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Ultrasound-Assisted Melt Extrusion of Polymer Nanocomposites

Carlos A. Ávila-Orta, Pablo González-Morones, Diana Agüero-Valdez, Alain González-Sánchez, Juan G. Martínez-Colunga, José M. Mata-Padilla and Víctor J. Cruz-Delgado

Abstract

A review of the latest developments in ultrasound-assisted melt extrusion of polymer nanocomposites is presented. In general, the application of ultrasound waves during melt extrusion of polymer in the presence of nanoparticles results in a more homogeneous dispersion of the nanoparticles in the polymer matrix. In spite of this, a lack of understanding in the field has hindered the development of this processing technique. Based on the analysis of literature on the field, key aspects are identified for a better understanding of the physical and chemical effects of ultrasound waves and the fabrication of polymer nanocomposites by means of melt extrusion.

Keywords: extrusion, ultrasound, melt, nanocomposites, cavitation

1. Introduction

The study of polymeric nanocomposites has grown during the last 10 years due to the remarkable properties that result from the combination of a continuous phase (polymer matrix) and a dispersed phase (nanoparticles), where at least one dimension of the dispersed phase is found in the scale of nanometric size (<100 nm). Such nanocomposites have attracted the attention of academic and industrial researchers due to their extraordinary electrical, thermal, chemical, and biological properties and potential applications in various sectors of the industry such as in the health sector, automotive industry, energy, construction, and food industry among
others [1, 2]. One of the most popular methods used to prepare such materials is melt extrusion, since it is a flexible and versatile process, which does not require the use of solvents and can be scaled up at industrial level.

However, even with all these advantages, the lack of homogeneous dispersion of nanoparticles in the polymer matrix is still a problem with melt extrusion. An alternative to improve the dispersion is the application of ultrasound waves during the polymer processing in the molten state, named ultrasound-assisted extrusion. The first report of the use of ultrasound coupled in extrusion was made by Isayev et al. for processing vulcanized elastomers devulcanization [3]. These authors reported that the ultrasound waves have the ability to cause an incision in the C-S and S-S bonds of the crosslinked rubber, causing the breaking of the reticulated network and thereby achieving the devulcanization of the rubber. Later, it was applied to the study of polymer mixtures in the molten state [4], and in the last decade, this technology has been used for the preparation of polymer nanocomposites. Although it has been proven that this technology improves the dispersion of nanoparticles and that it has a great potential for application, the fundamentals for applying this technology in melt extrusion process are still not well understood. For example, the effects observed by the application of ultrasound have been explained on the basis of acoustic cavitation, treating the molten polymer as a Newtonian system; however, polymer cannot be considered as Newtonian fluids. For this reason, a general overview of the basic principles of ultrasound, the development and use of this technology in the preparation of polymeric nanocomposites in the molten state, and the mechanisms that have been proposed so far for the understanding of the phenomenon that generates the dispersion of the nanoparticles in the polymer is described below.

2. Extrusion applied in the manufacture of polymeric nanocomposites

2.1. Polymers and nanoparticles

Thermoplastic polymers and nanoparticles are the main materials used to produce polymer nanocomposites by melt extrusion. Thermoplastic polymers include polyolefins, polyesters, and polyamides among other polymer families. On the other hand, the nanoparticles can be classified according to the number of dimensions in the nanometer range. Zero-dimensional (0D): it is defined as a particle that is measured within a nanoscale range, that is, less than 100 nm, among them are all the nanoparticles, for example ZnO, TiO$_2$, etc. One-dimensional (1D) has two dimensions in this scale, such as nanotubes and nanofiber. Finally, two-dimensional (2D) is referred to nanoparticles, where one dimension is in the nanometer scale, for example graphene and nanodisks [5].

2.2. Modification of nanoparticles

Unlike particles of micro size, in the nanoparticles, the interparticle forces such as Van der Waals and electrostatic forces, as well as the magnetic attraction, become stronger, which results in the nanoparticles forming agglomerates, which are difficult to disperse individually
and uniformly in the polymeric matrix; this implies obtaining compounds similar to conventional composites [6]. For this reason, various techniques in the modification of nanoparticles have been explored.

