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Polymer/clay nanocomposites

Summary — Polymer/clay nanocomposites consisting of a polymer matrix and a dispersed montmorillonite clay (MMT) were discussed. Use of MMT as filler for thermosetting and thermoplastic polymers improves rheological, structural and thermal properties of the resulting materials. Aminoacids, alkylammonium ions, silanes, imidazole salts and crown ethers were characterized as dispersion facilitator's modifying the MMT structure. The polymer matrices discussed include Polyamide 6, polyimides, epoxy resins, polystyrene and polypropylene. Resulting composites characterized by XRD and TEM. Flammability and thermal properties of the nanocomposites are of special importance. Combination of excellent barrier properties and transparency has led to wider application of the polymer/MMT nanocomposites in packaging.
Key words: polymer/clay nanocomposites, montmorillonite, surface modifiers, modifiers, properties of composites.

GENERAL CHARACTERISTICS OF THE PROBLEM

Flame retardants are used in polymers based on halogen, heavy and transition metal or phosphorus organic compounds manifest a number of problems, depending on the system. Halogen based fire retardant produce toxic and corrosive combustion products. Halogen as well as phosphorus based fire retardants increase the amount of carbon monoxide and smoke during the combustion process. Further, most currently used fire retardants normally lose most or all of their effectiveness at very high heat fluxes, so that new fire retardants without such shortcomings are needed. Researchers started to address new, environmentally friendly polymeric additives and the novel synthesis methods involved. Significant interest has been devoted in recent years to polymer/clay nanocomposites, due to their increased thermal stability, improved physical properties, reduced flammability, low toxic gas emission and a wide scope of possible applications.

Polymer/clay nanocomposites consist of filler in polymerized medium [1, 2]. The filler is an organo/clay, usually a cationic complex in which the clay's natural surface metal cations have been exchanged with an organic cationic surfactant. Intercalation behavior of montmorillonite clay is of interest and many attempts have been made to introduce macromolecules into the interlayer spaces of this layered clay mineral. Such fillers were prepared by ion exchange or adsorption of charged complex ions on layered clay [3—19]. Ion exchange properties of clay minerals have been investigated by several workers with different cations and also with charged large organic moieties [20—23].

GENERATION OF NANOCOMPOSITES

Many different polymers have already been used to synthesize polymer/clay nanocomposites; these can be divided into two main groups, namely: thermosetting and thermoplastic polymers. The first group includes primarily unsaturated polyesters [24], epoxy resins [25—29], poly(dimethyl siloxane) [30] and polyimides [31, 32]. The second group includes polypropylene [33, 34], poly(ε-caprolactone) [35, 36], poly(ethylene oxide) [37, 38], poly(methyl methacrylate) [39] and polystyrene [40—42].

Blumstein [43] was the first to demonstrate polymerization of vinyl monomers intercalated into montmorillonite. Usuki et al. [44] discovered the possibility of building a nanostructure from polymer and organophilic clay. Their new material based on Polyamide 6 and organophilic montmorillonite showed dramatic improvements of mechanical properties, barrier properties and thermal resistance as compared to conventional filled polymer and this at low clay content (4 wt. %). In result, polymer/clay nanocomposites have been become an attractive organic — inorganic materials, not only because of their obvious potential as technological materials, but

also due to providing a convenient macroscopic system to study fundamental scientific issues concerning confined polymers [45]. Polymer/clay nanocomposites were reported in literature and most of the methods used to prepare polymer/clay nanocomposites have been developed by several groups of scientists [25, 46—55]. In general, these methods achieve molecular — level incorporation of the layer silicate (*e.g.* montmorillonite or synthetic layered silicate) into the polymer by addition of a modified silicate, during the polymerization (*in situ*), or to a solvent swollen polymer or to the polymer melt. In many instances, resultant polymer/clay nanocomposites have improved thermal properties. Furthermore, most of the nanocomposite systems reported so far show reduced flammability, so, the most important aspect of nanocomposite approach is to combine improvement in flammability properties and physical properties [56—61].

