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Strategies for the preparation of polymer composites with complex alignment of the dispersed phase

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ABSTRACT
The design and production of anisotropic composites and nanocomposites has become increasingly relevant in materials science and engineering because they provide an opportunity of enhancing and adapting the properties of a material for specialized applications. This article reviews the strategies that have been developed to achieve anisotropy based on the position and orientation of the dispersed phase in polymer composites including polymer nanocomposites. Flow and electric field-driven alignment methodologies are briefly described, which is followed by a focus on magnetically oriented composites. The use of magnetic fields for this purpose has been of particular interest in recent years due to its ease of use and the variety of materials on which this method can be applied. Strong magnetic fields are required to align diamagnetic fillers. However, the modification of particles with low magnetic susceptibilities with magnetic nanoparticles (i.e. iron oxide nanoparticles) has been proven to be a successful approach to broaden the capabilities of magnetic alignment in polymer composites. The development of filler manipulation techniques opens the possibility to mimic complex biological structures that promise to improve the mechanical properties of bioinspired composites and even achieve advanced functionalities in self-shaping materials for example.

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1. Introduction
With the increasing need of better and more specialized materials, composites have emerged as a promising choice to fulfill those needs. In particular, polymer composites have become relevant mainly due to their high strength yet low density, as well as the fact that they display properties that can be tuned for a range of applications from automotive or aerospace industries to biomedical or environmental sectors [1].

Polymer composites refer to a phase acting as filler or reinforcement dispersed within a polymer matrix. Polymers have received special attention owing to their ease of processing, lightweight and low cost, as well as their wide variety of choices and hence various properties (e.g. high ductility for semi-crystalline thermoplastics and excellent chemical resistance for thermosets) [2]. The addition of fillers to a polymer matrix can not only improve its overall properties but in some cases provide...
added-value functionalities such as electrical conductivity [3].

The properties displayed by a polymer composite rely on six factors: (i) the intrinsic properties of the constituent phases, namely the polymer matrix and the filler, (ii) the volume fraction of filler, (iii) the shape of filler, (iv) the orientation of filler, (v) the distribution of filler, and (vi) the interface between the matrix and the filler [4]. Reinforcing particles can appear in different shapes and dimensions in polymer composites, from discrete spheres or clusters [5], to fibers [6], tubes [7], sheets [8,9], or aggregates of them. This variety of shapes and sizes makes it possible to not only tailor the overall properties of a composite but to create materials with anisotropic properties.

Polymer composites containing spherical particles are considered isotropic, while fibers, rods or sheets can form either iso- or anisotropic composites depending on their orientation, which is relevant to the processing method and conditions [10]. Isotropic composites display the same properties at all directions while anisotropic composites show varying properties along different axes [11]. Anisotropic composites are of significance due to the increasing need of materials with controlled and superior thermal [12], electrical [13], mechanical [14], optical [15], barrier [16], or even self-shaping properties [17] for a wide range of applications from aerospace engineering to medicine [3].

Producing anisotropic materials implies controlling the spatial distribution and orientation of the fillers, which is one of the current challenges in micro and nanoscale materials science and engineering [11]. Processes such as extrusion [18], fiber spinning [19–21], self-assembly via solvent-particle or particle-particle interactions [22], layer-by-layer assembly via dipping or spraying [23,24], or the use of external stimuli such as electric [25] or magnetic [26] field, have been used to develop anisotropic polymer composites.

2. Alignment strategies

In this section, the alignment of reinforcing elements in polymer composites by shear forces, extensional flows, and electric and magnetic fields will be described. These strategies will be explored through relevant examples and the mechanisms behind the alignment. The classic layer-by-layer assembly and self-assembly strategies have been widely reviewed before [27–29] and so will not be further explored herein.

2.1. Flow-assisted alignment of particles in polymer composites

Shear and extensional flows are the dominating forces when referring to orientation of fillers in composites under flow. It has been demonstrated that anisotropic particles such as short fibers, rods, and nanotubes can be aligned through extrusion and injection molding [11,18] which are shear dominant processes, and through fiber spinning or post-elongation processes in which extensional flow is observed [20,21,30,31]. In this section, both approaches will be reviewed.

