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Polymer Nanocomposites with Different Types of Nanofiller

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<http://dx.doi.org/10.5772/intechopen.81329>

Abstract

The development of polymer nanocomposites has been an area of high scientific and industrial interest in the recent years, due to several improvements achieved in these materials, as a result of the combination of a polymeric matrix and, usually, an inorganic nanomaterial. The improved performance of those materials can include mechanical strength, toughness and stiffness, electrical and thermal conductivity, superior flame retardancy and higher barrier to moisture and gases. Nanocomposites can also show unique design possibilities, which offer excellent advantages in creating functional materials with desired properties for specific applications. The possibility of using natural resources and the fact of being environmentally friendly have also offered new opportunities for applications. This chapter aims to review the main topics and recent progresses related to polymer nanocomposites, such as techniques of characterization, methods of production, structures, compatibilization and applications. First, the most important concepts about nanocomposites will be presented. Additionally, an approach on the different types of filler that can be used as reinforcement in polymeric matrices will be made. After that, sections about methods of production and structures of nanocomposites will be detailed. Finally, some properties and potential applications that have been achieved in polymer nanocomposites will be highlighted.

Keywords: nanocomposites, polymers, nanofillers, processing, compatibilization, morphology, structures, characterizations, properties, applications

1. Introduction

Polymer nanocomposites (PNCs) may be defined as a mixture of two or more materials, where the matrix is a polymer and the dispersed phase has at least one dimension smaller than 100 nm [1]. In

the last decades, it has been observed that the addition of low contents of these nanofillers into the polymer can lead to improvements in their mechanical, thermal, barrier and flammability properties, without affecting their processability [1, 2]. The ideal design of a nanocomposite involves individual nanoparticles homogeneously dispersed in a matrix polymer. The dispersion state of nanoparticles is the key challenge in order to obtain the full potential of properties enhancement [1, 2]. This uniform dispersion of nanofillers can lead to a large interfacial area between the constituents of the nanocomposites [2]. The reinforcing effect of filler is attributed to several factors, such as properties of the polymer matrix, nature and type of nanofiller, concentration of polymer and filler, particle aspect ratio, particle size, particle orientation and particle distribution [3]. Various types of nanoparticles, such as clays [3, 4], carbon nanotubes [5], graphene [6, 7], nanocellulose [8] and halloysite [9], have been used to obtain nanocomposites with different polymers.

The evaluation of the nanofiller dispersion in the polymer matrix is very important, since the mechanical and thermal properties are strongly related to the morphologies obtained. Depending on the degree of separation of the nanoparticles, three types of nanocomposite morphologies are possible (**Figure 1**) [10]: conventional composites (or microcomposites), intercalated nanocomposites and exfoliated nanocomposites. When the polymer is unable to intercalate between the silicate layers, a composite of separate phases is obtained (**Figure 1(a)**), whose properties are in the same range as those observed in traditional composites [1]. An intercalated structure, in which a single (and sometimes more than one) extended polymer chain is intercalated between the layers of the silicate, results in a well-ordered multilayer morphology with intercalated layers of polymer and clay (**Figure 1(b)**). When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated structure is obtained (**Figure 1(c)**) [10].

Exfoliated nanocomposites have maximum reinforcement due to the large surface area of contact between the matrix and nanoparticles. This would be one of the main differences between nanocomposites and the conventional composites [11].

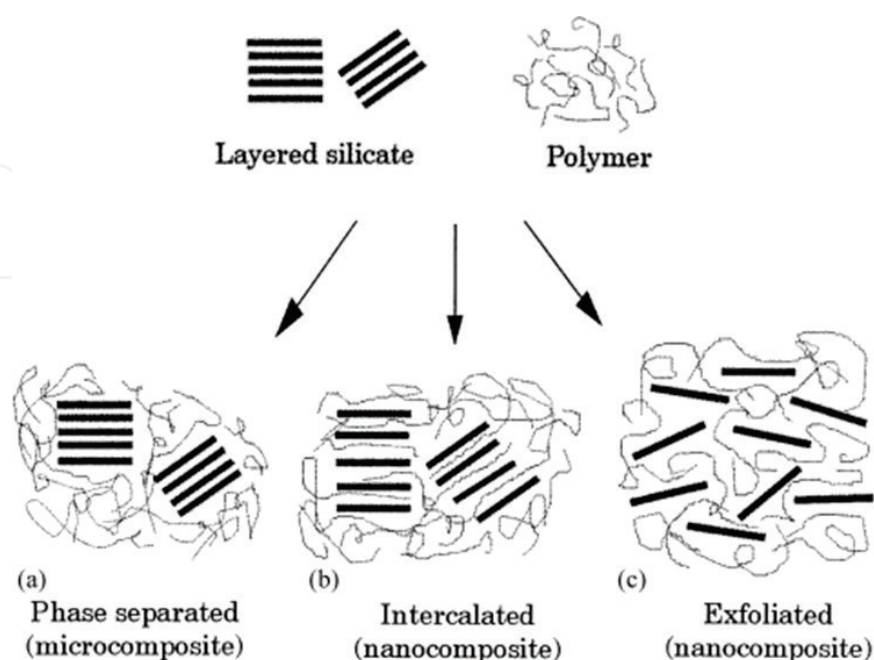


Figure 1. Possible structures of polymer nanocomposites using layered nanoclays: (a) microcomposite, (b) intercalated nanocomposite and (c) exfoliated nanocomposite [10].

The aim of this chapter is to review the common types of fillers used in nanocomposites, to provide an understanding of how nanocomposites are currently produced and characterized and, finally, to present some examples of applications of these materials.

2. Nanofillers and compatibilization of nanocomposites

2.1. Carbon-based nanofillers

2.1.1. Carbon nanotubes

Carbon nanotubes (CNTs) are ultrathin carbon fibers with nanometer-size diameter and micrometer-size length. CNTs were discovered in 1991 by Sumio Iijima, and since then, these nanomaterials have been used in various applications [12]. The structure of CNT consists of enroled graphitic sheet, which is a planar-hexagonal arrangement of carbon atoms distributed in a honeycomb lattice [12, 13]. The nanotubes can be classified into either multi-walled (MWCNT) or single-walled (SWCNT) depending on its preparation method [12, 14], as can be seen in **Figure 2**. MWCNTs consist of two or more concentric cylindrical shells of graphene sheets coaxially arranged around a central hollow core. On the other hand, SWCNT consists of a single graphene layer rolled up into a seamless cylinder [15, 16]. In addition to the exceptional electrical and conductive properties, the CNTs also present excellent mechanical properties, with an elastic modulus in the order of 1 TPa and maximum tensile strength can reach 300 GPa (for CNTs free of defects) [13, 17]. These properties are related to a strong covalent bond between carbons and its arrangement in cylindrical nanostructures [5].

Due to their excellent properties, considerable interest has been drawn on polymer nanocomposites with CNTs [18]. The incorporation of carbon nanotubes in polymer matrices has been explored as a strategy to obtain composite materials with electrical properties and with superior mechanical and thermal properties. However, these fillers are materials of difficult dispersion in polymeric matrices. Problems arising from agglomeration during processing are commonly observed due to the low polymer/CNT interaction (see **Figure 3**) [19]. The processing conditions may influence the dispersion state of these nanofillers in the resulting material. In addition, carbon nanotubes can be chemically modified to improve the interfacial interaction [19, 20].

