A PROJECT ON ADVANCED POLYMER NANOCOMPOSITES:SYNTHETIC AND NATURAL FILLERS

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CERTIFICATE

This is to certify that the project report entitled "ADVANCED POLYMER NANOCOMPOSITES:SYNTHETIC AND NATURAL FILLERS", submitted by SUMAN MISHRA , MRUTYUNJAY KUMAR RANA, GOUTAM KUMAR SAHOO, PARTHA SAHOO, SUBHASIS DAS, for the award of the degree of Bachelor of Science from NILAMANI MAHAVIDYALAYA, Rupsa, Balasore, Odisha, is a bonafide record of work carried out by him/her under my guidance. Neither this project report nor any part of it has been submitted for any degree or academic award elsewhere.

Basanta Kumar Pdhi.

(Signature of Guide)

ACKNOWLEDGEMENT

We would like to express our deepest appreciation to all those who provided me the possibility to complete this report. A special gratitude we give to our adorable Mr. Basanta Kumar Bhoi, H.O.D. department of the chemistry,NILAMANI MAHAVIDYALAYA, rupsa, balasore whose keen supervision and contribution in stimulating suggestions and encouragement,helped us to coordinate our project especially in writing this report.

We acknowledge, with highest sense of respect and regard to my parents, for their constant inspiration, moral support and necessary help throughout the study period.

Last but not least, many thanks go to all chemistry departmental staffs , whose have invested their full effort in guiding the team in achieving the goal , helped us to overcome all odds and improving our presentation skills , thanks to our comment and advices.

Despite all this co-operation generously by one and all , we are solely responsible for any and all the errors and shortcomings of this project.

ABSTRACT

The paper reviews current research, techniques for characterization and trends on the field of nanocomposites. Nanocomposites are new materials made with fillers which have nanosize. These materials have a big potential for application in the automotive and aerospace industry as well as in construction, electrical application and food packing. There is a tremendous interest for using bio-nanoparticles like cellulose microfibrils or whiskers to be applied in the new era of biocomposites.

CHAPTER-1

INTRODUCTION

INTRODUCTION

.1 Composite

A "composite" is when two or more different materials together to create a superior and unique material. This is an extremely broad definition that holds true for all composites, however, more recently the term composite describes reinforced plastics.

- Composite is something in which at least one of the phase has at least one dimension of the order of nanometers (The definition of term is related to polymer blends, composites and multiphase polymer).
- Multiphase solid materials where one of the phase has one, two or three dimensions of less than 100 nanometers (nm) or structures having nano-scale repeat distances between the different phase that make up the materials.
- In the broadest sense this definition can includes porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phases differing in properties due to dissimilarities in structure and chemistry.

1.1.1 Examples of Composites:- The most common example of a composite in a broad sense is concrete. In this use , structural steel rebar provides the strength and stiffness to the concrete, while the cured cement holds the rebar stationary . Rebar alone would flex too much and cement alone would crack easily.However, when combined to form a composite, an extremely rigid material is created. The composite material is most commonly associated with the term "composite" is Fiber Reinforced Plastics. This type of composite is used extensively throughout our daily lives.

1.1.2 Common Uses

- Aircraft
- Boats and marine
- Sporting equipment
- (Golf shafts, tennis rackets, surfboards, hokey sticks, etc.)
- Wind turbine blades
- Body arBulding materials
- Water pipes
- Bridges
- Tool handles
- Ladder rails

1.1.3 Benefit of Composites

- In comparison to common materials used today such as metal and wood, composites can provide a distinct advantage. The primary driver and advantage in the adoption of composite is the lightweight properties. In transaction, less weight equipment, lightweight composites allow for longer drives in golf, faster swing in tennis, and straighter shots in archery. While in wind energy, the less a blade weighs, the more power the turbine can produce.

  Besides weight saving, the most important benefits of composites include:
- Non-corrosive
- Non-conductive

- Flexible, will not dent
- Low maintenance
- Long life
- Design flexibility

1.2 Nanocomposite

Nanocomposites are a subset of composites that advantage of unique materials properties on the small scale . At nGimatTm, we use proprietary NanoSpraySM and |Combution Chemical Vapor Condensation (CCVC) processes to produce polymer matrix/ metal or ceramic nanoparticle nano- composite coatings.

