Polypropylene Clay Nanocomposites

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Contents

Keywords

Flameretardants • Isotactic polypropylene • Layared silicate nanocomposites • Maleic anhydride • Metallocene

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1 Introduction

Recently, research on polymer/layered silicate nanocomposites has been received great interest because they often show superior property improvements with respect to pristine polymers or conventional composites [1–11]. The extent of enhancement in properties depend on the interfacial interaction between the polymer matrix and the layered silicate layers. There are many types of silicate layers which have been used for the filling in polymers, such as montmorillonite (MMT), hectorite, saponite, laponite, halloysite, and kanemite, etc [9]. Unlike traditional filled polymer systems, nanocomposites require relatively low filler loadings to achieve significant improvements in the properties. These materials are called nanocomposites because of the finely dispersed nanometer thickness clay sheets in the polymer matrix. In addition to their properties, the discovery of simple processing methods such as melt compounding provided a potentially commercially viable method to produce nanocomposite materials on a large scale [12].

Isotactic polypropylene (PP) is one of the most important commodity polymers and has been extensively used in several applications, including as interior and exterior decoration materials of automobiles, home electric appliances, etc. PP has a simple chemical structure ($-[CH_2\text{-}CH(CH_3)]_n-$) and is one of the most basic and important polymers from both the industrial and scientific points of view [13]. From the commercial perspective, PP is one of the most important members of the polyolefin family due to its outstanding combination of low cost, low weight, moderate heat distortion temperature of about 100 °C, along with extraordinary usefulness in terms of properties applications and *recycling* [14–30]. To improve the range of its applicability, it is essential to improve its toughness and thermal resistance so that it meets the demands of engineering products. Therefore, it is proposed that the uniform dispersion of layered silicates in the polymer matrix must enhance its mechanical performance [19–30].

This chapter briefly describes the advancement in this area, along with possible future developments. The chapter mainly focuses on the preparation methods of polypropylene clay nanocomposites (PPCNs) and their significant aspects in terms of properties, structure, and morphology behaviors will be discussed.

2 Polypropylene/Layered Silicate Nanocomposites

In the layered silicate nanocomposites, the most commonly used clay is MMT (a smectite type), which contains 1-nm-thick layers, where alumina is located in the center as an octahedral sheet sandwiched between two silica tetrahedral sheets. The clays have negative charges generated on the surface by isomorphic substitution, balanced by cations, which is known as the cation-exchange capacity (CEC). Layered silicate clays are good candidates for the preparation of inorganic–organic hybrid nanocomposites because they are abundant in nature, inexpensive chemically, and thermally stable. The parallel-organized sheets exist in the form of stacks with regular van der Waal's gaps, called the interlayer space of the gallery where

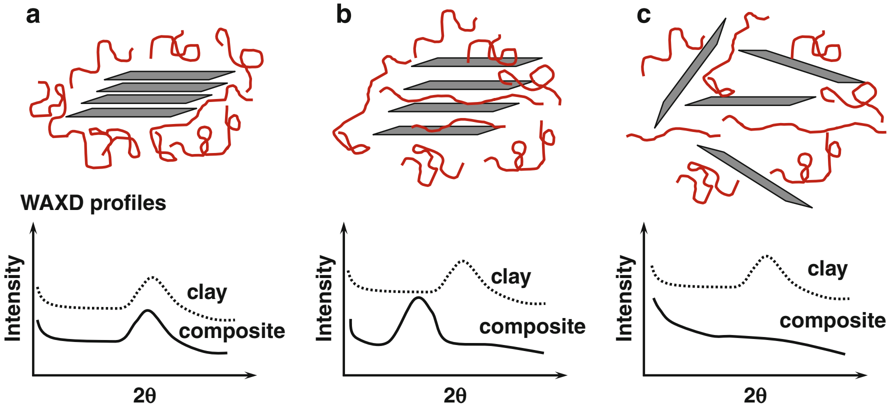

Fig. 8.1 Schematic representations of different states of clay dispersion and their corresponding WAXD profiles. (**a**) Phase-separated microcomposite. (**b**) Intercalated nanocomposite. (**c**) Exfoliated nanocomposite

the cations are located. The replacement of inorganic exchangeable cations with organic *onium* ions on the gallery surfaces decrease the attractive force between the clay galleries and enhance the compatibility between the clay and the polymer matrix [9, 31, 32]. Another method to improve the compatibility between the clay and the polymer matrix is that the polymer matrix can be functionalized either by grafting or by the incorporation of functionalized monomers in the main chains during the synthesis of the polymer. In particular, for non-polar polymers like PP, in addition to those primary modifications, many special efforts have been made, such as etching with acids, plasma modification, irradiation, etc. The use of a functionalized polymer as a master batch is another common method during the melt intercalation method. Maleic anhydride (MA) grafted on polyethylene (PE) or PP (MA-g-PP/PE) has been extensively used as a compatibilizer during nanocomposites preparation in the presence of peroxide as the initiator. This grafted material enhances the dispersion of clay in the polymer matrix and improves the interfacial adhesion between the filler and the polymer matrix, which ultimately helps in enhancing the material properties.

The ultimate aim of nanocomposites preparation is to attain the best properties by achieving a homogeneous and uniform distribution of silicate layers in the polymer matrix. As mentioned earlier, the layered silicates have a layer thickness on the order of 1 nm and very high aspect ratio (e.g., 10–1,000 nm), therefore, creating a large surface area between polymers and clay platelets, and enhancing the *polymer–filler* interaction more than in conventional microcomposites. Based on the extent of the layered silicate distribution in the polymer matrix, i.e., depending on the strength of the interfacial interaction between the polymer matrix and the layered silicate, three different types of structures are expected: phase-separated nanocomposites (microcomposites), intercalated nanocomposites, and exfoliated nanocomposites (Fig. 8.1).