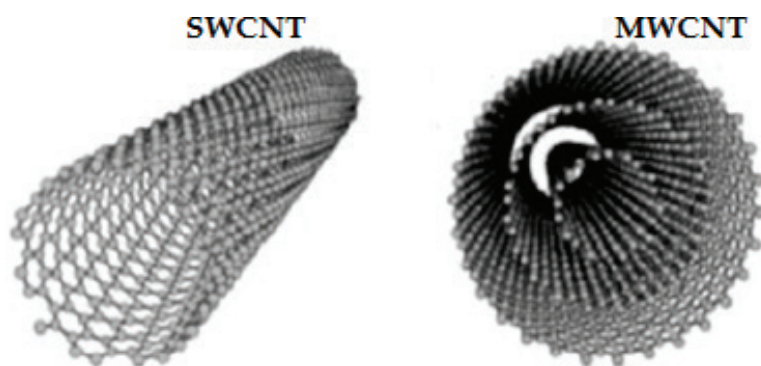


Figure 2. Representation of SWCNT and MWCNT [14].

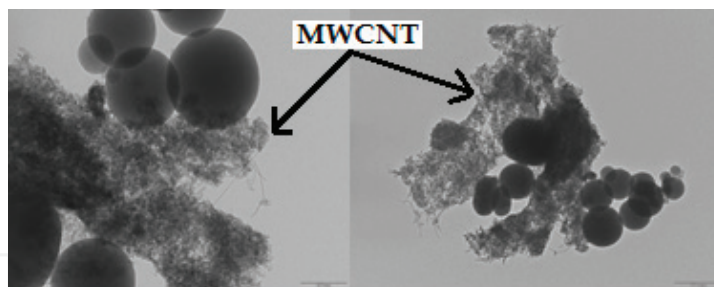


Figure 3. Micrographs obtained by transmission electron microscopy of nanocomposites with polyetherimide (PEI) and MWCNT [19].

The presence of functional groups on the side walls of CNTs increases the chemical reactivity between the filler and matrix, inducing to a better interface and consequently a better load transfer from the matrix to the reinforcement [5]. One route that has been considered for modification of carbon nanotubes is the surface treatment of these materials with a mixture of nitric and sulfuric acids ($\text{HNO}_3/\text{H}_2\text{SO}_4$), which results in the formation of carboxylic acid groups ($-\text{COOH}$) on the surface [5]. This treatment was developed by Goyanes et al [21] and can alter the nature of the CNTs surface making them more compatible with the polymer matrix. Besides the acid treatment, secondary particles, such as clay, have been used to improve the dispersion of carbon nanotubes and increase the electrical properties of composites containing these fillers [20]. In addition to obtaining nanocomposites using a single polymer matrix, the use of polymer/polymer blends as matrix has attracted the attention of researchers. It has been observed that polymer/polymer blends with carbon nanotubes have better electrical and thermal properties when compared to unfilled blends [18].

The electrical conductivity after the incorporation of CNTs in polymers occurs due to the formation of a three-dimensional network of CNTs inside the polymer matrix, which strength depends on the distribution and dispersion of the CNTs. When the concentration of the nanofiller reaches a critical value, known as the limit of electrical percolation, the electrical conductivity of the nanocomposite increases unexpectedly. After this abrupt increase in electrical conductivity, it will show modest increases as the conductive additive increases inside the polymer matrix [18, 22]. In nanocomposites based on polymer blends, the amount of CNTs required to achieve electrical percolation may be even lower than in nanocomposites with a single polymer matrix, provided that a selective location of the CNTs occurs in the matrix phase or at the interface of the blend [18, 23]. In addition, it is especially desired the formation of blends with co-continuous morphology, where a double phenomenon of electric percolation can be found. Thus, the limit of electric percolation in polymer blends is strongly influenced by the concentration of nanotubes and also by the final morphology of the blends, which in turn is a function of the composition of the blend, the compatibilizer and the processing conditions [18].

2.1.2. Graphene

Graphene was discovered in 2004 by Andre. K. Geim and Konstantin S. Novoselov and has revolutionized the scientific frontiers in nanoscience and condensed matter physics due to its exceptional electrical, physical and chemical properties. Graphene has sparked enormous

interest in many research groups around the world and has resulted in an abrupt increase in publications on the subject. This material consists of one atomic thick sheet of covalently sp²-bonded carbon atoms in a hexagonal arrangement [24, 25], as illustrated in **Figure 4**.

The primitive cell of graphene is composed of two non-equivalent atoms, A and B, and these two sub-lattices are translated from each other by a carbon-carbon distance $a_{c-c} = 1.44 \text{ \AA}$ [25]. Graphene can be produced from graphite by different methods, such as thermal expansion of chemically intercalated graphite, micromechanical exfoliation of graphite, chemical vapor deposition and chemical reduction method of graphene oxide [27]. Graphene has Young's modulus of 1 TPa, fracture strength of 125 GPa, thermal conductivity of 5000 W/m.fK and electrical conductivity up to 6000 S/cm [28]. These properties in addition to extremely high surface area (theoretical limit: 2630 m²/g) and gas impermeability indicate graphene's great potential for improving mechanical, electrical, thermal and gas barrier properties of polymer nanocomposites [28, 29].

The successful use of graphene depends on the exfoliation of bulk graphite into individual sheets. Several chemical-mechanical routes have been developed to produce individual exfoliated graphene sheets, for example, mechanical exfoliation, chemical exfoliation and chemical vapor deposition [30, 31]. Each method has its own advantages and drawbacks related to the purity and the presence of defects (oxygen and functional groups on the surface). The most common route to produce graphene involves the production of graphite oxide (GO) by oxidation chemistry followed by a reduction and mechanical exfoliation [6]. This is the basis of Hummers and Offeman's process [32]. GO is nonconductive, hydrophilic and can readily swell and disperse in water. Recently, several new methods of graphene functionalization were reported. Functionalized graphene sheets (FGS) demonstrate improved dispersibility in organic solvents and polymers [28, 30].

2.2. Layered nanoclays

Nanoclays belong to a class of materials generally made of layered silicates or clay minerals with traces of metal oxides and organic matter. Clay minerals are hydrous aluminum phyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths and others cations [33]. In the last decades, several published works have shown that the dispersion of exfoliated clays in polymer leads to a remarkable increase in stiffness, fire retardancy and barrier properties, beginning at a very low nanoparticle volume fraction [3]. Clays have been found to be effective reinforcing fillers for polymer due to lamellar structure and high specific surface area (750 m²/g) [2]. Smectite clays are layered silicates, and they are a

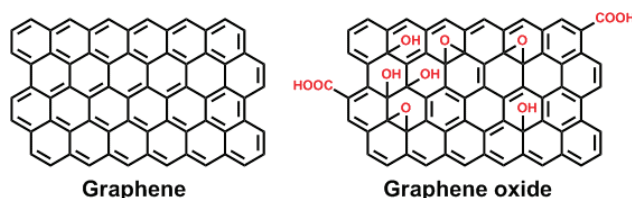


Figure 4. Honeycomb lattice of graphene [26].

required choice for the preparation of polymer nanocomposites due to their low cost, swelling properties and high cation exchange capacities. Some examples of these clays are montmorillonite, saponite, laponite, hectorite, sepiolite and vermiculite [16, 33]. Among these clays, montmorillonite is the most widely used clay in polymer nanocomposites, because of its large availability, well-known intercalation/exfoliation chemistry, high surface area and reactivity [33]. Montmorillonite (MMT) is composed of two tetrahedral silica sheets with an alumina octahedral sheet in the middle (2:1 layered structure), and the hydrated exchangeable cations occupy the spaces between lattices, as shown in **Figure 5**.

