

Preparation of Polymer-Based Nanocomposites by Different Routes

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Abstract

Since the eighties, polymeric nanocomposites have been intensely investigated due to the performance improvement achieved when a small amount of nanosized particles are added to a polymer matrix. The remarkable changes on physical and mechanical properties of polymers due to the addition of inorganic solid nanoparticles (typically in form of fibres, flakes, spheres or fine particles) is explained by the huge surface area, which increases the interaction between the nanoparticle and the polymer. Moreover, nanocomposites can be produced using conventional polymer processing techniques, which makes them particularly interesting from the production point of view. Therefore, this chapter will make an overview about different routes to prepare polymer-based nanocomposites by extrusion, mainly synthesis of nanoparticles by sol-gel reactions and dispersion of clays in polymer matrices.

Keywords: Polymeric nanocomposites; Preparation methods; Extrusion; Sol-gel reaction

Introduction

Nature has always combined organic and inorganic components, at the nanoscale, to construct smart materials with remarkable properties and functions (mechanics, density, permeability, colour, hydrophobicity, etc). Crustacean carapaces, mollusc shells, bone and tissues are examples of organic-inorganic natural materials [1,2]. Bones, for example, are composed by hierarchical nanocomposite built from ceramic tablets and organic binders. Oriakhi, in 1998, published a paper entitled "Nano sandwiches", writing, "Nature is a master

chemist with incredible talent" [3]. Looking to nature, scientists have been capable to develop new synthesis strategy to produce materials that can have several functions at the same time [4]. In the field of material science, the combination of an organic phase (generally polymers) with inorganic particles has drawn considerable attention since last decades. This interest arose since the addition of particles (typically in the form of fibres, flakes, spheres or fine particles) well dispersed at the nanosize scale, allows the development of new

materials with tailored properties [5, 6]. These materials belong to a new class of composites designated by Theng, in 1970, as nanocomposites [1, 7]. The idea of developing a multiple-phase nanocomposites to improve properties and materials characteristics is not recent. This has been a common practice since civilization started and humanity began to produce more efficient materials for specific purposes. Examples of man-made nanocomposites can be found in green bodies of china ceramics, blue Maya pigments and some prehistoric frescos. The Maya blue for example, is a man-made nanocomposite, which combines the resistance of the inorganic clay palygorskite with organic pigment blue indigo [8-10].

In industrial context, mixing organic and inorganic components started in 1940s in some companies, like, Toyota, Dupont, Dow Corning, 3M and others. Paints (where inorganic nano-pigments were suspended in organic mixtures), paper (metal oxo-species crosslinking with cellulosic polymers) and coupling agents (silanes, silicones or metallo-organic molecules) are products examples [2,11,12].

Nanocomposites structure is anticipated to be composed by solid structures dispersed at the nano scale in a matrix, in the case of polymers, typically an organic matrix containing inorganic nanoparticles. The nanostructure phases of nanocomposite structure can be defined as: zero-dimensional (embedded cluster), 1D (one-dimension; e.g. nanotubes), 2D (nanoscale coatings) and 3D (embedded network) [5]. Nanocomposites materials can be produced both by complex and simple processes. Complex nanostructures materials with complex hierarchical structure are building "block by block" with several preparation technics ranging from chemical processes to vapour phase deposition. Nevertheless, a simple dual-phase system where a catalyst is used to produce the inorganic nanoparticles in a ceramic can be obtained by simple evaporation of metal onto selected substrate or dispersed through solvents in solution medium.

Since nanocomposites are composed by nanosized particles with high surface area, the particles interface assumes as key point, which defines its final properties. Depending on the dispersion and particles surface, several interfaces can be observed, which can result in special properties. An example of this, is the anti-bacterial properties of some biodegradable polymers used for food packaging obtained by titanium nanoparticles dispersion onto polymer phase [13]. Nanocomposites can be produced by similar processes that used for conventional polymer composites, which makes them particularly interesting from the production point of view [3]. They can also be prepared by in-situ synthesis of inorganic nanoparticles, which are called hybrid polymer materials [14]. A correct definition of the design and the synthesis technics are critical to obtain nanomaterials with suitable properties [15]. Usually, the synthesis of polymer nanocomposites applies bottom-up or top-down methodologies. Nevertheless, the difference between nanocomposites and hybrid materials is not clear since inorganic clusters can form molecular building blocks that are larger to hybrid materials but are in nanometer length scale. Even though, the term nanocomposite is usually used when inorganic units are added to an organic matrix and the term hybrid nanocomposites

when the inorganic nanoparticles are formed in situ by a molecular precursor using, for example, the sol-gel method.

Nowadays, nanocomposites have good future perspectives, where new and exigent applications are imposed to achieve huge harmony between human activities and environment [1].

Polymer Nanocomposites

Polymer nanocomposites are materials with high industrial importance as described above. According to Schadler [16] at the beginning of the last decade, traditional micrometerscale composites reached the limits of properties optimization, since to achieve one required property involved the loss of another. Stiffness is traded for toughness or toughness could be reached but optical clarity would be loss. Moreover, agglomerates of micrometer-scale fillers, can promote macroscopic defects that can lead to breakdown or failure [16]. Contrarily, nanosized particles allow to improve electrical and/or mechanical properties, without scatter light significantly, due to its small size, letting the polymer to retain its optical clarity. Moreover, nanosize means that particles do not provoke high stress level not contributing for material failure during service.

Now a day scientists are able to define the size, shape, volume fraction, interface and degree of dispersion or aggregation, which generated great interest around this subject in recent years [14, 16-18]. A good selection of the basic components allows synergetic properties of the produced nanocomposites. Mechanical properties, like, yield stress, tensile strength and Young's modulus generally suffer a huge increase when compared to pure polymers [11, 19, 20]. Polyurethane when filled with silica nanoparticles in a weight fraction of 20 % shows an increase in the strain-to-failure of 500 % compared to pure polyurethane [20]. Gas barrier properties can be improved by 50 to 500 times by dispersion of small amounts of nanoclays into a polymer matrix [21]. Literature is full of examples of incredible changes on properties and many of them can be obtained without losing optical transparency.

Nevertheless, this complete control over the hierarchical structures of nanocomposites, as well as, over interface properties between matrix and filler are only achieved due to the developments on chemical processes, as the in-situ synthesis processes. Interface control means to be able to control the interaction between filler and polymer and consequently the material final properties.

Interface Role on Nanocomposites Final Properties

The interface plays a central role on the nanocomposites final properties. A simple mind game shows the importance of atom surface when particles become smaller (Fig. 1). Taking the example described by Kickelbick, if a cube of atoms packing $16 \times 16 \times 16$ atoms, this contains a overall number of 4096 atoms from which 1352 are located on surface ($\approx 33\%$ surface atoms) [14]. However, if the cube is divide into eight equal parts the overall atoms number is the same but the

number of atoms at the surface increase to 2368 (surface atoms); repeating the process we reach to 3584 surface atoms ($\approx 88\%$ surface atoms). Then, the inner interface has a direct impact on material properties.

Based on the interfacial chemistry two distinct categories of interfaces can be defined. While Class I has only weak bonds (hydrogen, van der Waals or ionic), Class II has covalent bonds between organic and inorganic components [3, 11, 22, 23].

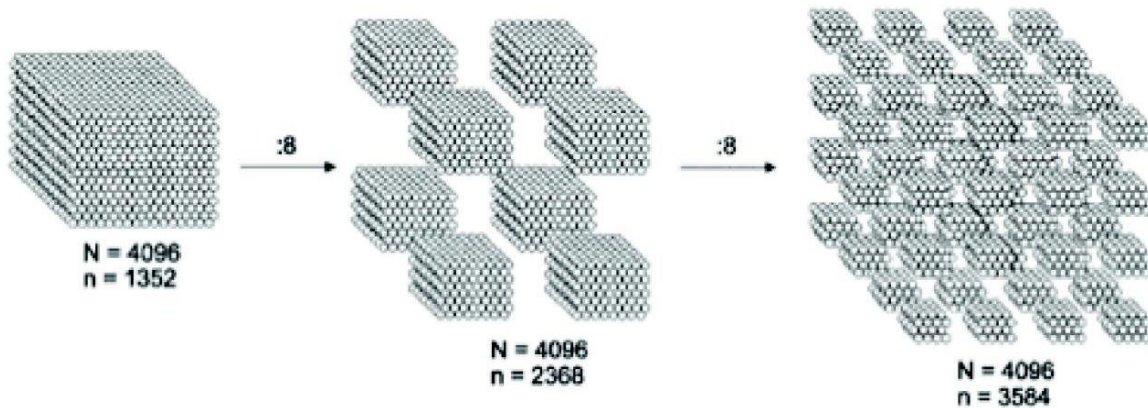


Figure 1. Surface statistic consequences [14].