The modification of the surface, in general, decreases the surface energy of the nanoparticles, improving the affinity between the polymer matrix and the nanoparticles. Natural clays have a stratified structure bonded by strong covalent bonds [7], thus hindering its homogeneous dispersion in many polymers. Therefore, a surface modification is needed, and in this case, it is carried out through a cation exchange process, in which the sodium and calcium cations present in the inter-clay galleries are replaced by alkylammonium species, usually quaternary ammonium containing alkyl, phenyl, benzyl, and pyridyl groups [8]. In metal nanoparticles such as nanoparticles of silicon dioxide, titanium dioxide and aluminum oxide are surface modified with organosilane coupling agents [9], while in carbon-based nanoparticles, surface modification is carried out by covalent functionalization or not covalent. In CNT for example, functionalization of the covalent bond of functional entities can be performed at the ends of the tubes or on their side walls. This process can be carried out by reaction with some molecules with high chemical reactivity, such as fluorine [10]. A non-covalent functionalization is the $\pi-\pi$ interactions with aromatic molecules, such as pyrene, widely used to modify graphene [11].

Another approach to modify the surfaces of nanoparticles is based on grafting synthetic polymers on the surface of the substrate, which improves the chemical functionality and alters the topology of the surface of the materials [12]. The graft can be done in two ways: (1) by means of obtaining a polymer with a reactive terminal group and subsequently it is grafted to the surface of the nanomaterial, and (2) the graft is made from the growth of the polymer from an initiator [13].

In spite of all the available modifications for nanoparticles, sometimes they are not usually enough and it is necessary to look for alternative or previous methods to the extrusion process that helps us to de-agglomerate the nanoparticles and to reduce the size of these. One of these methods is mechanical milling by high-energy ball mill. The alteration of the solids by mechanical grinding gives rise not only to the fragmentation of the particles but also to structural changes, polymorphic transformations, variation of the properties of the surface, generation of defects, increases of reactivity, induction of chemical reactions, etc. [14]. Mechanical grinding has been applied in phyllosilicates, for example some studies have been carried out on kaolinite, pyrophyllite and some smectites, finding that grinding originates first a disordered phase of the mineral and later a more amorphous phase giving a structural destruction of the same, resulting in an exfoliation of the clay layers [15, 16]. It has also been successfully applied to carbon materials either to modify the morphology of carbon nanotubes or to introduce functional groups, which allow an improvement in dispersion and compatibility with the polymer matrix.

Another way is to carry out a premixing of the nanoparticles with the polymer using by calendaring. This method has been used in the exfoliation and dispersion of montmorillonite in a DEGBA epoxy resin [17], as well as in dispersion of multiple-wall carbon nanotubes in an epoxy resin [18]. In both cases, a better dispersion of the nanoparticles in the polymer matrix was observed.
Mechanical agitation is a common technique for the dispersion of nanoparticles in liquid systems; however, after a while, the nanoparticles tend to agglomerate. To improve the efficiency of dispersion and exfoliation, the ultrasound waves have been applied to stir particles, taking as the separation of individualized nanoparticles results. Ultrasonication is an effective method to disperse CNT in liquids that have a low viscosity, such as water, acetone, and ethanol. In this stage of application of ultrasound, some power factors must be taken care of, for example, because in the case of nanotubes, it has been seen that ultrasound waves can induce defects such as the formation of amorphous carbon in the CNT [19]; recommendations have been made as a sonication of the low power bath to preserve the length and structure of the CNT [20].

After applying these methods to modify the nanoparticles aiming to improve their dispersion in the polymer, it is necessary to consider the conditions of the extrusion process where these nanoparticles are incorporated, since it can be in different modalities or extrusion conditions in order to avoid reagglomerations or degradations of the polymer.

2.3. Manufacture of nanocomposites

In general, the most used mixing methods for the preparation of nanocomposites are in-situ polymerization, solution, and melt mixing. In the in-situ polymerization method, the nanoparticles are first dispersed in the liquid monomer (or a monomer solution), and from there, they are mixed to carry out the polymerization, which can be initiated by heat or by the diffusion of an initiator. In the solution method, the polymer is dissolved in a solvent, and the filler is dispersed in the same solution. The intercalated nanocomposite is obtained by removing the solvent by vaporization or precipitation [21]. Because both processes use a solvent, it is not practical at the industrial level. The melt mixing method takes advantage of the melt temperature of the polymer matrix, and in this way, it achieves the mixing with the nanoparticles. Within this method, one of the most striking is the melt extrusion process [22].

Melt extrusion is a continuous process that consists of passing a material in the molten state through a profile or given geometry. The preparation of a large variety of polymeric nanocomposites has been reported through this process from varying the polymer matrix to modifying the geometry and size of the nanoparticles to be used. It has been observed that the size and dispersion of the nanoparticles in the polymer are related to the improvement in the properties of the final nanocomposite. A great challenge in the preparation of polymeric nanocomposites is to achieve the homogeneous dispersion of the nanoparticles in the polymer matrix, knowing that a complete dispersion of the nanoparticles allows a greater matrix-nanoparticle interaction responsible for the improved properties in the final material [23].