In the phase-separated nanocomposites, the polymer chains are confined in the clay and remain as tactoids. These tactoids act as stress concentrators, causing cartographic failure of the matrix and the properties of the resulting hybrids are either similar or reduced with respect to pristine polymers. In an intercalated nanocomposite, the polymer chains penetrate into the clay galleries. As a result, the clay galleries swell, but the clay still preserves its crystallographically regular structure, irrespective of the polymer to silicate layer ratio. The properties of such nanocomposites are similar to those of ceramic materials. In an exfoliated nanocomposite, the individual silicate layers separated in the polymer matrix by an average distance. In general, polymer clay nanocomposites often exhibit a mixed morphology, in which the three above-mentioned types of dispersion states coexist within the same composite material.

The degree of clay dispersion in the polymer matrix is established using wide-angle X-ray diffraction (WAXD) analysis and transmission electron microscopy (TEM) image observations. WAXD is the most commonly used technique because of its ease of use and possibility to probe the interlayer spacing of the clay in pristine clays, as well as in the composite materials. By measuring the diffraction angle (2θ), one can calculate the average interlayer spacing (d) of a clay using Bragg's equation $\lambda = 2d \sin \theta$, where λ is the wavelength of incident X-ray radiation. By knowing the position and shape of the clay's basal peaks, the extent of clay dispersion in the nanocomposites can be quantified. For example, in the case of exfoliated nanocomposites, the clay layers are homogeneously dispersed in the polymer matrix, which results in the absence of any coherent X-ray diffraction from the silicate layers. On the other hand, in the intercalated nanocomposites, the clay galleries are expanded due to the intercalation of polymer chains into the clay galleries, which result in the appearance of a new reflection or shift of the diffraction peak to the lower 2θ side in the WAXD profiles. In this way, WAXD is, undoubtedly, a convenient and precise method to determine the interlayer spacing of the silicate layers in polymer silicate nanocomposites. More often, TEM is used as a complement to WAXD to directly observe the level of clay dispersion in the intercalated nanocomposite, although how small a specimen area under examination can explain the dispersion states of silicates inside the matrix remains a significant area of research. More recently, small-angle X-ray scattering and Fourier transform infrared spectroscopy (FTIR) measurements have been used to reveal the extent of clay galleries dispersion in the polymer matrix [33, 34].

3 Preparation of Polypropylene/Layered Silicate Nanocomposites

Many efforts have been made to develop PP nanocomposites with organic silicates by utilizing various appropriate preparative methodologies. The preparation methods used for PPCNs are broadly classified into three main categories:

1. In situ polymerization
2. Melt compounding
3. Solution blending

In addition to these common processing methods, there have been several published reports on some special preparative methods. The most common methods used in the preparation of PP nanocomposites have been extensively reviewed. In this chapter, the discussion is limited to the various popular approaches that have been used for the preparation of PP nanocomposites.

3.1 In situ Polymerization

In this method, generally, the organic modified layer silicate (OMLS) is swollen in the monomer or a monomer solution, so that the polymer formation occurs in between the clay galleries. Polymerization can be initiated by either heating or radiation using a suitable initiator, or catalyst is fixed via the cation exchange process inside the inter layer before swelling the clay galleries with monomer. It is believed that an in situ polymerization is an effective method to obtain exfoliated PPCNs compared with melt and solution blending methods. Many efforts have been made to obtain PP nanocomposites via in situ polymerization [20, 35–44]. The in situ polymerization methods used for the preparation of PE nanocomposites can be extended to prepare PP nanocomposites. Mainly, two approaches have been reported for obtaining polyolefin nanocomposites by using the in situ polymerization method. The first route is the direct synthesis of the PP nanocomposites in the presence of the nanosheets/particles, where the clays are placed in contact with the catalytic system (metallocene catalyst/MAO) [35]. In the second route, the catalytic system is fixed on the surface of the clay prior to the initiation of the polymerization reaction [36–38]. Sun and Garces [39] proposed an original method for the preparation of high-performance PP nanocomposites, where no external activators, such as methylaluminoxane or perfluoroarylborates, are needed to initiate the olefin polymerization and high pressures or high temperatures during processing are also not required. The methodology can be readily extended to make other polyolefins, like PE and poly(1-butene) clay nanocomposites. Tudor and co-workers [40] demonstrated the in situ polymerization method. They showed that a soluble metallocene catalyst is intercalated into the layered silicates, followed by polymerization reactions. First, a synthetic hectorite was treated with methylaluminoxane (MAO) (a common cocatalyst used in metallocene catalyst-based polymerizations) in order to remove all acidic protons (acidic protons are also known to be poisonous to the catalyst), which enables the interlayer spacing to receive metallocene catalysts. By the addition of metallocene catalyst ($[Zr(\eta\text{-}C_5H_5)Me(THF)]^+$), a cation exchange reaction occurs between Na^+ in MAO-treated hectorite and the metallocene catalyst; as a result, an increase in the interlayer spacing of silicate clay is possible. In another attempt, by using synthetic fluorinated mica-type clay with a negligible proton in the clay galleries, the catalyst was intercalated directly with clay galleries without the need for MAO treatment. Yang et al. [20] demonstrated the effect of in situ polymer chain functionalization on the stability of the nanocomposite structure by copolymerizing a propylene monomer with 5-hexenyl-9-borabicyclo[3.3.1]nonane (5-hexenyl-9-BBN) with a Ziegler–Natta catalyst which was intercalated initially with organically modified montmorillonite (OMMT) and diphenyldimethoxysilane (DDS) as the external donor. The resultant hydroxyl-functionalized PP/MMT nanocomposites exhibit enhanced structural stability against processing conditions as compared with pristine or unfunctionalized PP nanocomposites. In a further attempt by He et al. [44] alkyltriphenylphosphonium-modified montmorillonite (PMMT) was used to prepare PP exfoliated nanocomposites in the presence of a heterogeneous compound catalyst $TiCl_4/MgCl_2$/PMMT. Before initiating the polymerization reaction, the compound catalyst system was pretreated with toluene, followed by $AlEt_3$, dipenyldimethoxylsilane, and, finally, pretreated catalyst slurry or powder were added successively to the monomer to initiate polymerization. Thus, the resulting PP/PMMT nanocomposites were found to be exfoliated (based on XRD and TEM experiments) with improved thermal stability.