The particles with small sixe in the range from a few to several tens of nanometers are called quasi zero – dimensionalmesoscopic system associated with quantum dots, quantixed Or Qparticles, etc (Sharma, et.al, 2004) . According to Jordon et. Al (2004) the nano- sixed are defined as those that have at least one dimension in the range ! to 100nm. Nanotechnology is now recognized asa one of the most promising areas for technological development in the 21st century. In materials research, the development of polumer nanocomposites is rapidly emerging as a multidisciplinary research activity whose results could broden the applications of polymers to the great benefit many different industries. |The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite woll differ markedly from that of the component materials. Size limits for these effects have been proposed, <5nm for catalytic activity, <20nm form making a hard magnetic material soft, <50nm for refractive index changes, and <100nm for achieving superparamagnetism, mechanical strenghthening r restricting matrix dislocation movemet.

Structure of as prepared layered Silicate Nanocomposite

1.3 Polymeric nanocomposite

Plymer nanocomposites (PNC) are polymers (thermoplastics, thermosets or elastomers) that have been reinforced with small quantities (less than 5% by weight) of nano –sized particles having high aspect ratios (L/h>300) (Denault and Labreque, 2004) Figure No 1 shows a classical layered silicate nanocomposites. PNCs represent a radical alternative to conventional filled polymers or polymer blends – a staple of the modern plastics industry. In contrast to conventional composites, where the reinforcement is on the order of microns, PNCs are exemplified by dicrete constituents on the order of a few nanometers. The value of PNC technology is not solely based on the mechanical enhancement of the neat resin nor the direct replacement of current filler or blend technology. Rather, its importance comes from providing value- added properties not present in the neat resin, without sacrificing the resin's inherent processibility and mechanical properties ,or by adding excessive weight. PNCs contain substantially less filler (1-5 vol %) and thus enabling greater retention of the inherent processibility and toughness of the neat resin (Vaia and Wagner, 2004)

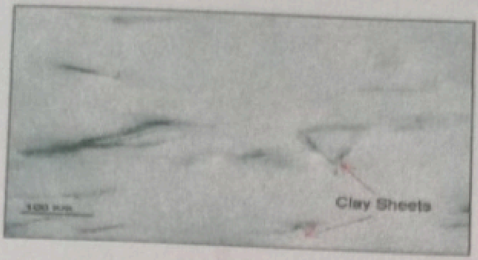


Figure N°1: *Transmission electron microscopy (TEM) of a polymer/layered silicate nanocomposites prepared in a twin screw extruder.*

Polymer nanocomposites, I especially polymer layered silicate nanocomposites, 2 represent a radical alternative to conventionally (macropically) filled polymers. Because of their nanometer – size dispersion, the canocomposites exhibit markedly improved properties when compared with the pure polymers conventional composites. These includes increased modululs and strength, decreased gas permeability, increased solvent and heat resistance and decreased flammability. For example, a doubling of the tensie modulus and strength is achieved for nylon- layered silicate nanocomposites increases by up to 100 C , extending their use to higher- temperature environments, such as automotive under-the – hood parts. 3 furthermore, the heat release rate in the nanocomposites in reduced by up to 63% at heat fluxes of 50 kW m-2 without an increase in the CO and soot produced during combustion.

There are three main material constituents in any composite: the matrix, the reinforcement (fiber), and the so-called interfacial region. The interfacial region is responsible for communication between the matrix and filler and in conventionally ascribed properties different from the bulk matrix because of its proximity to the surface of the filler (Vaia and Wagner, 2004)

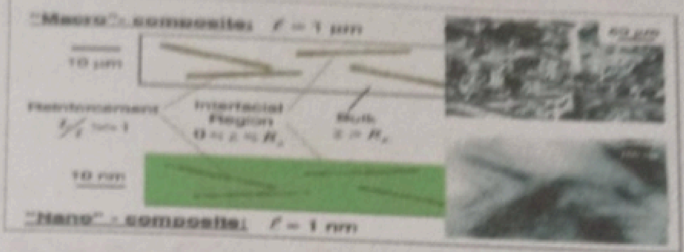


Fig no-2

Fig no-2 represents:

Schematic comparison of a macro-composite containing 1µm×25µm(×L)fibers in an amorphous matrix to that of a nano-composites at the same volume fraction of filler, but containing 1 nm x 25nm fibers. Constituents in any composite: the matrix (white), the reinforcement (fiber, red) and the so called interfacial region (green) .Scanning electron micrograph shows E-glass reinforced polyolefin(15µm fiber) and transmission electron micrograph shows montmorillonite- epoxy nanocomposite (1nm thick layers.)

