidly [5,11,12]. The coatings of magnetic particles are of special interest because of their significant applications, e.g., technological energy transformation, magnetic recording, magnetic fluids and magnetic refrigeration system etc [12,13].

Polymeric materials are filled with several inorganic compounds in order to increase properties like heat resistance, mechanical strength and impact resistance and to decrease other properties like electrical conductivity,

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dielectric constant thereby increasing the permeability for gases like oxygen and water vapor. In recent years considerable efforts have been devoted to the development of methods for the preparation of composite materials consisting of polymer cores covered with shells of different chemical composition. In these powders, particles covered with magnetic materials have been used as beads for gas separation, or as pigments, catalysts, coatings, flocculants, toners, raw materials recovery, drug delivery and corrosion protection [6,12,14]. Polymer composites containing ferrites are increasingly replacing conventional ceramic magnetic materials because of their mouldability and reduction in cost. These are also potential materials for microwave absorbers, sensors and other aerospace applications. The flexible magnets or rubber ferrite composites are also possible by the incorporation of magnetic powders in various elastomer matrices. It modifies the physical properties of the polymer matrix significantly. Solvent casting method is one of the easiest methods for the preparation of polymer nano-composites. It needs simple equipment and is less time consuming [14-16].

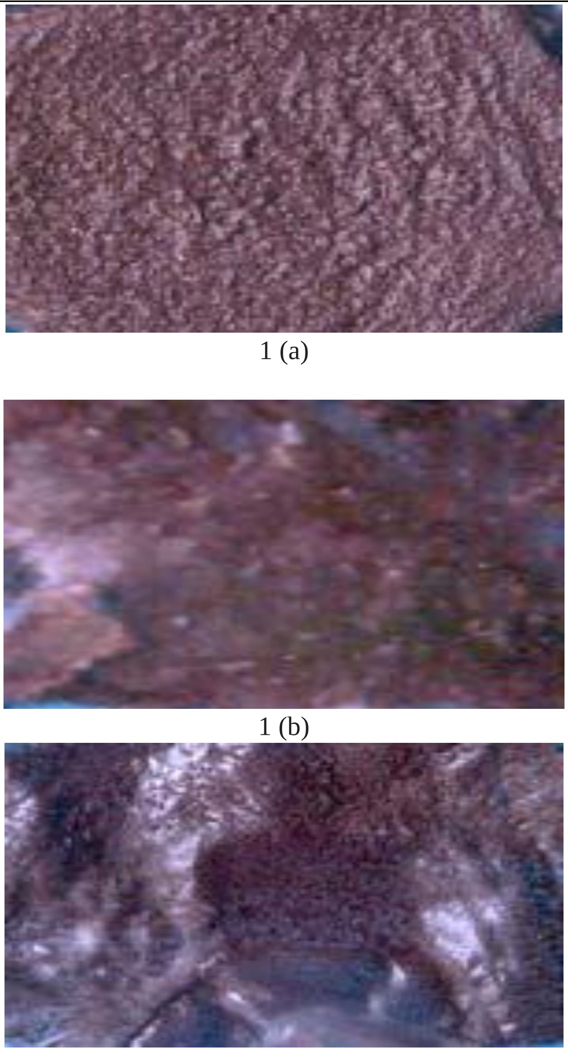
II. MATERIALS AND METHODS

In this work required polymers, nano-materials, clay, other ingredients, and apparatus used have been provided by R&D Lab, Berger Paints Limited, Kolkata and Nano Technology Application Centre, Allahabad University.

Incorporation of appropriate nano-ceramic particles into commercial grade acrylic polymer produced a high class of polymer nano-composite material. These nano-composites have been prepared by intercalation of the organoclay with a polymic acid. The clay polyimide hybrid composite films exhibit greatly improved CO_2 barrier properties at low clay content; clay less than 8.0 % by volume results in almost a ten-fold decrease in permeability. In the simplest case, appropriately adding nano-particulates to a polymer matrix can enhance its performance, often dramatically, by simply capitalizing on the nature and properties of the nano-scale filler. These materials are better described by the term nano-filled-polymer-composites. This strategy is particularly effective in yielding high performance composites, when good dispersion of the filler is achieved and the properties of the nano-scale filler are substantially different or better than those of the matrix.

