Polymer Nanocomposites

Arunkumar Lagashetty and A Venkataraman

The synthesis of polymer nanocomposites is an integral aspect of polymer nanotechnology. By inserting the nanometric inorganic compounds, the properties of polymers improve and hence this has a lot of applications depending upon the inorganic material present in the polymers. Solvent casting is one of the easiest and less time consuming methods for the synthesis of polymer nanocomposites. In this article we present different types of polymer composites, methods of synthesis, characterisation techniques and different applications of polymer composites.

Polymer nanocomposites are materials in which nanoscopic inorganic particles, typically 10-100 Å in at least one dimension, are dispersed in an organic polymer matrix in order to dramatically improve the performance properties of the polymer. Systems in which the inorganic particles are the individual layers of a lamellar compound – most typically a smectite clay or nanocomposites of a polymer (such as nylon) embedded among layers of silicates – exhibit dramatically altered physical properties relative to the pristine polymer (see *Box* 1 on p.58). For instance, the layer orientation, polymer-silicate nanocomposites exhibit stiffness, strength and dimensional stability in two dimensions (rather than one). Due to nanometer length scale which minimizes scattering of light, nanocomposites are usually transparent.

Polymer nanocomposites represent a new alternative to conventionally filled polymers. Because of their nanometer sizes, filler dispersion nanocomposites exhibit markedly improved properties when compared to the pure polymers or their traditional composites. These include increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability.

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Polymers that contain transition metal complexes either attached to or directly in a π-conjugated backbone are an exciting and a promising class of modern materials. These macromolecules are hybrid of π-conjugated organic and transition metal-containing polymers. π-conjugated organic polymers, such as polyacetylene, polythiophene, 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, electrocatalysis, batteries, smart windows and memory devices.

Layered silicate/polymer nanocomposites exhibit superior mechanical characteristics (e.g. 40% increase of room temperature tensile strength), heat resistance (e.g. 100% increase in the heat distortion temperature) and chemical resistance (e.g. ~10 fold decrease in O_2 and H_2O permeability) compared to the neat or traditionally filled resins. These property improvements result from only a 0.1-10 vol. % addition of the dispersed nanophase. Polyimide-clay hybrids represent another example of polymer nanocomposites. These nanocomposites have been prepared by intercalation of the organoclay with a polyamic acid. The clay-polyimide hybrid composite films exhibit greatly improved CO_2 barrier properties at low clay content; less than 8.0 vol. % clay results in almost a ten-fold decrease in permeability. Adding nanoscale ceramic powders to commercial products can produce another class of polymer nanocomposites. The addition of reinforcing agents is widely used in the production of commodities (packaging films and tyres). It is expected that the reduction of the added particle size down to nanometric 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) and in the production of barrier plastic film for food industry. Besides

structural applications, polymer nanoparticle compounds have very interesting functional applications. For instance, γ-Fe_2O_3/ polymer nanocomposites are used as advanced toner materials for high quality colour copiers and printers and as contrast agents in NMR analysis, memory devices. The key to forming such novel materials is understanding and manipulating the guest-host 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 and added particle surfaces. There have been major advances in solid state and materials chemistry in the last two decades and the subject is growing rapidly.

The coatings of magnetic particles are of special interest because of their important applications viz. technological energy transformation, magnetic recording, magnetic fluids and magnetic refrigeration system. Polymer materials have been 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, 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 particles consisting of polymer cores covered with shells of different chemical composition. In several of these powders, particles covered with magnetic materials have been used as beads for gas separation, or as pigments, catalysts, coatings, flocculents, toners, raw materials recovery, drug delivery and anticorrosion protection.

Polymer composites containing ferrites are increasingly replacing conventional ceramic magnetic materials because of their mouldability and reduction in cost. They are also potential materials for microwave absorbers, sensors and other aerospace applications. These flexible magnets or rubber ferrite composites are possible by the incorporation of magnetic powders in