2.3.1. Melt extrusion

In a broad definition, the extrusion process refers to any transformation operation in which a molten material is forced to traverse a nozzle to produce an article of constant cross section and in principle of indefinite length [24]. From the point of view of plastics, melt extrusion is clearly one of the most important processes of transformation, where the polymer is fed
in solid form; it is heated until reaching the molten state and leaves the extruder in the latest state. In this case, the extruder acts as a pump, providing the necessary pressure to pass the polymer through the nozzle.

An extruder must have a system for feeding the material, a system for melting-plasticizing it, a pumping and pressurizing system (which usually generates a mixing effect), and finally, a device for forming the molten material. Figure 1a shows a basic scheme of an extruder [25]. Depending on the pressure that is exerted along the barrel or extrusion barrel, three main zones can be identified as indicated in Figure 1b. The feeding zone is the closest to the feeding of the material, where it is gradually compacted at a certain speed. The transition zone is a zone of intermediate compression of the material where the fusion takes place, in addition to which the air that could be trapped in the same escapes by means of the feed hopper. Finally, there is the dosing zone, in which the molten material is homogenized and pressurized to exit the extruder by means of the forming nozzle [26].

2.3.2. Screw configuration

One of the most important parts in this process is the screw and the barrel, since they contribute to carry out the functions of transporting, heating, melting, and mixing the material. For this reason, the stability of the process and the quality of the final product depend to a great extent on the screw design. The screw consists of a long cylinder surrounded by a helical fillet (Figure 2). The most important parameters to design it are: the length (L), diameter (D), the angle of the propeller (θ), and the thread pitch (w). When only one screw is used, the machine is called single-screw extruder, while when two screws are used, the term double-screw or twin-screw extruder is used. The mixing is highly dependent on the number of screws and its configuration. In the case of twin-screw extruders, the screws can co-rotate or counter-rotate.
and have different degrees of interpenetration. In Figure 3, some possible variants are shown. The advantages of its use include a good mixing and degassing capacity, as well as good control of the residence time and its distribution. Some disadvantages of these extruders are their price superior to that of the single screw and the fact that their performance is difficult to predict.

It is important to mention that the selection of a twin-screw extruder to a single-screw extruder depends mainly on the efficient transport as a function of the friction of the material with the barrel and the extrusion screw. In a single screw-extruder, a high level of friction material/barrel and a low level in the screw provide a high carry per revolution. On the other hand, a poor carry per revolution will result in a low level of friction in the barrel and a high level in the screw. In addition, the amount of friction between the metal of the barrel or the screw and the performance of the extruder can change caused by a decrease in temperature. These troubles are minimized in a twin-screw extruder, where the interlock between the screws forms very close chambers, carrying the material forward [27].

2.3.3. Screw configuration modification

One aspect of great relevance is the definitive choice of the number and geometric design of the areas of the screw; this decision depends not only on the design of the nozzle and the expected flow rates but also on the melting characteristics of the polymer, its rheological behavior, and the speed of the screw. A simple screw, of three zones, is usually defined according to the number of turns of the propeller in the areas of feeding, compression, and dosing. An example of different screw configurations is shown in Figure 4.

2.3.4. Mixing lines

Most plastics need a previous stage of mixing before processing. Sometimes, it requires only extensive mixing, where the components of the formulation are mixed superficially and is made in fast mixers, and in other, intensive mixing of the different components of the formulation is necessary and is usually carried out in extruders. In some cases, both are necessary, extensive mixing prior to intensive. The use of twin-screw extruders is common in mixing lines. The configuration of the line is determined, among other things, by the type of additives to be combined in the extrusion. These lines usually have pelletizers at the extruder exit to obtain the material in pellet form. When additives or abrasive fillers have to be mixed with
the polymer, the polymer is usually added in the first feed hopper, and the filler is added once the plastic has melted, thereby reducing wear of the extruder caused by the filling. With large amounts of filler, the melt often has a large amount of air, steam, or gases, and so the extruder must have a vent zone (Figure 5).
The characteristics of the melt extrusion process both in the selection and configuration of the screw type, as well as the feeding of the materials, affect the pre-dispersion of the nanoparticles, since a homogeneous predispersion will improve the dispersion efficiency when using ultrasound.