The sheets have dimensions of 1 nm thickness and are 100–500 nm in diameter, resulting in platelets with high aspect ratio [35]. Stacking of the clay layers leads to a regular van der Waals gap between the layers called interlayer or gallery. Isomorphic substitution within the layers generates negative charges that are counterbalanced by alkali and alkaline earth cations (Li^+ , Na^+ or Ca^{2+}) situated inside the galleries. The extent of the negative charge of the clay is characterized by the cation exchange capacity (CEC) [36]. Natural montmorillonite is hydrophilic and most polymers tend to be hydrophobic, so the clay surface must be modified to yield organophilic clay in these cases. This is often done by exchanging the cations in the gallery with alkylammonium or alkylphosphonium salts (for example, dioctadecyl dimethyl ammonium bromide), typically with chain lengths longer than eight carbon atoms (C_8). The clay that was previously hydrophilic becomes organophilic after modification [35]. The replacement of inorganic exchange cations with organic ions on the gallery surfaces of smectite clays is useful to expand the clay galleries. This facilitates the penetration into the gallery space (intercalation) by either the polymer chains. Other type of modification that has been used in nanoclays is the process known as silanization. The modification of the clay with organosilanes promoted covalent bonds between polymer and clay by reactive extrusion favoring strong interactions between clay and matrix. Examples of those silanes that have been used to modify nanofiller are 3-aminopropyltriethoxysilane (APTES) and vinyltrimethoxysilane (VTMS) [37].

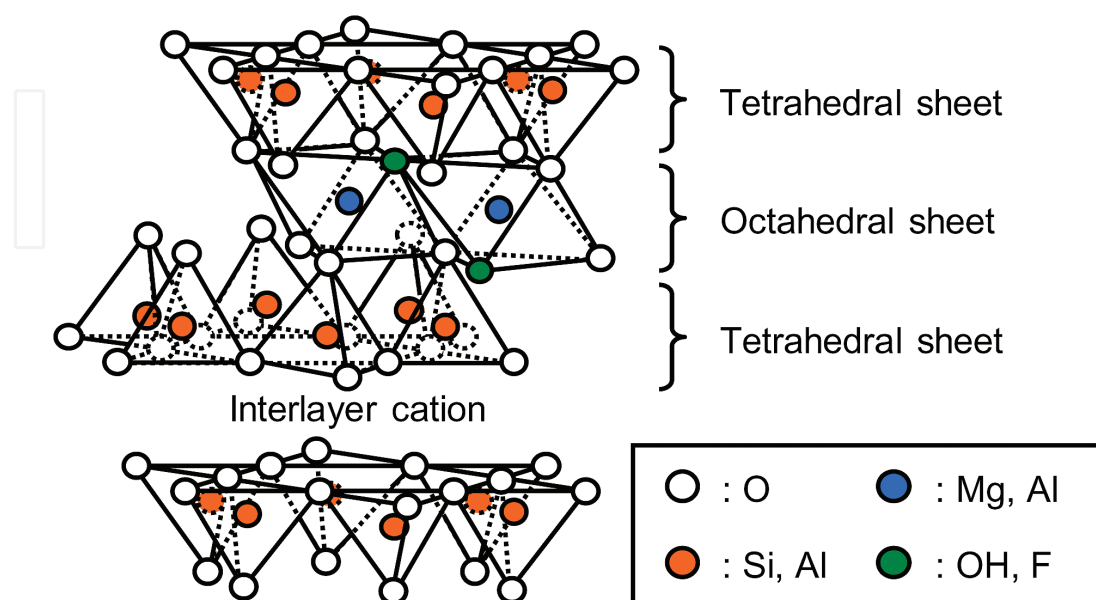


Figure 5. Structure of 2:1 layered silicates [34].

2.3. Porous and hollow nanoparticles

2.3.1. Halloysite

Halloysite nanotube (HNT) is an aluminosilicate with hollow micro- and nanotubular structure [38]. HNT is structurally much to kaolinite [39] and may intercalate a monolayer of water molecules, which is weakly held. It consists of sheets of SiO_4 tetrahedra with sheets of edge sharing AlO_6 octahedral [40], as shown in **Figure 6**. Consequently, the chemical composition of HNT is similar to nanoclays, while nanotubular geometry is similar to CNTs. Uniqueness of HNT exists in its tubular form with length up to few microns and diameter in nm range. It offers innovative possibilities for nanocomposite preparation [41]. Optimizing polymer properties by filler addition of low content has been the focus of industrial and academic research. HNT as nanofiller in polymeric materials has been found to significantly increase the mechanical, thermal, non-flammability and other physical properties of the nanocomposite [42]. Due to variety of characteristics, such as nanoscale size, shape, surface area and high length to diameter ratio, HNT has been discovered for numerous applications.

2.3.2. Zeolite

Zeolites are widely used as catalysts or catalyst supports in a variety of applications in refining and (petro)chemical industries [44]. Particularly, the faujasite-type framework is an aluminosilicate with cavities of 1.3 nm of diameter interconnected by pores of 0.74 nm, as illustrated in **Figure 7**. The cubic unit cell of these aluminosilicates contains around 192 $(\text{Si,Al})\text{O}_4$ tetrahedrons [45]. The development of zeolite synthesis methods to reduce the size of the particles has received special interest [46]. Micrometer-sized zeolites have a negligible external surface area compared with the large surface area in their internal microporous [47]. Zeolite nanoparticles lead to substantial changes in the material properties, increasing the intercrystalline space, the external and internal surface area and volume and pore mouths exposed. Therefore, the application of nanozeolites in some catalytic reactions can reduce diffusion path lengths and increase catalytic activity and selectivity, as well as improve reaction medium stability [48].

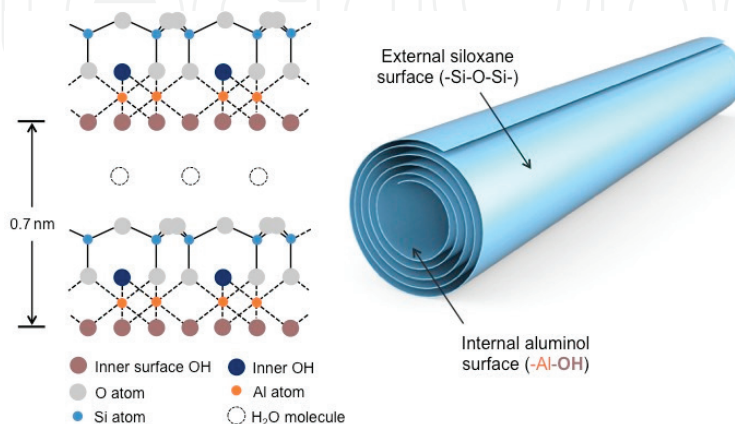


Figure 6. Structure of halloysite nanotube [43].