1.4 Significance of synthetic and natural fillers

Polymer matrix composites are a promising candidate in tribological applications due to possibility of tailoring their properties with special fillers. The comparative performance of Glass-Epoxy(G-E) composites with influence of synthetic fillers such as graphite(Gr) and silicon carbide(sic) and biobased natural fillers jatropha oil cake(JOC) was experimentally investigated. All the composites were fabricated using-assisted resin infusion (VARI)technique. The mechanical properties were studied in accordance with ASTM standards. The three-body abrasive wear studies were carried out with rubber wheel abrasion tester as per ASTM-G65 standard. Two different loads namely 22 N and 32 n ith different abrading distances viz. 135, 270 ,405 and 540 m are test parameters. The results reveal that addition of JOC in G-E composites has significant influence on wear under varied abrading distance/load. Further, it was found that Sic filled G-E composites exhibited better wear resistance compared to Gr/JOC filled G-E composites. The operating wear mechanisms have been studied by using scanning electron microscopy.

1.5 TYPES OF POLYMER NANOCOMPOSITES

Polymer/layered nanocomposites in general, can be classified into three different types, namely

I. Flocculated nanocomposites,
II. Exfoliated nanocomposites
III. Intercalated nanocomposites

1.6 MISCIBILITY / THERMODYNAMICS OF NANOCOMPOSITE FORMATION

Similarly to polymer blends, any mixture of polymer and layered silicate does not necessarily lead to a nanocomposite. In most the incompatibility of the hydrophobic polymer and the hydrophilic silicate leads to phase separation similar to that of macroscopically filled system. In contrast, by using surface- modified silicate, as noted earlier, one can fine-tune their surface energy and render them miscible (or compatible) with different polymers. The approach is based on a chemical(rather than a mechanical) driving force which leads to nanoscopic dispersion. What is then the driving force for polymer intercalation which leads to nanodispersion? To answer this question we have developed recently mean field model . Nanocomposites are formed if the free energy change, ΔG, of the process negative.

The change in free energy is composed of an enthalpic term, ΔH due to the intermolecular interactions and an entropic term. ΔS associated with the configurationally changes of the constituents, and $\Delta G = \Delta h - T\Delta S$, where T is the temperature. The entropy change of the organically modified inorganic component is calculated using a modified Flory- Huggins lattice model in which transmission electron micrographs of a polystyrene intercalated nanocomposite and an epoxy delaminated nanocomposite. The confinement of the polymer chains is similarly approximated using a self-consistent field treatment of a random- flight polymer between two surfaces.

CHAPTER-2

LITERATURE SURVEY

LITERATURE SURVEY

W Gachitua, A Ballerini, J Zhang- Maderas. Ciencia y technology, 2005-scielo. Conicyt.cl

This paper reviews current research, techniques for characterization and trends on the field of nanocomposites.

IL Ngo, S Jeon, C Byon- International journal of heat and mass transfer, 2016-Elsevier

It was found from the literature review that carbon- based fillers, particularly multi-walled carbon nanotubes, and ceramic fillers have been considered as the most promising filler.

MZ Rong, MQ Zhang, WH Ruhan- Materials science and...,2006-Taylor & Francis

This review is represented on the surface modification of nanoparticles.

K Prabhakar, S Debnath, R Ganesan...-IOP Conference...,2018-iopscience.iop.org

This review is weight of filler content to determine the tribiological (friction and wear) behavior of the polymer composite.

CHAPTER-3

TECHNICAL CONTRIBUTION-1

2. TECHNICAL CONTRIBUTION-1

2.1 TECHNIQUES FOR CHARACTERIZATION

The vigorous development of polymeric science and extensive utilization of polymeric material 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 investigation dealing with materials . 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. Characterization, therefore, describes 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 visits in solid state materials.

Experimental techniques used for the characterization of nanocomposites include NMR for materials behavior (giving greater insight into the morphology, surface chemistry, and to a very limited extent the quantification of the level of exfoliation in polymer nanocomposites), X-ray diffraction (due to ease and availability), transmission electron microscopy (TEM- allows a qualitative understanding of the internal structure, spatial distribution of the various phase, and direct visualization of defect structure), differential scanning calorimetry (DSC- to understand the nature of crystallization taking place in the matrix), FTIR(to detect functional groups and understand the structure of the nanocomposites), dynamic mechanical analysis (DMA- response of a material to oscillatory deformation as a function of temperature, giving storage modulus [corresponds to elastic response to deformation], loss modulus [correspons to plastic response to deformation], and $\tan^{\delta}$ [ratia of the previous two and an indicator of occurrence of molecular mobility transitions]), and resonance Raman spectroscopy(for structural studies).Among the several characterization techniques, X-ray diffraction (XRD), scanning electron micrography (SEM) infrared (IR) spectroscopy are taken into the account.

