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Polymer Nanocomposites

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Abstract

The development of polymer nanocomposites has advanced, especially due to their new properties after nanoparticle incorporation. Many nanocomposites composed of synthetic polymers and/or biopolymers have been studied after incorporation of a diversity of nanoparticles, which differ in form, shape, surface area and chemical organization. In this chapter, some examples of nanocomposites based on poly-vinyl alcohol (PVA); polycarbonate (PC) and matrixes of dental resins are presented. These nanocomposites could be obtained by three basic methods: in situ polymerization, solution casting and melt extrusion. The best method is determined by the relation and route to the polymer-nanoparticle pair. The dispersion and distribution of nanoparticles in the polymer matrix is the key to obtaining new materials with synergism of compounds properties. This synergism depends on how strong is the intermolecular interaction between the polymer matrix and nanoparticles. The evaluation of new nano systems can be done by different techniques, usually microscopy, X-ray diffraction, thermal analysis and so on. Low-field NMR relaxometry has been used to evaluate polymer nanocomposites. This technique provides valuable information related to the interaction of the nanoparticles with the polymer matrix, and it also indicates the dispersion and distribution of these nanoparticles in the matrix.

Keywords: nanocomposites, polymer, spin lattice relaxation

1. Introduction

Development of polymer nanocomposites has advanced quickly because these new materials normally present better properties when compared to pure polymers and/or polymer composites, due to the new architecture. Many natural polymers, synthetic polymers, biopolymers, and

elastomers have been used to prepare these materials, containing different nanoparticles incorporated in them, depending on the application [1–9]. To obtain these new materials with good characteristics, it is necessary to choose the right polymer-nanoparticle pair and preparation technique, because the new architecture depends on this.

To generate polymer nanocomposites, the following important information on the components need to be considered in order to understand the behavior of the new materials: (i) polymer mass; (ii) polymer chemical structure; (iii) polymer semi-crystallinity; (iv) polymer chemical solubility; (v) polymer thermal stability; (vi) nanoparticle surface area; (vii) nanoparticle chemical structure; and (viii) nanoparticle dispersion. There are several methods to obtain these materials, the most common being *in situ* polymerization, solution dispersion (including nanoprecipitation and spray drying) and melt extrusion. Each process has its own particularity. But the essence of all polymer nanocomposites is the final morphology, irrespective of the process, which depends on polymer-nanoparticle interactions that will promote good dispersion and distribution of the nanoparticles in the polymer matrix [10–14]. The final morphology also depends on the process of obtaining the polymer nanocomposite.

2. Different methods for synthesis of polymer nanocomposites

2.1. *In situ* polymerization

This method normally is suitable for polymers that cannot be produced economically or safely by solution methods because the solvents used to dissolve them are highly toxic. This method promotes good dispersion and distribution of the nanoparticles in the polymer matrix [10, 15]. Some important aspects of this method should be pointed out. The first is related to the cost of the process, which can require some changes compared to the normal polymer synthesis. Care is also necessary to choose the most appropriate catalyst. The apparatus used can be the same for polymerization without nanoparticles.

2.2. Solution method

This is a good method when the solvent used is less toxic (chloroform, acetone, alcohol or water). In this method, different quantities of nanoparticles can be dispersed due to the good interaction with the solvent and polymer. This is the easiest method to obtain good nanocomposites. Some care must be taken in the manipulation of the solvent since it must be completely eliminated afterward [8, 11, 13, 16]. The necessary apparatus (**Figure 1**) is very simple.