Although a lot of researches have been published about nanocomposites preparation, achieving homogeneous dispersion of the nanoparticles in polymeric matrices is still difficult [24]. In most cases the van der Waals attraction between nanoparticles promotes formation of clusters and agglomerates. In addition, hydrophilic nanoparticles and hydrophobic polymers are not compatible, which results in poor interfacial adhesion, consequently bad dispersion and poor properties. Therefore, sometimes nanocomposites exhibited worst properties than conventional polymers, which limits their effective application [25-27].

To overcome these interfacial problems, scientists have been draw considerable attention to the synthesis processes, as well as, the development of new combined methods to have higher control both on chemistry and morphology. Therefore, this chapter summarizes the different routes used to prepare polymer nanocomposites.

Synthesis Strategies towards Polymer Nanocomposites

Nanocomposites, can be prepared by in-situ synthesis of inorganic particles or by dispersion of fillers in a polymeric matrix [14]. A correct selection of the preparation technic is critical to obtain nanomaterials with suitable properties [15]. The synthesis of polymers nanocomposites usually applies bottom-up or top-down methodologies (Fig. 2). In the bottom-up approach, precursors are used to construct and grow, from the nanometric level, well organised structures.

Also, blocks-assembly or building block approaches can be used, where already formed entities or nano-objects are hierarchically combined to originate the desirable material. The building block approach has an advantage compared to in-situ nanoparticles formation, since at least one structural unit is well defined and usually does not have significant structural changes during the matrix formation. Chemical processes, such as, sol-gel, chemical vapour deposition (CVD), template synthesis or spray pyrolysis are employed as bottom-up methodologies [14, 15, 28]. Contrarily, top-down approach, bulk material is breaking down into smaller pieces or patterning using in most cases physical methods, as the dispersion layered silicates in polymer matrices.

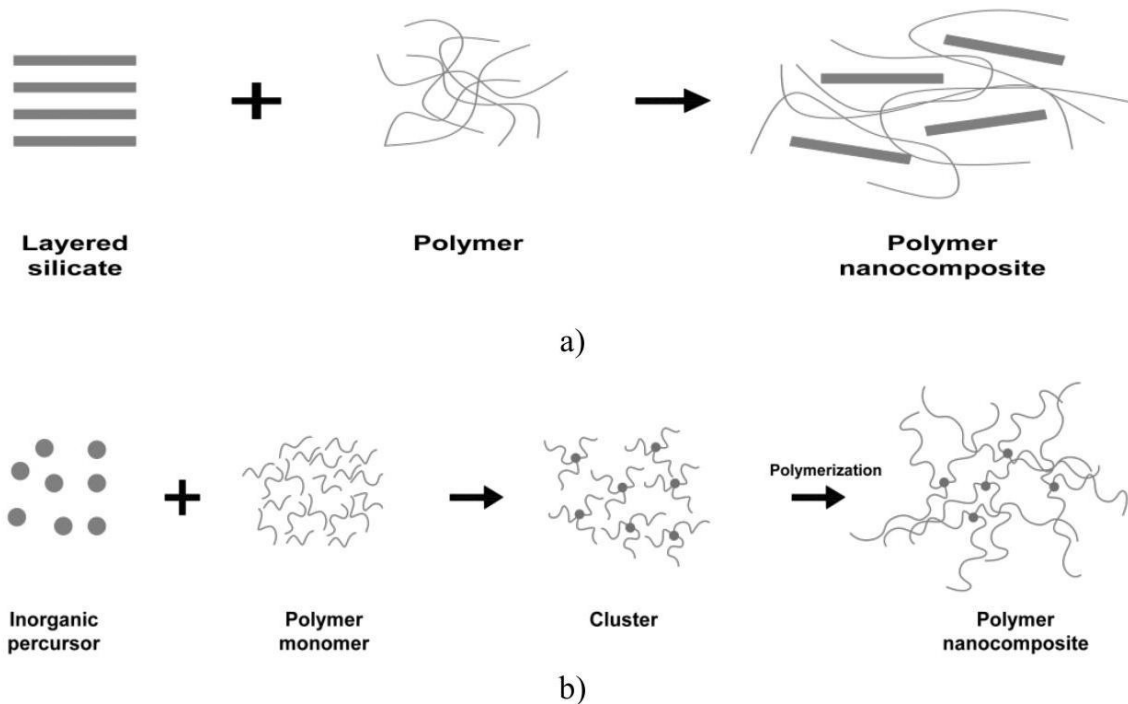


Figure 2. Schematic representation of a) top-down and b) bottom-up approaches.

Generally three ways are used to disperse inorganic nanoparticles into polymer matrices. The first uses the top-down methodology, which consists in the direct mixing of the filler into a polymeric matrix in solution or in melt. The second is based on in-situ polymerization in the presence of the nanoparticles previously obtained or in-situ synthesis of inorganic nanoparticles in the presence of polymer. The last one, inorganic and organic components are both formed in-situ. These two last methods are defined as bottom-up methodologies. Nevertheless, Fig. 3 makes a summary of the basic methods used to prepare nanocomposites.

Interpenetrating Network

Interpenetration networks (IPNs) can be formed between inorganic and organic elements either by a sequential two steps process, where a secondary network is formed in the primary, or by only one step, where both networks are formed simultaneously [29]. Nevertheless, the focus is on the inorganic network formation. However, some difficulties can occur during the incorporation of the inorganic system into the polymeric phase. When the inorganic component is obtained into the organic polymer by polycondensation reactions, the incompatibility between components can lead to phase separation. Additionally, inorganic systems are thermal stable and are formed generally at high temperatures, while most of polymers have a maximum temperature of 250° C and at higher temperatures degradation may occur. Therefore, organic-inorganic nanocomposites require synthesis strategies suitable for both phases.

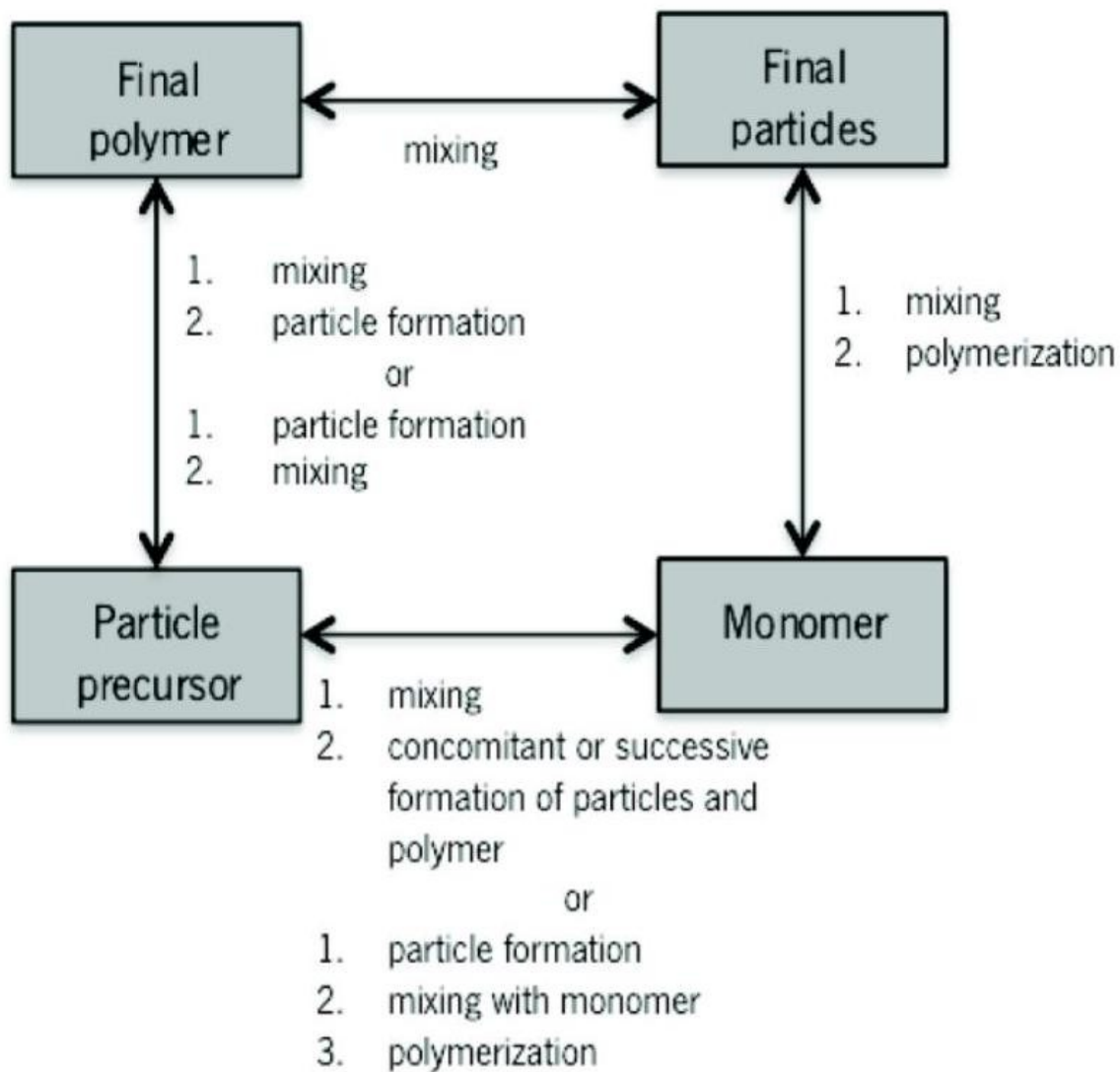


Figure 3. Summary of nanocomposites preparation methods [14].

