

ADVANCES IN POLYPROPYLENE BASED MATERIALS

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Polypropylene is an extremely versatile thermoplastic polymer known for its good performance/price ratio, excellent heat, moisture and chemical resistance, favorable processing characteristics and recyclability. Due to its universal properties, polypropylene is applied in numerous industrial fields such as electronic and electrical, automobile, textile, pipeline, etc. Furthermore, the progress in its synthesis and property modification in the last decade has contributed to the development of new polypropylene based materials with advanced performance. This review aims at reporting on some recent developments in polypropylene based materials, such as nanofibers, natural fiber reinforced composites, self-reinforced polypropylene and polypropylene/clay hybrids, that have replaced many types of engineering thermoplastics in high-performance applications.

Key words: polypropylene; synthesis; crystal structure; nanofibers; natural fiber reinforced polypropylene; polypropylene/clay nanocomposites

INTRODUCTION

Polypropylene (PP) is one of the most common thermoplastic polymers, known for its light-weight, good mechanical properties, excellent moisture, heat and chemical resistance, excellent dielectric properties, favorable processing and recycle characteristics and relatively low price. PP has had remarkable growth rate during the last decades, and it continues to be the fastest growing of the thermoplastic polyolefines. Estimates indicate that approximately 69.1 million tones of PP were manufactured globally in 2013 [1]. Due to its versatility and sustainability, PP has found extensive use in both commodity and engineering applications.

The progress in catalytic systems for its synthesis, development of new production technology and increasingly sophisticated performance requirements of the polymeric materials marketplace, have resulted in development of a new generation of advanced PP-based products. Innovative PP-based materials continue to reinforce the capability of PP not only to replace traditional materials (such as wood, metals, glass etc.), but also to introduce new application possibilities in diverse industrial fields.

SYNTHESIS

Propylene was first polymerized to a crystalline isotactic polymer by Giulio Natta as well as by the German chemist Karl Rehn in 1954. This pioneering discovery led to a large-scale commercial production of isotactic PP (iPP) in 1957 in Italy, Germany and USA. Its industrial importance results from the appearance of high molecular weight stereoregular PP, synthesized on complex organometallic Ziegler-Natta catalyst (a combination of transition metal compound, TiCl_4 with metal alkyl co-catalyst, $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$) [2, 3]. Ziegler-Natta catalysts were able to restrict linking of monomer molecules to a specific regular orientation, either isotactic, when all methyl groups are positioned at the same side with respect to the backbone of the polymer chain, or syndiotactic, when the position of the methyl groups alternate [3, 4]. The first isotactic polypropylene exhibited relatively low degree of crystallinity, 40%. It should be mentioned that the other commonly known catalysts for polymerization (free radical, cationic, etc.) typically produce low molecular weight amorphous PP that is of limited commercial value [2]. Since the first Ziegler-Natta catalytic

system, a numerous variations of formulae, consisting of the combinations of IVB-VIIIB transition metal compounds and IA-III A organometallic compounds, evolved [4]. However, a major improvement in catalytic activity was achieved by introduction of supported Ziegler-Natta catalysts in the 1970s [5]. Since then, several generations of these systems have been developed, allowing excellent stereochemical control and tunable morphology of PP. Among many inorganic compounds tested as support for polyolefine catalysts, anhydrous $MgCl_2$ remains the most widely employed in industrial Ziegler-Natta catalysis [2]. Due to enormous extent of industrial investigation, the catalyst's productivity has grown rapidly, from 0.1 kg PP/g catalyst in 1950s to 100 kg PP/g catalyst in 2010 [2].

The second class of catalysts being introduced for the production of PP is metallocenes, called also single site catalysts. They are soluble in aromatic hydrocarbons and usually contain two components, a metallocene complex and a special organometallic cocatalyst, methylalumoxane $[(O-Al(CH_3)_2)_n]$. The metallocene catalysts have the composition Cp_2MCl ($M = Ti, Zr, Hf$) such as titanocene dichloride, and the organic ligands are typically derivatives of cyclopentadienyl. Contrary to Ziegler-Natta catalysts, single site catalysts are homogeneous, and the property profile of single site catalyst derived PP is much better controllable, the chain structure is more uniform, and the molecular weight distribution of PP is very narrow (M_w/M_n of 2–3), compared to Ziegler-Natta (M_w/M_n of 4–8) [2]. Special group of single site catalysts has been developed in 1980s [6] to produce syndiotactic PP, sPP. sPP is less crystalline than iPP and it has smaller crystalline domains; as a consequence, its optical clarity is very good, and melting temperature ($\sim 128^\circ C$) is lower than iPP ($\sim 155\text{--}165^\circ C$) [6]. The polymerization mechanism of metallocene catalysts is similar to that of Ziegler-Natta catalysts: propylene monomer molecules coordinate with transition metal complexes and then insert between the chained segments and the metal to form the long chain polymer [1]. The most important technological characteristic of all the supported catalysts are high productivity and a high fraction of the crystalline isotactic PP they produce at $70\text{--}80^\circ C$ under standard polymerization conditions. Industrial manufacturing processes are usually carried out either in the medium of liquid propylene or in the gas-phase reactors, and differences in catalytic system and production conditions enable altering of molecular characteristics, morphology and properties of PP [2, 7]. The progress in the synthesis routes has nowadays resulted in a wide range of molecular masses, isotacticity index, molecular

mass distribution, rheological properties etc., and this is the reason why PP is fabricated into hundreds of consumer and industrial goods.