One interesting method is a combination of solution dispersion and spray drying. The dispersion containing the nanoparticles in the polymer solution, after some time for homogenization, is injected in the spray dryer, which dries the material into a powder. The major drawback of this technique is the final yield of the material. However, this procedure occurs in just one step after all conditions are adjusted and the final material presents good dispersion and distribution. In this process, drugs can be injected together with nanosystems for controlled or targeted delivery. The equipment used in this process is shown in **Figure 2**.
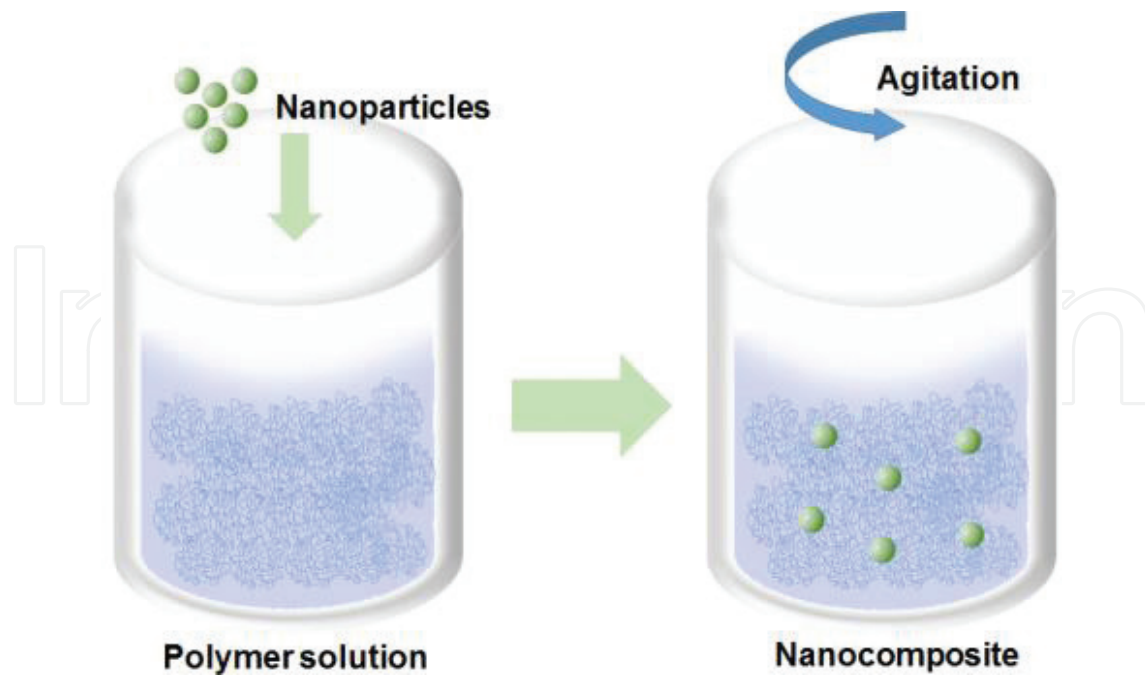
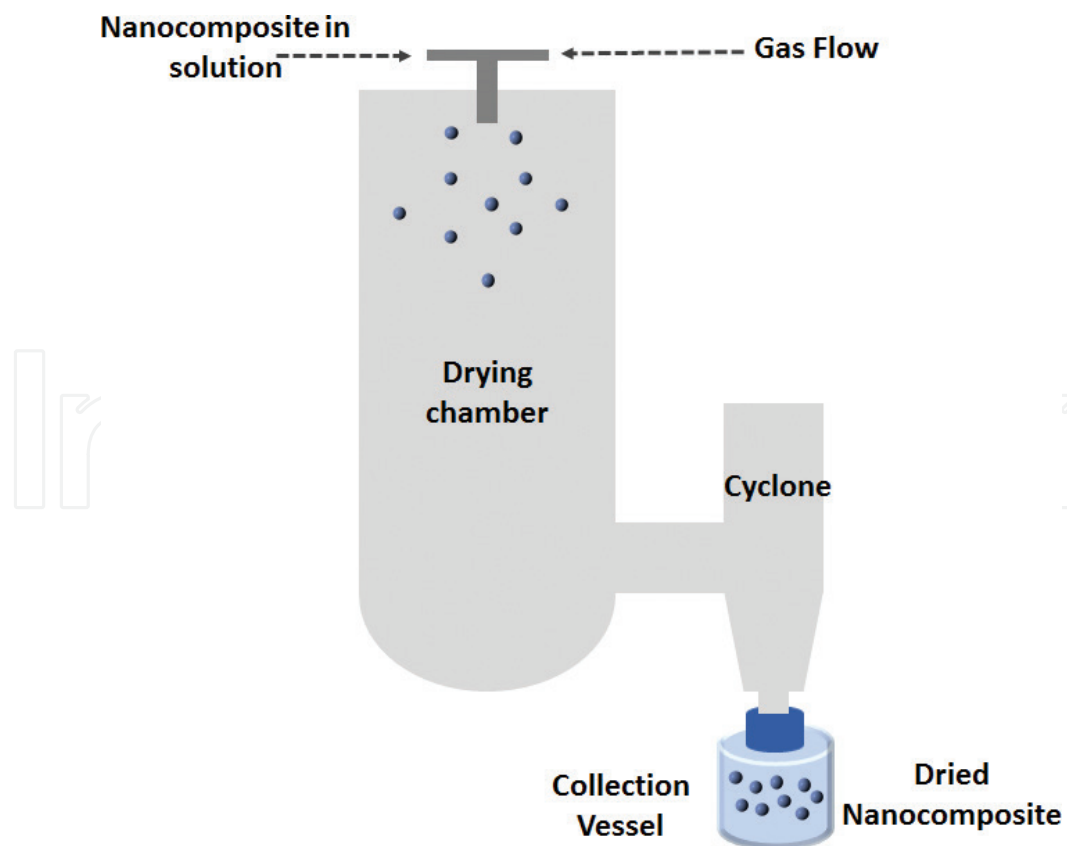**Figure 1.** Scheme of obtaining polymer nanocomposites by the solution method.