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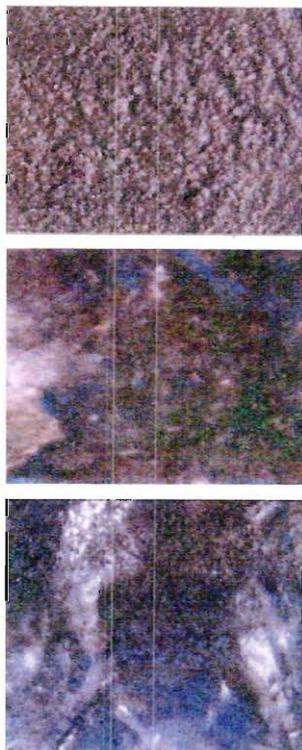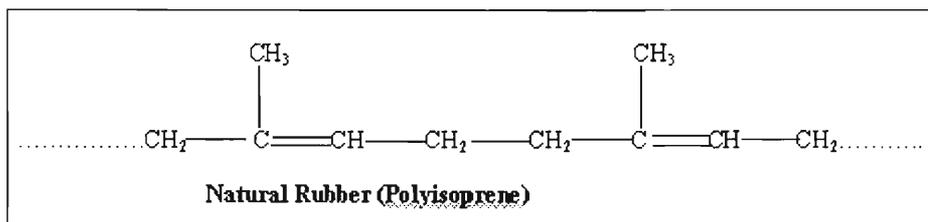
Figure 1. Optical micrograph images of γ-Fe$_2$O$_3$ dispersed (a) natural rubber. (b) polyethylene glycol (c) polycarbonate composite films.

Figure 1(d) Structure of natural rubber. (polyisoprene).

various elastomer matrices. This modifies the physical properties of the polymer matrix considerably.

Solvent casting method is one of the easiest methods for the preparation of polymer nanocomposites. It needs simple equipment and is less time consuming. *Figures* 1 (a-c) show the optical micrograph images of γ-Fe$_2$O$_3$ dispersed natural rubber (γ-Fe$_2$O$_3$-NR), γ-Fe$_2$O$_3$ dispersed polyethylene glycol (γ-Fe$_2$O$_3$-PEG) and γ-Fe$_2$O$_3$ dispersed polycarbonate(γ-Fe$_2$O$_3$-PC), nanocomposite 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 (natural rubber).

Characterization

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. 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 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 structure elucidation, have been stupendous and have opened new vistas in solid state materials. Among the several characterization techniques, X-ray diffraction (XRD), scanning electron

Natural Rubber (Polyisoprene)

micrography (SEM) and infrared (IR) spectroscopy are the three important techniques.

X-ray Diffraction

X-ray diffraction[1] 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 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 nanocomposites of amorphous polymer show sharp and highly intensed peaks. This is due to the development of crystallinity in the amorphous polymer. *Figures* 2(a-b) show the XRD pattern of pure natural rubber and γ-Fe_2O_3 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.

Scanning Electron Micrograph

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

Figure 2. XRD pattern of (a) pure natural rubber (b) γ-Fe_2O_3 dispersed natural rubber.
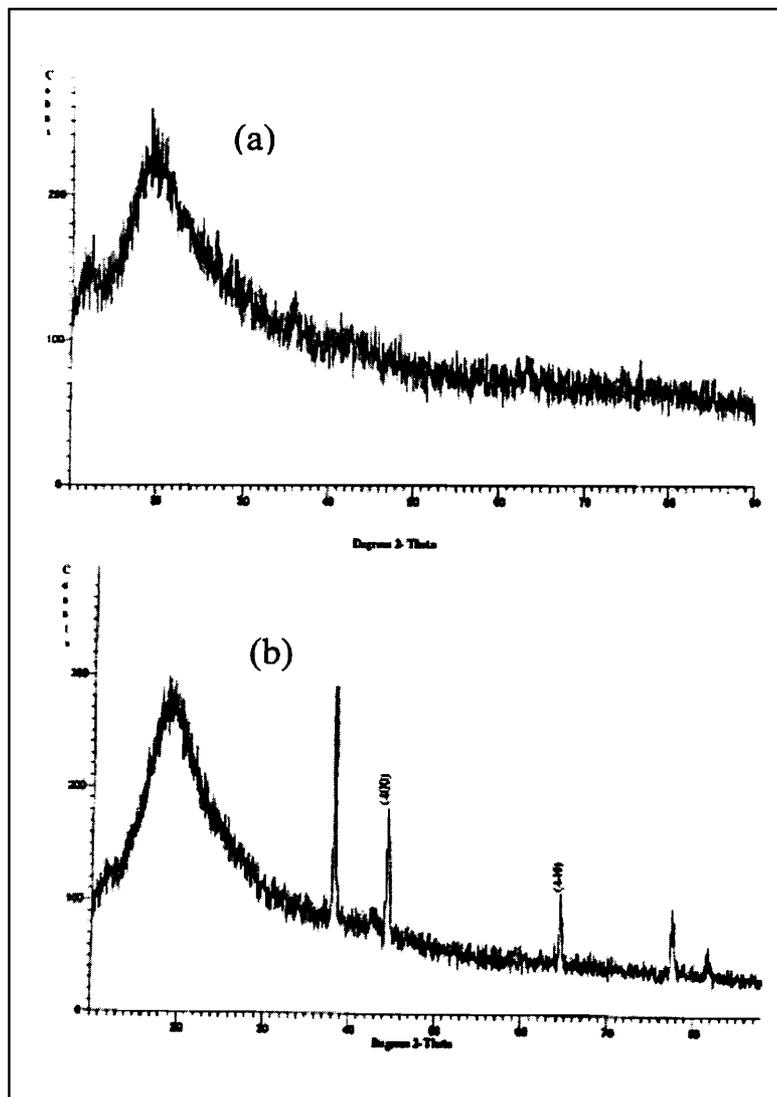
typical not only of crystalline, but also of amorphous polymers. Despite the complex morphology of structural formation in polymers it should not be forgotten that all these structures are built up of separate polymeric molecules. At a glance it seems self-evident that direct relations must exist between the properties of macromolecules and their ability to form super molecular structures. The shapes of most polymer molecules may 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. 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. 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-known 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 discerned between the unchanged and the oriented portions of a spherulite. In addition, secondary formations can be seen which have resulted from recrystallisation of the oriented parts, and these are also separated by sharp boundary lines.