2.1.1 X-ray Diffraction

x-ray diffraction has played a central 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 order of crystalline arrangements from the amorophous substances are largely derived from X-ray diffraction and thus it remains as a useful tool to obtain structural information-ray diffraction pattern of amorophous polymer will not show any sharp and highly intensed peaks whereas the nanocomposites of amorophous polymer show sharp and highly intensed peaks. This is due to the development of crystallinity in the amorophous polymer.Figures-2(a-b) shows the XRD pattern of pure natural rubber and ϒ-Fe_2O_3 dispersed natural rubber composite . Highly intensed peaks occour 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 .

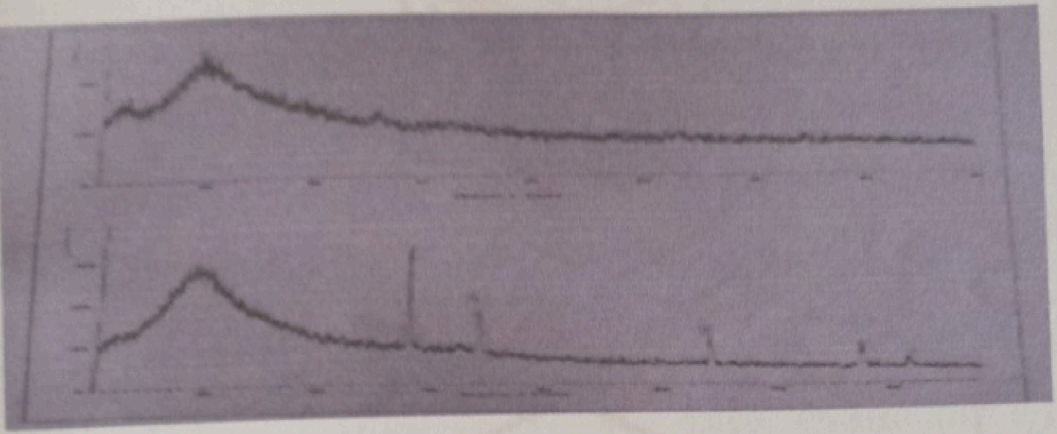


Figure 2. XRD pattern of (a) pure natural rubber (b) ϒ-Fe_2O_3

Dispersed natural rubber

2.1.2 Scanning Electron Micrograph

Structural phenomena play an important role in determining the properties of a polymer. Mechanical properties re determined not only by the changes in shape confirmation and by motion of individual molecules of the polymers, but by the behavior of large 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. Despite the complex morphology of structural formation in polymers it should not be forgotten that all these structures are built up of separate polymeric molecules. 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 very within wide limits when studying the simplest phenomenon of structures 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 .Evidently in majority of cases , they aggregate into chain bunches usually containing several dozen molecules. The phenomenon of structural transformations occouring during deformation is very typical of polymers.

A classic example of structural transformation is the formation of a 'neck' on deformation, described for the case of crystalline polymers some time ago by Kakina . 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 obscure for a long time, but electron microscopy revealed that neck formation 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-know example is that of 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 discemed between the unchanged and oriented portions of a spherulite. In addition, secondary formations can be see which have resulted from recrystallisation of the oriented parts, and these are also separated by sharp boundary lines.

2.1.3 Infrared spectroscopy

Infrared spectroscopy is one of the most powerful analytical the shape of most polymer molecules may vary within wide limits when studying the simplest phenomenon of structure formation. The phenomenon of structural transformations occuring during deformation is very typical of polymers. Techniques, which offers the possibility of chemical identification. This technique when coupled with intensity measurements may be used for quantitative analysis. One of the important advantages of infrared spectroscopy over the other usual methods of structural analysis (X-ray, diffraction, electron spin resonance, etc) is that it provides information about the structure of molecule quickly, without tiresome evaluation methods. This method can solve many problems in organic chemistry (polymeric materials) and cooridination chemistry, and also advantageously complements the results obtained by other methods. This technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region giving rise to close- packed absorption bands called an IR absorption spectrum, over a wide wavelength range. Various bands will be present in the IR spectrum, which will correspond to the characteristic functional groups and bonds present in a chemical substance. Thus an IR spectrum of a chemical substance is a fingerprint for its identification. IR spectrum of polymer nanocomposite shows the presence of both nanomaterials and polymers (depending upon the polymer chain) at various frequencies.