Crystal forms and morphology of PP

It is known that the overall properties of semicrystalline polymers are dictated by morphology, which is influenced by crystallization behavior of the polymer under certain conditions. PP belongs to the group of polymers with high tendency to crystallization due to its regular chain structure. The most important industrial polypropylene remains the isotactic one, although in some fields (such as, for instance, film-forming) the application of β -iPP is favourable [8]. Isotactic PP has been studied extensively for its polymorphic characteristics and crystallization behavior since 1960s [9] and the results of these studies are reported in many monographic [see, for instance summarized Ref. 10 and 11] and journal publications [12–19]. Its crystalline morphology influences greatly the overall polymer properties (rheological, physical and mechanical) and the properties of the final products made of PP. iPP crystallizes into several crystal modifications, such as monoclinic (α), hexagonal (β), triclinic (γ) and mesomorphic form (see Figure 1), depending on the conditions of crystallization and molecular characteristics.

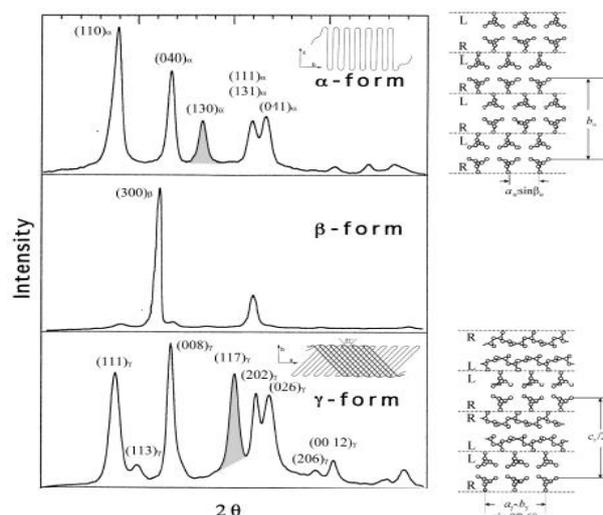


Figure 1. The WAXS patterns of the different PP phases and their crystal structures (Diagnostic reflections are shaded. Courtesy F. Auriemma and C. DeRosa, Naples University)

Commonly, under the processing conditions that occur in practice, it crystallizes into thermodynamically most stable monoclinic α -phase which is

responsible for its good strength and modulus. The trigonal β -form is metastable and can be obtained, or can become predominant, under specific crystallization conditions. The β -form PP exhibits lower strength but much higher impact toughness than the α -form PP [8, 20]. In most cases, the β -form can only be partially formed in samples mixed with α -form. A high content of the β -form in iPP can be achieved under special conditions such as rapid quenching, zone solidification, crystallization under a temperature gradient [12, 15] or in the presence of selective β nucleating agents [21–34]. Conformation of macromolecules in γ -form is analogous to α form, and it can be obtained as a result of crystallization under elevated pressure above 200 MPa and from iPP samples with a low molecular weight. The melting temperature of the β -form lamellae is near 152 to 164°C, while the melting of the α -form lamellae occurs above 164°C. Moreover, the α -form lamellae can still grow in the temperature range from 152 to 164°C. iPP can crystallize in a wide range of spherulite dimensions (from 10–50 μm to 280–370 μm) depending on the temperature of crystallization and crystallization conditions as well as the presence of nucleating agents [35–37]. The presence of maleic grafted PP (PP-g-MA), most often used as an adhesion modifier for PP composite applications, leads to alteration of the crystallization kinetics, without any significant changes in polymer spherulitic morphology (Figure 2) [16]. Selective nucleating agents are sometimes added to PP, before or during processing, to induce appearance of a certain polymorphic modification, to enhance the crystallization, to obtain more uniform morphology and to alter its mechanical properties or transparency. Derivatives of sorbitol are the most effective known nucleating agents of iPP, leading exclusively to the creation of the monoclinic α -form [26, 38, 39]. The best-known β -nucleating agents are the trans-quinacridone [21] and a bicomponent mixture of pimelic acid and calcium stearat [40]. A particularly important structural effect, usually observed if nucleating agents are introduced into semi-crystalline polymers, is an increase of crystallization temperature T_c . This effect is characterized by the creation of a larger number of smaller spherulites, and the shortening of the crystallization time, which is especially useful for the industrial application, where the economic benefit is related to shorter cycles time (for instance, about 30% shorter injection molding cycle was reported in [22, 41] due to heterogeneous nucleation induced by addition of nucleators).

The specific structural characteristics of α - and β -modifications of iPP may lead to significant

differences in the end-use properties. There is particular interest in adjustment of the optical properties (a so-called clarifying effect) achieved by the use of the derivatives of sorbitol [26, 42]. One can also affect mechanical properties, namely enhance the impact strength and lower the stiffness for β -nucleated iPP [21].

