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Aliphatic Polyester and Poly(ester amide) Clay Nanocomposites by *In-situ* Polymerization

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14.1

Introduction: Biodegradable Polymers and Their Nanocomposites

In recent years, interest in biodegradable polymers has grown because of their sustainability and specialized applications mainly in the biomedical field. These polymers are becoming crucial for different industrial sectors like agriculture, automotive industry, medicine, and packaging, which require the use of environmentally friendly materials and, in some specific cases, biocompatible polymers. Specifically, polymers susceptible to being employed in packaging seem to be receiving more attention since it is estimated that more than 40% of plastics are used in this area.

Biodegradable polymers can be classified into three categories according to their origin: (i) synthetic polymers, particularly aliphatic polyesters, such as poly(L-lactide) (PLA) [1–3], poly(ϵ -caprolactone) (PCL) [4–6], poly(*p*-dioxanone) (PPDO) [7–9], and poly(butylene succinate) (PBS) [10–12]; (ii) polyesters produced by microorganisms, which mainly correspond to different poly(hydroxyalkanoate)s (e.g., poly(β -hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate)); and (iii) polymers derived from natural resources (e.g., starch, cellulose, chitin, chitosan, lignin, and proteins).

Despite the large investment in biodegradable polymers, it is clear that they are still far from becoming ideal substitutes of conventional synthetic polymers applied as commodities. In general, the main limitations are their high manufacturing costs and disadvantageous physical properties (e.g., poor mechanical and thermal properties, high hydrophilicity, and poor processability). Therefore, it seems very necessary to modify their chemical nature and/or enhance their performance by nanotechnology. In the first case, the incorporation of amide groups into a polyester chain is an interesting option as poly(ester amide)s (PEAs) should establish strong intermolecular interactions that may improve properties and maintain degradability [13, 14]. In the second case, the incorporation of nanoscale particles into a polymer matrix should provide polymer/nanoparticle composites with enhanced properties. Although several preparation methodologies have been developed, *in-situ* polymerization in the presence of layered silicates appears more

appropriate to render exfoliated structures, which should have a greater impact on properties than intercalated structures [15].

This chapter reviews the state-of-art in the preparation of nanocomposites based on biodegradable aliphatic polyesters and PEAs by *in-situ* polymerization.

14.2

Aliphatic Polyester Clay Nanocomposites by *In-situ* Polymerization

14.2.1

Poly(ϵ -Caprolactone)-Based Nanocomposites

The *in-situ* polymerization technique has received much attention since the successful preparation of exfoliated nanocomposite structures from polyamides [16–18] by promoting polymerization from initiators located on the clay surfaces.

Early works on *in-situ* polymerization of ϵ -caprolactone were carried out by Messersmith and Giannelis [19]. A composite consisting of poly(ϵ -caprolactone)-intercalated silicate particles embedded in the same polymer matrix was synthesized by heating Cr^{3+} -fluorohectorite (a synthetic mica type of silicate) to 100°C in the presence of an excess of ϵ -caprolactone.

Intercalation of the monomer was revealed by powder X-ray diffraction (XRD), which showed an increase in the silicate d -spacing from 1.28 to 1.46 nm, in consistency with a perpendicular orientation of the ϵ -caprolactone ring to the silicate layers. XRD patterns after polymerization indicated a reduction in the silicate spacing from 1.46 to 1.37 nm, which suggested a dimensional change accompanying polymerization. Thus, the opening of the lactone ring in the monomer gave rise to a monolayer of fully collapsed poly(ϵ -caprolactone) chains (Figure 14.1).

The polymer matrix was isolated and found to be indistinguishable (except for chain end groups) from the bulk polymer obtained by metal-alkoxide-initiated polymerization. The polymerization reaction was postulated to proceed through cleavage of the acyl-oxygen bond catalyzed by the interlayer Cr^{3+} ions. The intercalated polymer was strongly adsorbed onto the silicate layers and showed no melting transition.

Messersmith and Giannelis [20] also reported the preparation of nanocomposites by reacting protonated 12-aminolauric acid-exchanged montmorillonite with ϵ -caprolactone monomer. The monomer ring was initially intercalated in the gaps

Figure 14.1 Changes in the silicate spacing as a consequence of monomer intercalation and subsequent polymerization.

between the aminolauric acid chains so that no gallery expansion was detected in the XRD patterns. During heating of this mixture at 170 °C, the organic acid groups initiated ring-opening polymerization of the heterocyclic monomer by nucleophilic attack on the ϵ -caprolactone carbonyl. Diffraction patterns of powdered composite samples showed no discernable (0 0 1) reflections due to the organomodified clay, suggesting that individual silicate layers were dispersed in the polymer matrix. It was also determined that water permeability through composite films containing modest amounts of silicate was dramatically reduced (e.g., by nearly an order of magnitude at only 4.8 v %) due to dispersion of impermeable high aspect ratio of silicate layers in the polymer matrix.

