

Study on the Optical and Rheological properties of polymer- layered Silicate Nanocomposites

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ABSTRACT

This review reports recent advances in the field of polymer-layered silicate nano composites. These materials have attracted both academic and industrial attention because they exhibit dramatic improvement in properties at very low filler contents. Herein, the structure, preparation and properties of polymer-layered silicate nanocomposites are discussed in general, and finally the effect of clay nanoparticles on optical and *Rheological* properties of polymeric products were also discussed.

Keywords: Optical properties; Clay; Layered silicate; Nanocomposites

INTRODUCTION

Polymer nanocomposites have attracted great attention worldwide academically and industrially due to the exhibition of superior properties such as modulus, strength, toughness and barrier far from those of conventional micro composites and comparable with those of metals. However polymer nanocomposites have added advantage of lower density and ease of processability. In polymer nanocomposites, the filler has at least one dimension in the nanometer scale and its nanoscale dispersion within the polymer matrix leads to the tremendous interfacial contacts between the polymer and inorganic filler which causes to the superior properties than those of bulk polymer phase. When the dimensions of

filler particles are decreased to the nanoscale, their properties change also significantly [1]. Clay is a general word used to describe mineral crystalline particles consisting mainly of hydrous aluminum silicates with substitution of aluminum by magnesium, iron, alkalies, or alkaline earth elements. It is a familiar name in the different industries such as petrochemistry, oil production, paper production, ceramic, plastic, rubber, and paint. This natural material has different types, but its three kinds are used mostly in paint industry namely attapulgite, kaolin and smectite [2].

Attapulgite is a hydrated magnesium aluminum silicate with a formula of $(Mg, Al)_5Si_8O_{22}.4H_2O$. The needle-like particles

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of attapulgite are used in paints to provide thixotropy property. These particles form a network through hydrogen bonding and van der waals forces that can break on effect of high shear forces. Figure 1 shows acicular particles of attapulgite and network formation by its particles in a water borne paint [2].

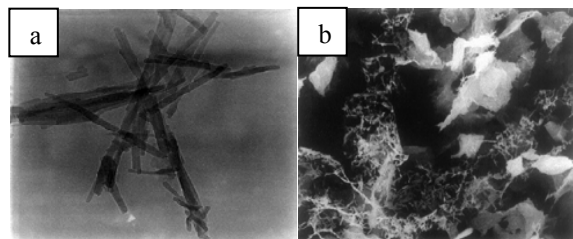


Fig. 1. (a) Acicular particles of attapulgite and (b) Network formation by particles in a paint.

Kaolin has plate like structure and chemical formula of $Al_2Si_2O_5(OH)_4$. It is made up of tetrahedral sheets attached to octahedral sheets. Tetrahedral sheets are composed of silicon-oxygen units that are linked to form hexagonal rings. These rings repeat in two dimensions to form a sheet. Octahedral sheets consist of aluminum and oxygen units. The schematic of a layer of kaolin is presented in figure 2. These layers are held together through hydrogen bonding between hydroxyl groups in the octahedral sheets and oxygen in the tetrahedral sheets of the adjacent layers [2, 3].

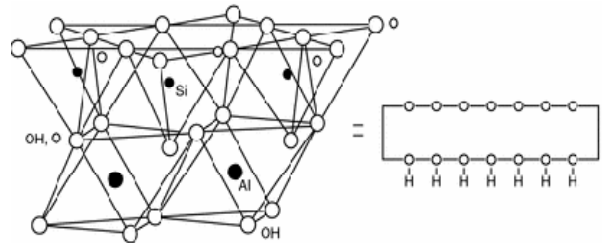


Fig. 2. The schematic structure of Kaolin [4].