Figure 2. Scheme of obtaining polymer nanocomposites by spray drying.

2.3. Melt extrusion

This method has a major advantage in relation to the others since no solvent is necessary. However, the quantity of nanoparticles to be dispersed is very important. This method requires close monitoring of the nanoparticles' dispersion, because these agglomerate easier than in other methods. The apparatus is the same used for polymer processing without nanoparticles. Therefore, the researcher needs to pay attention to the temperatures used so as not to degrade the polymer during extrusion and also must pay attention to the time necessary for the nanoparticles to disperse properly. For natural polymers and few biopolymers, the degradation and melting temperatures are very close [7, 12, 17]. A typical extruder is shown in **Figure 3**.
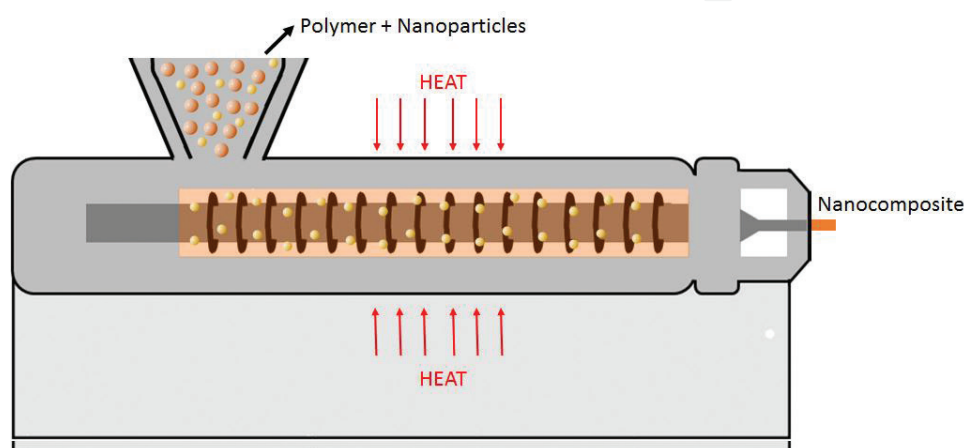

Figure 3. Scheme of obtaining polymer nanocomposites by melt extrusion.

3. Examples of obtaining nanocomposites by different methods and determination of their characteristics

This section gives examples of the three methods and discusses a new technique for their characterization: nuclear magnetic resonance relaxometry to measure proton spin-lattice relaxation time, with a time constant of T_1H.

The spin-lattice relaxation time is the time that the longitudinal magnetization takes to recover about 63% of its initial value after being flipped into the magnetic transverse plane by a perpendicular radio-frequency pulse. This is an enthalpy process where the energy of the spins is passed to the whole network to which the material conforms. Thus, T_1H can indicate the change in molecular mobility caused by intermolecular interactions and the distribution of the components of the material. Longer times refer to more rigid domains and shorter times indicate greater mobility [4–8, 18].