MODIFICATION OF MONTMORILLONITE AND MODIFIERS

Montmorillonite clay belongs to a family of clays known as the 2:1 layered silicates, forms naturally from plates, with the spaces between plates called gallery spaces. The montmorillonite group of clays, having the general formula $Al_4Si_8O_{20}(OH)_4 \cdot nH_2O$, show cation exchange properties and can also take up extraneous molecules between its structural layers [2, 62, 63], where the polymer can easy diffuse into the particles. Montmorillonite and other layered silicates clays, are naturally hydrophilic; this makes them incompatible with most polymer materials. Moreover, modification of the clay, makes it more compatible with an organic matrix, through ion exchanging of alkali cation of the clay with virtually any other cation [64, 65]. Popular specie chosen, as organic cations for exchange with montmorillonite include alkyl ammonium ions with long alkyl chains. The mechanical and thermal characteristics of the nanocomposites depend on degree of dispersion. An optimum characteristic clay surface area is made available for cation exchange and when it maintained during the subsequent polymerization, then, the clay mineral should be separated into its constituent platelets in the nanocomposites precursor state. An extended polymer chain is inserted between the silicate layers resulting in a well ordered (intercalated) multilayer with alternating polymer—inorganic layers, or disordered (exfoliated) multiplayer, in which the silicate layers are uniformly dispersed, with random orientation throughout the polymer matrix. Thus, nanocomposites can be made from the intercalated or exfoliated clay.

Montmorillonite clay should be surface — modified to disperse clay within the polymer. Preparation of the nanocomposites involves the use of certain compatibilizing modifying agents. The role of such agent is to convert the surface of clay from hydrophilic to organophilic

status. Alkylammonium substances are common organic cationic molecules used in exchange reactions with montmorillonite; they constitute of one or more alkyl chains containing of 3—18 carbon atoms. The clays with exchanged alkylammonium ions have spacing larger than natural clay, increasing with growing alkyl chain length. These alkylammonium exchanged forms of montmorillonite are generally organophilic and, therefore, compatible with organic materials.

Amino acids

Amino acids molecules contain an amino group (-NH$_2$) and acidic carboxyl group (-COOH). In acidic medium, a proton is transferred from the -COOH group to the intramolecular -NH$_2$ group. A cation-exchange process is, thus, possible between the (-NH$_3^+$) function formed and a cation (*i.e.* Na$^+$, K$^+$) intercalated between the clay layers, thus making the clay organophilic.

A wide range of α,ω-amino acids (H$_3$N$^+$(CH$_2$)$_4$COOH) have been intercalated between the layers of montmorillonite [64]. Amino acids were successfully used in the synthesis of Polyamide 6/clay hybrids [65] because their acid function has the ability to polymerize with ε-caprolactam intercalated between the layers. Thus, such intra-gallery polymerization delaminates the clay in the polymer matrix and a nanocomposite is formed.

The Usuki research group [44] was first to use an amino acid as a compatibilizing modifying agent in the syntheses of nanocomposites, specifically for Nylon 6.

The ion exchange reaction was effected using an amine salt of an amino acid. The aminododecanoic acid replaces all sodium ions on the clay surface, which is subsequently swelled in ε-caprolactam, allowing caprolactam to enter the clay gallery. During the polymerization process the carboxyl end of the molecule is free to participate in the reaction, leading to formation of the nanocomposite.

Alkylammonium ions

Montmorillonite exchanged with long chain alkylammonium ions can be dispersed in polar organic liquids, forming gel structures with high liquid content. Alkylammonium ions can be intercalated easily between the clay layers and offer a good alternative to amino acids for the synthesis of nanocomposites based on polymer systems other than Polyamide 6. The most widely are used alkylammonium ions are based on primary alkyl amines placed in an acidic medium to protonate the amine function. Their basic formula is CH$_3$(CH$_2$)$_n$NH$_3^+$, where n is between 1 and 18. It is interesting to note that the length of the ammonium ions has a strong impact on the resulting structure of nanocomposites.

Usuki research group [66] has designed a polyimide/clay hybrid and many alkylammonium ions were em-

ployed in the cation exchange process with montmorillonite, including a dodecylammonium salt, *n*-decyltrimethyl ammonium chloride, and 12-aminododecanoic acid.

To perform the ion exchange reaction, the naturally hydrophilic montmorillonite clay was first dispersed in deionized water at 80°C, a solution of intercalating agent in water with a small amount of acid (HCl) were added, and the mixture allowed to stir for one hour. The ion exchanged clay was then recovered by filtration and washed several times to remove any excess of the intercalating agent. Once clean and dry, the organo/clay was dispersed in dimethylacetamide (DMAc) to a solids content of *ca*. 3 wt. %. This dispersion was blended with a DMAc solution containing poly(amic acid). A film was then cast followed, by heating to high temperatures where the amic acid can imidize forming the polyimid/clay hybrid.