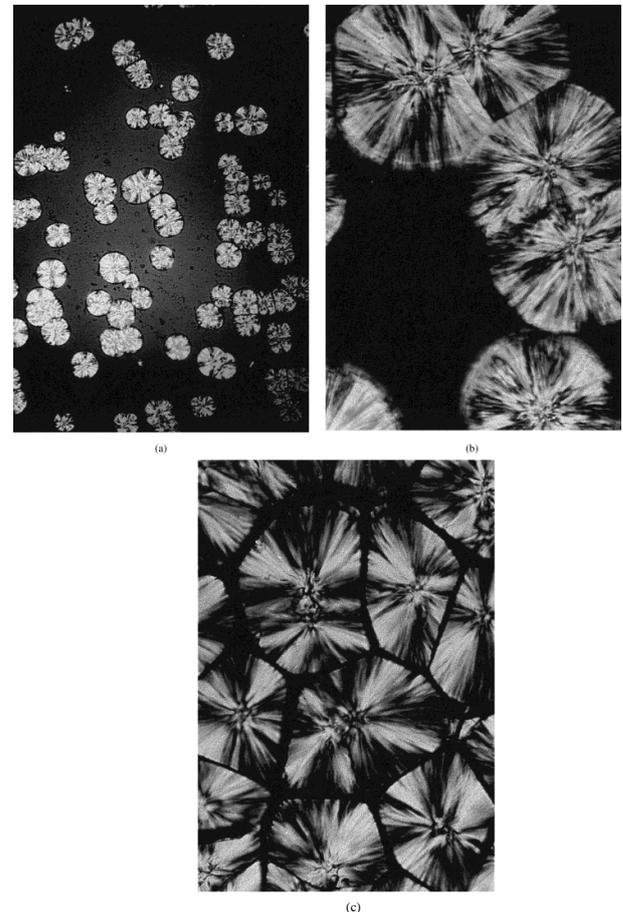


Figure 2. Polarizing optical microscopy of spherulitic morphology of PP-g-MA (typical for iPP) crystallized isothermally at $T_c = 135\text{ }^\circ\text{C}$ after (a) 150 min, (b) 190 min and (c) at the end of crystallization

The effects of various additives on the crystallization of iPP have also been investigated. These additives include not only different nucleating agents, but also mineral fillers (talc, CaCO_3 , sepiolite, mica), various pigments, carbon black, certain flame retardants and other ingredients. Numerous results are also reported on fiber reinforced/iPP composites, where fiber surface generally favors heterogeneous nucleation, sometimes resulting in a specific transcrystalline layer on the surface with characteristics different from those in the bulk polymer [8]. During the crystallization of fiber-reinforced polymers, fibers have dual effect, which

depends on the interplay between their enhancing impact on nucleation and their depressing effects on spherulitic growth caused by an impingement mechanism [43]. The nucleation activity of glass and PET fibers, used to produce special textile composite preforms, was also analyzed and it was shown that differently treated and sized fibers might exhibit different nucleating ability toward isotactic PP, resulting in lower energy for formation of a stable nucleus and its lower critical dimensions. Predominant nucleating effects were exhibited by glass fibers surface treated with PP compatible sizing, pointing out to the possible reactive coupling effects between its components and the functional groups of maleic anhydride modified PP, used as a matrix in the composite material [44, 45].

Recently, much attention has been paid to PP-nanocomposites, produced by different techniques and containing mainly carbon nanotubes/nanofibers or layered silicates [46–56]. Numerous reports describe the fabrication of a range of PP-nanocomposites, and, in particular, the impact of nanofillers on the crystallization of a matrix. In general, the results obtained by DSC analysis, applying the known theoretical approaches of polymer crystallization, demonstrate nucleation ability of nanofillers resulting in a change of polymer morphology, similarly to the action of glass and carbon fibers (see Figure 3) [56–60].



Figure 3. Shear-induced transcrystallization of PP in glass fiber/PP composites, showing the appearance of α -crystalline modification of iPP on the fiber's surface (polarizing optical micrograph of a single glass fiber after partial melting of the matrix) [59]

Biopolypropylene and "programmed degradable" PP

Polypropylene belongs to nonbiodegradable thermoplastics. In fact, most of the synthetic polymers produced from petrochemicals are inherently nonbiodegradable, and through processing and fabrication they are turned into plastics that are envi-

ronmental nonbiodegradable. Due to the increased environmental concern, a new class of biodegradable plastics appeared at the end of the last century, mainly produced from biomass sources [61]. Thermoplastic synthetic polymers produced from biomass are promoted as environmentally friendly alternatives to plastics derived from petroleum, and they are known as "synthetic biopolymers", similarly to biological polymers (biopolymers) produced by plants, animals and microorganisms through biochemical reactions [61, 62]. Among them, polylactic acid (PLA), one of the most highly developed biopolymer, is presently produced mainly from corn, i.e. by condensation polymerization of lactic acid monomer obtained through the conversion of starch from corn, wheat, rice or some other starch source [63]. Recently, production of PP using propylene synthesized from ethanol (obtained by fermentation of sugar cane), so called "biopolypropylene", has been also announced [64–67]. Biopolypropylene is tough and flexible and is commonly used in the packaging industry, but other uses include also textiles, bottles, and even polymer banknotes.

The idea of "programmed degradable plastics" (plastics with controlled life times that degrade in a predetermined time under specific conditions) has been also developed, by making synthetic nonbiodegradable polymers photosensitive: the sensitizing group, such as a ketone group, is introduced into the polymer chain by copolymerization with an appropriate monomer [61]. Another approach, not relying on photodegradation, is based on incorporation of special additive formulations that promote environmental degradation through the chemical processes of oxidation and hydrolysis [64].