3. Ultrasound-assisted extrusion applied to the manufacture of polymeric nanocomposites

In the last decade, the application of ultrasound waves for the preparation of polymer nanocomposites by melt extrusion has shown a growing interest. It seems that the scientific interest is ten times larger than the industrial interest, since only 3 patents have been registered in comparison to 36 published articles, as can be seen in Figure 6. This gives us a perspective of the relevance that this technology has had in recent years. Several studies report the preparation of polymer nanocomposites by means of ultrasound-assisted extrusion, resulting in the break nanoparticle agglomerates as nanoclays, as well as improvements in the dispersion of nanoparticles in a polyamide 6 [28]. Another study reported an improvement in both rheological and mechanical properties after the ultrasonic treatment, where it is also shown that this change in properties is attributed to the decrease in the size of the clay agglomerates in HDPE [29].

Other authors argue that the application of ultrasound to extrusion has to be carried out in stages to favor the dispersion of the nanoparticles, as in the case of carbon nanotubes (CNT), where it has been found that the dispersion of CNT can be favored when using two stages of processing. The first is the preparation of a masterbatch (concentrate method), which is then diluted in the polymer to increase the dispersion of CNT. It is generally accepted that the dispersion is improved due to the high voltage of cutting that acts on the agglomerates during the second stage [30]. The combination of the masterbatch technique with assisted ultrasound has been an important improvement for the dispersion of nanoparticles in polymeric matrices, mainly tested in polymer-CNT systems [31]; in turn, it has also been shown that ultrasound can favor the hybridization of polymer chains on the nanoparticles [32].
3.1. Fundamentals of ultrasound applied to the manufacture of nanocomposites

Before delving into the subject, it is necessary to mention that sound is a mechanical wave that needs a medium for its propagation. This medium can be liquid, solid, or gas. The propagation of the sound according to the medium can be transverse and longitudinal, and this will depend on the direction in which the energy travels. The frequency of audible sound for humans is between 20 Hz and 20 kHz. That inaudible sound with values of frequencies above 20 kHz is known as ultrasound. The ultrasound of low power or high frequency corresponds to the sound of low amplitude (higher frequency) and is related to the physical effect of the medium on the wave and is in a range of 2–10 MHz; these frequencies are widely used in the medical area for obtaining images and chemical analysis. On the other hand, ultrasound of high power (low frequency), between 20 and 100 kHz, is used for cleaning, plastic welding, as well as for the area of sonochemistry, which with the development of high-performance equipment power, can reach frequencies up to 2 MHz [33].

Chemical and physical effects of ultrasound in liquid systems are typically explained in terms of acoustic cavitation. The definition of cavitation is complicated. In some cases, acoustic cavitation is defined as an isothermal transition of the liquid-vapor phase limit in a fluid due to a decrease in pressure, as a response to the change below of the vapor pressure of the liquid, or when the temperature has risen above the boiling point [34]. In both cases, acoustic cavitation
is presented as a response to the decrease in pressure due to the propagation of an acoustic wave. In other words, during the expansion and compression characteristic of ultrasound waves, there is a formation, growth, and the implosive collapse of bubbles. But how is this bubble formed? The nucleus theory states that any liquid contains intrinsically tiny spaces (cavitation nuclei) full of gases, which undergo a change of pressure to quickly grow to cavities and then to bubbles. However, this principle has evolved, and it is accepted that a nucleus is needed that originates cavitation. The formation of this core can occur in two ways: for pure homogeneous liquid that does not contain impurities or gas, cavities will form due to the effect that the acoustic pressure will have on the liquid called homogeneous nucleation. In real systems or practical experiments, it is thought that a heterogeneous nucleation occurs, in which the neighboring liquid molecules are broken because the liquid contains “weak sites,” in the limits of the liquid and a solid or in the liquid-solid-gas interfaces, where cavitation can start more easily [35]. These cavitation cores generate bubbles that expand during the phase of rarefaction and collapse during the compression phase; stable and transient bubbles are formed [36]. Stable bubbles can remain oscillating during many cycles of acoustic pressure. On the other hand, transients generally exist for less than one cycle; during this cycle, they expand at least twice their original size and then collapse violently. It is said that the pressure and temperature inside the bubble increase to more than 1000 atm and 5000 K [37] during cavitation (Figure 7). The collapse of the bubble is a violent process which generates localized shock waves, which results in an effect on the liquid or solid.