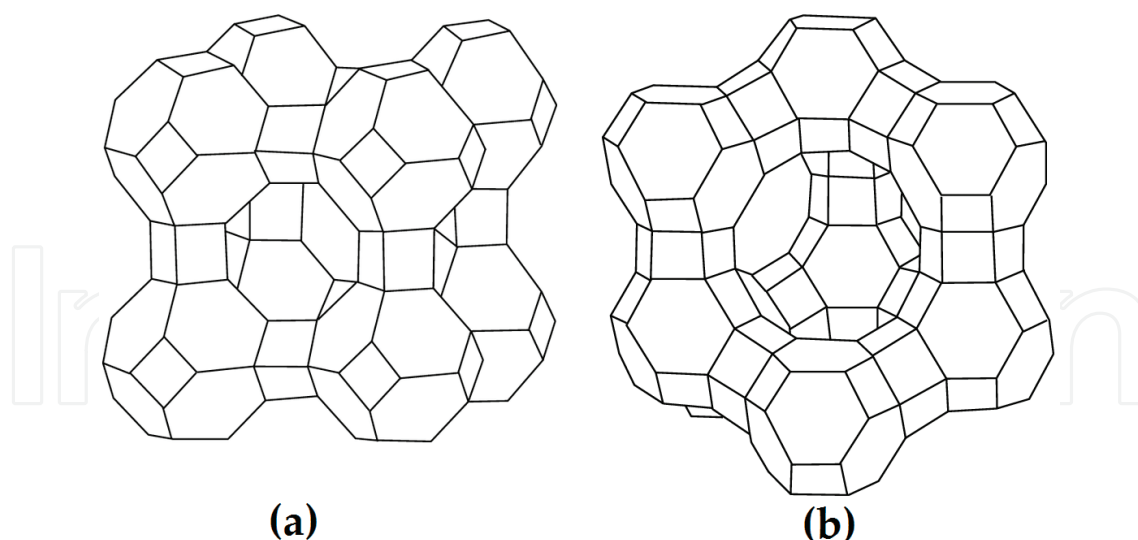


Figure 7. (a) Zeolite A and (b) faujasite-type zeolites X and Y [45].

2.4. Nanocellulose

There is an interest in the use of biomass as a source of renewable energy and materials. A promising source of biomass is cellulose. By suitable chemical and mechanical treatments, it is possible to produce fibrous materials with one or two dimensions in the nanometer range from any naturally occurring sources of cellulose [49]. The term “nanocellulose” is used to cover the range of materials derived from cellulose with at least one dimension in the nanometer range. This material has been described as a new bionanomaterial [50]. Isolation of crystalline cellulosic regions, in the form of monocrystals, is done by an acid hydrolysis process [51]. The first report on the mechanical destructurement of cellulose fibers was published in 1983 in two companion papers [52]. Nanocellulose-based materials have a low carbon footprint and are sustainable, renewable, recyclable and nontoxic; they thus have the potential to be truly green nanomaterials with many useful and unexpected properties. **Figure 8** shows the illustration of the crystalline structure of cellulose.

2.4.1. Cellulose nanofibrils

The mechanically induced destructurement strategy consists of applying severe multiple mechanical shearing actions to a cellulosic fiber slurry to release more or less individually

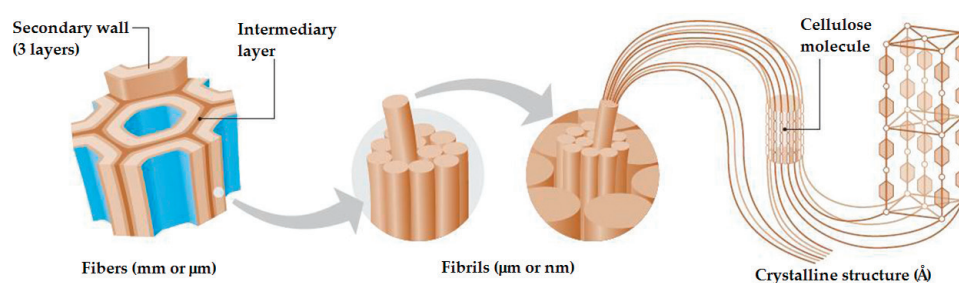


Figure 8. Crystalline structure of cellulose [53].

the constitutive microfibrils. Different shearing types of equipment, such as a homogenizer, microfluidizer or ultra-fine friction grinder, are generally used. This material is usually called nanofibrillated cellulose (NFC) or cellulose nanofibrils (CNF) and is obtained as an aqueous suspension [49]. The width is 3–100 nm depending on the source of cellulose, defibrillation process and pretreatment, and the length is usually higher than 1 μm [53].

2.4.2. Cellulose nanocrystals

The chemically induced destructure strategy consists of applying a controlled strong acid hydrolysis treatment to cellulosic fibers, allowing dissolution of amorphous domains and therefore longitudinal cutting of the microfibrils. The ensuing nanoparticles are called cellulose nanocrystals (CNCs) and are obtained as an aqueous suspension [51]. These nanoparticles have high aspect ratio rod-like nanocrystals (whiskers). Their geometrical dimensions depend on the origin of the cellulose and hydrolysis conditions. Sulfuric acid is used for the preparation of CNC, and this process induces the formation of negatively charged sulfate groups at the surface. The average length is of the order of a few hundred nanometers and the width is of the order of a few nanometers [53]. An important parameter for CNCs is the aspect ratio, which is defined as the ratio of the length to the width [49].

2.5. Nanoparticles of metallic alloys

The possibility of using metal hydrides (MH) alloys in hydrogen technology has been attracting interest [54]. These types of material react with hydrogen reversibly, thus being successfully utilized in the solid state storage of the gas. However, MH alloys under repeated hydriding/dehydriding cycling suffer from a pulverization phenomenon due to a large volume mismatch between the hydride and the metal compound [55]. As a consequence, repeated hydrogen loading/unloading cycles produce free metal powder particles in nanoscale size. Particle fragmentation results in a considerable increasing of the metal surface area with a consequent enhancement of some properties. Among these, the hydriding kinetics is expected to improve even if a parallel increasing of undesired degradative phenomena (such as oxidation) can result in a detriment of the overall storage capacity of the material. Furthermore, from a technological point of view, the presence of unconfined nanoparticles inside the device can constitute an obstacle to the gas flow through the material [55]. Anyway, storing hydrogen in MH beds as a chemical compound appears to be a promising, cost-effective and safe method of hydrogen storage in the near future [56]. An example of polymer nanocomposite with MH alloy is shown in **Figure 9**.

2.6. Compatibilization in polymer nanocomposites

To obtain a polymer blend or nanocomposite with the desired properties, compatibilization is an important issue. Actually, the differences in chemical nature between the polymers or the polymer matrix and the nanoparticles give rise to systems with poor properties [58]. Compatibilization gains importance in order to improve the properties. The degradation, which must be minimized, involves the decomposition of the organomodifier and the interactions among the degradation products and the polymers. These, together with the processing conditions, influence the morphology and the properties of the material [59, 60] (**Figure 10**).