PP nanofibers – a new important class of materials

The PP fiber industry occupies more than 30% of global PP market share. PP fibers are used in a wide range of fibrous materials, such as woven or knitted fabrics, nonwovens and special 3D-structures for technical application [68]. The diameter of conventional fibers made by typical industrial melt spinning manufacturing processes is usually about 10–20 micrometers, and this greatly limits their application in engineering purposes. However, progress has been made lately in the field of nano-dimensional fibers and fibrous materials, which represent a new class of important materials with potential use in numerous fields [69]. Newly developed phase separation method provides a promising tool for preparation of PP fibers with

diameter range in nanoscale (~ 100 nm) [70]. Thus, iPP nanofibers were prepared by this method using blends of iPP with cellulose acetate butyrate [71], polyethyleneterephthalate [72], polyamide 6 [73] and polylactide [74] as a matrix material, that is selectively removed as a result of phase separation to form PP nanofibers. Another method applied recently for preparing nanostructured PP material (150–400 nm) is the template synthesis [75]. So far, electrospinning is the most used method for producing nanofibers, and progress has been made in electrospinning of both syndio- and isotactic PP monofibers [76–78]. For instance, uniform nanofibers of syndiotactic polypropylene (sPP) with diameters between 140 and 350 nm were successfully obtained from high-temperature solution electrospinning [79]. However, the wide-spread commercial use of electrospinning is still limited, mainly due to its low production rate [79]. Centrifugal spinning is an alternative method for producing nanofibers from various materials at high speed and low cost. In centrifugal spinning, the spinning fluid is placed in a rotating spinning head. When the rotating speed reaches a critical value, the centrifugal force overcomes the surface tension of the spinning fluid to eject a liquid jet from the nozzle tip of the spinning head. The jet then undergoes a stretching process and is eventually deposited on the collector, forming solidified nanofibers. Centrifugal spinning is simple and enables the rapid fabrication of nanofibers for various applications [80]. The Forcespinning® unique technology [81] has only recently been developed to commercial-level production by FibeRio Technology Corp., McAllen, Texas, and it has already gained significant momentum with reporting of PP nanofibers with average diameters of less than 500 nanometers. Furthermore, a 100-fold increase in productivity rate has enabled the technology to be viewed for more than air filtration applications. Dramatic productivity gains have been demonstrated with both the melt-based process and solution spinning.

Application of PP fibers and fabrics is versatile, and recently has expanded rapidly due to these innovations in nanofibers production, but also as a result of easily modulated surface functionality by means of chemical and physical modification of PP. Thus, nano-PP fibers and nonwovens are used in variety of applications, including protective clothing, battery separators, tissue engineering, energy storage, filtration and waste water treatment [68, 82, 83], bioseparation, and also for production of various biomedical textiles after proper chemical modification or incorporation/deposition of antibacterial components onto their surface [84–89].

Natural fibers' and self-reinforced polypropylene composites

Environmental regulations have forced the search for new composites and "green" materials, compatible with the environment. As a result, new eco-friendly lightweight materials and technologies have been developed in the last decades. Natural fibers reinforced thermoplastics and self-reinforced thermoplastics represent the two major groups that have already penetrated the global market of composite materials. Natural fiber composites consist of biodegradable or easy recyclable polymer matrices and different natural fiber reinforcement [90–92]. Polypropylene, on the other hand, is one of the most widely used thermoplastic polymer due to its versatility. It is tough and flexible but has to be filled and reinforced to compete with engineering plastics. To improve its properties, glass fiber is commonly used, however, recycling of PP/glass fiber composites is difficult, especially when energetic recycling is targeted. Moreover, reprocessing through melt compounding is accompanied by substantial property losses because of breakage of the fibers.

Natural plant fibers, such as flax, hemp, kenaf, ramie have been extensively investigated as a renewable alternative to traditional glass fibers reinforcement. For the application, especially in the transport sector, the lower density of plant fibers (usually, less than 1.5 g cm^{-3}) compared to glass fibers ($\sim 2.5 \text{ g cm}^{-3}$) is attractive: plant fibers allow to produce lightweight structures and subsequently to reduce the fuel consumption of the vehicle. On the other hand, their mechanical properties are adequate for reinforcement of thermoplastic polymer matrices: fracture stress of natural fibers is between 280 MPa and 1000 MPa (see Table 1 and Table 2), in dependence of the fiber type, its constituents, fibrillar structure and amount of cellulose. Among natural fibers flax fibers have attracted great interest due to their very high specific modulus ($71 \text{ GPa g}^{-1} \text{ cm}^{-3}$) as compared to glass fibers ($28 \text{ GPa g}^{-1} \text{ cm}^{-3}$). In eco-composite materials PP takes an important place since its recyclability represents an important advantage from environmental point of view. It has been demonstrated that the PP/natural fiber composites have the potential to replace glass fiber/PP composites [93–105]. For instance, PP/sugar cane composites containing 20 % natural fibers have strength of 17 MPa and modulus of 600 MPa, while the modulus of bamboo fiber reinforced PP reaches 2.5 GPa [91]. Bagasse/polypropylene and china reed/PP composites contribute to further weight reduction and energy saving compared to glass fiber reinforced plastics [92]. Currently, the widely favored PP is used for great number of recyclable

eco-composites [95, 106–107]. Although PP could not be classified as a biodegradable polymer, by introducing thermo-sensitive catalysts to increase its degradability (as reported earlier in this paper), PP continues to take an important place in eco-composite materials.

The production procedures for natural fiber composites are quite similar to those for the production of conventional glass fiber composites, and they include injection and compression molding, vacuum injection molding, structural reacting injection molding and resin transfer molding [94, 106–108].