Kaolin is often treated with various surface active agents, such as silanes, stearates or polyacrylates to provide

hydrophobicity and ease of dispersion in paints. Kaolin is used in paint as extender, anti-settling and gloss control agent. It may also improve opacity, stain resistance and brush-ability [2]. The crystal structure of smectite is very similar to kaolin. It is formed of two tetrahedral sheets fused to an edge-shared octahedral sheet. Smectite mostly consist of sodium and calcium montmorillonites. In montmorillonite (MMT), some aluminum or silicon ions of octahedral and tetrahedral were substituted isomorphically by ions having lower valency such as magnesium. These substitutions give an overall negative charge to each three sheets layer. This negative charge can be counterbalanced by cations such as Na^+ and Ca^{2+} existing in the interlayer space. The schematic structure of MMT is shown in figure 3. MMT is a hydrophilic material, but it can be an organophilic one by ion exchanging the inter-layered cations with organic alkyl amines. The resultant clays are called organoclays. Organoclays are used mostly in paints to provide sag resistance and increase viscosity [2, 5].

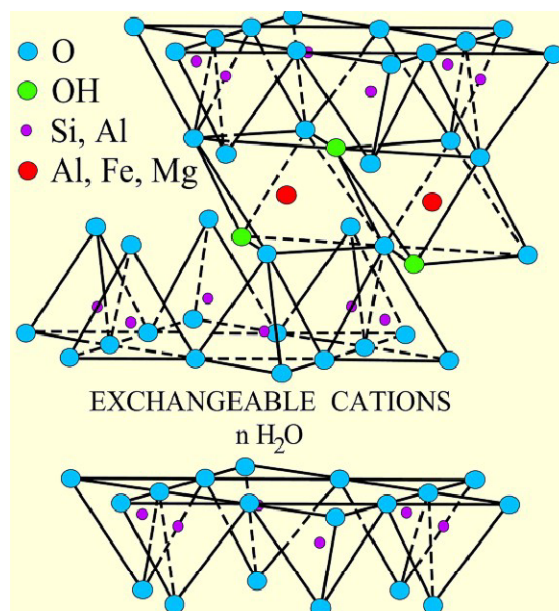


Fig. 3. The schematic structure of montmorillonite [4].

Layers of MMT have dimensions about 1 nm thickness and one hundred to several hundred nanometers in length. They align themselves in a parallel manner, form stacks, and are attracted to each other by van der Waals forces. The gap and distance between the layers are called gallery and d_{001} spacing, respectively. The d_{001} spacing varies over a wide range 10–30 Å depending on the size of the absorbed cations in the interlayer space. Nanometer-sized layered structure of MMT can utilize to produce nano coatings. These coatings are often named layered-silicate nano coatings or nano clay coatings [3, 6].

ORGANIC MODIFICATION OF CLAY

Generally clays are hydrophilic in nature. In order to make compatible with organic polymers, the surface of the clay minerals should be modified to organophilic prior to its use. Organic cations such as an ammonium ion or phosphonium ion are the commonly used organic modifiers for clay minerals [7]. Modification involves the exchange of interlayer inorganic cations with organic onium salts. The organic modification causes the expansion of the interlayer space and thereby increases the d spacing to certain extent (normally over 2 nm). Thus the organic modification favors the diffusion of polymer or its precursor into the interlayer space. Fig. 4 shows the schematic representation of the organic modification of clay. Alkyl ammonium ions are most popular since they can easily be exchanged with the ions situated between the layers. Depending on the layer charge density of the clay, the alkyl ammonium ions may adopt different structures between the clay layers. Alkyl ammonium ions reduce the electrostatic interactions between the silicate layers thus facilitate diffusion of the polymer into the

galleries. In general, the longer the surfactant chain length, the more will be the d spacing of the clay layers [8].

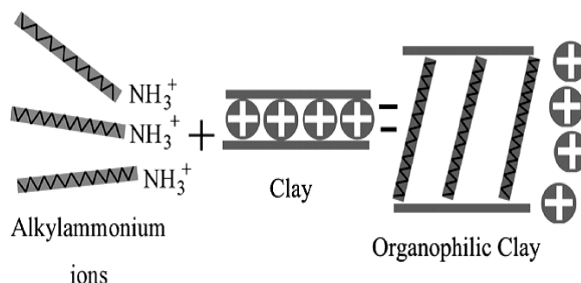


Fig. 4. Organic modification of clay.