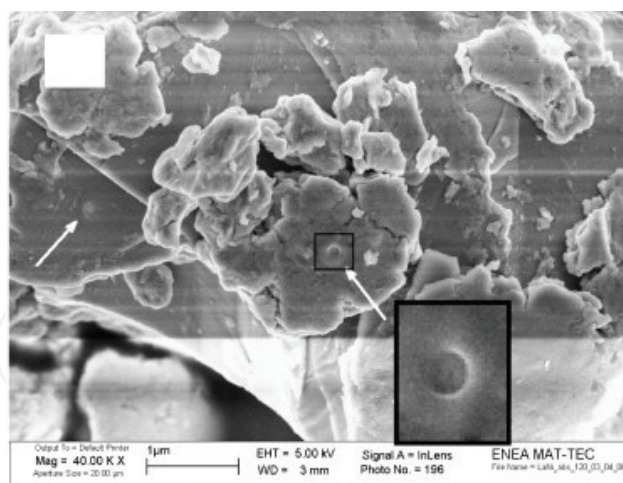


Figure 9. LaNi₅/ABS after a mechanical-dry particle coating process in a tumbling mill [57].

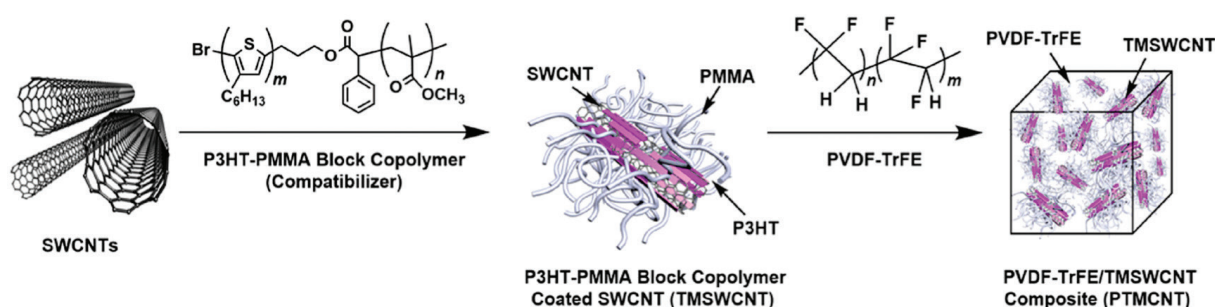


Figure 10. Scheme of production of compatibilized nanocomposite of PVDF/SWCNT [60].

3. Processing of polymer nanocomposites

Polymer nanocomposites can be produced by three methods: in situ polymerization, solution and melt blending. An appropriate method is selected according to the type of polymeric matrix, nanofiller and desired properties for the final products [61].

3.1. In situ polymerization

During the in situ polymerization, the nanofiller must be properly dispersed in the monomer solution before the polymerization process starts, ensuring the polymer will be formed between the nanoparticles. Polymerization can be started using several techniques (heat, use of an appropriate initiator, etc.) [62]. Using this technique, a polymer grafted nanoparticle and high loading of nanofillers without aggregation can be carried out [63]. Organic modifiers may be used to help the dispersion of the nanoparticles and take part in the polymerization [64]. It can be an alternative way for the production of nanocomposites using polymers that are non-soluble or thermally unstable [65]. In some cases, this technique can be applied in solvent-free form [66]. It is also a technique which can result to higher performance products [67]. Mini-emulsion polymerization is based on the creation of monomer droplets that are dispersed in a solution in a nanoscale [68]. The procedure for the production of polymer nanocomposites by this technique is shown in **Figure 11**.

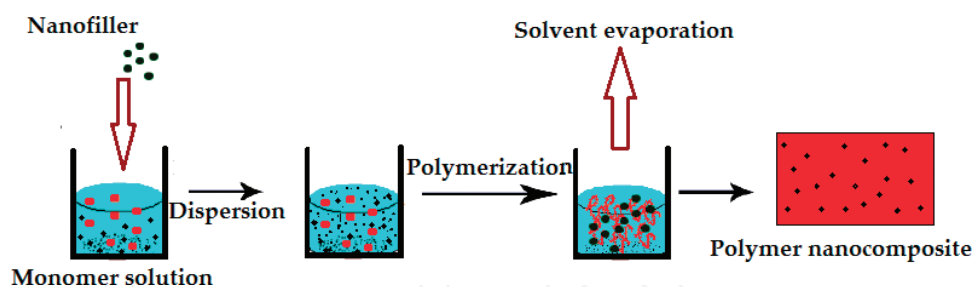


Figure 11. Schematic illustration for the in situ polymerization method.

Some of the benefits are controllable particle morphology [69], good interfacial adhesion of the nanofillers [70] and high transparency [71, 72]. When using this method, it is possible to [61] apply higher contents of nanofillers without agglomeration, have better performance of the final products, expand to the solvent-free form, have covalent bond among the nanoparticle functional groups and polymer chains and use both thermoset and thermoplastic polymers. One main limitation is the ease of agglomeration [63, 65].

3.2. Blending

This method is widely used for the production of polymer nanocomposites due to its simplicity. However, reaching a proper dispersion of the nanofiller in the polymer matrix can be more difficult when compared to other methods [61, 62].

3.2.1. Solution blending

Solution blending is actually a system including the polymer and nanofiller, which are easily dispersed in an appropriate solvent [62]. Ultrasonic irradiation, magnetic stirring or even shear mixing can be used to disperse the nanofiller within the polymer [63]. In this method, when the solvent evaporates, the nanoparticle remains dispersed into the polymer chains, as shown in **Figure 12**. The produced nanocomposite can also be obtained as a thin film [61].

There are some problems for the solution blending from the economic and environmental point of view. A proper decision must be taken to choose a correct method according to the situation and the desired product [73]. Some of the benefits of using solution blending are [61]

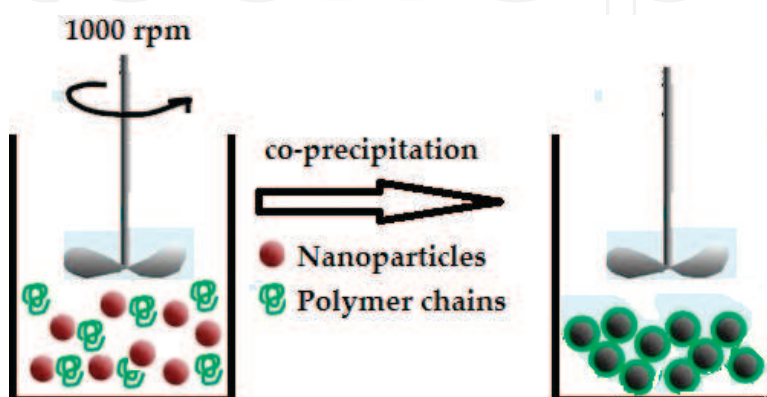


Figure 12. Schematic illustration for the solution blending method.

reduction in the permeability of gases [74], easy operation, and general technique for all types of nanofillers and to both thermoset and thermoplastic polymers [75]. The main limitations are aggregation and environmental constraints [73, 76]. This technique will likely be limited to polymers that are soluble in water [77].