In-situ Nanoparticles Formation

The in-situ components formation, based on the bottom-up approach, allows us to build well defined multidimensional structures, which have completely different properties from the original precursors. Typically, organic polymer acts as reaction medium where metal and/or metal oxide particles are generated. The desired nanoparticles are then obtained by chemical conversion of the metal precursor [14, 30]. Metals and metal oxide nanoparticles generally are excellent sorbents, catalysts, sensors, reducing agents and bactericides [30]. On the other side, polymers are robust and chemically stable organic materials. Thus, the resulting hybrid nanocomposites exhibit synergetic properties and applications that could not be achieved either by the polymeric material or by the metal nanoparticles individually (Fig. 4).

The incorporation of metal nanoparticles into a polymeric matrix can be done using two different approaches: ex-situ or in-situ (Fig. 5). In the ex-situ, the inorganic nanoparticles are first synthesized and then introduced in the polymer solution or melt. This is based on physical entrapment of the metal or metal oxide nanoparticles into the polymer network, but homogenous dispersion are difficult to obtain. To overcome this difficulty, the in-situ approach can be used. Here, the metal or metal oxide particles are generated inside the polymer phase using a metal precursor, which is converted in the desirable nanoparticles. The in-situ method allows control over the particle size and the morphology [30]. One of the most successfully chemical processes that allows us to incorporate metal nanoparticles into organic phase is the sol-gel process.

Sol-Gel Process

The term sol-gel is associated to two reaction steps, sol and gel. Sol is a colloidal suspension of solid particles in a liquid phase and gel the interconnected network formed between phases [31, 44].

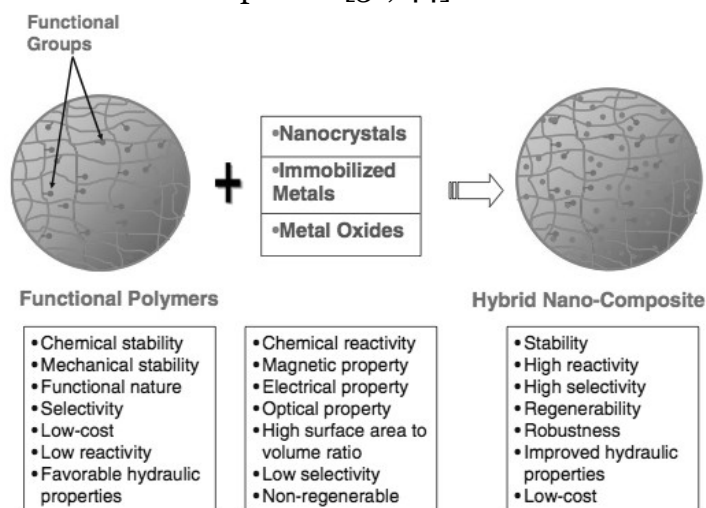


Figure 4. Synergetic effects of polymer-metal hybrid nanocomposite [30].

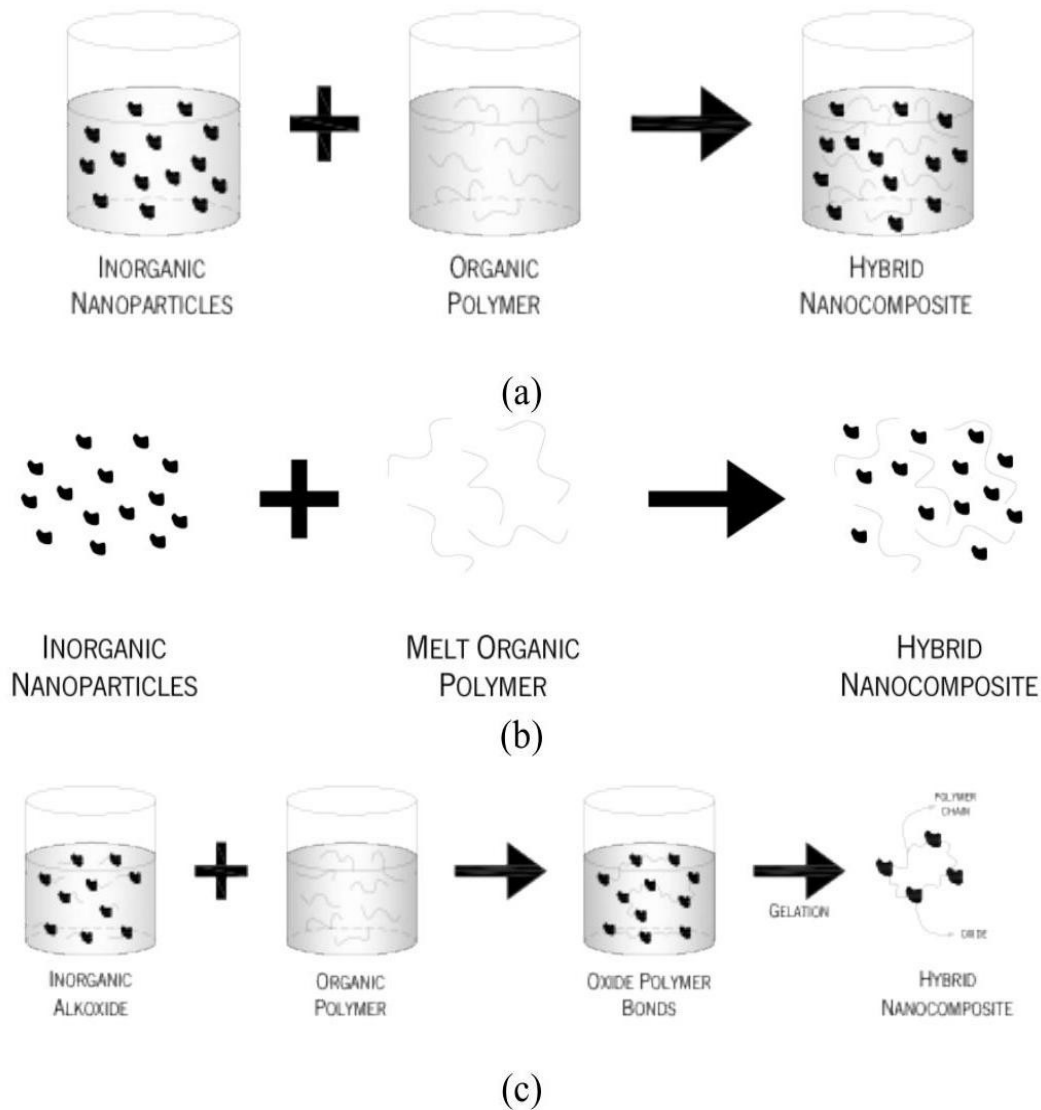


Figure 5. Methods for nanocomposites preparation: ex-situ process a) solution dispersion and b) melt dispersion; in-situ process c) sol-gel process.

The sol-gel technic allows engineers and scientists to design a new generation of advanced materials with unique properties [11, 31, 32]. Nevertheless, the use of sol-gel method to prepare functional materials is very old, and it was used 17,000 years ago [32]. However, only in 1644, sol-gel method got scientific relevance with the discovery of the "water glass" by von Helmont [33]. Later, 1779, Bergman reported that silica gel could be created by a mixture gelled on acidification, if the correct amount of diluted acid was added [34]. This discovery allowed, at that time, to develop a process very similar to the actual solgel chemistry [32]. Then, in 19th century the sol-gel process was finally established due to two main developments: physician masters, as Becquerel and Faraday, undergone an intensive study on the physical properties of colloids (some of the prepared sols, as gold sols, were so stable that still exist at the Royal Institution in

London) and the chemistry science become very sophisticated with important improvements. Ebelman, 1846, prepared the first silicon alkoxide precursor from the reaction between silicon tetrachloride and alcohol, observing a gelled compound when exposed to the atmosphere [35]. However, these materials only had interest to the chemists, until Geffcken, in 1930s, demonstrated that alkoxides could be used to obtain oxide films, a process that was developed by the Schott glass company [36]. After, Roy, popularized the sol-gel process in the ceramic community to prepare homogenous powders [37-39]. However, the growth of the sol-gel method applied to ceramics continues until today due to Yoldas and Yamane works [40, 41]. They demonstrated that careful drying of gels could produce monoliths, which led to an increase in sol-gel process research, being still very important nowadays [42, 43].