The high average grafting density (with the areal grafting density $\times$ unperturbed radius of gyration $\gg 1$) of the obtained nanocomposites made these systems excellent models to understand the static conformations and dynamics of polymer brushes, which is a focus of intense theoretical, experimental, and simulation interest. Similarities in the rheological response of end-tethered nanocomposites and block copolymers and smectic liquid crystals were demonstrated. The rheology of these end-tethered silicate nanocomposites was investigated using linear viscoelastic measurements in oscillatory shear with small strain amplitudes [21]. It was found that the storage and loss moduli increased at all frequencies with increasing silicate loading. However, their power law dependence on the terminal zone was different from that observed in homopolymers and decreased with increasing silicate loading. At low frequencies, the rheological response became almost invariant with frequency, which suggested a solid-like response. Interestingly, the system exhibited a nonterminal rheological behavior and had molecular weights which suggested a marginal entanglement. This was in close agreement with claims concerning lamellar block copolymers and smectic liquid crystals according to which the presence of entanglements was not required to observe nonterminal behavior.

The *in-situ* polymerization technique has recently been applied for the preparation of PCL/layered aluminosilicate nanocomposites. Tin(II) octoate and dibutyltin(IV) dimethoxide were reported as appropriated transesterification catalysts to promote the polymerization of ϵ -caprolactone in the presence of organomodified clays [22–25]. Montmorillonites with surfaces modified by ammonium cations bearing hydroxyl groups (e.g., bis(2-hydroxyethyl)methyl (hydrogenated tallow alkyl) ammonium) were found to be highly efficient in initiating the polymerization and “grafting” the PCL chains onto the layered silicate surface. Lactone polymerization was postulated to be initiated by all the hydroxyl functions available at the clay surface after activation into either tin(II) or Al(III) alkoxide active species. Hybrid nanocomposites were accordingly generated through covalent grafting of every polyester chain onto the filler surface. Surface-grafted polycaprolactone (PCL) chains were untied and isolated by ionic exchange reaction with LiCl in THF solution, and molar masses were measured by size exclusion chromatography. The PCL molecular weight and the extent of clay exfoliation could be controlled and readily tuned by the content of hydroxyl groups available at the clay surface [25]. Another interesting conclusion was that the initiation reaction by

aluminum trialkoxide active species yielded grafted PCL chains characterized by a very narrow molecular weight distribution ($M_w/M_n \sim 1.2$).

Transport properties of water and dichloromethane vapors and mechanical properties were investigated for PCL chains grafted by *in-situ* polymerization onto clay modified by ammonium salts bearing hydroxyl groups. The clay content was fixed at 3 wt% in inorganics, whereas the hydroxyl functionality ranged between 25 and 100%, always leading to clay delamination [26]. The increase in polymer chain grafting density resulted in a better exfoliation of the clays, limiting, for example, the diffusion of permeant water molecules. In the same way, the diffusion parameters of dichloromethane exhibited a decreasing value on increasing the hydroxyl content in the nanocomposites. Mechanical and dynamic mechanical analyses showed improvement in the nanocomposite elastic modulus in a wide temperature range. Interestingly, for the higher hydroxyl contents (50, 75, and 100%), the modulus could be measured at up to 120 °C (i.e., a much higher temperature than the melting temperature of pure PCL).

A surfactant mixture that contained varying proportions of hydroxyl-substituted alkylammonium and unsubstituted alkylammonium cations to exchange the initial Na^+ counterions of the natural montmorillonite was employed to have a tunable amount of hydroxyl functions at the surface of the clays. As previously indicated, those functions were then derivatized into aluminum alkoxides in order to initiate the ring-opening polymerization of ϵ -caprolactone directly from the clay surface, which was swollen in an organic solvent. Atomic force microscopy measurements on the resulting polymer-grafted nanoplatelets demonstrated the strong dependence of the coating of individual clay particles on the composition of the surfactant mixture used for the cationic exchange [27]. This allowed the generation of a range of morphologies varying from polymer islands distributed over the clay surface to homogeneous polymer layers thoroughly coating the platelets (Figure 14.2). Direct visualization of the polymer grafted onto the clay platelets gave relevant information on the structure of the obtained nanohybrid materials. First, the grafting density increased drastically as the proportion of OH-substituted alkylammonium cations used to organomodify the clay was raised. Second, the polymer deposit was not simply a continuous film growing in thickness with increased OH content. Instead, separate polymer islands formed in the low-OH-content systems, probably as a result of a phase separation process between the ammonium ions induced by the polymerization reaction. Homogeneous coverage and subsequent thickening only took place from 50% OH content. When this situation was achieved, adjacent platelets became fully independent of each other since they were fully covered by the polymer and exfoliation was greatly favored.