3.1. *In situ* polymerization

Obtaining poly-vinyl alcohol (PVA) and clay systems and use of relaxometry: The nanomaterials were prepared by *in situ* polymerization employing different clay ratios, from 0.25 to 10%

w/w. Solutions of vinyl acetate were poured into Erlenmeyer flasks containing the clay dispersions. After 2 hours of heating at 60–65°C, 5 ml of benzoyl peroxide solution in methanol was add to acetate vinyl solution and the polymerization reaction occurred during 24 hours.

The main characterization was performed by measuring T_1H, with the following conditions. The Free Induction Decay (FID) amplitude was 40 points, ranging from 0.1 to 5000 ms, with four measurements for each point and a recycle interval of 5 s. **Table 1** reports the T_1H values for PVA and its nanocomposites with clay obtained by *in situ* polymerization.

Analysis of the T_1H data for the PVA-clay systems of the material containing 3% clay showed a significant decrease in the relaxation parameter, indicating good interaction between clay lamellae and the polymer matrix, in turn promoting good dispersion and distribution of the nanoparticles in the polymer matrix. The nanocomposite formed was exfoliated since the polymer's main chains were free to move around the clay lamella. This can also be explained by the presence of a paramagnetic metal in the clay structure, which acts as a relaxing agent. After this proportion, a tendency to increase the relaxation value was observed, showing that these proportions produce a predominance of intercalated chains, because they are not free to move since they are constrained among the clay lamellae.

3.2. Solution method

3.2.1. Obtaining PVA-clay films by solution casting

The films obtained by solution casting were prepared mixing a polymer solution and clay dispersion in water. After homogenization of both the solution and dispersion, the solvent was eliminated by heating in oven at 80°C. The films were also analyzed by measuring the proton spin-lattice relaxation time (**Table 2**) employing the same conditions as for the *in situ* polymerization.

According to the relaxation data in **Table 2**, the same behavior was found for the samples generated by *in situ* polymerization. Therefore, the effect was more pronounced and the samples obtained by solution intercalation showed better exfoliation for 3 and 5% clay in the PVA matrix. For 5% clay, the dispersion and distribution of the clay lamellae in the polymer matrix were very good and a predominance of exfoliated nanocomposite was obtained for both proportions, although at 5% this was more accentuated.

Sample/PVA-clay	T_1H (ms)
PVA	115
PVA-0.25	110
PVA-0.75	120
PVA-1.5	105
PVA-3.0	100
PVA-5.0	105
PVA-7.0	115

Table 1. T_1H values for PVA and its nanocomposites obtained by *in situ* polymerization.

Sample/PVA-clay	T_1H (ms)
PVA	120
PVA-0.25	115
PVA-0.75	105
PVA-1.5	105
PVA-3.0	95
PVA-5.0	70
PVA-7.0	90

Table 2. T_1H values for PVA and its nanocomposites obtained by solution casting.

3.2.2. Obtaining PC-organoclay films by solution casting

The PC films and PC-organoclay were obtained using chloroform as solvent and mixing the polymer solution and organoclay dispersion. The films were dried at room temperature under air circulation and the materials obtained were evaluated by measuring the T_1H values. The results are listed in **Table 3**.

Evaluating the T_1H Values, one can see that the incorporation of the organoclay in the polycarbonate through intercalation by solution promoted the generation of mixed nanomaterials, that is, with an exfoliated part and intercalated part, since there was no significant decrease in the spin-lattice relaxation time of the hydrogen nucleus, except at the proportion of 5%, which presented a higher degree of exfoliation. This can be explained because when the polymer chains are around the clay lamellae, the metals present in the clay composition (such as iron, calcium and magnesium) act as relaxing agents, causing a decrease in the relaxation times.

3.2.3. Obtaining PC-TiO₂ films by solution casting

Films of PC and PC-TiO_2 were obtained using chloroform as solvent by mixing the polymer solution and TiO_2 dispersion. The films were dried at room temperature with air circulation and the materials obtained were evaluated by measuring the T_1H values. The results are listed in **Table 4**.

Sample/PC-organoclay (%)	T_1H (ms)
PC	100
PC-1	105
PC-3	90
PC-5	95

Table 3. T_1H values of PC films and PC-organoclay obtained through solution casting.

Sample /PC-TiO$_2$ (%)	T$_1$H (ms)
PC	100
PC-1	95
PC-3	98
PC-5	90

Table 4. T$_1$H measurements of PC and PC-TiO$_2$ films.