The sol-gel process consists in two main reactions: hydrolysis (Equation 1a) and condensation (Equation 1b). Both are multi-steps processes and occur sequentially. Hydrolysis is a cleaving of organic chain bonding to metal and subsequent replacement with OH groups through nucleophilic addition. The protonated species leaves the hydrolysed metal as an alcohol (alcoxolation). Condensation is based on oxygen, metal, oxygen bond formation (-O-M-O-). By definition, condensation reaction releases small molecules, such as, water or alcohol [31, 36, 44, 45].

Equation 1a) $M-OR + H_2O \rightarrow M(OH)_n + nROH$

Equation 1b) $M(OH)_n + M(OR)_m \rightarrow M_nO_{n+m} + nH_2O$

The metal reactivity, amount of water, solvent, temperature and the use of complexing agents or catalysts are the reaction main parameters. To use or not a catalyst depends on the chemical nature of the metal atom and steric hindrance of the alkoxide group. Electrophilic character of the metal atom and its ability to increase the coordination number, seems to be the main parameters [24,31].

One of the most interesting advantages of the use of sol-gel method is its compatibility with polymers and polymerization processes, which allows the formation of nanoparticles in the presence of organic molecules [46].

Sol-Gel Precursors

Precursors can be either metals alkoxides or inorganic and organic salts. The silicapolymer hybrid materials are the most studied class of sol-gel prepared inorganic-organic hybrids. Nevertheless, silica incorporation only promotes changes on mechanical and thermal stability of the polymer matrix [46]. Contrary, metal alkoxides, in particular transition metal alkoxides, give new functions, such as, electronic, magnetic or catalytic properties. Metal alkoxides are much more reactive than silicon alkoxides due to the presence of the highly electronegative OR groups, which stabilize the metal atom in its highest oxidation state and make it more susceptible for nucleophilic attack [44]. Therefore, usually no catalysts are required for the hydrolysis condensation reactions and it is

necessary to limit the metal alkoxide reactivity by coordination with bidentate ligands [46]. Although the higher reactivity could be a problem to control sol-gel process, this also gives the possibility to polymer science to tailor the macromolecules, playing with interactive groups and sterical demand of the polymer, in such way that it is possible to control the metal alkoxide reactivity. Metals with alkoxide ligands type $-O-CH_2-R$, where R is $n-C_4H_9$, $i-C_4H_9$, $n-C_5H_{11}$, etc., have lower steric hindrance due to molecules symmetry. However, if the alkoxide groups has OR as secondary or tertiary, the conversion of the tetrahedral metal atoms to penta or octahedral coordination, results in the formation of less species, like dimers or trimers and consequently lower reactivity [31].

Synthesis of Hybrid Nanocomposites Based on Sol-Gel Process

Applied first in the processing of inorganic ceramics and glasses materials, as described above, the sol-gel method started to be employed to prepare hybrid polymers in 1980 [47]. However, until the beginning of last decade, the synthesis of inorganic-organic hybrid involved always the use of solvents, which rise problems of polymers solubility and compatibility of the solvent with the sol-gel process [32]. Wu and Liao were the first to propose the sol-gel process in the melt [48]. To overcome the recognise limitations of polyethylene, as low melting point, stability in hydrocarbons and tendency to crack under stress, they modified polyethylene-octene elastomer (POE) by incorporation of silica nanoparticles. Then, POE/SiO_2 and maleic anhydride-grafted polyethylene-octene elastomer (POE-g-MA) \wedge SiO_2 hybrids were prepared by incorporation of a solution containing silica precursor, water and catalyst into the molten polymers. The reaction mechanism of Fig. 6 was proposed.

The synthesis of POE/SiO_2 and $(POE-g-MA)/SiO_2$ resulted in an increase of the initial decomposition temperature, as shown in Fig. 7. Moreover, they concluded that the interfacial bonds between the polymer chain and silica network changed from hydrogen bonding to strong covalent $Si-C-O$ bonds, when POE-g-MA was used instead PEO. Also, the optimal silica content was determined, higher than 9 % (wt%) does not have significant change in initial decomposition temperature and has a negative effect on tensile strength (Fig. 8), which was attributed to the phase separation.

Bounor-Legaré, in 2004, described the synthesis of ethylene-co-vinyl acetate (EVA) and silica hybrid without the presence of solvents [49]. Using tetraalkoxysilane (TEOS) as silica nanoparticles precursor, EVA and TEOS were mixed during 3 min at $110^\circ C$ in an internal mixer in the presence of catalyst dibutyltin oxide. However, under these conditions EVA crosslinking did not occur and only a physical mixing of the three compounds was achieved. The crosslinking reaction (Fig. 9) was then carried out at $150^\circ C$ during 45 min between the plates of a heating press. Nevertheless, after 45 min of curing they realised that crosslinking did not happen, since by assessing the propyl acetate concentration

by gas chromatography between 90 to 92 % of TEOS was free and dispersed on EVA network. A third step had necessary to promote the hydrolysis condensation of alkoxide groups.

A: Hydrolysis



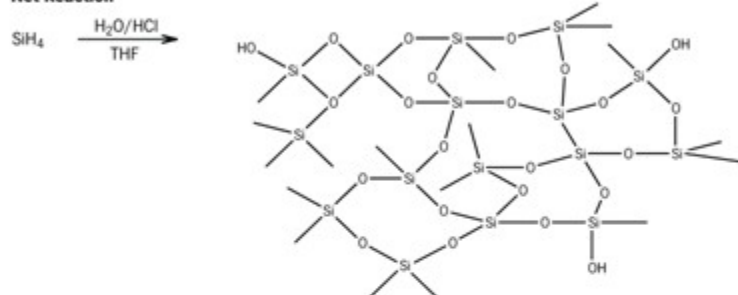
Condensation



and/or



Net Reaction



B:

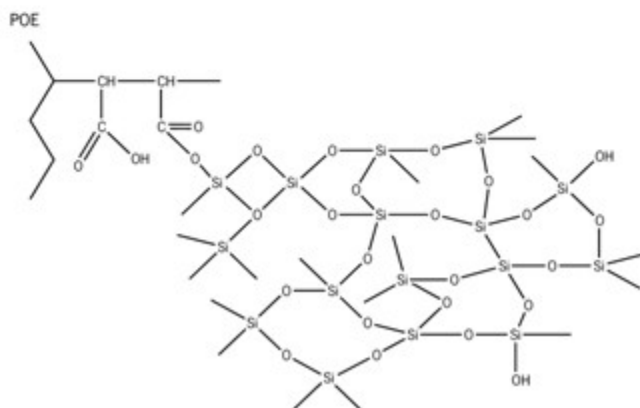
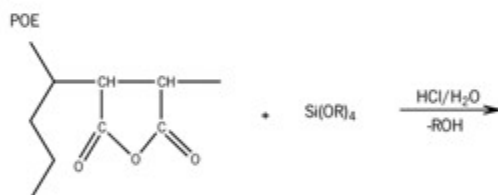


Figure 6. Sol-gel synthesis mechanism of *POE/SiO₂* and (POE-g-MA)/ *SiO₂* [48].