2.2 Importance of Thermo gravimetric Analysis and Z-Ray diffraction for filler and Nanocomposite Microstructure Characterization

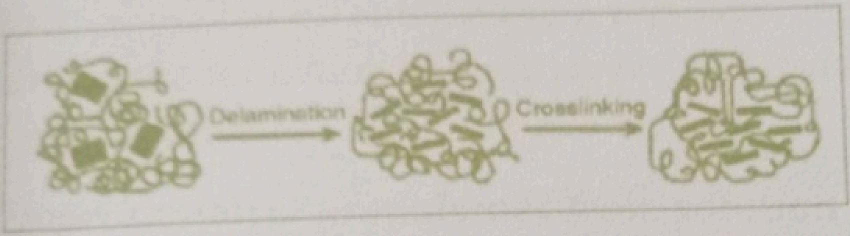
Both, XRD and TGA, are important techniques used to characterize the microstructure of nanocomposites. In general, TGA is used to assess the amount organic matter exchanged on the clay surface during the surface modification process. High – resolution TGA can also be used to ascertain if there is presence of any excess of surface modification molecules present as a pseudo bilayer, but unbound to the surface. XRD is also used quantify increases I basal plane spacing in the filler following surface modification, and also after composite generation. The increased basal plane spacing that occurs after surface exchange leads to information regarding the possible alignment of the modification molecules inside the clay interlayers , whereas the presence and absence of diffraction peaks in the composites used to provide information concerning the microstructure of the composites. Although XRD also provides information relation to the amount of organic matter present in the clay interlayers, it cannot provide information on the excess of surface modification molecules present on the clay surface, as does TGA. Information relating to excess modification is very important especially when the filler must compounded with the polymer at high temperature as any free modification present on the surface would have a much lower thermal degradation temperature and may impact negatively on the composite's properties. Figure 1.3 shows a comparison of the XRD and TGA of the fillers, which were modified with octadecyltrimethylammonium, dioctadecyldimethylammonium and trioctadecylmethylammonium. The modification differed in terms of the increasing number of octadecyl chains in the molecule. As shown in Figure 1.3 a the basal plane spacing of the filler increased as the chain density in the molecule increased .The cation-exchange capacity (CEC) of the clay also has a major impact on the basal plane spacing of the filler, with a low-CEC filler generally having a lower basal plane spacing as compared to a high- CEC counterpart. The fillers in Figure 1.3 a had CEC – values of 680 and 880μEqg^{-1} .Figure 1.3 b shows the TGA thermograms of the same fillers modified with the above-mentioned surface modifications, and using MMT with a CEC of 880μEqg^{-1} . The increased amount of organic matter was clearly visible in the TGA thermograms when the chain density was increased in accordance with the increase on basal plane spacing in the XRD. Yet , the TGA thermograms can provide additional information on the state of surface of the MMTs, with those of the trioctadecylmethylammonium- modified MMT showing a sharp degradation peak at low temperature. This effect is due to a small amount of the ammounium modification being present as a pseudo-bilayer, and not bound ironically to the clay surface. As noted above, these molecules degrade at much lower temperatures than those which bind ironically to the clay surface; however such information cannot be obtained from the X-ray diffractograms. Thus, it is very important to quantify the state to the filler surface by using a combination of high -resolution TGA and XRD.

2.3 PROCESSING CONDITIONS

The traditional routes to prepare nanocompositess using layered compounds as reinforcement, especially days, can be summarized as follows.

2.3.1 Exfoliation/adsorption

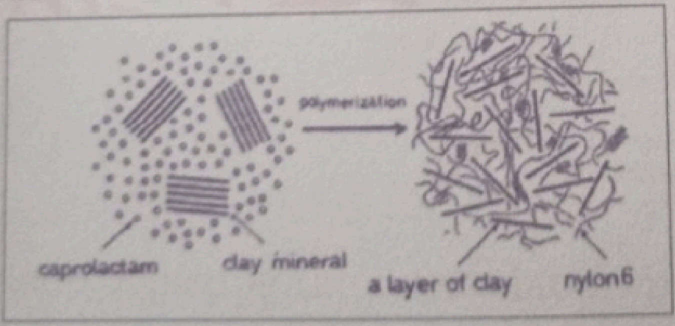
First the layered host is exfoliated in a solvent, in which the polymer is soluble (water, toluene, etc). the polymer is adsorbed onto the single layer surfaces and after evaporation of the solvent or a precipitation procedure, the single layers are restacked, trapping the polymers and the hydrated/ solvated ionic species.