STRUCTURE OF POLYMER CLAY NANOCOMPOSITES

Depending on the nature of the components, processing condition and strength of the interfacial interactions between polymer and layered silicates (modified or unmodified), either conventional composites or nanocomposites can be formed as shown in Fig. 5 [9, 10]. In a conventional composite, the polymer cannot diffuse between the clay layers and the clay particles exist in their original aggregated state. Properties of these composites are similar to the micro particle filled composites.

An improvement in modulus is normally achieved in conventional clay composite but this reinforcement benefit is usually accompanied with a deficiency in other properties such as strength or toughness. If there is a favorable condition for the mixing of clay minerals with polymer, two extremes of nanocomposites are formed, i.e., intercalated and exfoliated nanocomposites. In intercalated nanocomposites, the clay layers retain the well ordered multi structure of alternating polymeric and clay layers with a d spacing of 20–30 Å. On the other hand, in exfoliated nanocomposites, the individual clay layers are well separated and

randomly distributed in the continuous polymer matrix with a d spacing of more than 50 Å. The intercalation and exfoliation of the clay layers in the polymer matrix can be identified through wide angle X-ray diffraction (WAXD) and Transmission Electron Microscopy (TEM). The characteristic WAXD of unmodified clay (Cloisite Na), organically modified clay (Cloisite 30B and clay 3) and organically modified clays swelled by epoxy resin is shown in Fig. 6 [11]. Here it is clear that the d spacing increases with the organic modification of clay and it further increases when it swelled in epoxy resin. After curing, the epoxy clay

nanocomposites can give either intercalated or exfoliated structure, where the d spacing will be increased further for intercalated structure or the peak corresponding to the d spacing in the WAXD will be disappeared in exfoliated structures as shown in the case of epoxy-5 wt.% Cloisite 30B (clay 1) mixtures cured at different temperatures (Fig. 7) [11]. Lingaiah et al. suggested that air plasma etching followed by scanning electron microscopy (SEM) imaging is a promising technique for visualizing the exfoliation and dispersion of inorganic nanofillers like clay and CNT in polymer nanocomposites [12].

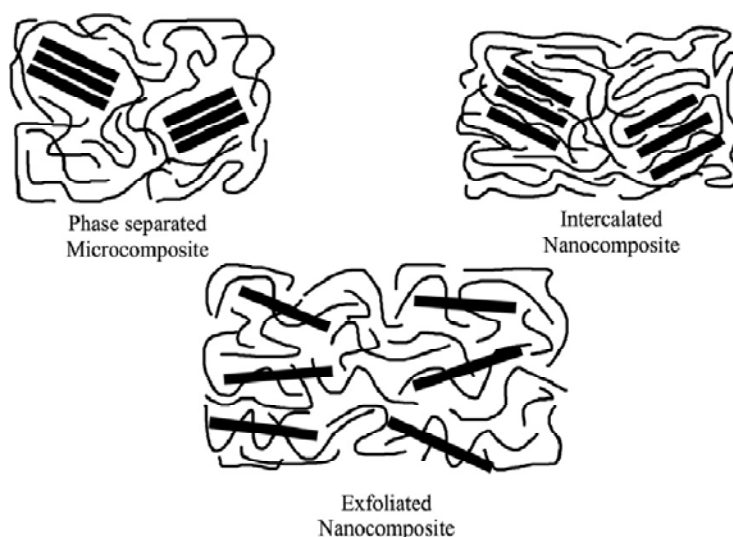


Fig. 5. Types of polymer clay nanocomposites.