Figure 3 shows the SEM images of γ-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.
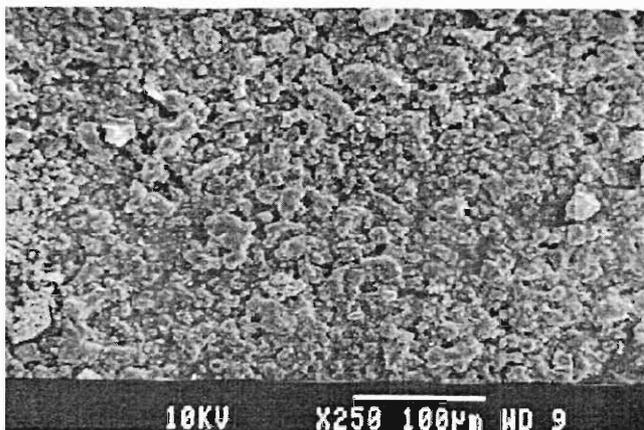
Infrared Spectroscopy

Infrared spectroscopy is one of the most powerful analytical

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The phenomenon of structural transformations occurring during deformation is very typical of polymers.

Figure 3. SEM image of γ-Fe_2O_3 dispersed natural rubber.

10KV   X250 100µm WD 9

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 a molecule quickly, without tiresome evaluation methods. This method can solve many problems in organic chemistry (polymeric materials) and coordination 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.

Thermal Analysis

Thermal analysis may be defined as the measurement of physical and chemical properties of materials as a function of tempera-

ture. The two main thermal analysis techniques are thermo-gravimetric analysis (TGA) which automatically records the change in weight of a sample as a function of either temperature or time, and the differential thermal analysis (DTA), which measures the difference in temperature, ΔT, between a sample and an inert reference material as a function of temperature; DTA therefore detects change in heat content. A technique closely related but modified to DTA is differential scanning calorimetry (DSC). In DSC, the equipment is designed to allow a quantitative measure of the enthalpy changes, (ΔH), that occurs in a sample as a function of either temperature or time.

DSC is an analytical tool which helps to understand the thermal behavior of polymer nanocomposites. It helps in finding glass transition temperature (T_g) of polymer and its polymer composites. The increase in T_g values shows the presence of inorganic materials in the polymer matrix.

Exciting developments can be expected in the area of polymer nanocomposites and structures in the near future. Investigations on polymer nanocomposite can thus pay rich dividends.

Suggested Reading

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[2] *Polymer Nanocomposites: Synthesis, Characterization, and Modeling,* ACS Symposium Series 804.
[3] Ramanan Krishnamoorti and Richard A. Vaia, eds. ISBN: 0 841237689 Publisher: American Chemical Society Copyright: 2001.

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Box 1. Polymer/Clay Nanocomposites

This box briefly explains the advent of polymer/clay nanocomposites 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 nanocomposites.

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 nanocomposites, 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 nanocomposite materials in recent times.