Bulk polymerizations of ϵ -caprolactone were also conducted at 170 °C in the presence of catalytic traces of water and 10, 30 and 50 wt% of hydrated synthetic montmorillonite SOMASIF ME100 without additional catalysts [28]. ^1H NMR and GPC analyses suggested that the montmorillonite present in the system induced both significantly higher lactone hydrolysis and polymer chain growth rates. All systems gave rise to low molecular weights ($M_w = 5360\text{--}22432 \text{ g mol}^{-1}$), which

Figure 14.2 Scheme of the polymer surface grafting onto individual clay platelets and concomitant phase separation, as explained in detail in Ref. [26].

seemed to indicate a hindrance effect in diffusion caused by increasing amounts of silicate in the system. Wide-angle XRD data revealed that within the interlayer regions of silicate, ϵ -caprolactone was arranged in weakly ordered bimolecular pseudo-layers. It is worth noting that the interlayer spacings of montmorillonite in the nanocomposites were slightly smaller than for silicate dispersed in ϵ -caprolactone. Such results were attributed to an unfavorable polymerization of ϵ -caprolactone in the interlayer region of the silicate (i.e., chains remained small and unable to open the clay layers to give rise a delaminated structure). The comparison between measured values of gallery height and calculated dimensions of the poly(ϵ -caprolactone) chain indicated that polymer chains were flatly arranged on each side of the silicate platelet, creating pseudo-bilayers inside the montmorillonite gallery.

Comprehension of the nanocomposite structure and interactions at the polymer–nanofiller interface is crucial in controlling nanocomposite properties. In all cases, nanocomposites are characterized by the presence of a polymer layer at the interface with the inorganic surface whose properties clearly differ from those of the bulk polymer. Pucciariello *et al.* [29] conducted a detailed surface analysis of poly(ϵ -caprolactone)–montmorillonite clay nanocomposites obtained by *in-situ* polymerization. The organophilic clay was prepared by treating the natural montmorillonite with a solution of protonated 12-aminolauric acid. *In-situ* polymerization of ϵ -caprolactone was performed under a nitrogen atmosphere at room temperature for 2 h and then at 170 °C for 48 h. The organomodified montmorillonite concentration was close to 18% as this was previously determined as the maximum content at which the silicate was exfoliated [30, 31]. The X-ray photoelectron spectroscopy technique gave information on atom concentrations in the surface layer, the valence state of these atoms, and the bonding of their nearest neighbors. Spectroscopic data indicated a great polarization of Si–O and Al–O bonds in the organomodified montmorillonite, which was attributed to the electron-attracting and electron-donor effects of the NH_3^+ and COOH groups of the aminolauric ion, which efficiently coordinated the partially negatively charged oxygen and the partially positively charged silicon (aluminum) of the clay (Figure 14.3a). X-ray photoelectron spectroscopy data of the nanocomposite revealed lower binding energies of Si–O and Al–O bonds, and consequently a reduced ionicity of such bonds with respect to the organophilic clay. Thus, the presence of the polymer limited the polarizing effect of the aminolauric cation because of the electron-donor/electron-attracting effects of the ester group oxygen (Figure 14.3b).

Poly(ϵ -caprolactone) was studied as a polymer biodegradable matrix which adds potential to the use of derived nanocomposites as biodegradable packaging materials. The synthesis of a series of montmorillonite–PCL nanocomposites in which the content of the inorganic material was varied regularly from 0 to 44 wt% was performed to find some basic structure–property correlations of the multiphase nanocomposites and investigate the permeability to organic (e.g., dichloromethane) and inorganic (e.g., water) solvents of the multiphase polymers [32]. *In-situ* polymerization was carried out at 85 °C using a montmorillonite modified with protonated 12-aminolauric acid. Permeability to water and dichloromethane was found to decrease significantly with increasing clay content. In particular, the water permeability behavior was largely dominated by the diffusion parameter. The diffusion path of the polar molecules of water was assumed to be slowed down with respect to dichloromethane vapor because of not only the physical barrier of the clay layers but also the hydrophilic character of the platelets. Barrier properties associated with the biodegradability of poly(ϵ -caprolactone) play an important role in enhancing interest in these nanocomposites as biodegradable packaging materials.

PCL is thermodynamically miscible with many other polymers (e.g., PVC or SAN copolymer) and can be used as an environmentally decomposable additive that facilitates plastic degradation [33]. A study was recently undertaken to dissolve PCL–clay systems prepared by *in-situ* polymerization in a SAN matrix and evaluate

Figure 14.3 Schemes explained in detail in Ref. [30] showing: (a) Coordination of the aminolauric cation $\text{HOCO}-(\text{CH}_2)_{11}-\text{NH}_3^+$ to the clay. (b) Model of the interactions occurring in the polymer-alkylammonium cation-clay system.

the structure and mechanical properties of these ternary nanocomposites [34]. The *in-situ* polymerization was performed at 170°C using a commercial montmorillonite modified with hexadecyltrimethylammonium bromide. Clay content was of 10, 30, or 50 wt% since nanocomposites were then used as masterbatches to obtain SAN-(PCL-clay) ternary blends containing 0.66–5.65 wt% of the organomodified clay. Blends of PCL nanocomposites with SAN copolymer gave rise to intercalated and semi-exfoliated structures, as deduced from XRD and TEM techniques. The increase of clay in the system led to higher values of Young's modulus. Thus,

compared to unmodified SAN, the addition of only 0.66 wt% resulted in approximately a 10% increase in stiffness modulus, whereas at 5.65 wt%, a 40% increase was obtained.

Supercritical CO₂ has been studied as an alternative polymerization medium (e.g., for ring-opening polymerization of lactones [35, 36]) for more conventional organic solvents due to its well-known advantages [37]. Thus, it is environmentally friendly, nontoxic, nonflammable, and economical since its critical parameters are relatively easily obtained. Furthermore, its fluid/solvent properties can be tuned by small changes in temperature.