The addition of titanium dioxide caused a greater decrease in the spin-lattice relaxation time of the hydrogen nucleus, mainly at the 5% ratio, which can be related to good dispersion of this oxide in the polymer matrix.

3.3. Melt extrusion

3.3.1. Obtaining PC-organoclay systems by extrusion

The materials were processed in a twin-screw extruder. The polymer and the organoclay (PC/organoclay) were mixed together at 270°C. The relaxometry characterization was done by measurement of T$_1$H (**Table 5**).

In the melt intercalation at 270°C, the systems containing 3 and 5% organoclay showed formation of hybrid nanomaterials with some tendency of exfoliation. This system, when compared to the same system obtained by solution, presented higher intercalation.

3.3.2. Obtaining PC-TiO$_2$ systems by extrusion

The PC/TiO$_2$ systems were processed in a twin-screw extruder at 270°C. The relaxometry characterization was done by measuring T$_1$H. The results are reported in **Table 6**.

The addition of titanium dioxide did not interfere in the relaxation time of the polymer matrix, so the values are similar to those for PC. This behavior may indicate that the particles were not well dispersed in the polymer matrix, probably because the processing temperature was not high enough to promote good dispersion of the particles in the polymer matrix.

Sample/PC-organolay (%)	T$_1$H (ms)
PC	95
PC-1	95
PC-3	90
PC-5	90

Table 5. T$_1$H measurements of the PC-organoclay nanocomposites obtained by melt intercalation.

Sample/PC-TiO$_2$ (%)	T$_1$H (ms)
PC	95
PC-1	93
PC-3	95
PC-5	93

Table 6. T$_1$H measurements of the nanocomposites formed by PC/TiO$_2$ obtained by melt intercalation at 270°C.

4. Some applications of nanocomposites

Nanocomposite materials can be applied in many areas, such as manufacture of plastic articles, medical devices, drug delivery systems, dental materials, military materials, sensors, automotive parts, biodegradable materials and others. In the health area, the use of these materials has been gaining prominence in recent years. The application of nanotechnology enables earlier diagnosis and better treatment of some diseases. The principal application of this technology involves controlled drug release and restoration or regeneration of tissues (epithelial, bone and dental tissues) [19–22].

4.1. Dental restoration

The incorporation of nanoparticles in dental composites has led to important improvements in clinical practice. The application of nanoparticles in these materials can improve mechanical properties, surface smoothness and gloss and reduce the polymerization shrinkage [23–25].

Mechanically speaking, the incorporation of nanoparticles in dental composites can improve several properties, such as wear resistance, elastic modulus, flexural strength, diametral tensile strength and fracture toughness. The use of nanotechnology in polymeric materials includes the use of many nanofiller types and several studies have shown the ability of these fillers to increase the hardness and decrease the roughness of the final restoration.

The use of nanocomposites in dental restoration aims to mimic the natural composition of the tooth tissues. The human teeth are formed mainly by two highly mineralized tissues, dentin and enamel (**Figure 4**). These tissues have an inorganic portion composed mainly of natural calcium-based nanoparticles such as hydroxyapatites and calcosperites.

The enamel is formed mostly (96–99%) of hydroxyapatite nanocrystals. Dentin, on the other hand, has a more complex composition, presenting lower percentage of nanohydroxyapatite and calcospherites, which compose about 70% of the tissue. They are dispersed between the organic matrix, which is composed mainly of extracellular matrix and collagen fibrils.