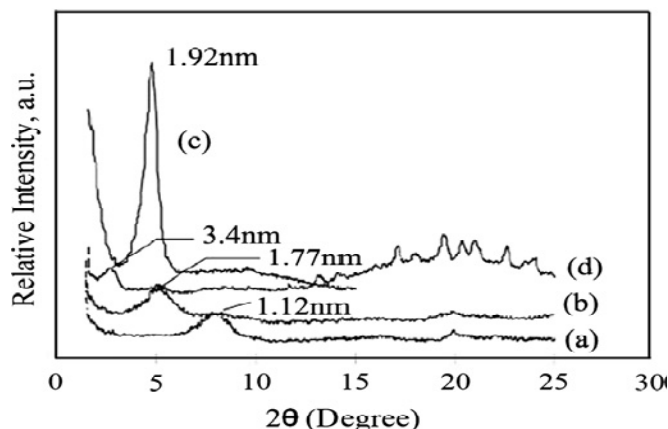


Fig. 6. The characteristic WAXD of (a) unmodified clay (Cloisite Na), (b and c) organically modified clay (Cloisite 30B (b) and clay 3 (c)) and (d) organically modified clays swelled by epoxy resin (Epon 828).

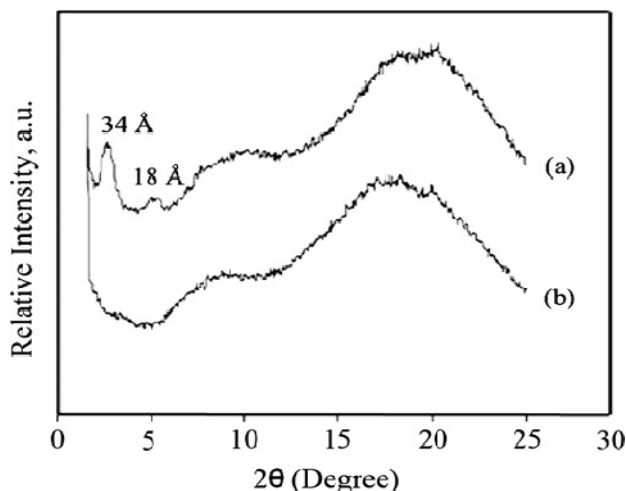


Fig. 7. WAXD patterns showing (a) intercalated and (b) exfoliated clay structures obtained by curing Epon 828–5 wt.% clay 1(Cloisite 30B) mixtures using Jeffamine D230 respectively at 50 °C for 5 h and at 100 °C for 2 h.

PREPARATION OF NANOCOMPOSITES

There are several methods to prepare clay based polymer nanocomposites. These include in situ polymerization, melt intercalation and solution casting.

In situ polymerization

In this method, the liquid monomers or prepolymers (epoxy resin) are intercalated into clay layers and polymerizes within the clay layers resulting the expansion of the interlayer distance (d spacing). Polymerization can be initiated by heat or a suitable initiator. Most of the exfoliated nanocomposites are produced by this method because it provides to select suitable reagents and polymerization routes resulting a good affinity between clay and polymer. In situ polymerization technique has been used for the preparation of nanocomposites based on polyamide (PA) [13], poly (ε-caprolactone) [14], polystyrene (PS) [15], polyolefin (PP and PE) [16] polyethylene terephthalate (PET) [17], epoxy [9].

Melt intercalation

The melt intercalation involves the blending of clay with the polymer matrix

in molten state. If the layer surfaces have sufficient affinity with the polymer, the polymer can diffuse between the clay layers and form either an intercalated or an exfoliated nanocomposite. Melt intercalation technique is used for the preparation of nanocomposites based on polyamide such as nylon 6 [18] and nylon 66 (PA66) [19], and polyethylene terephthalate (PET) [20]. This method is more economical and simpler than other methods.

The melt intercalation process has become increasingly popular because of its great potential for application with rapid processing methods such as injection molding [21] and twin screw extrusion [22]. Melt blending technique is more efficient and produces nanocomposites with improved mechanical properties when it is processed under the aid of super critical carbon dioxide [23].