Preparation of nanocomposites by redispersion of masterbatches of exfoliated PCL nanocomposites into polymers miscible with PCL, such as the styrene-acrylonitrile copolymer [34], showed encouraging results but also drawbacks, for example, difficulty in recovering the aggregated bulk masterbatch and need to purify it before use. Detrembleur *et al.* [38] proposed an alternative method based on the preparation of PCL-clay masterbatches by *in-situ* intercalative polymerization in supercritical carbon dioxide. The specific properties of this solvent allowed *in-situ* polymerization at high clay content without viscosity problems. This is never the case for bulk polymerization processes, in which clay loading is usually limited to 30 wt%. Furthermore, the product obtained after depressurization was an easily recoverable fine powder and supercritical CO₂ was able to extract the residual monomer during depressurization, directly providing a ready-to-use dry powder. The ring-opening polymerization of ϵ -caprolactone in supercritical carbon dioxide occurred as a dispersion polymerization since only the monomer was soluble in this medium under typical supercritical conditions [39]. Catalysts like Sn(Oct)₂ were preferably used as they should have low sensitivity to the carbonation reaction and protic impurities. Polymerizations of ϵ -caprolactone were carried out in supercritical CO₂ (85 °C, 28 MPa) using the natural montmorillonite and the clay organomodified with a nonfunctional (Cloisite 20A) or a functional (Cloisite 30B) quaternary ammonium salt. In all cases, nanocomposites were qualified as “pre-exfoliated” masterbatches since true exfoliation could not be reached at high clay contents. Redispersion of organomodified clay-polymer masterbatches into chlorinated polyethylene was proved to be more efficient in terms of quality of clay delamination than direct blending of commercial clay.

Starch, a natural polymer constituted by linear α -glucan amylose and highly branched amylopectin, is considered one of the most promising candidates to be used as environmentally friendly materials. It has an attractive combination of availability, price, and performance, but its mechanical properties are poorer than those of synthetic polymers mainly due to its hydrophilic nature, which makes it sensitive to moisture content. For this reason, starch has been modified by blending with synthetic polymers such as poly(ϵ -caprolactone) and even with layered silicates [40, 41]. Namazi *et al.* [42] have recently prepared starch-g-polycaprolactone by *in-situ* ring-opening polymerization of ϵ -caprolactone in the presence of starch, Sn(Oct)₂, and an organomodified montmorillonite (i.e., Cloisite 15A) at reaction temperatures between 100 and 150 °C. Results suggested a slight improve-

ment in thermal stability but intercalation of the copolymer into clay galleries was less effective than the solution intercalation method.

14.2.2

Poly(lactide)-Based Nanocomposites

Poly(lactide) (PLA) is a well-known green polymer that receives great attention from the polymer industry since it can be produced from renewable resources (e.g., corn starch and other carbohydrate-rich substances like maize, sugar, or wheat) and is biodegradable and compostable. These advantages make PLA an attractive alternative to classical commodity polymers (e.g., in the production of loose-fill packaging, compost bags, food packaging, and disposable tableware). However, several properties need to be improved to widen its range of applications. For example, PLA is too brittle and permeable to gases to render optimal application performances, especially for packaging purposes. Despite this, PLA is currently one of the most widely used specialty polymers in the biomedical field (e.g., for sutures, stents, dialysis media, drug delivery devices, and even for tissue engineering).

The introduction of a few percent of nanofillers, such as layered aluminosilicate clays, has been extensively considered to enhance PLA properties. However, the greatest improvement is usually achieved when nanoparticles are fully and uniformly delaminated (exfoliated) in the polymer matrix, a challenge that cannot be fully met by direct melt blending of the clay as this usually leads to intercalated nanocomposites [43, 44]. The use of *in-situ* polymerization techniques appears fully justified since the monomer can penetrate and then polymerize inside the clay sheets, enhancing the delamination efficiency.

In-situ ring-opening polymerization of the lactide monomer in the presence of clay has been extensively studied [45, 46]. For instance, PLA–MMT nanocomposites were prepared in bulk with catalysts such as tin(II) octoate ($\text{Sn}(\text{Oct})_2$) or triethylaluminum in the presence of montmorillonite clays (e.g., Cloisites 25A and 30B) organomodified with an ammonium salt functionalized or not with hydroxyl groups. When Cloisite 30B was used, polymerization was coinitiated by a molar equivalent of AlEt_3 or $\text{Sn}(\text{Oct})_2$ with respect to the hydroxyl groups borne by the ammonium cations of the filler, which was added before the L,L-lactide monomer. The presence of hydroxyl groups was found to be critical because these led to aluminum alkoxide or tin alkoxide active species (Figure 14.4 and Eq. (14.1)), which acted as initiators and led to polylactide chains grafted onto the clay surface

The molar ratio between hydroxyl groups and aluminum cations was crucial in promoting a controlled polymerization. Thus, a defect of aluminum cations should lead to more efficient aluminum trialkoxides, but this was not the case when polymerizations were performed from lactide rings [46]. It was claimed that the probability to form a large amount of trialkoxide species from the anchored hydroxyl groups was rather low, and most probably a mixture of aluminum mono-

Figure 14.4 (a) Scheme of the *L,L*-lactide *in-situ* polymerization performed from Cloisite 30B using triethylaluminum (AlEt_3) as the initiator (R stands for tallow alkyl chain).