Carbon nanotubes (CNTs) have attracted the attention of researchers in many fields because of their high strength, high aspect ratio, and electrical conductivity [11]. Achieving alignment has become important to enhance the load-carrying efficiency and electrical conductivity of their polymer composites, especially in the direction in which they are aligned [32,33].

Sulong and Park [18] studied the influence of shear rate on CNT alignment in a polymer matrix through extrusion. Polyethylene (PE)/multi-walled CNT (MWCNT) composites were produced through extrusion using a self-build system with varying shear rates. It was found that higher shear rates produced a higher degree of alignment on the extrusion direction. PE nanocomposites containing 1 wt% unidirectional aligned CNTs displayed increased Young’s modulus, tensile strength and elongation at break by 27%, 40%, and 39%, respectively, in comparison to randomly dispersed composites. These improvements are related to the axial load-carrying efficiency of CNTs (~1 TPa Young’s modulus), which is transferred from the polymer matrix during the tensile loading [18,34].

An interesting research on the use of helical flow to create a helical fibrous structure in a polymer matrix during extrusion was presented by Zhang et al. [35]. During extrusion, fibers align along the axis of extrusion. This represents a disadvantage when producing tubular structures as the alignment decreases the resistance to hoop load [36]. Hence, there is a need to develop materials that enhance hoop properties and therefore kink resistance. In the work of Zhang et al. [35], polypropylene (PP) tubes containing either TiO₂ or TiO₂-Ag fibers arranged in a helical architecture were produced by mandrel rotation in addition to the longitudinal extrusion (Figure 1). Their self-designed equipment allowed the production of composite tubes of 3 mm diameter and 0.5 mm thickness that displayed superior kink-resistance to their conventionally extruded counterparts and antibacterial activity, which makes the material useful for medical devices [35].
Hoop strength for the neat PP tubes increased from 16 to 19 MPa using this rotational extrusion approach, and from 18.1 to 22.4 MPa for the PP composite tube with 5 wt% TiO₂. It was also observed that axial strength exhibited an opposite behavior with a decrease from 26.5 MPa for conventionally extruded PP composite tube to 24.7 MPa for PP composite tube produced through rotational extrusion. A similar decrease was observed in PP-TiO₂ composites, where the axial strength of rotation-extruded samples was 25.9 MPa, similar to the value of conventionally extruded neat polymer. Composite tubes with silver-modified TiO₂ fibers displayed almost identical mechanical properties to the cases with unmodified fibers, whilst also showing enhanced antibacterial properties against S. aureus and E. coli. In general, kink-resistance, antibacterial invasion and colonization prevention are desirable properties for medical applications [35].

Another research in relation to extrusion alignment is multilayer coextrusion, a process where two or more extruders inject different polymers into a feed block and then into a series of multiplier dies, where the polymer melt is vertically sliced, stretched and recombined one on top of the other [37,38]. Gao et al. [37] adopted this process to produce poly(lactic acid) (PLA)/PLA-graphene composites made up of up to 128 alternating layers of pristine polymer and aligned polymer-graphene nanocomposite. Li et al. [38] produced alternating layers of poly(methyl methacrylate) (PMMA)/polystyrene (PS)-graphene composite and PMMA/PMMA-graphene composite respectively, each of which consisted of 2049 layers with a thickness of 290 nm for the former and 35 nm for the latter. Reinforcement in the extrusion flow direction for both systems was confirmed through quasi-static tensile tests and dynamic mechanical analysis. These showed a ratio of approximately 2 for the tensile Young's modulus for the PMMA/PMMA 0.2 wt% graphene composite to the value of the neat polymer. PMMA/PS-graphene composites showed similar results, however, these materials tended to weaken over time due to the weak interaction between matrix and filler [38].