3.2.2. Melt blending

In the melt blending method, the nanofillers are directly dispersed into the molten polymer. During mixing in the melt state, the strain that the polymer applies on the particles depends on its molecular weight and weight distribution. High levels of shear stress reduce the size of the agglomerates [61]. The mechanism for the action of shear flow during the dispersion and distribution of nanoparticles is shown in **Figure 13**. Initially, large agglomerates break down and form smaller ones dispersed through the polymer matrix. The transfer of strain from the polymer to these new agglomerates leads to stronger shearing, which breaks them into individual particles; this step depends fundamentally on time and on the chemical affinity between the polymer and the surface of the nanoparticles [59, 78].

Both single and twin-screw extruders are usually applied for melt blending [79], although it must be noted that in some cases high temperatures can have unfavorable effects on the modified surface of the nanofiller and an optimization must be employed [80]. Intermeshing co-rotating twin-screw extruders are quite popular for this purpose. This method has some drawbacks that involve parameters that are not easy to control, such as the interaction between the polymer and the nanoparticles and the processing conditions (temperature and residence time) [81]. Therefore, in some cases, it can be difficult to obtain well-dispersed nanoparticles. An example of a medium dispersive screw profile for a twin-screw extruder is shown in **Figure 14**. It was designed with transport and kneading block elements and one turbine element at the end of the melting zone [82].

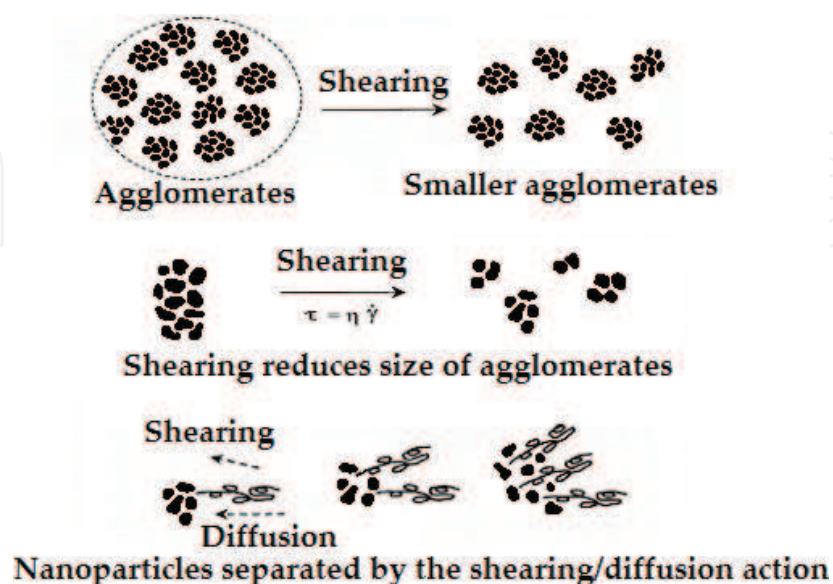


Figure 13. Effect of shearing on the dispersion of the nanoparticles during melt blending.

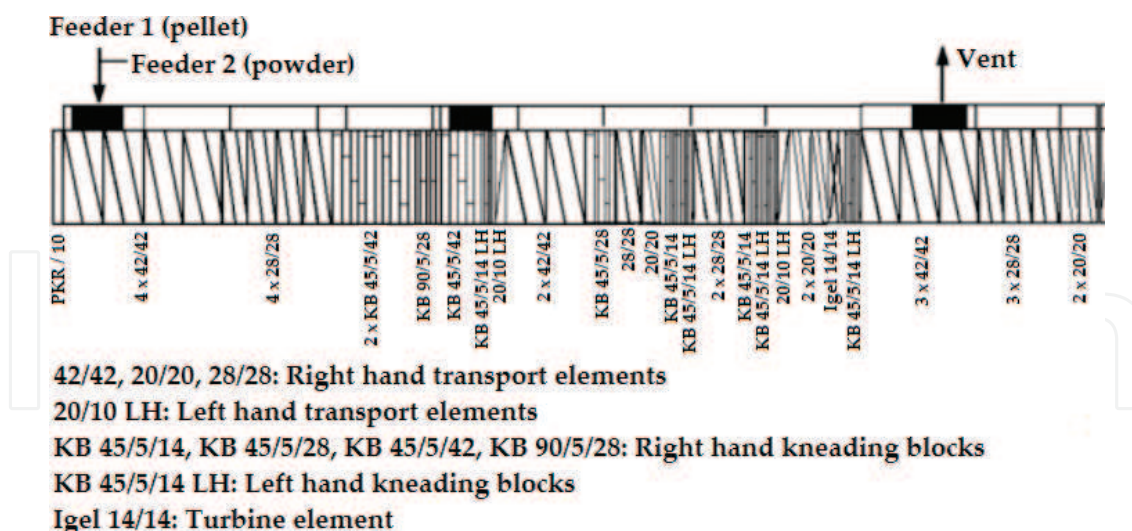


Figure 14. Schematic illustration of a screw profile of a twin-screw extruder [82].

Melt blending has been used for the production of polymer nanocomposites with different types of matrices: polypropylene [83–85], poly(methyl methacrylate) [86], poly(lactic acid) [75], poly(vinyl chloride) [87], polycarbonate [88, 89], polyamide 6 [4, 90, 91], etc.

The melt blending is well matched with several industrial operations, such as extrusion and injection molding, and consequently, it can be commercialized [61]. Some of the benefits of this technique are good dispersion of the nanoparticles [92], enhancement of the heat stability [93], improvement of mechanical properties [83–86] and low cost-effectiveness and eco-friendly (do not use solvent). A considerable limitation is the use of high temperatures, which can damage the modified surface of the nanofillers [94].

By and large, each technique has some advantages over the others and can be selected as the best method according to the conditions and applying materials [61].

4. Techniques of characterization

The knowledge and use of techniques of characterization is determinative to understand the basic physical and chemical properties of polymer nanocomposites. For several applications, it facilitates the study of emerging materials by giving information on intrinsic properties [95]. Various techniques have been used extensively in polymer nanocomposite research.

4.1. Structural and morphological characterization

The commonly used techniques are wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) [10, 96, 97]. The SEM provides images of surface features associated with a sample. The atomic force microscope (AFM) uses a sharp tip to scan across the sample. Raman spectroscopy has proved a useful probe of carbon-based material properties [95, 98].

Due to the easiness and availability, WAXD is most commonly used to probe the nanocomposite structure [99, 100] and to study the kinetics of the polymer melt intercalation, when using layered silicates [100]. In these systems, a fully exfoliated system is characterized by the absence of intensity peaks in WAXD pattern [101]. Therefore, a WAXD pattern concerning the mechanism of nanocomposite formation and their structure are tentative issues for making any conclusion. On the other hand, TEM allows a qualitative understanding of the internal structure, spatial distribution of the various phases and views of the defective structure through direct visualization. Thus, TEM complements WAXD data [102]. **Figure 15** illustrates some results obtained from both analyses.