(Schematic illustration of nanocomposite synthesis)

2.3.2 In situ intercalative polymerization

Polymer is formed (initiation of polymerization by heating or radiation or by diffusion) between the layers by swelling the layer hosts within the liquid monomer or monomer solution.



(Schematic illustration for synthesis of Nylon-6/clay nanocomposites)

2.3.3 Melt intercalation

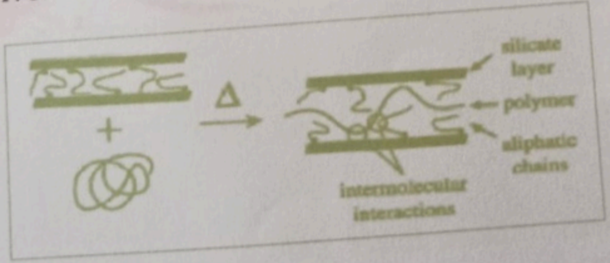
This method an environmentally benign one, uses all types of polymers as well as being compatible with practicing polymer industrial processes such as injection molding being the most popular to prepare nanocomposites for industrial applications. In this method polymers, and layered hosts are annealed above the softening point of the polymer.

2.3.4 Template synthesis :-

In situ layered double hydroxide (LDH) based nanocomposites can be obtained in a template of polymer aqueous solution for the formation of host layers and usually employed for water soluble polymers.

2.3.5 intercalation of prepolymer from solution

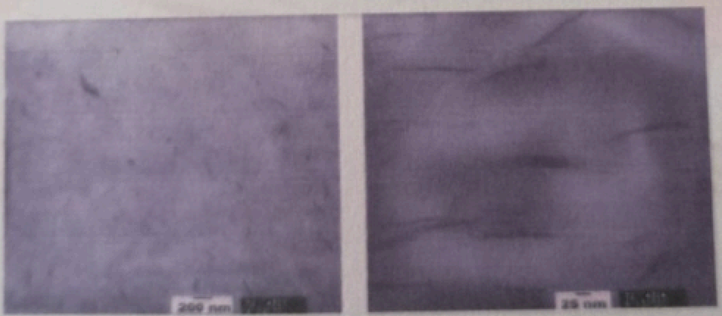
The layered host is to be swelled in a solvent (water ,toluene ,etc) followed by its mixture with polymer or prepolymer, whereby the chains of the latter intercalate while displacing the solvents used for swelling. Polymer layered nanocomposite results when the solvent within the interlayer is removed.



(Schematic depicting the intercalation process between a polymer melt and an organic modified layered silicate.)

2.4 FORMULATIONS AND FUNCTIONS

Experimentally polypropylene(PP) nanocomposites was prepared and characterized by Ellis and D' Angelo in 2003, containing approximately 4 wt % of an organophilic montmorillonite clay, and their properties were compared with of tale- filled (20-40 wt%) compositions. They found that it is possible to reduce weight maintaining or even improved flexural and tensil modulus, especially at temperature up to 70 c . Also TEM" micrographs shown in Figure N 8 also support the inference of an intercalated PP nanocomposites rather than a fully exfoliated nanocomposite. The micrographs indicate a well-dispersed morphology with incomplete exfoliated nanocomposite. The classical view of fiber reinforced composites implies that strong fiber-matrix interfaces lead to high composite stiffness and strength, but also to low composite toughness because of the brittleness of the fiber and the absence of crack deflection at the interface. Vice versa, composites with weak interfaces usually have relatively low stiffness and strength, but higher toughness. One of the most difficult problem in the physics of polymer nanocomposites is the measurement of the extent and efficiency of stress transfer through the interface between nanoparticles and matrix.



(TEM micrographs of the pp nanocomposites)

It is a general knowledge that the larger is there is their internal surface and hence their tendency to agglomerate rather than to disperse homogeneously is a matrix. Also , the contact surface in such dispersion between the elements and matrix material grows dramatically band consequently the problems in creating an intense unteraction at his interfaction at this interface (Fischer, 2003). Fischer reported that an agglomeration of the clay platelets in the organic- inorganic hybrid coatings did not occure up to an amount of 20 wt % based on the solid content of the coating materials; the nanocomposites coatings of organic and organic – inorganic hybrids remained transparent up to an amount of 15 wt % of clay.

A homogeneous dispersion of the clay platelets (5.0 wt % based on solid coating material) in an organic-inorganic hybrid coating was observed using . TEM . Current micromechanics theories rely on the idea that the effective properties of composite materials, such as Young's modulus, are functions of properties of constituents, volume fraction of components, shape and arrangement of inclusions, and matrix-inclusion interface. These theories, therefore, predict that the properties of composite materials are independent of the size of inclusions. In general, this is correct for systems with micron size reinforcement, but ,as mentioned above may not be true for nanocomposite systems.