The following example provides a better understanding of the role of nanoparticles in the properties of dental restorative materials.
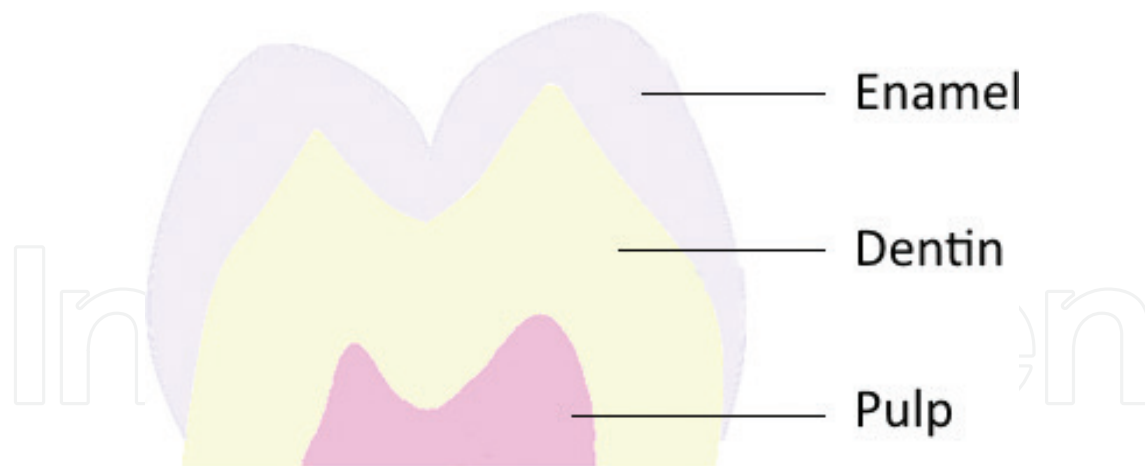
Figure 4. Dental tissue structure.

4.1.1. Dental resin with nanoparticles

To obtain these systems, a standardized resin matrix was used containing a mixture of bisphenol A glycidyl methacrylate (Bis-GMA), urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA) in the proportion 35:40:25wt%, associated with a camphorquinone as photoinitiator. As fillers were organo-modified clay and organo-modified silica. These nanoparticles presented diameters between 100 and 200 nm and thickness of 1 nm for the clay and a diameter of 16 nm for the silica.

In all groups, the proportion of nanofiller in the matrix was 2.5, 5 or 10% wt/wt to evaluate the influence of nanofiller in these systems. The resulting materials were compared with a resin with alumino-silicate microfillers (4 μm) [26–32]. The filler and matrix were mixed using a centrifugal mixing device. After obtaining these systems, they were evaluated by measuring the microhardness of each one.

In the Knoop hardness test (**Figure 5**), the best results were attained for the resins containing nanoparticles for all concentrations evaluated. Among the nanoparticle concentrations, the most promising results were observed in the groups containing 2.5% nanoclay and in groups containing 10% silica.

The addition of these fillers increases mechanical properties because they have a higher relative surface area than micro-particles. In this case, when the nanofiller presents good intermolecular interaction with the polymer matrix, it can be better dispersed and distributed, producing a larger polymer/nanofiller interfacial area and facilitating the transmission of forces between them.

The resin's properties need to mimic as closely as possible the physical and mechanical characteristics of dentin and enamel, so that the restorations can resist occlusal stresses. Materials containing nanoparticles are a promising alternative since the particles promote a greater durability and longevity of restorations.
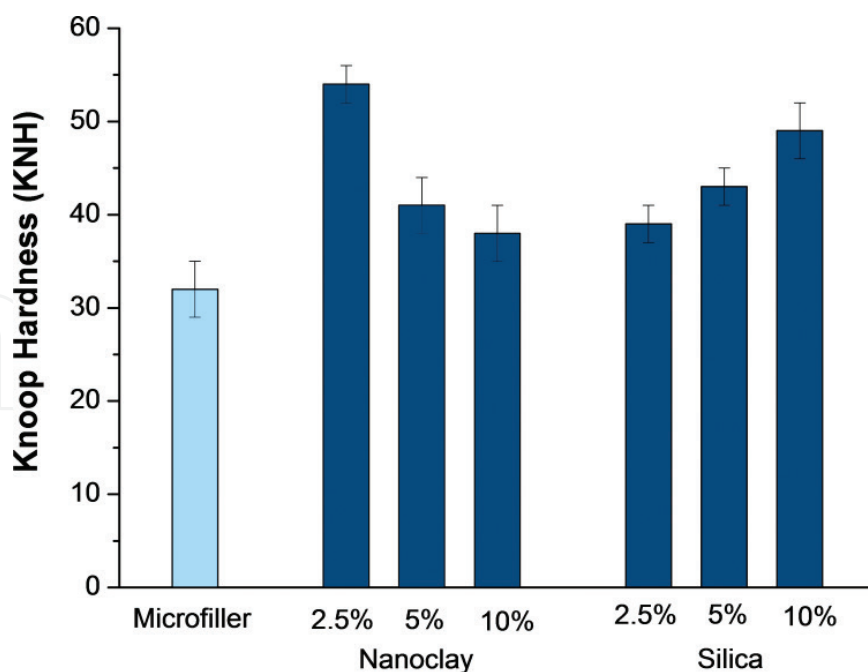
Figure 5. Knoop hardness results of dental resins with clay and silica nanoparticles.