However, the use of shear to achieve alignment has limitations; not all polymers are suitable for shear processing. In general, the alignment is defined by the viscosity of the matrix, the filler shape and concentration, screw design, screw speed, the shape of the die in extrusion and/or the shape of the mold in injection molding [11,18,39–41]. In extrusion or injection molding processes, the shear forces run parallel to the die or mold walls, so these processes are limited to thin components as alignment decreases towards the core of the specimen. Changes in rheology during extrusion also generate a drag force that opposes alignment [18]. Moreover, complex geometries can generate streamlines that result in undesired alignment (i.e. presence of Jeffrey’s orbits) [42]. It has been proven difficult to create complex architectures that show controlled multidirectional alignment during shear-driven processes [39].

Extensional flow can also control the alignment of particles in polymer composites. This type of flow behavior is fundamental in processing techniques such as blow molding and thermoforming. It is also the dominant phenomenon in fiber spinning processes including electrospinning [20,21,43]. With electrospinning, it is possible to produce polymer fibers with thickness from tens of nanometers to several microns and has the potential of aligning embedded particles in direction of the flow. Orientation of the filler in the composite fibers depends on its shape and dispersion. Carbon nanotubes and graphene oxide sheets have been widely studied in electro-spun systems, some of which have been previously reviewed [20,21].

Apart from shear and extensional flows during processing, post-elongation has also been introduced to improve the alignment of nanoparticles in polymer composites. Okamoto et al. [30] described the formation of a house of cards structure in polypropylene/clay nanocomposites through an extrusion process followed by elongation at a constant strain rate on an elongational rheometer immediately after annealing above glass transition temperature. Elongated specimens were recovered, and transmission electron microscopy showed alignment of the

Figure 1. Scanning electron micrographs of (a) conventional extruded PP-TiO₂ composites and (b) helically extruded PP-TiO₂ composites. (c) Schematic representation of the flow pattern in pink and fiber alignment in black during rotation extrusion. Reproduced with permission from [35]. Copyright (2018) Elsevier.
dispersed clay sheets perpendicular to the elongation direction. This unusual orientation was presumably related to the strong strain-induced hardening behavior of the material under elongational flow [30].

Park et al. [31] later also studied the orientation that clay layers adopt under uniaxial elongational flow in different polymer/clay composites by elongational rheometry. The composites investigated were polypropylene (PP)/maleic anhydride modified PP (MAPP)/Cloisite20A (C20A), MAPP/C20A, polystyrene (PS)/C20A, MAPP/Cloisite Naþ (CNa), and PP/MAPP/CNa, the first two being exfoliated systems, the third intercalated, and the last two microcomposites. 2D small-angle X-ray scattering showed that exfoliated composites had clay sheets aligned parallel to the elongation direction, the intercalated also had orientation but at a smaller degree and micro-composites did not show orientation. This can be explained through the fact that this postelongation produced a strong streamline that forces particles with a high aspect ratio to align. In the case of MAPP/CNa and PP/MAPP/CNa materials, the lack of alignment is caused by the incompatibility between clay and polymer [31].

2.2. Electric field-assisted alignment of particles in a dielectric fluid (i.e. liquid resin)

Since the end of the 1990s, the alignment of single-wall carbon nanotubes (SWCNTs) under electric and magnetic fields was reported for dilute solutions [44]. It was not until one decade ago that Park et al. [45] reported the synthesis of urethane dimethacrylate/1,6-hexanediol dimethacrylate/SWCNT nanocomposites with 0.03 wt% aligned SWCNTs (Figure 2). The uniform orientation of the nanoparticles was achieved through the application of an AC electric field before and during photopolymerization of the acrylate monomers. At a frequency of 1 Hz, the electrical conductivities of neat epoxy and randomly oriented composites were reported to be $1.4 \times 10^{-13}$ and $3.3 \times 10^{-13}$ S cm$^{-1}$, respectively, in the same work [45]. Conductivities up to $10^{-6}$ S cm$^{-1}$ can be achieved by composites prepared under 200 V$_{p-p}$ fields and 100 Hz. Interestingly, the conductivity perpendicular to the direction of alignment also increased, but only by two orders of magnitude. The dielectric constant of pristine epoxy was 5.2 S cm$^{-1}$ and that of unaligned composites at 1 Hz was 25.2 S cm$^{-1}$. For 150 V$_{p-p}$ aligned composites, the dielectric constant reached 1500 at 1 Hz. This research illustrates that the electrical conductivity and dielectric constant can be tuned by controlling the alignment of SWCNTs through varying the strength and frequency of the applied electric field [45].