3.2 Melt Compounding

This method became popular since its invention by Giannelis et al. in 1993 [13]. It has been the most popular way to prepare PP nanocomposites due to its flexibility with the existing processing techniques, like extrusion, blow, and injection molding. Melt blending involves mixing of the clay or modified clay with PP at above the melting temperature of PP, in an extruder or mixer, preferably under shear. The level of clay dispersion in the nanocomposite depends on the mixing conditions and the compatibility between the polymer and the layer silicates. Favorable enthalpy of mixing between the polymer and layered silicates can be expected when the polymer–clay interactions are more enhanced than the surfactant–clay interactions. In order to improve the polymer–clay interaction in PP nanocomposites, many modifiers or compatibilizers have been reported [16, 21–30, 45–54]. Moad et al. [54] used various copolymers as dispersants/intercalants/exfoliants in PP clay composites without clay modification. Polyethylene oxide (PEO)-based nonionic surfactants and amphiphilic copolymers based on a long chain (meth)acrylate (e.g., octadecyl acrylate) and a more polar comonomer (e.g., *N*-vinylpyrrolidone, methyl methacrylate) were applied during melt mixing. Nanocomposites were prepared by melt mixing in a twin-screw extruder by first forming a master batch having 10–70 wt% clay and other components, which was then melt-blended with PP to obtain a composite of the required clay content. The properties of nanocomposites were found to depend strongly on both the level of dispersant and its overall composition. The tensile modulus increased up to 40 % in comparison to organically modified clays. The additives provide substantially improved clay dispersion and cause partial exfoliation. Cui and Paul [23] prepared a PP-g-NH_3^+ functional compatibilizer from PP-g-MA by reacting with 1,12-diaminododecane and followed nanocomposite preparation by the melt mixing method. In the prepared nanocomposites, the NH_2 or ionic $–NH_3^+$ groups do not induce a better interaction for a better clay dispersion than the usual PP-g-MA compatibilizer. The PP-g-MA/organoclay and PP/PP-g-MA/organoclay

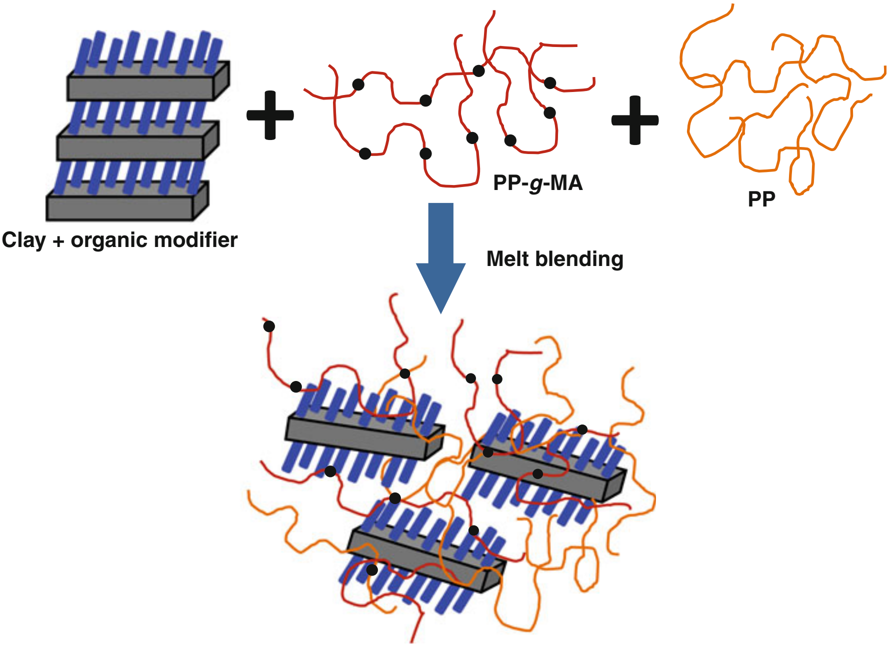

Fig. 8.2 Schematic representation of the melt compounding method used to prepare PPCN in the presence of PP-g-MA compatibilizer

hybrids showed the most substantial increases in mechanical properties and clay dispersion as compared to other polymer clay hybrids. In another attempt, Mulhaupt et al. [55] suggested that octadecylamine reaction with the anhydride group facilitates strong hydrogen bonds between silanol groups of the clay surface. They also discussed the effect of carbon chain length on the clay dispersion.