3.2. Preparation of nanocomposites by means of ultrasound-assisted extrusion

The incorporation of ultrasound in melt processing methods requires, in its simplest form of a processing system or equipment, a sonotrode, and an ultrasonic wave generator. At present,

![Figure 7. Acoustic cavitation phenomenon in Newtonian fluid.](image)
double or single screw extruders with different arrangements in their mixing zones are used, at speeds ranging from 50 to 100 rpm, in order to improve the efficiency in the dispersion of nanoparticles, while temperature profiles vary according to the polymer-nanoparticle system. As for the treatment with ultrasound, a specially designed camera to contain a sonotrode is attached to the extruder, which in general according to the literature is usually made of titanium. This chamber has a controlled temperature and a nozzle to extract the molten nano-composite. The sonotrode is connected to an ultrasonic generator, which operates at frequency intervals that can range from 10 to 100 kHz and with powers that can reach 1000 W. The data obtained are usually collected by means of an oscilloscope. Figure 8 shows a system developed by Ávila-Orta et al. [38].

3.2.1. Technical characteristics of the design of the process of ultrasound-assisted extrusion

Ultrasound has been applied to molten polymers as a very efficient way to reduce the resistance of the shaping channels by decreasing the viscosity of the polymers. The results showed that the application of ultrasound disturbs the convergent flow of molten polymer in the entrance zone and changes the flow patterns, which leads to lower elastic stresses, increasing the movement of the molecular chains, so that the elastic recovery is faster. Guo et al. [39] demonstrated significant changes in the properties of polymeric materials by applying ultrasound during the extrusion process and applying ultrasonic oscillations in the direction parallel to the polymer melt flow (Figure 9). Scientists at the University of Akron have applied longitudinal vibrations in the direction perpendicular to the direction of flow using two sonotrodes symmetrically in the nozzle during the extrusion double screw of polymer nanocomposites containing carbon nanotubes and polypropylene clays (Isayev et al. [30]; Figure 10). In addition to dispersing nanocomposites, the application of ultrasound to the polymer has resulted in an increase in crystallinity, the reduction of structural defects, and the improvement of mechanical properties.

Ultrasound in the extrusion process has been used to improve the compatibility and dispersion of additives. The effects of ultrasound on polymers can be both physical and chemical.
Some physical changes induced by ultrasound in polymer systems are the dispersion of loads and other base components. Several systems have been developed, where good results of nanoparticle dispersion are obtained. Different ways of feeding and positions of the ultrasound along the zones of the extruder have been tested, aiming to find out the behavior of the nanoparticles in the matrix depending on the type of configuration. Some configurations of ultrasound-assisted extrusion of equipment that have been patented are

Figure 9. Schematic diagram of the ultrasonic irradiation extrusion system used by Guo et al. [39].

Figure 10. Schematic diagram of the ultrasonic irradiation extrusion system used by scientists at the University of Akron, Isayev et al. [30].
shown in Figure 11. It is important to mention that within the aspects that modify the dispersion of the nanoparticles is the intensity of the applied ultrasound, where it has been demonstrated that the power of the ultrasound is a function of the reduction in the size of the agglomerates of nanoparticles, which favors the dispersion. It has also been found that a good exfoliation and dispersion are improved at low extrusion rates in order to increase the time of the ultrasonic treatment [44]. However, high exposure times to ultrasonic vibrations produce a degradation of the polymeric material, that is, there is a breakdown of the polymer chains, as demonstrated by means of rheological studies.

3.2.2. Characteristics and final properties of NCPs produced by ultrasound-assisted extrusion

In the last two decades, the effect of ultrasound in the preparation of nanocomposites has been studied. In 2003, Isayev and Hong employed for the first time the ultrasonic vibration to prepare nanocomposites. This study reported that the application of ultrasound improves the dispersion and reduced size of silica agglomerate (0.3 μm). The viscosity of the ultrasonically treated mixtures was found to be higher than that of the silane-treated mixtures.

Table 1 summarizes information from publications involving the use of the ultrasonic treatment technology for the preparation of polymer nanocomposites. The information shows the polymer matrix studied, the nanoparticles, the focus of the study, and improved properties. It is evident that the most studied structures using ultrasound are clays and those based on carbon such as graphene and nanotubes.
Regarding the use of ultrasound in the preparation of nanocomposites with clay, improvements in degree of clay dispersion have been found. Kim and co-workers made use of the ultrasonic-assisted continuous extrusion process to the preparation of polypropylene (PP) and polystyrene (PS) nanocomposites with 3% loading of organophilic montmorillonite clay.