As described in the previous section, alignment of CNTs in composites had been achieved through shear forces during extrusion [18,42]. However, shear alignment resulted in a low statistical probability of contacts among adjacent nanotubes caused by their excluded volume as predicted by Balberg, Binenbaum and Wagner [46], limiting the electrical conductivity of this kind of composites. The use of an electric field overcomes this obstacle due to the interaction between induced dipoles [45].

Electric field-assisted alignment has been focused on the production of 2D architectures. Recently, an interesting research was produced by Holmes and Riddick [47] who created a 3D composite using aluminum microparticles embedded in an ultraviolet curable acrylate polymer resin through the Field-Aided Laminar Composite (FALCom) process (Figure 3). Following a layer-by-layer technique, the resulting specimen displayed a complex shape and a multidirectional orientation of the filler. Microparticles arranged themselves into chain-like structures along the direction of the applied electric field. This kind of advanced manufacturing will enable the production of novel, tunable structures based on hierarchical design and synthesis principles.

This alignment strategy is useful for systems formed by a dielectric fluid and conductive and
dielectric fillers, such as metal, ceramic, glass, and carbon particles [11,25,47]. The physics behind the alignment mechanism has been studied since. When particles within a liquid are subjected to an electric field, they become polarized with opposing charges at opposing ends. If the particles possess shape anisotropy, the interaction of this dipole with the electric field generates a torque that attempts to align said dipole parallel to the field. The efficiency of such alignment depends on the shape anisotropy of the particles (aspect ratio), as well as their dielectric properties, electrical conductivity and concentration [11,25,47,48].

2.3. Magnetic field-assisted alignment for particles

Even if shear-driven and electrical alignment have been explored as a possibility to induce the distribution and position of fillers in polymeric composites, magnetic fields have proven to be the top alternative to achieve it. The advantages of magnetic control have been well established by Rikken et al. [49]. First, magnetic fields are non-invasive or contactless so the structural integrity of the specimens is preserved throughout the process. Secondly, the use of homogeneous, inhomogeneous, rotating, or oscillating magnetic fields allows a variety of responses, hence a variety of structures either constant across the sample or with progressive variations. Thirdly, response can be further tailored through the type of magnetism of the materials, which depends on the magnetic susceptibility of the filler (i.e. diamagnetic, ferromagnetic). Fourthly, magnetic fields are not as sensitive to surface changes and pH as electric fields and do not produce chemical changes, which allows its application on a wider variety of systems [49].

The use of magnetic fields to control the position of filler particles in composites has been studied through different approaches and at different degrees. From unidimensional fillers, such as micro- and nano-spherical particles [50–54], to fibers [55], nanotubes and microsheets [11], this section attempts to provide a relatively comprehensive analysis of the existing research on this matter.

2.3.1. Magnetically aligned composites with simple 2D structures

Composites containing magnetic particles have been studied for their applications in micro- and nanoelectronics and medicine. In this regard, anisotropic polymer nanocomposites were produced by inducing the alignment of Fe3O4@TiO2 core-shell nanoparticles within an epoxy resin DER 321 [50]. This was achieved through the application of an inhomogeneous magnetic field generated by a strong permanent magnet (10 kOe) during the curing process. The resulting nanocomposites showed micro-chains formed by the nanoparticles, aligned in direction of the magnetic flux lines as observed in Figure 4 [50]. The closer to the magnet, the longer the chains [50].

The effect of dipolar interaction aligns the magnetic particles in chains, which then behave as magnetic entities. This provides distinctive magnetization depending on the direction of the applied field [50]. The magnetic properties of the resulting ordered composites were measured parallel and perpendicular to the chains. Room temperature hysteresis loops showed magnetic anisotropy. It was also found that the coercive field $H_c$ decreases with increasing temperature and it is slightly higher when the field is applied parallel to the chains [50].