III. RESULTS AND DISCUSSION

Figures 1a, 1b & 1c show the optical micrograph images of R-Fe_2O_3 dispersed natural rubber (R-Fe_2O_3-NR), R-Fe_2O_3 dispersed polyethylene glycol (R-Fe_2O_3-PEG) and R- Fe_2O_3 dispersed polycarbonate (R-Fe_2O_3-PC), nano-composite films. The fine dispersion of the magnetite inside the polymer matrix makes it a magnetic polymer. Figure 1(d) shows the structure of the polymer polyisoprene (i.e. natural rubber) [1, 2]. The vigorous development of polymeric science and extensive utilization of polymeric materials in technology has led in recent years to the increased interest in the preparation and characterization of polymer and its composite films. Characterization is an essential part of all investigations dealing with materials [2-4].

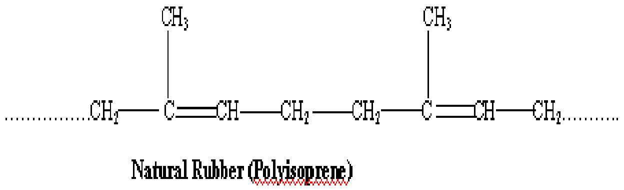

1 (a)

1 (b)

1 (c)

Figure 1 (a, b & c): Optical micrograph images of R-Fe_2O_3 dispersed: (a) natural rubber, (b) poly-ethylene glycol, and (c) poly- carbonate composite films.

The important aspects of characterization are chemical composition and compositional homogeneity (chemical homogeneity), structure (including crystal system where possible atomic coordinates, bonding and ultra structure) and identification and analysis of defects and impurities influencing the properties of the materials [4, 5]. Characterization, therefore, describes all those features of composition and structure of a material that would suffice for reproducing the material. The advances made in the last few years in characterization techniques, especially in the structure elucidation, have been stupendous and have opened new vistas in solid state materials. Among the several characterization techniques, X-ray diffraction (XRD) and scanning electron micrography (SEM) are the two important techniques [5-7].



$$\ldots CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\ldots$$

Figure 1(d): The structure of the polymer poly-isoprene (natural rubber).

X-ray diffraction study– X-ray diffraction1 has played a vital role in identifying and characterizing solids since the early part of this century. The nature of bonding and the working criteria for distinguishing between short-range and long-range order of crystalline arrangements from the amorphous substances are largely derived from X-ray diffraction and thus it remains as a useful tool to obtain structural information. X-ray diffraction pattern of amorphous polymer will not show any sharp and highly intensed peaks whereas the nano-composites of amorphous polymer show sharp and highly intensed peaks. This is due to the development of crystallinity in the amorphous polymer [8,9].

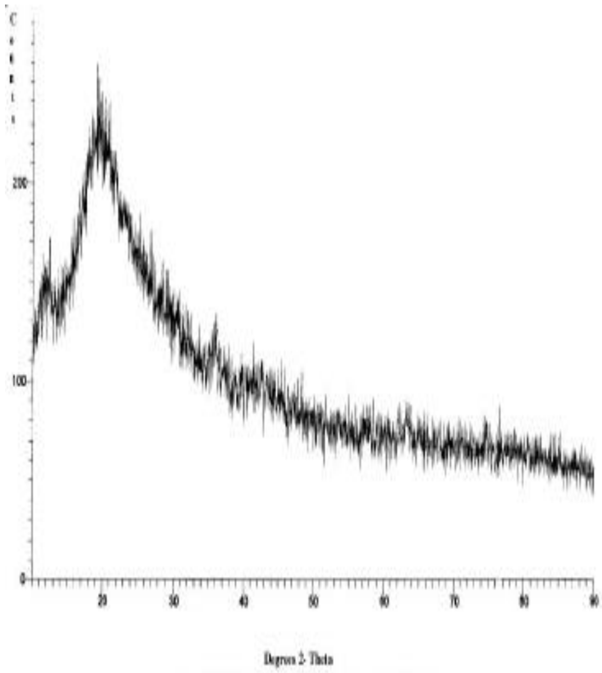


Figure 2(a): XRD pattern of pure natural rubber

Figures 2(a) & 2(b) show the XRD pattern of pure natural rubber and R-Fe2O3 dispersed natural rubber composite. Highly intensed peaks occur in the pattern due to the presence of inserted gamma iron oxide materials in the rubber matrix. X-ray diffraction has been most commonly used for routine characterization as well as for detailed structural elucidation. In order to obtain detailed structural information, knowledge of X-ray diffraction intensities is also essential, the intensities being related to the structure factor [9,10].