Table 1. Basic properties of some natural fibers [91]

Fiber	Density g cm^{-3}	Elongation at break %	Fracture stress MPa	Young modulus GPa
Cotton	1.5	7.0–8.0	287–597	5.5–12.6
Jute	1.3–1.46	1.5–1.8	393–800	10–30
Flax	1.4–1.5	2.7–3.2	345–1500	10–80
Hemp	1.48	1.6	270–900	20–70
Sisal	1.2–1.5	2.0–2.5	511–700	3.0–98
Bamboo	0.8	/	391–1000	48–89
Soft wood	1.5	/	1000.0	40.0
Ramie	1.5	3.6–3.8	400–938	44–128

Table 2. Mechanical properties of sisal and flax fibers in comparison with conventional reinforcing fibers (glass, Kevlar and carbon) [91]

Fiber	Specific gravity g cm^{-3}	Tensile strength GPa	Tensile modulus GPa	Specific strength $\text{GPa g}^{-1}.\text{cm}^{-3}$	Specific modulus $\text{GPa g}^{-1}.\text{cm}^{-3}$	Cost ratio
Sisal	1.2–1.5	0.08–0.5	3–98	0.07–0.42	3–82	1
Flax	1.4–1.5	2.00	85	1.60	71	1.5
E-glass	2.60	3.50	72	1.35	28	3
Kevlar	1.44	3.90	131	2.71	91	18
Carbon (standard)	1.75	3.00	235	1.71	134	30

In PP-based composites, natural fibers are used in the form of nonwoven textiles, fabrics, mat, SMC (sheet molding compounds) and BMC (bulk molding compounds) for compression molding, and hybrid mats (both the reinforcement and the matrix polymer are in fibrous form), but also as UD-reinforcing fibers [109]. Thus, the innovative "LFT-D/NF"-technology represents a process of reinforcement of thermoplastic polymers with direct introducing of long natural fibers, resulting in a compound that could be processed and pressed in one stadium. It is very important to note that the cycle time of one natural fiber thermoplastic mat is comparable with the cycle time for production of thermoplastics reinforced with synthetic long fibers.

Numerous companies (Technilin, Visteon, Tech-Wood International, Wageningen UR, etc.) have already developed industrial production of natural fiber/polypropylene composites, applicable in car industry, furniture, building materials, door

panels, trims, office cabinet, marine flooring, and various artificial wood products [110–115].

Analogously to conventional carbon and glass fiber reinforced composites, the interfacial adhesion in natural fibers PP composites plays a crucial role for the mechanical behavior of the material. Therefore, prior to their use in PP-composites, natural fibers are subjected to chemical treatments such as dewaxing, bleaching, steam explosion, silane treatment, etc. in order to enhance adhesion with a polymer matrix and to improve their, otherwise, low dimensional stability (due to the moisture absorption) [116, 91]. Also, it has been reported that the modification of the matrix PP by maleic anhydride provides polar interactions and covalently links PP to the hydroxyl groups of the cellulose, thus enhancing the composite strength and modulus [95, 108].

The future research on natural fibers reinforced PP composites is mainly focused on a cost-

effective modification of fibers, since the main market attraction of eco-composites is the competitive cost of natural fibers. The reports, related to the comparison of LCA (life cycle assessment) of natural fiber composites with glass fiber reinforced composites, have found that natural fiber composites are superior in the specific automotive applications, first of all due to their lower weight and possibility of recycling [90, 91, 117–120].

Another class of new PP based materials, 'all-PP' composites, has attracted great industrial interest. They represent an easy-to-recycle alternative, because both reinforcement and matrix are made from the same polymer: they have identical chemical structures but different melting region [121–127]. Hence, the polymorphism of iPP represents an advantage, since its α - and β -crystal forms exhibit not only different mechanical properties, but also different melting temperatures [122, 123]. This class of recyclable PP composites was developed in the 1990s and they are known as self-reinforced polymer composites, SRPs. Nowadays, they are commercially available (for instance, Curv® of Propex, Armordon® of Don and Low Ltd., Goodfellow PP products, Tegriss™ of NASCAR®, etc.) in a form of fabrics or pre-consolidated sheets [128–131]. The PP-based SRPs exhibit a unique set of properties including: low density, good tensile strength, outstanding impact strength (even at low temperatures) and recyclability. The key characteristic of SRP materials is that the matrix and reinforcement are made of the same polymer. The matrix PP is a lower melt temperature version and the PP-reinforcement is a higher melt temperature version, which is also highly drawn to give a high-tenacity fiber. SRP composites are lightweight, impact resistant and more recyclable than thermoplastic composites which have glass or carbon fiber as reinforcement. The woven SRP fabrics are produced using co-extruded tapes. Each individual co-extruded tape consists of a high melting point polymer core, surrounded by a lower melting point copolymer "cap" coat. Armordon® fabric utilises the technology of the co-extruded tape within fabric. In this way, the technology does not rely on resin impregnation, but on the welding of flat tapes. Thermal consolidation (usually performed under pressure) of the fabric melts the "cap" coat of the individual tapes and fuses the tapes together within the weave of the material.

SRP composites are currently in use to manufacture luggage (Samsonite, Tumi), for anti-ballistic and blast panels, for sports goods (body protection pads) and automotive body panels (Porsche, NASCAR). Comparable data of commercially available self-reinforced PP sheet and other PP-

based materials (isotropic PP, short glass fiber reinforced PP mat, with 40 % fibers, and UD glass fiber reinforced material with 60 % reinforcing fibers) are available on the matweb [132].

The properties of PP and PP-based products greatly depend on polymer morphology developed during the process of manufacturing [133–135]. The works of Verpoest et al. [136] and Czigany et al. [137] have demonstrated a wide property range of self-reinforced PP composites, depending on the processing parameters. For instance, an increased compaction temperature allows more molecular relaxation, thereby melting more matrix and creating a stronger interlayer bonding. These results might help in further tailoring of self-reinforced composite properties for certain specific applications.