Solution casting

In the solution method, polymer clay nanocomposites are prepared by using a suitable solvent such as water, acetone, and chloroform, in which the polymer is soluble and the clay is dispersible.

When the polymer solution and the clay-dispersed solution are mixed, the

polymer chains will be intercalated between the clay layers by replacing the solvent molecules. Intercalated polymers will remain in the clay layers upon the removal of solvent. It is reported that the increase in entropy by desorption of solvent molecules is the driving force for the intercalation of polymer from solution [24]. Water soluble polymers such as poly (ethylene oxide) [25], and poly (ethylene vinyl alcohol) [26] have been intercalated between the clay layers by this method. Nanocomposites based on cellulose [28], high-density polyethylene [27], etc. have been synthesized by this method using non-aqueous solvents. The major advantage of this method is that it offers the possibility to synthesize intercalated nanocomposites based on polymers with low or even without polarity.

PROPERTIES OF POLYMER/CLAY NANOCOMPOSITES

The aim for the addition of clay minerals to the polymers is to improve the polymer properties and to produce the polymer/clay nanocomposites with demand characteristics for desired applications. Almost it is wanted to obtain a nanocomposite with demand properties and characters or overcome the drawbacks of polymers while remaining the intrinsic advantages of primary polymer matrix. Because of the low price, availability, high aspect ratio as well as desirable nanostructure and interfacial interactions, clays can provide dramatic and adjustable improved properties at very lower loadings which help to the more remaining of polymer original useful properties. The nature and properties of components as well as preparation methodology and conditions affects on the final properties of polymer/clay nanocomposite [29]. In this section the various improved properties of polymer/clay nanocomposites as well as

the mechanism and effective parameters are discussed.

Rheological properties

The measurement of the rheological properties of any polymeric material is crucial to gain fundamental understanding of the processibility of that material and is usually conducted by either dynamic oscillatory shear or steady shear measurements [30]. In the case of polymer-layered silicate nanocomposites, the study of rheological properties is instructive for two reasons: First, these properties are indicative of melt processing behavior in unit operations, such as injection molding. Second, since the rheological properties of particle-filled materials are sensitive to the structure, particle size, shape and surface characteristics of the dispersed phase, rheology potentially offers a means to assess the state of dispersion in nanocomposites, directly in the melt state. Thus, rheology can be envisaged as a tool that is complementary to traditional methods of materials characterization [30].

It is generally established that when nanocomposites are formed, the viscosity at low shear rates increases with filler concentration [31]. Very often, solid-like behavior is observed, which is attributed to the physical jamming or percolation of the randomly distributed silicate layers, at surprisingly low volume fraction, due to their anisotropy [32]. On the other hand, at high shear rates, shear thinning behavior is usually observed [31]. It has been suggested that this is the result of the alignment of silicate layers towards the direction of flow at high shear rates. Such observations support the percolation argument used in the case of nanocomposite rheological behavior under low shear [32]. Typical shear viscosity curves as a function of shear are presented

in Fig. 8 for PBS-based nanocomposites with various clay loadings.

Shear thinning behavior at high shear rates has also been observed for a PA6 nanocomposite. In fact, this behavior is similar to that of neat PA6 and the composites with the same amount of glass fiber or unmodified MMT. It is of great interest to note that the absolute value of the melt viscosity of the nanocomposite is significantly lower than that of neat nylon 6 or the other composites—which implies good melt processibility over a wide range of processing conditions. One possible reason for reduction of melt viscosity in the nanocomposite is slip between the PA6 matrix and the exfoliated organoclay platelets during high shear flow. Another possibility is a reduced molecular weight of the nylon 6 due to degradation (e.g. hydrolysis) in the presence of clay [31]. Similarly, capillary data revealed that nanocomposites based on medium and low molecular weight PA6 exhibited lower viscosities than the corresponding pure polymers [9].