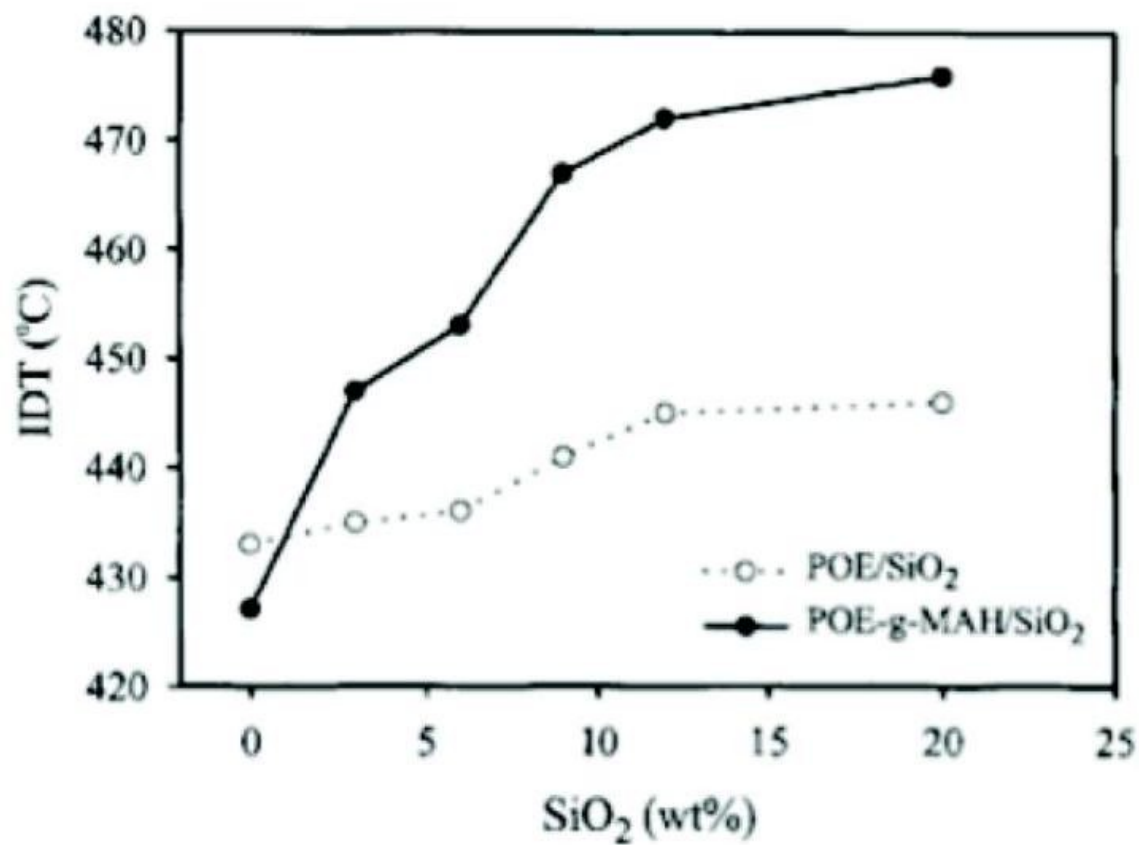


Figure 7. Initial decomposition temperature as a function of silica content for *POE/SiO₂* and *(POE-gMA)/ SiO₂* hybrids [48].

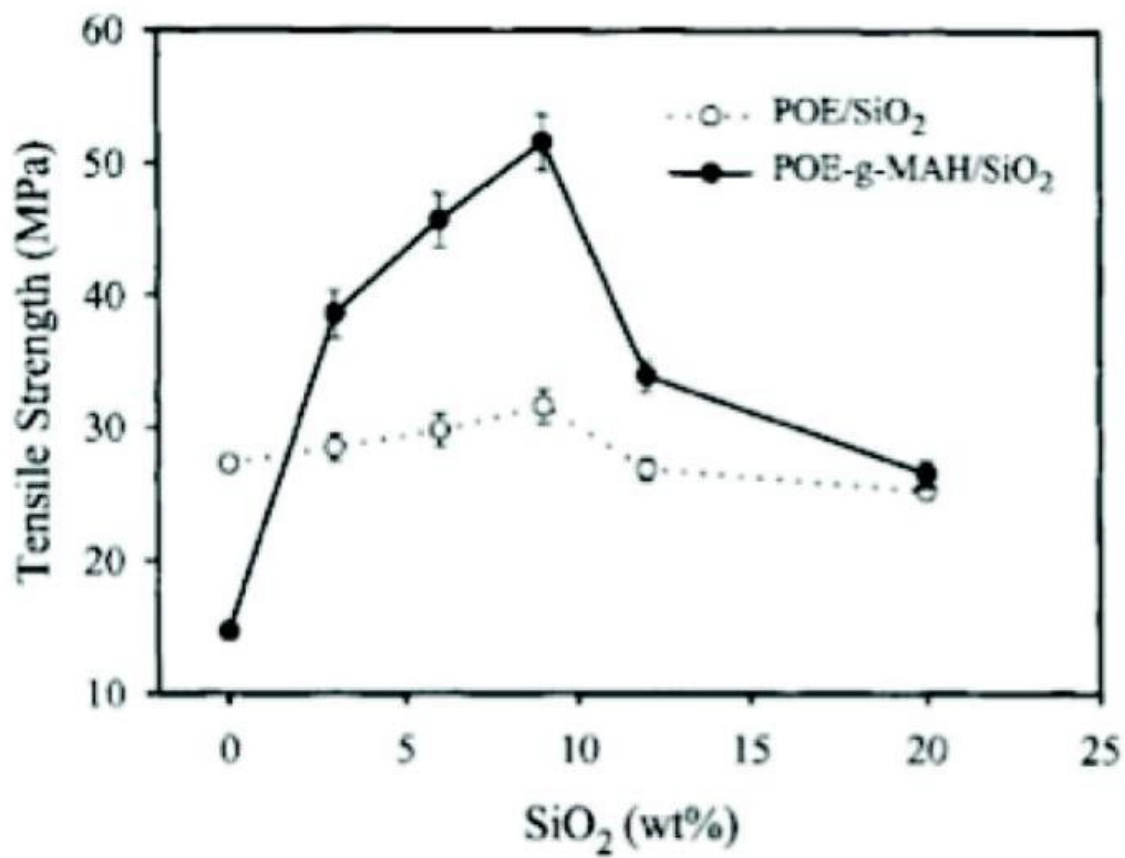


Figure 8. Tensile strength at break as a function of silica content for *POE/SiO₂* and (POE-g-MA) *SiO₂* hybrids [48].

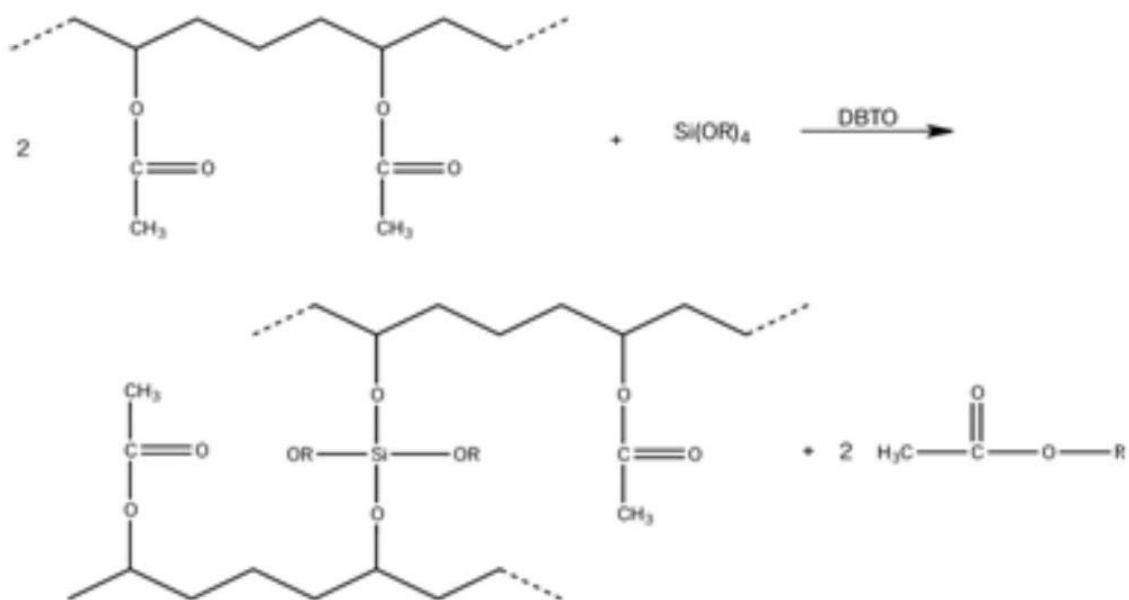


Figure 9. Reaction scheme of EVA crosslinking through ester-alkoxyane interchange reaction ($R = \text{propyl}$) [49].

A third step was carried out at 80°C in acidic water, following the Sioplas process [50], leading to silica network formation according to scheme described in Fig. 10.

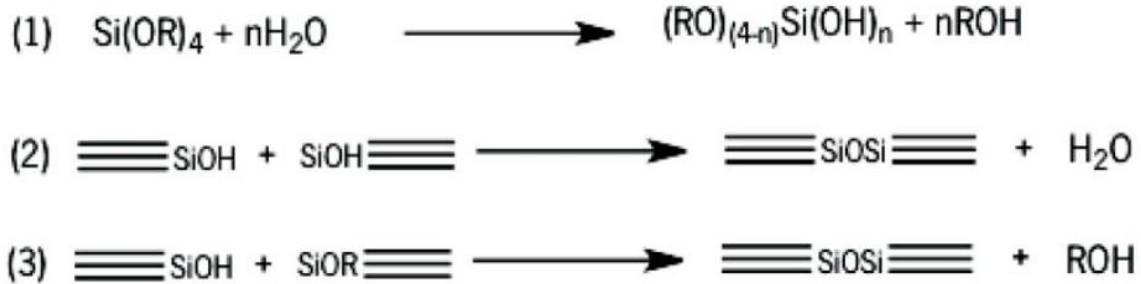


Figure 10. Reaction scheme of alkoxy silane showing the hydrolysis (1) and the condensation (2) and (3) [49].