<table>
<thead>
<tr>
<th>Polymer nanocomposite</th>
<th>Focus of the study</th>
<th>Property improvement(s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon nanoparticles</td>
<td>MWCNT Effect of ultrasound on thermal, electrical, mechanical and rheological properties.</td>
<td>Improvement electrical and thermal conductivity, Young’s modulus. Storage modulus and complex viscosity generally increased.</td>
<td>[30, 45–54]</td>
</tr>
<tr>
<td>CNF</td>
<td>Effects of the variation of the ultrasonic amplitude and concentration on CNFs (morphology), rheology, electrical resistivity, abrasion and mechanical properties.</td>
<td>Improved dispersion, elongation at break, Young’s modulus and tensile strength. The abrasion resistance was improved at certain amplitudes at low CNT loadings only.</td>
<td>[55, 56]</td>
</tr>
<tr>
<td>GNP</td>
<td>Effects of the ultrasound vibration on exfoliation, and dispersion of GNP’s in the polymer matrix.</td>
<td>Increased the exfoliation and dispersion of GNPs on the polymer. Thermal and conductivity properties were increased.</td>
<td>[47]</td>
</tr>
<tr>
<td>Ceramic nanoparticles</td>
<td>Cloisite 20A Effects of ultrasound on clay dispersion, morphology, mechanical and rheological properties.</td>
<td>Improved clay dispersion compared with non-treated ones, intercalated-exfoliated structures was found. Young’s modulus enhanced and increase viscosity in most studies.</td>
<td>[57–60]</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>Effect of ultrasound on dispersion and mechanical properties of polymer matrix</td>
<td>Improves nanoclay dispersion, which results in an enhancement of the reinforcement of the fillers and decreases the viscosity of the composites during the process.</td>
<td>[61]</td>
</tr>
<tr>
<td>Nanosilica</td>
<td>Effects of ultrasound on the morphology, as well as the rheological and mechanical properties of the composites</td>
<td>Improve strength and elongation of the composites at break, ultrasound-induced homogeneous dispersion of nanoparticles in the polymeric matrix</td>
<td>[62]</td>
</tr>
<tr>
<td>Other nanoparticles</td>
<td>Flash aluminum flake pigments (FAFP) Effects of the ultrasound intensity, experimental temperature, filler content, and particle size on the composite viscosity</td>
<td>Composite viscosity decreased as the ultrasound intensity and the filler content decreased.</td>
<td>[63]</td>
</tr>
</tbody>
</table>

Table 1. Summary of the experimental results of some reviewed publications involving the application of extrusion assisted by ultrasound for preparation of polymer nanocomposites, last 10 years.
They found that the waves of ultrasound improve the compatibility between PP and PS and breakup of the clay agglomerates and as a result exfoliated the clay layers in the PP/PS matrix [64]. Similar observations were made for PP/clay nanocomposites. Two methods for the fabrication of polypropylene/clay nanocomposites are compared. In the first approach, a two-stage process was implemented. First, the nanocomposites were prepared using a co-rotating twin-screw extruder followed by a single-screw extruder, in which the ultrasound was implemented. In the second method, a single-stage process was used. In addition, two regimens of feeding were used in the process. In both processes, it was observed that the ultrasound generates a degradation of the polymer matrix and intercalation/exfoliation of clay; however, the single-stage process led to a minor polymer degradation [65]. Li et al. [28] prepared polyamide 6/montmorillonite nanocomposites by using a conventional and an ultrasonic extrusion technology. The results showed that the elongation at break and impact strength of the ultrasonicated nanocomposites increase due to the improved dispersion of montmorillonite and decreased size of spherulites [28]. Other works have focused on the preparation of clay nanocomposites with different polymer matrix as a HDPE and LLDPE. For example, Niknezhad and Isayev [59] applied ultrasound continuous method for the production of films polymer/clay nanocomposites. In this process, compounding, ultrasonic treatment, and film casting were combined in a single-step process. It has been found that the effect of the dispersion of the clay depends on the amplitude of ultrasound used, affecting the crystallinity and the mechanical properties of the material, as well as the permeability to gases [59]. On the other hand, the application of ultrasound irradiation and maleic anhydride (MA) addition, during the preparation of PP/Clay nanocomposites in a twin screw extruder, showed to have a very significant effect on the simultaneous grafting of MA onto the PP chains and in the exfoliation/dispersion of the clay. The tensile modulus increased with ultrasound intensity, and an opposite effect occurs with elongation, which decreases with the applied ultrasound [58].