Pinnavaia and coworkers [31] have synthesized identical polyimide clay in excellent agreement with Usuki; they had shown that alkyl ammonium ions with chain length longer than eight carbon atoms support the synthesis of delaminated nanocomposites, whereas alkyl ammonium ions with shorter chains lead to the formation of intercalated nanocomposites. Alkyl ammonium ions based on secondary amines have also been successfully used [67]. The cation-exchange process involving linear alkyl ammonium ions depends on the layer charge density of the clay, alkyl ammonium ions lead to formation of different structures between the clay layers [68] (monolayers, bilayers, pseudo trimolecular layers, and paraffin type monolayers). Alkyl ammonium ions decrease the surface energy of the clay so that organic species with different polarities may undergo intercalation between the clay layers.

Silanes

Silanes have been used in the synthesis of unsaturated polyester/clay nanocomposites. Silane coupling agents comprise a family of organosilicon monomers characterized by the R-SiX$_3$ formula, where R is an organofunctional group attached to silicon in a hydrolytically stable manner and X designates hydrolysable groups which are converted to silanol groups on hydrolysis. Silane coupling agents interact with receptive inorganic surfaces forming tenacious bonds at the interface. These receptive inorganic surfaces are characterized by the presence of hydroxyl groups (OH) attached principally to silicon and aluminum, having particular affinity to bonding with silane. In the clay, hydroxyl groups may be on the surface of the layers but also, and in particular, on their edges. The silane-coupling agent is first converted by hydrolysis into the reactive silanol form, which then reacts with the hydroxyl groups present on the inorganic surface. It is still not clearly established whether oxano bonds are formed or whether only hydrogen bonds exist [69].

Other modifying agents

Other compatibilizing agents have recently been used in the synthesis of polymer/clay nanocomposites. Recently, imidazole salts were used for treating the sodium derivate of montmorillonite (NaMMT) *via* standard ion exchange to give a series of imidazole-MMTs (IM-MMT). The crown ether treatment of NaMMT organically modified the clay but left the sodium cation in the gallery. The modified 18 Crown 6/NaMMT and several IM-MMT composites were analyzed by XRD showing that the spacing between the clay layers had changed. It appears that the Crown 6/Na montmorillonite gallery is sufficiently hydrophobic to be compatible with Nylon 6 giving well dispersed nanocomposites. Two of the new modified montmorillonite materials, 18 Crown 6/Na montmorillonite and 1,2-dimethyl-3-*N*--hexadecyl imidazole/montmorillonite, were blended with Nylon 6 and polystyrene to form a well dispersed nanocomposites [61, 69]. A review by Ogawa *et al.* [70] gives further information about other suitable compatibilizing modifying agents for the synthesis of nanocomposites.

POLYMERS USED IN NANOCOMPOSITES SYNTHESIS

However, it was noted that the exfoliated and homogenous dispersion of the clay layers could be achieved only in few cases, due to presence of polar hydroxy groups within the silicate layers of clay have, resulting in compatibility with polymers containing polar functional groups such as amides and imides [71]. The deals with certain thermosetting and thermoplastic polymers are used in the preparation of nanocomposites is discussed below.

Nylon6/clay nanocomposites

Certain Nylon 6/clay nanocomposites have been synthesized by first intercalating the monomer into the clay interlayer and subsequently polymerizing it, what may result in delamination upon chain growth. For example, organically modified montmorillonite clay will ingest ε-caprolactam forming an intercalated hybrid (modified montmorillonite can be swollen with large quantities of molten ε-caprolactam at 200°C) [66]. Increasing the temperature to 260°C for six hours under nitrogen in the presence of an accelerator (6 aminocaproic acid) polymerizes the ε-caprolactam forming a Nylon 6/clay hybrid. The polymerization process causes delamination of the silicate layers leading to a fairly well dispersed system, as seen by transmission electron microscopy (TEM) [65]. Usuki *et al.* [72] have developed a "single pot" synthesis route for the hybrid. Annealing Nylon 6/clay hybrids at elevated pressures produced a high melting temperature phase (observed by DSC) corresponding to a different unit cell [73]. Nylon 6 has two

crystal forms, α and γ. After annealing the hybrid under elevated pressure, content of the g form decreased, while a high melting a phase emerged. This same phenomenon was observed upon high-pressure injection molding of the hybrid [74].