CHAPTER-4

TECHNICAL CONTRIBUTION-2

3. TECHNICAL CONTRIBUTION-2

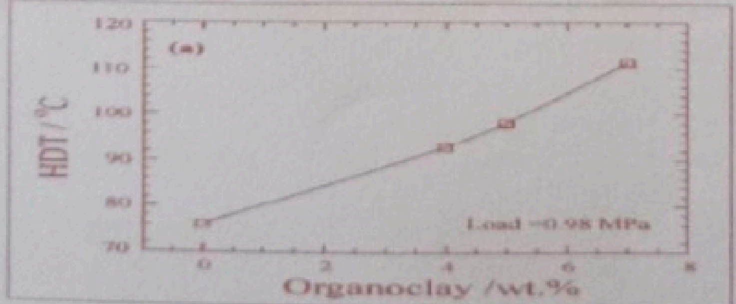
Current research

Jordon et al. in 2005 reported result of composites with polypropylene matrix and calcium carbonate (caco3) nano particles. In their system the CaCO3 inclusions had an average sixe of 44 nm and a strong interaction with the polymer matrix. The addition of Caco3 nano particles to a PP matrix produced an increase in the elastic modules compared to the pure matrix. The increase in modulus coincided with an increase in nano particles volume fraction.

Clay- reinforced nanocomposites have received considerable attention in recent years (more than 100 articles have been published in the literature on clay composites in the past three years). A number of polymers, such as PC , PAN, PP, etc were used as the matrix. Shelley et al. in 2001 examined a Polymide-6 system with clay platelets. The platelets constituted 2% and 5% weight fraction and were 1 nm×10nm×10nm in size. Good interaction was found between the matrix and inclusions. With this setup, the elastic modulus was found to improve for both the 2%and 5% samples. For the smaller Weight fraction(2%), the increase in effective elastic modules was 440% over the modulus of the pure polymer system. The larger weight fraction (5%) improved the effective modulus by a factor of two as compared to that of pure polymer. These results were for tensile specimens cut in both longitudinal and transverse directions. In addition, the yield stress also improved for both weight fractions, with the greatest improvement found for the higher concentration of inclusions. The other property studied was the strain-to-failure. The 2% system was found to give higher strain-to –failure than the pure system in the longitudinal direction but close to that in the pure system in the transverse directions. The higher filler content resulted in a decline in strain-to-failure from the pure system in both directions.

From the above discussion, it is possible to extract a few trends for the behavior of polymer matrix nanocomposites based on the nature of the polymer matrix, particularly crystalline or amorphous nature of the polymer, and the interaction between the filler and matrix. The elastic modulus tends to increase with the volume fraction of inclusions in every case. In some systems, there is a critical volume fraction at which aggregation occurs and the modulus goes down. In general, there is also an increase in modulus as the size of the particle decreases. Interaction between matrix and filler may play an important role in the effects of the nanoparticles on composite properties. The overall trend of the modulus of polymer nanocomposites is not found to be greatly dependent upon the nature of the matrix nor the interaction between filler and matrix. An examination with good interaction between filler and matrix, the yield stress tends to increase with increasing volume fraction and decreasing particle size, similarly to the increase in modulus under same conditions. The pattern changes when there is poor interaction between the matrix and particles. The addition of nanoparticles with poor interaction with the matrix causes the yield stress to decrease, compared to the neat matrix, regardless of the fuller concentration or size. The ultimate stress follows a similar pattern as that observed for the yield stress. It generally increases in general as particle size decreases. There is no uniform trend with respect to the volume fraction of particles for the ultimate stress. A poor filler-matrix interaction leads to a decrease in the ultimate and yield stress as compared to the pure matrix system (Jordon et. Al, 2005). Jordon et. Al in 2005 state that in general, viscoelestic properties tend to be higher in nanocomposites than in pure polymer systems. When there is good filler-matrix interaction, the storage modulus generally increases with increasing volume fraction. |The modulus also seems to increase as the particles size decreases. However, there is little experimental work in this area for composites with poor filler-matrix interaction. Overall, the storage modulus tends to increase with the presence of nanoparticles in a composite system. Morphological details, such as exfoliation, intercalation, or cross-linked matrix versus uncross-linked matrix, have a significant effect on the viscoelastic properties of nanocomposites.