As for carbon-based nanocomposites, polyetherimide (PEI) systems with 20% carbon nanofibers (CNF) have been studied. It was established that ultrasound with high power is effective in obtaining relatively more homogeneous dispersion with improved electrical and thermal conductivity in the CNF/PEI nanocomposites in comparison with extruded untreated ones. An increase in Young’s modulus was observed while retaining tensile strength up to 15% of CNF [54]. In another study, it was mentioned that the effect of ultrasound on the rheological, electrical, morphological, and mechanical properties of the Polyetherimide (PEI) matrix with multiple-wall carbon nanotubes (MWCNT) has been carried out from 1 to 10% by weight. In ultrasound-treated nanocomposites, an increase in viscosity and storage module was observed. As for the mechanical properties, the authors conclude that there is a relationship between the content of MWCNT and the application of ultrasound because the Young module and the resistance showed an increase by using 5 and 10% load. The authors also notice that working amplitudes are important factor to improve the dispersion. Rheological and electrical percolations were found between 1 and 2% in load weight of MWCNT. The observed effect is attributed to the fact that the ultrasound breaks the agglomerates of MWCNT improving its dispersion, which affects to a greater degree the rheology of the material than to the electrical conductivity [30]. Blanco et al. [53] mention that ultrasonic vibration has a significant effect on the conductivity of PA/MWCNT systems; in these nanocomposites, the percolation rate is reduced from 7 to 3 wt% when ultrasound is applied. This is attributed to a better
dispersion of nanotubes in the matrix, resulting in an increase of three orders of magnitude in the electrical resistivity for the system PA6/MWCNT at 7 wt%. These authors concluded that the application of ultrasound improves the processability of the material and that it is possible to reduce the percentage of nanotubes in the preparation of nanocomposites with conductive properties without affecting thermal properties [53]. Ávila-Orta et al. [51] used polypropylenes with different flow rates (MFI) and 10% multiwall carbon nanotubes for the preparation of nanocomposites. Four different fabrication methods based on melt extrusion were used. In the first method, melt extrusion fabrication without ultrasound assistance was used. In the second and third methods, an ultrasound probe attached to a hot chamber located at the exit of the die was used to subject the sample to fixed frequency and variable frequency, respectively. In the fourth method, the carbon nanotubes were treated in a fluidized air-bed with an ultrasound probe before being used in the fabrication of nanocomposites. It was found that the MFI decreases regardless of the method used in processing, the same is not the case with the other properties. For example, as to the size of agglomerates, the smallest value was found using PP of MFI = 2.5 using variable ultrasound frequency in processing; in this sample, it was found a lower surface/agglomerate ratio and a higher value of electrical charge (1040 V) [51]. A similar study showed that the electrical properties in nanocomposites of PP/MWCNT with different values of MFI of the polymer matrix depend on the methods used in the ultrasound-assisted extrusion because the ultrasound waves decrease the agglomerates of nanotubes producing conductive materials and static dissipators with a negative dielectric constant [66].

In summary, the application of ultrasound in the preparation of nanocomposites by extrusion generates an increase in some properties of great importance. However, the mechanisms by which ultrasound helps in the dispersion of nanoparticles is not known with precision, which is a significant aspect and would help to improve and create innovative methodologies aimed at the implementation of more specific nanocomposites.

3.3. Models of the mechanism of dispersion of NPs in ultrasound-assisted extrusion

The effect of ultrasound on fluids and Newtonian systems has been explained in terms of acoustic cavitation. This process, as mentioned above, involves at least three stages: nucleation, bubble growth, and the implosive collapse of the same, propitiating stable and transient acoustic cavitation events that are the cause of the effect of ultrasound. However, these physical or chemical effects will not be presented if ultrasound-led energy is less than the cavitation threshold [67]. In non-Newtonian fluids, the bubble in polymer solution implodes less violently compared to a Newtonian fluid such as water (Figure 12), which makes the impact of the liquid jet on the limit very small or even null. In particular, the dynamics of the collapse of bubbles near a solid boundary appears to be a critical problem in the dispersion of nanostructures in liquid systems, since the impact of the liquid jet on the surface of the agglomerates is considered mechanism dominant for the reduction of agglomerate size during acoustic cavitation [68].

If a solid is within the sample, the cavitation is given in a different way, due to the liquid–solid interface. An accepted explanation is that the cavitation that takes place near the solid
surface will generate microjets of fluid of high velocity, directed toward the solid surface. The impact of microjets of fluid on the solid surface causes localized erosion. In addition to this effect, we have the formation of shock waves, inducing effects such as breaking aggregates of particles [69].