The connectivity between EVA network and silica growing domains was established through $\text{Si}-\text{O}-\text{C}$ bonds. However, due to the sensitivity of $\text{Si}-\text{O}-\text{C}$ bonds to hydrolysis a decrease of connecting bonds between organic and inorganic phases occurred, which resulted in the formation of pendant alcohol groups. Thus, the crosslinking density of EVA network decreased with hydrolysis-condensation treatment, relatively to the first curing treatment. Moreover, the EVA hybrid showed a permanent elasticity for temperatures above the melting temperature, but with the hydrolysis progress, the equilibrium rubber plateau slightly decreased (Fig. 11).

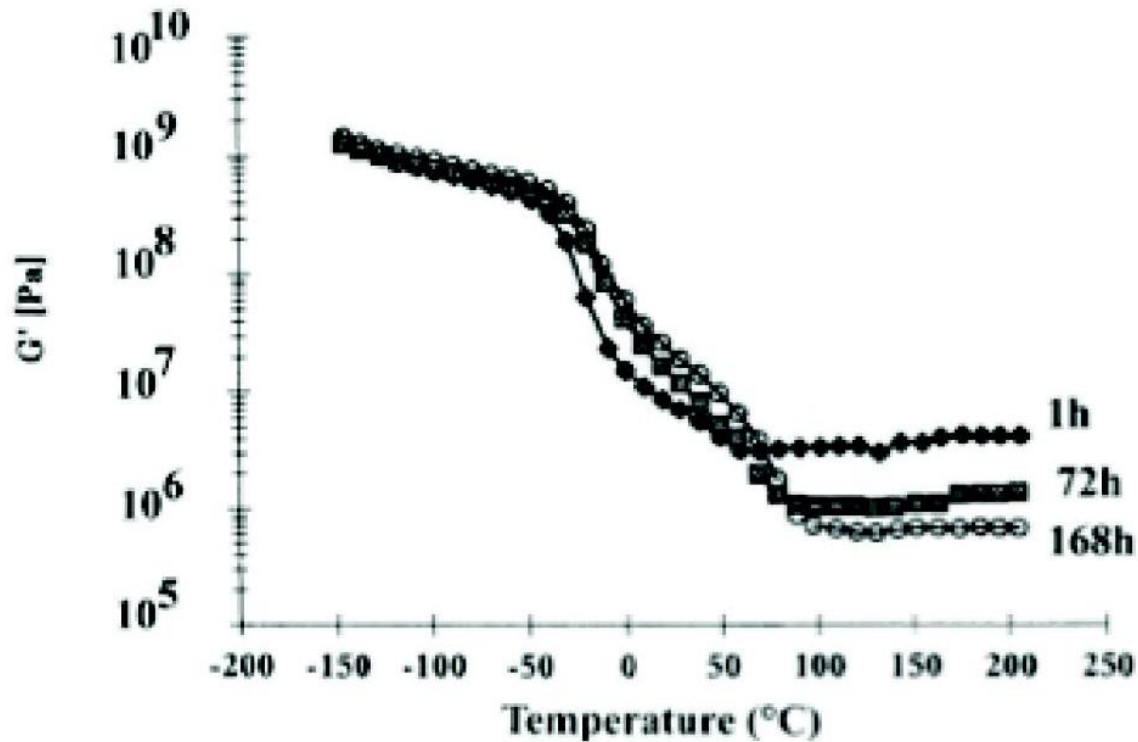


Figure 11. Storage modulus (G') as a function of temperature for organic-inorganic hybrid after 1,72 and 168 h of hydrolysis [49].

Bahloul and co-workers studied the synthesis of polypropylene titanium nanocomposite (PP/TiO_2) by direct sol-gel reaction under molten conditions [42, 51, 52]. The nanocomposites were prepared using a co-rotating twin-screw extruder, where titanium nbutoxide was added as liquid to molten PP by a side feeder. In this case, neither water or catalyst was added, the hydrolysis-condensation reaction was initiated by the surrounding humidity. Authors reported that at the die exit of the extruder the extent of the hydrolysis was higher than 70 %, but the complete hydrolysis-condensation process was only achieved after samples immersion, in hot water ($80^\circ C$) for three days. The viscoelastic properties of the synthesised nanocomposite were compared with the nanocomposites prepared by addition of TiO_2 particles to PP. The results obtained showed that, in this case, there was no interaction between particles and polymer matrix (Fig. 12 a)). On the opposite, the nanocomposite prepared in-situ exhibits a clear modification of the viscoelastic behaviour (Fig. 12 b)). More precise, for higher concentrations of TiO_2 , G' depicted similar values for all frequency range, which corresponds to a typical solid-like behaviour.

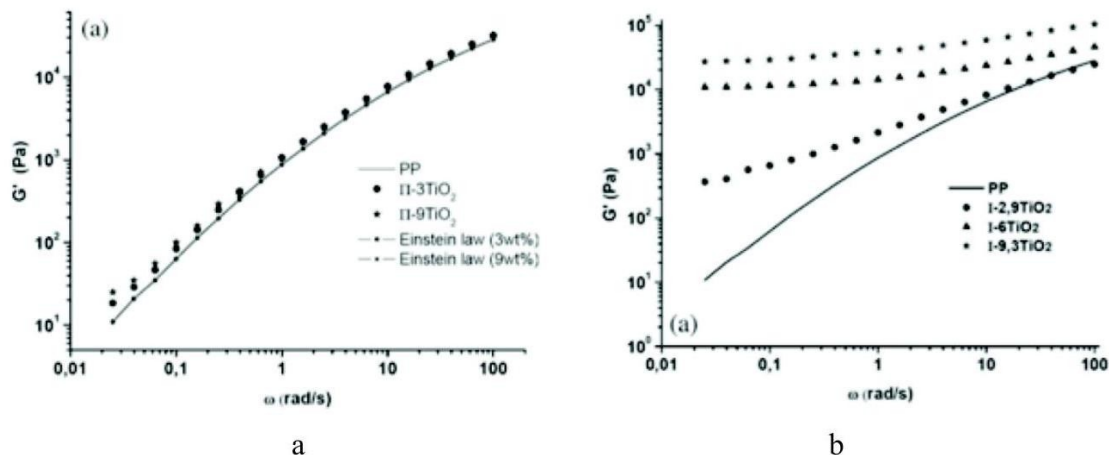


Figure 12. Viscoelastic behaviour a) PP/TiO_2 nanocomposite prepared by particles addition, b) PP/TiO_2 nanocomposite prepared by sol-gel process [42].

Oliveira prepared nanocomposites of polypropylene containing aluminium by single step directly in the extruder [6, 53]. Polypropylene grafted with maleic anhydride (PP-g-MA) reacted with aluminium isopropoxide, which allowed the introduction of aluminium and crosslinking formation (Fig. 13).
2-propanol

Figure 13. Simplified scheme of PP-g-MA aluminium isopropoxide reaction. Moreover, a drastically change of the rheological properties evidenced the effect of the inorganic particles in the polymer matrix. The increase in viscosity and storage modulus (Fig. 14) could be associated to three sources: first due to the presence of inorganic filler dispersed in the polymeric matrix, second due to physical interaction and third by the formation of a branched/crosslinking structures. However, gel content and the crosslinking density values confirmed that crosslinking occurred.