RAY AND Okamoto in 2003 presented a brief discussion about heat distribution temperature (HDT) of nanocomposites. HDT of a polymeric material is an index of heat resistance towards applied load. Most of the nanocomposite studies report HDT as a function of clay content , characterized by the procedure gives in ASTM D-648 (see figure N°13). Ray and Okamoto state that increasing HDT due to clay dispersion is a very important property improvement for any polymeric material, not only from application or industrial point of view, but also because it is very difficult to achieve similar HDT enhancements by chemical modification or reinforcement by conventional filler.

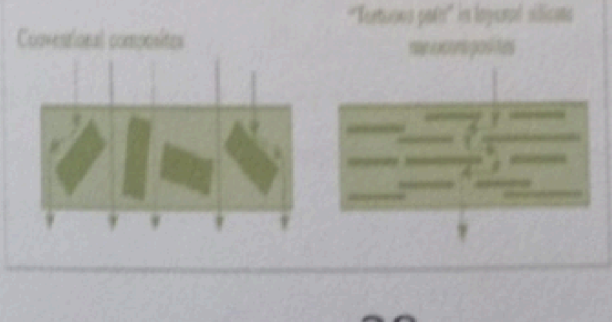


Organoclay (wt %) dependence of HDT (Ray and Okamoto,2003)

Tidjani in 2005 found a dramatic reduction in peak heat release rate for the nanaocomposites compared to pure polypropylene-graft-maleic anhydride and is hybrid. He states that the improved flammability happens in the condensed phase and is not likely to be due to a higher thermal stability of the nanocomposite. The impermeability of the silicate layers in the polymer , which reduced the diffusion of gases in the nanocomposites, may participate in the reduction of the flammability.

Using an intercalated thermoplastic polyolefin(TPO)/ organically nanocomposite with maleic anhydride functionalized pp as a compatibilizer , Mishra et al. in 2005, established that the compatibilizer not only enhances the intercalation of the polymer chain inside the clay gallery but also changes the thermoplastic elastomer composition (which is very important for end use application) of the TPO/clay nanocomposite. The tensile modulus as well as storage modulus of TPO/organoclay nanocomposite was substantially higher over a 20% talc based microcomposite.

From the point of view of gas barrier properties , nanocomposites offer interesting features. Ray and Okamoto in 2003 proposed that clays increase te barrier properties by creating a maze or "tortuous path"(see figure N°1.6) that retards the progress of the gas molecules through the matrix resin.



Fig(1.6): Formation of tortuous path in polymer layered silicate nanocomposites

In the field of nanocomposites using carbon nanotubes(CNTs),it has already been established that CNTs possess remarkable properties. Nowadays , the main challenge is to be able to implement these properties in composites on a macroscale, combining the choice of materials with the appropriate processing method. Table N°2 shows a comparison between CNTs composite and polypropylene matrix.

Properties Of Fibers From Polypropylene(PP) and PP/CNT Composites

Sample	Tensile strength (MPa)	Tensile Modulus (GPa)	Elongation to break(%)	Compressive strength (MPa)
PP control	490±60	4.6±0.7	23±5	25±1
PP/5wt% nano carbon fiber	570±70	7.1±0.9	16±2	48±10

Studies about photodegradation of nanocomposites found that photo-oxidation at long wavelengths of polypropylene-based nanocomposites produces the same photoproducts as those of the pristine polypropylene and in the same quantities. The maleic anhydride grafted PP used as compatibilizer and the organically modified nanoclay do not significantly modify the rate of the samples. However , the efficiency of additivies is considerably reduced. This could result from the location of the additivies close to the organoclay due to the spreading of these polar species onto the hydrophilic nanoplatelets.

CHAPTER-5

CONCLUSIONS

AND

FUTURE WORKS

4.CONCLUSIONS AND FUTURE WORKS

Novel polymer/clay nanocomposites can be prepared by varying two parameters; first by optimizing polymer to clay ratio and second by varying the processing techniques. An exploration in making the polymer/clay nanocomposites with different clays, surfactants and polymer is continuing subject of research and interest to both academia and industry. Significant research is needed to figure out the behavior of nano-interfaces, and this field can still be considered to be in its beginnings. In particular the development of accurate nanomechanical models, and understanding of the properties of the polymer at the interface are required to address the outstanding issues of the polymer nanocomposites. It is believed that one of the main issues in preparing good polymer matrix nanocomposite samples is the good dispersion of the nanoparticles in a polymer matrix . nanoparticles obtained from wood cell offer a great potential to make nanocomposites with biodegradable characteristics.

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6. BIBLIOGRAPHY

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