SAXS is used to observe structures on the order of 10 \AA or larger, in the range of $0\text{--}5^\circ$. The TEM, AFM and SEM are also required to characterize the dispersion and distribution of nanoparticles. WAXD has found relatively limited success in CNT research [95]. In the Raman spectra of graphite and SWNTs, there are many features that can be identified with specific phonon modes that contribute to each feature. The Raman spectra of both materials can provide much information about the exceptional 1D properties of carbon materials, such as their phonon structure and their electronic structure, as well as information about sample imperfections. Since mechanical, elastic and thermal properties are also strongly influenced by phonons, Raman spectra provide general information about the structure and properties of SWNTs [98].

4.2. Thermal, mechanical, rheological and other techniques of characterization

For further characterization of polymer nanocomposites, the commonly used techniques are Fourier-transform infrared (FTIR), rheometry [82], differential scanning calorimeter (DSC), thermogravimetric (TGA), thermomechanical (TMA) and dynamic modulus analysis (DMA) [96].

Because viscoelastic measurements are highly sensitive to the nano- and mesoscale structure of polymers, when combined with WAXD, TEM, DSC, TGA and DMA, they will provide fundamental understanding of the state and mechanism of dispersion of the nanoparticles in the

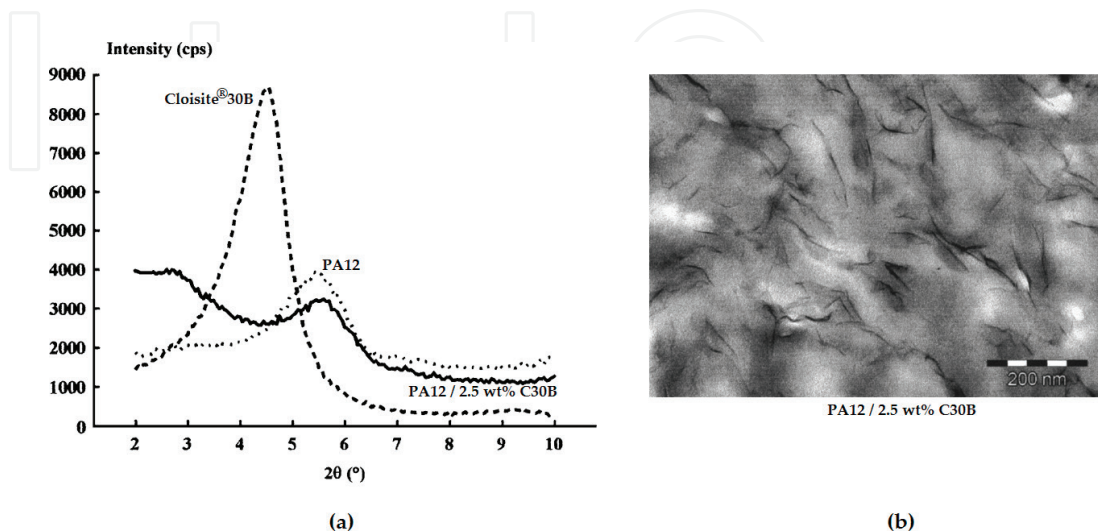


Figure 15. (a) WAXD diffractograms and (b) TEM micrograph of a 2.5 wt% MMT-PA12 nanocomposite [103].

matrix [104]. In addition, understanding rheological properties of nanocomposites is crucial for application development and understanding polymer processability. The nanocomposites usually demonstrate a change of pattern in dynamic mechanical spectrum, as a function of the degree of exfoliation/dispersion, from typical polymer response [$G' \sim \omega^2$, $G'' \sim \omega^1$] to a terminal response [$G' \sim \omega^1$, $G'' \sim \omega^1$], then to a pattern with double crossover frequencies, and

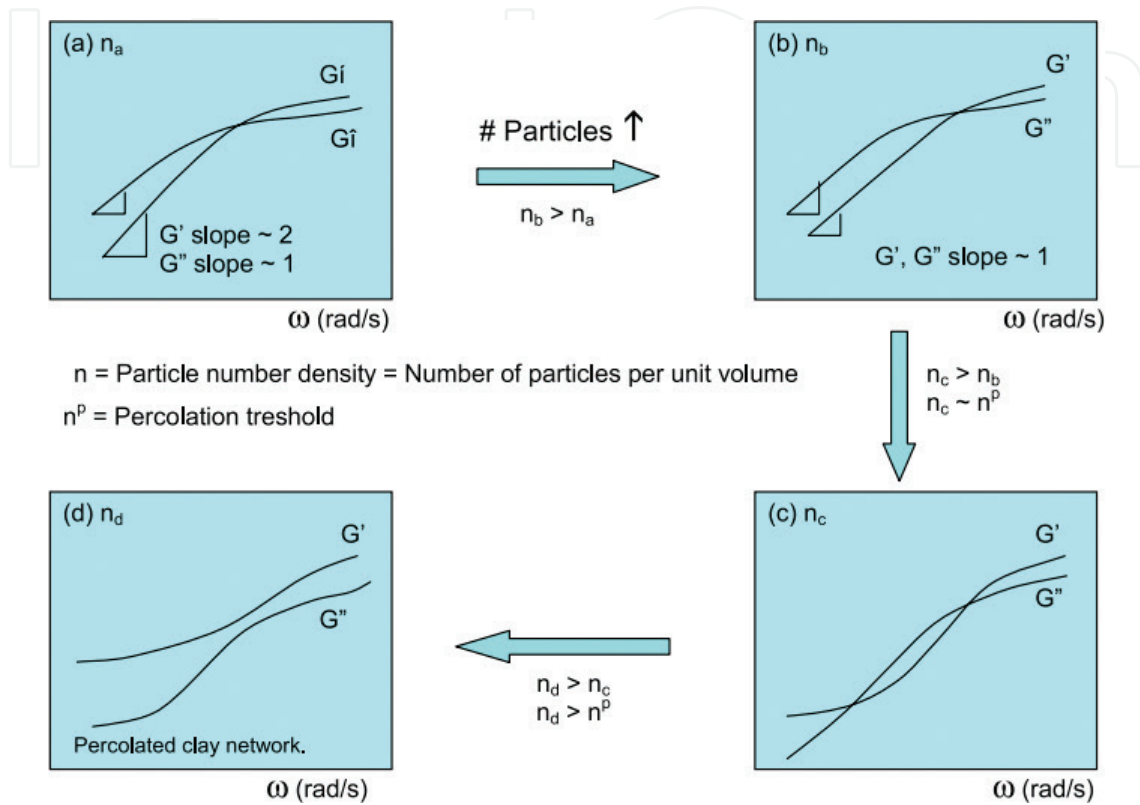


Figure 16. Schematic representation of the rheological response to the increase in the number of particles per unit volume [104].