Among the many compatibilizers, maleic anhydride grafted polypropylene (PP-g-MA) is the most widely used for the development of PP nanocomposites [16, 21–30, 45–53]. This is due to the strong hydrogen bonding formation between the maleic anhydride (or COOH groups generated after hydrolysis) and the oxygen groups of the clay surface. The interaction between PP-g-MA and clay layers help to expand clay galleries; as a result, the interaction between clay layers weakens. In many approaches, first, a master batch with high clay loadings of PP-g-MA is prepared, which is then mixed with PP to form a composite with the required clay content. In this process, when the PP-g-MA intercalated clay contacts with PP under processing, due to a strong shear fields, delamination of the clay layers may be facilitated if there is a great enough interaction strength existing between the PP and PP-g-MA to form a molecularly dispersed clay nanocomposite (Fig. 8.2). Manias et al. [6] reviewed the preparation of PPCNs with the coexistence of exfoliated and intercalated MMT layers by the melt compounding method. In their approach, they applied two steps to prepare the nanocomposites: (i) by introducing functional groups in PP and the use of common alkylammonium

MMTs, and (ii) by using neat/unmodified PP and a semi-fluorinated surfactant modification for the MMT. The PP nanocomposites showed better concurrent improvement in several properties, including tensile characteristics, higher heat deflection temperature, high barrier properties, better scratch resistance, and increased flame retardancy. Okamoto et al. [56] prepared PP nanocomposites using PP-g-MA (0.2 wt% MA) and C18-MMT in a melt extrusion method using a twin-screw extruder at 200 °C. The prepared nanocomposites with 2 wt% clay showed an exfoliated structure; with 4 wt% clay, a disordered intercalated structure; and with 7.5 wt% clay content, the nanocomposite showed an ordered intercalated structure.

3.3 Solution Blending

In this method, the layered silicate or organic modified silicate is first swollen in solvent in which the polymer also soluble. The swollen clay enables the polymer chains to intercalate in between the clay layers by replacing the solvent molecules in the galleries. When the solvent is removed under vacuum, the intercalated structure remains to form intercalated nanocomposites. There are several reports published on the preparation of PP nanocomposites based on the solution blending method [57–61]. Avella et al. [57] prepared nanocomposites by dissolving PP in *O*-dichlorobenzene at 180 °C in a specially made cylindrical flask. The modified organoclay (OMMT) was dispersed in *O*-dichlorobenzene by ultrasonic mixing, followed by mixing of the PP solution. The PP/organoclay nanocomposites were separated by precipitation in cold ethanol, and the solvent was removed in a separating funnel. It was found that, in the nanocomposites with high clay contents (5 %), the clay tactoids remain as clusters in some regions, which cause inhomogeneity, poor adhesion, and, as a result, deterioration of mechanical properties. In another attempt, Chiu and Chu [58] prepared nanocomposites by dissolving PP and clay in 1,2,4-trichlorobenzene (TCB). The solutions were kept at high temperature until clear solutions were formed, and these solutions were cast onto stainless dishes that were kept around 140 °C to evaporate the TCB solvent. XRD and TEM results revealed that the clay layers were dispersed finely (at the nano level), even without using compatibilizer. In another attempt, Oya and Kurokawa [60] demonstrated another somewhat complex procedure to prepare hydrophobic PPCNs. In addition to the solution technique, diacetoneacrylamide was polymerized prior to the addition of PP solution in toluene. However, the expected clay dispersion was not achieved, but, still, the formed nanocomposites had excellent mechanical properties.

3.4 Other Methods

In addition to those common methods to prepare PP nanocomposites, there are several other methods incorporating specially designed instruments and accessories. Nowicki and coworkers [26] introduced radiation-induced modification of

MMT to improve the compatibility between inorganic fillers and the polymer matrix, where the filler was modified with MAH, followed by irradiation with an electron beam. It has been demonstrated that the method is an effective approach in overcoming the organophobic character of inorganic fillers. In polymeric composites, the radiation treatment generates stable carbon-centered free radicals in the organic modifier, which induce filler–matrix linkages. Kato and co-workers [62, 63] developed a direct compounding method for the preparation PP nanocomposites, in which a specially designed twin-screw extruder, equipped with four geometrical sections and a much longer length-to-diameter (L/D) ratio (77:1), is used. In the first section of the extruder, all the materials, comprising PP, PP-g-MA, pristine clay, and alkylammonium salt, are fed and premixed. In the second stage, water is injected into the extruder to disperse the clay into PP in a slurry state, followed by the evaporation of water in the third and fourth sections. With this method, it was found that the clay was dispersed finely in an exfoliated structure. The PP nanocomposites prepared by this method showed better improvement in the properties as compared to composites prepared by the conventional method. Lapshin and Isayev [64] demonstrated an ultrasound-aided extrusion process for the preparation of PPCNs. The nanocomposites were prepared using a co-rotating twin-screw extruder followed by a single-screw extruder equipped with an ultrasonic die. The thus formed nanocomposites showed enhancement in the properties. Wang et al. [65] prepared the PP nanocomposites using a dynamic packing injection molding technique. It was found that, in the nanocomposites prepared by this method, the exfoliation structure increase from the skin to the core.

Marchant and Jayaraman [66] quantitatively studied the role of compatibilizer in the preparation of PPCNs. They found that a significant exfoliation of clay in the composites occurs at an optimum compatibilizer concentration of 10 wt%. Wang and co-workers [67] synthesized end-functionalized PP that contained a functional group (like Cl, OH, COOH, etc.) at the chain end. The ammonium (PP-t-NH_3^+)-terminated PP is directly compounded with clay. The resultant nanocomposites had an exfoliated structure.