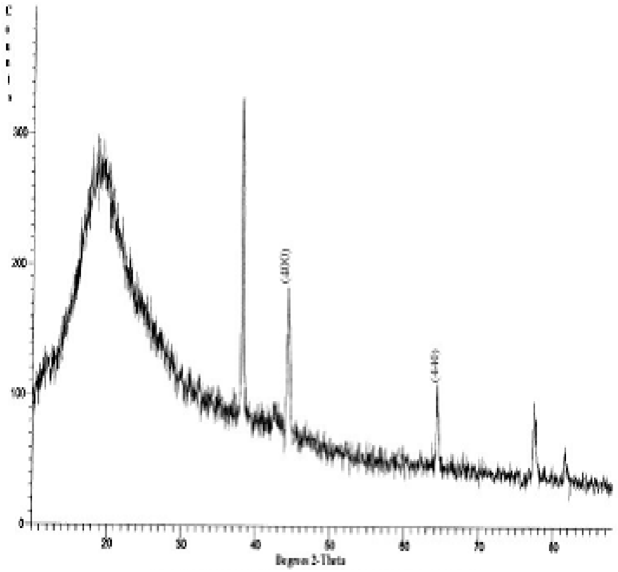


Figure 2(b): XRD-pattern of Fe_2O_3 dispersed natural rubber

Scanning electron micrographs study- The complex morphology of structural formation in polymers should not be forgotten that all these structures are built up of separate polymeric molecules [10,11]. At a glance, it seems self-evident that direct relations must exist between the properties of macromolecules and their ability to form super molecular structures. The shapes of most polymer molecules may vary within wide limits when studying the simplest phenomenon of structure formation. Quite a long time ago it was found that there are two ways by which structures can form. Sufficiently flexible molecules roll up into spherical coil globules, which form in very much the same way as the drops of a liquid under the action of surface tension. But if the macromolecules are sufficiently rigid, the simplest linear structures result. No separate linear polymer molecules have been observed so far [12,13]. Evidently in majority of cases, they aggregate into chain bunches usually containing several dozen molecules. The phenomenon of structural transformations occurring during deformation is very typical of polymers. Structural phenomena play an important role in determining the properties of a polymer. Mechanical properties are determined not only by the changes in shape confirmation and by motion of individual molecules of the polymers, but by the behavior of larger and more complex structural formations as well. The interface boundaries of these formations, known as super molecular structures, are the sites where chemical reactions in the polymer are most likely to begin and centers of crack formation and incipient destruction are likely to arise. It has been found that extensive occurrences of ordered structures are typical not only of crystalline, but also of amorphous polymers. It is also observed in the case of amorphous polymers with developed structures and it is firmly described as a phase transformation.

The nature of this phenomenon remained difficult to understand for a long time, but electron microscopy revealed the composite formation, that is actually a jump wise transition from one super molecular structure to another with a sharp interfacial boundary which is also observed on a microscopic scale. A well-known example is of a poly-methyl methacrylate, where a sharp boundary can be seen between the isotropic and the oriented parts of the specimen. The formation of a ‘neck’ on deformation of a large spherulite of isotactic poly (methyl methacrylate) takes place and a sharp boundary can be discerned between the unchanged and the oriented portions of a spherulite. In addition to this, the secondary formations can be seen which have resulted from recrystallization of the oriented parts, and these are also separated by sharp boundary lines [13,14].

Figure 3 shows the SEM images of R- Fe_2O_3 dispersed natural rubber composite. From the figure, one can observe the fine dispersion of iron oxide particles in the rubber matrix. The dispersed particles have irregular shape and show agglomeration [14,15].

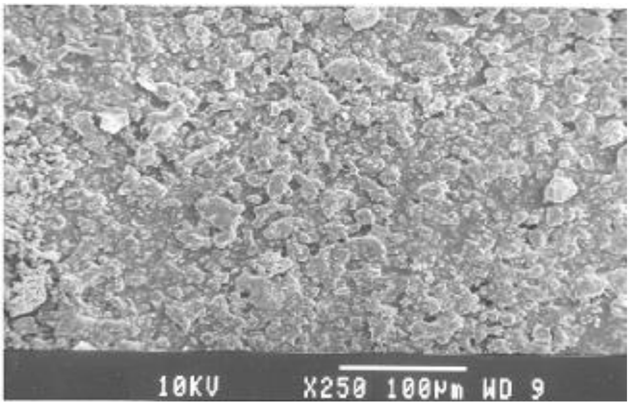


Figure 3: SEM image of R-Fe_2O_3 dispersed natural rubber.