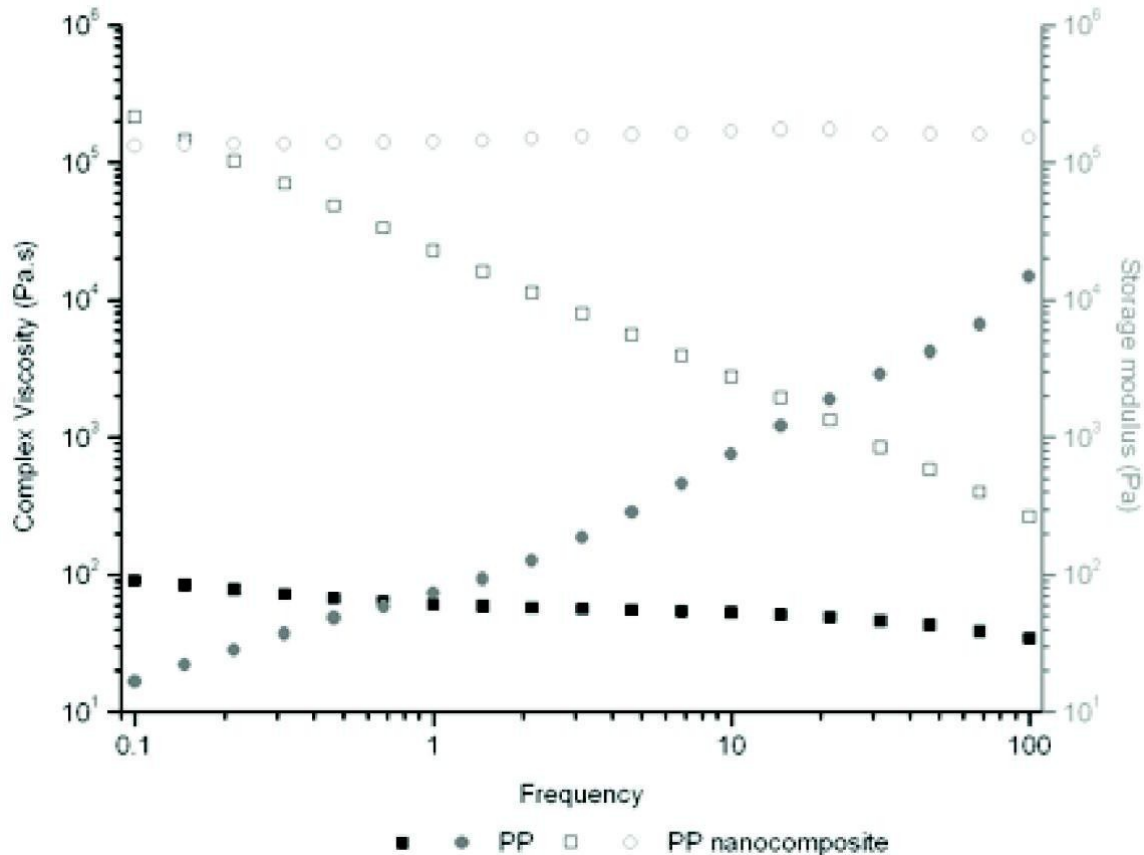


Figure 14. Rheological behaviour of PP and PP nanocomposite.

Intercalation Polymer-Layered Silicate Materials

LeBaron, 1999, affirmed that layered silicates dispersed as reinforcing phase in a polymer matrix were one the most important nanocomposites [54]. It is well established that clays incorporation into polymeric matrices improves the bulk properties, such as, shrinkage on moulding, stiffness, heat resistance and flammability, decrease of electrical conductivity or permeability of gases (oxygen or water vapour) [29]. In the final of the 1980s, Toyota researchers described for the first time the exfoliation of a nanoclay in nylon-6. Performed in solution, they studied the ability of Na-montmorillonite nanoclay to swollen ϵ -caprolactone monomer and subsequently promote its ring opening polymerization to obtain nylon-6-based nanocomposites [55]. Later, 1993, Vaia and co-workers reported that the clays could be dispersed by direct melt mixing [56]. Since that, lot of studies has been reported describing several preparation strategies. Alexandre and Dubois enumerate the four main processes to prepare nanocomposites of polymer-layered silicates: exfoliation-adsorption, in situ intercalative polymerization, melt intercalation and template synthesis (Fig. 15) [57]. Nevertheless, the selection of the process depends on the polymer and clay compatibility [58]. Since the clays surface is mainly composed by a hydrophilic silicate layer and most of the polymers are hydrophobic, a direct mixing of both is only possible by modification of one or both components. The most common

consists on clay modification using amino acids, organic ammonium salts or tetra organic phosphonium to change the clay surface from hydrophilic to organophilic. The clays subjected to this treatment are known as organoclays [54, 58, 59]. Common polymer without functional groups, such as PP, usually requires the addition of a dispersion agent that contains polar groups on main chain, like PP grafted with maleic anhydride [27, 60].

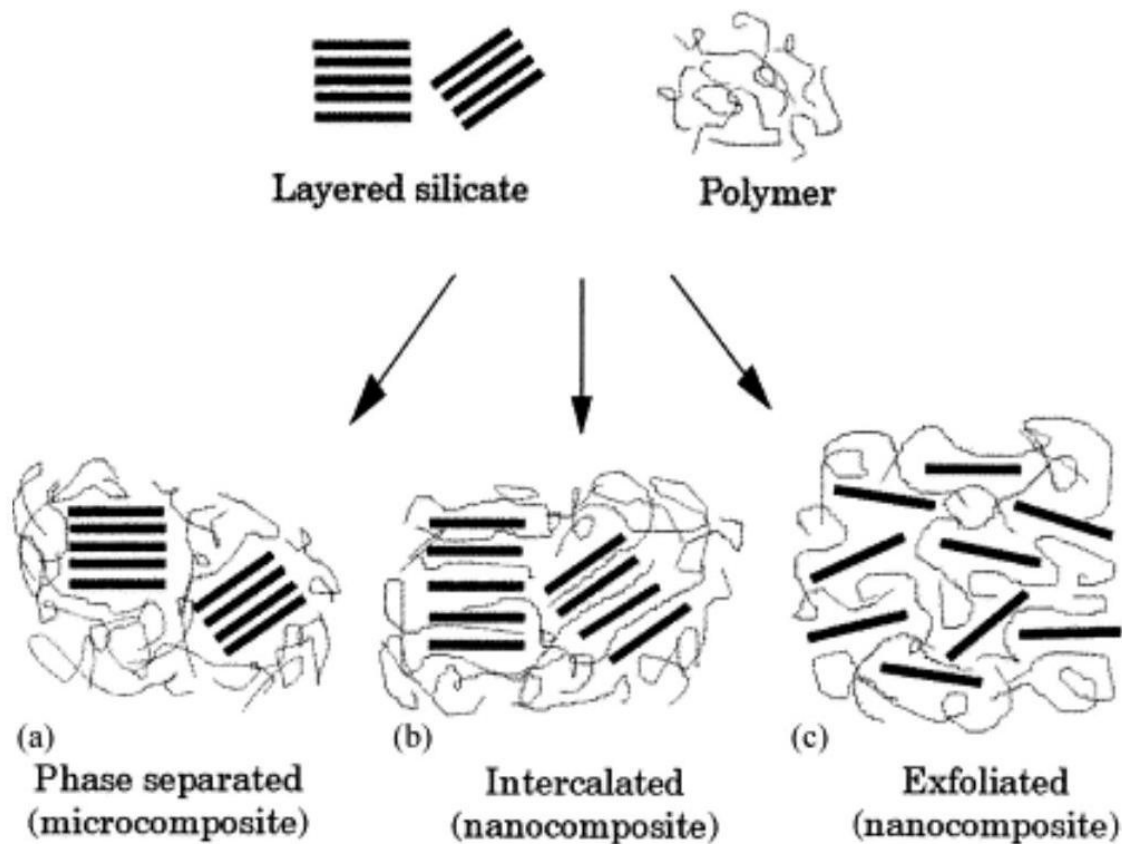


Figure 15. Schematic view of preparation methods for polymer silicates nanocomposites [61].

Exfoliation-Adsorption

This process involves the use of solvent, in which polymer or prepolymer is soluble, to promote the exfoliation of layered silicate into single layers (Fig. 16). When the appropriated solvent is used, it is possible to break the weak forces that stack the layers together. Then, the polymer is easily absorbed onto the laminated sheets. After solvent evaporation, a sandwich of polymer is obtained by sheets reassemble [3, 57]. However, this process reveals commercial handling problems due to the solvents high costs and phase separation of the synthesized product from the solvent [58]. Emulsion polymerization, where silicate layers are dispersed in the aqueous solution, is also included in this process.

In Situ Intercalative Polymerization

In this process monomer is in solution where silicate layers are swollen within. The polymerization is initiated between layers, expanding and dispersing the clays into the polymer (Fig. 16) [62]. An advantage of this method is the tethering effect, which allows nanoclays with chemical active surface to link polymer chain during polymerization [3].

Melt Intercalation

Melt mixing is the most promising and practical method to be used in industry. Since solvents are not required, this can be applied to polymer processing industry to produce nanocomposites based on usual compounding devices, such as, extruders or mixers [14, 57, 58, 63]. Direct mixing due to simplest, economical, and environmentally friendly technic, is the mainstream for the fabrication of polymer silicates nanocomposite [16, 63, 64]. Usually during extrusion the clay is mixed with the molten polymer, whose chains penetrate inside the galleries of clay layers inducing its intercalation as shown in Fig. 16. According to the compatibility between layers surface and polymer, either intercalated or exfoliated nanocomposites can be obtained, depending the degree of layers separation (Fig. 2). This method, commonly requires "trial-and-error-based" experiments to test different process conditions to optimize dispersion [62]. Processing equipment and processing conditions have important role since the combination of shear stresses, residence time and temperature improve clay dispersion [65]. Other important parameter for effective clay dispersion is the polymer molecular weight. Polymers with high molecular weight enhance clay dispersion since these can transfer shear stress to the clay. Nevertheless, normally lower levels of exfoliation are achieved when compared with in situ polymerization.

Polymers that are not suitable for adsorption or in situ polymerization methods, nanocomposites can be prepared by melting intercalation process [3]. Thermoplastics with strong polar groups, as polyamide-6, ethylene vinyl acetate and polystyrene have been intercalated/exfoliated. However, polyolefins, the main volume of produced polymers, only in specific cases intercalation was successful achieved, until now [66].