(b) Scheme of a mixture of aluminum mono-, di-, and trialkoxides produced by addition of AlEt_3 onto Cloisite 30B in a $n_{\text{OH}}/n_{\text{Al}} = 3$ molar ratio.

di-, and trialkoxides was formed (Figure 14.4b). This distribution was responsible for the observed low monomer conversion, loss of polymerization control, and bimodality of the molecular weight distribution.

The grafted chains pushed the lamellar sheets apart from each other and led to the achievement of an excellent degree of clay exfoliation, which, for example, leads to improved thermal stability compared to unfilled PLA and even intercalated counterparts. Moreover, while the T_g and T_m of the PLA matrix were not influenced by the nanofiller, the degree of crystallinity of the polyester in the exfoliated structure was significantly higher than in the intercalated nanocomposite [45].

The grafting reaction was confirmed by the impossibility of dissolving the so-produced PLA chains in good solvents like toluene, THF, or CHCl_3 . In fact, a specific cationic exchange reaction with LiCl was required to recover the PLA chains, suggesting that polyester chains were attached to the ammonium cations localized in close vicinity and in electrostatic interaction with the montmorillonite surface. Interestingly, polymerization conditions (e.g., bulk with 3 wt% of Cloisite) allowed the synthesis of PLA grafts with a number average molecular weight close

to 14000 g mol^{-1} and a relatively narrow distribution for such a heterogeneous initiation process (i.e., polydispersity index was close to 1.5).

Dubois *et al.* [46] also used *in-situ* polymerization to prepare a PLA–MMT masterbatch and confirmed that its dilution with the neat PLA during melt processing was an effective technique for improving clay dispersion.

It is well known that brittleness is a strong limitation for the application of PLA. The use of plasticizing agents is a usual procedure that may allow PLA to fulfill mechanical requirements. Considerable efforts have been made to improve PLA brittleness to make it competitive with low-cost flexible commodity polymers (e.g., polyethylene and polypropylene). Several types of compounds such as citrate ester, poly(ethylene glycol) (PEG), glucose monoesters, partial fatty acid esters, oligomeric lactic acid, and glycerol have been studied as plasticizers for PLA [47–49]. However, the addition of a plasticizer generally reduces strength and modulus. Moreover, despite the increase of deformation, PLA-based materials having a good balance of stiffness and high deformation are still required for wide applications. For this reason, the possibility of preparing nanocomposites based on the PLA matrix and adding a plasticizer compound has been considered, specifically, the preparation of nanocomposites by melt blending a PLLA matrix, a plasticizer like PEG, and a nanofiller.

Nevertheless, PEG tends to diffuse out of the material and accumulates at the nanocomposite surface, leading to structural matrix changes upon aging [50]. Thus, *in-situ* polymerization of L,L-lactide in the presence of both dihydroxylated PEG ($M_w = 1000 \text{ g mol}^{-1}$) and Cloisite 30B has been studied as an interesting alternative since it leads to nanocomposites based on a triblock copolymer matrix in which the central polyethylene block affords flexibility and is not susceptible to diffusing out of the material [45]. Results showed that intensive clay platelet destructure was achieved independent of the PEG weight ratio. The plasticizing effect of the PEG sequence (entrapped in the triblock copolymer) was highlighted by the significant T_g decrease of the nanocomposite (e.g., from 60 to 12°C at 16.2 wt% content in PEG). Moreover, the thermal degradation of the resulting nanocomposites was dependent on the relative content in PEG blocks and decreased as the polyether level increased within the triblock copolymer.

Poly(lactide–vermiculite) nanocomposites were also prepared by *in-situ* intercalative polymerization of L,L-lactide in the presence of vermiculite clay particles (VMT) that were treated with an alkylammonium surfactant in order to decrease their highly hydrophilic character and favor diffusion of the cyclic monomer into the clay interlayer spaces [51]. XRD suggested that exfoliated structures were attained and TEM observations revealed that VMT layers were exfoliated and dispersed uniformly in the polylactide matrix. TGA indicated a slight improvement in thermal stability (i.e., the onset temperature increased from 279 to 314°C when 5 wt% of organomodified clay was added). Dynamic mechanical analyses showed an increase in storage and loss moduli caused by the reinforcing effect of the nanoscale VMT layers, as well as a slight increase of T_g by increasing the clay content.

Nanocomposites based on anionic clays or layered double hydroxides (LDHs) have also been widely studied. These clays are composed of positively charged

layers with anions and water molecules in the interlayer region. Compounds were defined with the general formula $(\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2)^{x+}(\text{A}^-)_x \cdot n\text{H}_2\text{O}$, in which A^- represents an interlamellar anion (e.g., carbonate) [52]. Although LDHs occur naturally, they are usually synthesized under controlled conditions in order to obtain materials with a known, homogeneous composition [53]. LDH platelets have a high aspect ratio, tuneable layer charge density, and can be prepared by low-cost processes. The potential suitability of organo-LDHs for the intercalation of hydrophobic polymers, the potentially greater susceptibility to complete exfoliation than that of cationic clays, and the catalytic activity for polymerization of lactides in the interlayer are also worth mentioning [54, 55].