4 Structure and Crystallinity of PP Nanocomposites

Semicrystalline polymers are unique among engineering materials, since they are the only common technological materials in which a complicated higher-order structure consists of stacks of lamellar crystals, with amorphous and intermediate regions intercalated between them. For semicrystalline polymers, this structure plays an important role in controlling the mechanical properties of the product. PP has a simple chemical structure ($-[CH_2\text{-}CH(CH_3)]_n-$) but complicated higher-order structure, which may be because it exhibits polymorphism. By adding nanoclay to the PP matrix, the situation becomes more complicated. In this section, the structure and properties exhibited by PP nanocomposites and the mechanism for the formation of such structures will be discussed. That is to say, it is essentially important to reveal the crystal structure, morphology, and orientation of

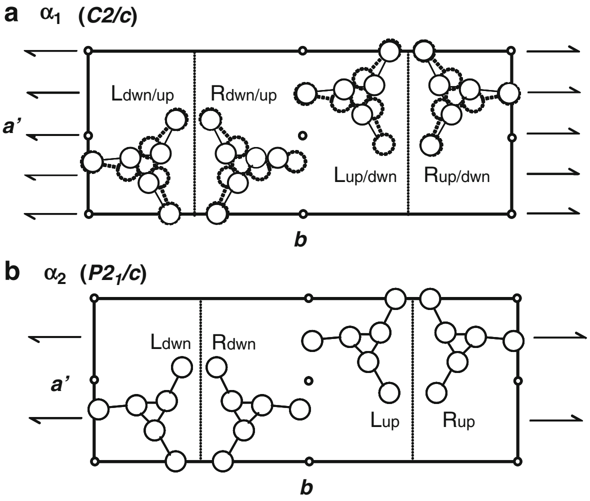

Fig. 8.3 Schematic representation of the crystal structures of iPP. (**a**) α_1 form with statistically random packing of upward and downward chains (space group $C2/c$). (**b**) α_2 form with regular chain packing structure (space group $P2_1/c$)

polymer chains developed in the crystalline state, as well as the orientation of silicate layers in the amorphous state, because these microstructures sensitively affect the properties.

4.1 Crystal Structure of PP and Its Effect on Nanofiller Dispersion

The crystalline structure of PP is complex because it crystallizes in several crystalline modifications, depending on the crystallization conditions. It crystallizes in four different crystalline modifications of monoclinic (α_1, α_2), trigonal (β), orthorhombic (γ), and hexagonal (smectic) systems (Fig. 8.3) [68]. In all of the crystal structures, the chains are packed in the crystal lattice as left- or right-handed (or both) (3/1) helix conformation with upward or downward directions of methyl groups. The disordered α_1 is obtained by slow cooling of the melt. The α_1 form exhibits the crystal structure of space group $C2/c$ or Cc, in which the (3/1) helical chains with $(TG)_3$ conformation are packed upward and downward randomly with 50 % probability, where T and G are *trans* and *gauch*e bonds, respectively [68–71]. When the α_1 sample is annealed at higher temperatures, it transforms into the α_2 form with a structure in which the (3/1) helices are packed regularly upward and downward with the space group $P2_1/c$ (Fig. 8.3) [69, 71]. The γ form is obtained relatively easily for the iPP sample polymerized with Ziegler–Natta catalyst under high pressure [72, 73], for the low-molecular-weight compounds at atmospheric pressure [74, 75], and for the ethylene–polypropylene copolymers [76, 77]. The γ form (with space group F_{ddd} and orthorhombic unit cell) can also be obtained from the iPP samples polymerized with the metallocene catalyst system and contains the *regio* and *stereo* defects [77, 78]. The β form (with space groups $P3_1$ or $P3_2$ and trigonal unit cell) can be obtained by adding special nucleating agents [79]. In the actual structure, these crystal forms are created in a mixed fashion at different ratios, depending on the sample preparation conditions.

4.2 Crystalline Morphology and Crystallization Behavior

Zheng and co-workers [80] studied the effect of clay on the polymorphism of PP in PPCNs. They found that, in both extruded PP and PP nanocomposite samples, only α-form crystallites were formed. They also prepared the samples of PP and PPCNs under compression. It was found that, in the pure PP samples which were compressed at 200 °C and crystallized at various temperatures and times, the maximum amount of β crystallites were formed. This indicates that the crystallization temperature has a significant effect on the formation of β-phase crystallites in neat PP. In the compressed films of PPCN, prepared under the same thermal and processing conditions, no β-phase crystals were detected. This reveals that the clay galleries significantly inhibit the formation of β-phase PP crystallites in the nanocomposites (Fig. 8.4). The results also indicated that the clay might support the formation of γ-phase crystallites in PP nanocomposites, as the γ-phase crystallites are nucleated on the α-phase lamellae, which is similar to the case of γ-phase crystal formation in neat PP under pressure. In fact, Nam et al. [56] observed an enhancement in the formation of γ-phase crystals in PP nanocomposites. However, they proposed a different mechanism of γ-phase formation, which is due to the narrow space in the clay galleries of the nanocomposite.