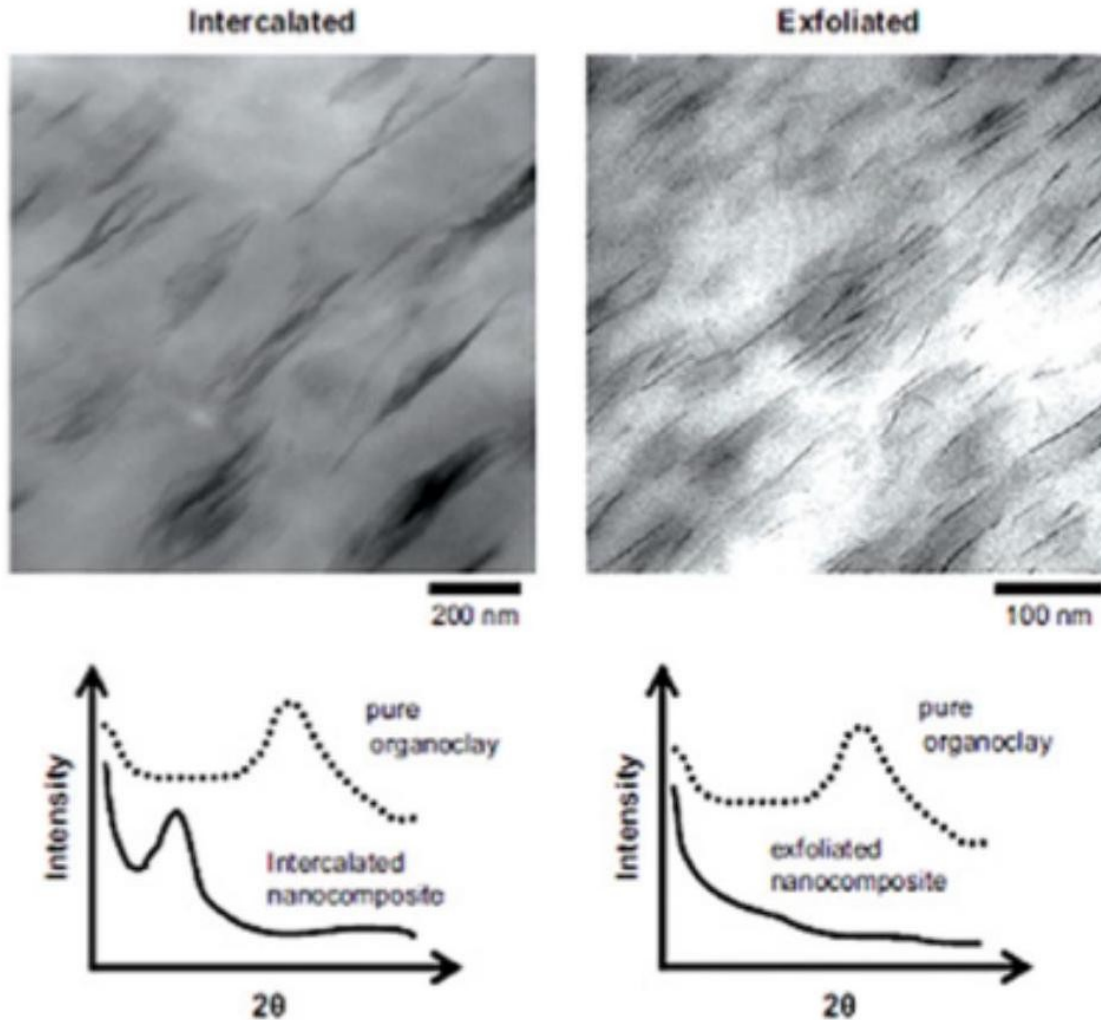


Figure 16. TEM micrograph and WAXS of intercalated and exfoliated organoclay in polymer [67].

Template Synthesis

Template synthesis technic, a method completely different from other described above, is based on sol-gel technic. Using an aqueous solution (or gel) containing the silicate building blocks and polymer, clay is synthesized within the polymer matrix. During the process, polymers act as template helping the nucleation and growth of silicates crystals, being trapped inside the layers as they grow [57, 62, 68-70]. Theoretically, template synthesis should promote the dispersion of the silicate layers in a one-step process, but some serious drawbacks have been observed.

Carbon Nanotubes Based Nanocomposites

Carbon nanotubes (CNTs) are recognised as the stiffest and strongest man-made materials known to date [70]. Recognised by high flexibility, lower mass density and large aspect ratio (typical >1000) and extremely high tensile moduli and

strength. Additionally, single-walled carbon nanotubes (SWCNTs) can transport current for long length without significant loss of strength making them more conductive than copper [71-73]. Ajayan and coworkers, 1994, reported for the first time polymer nanocomposites using CNTs as a filler [74]. Since then, many studies related with processing and resulting mechanical and/or electrical properties of polymer/CNTs nanocomposites have been published. Nevertheless, to obtain polymer/nanotubes nanocomposites with good properties depends on many parameters, such as, carbon nanotube production, length, diameter and chirality. Moreover, the dispersion of carbon tubes in polymeric matrices is recognised as the main difficulty. The failure of tubes dispersion means phase separation and consequently poor mechanical and electrical properties. Then, the outstanding CNTs properties, as high strength and stiffness, could not yet be full transfer to the final products [70, 75].

Aiming to improve the dispersion of CNTs on a polymer matrix, research has been performed on its functionalization. The CNTs functionalization is divided in two main approaches: covalent or non-covalent modifications [76-78]. As illustrated in Fig. 17, noncovalent modification covers physical interactions, van der Waals forces and charge-transfer interactions that can be used to wrap polymers around the nanotubes. Covalent modification involves the chemical reaction of CNTs surface and the incorporation of new species.

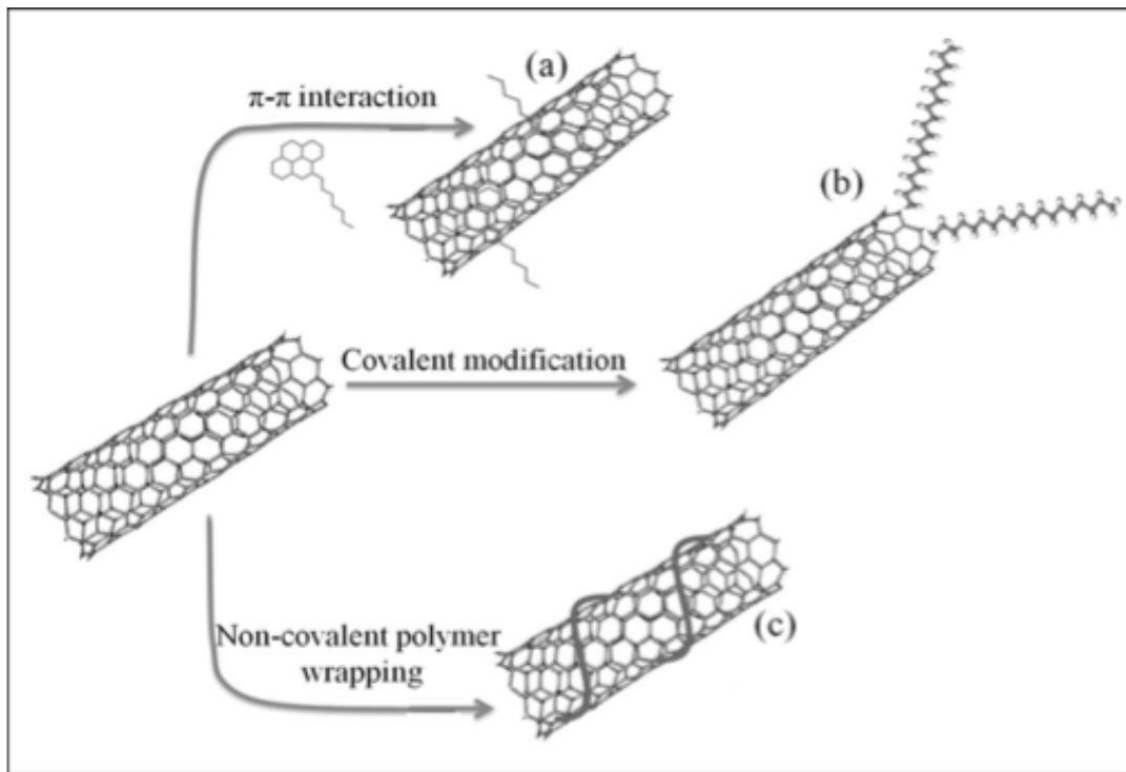


Figure 17. CNTs functionalization approaches; a) and b) non-covalent modification; c) covalent modification [79].

CONCLUSION

Depending on the nature of inorganic particles and properties to be accomplished, a variety of routes can be used to prepare polymer nanocomposites with high homogeneity. The key point is to find out the best conditions to improve the interaction between the polymer matrix and the dispersed particles. Moreover, there is not a general route that allows us to produce materials with homogeneous dispersion, it is necessary to optimize the various steps to reach the targeted properties.

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