Polyimide/clay nanocomposites

Of nine different intercalating agents employed by Usuki, et al. [66] in designing their polyimide/clay hybrid, only one was found to allow dispersion of the organoclay in DMAc. The intercalating agents varied mostly on the basis of carbon chain length attached as side groups. Increasing the aliphatic chain length produces an organoclay with decreased hydrophilicity. The cation that successfully afforded dispersion in DMAc contained a 12-membered carbon chain. TEM investigations into the structure of this hybrid showed that the all silicate layers had parallel orientation. Giannelis [30] showed that clay nanocomposites improved thermal stability; the intercalated polyimide/clay nanocomposites are more stable than the delaminated nanocomposites.

Epoxy/clay nanocomposites

Epoxy/clay nanocomposites have been extensively studied recently [25—29]. The reactants of epoxy systems have a suitable polarity allowing their diffusion between the clay layers and forming of a delaminated nanocomposite upon polymerization. Pinnavaia et al. [28, 75, 76] has studied phenomena occurring in epoxy/clay nanocomposites in great detail and they have also generated epoxy/clay hybrids. Acidic forms of exchanged montmorillonite permit the epoxy resin to enter the clay [47].

Intercalating agents such as aminocarboxylic acids and primary amines can react directly with the epoxy resin, so no curing agent was added. Studies with this group showed that the nature of the alkylammonium ions could influence the final structure of the nanocomposite. Tertiary and quaternary amines were the least favorable, with protonated primary and secondary amines preferred [28]. They concluded that this was due to the fact that the primary amine is the most reactive with the epoxy resin, and the quaternary amine is the least reactive. Hence the organo/clay has a catalytic effect on the epoxy reaction within the gallery regions. Self-polymerization of epoxy resin in organophilic specie clays due to the presence of the alkyl ammonium ions was one of the most important phenomena reported [29, 76]. Ten weight percent or less of alkyl ammonium chloride exchanged clay was blended with the epoxy resin (at 90°C) and sonicated for ca. 2 minutes. Massive increase in the viscosity of the mixture was noted after sonication, attributed to a "house of cards" structure formed by the silicate sheets.

Wide angle X-ray scattering led to the conclusion that intercalation, but not delamination, of the epoxy occurred. Therefore, a curing agent capable of reacting with the epoxy resin and causing delamination of the crystalline sheets had to be chosen. Two such curing agents were found, i.e. nadic methyl anhydride and benzyldimethylamine. Wide angle X-ray scattering of these nanocomposites after curing show no reflections corresponding to a correlation length between silicate sheets.

Polystyrene/clay nanocomposites

Giannelis' research group has also published results on direct polymer melt intercalation into an organo/clay [40]. Ion exchange of montmorillonite clay with dioctadecyldimethyl ammonium bromide (Od_2Me_2AmBr) changed the clay to organophilic. 25 wt. % polystyrene powder, $M_w = 35$ kg/mol, was mixed with 75 wt. % organo/clay and pressed into a pellet. The pellet was then subjected to 165°C in a vacuum oven, and X-ray diffraction experiments were performed as a function of time. X-ray data as a function of time over 25 hours show a disappearance of the peak associated with the Od_2Me_2AmBr exchanged clay at the expense of a new peak corresponding to the PS/intercalated clay. Gilman and his co-worker studied the effect of nanocomposites structure on the flammability of polystyrene-layered silicate and showed that only the delaminated polystyrene/nanocomposites have reduced flammability properties of polystyrene clay nanocomposites [61, 77, 78].

Polypropylene/clay nanocomposites

Initial attempts to create polypropylene/clay hybrids were based on the introduction a modified polypropylene with polar groups to mediate the polarity between the clay surface and bulk polypropylene [33, 48]. However, an organic solvent has to be used in order to facilitate the formation of a modified polypropylene intercalate and only a limited degree of clay nanolayer dispersion was observed. A successful polypropylene/clay hybrid was obtained when the mixture of stearylammonium-exchanged montmorillonite, maleic anhydride modified polypropylene oligomer and homopolypropylene was melted and the resulting clay nanolayer was found to be exfoliated [33, 71]. Maleic anhydride imparts a sufficient polarity to the modified polypropylene in order to generated intercalated nanocomposites. Gilman et al. [38] reported 54% lower peak Heat Relase Rates (HRR) for a PP-g-MA-MMT nanocomposites made by compression molding and 75% lower peak HRR for a PP-g-MA-MMT (4%) nanocomposites prepared by mixing head, which had dispersed the layer silicate particles into molten polymer under shear. Polypropylene based nanocomposites are particularly attractive for application as packing materials, displaying enhanced barrier

properties (improved mechanical and physical properties) and improved flammability.