4.2. Drug delivery systems

Polymeric nanoparticles or nanocomposites have promising features for drug delivery systems, including longer drug circulation time, better targeting to a specific tissue and reduced toxicity and adverse events, making disease treatment more tolerable to patients [19, 21].

In this context, nanocomposites using clay particles have drawn interest in recent years due to the significant changes promoted by small amounts of clay. These loads have several applications, including in polymer matrices aiming at improving mechanical properties, as also seen for dental restorations. To better understand the role of clay nanoparticles in drug delivery systems, the following example can be cited.

4.2.1. Chlorhexidine/nanoclay adhesive systems

To obtain these systems a standardized adhesive matrix composed of a dimethacrylate copolymer was used. The drug chlorhexidine diacetate was added to this material in the presence or absence of nanoclay particles. The nanofiller was used at 0.2% wt/wt in relation to the matrix, and the drug was tested in two different concentrations (0.5 and 1.0% wt/wt).

The *in vitro* drug release profiles of the systems containing chlorhexidine and doxycycline in the presence or absence of clay nanoparticles were analyzed and the results are shown in **Figure 6**.

The systems containing clay allowed prolonged drug release. This behavior occurs due to the lamellar conformation within the polymeric matrix. The clay layers interfere in the preferential diffusion pathways of the drug, creating more tortuous pathways, delaying the drug diffusion (**Figure 7**). Thus, after the release of the more external drug molecules, the more internal ones will be gradually released.
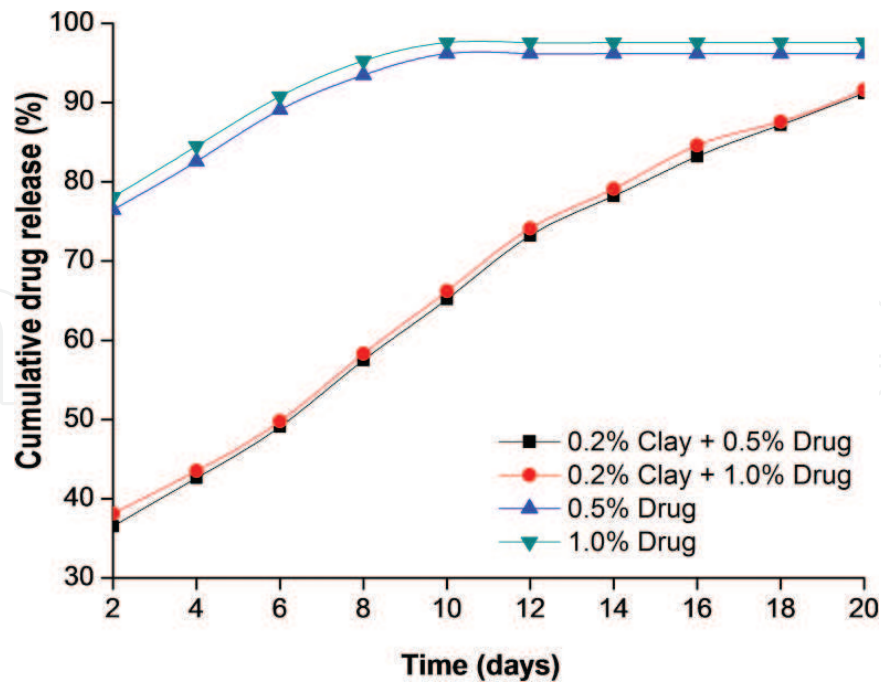
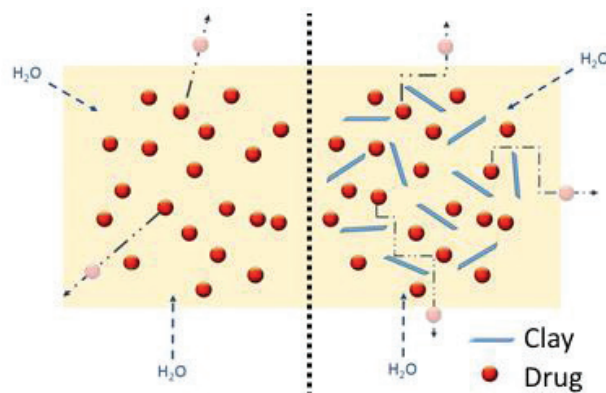**Figure 6.** Drug release of the systems containing clay.