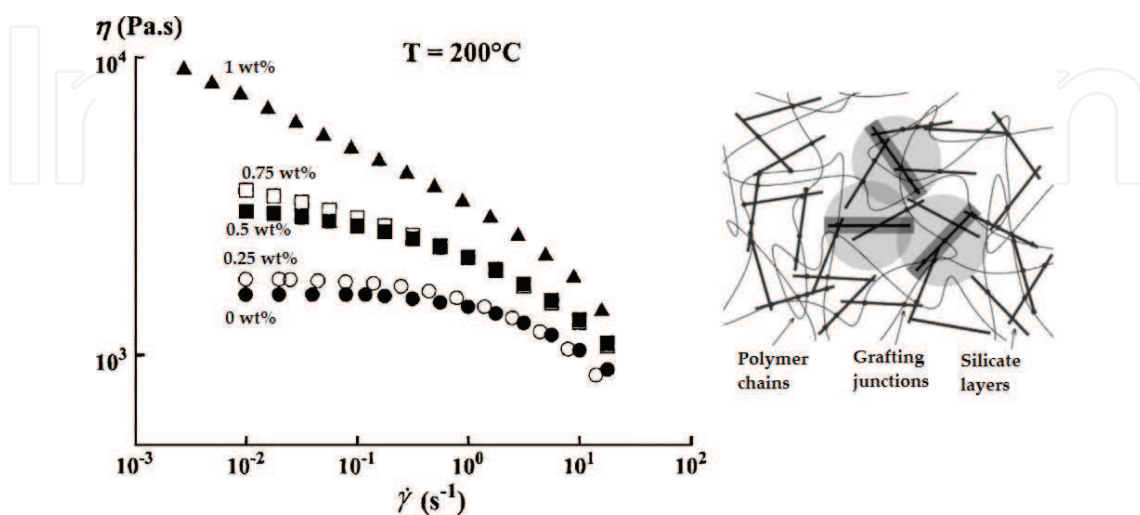


Figure 17. Steady shear viscosities as a function of shear rate at different montmorillonite concentrations in PA12 and a scheme of a percolated network in a nanocomposite [103, 105].

finally to a solid-like response with $G' > G''$ in all frequency ranges, as seen in **Figure 16**. The number of particles per unit volume is a key factor determining the characteristic response of nanocomposites [82, 104].

The presence of nanofillers caused these nanocomposites to have solid-like behaviors and slower relaxation. This behavior can be explained in terms of the development of a grafting-percolated nanoparticle network structure [105]. Its formation is a consequence of physical interactions between dispersed nanoparticles, polymeric chains and surfactants, which promote a considerable resistance to flow [103]. This behavior is shown in **Figure 17**.

The next section will briefly discuss the main properties and characteristics of some polymer nanocomposites, which have been used in relevant applications.

5. Properties and potential applications

Polymer nanocomposites have advantages: (1) they are lighter than conventional composites because high degrees of stiffness and strength are realized with far less high-density material, (2) their barrier properties are improved compared with the neat polymer, (3) their mechanical and thermal properties are potentially superior and (4) exhibit excellent flammability properties and increased biodegradability of biodegradable polymers [106].

There are many applications of polymer/clay nanocomposites and an increasing number of commercial products available on the market. Notable examples are automotive parts [16, 20], packaging [2, 8, 107], construction materials [36], biotechnology [108], medical devices, etc. [3, 36, 108]. One important property observed due to the incorporation of clay particles in polymers is a significant level of flame retardancy. This property also provides avenues for applications in many other areas, such as building materials, computer housings and car interiors [36]. Moreover, balanced mechanical properties, functionalities and biocompatibility of bionanocomposites provide an exciting platform for the design and fabrication of new materials for biomedical applications [36]. Another area of interest for nanocomposites is the packaging industry. The impermeable clay layers mandate a tortuous pathway, which difficult the diffusion of molecules throughout the matrix [109]. Improving food quality and shelf life, while reducing plastic waste, has stimulated the development of biodegradable polymer-based PCNs as advanced and smart packaging materials [109].

There are also several applications with carbon nanotubes and graphene. An area of notable application of these materials is in the optoelectronic industry [110, 111]. There is a wide range of applications which include fiber lasers, supercapacitor, field emission devices and photovoltaics, where the combination of tunable optoelectronic properties as well as structural and chemical stability, high surface area and low mass density of nanofillers with the processability of polymers offers a new class of materials [110, 111].

Nanocomposites of an organic-modified MMT and PA6 with a residual monomer were once produced by melt blending in a torque rheometer [112]. By WAXD, intercalated structures were observed in the nanocomposites with 3 and 5 wt% of MMT; on the other hand,

when 7 wt% of MMT was added, an exfoliated structure was obtained due to the predominant linking reactions between the residual monomer and the polar organic surfactant. Solutions of these nanocomposites in formic acid were prepared, and the 3 and 5 wt% nanocomposites were successfully electrospun; however, electrospinning of the 7 wt% nanocomposite was not possible. WAXD, SEM and TEM results showed that the 3 and 5 wt% nanofibers with average diameter between 80 and 250 nm had exfoliated structures. These results indicate that the high elongational forces developed during the electrospinning process changed the initial intercalated/exfoliated structure of the nanocomposites to an exfoliated one [112].

The use of an aqueous dispersion of polyethylene copolymer with a relatively high content of acrylic acid as a compatibilizer and as an alternative medium to obtain polyethylene NFC nanocomposites was a matter of recent study [113]. The NFC content was varied from 1 to 90 wt%, and the appearance, optical, thermal, mechanical and rheological properties, as well the morphology of the films, were evaluated. The PE/NFC films were transparent up to 20 wt% of NFC indicating a good dispersion of NFC, with PE-rich and NFC-rich regions observed by SEM. Improved mechanical properties were achieved with an increase in the Young's modulus. The rheological behavior indicated good melt processability [113].

Water suspensions of NFC with xylan, xyloglucan and pectin were studied for foaming and structural properties as a new means for food structuring [114]. They were analyzed by rheometry, microscopy and optical coherence tomography (OCT). A combination of xylan with TEMPO-oxidized NFC produced a mixture with well-dispersed air bubbles, while the addition of pectin improved the elastic modulus, hardness and toughness of the structures. Shear flow caused NFC to form plate-like flocs in the suspension that accumulated near bubble interfaces. This tendency could be affected by adding laccase to the dispersion. Xyloglucan interacted strongly with TEMPO-oxidized NFC (high storage modulus) [114].

6. Conclusions

Polymer nanocomposites offer excellent opportunities to explore new functionalities beyond those of conventional materials. The field of nanocomposites has been one of the most promising and emerging research areas. They find special attention due to the unique properties such as light weight, ease of production and flexibility. A defining feature of polymer nanocomposites is that the small size of the fillers leads to an enormous increase in interfacial area as compared to traditional composites. The interfacial area creates a significant volume fraction of interfacial polymer with properties different from the bulk polymer even at low loadings of the nanofiller. Interfacial structure is known to be different from bulk structure, and in polymers with nanoparticles possessing high surface areas, most parts of the polymers are present near the interfaces, in spite of the small weight fraction of the filler. This is one of the reasons why the nature of reinforcement is different in nanocomposites. The crucial parameters which determine the effects of fillers on the properties of composites are filler size, shape and aspect ratio and filler-matrix interactions.

Acknowledgements

The authors would like to thank the Coordination for the Improvement of Higher Education Personnel (CAPES, process PNPDP20131474-33001014004P9) for the financial aid.

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