Clay, in particular montmorillonite (MMT), a 2:1 phyllosilicate as illustrated in *Figure* A, 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 onium 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 10Å thick, but over 200 times more in width. The gallery spacing separates each platelet. These spaces in MMT can be enhanced to 2-3nm 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* B. 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* C. 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 of caprolactum, along with modified MMT, resulted in the first synthesis of an exfoliated Nylon-6 polymer/clay nanocomposite prepared at Toyota R&D in Japan in 1989 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°C to
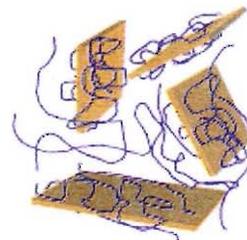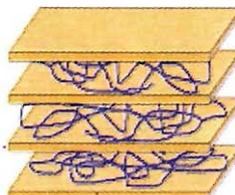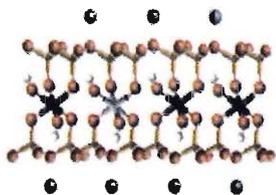

Figure A. MMT structure.   *Figure B. Intercalated structure*   *Figure C. Exfoliated structure*

152°C. This nanocomposite is being used commercially in making tough, heat resistant, nylon timing belt covers. Since then large number of new polymer/clay nanocomposites have been developed like polyurethane, PVC, polyesters, polystyrene and polypropylene. Also, some biocompatible polymers like PLA, poly (ε-caprolactone) to mention a few, have been synthesized by varying methods and with different clay loadings (%by weight). The hydrophobicity /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 nanocomposites has to consider the extent of intercalation/exfoliation which determines the properties of the new-formed materials.

Many methods have been devised to prepare polymer/clay nanocomposites. In general, these methods (as shown in *Figure* D) 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 nanocomposites. 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, polysiloxanes, polyesters, nitrile rubbers, polyurethanes,
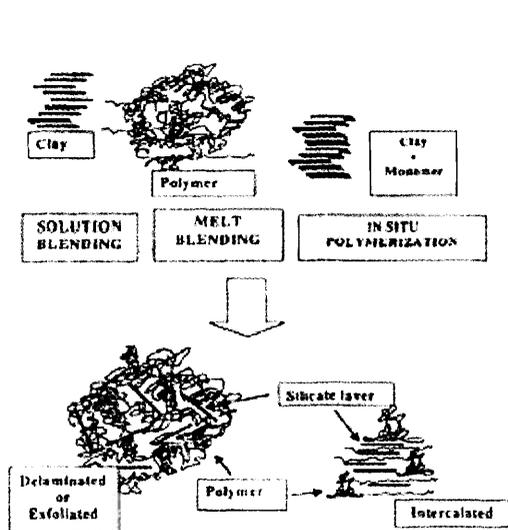

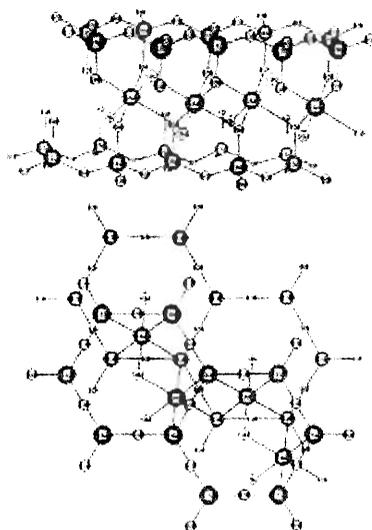*FigureD. Various methods used to prepare polymer layered-silicate nanocomposites*

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

PS-PMMA blends, polyamide 6-PP blends, polyisoprene-PEO blends. These novel materials have shown drastic enhancements in the mechanical, electrical, optical and thermal properties. For example, dramatic 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 reported. Even hyperbranched polymer/clay nanocomposites have been synthesized and exhibit enhancement in their properties. Rheological properties of nanostructured polymer/clay nanocomposites are strongly influenced by the morphology of the materials, which depends on the clay dispersion in the polymer matrix as illustrated in *Figures* B and C.

Several methods like SAXS, XRD, TEM, TGA/DTA 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 d_{001} spacing in the modified clay and provides information on the degree of hybrid structure generated. Diffraction peaks in the low angle region (SAXS) indicate the d-spacing (basal spacing) of ordered intercalated and ordered delaminated nanocomposites: disordered nanocomposites 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.

Conclusion

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 polymers is a continuing subject of research and interest to both academia and industry.

Suggested Reading

[1] EP Giannelis, R Krishnamoorti and E Manias, Polymer-Silicate Nanocomposites. Model Systems for Confined Polymers and Polymer brushes, *Advances in Polymer Science*, Vol.138, pp.107-148, 1998.
[2] TJ Pinnavaia and GW Beall, *Polymer-clay nanocomposites*, John Wiley and Sons, 2001.

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