CHARACTERIZATION OF POLYMER/CLAY NANOCOMPOSITES

Polymer/clay nanocomposites are characterized by employing mainly two methods, i.e. X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD is most straightforward, allowing good evaluation of spacing between the clay layers. Sample preparation is relatively easy and the X-ray analysis can be performed within a few hours. However, one needs to be very careful with the interpretation of the results. Low of sensitivity of the analysis and limitations of the equipment can lead to mistaken conclusions about the nanocomposite structure. Therefore, TEM is a necessary complement to XRD. TEM gives a direct measure of the spatial distribution of the layers but it requires substantial skills in specimen preparation and analysis.

PROPERTIES OF POLYMER/CLAY NANOCOMPOSITES

The increasing interest devoted to polymer/clay nanocomposites arises from the fact that delamination of a relatively low quantity of clay may result in substantial alteration of not just the mechanical properties of the polymer, but also some of its physical properties. Usuki's group [44, 66, 79] observed that exfoliation of layered silicates in Nylon 6, improved the thermal, mechanical and barrier properties of polymers. Nanocomposite technology has been applied to other polymers such as polypropylene [71], polystyrene [78], polyimide [66], epoxy [25, 67] and unsaturated polymer resins [80], with similar results. These polymer — layered silicates materials displayed increased thermal stability and reduced flammability.

Thermal Properties

Usuki's group showed that their new materials had an improved thermal stability [44, 66, 71]. The heat distortion temperature of their nanocomposite was 87°C higher than that of unfilled Polyamide 6, extending the use of this polymer to under-the-hood structural parts in the engine compartment. This property was combined with a reduction of the thermal expansion coefficient of up to 45%. The improvement of heat distortion temperature increases with the length and the content of silicate layers and was attributed to the presence of a constrained region in the nanocomposite [49]. The mechanical properties of Nylon 6/layered silicate nanocomposites, with a silicate mass fraction only 5 wt. % show excellent improvement over those for pure Nylon 6; nanocomposites exhibit increased thermal stability and improved physical properties. In general, the mechanical properties of nanocomposites were improved as

compared with the pure polymer and this at very low clay content (2—10 wt. %).

Flammability

Polymer/clay nanocomposites exhibit decreased flammability. Thus, Cone Calorimeter results indicate that the peak and peak of HRR curves during the combustion of Polyamide 6/clay nanocomposite is reduced by 63 wt. % at only 5 wt. % of clay [60]. Moreover, the nanocomposite structure appears to enhance the performance of the char through reinforcement of the char layer. This means that nanocomposite parts maintain their shape during combustion. After 2 hours of combustion at 100°C, it is still possible to distinguish the shape that the epoxy/clay nanocomposite samples had prior to ignition. A study performed on polyetherimide nanocomposites [50] demonstrated that intercalated nanocomposites showed the highest char yield and a self-extinguishing behavior. Thus, polymer/clay nanocomposites offer a new environmentally benign approach to improve fire resistance of polymers.

CONCLUSIONS

Polymer/clay nanocomposites have undergone important development over the past 10 years in laboratories across the world. A wide range of clays and polymers have been successfully used for the synthesis of nanocomposites and new methods of synthesis have been developed. The substantial improvements in mechanical and physical properties brought by polymer/clay nanocomposites may increase the use of polymers in industry. Their excellent barrier properties combined with good transparency make them ideal for packaging applications. Until now, only few commercial successes have been achieved with these new materials, but more is still to come. The next decade might see the emergence of nanocomposites in our everyday life.

Polymer/clay nanocomposites are materials consisting chemically of modified montmorillonite clay, with some compatibilizing modifying agents used in the synthesis of nanocomposites. The role of clay modifiers is to convert the surface of clay from hydrophilic to organophilic condition.

Current research is carried out in our laboratory to develop other types of flame retardant polymer/clay nanocomposites using metal chelates treated montmorillonite avoiding environmental problems through the nanoscale flame retardant approach.

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