Leroux and coworkers [56] suggested *in-situ* polymerization as an appropriate method for preparing polymer-LDH compounds because of the more confined interlayer spacing compared to a typical unmodified montmorillonite clay (0.78 vs 1.26 nm). The high charge density in LDHs and their dense packing favor the insertion of small molecules such as the lactide dimer over the insertion of long PLA chains. This should lead to an effective dispersion of LDH platelets in the growing polymer matrix. Efforts have also focused on the insertion of new organic anionic species in LDH interlayers to enhance or modify hydrophobicity of LDHs [56, 57].

Plackett *et al.* [58] studied *in-situ* polymerization of the lactide dimer in the presence of LDHs modified with carbonate (LDH- CO_3) or laurate units LDH (LDH- C_{12}). LDH- CO_3 was synthesized by a conventional coprecipitation method [59], whereas LDH- C_{12} was prepared using the reconstruction method. In this procedure, the previously synthesized LDH- CO_3 was calcined to form a mixed metal oxide and then dispersed into an ethanol-water solution containing sodium laurate. This process involved fast rehydration of the layered structure, followed by a slower anion exchange reaction, giving rise to the so-called memory effect mechanism [60]. XRD, scanning electron microscopy and transmission electron microscopy revealed that exfoliated nanocomposites were obtained when using LDH- C_{12} but that LDH- CO_3 gave a partly phase-separated morphology (Figure 14.5).

Thermogravimetric analysis showed that PLA-LDH combinations exhibited higher degradation onset temperatures than unfilled PLA. Differential scanning calorimetry indicated that both crystallinity and temperature of crystallization increased on adding LDH- C_{12} or LDH- CO_3 , suggesting that these additives have a nucleating effect. Although *in-situ* polymerization of lactide in the presence of 1–5 wt% LDH- C_{12} could be a promising method for producing nanocomposites with an exfoliated structure, the molecular weight was significantly reduced when compared with the polymer synthesized in the absence of LDHs. Since this phenomenon also occurred when $\text{Mg}(\text{OH})_2$ was used instead of LDH, a chain-termination mechanism via LDH surface hydroxyl groups and/or metal-catalyzed degradation was proposed.

From an industrial point of view, the melt-intercalation technique is usually preferred to *in-situ* polymerization because it is simpler and uses already existing technologies. In this sense, methods that combine the efficiency of the *in-situ*

Figure 14.5 Ring-opening polymerization of lactide rings in the presence of layered double hydroxides modified with carbonate or laurate units.

polymerization approach and the practicability of the melt-intercalation technique are currently being applied. Thus, a highly filled polymer–clay masterbatch was first synthesized using an appropriate solvent and then dispersed into the commercial polymer by melt blending.

Detrembleur *et al.* [61] used supercritical carbon dioxide as a polymerization medium for *in-situ* polymerization of D,L-lactide in the presence of different organomodified clays (e.g., C20A and C30B). Polymerizations were performed at 85 °C and 240 bar at which the lactide monomer was partially soluble whereas the formed polymer precipitated. The polymerization kinetic rate was observed to decrease with increasing the clay amount due to significant hindrance of the clay. A slightly higher conversion was observed in the C30B-based systems since its hydroxyl groups acted efficiently as polymerization initiators. Studies carried out at low clay levels (3 wt%) demonstrated that final structures were also strongly influenced by the nature of the organomodifier compound since intercalated and exfoliated nanocomposites were obtained using C20A and C30B, respectively. Nanocomposites were also successfully obtained with clay levels as high as 35–50% and were then useful as masterbatches to be mixed with the commercial PLA matrix. In this way, well-delaminated nanocomposites with 3 wt% of Cloisite 30B were attained, as deduced from TEM and XRD analysis. The nanocomposites showed significant improvement in both stiffness (up to 20%) and toughness (e.g., from 5.1 to 6.0 kJ m⁻²) compared with the unfilled matrix.

14.2.3

PBS-Based Nanocomposites

PBS is currently one of the most commonly applied biodegradable polyesters of the poly(alkylene dicarboxylate) family. It is commercialized by Showa Highpolymer as BIONOLLE and is usually copolymerized and blended to improve mechanical properties and biodegradability [62–65]. However, these methods (i.e., copolymerization and blending) often cause problems that affect crystallinity and melting point since the incorporation of a second component results in imperfect packing and/or isomorphism, and adversely affects the temperature range over which the resulting materials can be used [66, 67]. Preparation of nanocomposites appears as a promising alternative method to the production of commercial PBS-based polymers. In this case, the aggregation trend of inorganic materials caused by strong hydrophilic interactions should be avoided.