In their report, Medellin-Rodriguez and co-workers [81] studied the effect of nanoclays on the nucleation, crystallization, and melting mechanism of PP. The prepared nanocomposites had tactoid-like morphology because no compatibilizer is used. After the isothermal crystallization of samples, an inverse relationship between nanoclay concentration and the formation of the β-crystalline structure (Fig. 8.5) was observed. These results are not comparable with the results observed by Zheng et al. [80]. It was, therefore, proposed that the exfoliated individual layers, which are present at relatively high amounts at low nanoclay concentrations, must meet the crystallographic requirements for the nucleation and formation of the β-structure of PP in PP nanocomposites. Further increase in the amount of clay in the nanocomposite inhibits the formation of β-crystalline structure. In another attempt, Dong and Bhattacharya [82] studied the effect of clay content and maleated PP content on the PP crystalline structures in nanocomposites. It was found that the presence of clay enhanced the preferred orientation of PP crystals, which is believed to have contributed to the enhancement of tensile and flexural properties of nanocomposites with increase in clay content. It was also observed that MA-g-PP hinders the growth of α-phase crystals, reducing the tensile properties of nanocomposites with high MA-g-PP contents.

Misra and co-workers [83] discussed the effect of silicate layers on the pressure-induced crystallization of PP. It was found that, in neat sample at high pressures exceeding 60 MPa, γ-phase crystal formations are promoted. In the presence of nanoclay, γ-phase is formed, even at a low crystallization pressure of 0.1 MPa, implying the ability of nanoclay to encourage γ-phase nucleation [84]. Maiti and co-workers [49] discussed the effect of crystallization temperature on the morphology of PPCNs. The dispersed clay nanocomposites acted as a nucleating agent for the PP-g-MA matrix. As a result, the spherulite sizes decreased with the increase of clay content known from the light scattering experiments.

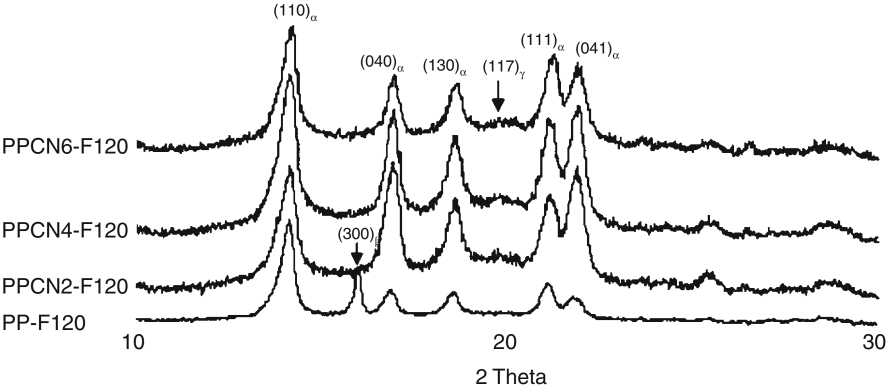

Fig. 8.4 XRD patterns of the neat PP and PPCN film samples prepared by isothermal crystallization at 120 °C on a hot press. Here, PPCN2-F120 identifies the PP sample with 2 wt% clay and annealed at 120 °C on a hot press (Reproduced from Zheng and co-workers [80] with permission)

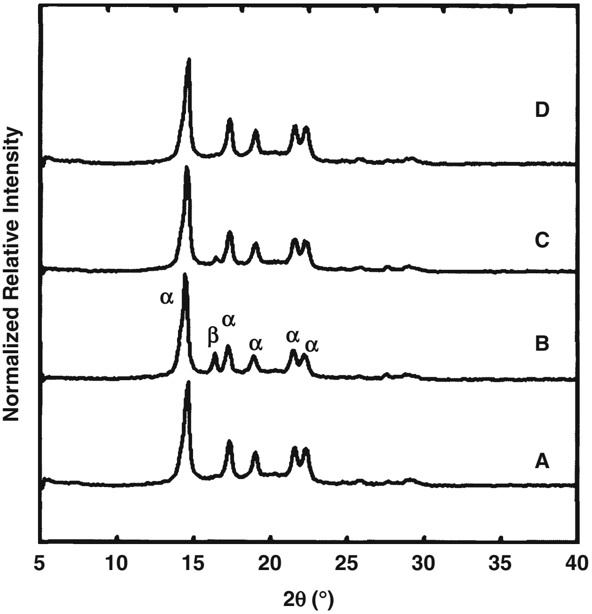

Fig. 8.5 WAXD profiles of the neat PP and PP nanocomposites after isothermal crystallization at (125 °C, 15 min). (*A*) iPP homo polymer. (*B*) iPP + 2 wt%. (*C*) iPP + 4 wt%. (*D*) iPP + 6 wt% nanoclay (Reproduced from Medellin-Rodriguez and co-workers [81] with permission)

The clay particles are well dispersed in the PP composites crystallized at low crystallization temperature (T_c) and the segregation of silicate layers occurs at high T_c. It was also observed that the equilibrium melting point was not affected by the clay content.

The crystallization behavior of PPCNs using differential scanning calorimetry (DSC) in the isothermal crystallization process has been studied by several authors. The crystallization process of pure PP itself is complex, due to the presence of various crystalline modifications in the final product. So, it is very important to reveal the structural evolution process in the presence of nanoclays in the crystallization process from various points of view. It was reported by several authors that the presence of clay layers enhance the crystallization rate of PP in the PP nanocomposites [85, 86]. This is due to the nucleation (heterogeneous nucleation) effect of clays in the crystallization process PP in nanocomposites.