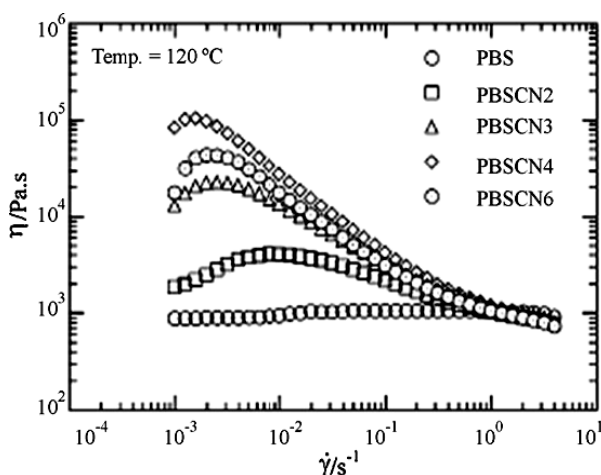


Fig. 8. Shear viscosity as a function of shear rates.

Photo-degradation

The degradability of nanocomposites under UV light is a serious problem that may limit their applications. In the few studies addressing this issue, it has been found that

nanocomposites exhibit lower stability than the corresponding neat polymers [33]. For example, Huaili et al. [34] studied the photooxidative degradation of PE/MMT nanocomposites compared with neat polyethylene. Since it is well established that the degradation of hydrocarbon chains leads to the formation of hydroxyl and keto groups, they studied the extent of photo-degradation by FTIR observations. As is shown in Fig. 9, the degradation of PE/o-MMT nanocomposite was greater than that of pure PE polymer after 200 h irradiation.

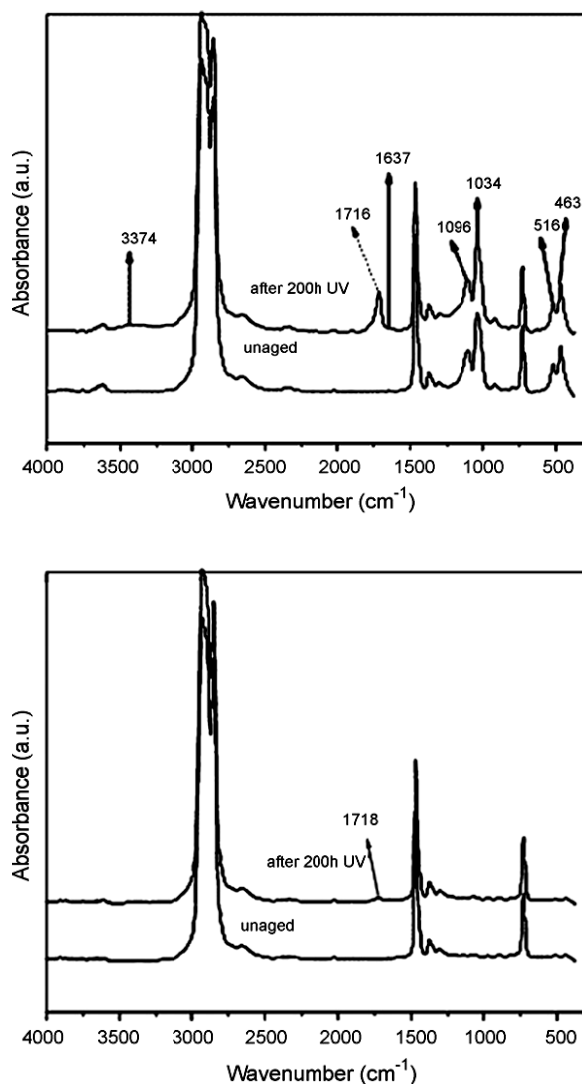


Fig. 9. (a) FTIR spectra of PE/o-MMT nanocomposites before and after 200 h irradiation. (b) FTIR spectra of pure PE before and after 200 h UV irradiation.