Kim *et al.* [68] prepared nanocomposites by *in-situ* polymerization of 1,4-butanediol and succinic acid in the presence of Closite 25A or a twice functionalized organoclay (TFC) using titanium(IV) butoxide as a catalyst. TFC was prepared by reaction of C25A with a silane coupling agent that gave rise to epoxy functional groups. These were expected to enhance the chemical bonding of TFC layers with PBS end groups, and consequently lead to better dispersion and exfoliation of the clay layers in the PBS matrix. Furthermore, the thermal stability of PBS–TFC was clearly improved, which was attributed to the increased interaction between the inorganic components and the polymer. Lower thermal stability and an intercalated structure were characteristic of PBS–C25A nanocomposites.

Nanocomposites based on the PBS matrix were prepared by two-step polymerization consisting of direct esterification and polycondensation from succinic acid, 1,4-butanediol, titanium tetrabutoxide, and fumed silica [69]. The first step was carried out at 190°C for 2 h and the second under vacuum at 240°C for 3–5 h. Solid-state ^{29}Si NMR and FTIR analyses indicated that silanol-bonded carbonyl groups were established within PBS–silica nanocomposite materials. Rheological effects inherent to the silica filler were evaluated and showed that despite high shear force, PBS–silica nanocomposites maintained a relatively high melt viscosity attributable to a network structure resulting from covalent bonding between silica and the polymer chain. Greatly improved mechanical properties were attained with only addition of 3.5 wt% of silica. Thus, an increase in both tensile strength (from 26.3 to 38.6 MPa) and elongation (from 56% to 515%) at break compared with parent PBS was reported. PBS–silica nanocomposites showed composition dependency on biodegradation ascribable to reduced crystallinity and preferential microbial attack.

Im *et al.* [70] treated Closite 30B with the coupling agent 1,6-diisocyanatohexane to form covalent bonds between silanol groups on the clay side and between a silanol group and the hydroxyl group of the organomodifier in the silicate layer (Figure 14.6). In this way, it was possible to increase both basal spacing and the favorable interaction between clay and PBS. Nanocomposites were prepared by two-step *in-situ* polymerization, as previously indicated. It was found that, at the

Figure 14.6 Formation of covalent bonds between 1,6-diisocyanatohexane and the silanol and hydroxyl groups in an organomodified montmorillonite as explained in Ref. [70].

same level of clay content, these nanocomposites showed a higher degree of exfoliation and improvement in all mechanical properties including tensile strength, storage modulus, and elongation at breaks compared with PBS and C30B nanocomposites.

Dubois *et al.* [71] demonstrated that the enhancement of *in-situ* transesterification reactions was a highly effective method to improve organoclay dispersion and exfoliation in a polyester matrix. Thus, Bionolle–Cloisite 30B nanocomposites were prepared by melt intercalation with addition of dibutyltin dilaurate ((Bu)₂Sn(Lau)₂) as a catalyst. Polyester chains were covalently linked to the organomodifier as a result of effective transesterification reactions occurring between the polymer chains and the hydroxyl groups of the organoclay. As a consequence of this process, clay exfoliation was enhanced and stiffness of the final compound clearly increased (i.e., Young's modulus showed an increase of 60% compared with the neat polyester).

14.2.4

PPDO-Based Nanocomposites

PPDO is a biodegradable polymer of great interest for applications in the biomedical field (e.g., bioabsorbable surgical sutures, bone fixation devices, and drug delivery systems) due to its outstanding mechanical properties, for instance, high tensile strength and excellent flexibility [72]. This polymer has also been applied as a drug delivery system and has great potential for general use in systems such as films, molded products, laminates, foams, nonwoven materials, adhesives, and coatings [73]. However, PPDO has some unfavorable characteristics (e.g., high hydrophobicity, low crystallization rate, and low melt strength) that may limit its

application and processing. Modifications based on the preparation of nanocomposites now appear as an ideal method to improve physical properties and avoid some of the above limitations. In this line, Wang *et al.* [74] studied the *in-situ* ring-opening polymerization of PPDO with organomodified montmorillonites (natural sodium montmorillonite, montmorillonite modified by octadecyltrimethyl ammonium chloride, and montmorillonite modified by hydroxyethylhexadecyldimethyl ammonium bromine) in the presence of triethylaluminum. Reactions were performed for approximately 20 h at 50 °C. Interestingly, montmorillonites accelerated the polymerization reaction and led to a viscosity-average molecular weight of PPDO of 44 900 g mol⁻¹ in only 0.5 h. Furthermore, a nucleating effect of montmorillonites was clearly observed and the crystallization temperature of PPDO increased by approximately 18 °C. All three montmorillonites improved the thermal stability of PPDO and increased its glass-transition and melting temperature. In addition, the melt strength of the PPDO–MMT nanocomposites increased dramatically when compared with that of the neat PPDO [73]. These results suggested that biodegradable PPDO–MMT thin films could be prepared by blowing process since low crystallization rate and low melt strength limitations can be overcome.