Figure 7. Schematic representation of drug release in the absence and presence of clay lamellae.

5. Polymer nanocomposite degradation

The statement that "polymers do not degrade" is not correct. Polymers are a large group of macromolecules and this group can be split into some categories: natural polymers, biopolymers, synthetic polymers and elastomers. Biopolymers without treatment degrade faster than synthetic polymers. This characteristic makes them attractive as substitutes for many products. The main degradation agent is oxygen, but it is not alone. Light, stress and bio-organisms can have the same effect. Each kind of degradation has a specific agent or combination of agents. In this context, the following causes of degradation are highlighted:

(a) Photodegradation: This is the degradation process that happens when the polymer molecules absorb photons from sunlight [33–36].

(b) Oxy-degradation: This degradation is caused by the action of oxygen on the materials, as happens to metals. In practice, it is easy to confirm this degradation because it can promote the appearance of chromophore groups that change the material's color [33, 35].

(c) Photo-oxy-degradation: This degradation process is a combination of the two previous ones. In some polymers, after the light radiation creates free radicals the oxygen reacts with them, generating carbonyl groups [33, 35].

(d) Biodegradation: It is caused by the action of enzymes produced by microorganisms in materials susceptible at enzymatic rupture [37].

(e) Thermal degradation: High temperature gives molecules energy, which vibrates and deforms them, but it also can break the chain bonds, prompting the loss of properties. It depends on the chemical structure and molar mass [38].

(f) Chemical degradation: Each polymer has its own chemical structure and this structure is susceptible to chemical attack that can change or break the molecular structure due to the interaction with chemical compounds that are stronger than the chemical bond [39].

Nanoparticles have different properties. Their small size changes many properties of materials, even in small amounts. The interactions between matrix and nanoparticles can promote interesting results.

Polymer nanocomposites often present synergism between the polymer and nanoparticles, which can change how the matrix degrades. This characteristic can extend or shorten the life of the biopolymer matrix, enabling tailoring materials for specific uses. For instance, faster degradation reduces the pollution generated by these materials [39].

5.1. Clay polymer nanocomposites

Various types of clay are widely used because they are versatile and can cause chemical modification of the matrix by changing the exchangeable cations. The small size of clay nanoparticles promotes better compatibility between clay and polymer matrix. This helps to disperse the clay in the matrix, which can reduce photo-oxy-degradation by acting as a physical barrier to oxygen and reflecting UV light because of the particles' large aspect ratio. Also, they can reduce the effect of thermal and chemical degradation due to stronger interactions between clay and matrix.

5.2. Silver nanocomposites

Silver in nanoscale has bactericidal properties and provides UV light protection. This former happens because in nanoscale the asepsis of the oligodynamic effect is improved, killing bacteria. The latter effect is due to reflection of light, blocking photodegradation.

5.3. Silica nanocomposites

Silica is hydrophilic due to the presence of Si-OH. It can be used to speed up the degradation of synthetic polymer matrixes by microorganisms that need water. Alternatively, the surface can be modified to change it from hydrophilic to hydrophobic, thus improving the resistance of biopolymers against microorganisms.

5.4. Carbon nanotube nanocomposites

Carbon nanotubes can have a single wall (CNTs) or multiple walls (MWCNTs). These nanoparticles are commonly used to change polymers that are nonconductors to semi-electrical conductors. Also, CNTs improve the resistance of polymers to UV degradation, mechanical stress and chemical degradation as well as reducing thermal stress.

6. Final Comments

The focus of this chapter has been on providing a basic understanding of polymer nanocomposites, especially methods to obtain them, with some examples of each one, and comparing the results obtained by each method for the same polymer system and the effects of degradation in the presence of each nanoparticle cited. It also covers low-field NMR relaxometry, a characterization tool that can efficiently evaluate nanoparticles' dispersion and distribution in the polymer matrix, according to the preparation method.

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