Hegde et al. [87] studied the effect of clay on the crystallization mechanism of PP in PPCNs using a combination of DSC, scanning electron microscopy (SEM), TEM, and polarized optical microscopy (POM). The nanocomposites, prepared with varying clay contents in the range 1–15 wt%, showed intercalated and flocculated morphology for all concentrations. At low wt% (1–5 wt%), well-dispersed clay platelets act as the antinucleating agent (or diluent) and reduced polymer chain mobility, as known from the longer half-time of crystallization or maximum time for crystallization. On the other hand, in the nanocomposite samples with higher (10–15 wt%) clay loadings, due to the high nucleation effect of clay platelets, the polymer chain mobility increased and, as a result, the crystallization rate increased. The phase segregation and phase separation of clay is observed in the inter-spherulite region of samples with a larger amount of clay sample. Solomon et al. [88] studied the flow-induced crystallization phenomenon of PP nanocomposites with intercalated structure using time-resolved small-angle light scattering measurements. It was observed that there was a significant increase in the flow-induced crystallization kinetics for the polymer nanocomposite at applied strain rates. However, a similar flow rate has only a modest effect on pure PP crystallization. Nowacki et al. [89] observed similar results for the crystallization of PP nanocomposites with OMMT and MA-g-PP in isothermal conditions. It was found that the nucleation ability of MMT was enhanced in shear-induced crystallization as compared to the static crystallization conditions.

4.3 Orientation

Wang et al. [90] observed highly oriented structure with both PP and clay platelets along the shear flow direction of PP nanocomposite samples obtained via dynamic packing injection molding. A much higher degree of orientation of PP was observed in the composites as compared with pure PP based on the analysis of the 2D WAXD results. The fibers made from PP and PP nanocomposites (intercalated structure) were studied by Ajji et al. [91]. It was observed that the [001] (normal to the clay platelets plane) plane of clay was oriented perpendicular to the machine direction. The orientation of the *c*-axis of PP in the fibers was slightly higher in the nanocomposite fibers. Preferential orientation of the PP chains is observed in the films of PP nanocomposites (extruded film) based on the XRD studies [92]. The uniaxial drawing in PP nanocomposites induced the silicate surface to align parallel to the sheet surface. The *c* and *a** axes of PP crystals were oriented bimodally to the flow direction (draw direction), and the *b*-axis was oriented to the thickness direction of the specimen [93].

5 Properties of PP Nanocomposites

5.1 Thermal Properties

It is believed that the presence of a small amount of clay can extraordinarily improve the properties of polymers if the clay platelets are dispersed finely. Due to their very high aspect ratio, the silicate layers are capable of dissipating energy rapidly if the silicate layers and the host matrix have interphases at *nano-level* thickness. It was proposed that the thermal resistance of PP increases by filling with clay, which brought about an increase of thermal stability in oxidizing atmosphere [48, 94–105]. The thermo-oxidative degradation of PP nanocomposites was widely investigated using thermogravimetric analysis (TGA). The TGA traces in oxidizing atmosphere showed a shift of the weight loss curves of nanocomposites towards higher temperatures with respect to neat polymer. These results are attributed to the nanoclays bringing about significant improvements in the thermal stability of the PP matrix in oxidizing atmosphere [99]. The shift towards higher temperatures was attributed to the formation of a high-performance carbonaceous silicate char that builds up on the surface, which insulates the underlying material and slows down the escape of volatile products generated during decomposition.

The thermomechanical properties of a polymer material are studied using dynamic mechanical analysis (DMA). The dynamic mechanical behaviors of PP nanocomposites have been studied in order to discover the effect of clay on the viscoelastic behavior of the polymer matrix. It is predicted that, with the increase in the confinement of polymer chains, the viscosity and mechanical properties of the system increases. Maiti et al. [49] measured the dynamic behavior of PP nanocomposites and found that that the storage modulus G' of a nanocomposite with 4 wt% of clay is higher than that for pure PP samples. Also, with an increase of T_c, G' increases, wherein the enhancement is maximal (30 %) for a PP nanocomposite with 4 wt% clay content. For further increases in the clay content, the G' decreases and is found to be 13 %. They attributed that the greater increase of the storage modulus is related to the extent of clay dispersion (amount of intercalation). Kawasumi et al. [50] discussed the temperature dependence of the storage modulus of PPCNs in the presence of PP-g-MA as a compatibilizer.

5.2 Mechanical Properties

The enhancement of the mechanical properties of polymer clay nanocomposites is mainly dependent on the dispersion state of clay, the reinforcing effect, and the interfacial interaction between the clay and the polymer matrix. PPCNs have been investigated in terms of their mechanical properties [106–116] and have been examined by taking into consideration the effect of the extent of clay exfoliation on nanocomposite properties [109]. PP nanocomposites often exhibit improved strength and stiffness by incorporating clay platelets into the PP matrix. To investigate the role of silicate modification and compatibilizer addition on the mechanical properties, clays were synthesized with varying modifier alkyl chain lengths [115]. In order to examine the effect of the alkyl chain length of the silicate modifier on the morphological and mechanical properties, the content of the organophilic layered silicates MEC*n* was varied from 0 to 10 wt% at a MAH-g-PP compatibilizer content of 20 wt%. The significant impact of both MAH-g-PP compatibilizer content and alkyl chain length on the Young's modulus was observed, where MAH-g-PP compatibilizer addition afforded substantially higher stiffness. Silicate modification with C12 amine gave much greater stiffness with respect to that obtained using C8 ammonium-modified silicate MEC8. In the absence of compatibilizer, both the Young's modulus and yield stress were very similar, a result of which improved the exfoliation and stabilization of uniformly dispersed anisotropic nanoparticles. It was concluded that a uniform distribution of clay was the most important for property enhancement. Joshi and Viswanathan [107] observed that the PP clay composite filaments produced by the melt spinning method displayed a substantial improvement in the tensile and dynamic mechanical properties, as well as creep resistance, over neat PP filaments.