It is well known that the mechanical properties of thermoplastic composites depend not only on the properties of the reinforcing fibers and polymer matrix, but also on the interfacial characteristics. Having in mind that the self-reinforced PP is, by its morphology, a kind of a "composite" material, it becomes clear that for the future development of SRP it would be necessary to elucidate the role of a transcrystalline zone, which is a common feature in fibers reinforced crystallizable thermoplastics [138, 139].

Polypropylene/clay nanocomposites – a new class of organic/inorganic hybrids

The field of nanotechnology is one of the most popular area for current research and development in basically all technical disciplines, including polymer science and technology [140]. An increasing number of review articles has been published on polymer nanocomposites, their synthesis, properties and potential application [see, for instance the Ref. 141–144], due to their new and often much improved properties as compared to their macro- and micro-counterparts. The synergistic advantage of nanoscale dimensions (which represent a transition zone between the macro-level and the molecular level) relative to larger scale modification is an important consideration in polymer nanocomposite materials [140].

In the past decade polymer/layered silicates (most often, clay) nanocomposites have attracted especially great interest, both in academia and industry, because they usually exhibit remarkable mechanical properties [140, 142, 146–148], good heat resistance [140], gas permeability resistance [149, 150] and significantly reduced flammability [151, 152], when compared with virgin polymer or conventional composites. Due to extremely high aspect ratio (length/thickness), when the clay struc-

ture is delaminated into individual platelets during processing, the polymer properties can be improved even at very low clay loadings (less than 5 wt%), compared to conventional composites, which employ reinforcing fibers loading of 20–40 wt%. Additionally, because of the platelet orientation, polymer/clay nanocomposites also exhibit dimensional stability in two dimensions instead of one, known for isotropic fillers. Furthermore, in spite of their submicrometer lateral size, clays are only 1 nm thin, and when single layers are dispersed in a polymer matrix, the resulting nanocomposite is optically clear in the visible region.

The driving force for the permanently increasing research work in the field of polymer nanocomposites was the report from the Toyota research group in the 1990s of a Nylon-6/montmorillonite nanocomposite [153], for which very small amounts of layered silicate loadings resulted in pronounced improvements of thermal and mechanical properties. Although first demonstrated for Nylon, polymer/clay nanocomposites have since been prepared for a range of thermoplastic and thermoset polymers. The improved properties of nanocomposites are related to the modification of the structure and dynamics of the polymer at and near the particle surface. Because of the large surface area, this fraction of the polymer contributes significantly to the properties of the whole nanocomposite, even at low filler content. In this respect, polymer nanocomposites are somehow similar to semicrystalline polymers where the crystals can be considered as nanofillers too [147].

The reinforcement of polypropylene and other thermoplastics with inorganic particles, such as talc and glass, is a common method of material property enhancement, but polymer/clay nanocomposites have extended this strategy to the nanoscale. In an attempt to overcome its relatively low toughness and low service temperature, isotactic polypropylene has become one of the pioneer researched nanocomposites. On the other hand, PP has a great potential for composite materials, since it can be processed by conventional technologies, such as injection molding, extrusion and many others. One of the most commonly used layered silicates is natural montmorillonite (i.e. natural smectic clay, 2:1 phyllosilicate), which consists of regular stacks of aluminosilicate layers with a high aspect ratio (thickness between 1.2–1.5 nm and a lateral dimension of 100–200 nm) and a high surface area. Because of the hydrated sodium cation in the clay galleries, natural montmorillonite is hydrophilic, which is a problem to have it homogeneously dispersed in non-polar organic polymers. Therefore,

the surface treatment of silicate layers is necessary to render its surface more hydrophobic, which facilitates exfoliation. Generally, this can be done by ion-exchange reactions of the interlayer inorganic cations with organic cationic surfactants, including primary, secondary, tertiary and quaternary alkylammonium compounds [see, for instance Ref. 154]. This modification also leads to the expansion of the basal spacing between the silicate layers, due to the presence of alkyl chain intercalated in the interlayer, and such organo-modified clays are already available commercially in several varieties, tailor made for different applications.

Following the procedure of Toyota researchers, the in situ intercalative polymerization for the preparation of PP/clay nanocomposites was first applied by Tudor et al. [155]. They demonstrated the ability of soluble metallocene catalysts to intercalate inside silicate layers, and to promote the coordination polymerization of propylene. In this method, the clay is used as a catalyst carrier, and the monomer intercalates into the interlayer gallery of the clay and then polymerizes there. Many other attempts for in situ synthesis were published since then, and they are reviewed in [156, 157]. Recently, polypropylene nanocomposites were synthesized using metallocene catalysts supported on commercially available organophilic clays [158]. Yet, the influence of the monmorillonite layered silicates on the termination rates of propylene polymerization has made the method of in situ polymerization less applicable option for synthesis of PP/clay nanocomposites [159].

A novel approach to prepare PP/clay nanocomposites using a functional oligomer (PP-OH) with polar telechelic OH groups as a compatibilizer was first reported by Usuki et al. [160]. In this approach, PP-OH was intercalated between the layers of organo-modified montmorillonite, and then the product was melt mixed with PP to obtain the nanocomposite with intercalated structure. Many further investigations were reported on melt blending of PP, modified by maleic anhydride grafted polypropylene (mPP) used as a compatibilizer, with organo-clays [161–167]. A wide range of systems was investigated in order to promote polymer intercalation into the clay galleries, with variables being molecular weight of the PP, maleic anhydride content in the compatibilizer, clay modification and content, etc. According to Okamoto et al. [141] and Okada et al. [168], the driving force of the intercalation originates from the maleic anhydride group and oxygen groups of the silicate through hydrogen bonding. It was found that the lower the molecular

weight of the maleated PP and the higher the maleic anhydride ratio of the mPP were, the better was the dispersion of the clay. However, this could affect inversely the miscibility between the high-molecular weight matrix PP and the compatibilizer. Depending on a nanoscale dispersion of the layered silicate, the whole spectrum of structures, ranging from intercalated to exfoliated PP nanocomposites, have been observed by WAXD, SAX (see, for instance, Figure 4) and TEM [166, 169–172]. It is well known that functionalization with mPP could lead to chain scission of the PP, which, in turn, can drastically diminish the mechanical properties of final composite [172]. Therefore, much care is needed in optimizing the polymer matrix modification system.