Fig. 10 shows FTIR spectra in the carbonyl region upon UV irradiation. Obviously, there is a considerable increase in the intensity of the carbonyl region with an increase of irradiation time in PE/o-MMT, which means that the material is undergoing degradation. In the pure PE, on the other hand, the intensity in the carbonyl region was significantly less, which indicates less degradation.

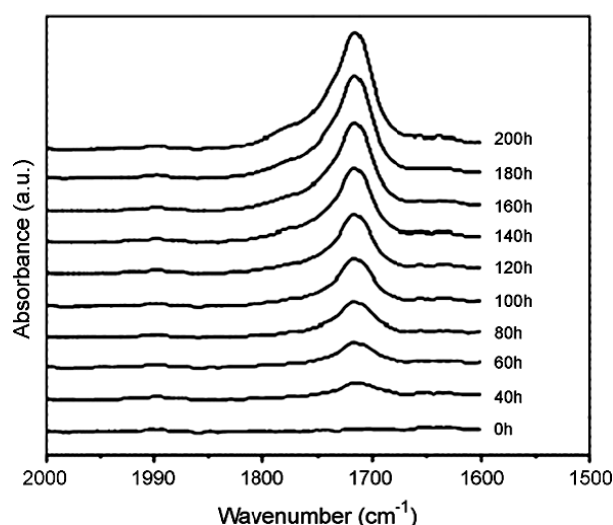


Fig. 10. FTIR spectra of PE/nanocomposite at carbonyl region during photo-degradation.

Morlat [35] and Mailhot et al. [36] studied the effect of compatibilizers on photo-degradation and its

Kinetics by comparing PP nanocomposites with neat polymer.

The increase in the absorbance at 3200–3600 and 1600–1800 cm^{-1} was rapid in nanocomposites in comparison with neat polymer. It was observed that the induction period decreased from 8 to 4 h by using PP-g-MA as compatibilizer and a two-phase degradation mechanism was observed. In the first stage (up to 40 h) there was no evidence for hydroxyl band formation in the IR spectra, which implies the absence of degradation on polymer backbone, whereas in the second stage a dramatic increase in the rate of photo-oxidation was found. The degradation

products were the same in the composite and the neat polymer. According to Patterson et al. [37], the incorporation of layered silicates in polycarbonate appeared to increase the rate at which chain scission occurs. Furthermore, these carbonate scissions produced a yellowing of the polycarbonate, which could inhibit its use in applications where optical clarity is important. However, in another study, the effect of accelerated weathering of polycarbonate nanocomposites was investigated. The silicate content used ranged from 0 to 3.5 wt.%. A UV-accelerated weathering tester programmed to cycle for 8 h of UV radiation and 4 h of dark condensation was

selected for the exposure study. The materials were characterized by UV/vis spectroscopy and FTIR spectroscopy and it was concluded that the degradation of the nanocomposite was less than that of the neat polymer [38]. In any case, although no explanation has so far been given for the differences in photo-degradation stability between the nanocomposites and the pure polymers, it has been suggested that the best way to increase the outdoor durability would be to develop nanocomposites by modification of the clay rather than functionalization of thermoplastics [33].

CONCLUSION

Polymer-layered silicate nanocomposites, although known for many years, have attracted recent attention due to the report of the Toyota research group on the improved properties of PA6 nanocomposites. Other preparation routes include intercalation of polymer or prepolymer from solution, in situ intercalative polymerization and template synthesis. In most cases, layered silicates first need to be modified with cationic-organic surfactants, in order to become miscible with polymeric matrices. Then,

whether a nanocomposite will form or not, and whether this will be intercalated or exfoliated, depends on a variety of factors. These include the type of polymer, layered silicate and organic modifier, the preparation technique and processing conditions. Researches in this filed showed that surface modifier agents used play an important role in improvement of optical resistance of clay nanocposites. Rheological stability was significantly improved by the incorporation of clay particles to polymeric systems.

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