Similar studies were also reported by Martin et al. [51], Fang et al. [52], Fragouli et al. [53], and Krommenhoek and Tracy [54] for epoxy resin Epon 828/carbonyl iron (150 G), acrylic resin/Fe3O4 (281-1030 Oe), poly(ethylmethacrylate-co-methacrylate)/Fe2O3-Fe3O4 (160 mT) and poly(lauryl methacrylate)-ethylene glycol dimethacrylate/Fe3O4 (10 kOe) composites, respectively. In such studies, a magnetic anisotropic response was observed when applying a magnetic field either along the chains or perpendicular to them.

To further increase the function of magnetically oriented composites (i.e. enhanced mechanical, thermal or electric properties), the use of electrically
Conductive carbon-based fillers has been documented [55, 56]. These studies consider two main fillers: carbon fibers (CFs) and carbon nanotubes. Their graphite-like structure produces a high diamagnetic anisotropy, which facilitates their magnetic alignment [11].

The magnetic alignment of CFs and other fibrous materials in suspension has been reported since 1972 [57]. Recently, their incorporation into polymer composites has been described. In 2010, Kimura, Umehara and Kimura [58] published a research where they produced agarose-CF composites in which the fibers were aligned using a Neodymium magnet (0.75T). Such magnet produced a field with radial distribution which oriented CFs at different angles as shown in Figure 5 [58].

In this study, it was found that the material could deform when subjected to a homogeneous magnetic field up to 8 T [58]. CFs possess a large diamagnetic anisotropy that is capable of producing a strong torque when exposed to a magnetic field. The torque of CFs towards the direction of the applied magnetic field produces the curvature of the composite film. The Young’s modulus was determined by measuring the deformation caused by the sample’s own weight when placed horizontally between two supports. It was determined that the modulus varied between 40 and 100 kPa depending on the distance between the supports. This kind of magnetostrictive material is of interest for magnetically driven actuation devices [58].

Later in 2016, Stainer, Ciamberla and Rahatekar [59] synthesized the polydimethylsiloxane-NiCF composites shown in Figure 6 where the fibers were aligned parallel to the direction of the magnetic field produced by four Neodymium N52 magnets (<200

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**Figure 4.** (a) Scanning electron microscopy (SEM) cross-sectional images of epoxy/Fe$_3$O$_4$@TiO$_2$ isotropic composites. (b) Synthesis diagram for anisotropic samples. (c, d) SEM cross-sectional images of epoxy/Fe$_3$O$_4$@TiO$_2$ anisotropic composites. Reproduced with permission from [50]. Copyright (2016) Elsevier.

**Figure 5.** (a) Schematic representations of the synthesis and structure of agarose-CF composites. (b) Photographs showing the deformation of agarose-CF composites under different magnetic fields. Reproduced with permission from [58]. Copyright (2010) Elsevier.
mT). The purpose of this study was to enhance the mechanical properties of an elastomer and to study the actuation capabilities of the composites. The tensile modulus varied according to the angle between the long axis of the fibers and the tensile axis. At an angle of 90°, the modulus was about 0.8 MPa while at 0°, it increased to 2.2 MPa. Also dependent of the angle at which fibers are oriented is the actuation behavior. At 0° a bending response is observed and it evolves towards a twisting deformation at 90° as shown in Figure 6 [59]. A follow-on research, including a mathematical description of the motion of NiCF in a viscous fluid, was published by the same group [60].

However, the carbon fibers used for these studies had a diameter of 10 μm and a length of 100 μm. The effects of introducing nano- instead of microfil-lers have been well described [61–63]. Their higher specific surface area offers a greater interfacial area, thus allowing a more significant enhancement of the mechanical and other properties (i.e. electrical, as in carbon-based fillers) at much lower loadings [63].

Polymer-CNT composites aligned by a magnetic field were first prepared in 2002 by Kimura et al. [64]. In this study, MWCNTs were synthesized by chemical vapor deposition and mixed with an unsaturated polyester resin and a styrene monomer. The mixture was then copolymerized in the presence of a strong magnetic field (10 T) produced by a superconducting magnet. It was found that for 1 and 2 wt% MWCNTs the conductivity measured parallel to the CNT alignment axis was higher than the one measured perpendicularly, by one order of magnitude. Dynamic mechanical analysis showed that the storage modulus measured parallel to the alignment was around 5 GPa while 4.5 GPa perpendicularly. These CNT composites have been considered for polymer-based optical devices (i.e. LEDs, photodiodes) [64].