Many reports on the different ways of preparations and characterizations of iPP-mPP/clay nanocomposites have been already published [173–177]. Recently a new approach based on latex technology was introduced, which has been successfully applied for preparation of single- and multi-walled carbon nanotubes/polymer (CNTs) conductive composites in a polymer matrix of choice, with very low percolation threshold and potential application in electronics [178].

This technique allows a use of third component such as surfactant molecules, to assist the exfoliation of CNTs into the polymer matrix without altering the intrinsic properties of the CNTs. The versatility of the ‘latex concept’ was demonstrated for semicrystalline PP/CNT nanocomposites, prepared

from aqueous PP emulsions. For this system, a low percolation threshold was found, and the extremely well-dispersed CNTs proved to be excellent nucleating agents for PP, raising significantly the crystallization temperature [179, 180]. It has been demonstrated that the latex technology (see Figure 5) could be successfully applied for preparation of PP/organo-modified clay nanocomposites as well [181].

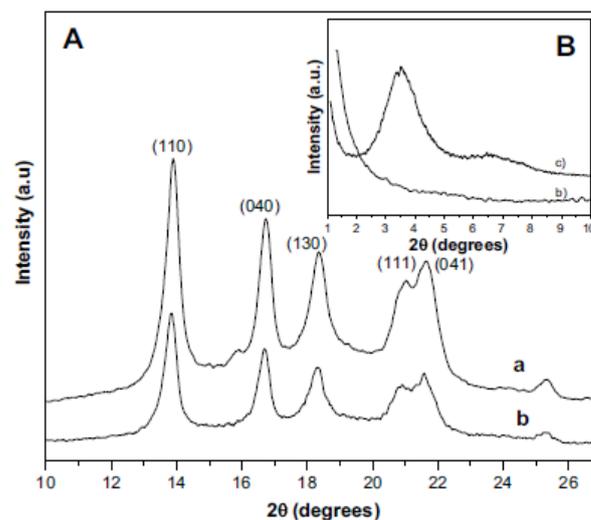


Figure 4. WAXD patterns for:

A – neat iPP (a) and iPP/montmorillonite nanocomposite containing 1 wt% clay (Cloisite C93A) (b) in $2\theta = 10\text{--}26^\circ$, B – nanocomposite (b) and Cloisite C93A (c) in $2\theta = 1.0\text{--}10^\circ$, showing the absence of clay characteristic peak at $2\theta \sim 3.5^\circ$ (an evidence of effective exfoliation of the clay) [169]

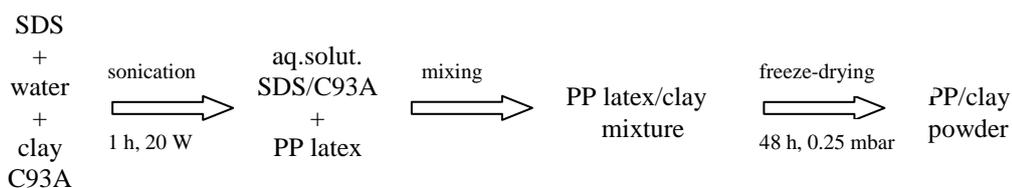


Figure 5. The schematic representation of the multi-step preparation of PP/clay (organically modified clay, Cloisite C93A) nanocomposites by latex technology [181]

After ultrasonication-driven exfoliation of clay nanoparticles, mixing with PP-latex, freeze-drying and subsequent compression molding, dispersion of organo-clay particles at nanoscale level in the matrix polymer was confirmed by morphological analysis carried out by WAXD and TEM/SEM. According to the obtained results, complete exfoliation of clay in the matrix has resulted in improved thermal stability of the hybrid. Dynamic mechanical analysis reveals an increase in storage modulus of PP matrix in the nanocompo-

sites for 30% over a temperature range, indicating an increase in the stiffness of the material with the addition of clay (see Figure 6).

Extensive research has shown that the morphology of iPP in fiber/filler-reinforced composites, as well as its crystallization and melting behaviour, is affected by the presence of reinforcing fibers (carbon, glass, polyethylene terephthalate, etc.). Similarly, the addition of different nanofillers (such as carbon nanotubes and layered silicates) can induce enhanced nucleation in the matrix and thus,

changes in crystallization kinetics, and appearance of a transcrystalline layer as well (see Figure 7) [140, 141, 182]. In general, crystallization is one of the most effective processes to control the extent of intercalation of polymer chains into silicate galleries, and hence to control the mechanical and various other properties of the nanocomposites [141].