Researchers have tried to explain the phenomenon of the dispersion of nanoparticles in polymeric matrices when using ultrasound in molten state. In this context, Zhong et al. argue that the propagation of the ultrasonic wave in a material generates waves of oscillatory pressure and induces the expansion and contraction of bubbles in the polymeric matrix that leads to a possible rupture of the agglomerates of nanoparticles, which would give place to a better dispersion. A small amount of bubbles usually dissolves or is trapped in the polymer that melts during extrusion [70]. In polymeric compounds, the particles are easily present in the form of porous agglomerates that introduce more gaps in the system. The existence of bubbles in the nanocomposites decreases the speed of the ultrasound and therefore the energy consumption. Based on experimental observation, a possible cavitation mechanism is suggested, depicted in Figure 13. The cavitation of bubbles in compounds can occur by internal and external cavitation mechanisms. The cavitation of the outer bubble could remove the particles from the primary agglomerates (Figure 13a), while the cavitation of the inner bubble would break the agglomerates from the inside (Figure 13b). One or both of these mechanisms would lead to better dispersion seen after ultrasonic treatment [71].

Espinoza-González proposed [72] a mechanism based on mechanochemistry to explain the physical and chemical effects of ultrasound in polymer matrices, as well as for the dispersion mechanism of nanostructures. This mechanochemical mechanism is mainly based on the deformation or stress experienced by the chemical bonds during the vibration movement. The generated vibration movement causes the appearance of different fatigue points along the polymer chain called nodes, in which the greatest deformation occurs between the links of the chain, reducing the energy of link dissociation leading to the activation of multiple reaction mechanisms, degradation, or chain extension.
Ultrasound-assisted extrusion process turns out to be a very promising technology and that in the last 10 years has shown great advances in its application to the elaboration of polymeric nano-composites. However, the mechanism to achieve the deagglomeration of nanoparticles and their dispersion in the polymer remains unknown. The phenomenon of acoustic cavitation is mainly proposed for the explanation of bubble dynamics, but it is possible to find in the literature and as mentioned above that the strict notion of cavitation is an isothermal transition of the liquid–vapor phase limit in a fluid of a single component, due to a decrease in pressure [34, 35, 73]. In other words, the cohesion between the fluid particles is overcome by an externally applied stress, which causes the homogeneous nucleation of the vapor. Based on this argument and answering the initial question of the text on the phenomenon by which the dispersion of nanoparticles in polymeric systems results, the phenomenon of acoustic cavitation is questionable, since it is not enough to be able to explain the dispersion of nanoparticles during the ultrasound-assisted extrusion process to produce nanocomposites, since there is no phase change and also due to the viscoelastic characteristics of the polymer matrices that imply higher cutting efforts, which would hinder the formation of bubbles. However, it has been proven that in polymeric solutions, there is poor bubble formation due to cavitation effects [74]. On the other hand, there is also the idea that ultrasound causes vibrational effects on the polymer related to relaxation times at the chain level [75], which could help explain that the effects of friction in the polymer are the main causes of the dispersion of nanoparticles in the formation of nanocomposites.

A number of researches are still necessary to understand the effects of the different parameters (power, amplitude, and working frequencies) of the ultrasound waves in the preparation of nanocomposites, as well as the mechanism of action. To understand the nature of a
system as robust as ultrasound-assisted extrusion, it is necessary to simplify the system, so that the dispersion phenomenon can be analyzed from the simplest possible perspective. For example, studies can be carried out in batch systems of polymer melts and nanoparticles.

4. Conclusions

In the last decade, the use of the ultrasonic assisted extrusion process has been used in the preparation of polymeric nanocomposites. This process has shown improvements in the dispersion of nanoparticles in the polymer matrix, which has led academics to make improvements in the design to achieve a greater effect on the properties of the final compound. Although the technique of ultrasound is known, it has not been possible to clearly explain the mechanisms of its action in polymer-nanoparticle systems, where despite the efforts made to achieve an adequate understanding of how the dispersion of nanoparticles occurs, it is still insufficient for the polymer nanocomposite theory to explain this phenomenon, and this limits the application of ultrasound in the manufacture of nanocomposites with specific properties. However, the large number of satisfactory results obtained in scientific articles on the novel properties and innovations that are made in patents on equipment and processing of nanocomposites provides a broad perspective of the evolution of this technology and its potential applications.

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Conflict of interest

The authors declare no conflict of interest.

Author details

Carlos A. Ávila-Orta¹*, Pablo González-Morones¹, Diana Agüero-Valdez¹, Alain González-Sánchez¹, Juan G. Martínez-Colunga¹, José M. Mata-Padilla¹ and Víctor J. Cruz-Delgado²

*Address all correspondence to: carlos.avila@ciqa.edu.mx

1 Centro de Investigación en Química Aplicada (CIQA), Saltillo, Coahuila, México
2 CONACYT—Unidad de Materiales, Centro de Investigación Científica de Yucatán (CICY), Mérida, Yucatán, México
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