The phenomenon of structural transformations occurring during deformation is very typical in polymer nano composites. This part briefly explains the advent of polymer/clay nano-composites into the field of nanotechnology. It highlights the 3M's, that is, the mechanism, methodology and the measurement techniques involved in preparing novel polymer/clay nano-composites [3-5].

Clay, a natural source, with small loadings (%by weight) can substitute reinforcers which are being used in polymers. The commercial importance of polymers has led to an intense investigation of polymeric material nano-composites, of sizes varying from 1 to 100nm. These are being reinforced by particulates, fibers and layer inorganic fillers. In particular, in the case of layer inorganic fillers, talc and mica are of maximum interest. There have been also recent advances in polymer/clay and polymer-layered silicate nano-composite materials in recent times [6, 7]. Clay, in particular montmorillonite (MMT), a 2:1 phyllo-silicate as illustrated in Figure 4A, naturally occurs as stacks of platelets as in talc and mica but possesses different layer charge. This leads to isomorphic substitution within layers (e.g. Al^{3+} is replaced by Fe^{2+}or Mg^{2+}) and generates a negative charge exchange capacity (CEC) and for MMT. The replacement of inorganic exchange cations with organic ions on the gallery surfaces of clays not only serves to match the clay surface polarity with the polarity of the polymer, but it also expands the clay galleries. Each platelet is less than 10 nm thick, but over 200 times more in width. The gallery spacing separates each platelet. These spaces in MMT can be enhanced to 20-30nm using quaternary ammonium salts. This facilitates the penetration of the gallery space by intercalation or exfoliation of either the polymer precursor or preformed polymer. If the extended chains are inserted in the self-assembled, well ordered gallery spaces, it is termed as intercalated structure as illustrated in Figure 4B. If the individual silicate layers are no longer close enough to interact with adjacent layers it is termed as delaminated or exfoliated structure as explained in Figure 4C [7,8,9].

Both of these hybrid structures can coexist. The enhancement in properties of polymer with modified MMT is mainly due to the clay which swells enormously in water and which in turn creates large surface area in which the polymer resides. Polymerization along with modified MMT resulted in the first synthesis of an exfoliated Nylon-6 polymer/clay nano-composite prepared in R&D Lab with just 5% (by weight) loading of clay. They reported 40% higher tensile strength, 68% higher tensile modulus, 60% higher flexural strength, 126% higher flexural modulus and increase of heat distortion temperature from 65^0 to 152^0.

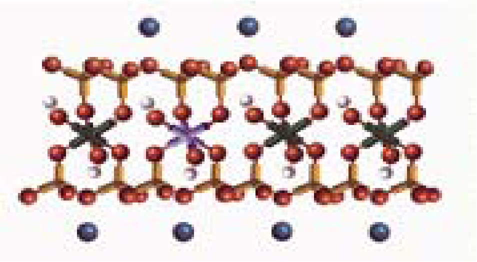


Figure 4A: MMT structure

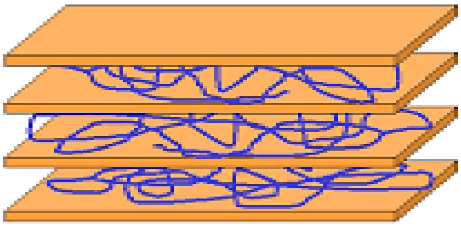


Figure 4B: Intercalated structure

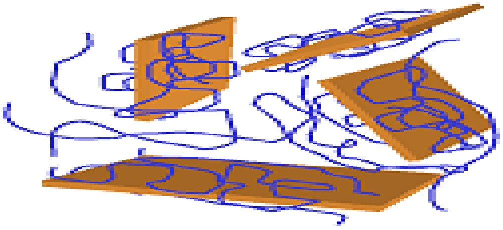


Figure 4C: Exfoliated structure

This nano-composite is being used commercially in making tough, heat resistant, nylon timing belt covers. Since then large number of new polymer/clay nano-composites have been developed like polyurethane, PVC, polyesters, polystyrene and polypropylene. The hydrophobicity or hydrophilicity of the polymer affects its dispersion in the clay layers leading to the exfoliated or intercalated structure.