14.3

PEAs Clay Nanocomposites by *In-situ* Polymerization

PEAs are a new class of polymers that combine the good degradability of polyesters with the high thermal stability, high modulus, and high tensile strength of polyamides, which makes it possible to obtain good material and processing properties while maintaining degradability. PEAs are also highly attractive since their properties can be tuned due to the large variety of monomers that can be used (e.g., α -amino acids, α,ω -aminoalcohols, and carbohydrates). Thus, polymers can be synthesized with variable ester/amide ratio, variable aliphatic/aromatic ratio, variable hydrophilicity (e.g., incorporating poly(ethylene oxide) blocks or changing the length of polymethylene sequences), variable stereochemistry, and variable monomer distribution. Thermoplastic elastomers and amorphous and semicrystalline materials can be obtained from segmented, random, and ordered microstructures, respectively. PEAs are now being considered for use as biodegradable matrices in nanocomposite preparation, although few works focus on the *in-situ* polymerization method.

Nanocomposites of organomodified montmorillonites (C20A, C25A, and C30B) and a biodegradable PEA were obtained by *in-situ* polycondensation of sodium chloroacetylaminohexanoate [75]. This synthesis was based on a thermal polycondensation reaction in which the formation of a metal halide salt became the driving force of the process [76, 77].

Figure 14.7 (a) WAXD profiles taken during *in-situ* polymerization of the monomer/C25A mixture at 125°C . It can be observed that the disappearance and appearance of reflections associated to the monomer and polymer structures, respectively, and the evolution of the (1 0 0) reflection of the NaCl structure. Sodium chloride was produced during polymerization according to Eq. (14.2).

(b) Plot of $\ln k$ versus the reciprocal of the polymerization temperature for the neat monomer and its mixture with C25A. Clear differences were observed between the intersections with the ordinate axis, but no significant differences were found between slopes and consequently the corresponding activation energies.

The great simplicity of this method raises interest in this family of polymers characterized by a semicrystalline character due to the regular distribution of the two units involved, which contrasts with the more amorphous nature of copolymers prepared by ring-opening polymerization. Exfoliated or intercalated structures were attained depending on the organomodifier (i.e., the most dispersed structure was obtained by addition of Cloisite 25A). Polymerization kinetics was strongly influenced by the presence of organomodified montmorillonites under both non-isothermal and isothermal conditions. Both FTIR and WAXD experiments were used to study the polymerization process following the time evolution of the 1742 cm^{-1} absorption band of the ester group and the diffraction intensity of characteristic NaCl reflections (Figure 14.7a), respectively. The temperature dependence of the polymerization kinetic constant allowed inferring that kinetic differences between the polymerization of the neat monomer and its mixture with C25A could be attributed to the preexponential frequency factor (Figure 14.7b). In this way, clay particles seemed to reduce chain mobility and the frequency at which reactive groups were close enough to facilitate the condensation reaction. The thermal stability and crystallization behavior of the neat polymer and its nanocomposites were significantly different. In general, exfoliated structures decreased both primary nucleation and crystal growth rate, whereas intercalated structures increased the density of primary nuclei. These nanocomposites were also prepared by the melt mixing technique, which rendered intercalated structures with a higher overall crystallization rate [78].

14.4

Conclusion

The increasing demand for biodegradable materials in the world market is leading to the development of products with better properties than those of existing materials. Efforts mainly focus on the synthesis of new biodegradable polymers with potential applications as both commodity and specialty materials. In this sense, PEAs can be considered a modification of conventional biodegradable polyesters that may provide enhanced properties. Incorporation of nanoparticles into biodegradable polymer matrices is another effective approach to improve the properties of pristine polymers remarkably. There is now a considerable body of literature concerning the preparation of nanocomposites from the more usual biodegradable polyesters (e.g., poly(ϵ -caprolactone), polylactide, poly(butylene succinate), and poly(*p*-dioxanone)) and silicate clays by *in-situ* polymerization. In general, this results in polymers grafted onto the silicate layers, favoring a subsequent exfoliation. Thus, *in-situ* polymerization seems to be more appropriate than other methodologies (i.e., melt or solution intercalation) that usually render intercalated structures. Despite the increasing interest in developing new biodegradable polymers, few works deal with the preparation of nanocomposites based on PEAs matrices. Thus, this may be a very promising topic for future research.

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In-situ Synthesis of Polymer Nanocomposites

The book series "Polymer Nano-, Micro- and Macrocomposites" provides complete and comprehensive information on all important aspects of polymer composite research and development, including, but not limited to synthesis, filler modification, modeling, characterization as well as application and commercialization issues. Each book focuses on a particular topic and gives a balanced in-depth overview of the respective subfield of polymer composite science and its relation to industrial applications. With the books the readers obtain dedicated resources with information relevant to their research, thereby helping to save time and money.

In-situ intercalative polymerization in the presence of filler provides distinct advantages when compared to other nanocomposite synthesis techniques including the possibility to polymerize a large range of thermoplastic and thermosetting polymers, improved handling of gaseous or liquid monomers or high pressure polymerization and improved control of heat of polymerization. This volume aims to highlight these advantages of the generation of polymer nanocomposites with a large spectrum of polymer matrices. Following an overview of the synthesis methodologies, the text goes on to discuss the most relevant polymer materials, including polyamides, polyolefines, polyacrylates, polyethylenes, polyurethanes, polyesters and polyepoxides.

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