From then, several publications arose reporting the alignment of CNTs in different polymer matrices. Thixotropic epoxy/SWCNT nanocomposites were synthesized (25 T) and their morphology and crystallinity studied [65]. SWCNTs or MWCNTs were embedded into Aeropoxy or Caldofix epoxies and cured under a magnetic field (0-25 T) and their thermal and mechanical properties analyzed [66]. Polyethylene terephthalate (PET)-SWCNT nanocomposites were produced (3 and 9.4 T) and characterized in terms of morphology and electrical conductivity [67]. EPON 815 C epoxy resin-MWCNT nanocomposites were magnetically processed (9.4 T) and their morphology, mechanical and thermal properties investigated [68]. Based on these examples, it is evident that a strong magnetic field is required to align diamagnetic or paramagnetic materials. The need of magnetic fields of several Teslas limits the application of this technique because of the need of specialized equipment. Therefore, it has become a popular practice to functionalize materials that exhibit low magnetic susceptibilities with superparamagnetic nanoparticles (i.e. iron oxide-based species) [13,55,56].

Kim et al. [69] synthesized Aeropoxy resin/MWCNT-γ-Fe₂O₃ nanocomposites with 0.1–3.0 wt% filler by first tethering γ-Fe₂O₃ nanoparticles onto the surface of MWCNTs through a sol-gel process, then embedding them into the resin and finally curing them under a magnetic field (0.3 T). Conductivity parallel and perpendicular to the CNT alignment was measured at 0.1 Hz. For 0.1 wt% load, conductivity was $6.0 \times 10^{-11} \text{ S m}^{-1}$ on both directions; this corresponds to a dielectric behavior due to the low filler content. Parallel and perpendicular conductivities for 1.0 wt% loadings were $4.1 \times 10^{-7} \text{ S m}^{-1}$ and $1.0 \times 10^{-7} \text{ S m}^{-1}$, and for 3 wt% $1.0 \times 10^{-6} \text{ S m}^{-1}$ and $8.5 \times 10^{-7} \text{ S m}^{-1}$, respectively. It is important to notice that conductivities for 3.0 wt% samples are quite similar on both directions, presumably because the viscosity of the composite solution increases with the loading of the nanoparticles hence hindering their mobility for alignment. Besides, iron oxide possesses high resistivity [69]. Figure 7 shows MWCNT-γ-Fe₂O₃ hybrids and their behavior under a magnetic field, confirming alignment occurs at relatively low field strengths [69].
Similarly, Fe$_3$O$_4$@CNF were prepared by co-precipitation method and aligned in an epoxy resin under a magnetic field (20–50 mT) produced by a pair of permanent magnets at varying distances. Their morphology, electrical conductivity and mechanical properties were obtained [55]. In another study [70], amino-functionalized MWCNTs were decorated with Fe$_3$O$_4$ nanoparticles coated with oleic acid and then aligned in a bisphenol A diglycidyl ether-based epoxy resin (0.3 T). Their morphology, electrical conductivity, thermal, and mechanical properties were determined. For these composites, in addition to similar electrical and mechanical behaviors to the ones reported in other polymer-CNT systems, a decrease in the glass transition temperature was found. For neat epoxy, $T_g$ was found to be 181.4$^\circ$C while for composites containing 0.25 wt% of unoriented and aligned MWCNT-Fe$_3$O$_4$ it was 170.0$^\circ$ and 168.8$^\circ$, respectively. This decrease can be explained through a stoichiometric decompensation arising from the absorption of monomers on the nanotubes or the acid groups of magnetite that can react with them [70].

Although fibers, rods or tubes reinforce in direction of their long axis, they weaken the composite in the other two directions [71]. Additionally, it has also been reported that aggregation is common for such kind of fillers [72]. Hence, two-dimensional particles (sheets) have been used to achieve a better reinforcing effect [73,74].