Different methods using (Na + MMT) or OMMT (organically modified clay by surfactants) have been used to overcome this problem. The method of preparation of these polymer/clay nano-composites has to consider the extent of intercalation/exfoliation which determines the properties of the new-formed materials. Many methods have been developed to prepare polymer/clay nano-composites. In general, these methods (as shown in Figure 4D) achieve molecular level incorporation of the layered silicate (e.g. MMT-clay, or synthetic layered silicate) into the polymer by addition of a modified silicate during the polymerization (in situ polymerization). Several other methods like sonication, adsorption via sonication, extrusion and spin casting techniques have been also reported as better methods to prepare polymer/clay nano-composites. Additionally, a method has been developed to prepare the layered-silicate by polymerizing silicate precursors in the presence of a polymer. Most of the studies have been performed on polymers/polymer blends like polystyrene (PS), polypropylene (PP), epoxy resins, polyamides, PVC, PET, poly-siloxanes, polyesters, nitrile rubbers, polyurethanes etc.

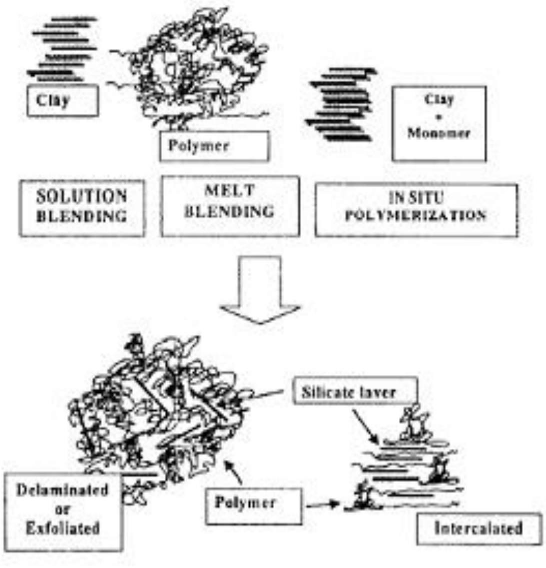


Figure 4D: Various methods used to prepare polymer layered-silicate nano-composites

Several methods like XRD, TEM, SEM etc to mention a few, determine the extent of the hybrid structure that is formed. Among them is X-ray diffraction technique (XRD), which determines the d001 spacing in the modified clay and provides information on the degree of hybrid structure generated.

Diffraction peaks in the low angle region indicate the d-spacing of ordered intercalated and ordered delaminated nano-composites: disordered nano-composites show no peak in this region due to the loss of structural registry of the layers and (or) the large d-spacing (> 10 nm). This can further be verified using the TEM analysis. TGA/DTA analysis is performed to ascertain the thermal stability [15-17].

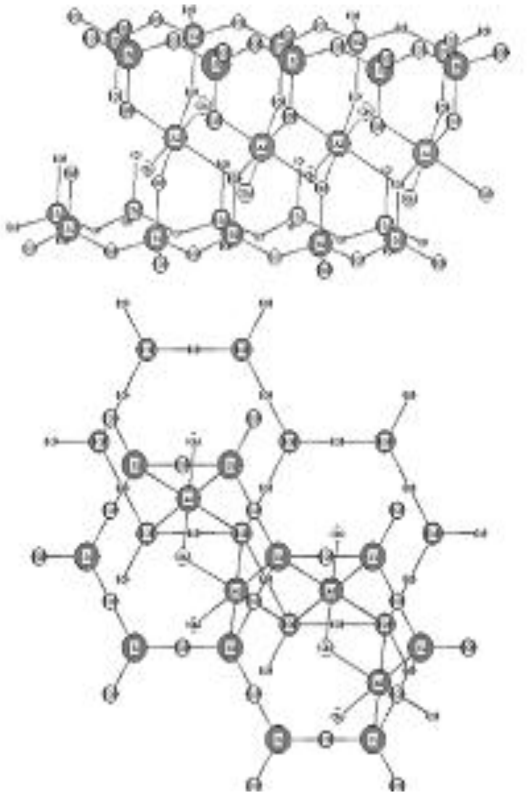


Figure 4E: Crystal structure of MMT; a) View along b-plane; b) View normal to ab-plane.

IV. CONCLUSION

New polymer-clay-nano-composites have been prepared by varying parameters; first by optimizing polymer to clay ratio and second by varying the processing techniques. An exploration in making the polymer-clay nano-composites with different clays, surfactants and polymers is a continuing research methodology. These novel materials have shown strong enhancement in the mechanical and thermal properties. For example, remarkable improvements in the stiffness and strength, increased dimensional stability, improved flame retardancy, improved solvent and UV resistance, and reduction in permeability of gases have been observed. Even hyper branched polymer/clay nano-composites have been synthesized and exhibit enhancement in their properties. Rheological properties of nano-structured polymer/clay nano-composites are strongly influenced by the morphology of the materials, which depends on the clay dispersion in the polymer matrix.

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