The impact strength of the PPCNs increased at low clay (0.5–2 wt%) loadings, which may be due to the exfoliated or intercalated clays hindering crack growth under impact. This effect should increase under more favorable interaction between the clay and the PP matrix or by adding a compatibilizer. By increasing the clay concentration further, a reduction in the impact strength is observed, which is mainly due to poor clay dispersion. Analyses of the fracture and failure mechanisms of PP nanocomposites have been carried out by Bureau et al. [116] through the essential work of fracture (EWF), where tensile testing showed 25–50 % improvements corresponding to the nanoparticle reinforcement effects.

5.3 Other Properties

In general, PP exhibits good water vapor barrier properties, but oxygen, carbon dioxide, and hydrocarbons easily permeate through PP. The presence of the silicate layers must be expected to decrease the permeability due to the more circuitous path for the diffusing molecules that must bypass impenetrable clay platelets. Several authors observed an enhancement in the barrier properties of PPCNs with respect to pristine PP. Sirousazar et al. [46] concluded that adding organoclay into the PP matrix enhances the barrier property of the matrix against O_2, CO_2, and water vapor. A nanoclay master batch has been used to make PP nanocomposite films

Upon the burning of nanocomposites, a carbonaceous char layer is formed, which acts as an excellent insulator to the mass transfer barrier, and, further, increases the flame retardancy of the resulting product [117]. Char formation impedes the movement of volatilized polymer from the interior of a plastic matrix, denying fuel at the air–surface and interface. A flame-retardant formulation containing nanoclay (Nanomer®) has been reported [26–29]. Nanoclays are very effective as a flame-retardant additive as compared to those of the traditional flame retardation chemical systems. Nanoclay also enables the reduction of traditional flame-retardant agents, to reduce toxicity, specific gravity, and provides easy processing for some flame-retardant systems.

6 Degradation of PP Nanocomposites

There are very few reports on the degradation behavior of nanocomposites, in particular, photodegradation [117–121]. The effect of compatibilizers on the photostability of PP nanocomposites has been studied. It was observed that the induction period decreased from 8 to 4 h by using MAH-g-PP as a compatibilizer and a two-phase degradation mechanism was observed based on the infrared spectral changes in the hydroxyl and carbonyl regions. In the first stage (up to 40 h), there was no evidence of the hydroxyl band formation in the infrared spectra, which implied the absence of degradation on the polymer backbone, whereas in the second phase, a dramatic increase in the rate of photooxidation was found. The degradation products were the same in both the composite and the neat polymer [118, 119]. As a whole, PP nanocomposites are less stable against photodegradation as compared to the neat PP. In another report, Lonkar et al. [120] studied the effect of layered double hydroxides (LDH) on the photodegradation of PP nanocomposites under accelerated ultraviolet irradiation. The rates of oxidation are influenced by the nanofiller, depending on the divalent cations of the LDH layers. The LDH phases containing Mg^{2+} have a positive effect on the nanocomposite material, whereas LDH with only Zn^{2+} has no influence on the rate of oxidation of the polymer matrix. Zanetti et al. [121] reported on the thermo-oxidative degradation of PPCNs by using TGA. They found that the nanocomposites were more thermally stable (>50 °C) in comparison to neat polymer. It was speculated that oxygen attacks the carbon radicals within the chain by H abstraction. Around 200–250 °C, hydrogen abstraction becomes more likely, thus, resulting in oxidative dehydrogenation. As the temperature increases, the concentration of chain end radicals increases due to the beta scission of radicals. Direct thermal scission of carbon–carbon bonds was also possible above 300 °C.

7 Applications of PP Nanocomposites

PP and its copolymers are important materials for industrial use because of their combination of properties and light weight as compared to metals, in particular, in the automotive industry. A decade ago, it was General Motors who first introduced commercial PP nanocomposites in automotive applications. The presence of clay enhances not only the mechanical properties but also the heat distortion temperature (HDT). PPCNs are suitable to replace nylon in applications where high HDT is needed. The synergistic enhancements (in terms of the flame-retardant property) of clay nanocomposites for fire safety applications have led to the development of commercial products: a series of polypropylene + organoclay + flame-retardant systems (Maxxam™ FR) produced by PolyOne® [122, 123]. Another important application field is gas barrier materials (packaging materials). Since the addition of clay improves the gas barrier property, their use in the food and drink industry as packaging film to keep foods fresher and for longer should increase tremendously.

8 Future Directions

In this chapter, the author comprehensively summarized reports published on the preparation, structure, crystallization performance, and application of PPCNs. It has been found that the material properties sensitively depend on the dispersion of clay in the matrix. Better clay dispersion in the PP matrix can be achieved through the introduction of functional groups in the main chain or by blending a compatibilizer (PP-g-MA) or by choosing suitable clay modifiers. The addition of nanoclays to the PP matrix not only enhances the crystallization rate and change in the morphology, but it also enhances the mechanical and thermal properties. Although much research has been devoted to develop PP nanocomposites for various applications by achieving fine dispersion of clay platelets, it is still far from addressing various problems such as filler–polymer interactions. So, it is essentially important to understand fundamentally the interaction between polymer–compatibilizer, polymer–filler, or filler–compatibilizer in order to understand structure–properties relationships in PP nanocomposites. Future research essentially requires focusing on better control over the structure and morphology of PP nanocomposites, which is key in achieving the current demands of PP nanocomposites with excellent mechanical properties.

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