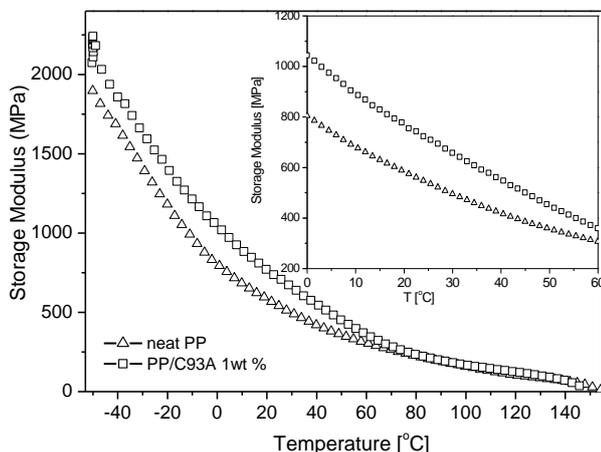


Figure 6. Dynamic mechanical thermal analysis (DMTA): Temperature dependence of dynamic storage modulus E' for neat PP matrix and PP/C93A 1 wt% nanocomposites prepared by latex technology [181]

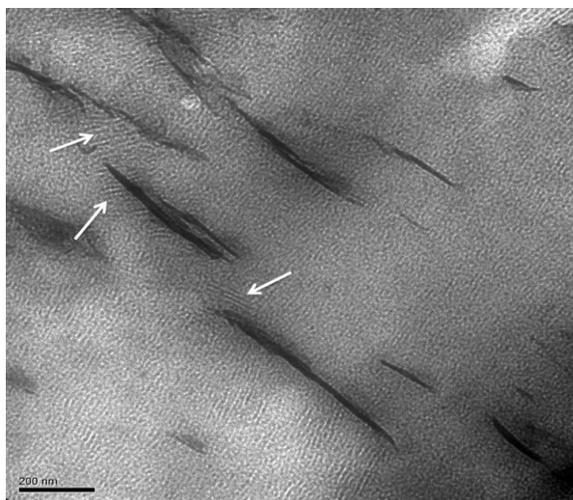


Figure 7. TEM bright-field micrograph of PP/clay nanocomposite (1 wt% clay). White arrows indicate the presence of transcrystalline layer of iPP with different orientation around the clay platelets [19]

In the last few years, there have been many reports concerning crystallization behaviour and morphology development of polypropylene in PP/clay nanocomposites [146, 183–191]. With nanoparticle incorporation in a polymer matrix, similarities to confined crystallization (crystallization in

nanopores) exist as well as nucleation effects and disruption of attainable spherulite size [140]. A recent review of the crystallization behaviour of layered silicate clay nanocomposites noted that while nucleation is observed in many systems, the overall crystallization rate is generally reduced, particularly at higher levels of nanoclay addition [192]. Another effect of layered silicates and some other nanofillers, such as halloysite nanotubes, observed in polypropylene nanocomposites, is the appearance of β - and γ -crystalline forms under certain crystallization conditions and/or clay content [159, 193, 194].

To take full advantage of the reinforcing effect of clay platelets, they have to be oriented in the appropriate direction, and this is affected by the type of processing, e.g. extrusion, injection molding, etc. [140]. It was recently found that shear flow, induced by a special water-assisted injection molding technique [195], can greatly enhance the dispersion and orientation of nanofillers, resulting in interfacial crystallization of the matrix [193]. This contributed largely to the increased thermal stability of the nanocomposite. To obtain a more complete characterization of the structure-property relationship of a polymeric nanocomposite based on polypropylene, and especially on the role of polymer/filler interface, Purohit et al. have applied thermal and dielectric spectroscopy methods [196]. A presence of immobile polymeric segments in close proximity of the nanofiller was clearly confirmed, thus providing an evidence of nanomorphology features in these systems. Nevertheless, the interaction between clay platelets and polymer crystallization requires further attention, because these interactions are likely a significant determinant of the end-use properties of PP/clay nanocomposites [154].

Despite the proven benefits of nanocomposites such as mechanical properties, barrier properties, fire retardancy, polymer nanocomposites are used today only in niche applications [197]. Commercial products by direct melt intercalation, which remains the most ecologically and economically desirable method, were manufactured by the RTP Company, Southern Clay Products, Nanocor and Honeywell Polymer, among others [198]. PP/clay nanocomposites are being produced by GM, Montell, Nanocor and SCP, mainly suitable for automotive, construction and packaging applications. An important issue for industrial application of PP/clay nanocomposites is also their environmental durability, an issue widely reviewed in the literature, but still without undivided conclusion [199–203].

It is expected that the commercialization and application of PP/clay nanocomposites will expand,

following the challenges of the future in terms of development of effective processing methods and gaining deeper knowledge on the mechanisms governing the behaviour of these advanced materials.

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РАЗВОЈОТ НА МАТЕРИЈАЛИ НА БАЗА НА ПОЛИПРОПИЛЕН

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Полипропиленот е повеќенаменски термопластичен полимер со добар однос својства–цена, познат по својата одлична отпорност на топлина, влага и хемикалии, погодни процесни карактеристики и можност за рециклирање. Поради универзалните својства, полипропиленот се применува во бројни подрачја: електрониката и електро-индустријата, автомобилската и текстилната индустрија, производството на цевки и цевководи. Покрај тоа, напредокот во начините на негова синтеза и модификација во последната декада придонесе за развојот на материјали на база на полипропилен, кои поседуваат нови супериорни својства. Во овој преглед се разгледуваат некои од поновите достигнувања кај материјалите на база на полипропилен како што се нановлакната, композитите зајакнати со природни влакна, самозајакнувачкиот полипропилен и нанокомпозитите со глина, кои го преземаат местото на многу видови инженерска пластика во примените кои бараат високи перформанси.

Клучни зборови: полипропилен; синтеза; кристална структура; нановлакна; полипропилен зајакнат со природни влакна; полипропилен/глина нанокомпозити