More recently, carbon-based sheet structures, namely graphite and graphene, have also been modified with iron oxide nanoparticles and used to prepare composites with different applications. Epoxy/graphite-Fe$_3$O$_4$ ordered composites (Figure 8b) were synthesized under a weak magnetic field (40 mT) [75]. This report focused on the gas barrier properties of 0.1, 0.5, and 1.0 wt% graphite-Fe$_3$O$_4$ composites, with their permeation coefficients determined at different gas pressures. At 2 MPa, the barrier properties improved by an order of magnitude compared to pristine polymer and around 65% in comparison to the randomly aligned composites (Figure 8a). It was also observed that barrier properties decreased significantly as the gas pressure increased from 2 MPa to 8 MPa. According to the authors, this could be explained considering that the presence of magnetite weakens the interface between graphite and polymer, which leads to micro-cracks that propagate. Gas barrier properties are of interest for storage tanks, which usually have a metallic layer...
that prevents leaking but increases the weight and is susceptible to delamination and buckling [75].

Thermal management is important for packaging of high-performance miniaturized devices. Related to this need, the synthesis of epoxy/graphene-Fe$_3$O$_4$ under a weak magnetic field (300 mT) was reported by Yan et al. [76]. They produced nanocomposites with improved thermal conductivity that depended on orientation. Thermal conductivity in the direction of alignment of the nanocomposites containing 1 vol% nanoparticles showed 139% and 41% increases compared to the ones measured perpendicularly and in randomly aligned samples, respectively [76].

More recently, epoxy/polyvinylpyrrolidone/graphene-Fe$_3$O$_4$ composites were synthesized with an enhanced toughness and electrical conductivity in the alignment direction [77]. The fracture energy increased by ∼20% and ∼50% in the direction of alignment for the nanocomposites containing 0.5 wt% and 1 wt% nanoparticles, compared to randomly aligned samples. In contrast, it decreased by ∼15% when measured perpendicular to the alignment. Results also showed that electrical conductivity increased by two and three orders of magnitude for the composites with 0.5 wt% and 1 wt% loads in alignment direction; and it slightly decreased when measured perpendicularly [77].

The spatial control of magnetic fillers has also been researched and proven successful for inorganic sheets functionalized with iron oxide nanoparticles as it is described below. The main purpose of this kind of fillers is to act as reinforcing agents and improve the mechanical properties of the composites.

Frank et al. [78] reported the magnetic freeze casting of porous scaffolds. Alumina sheets were modified with an anionic ferrofluid and then mixed with organic binders: poly(vinyl alcohol) and poly(ethylene glycol). The slurry was then freeze-cast under a weak magnetic field (75 mT) in direction perpendicular to the freezing direction. The Young’s modulus and strength were improved in the direction of alignment. The specific Young’s modulus (Young’s modulus divided by average relative density) in the direction of alignment was enhanced by ∼125% for ordered composites compared to randomly dispersed ones. The specific tensile strength was improved by ∼35% [78].

In another study, Lin et al. [79] modified hexagonal boron nitride (BN) sheets with a ferrofluid and prepared epoxy composites containing 20 wt% BN under a magnetic field (400 mT). These materials displayed increased thermal conductivity and Young’s modulus in the alignment direction. For aligned composites, the thermal conductivity was enhanced by a factor of 5.7 in direction of alignment, compared to pristine polymer. Randomly oriented composites displayed an increase of only 2.8. Young’s modulus was 4.55 GPa in direction of alignment, which is higher than the ones measured perpendicular to the alignment (3.52 GPa), in randomly oriented samples (3.45 GPa) and neat epoxy (2.70 GPa) [79]. The microstructures of these composites are shown in Figure 9 [79].

These are promising materials to satisfy the increasing thermal needs in electronic encapsulation. In this research, the application of these composites of underfill (encapsulation material for solder interconnects) was studied through finite element analysis. Solder joints often experience a high thermomechanical stress and strain. It was found that aligned composites stored less plastic strain, hence their predicted life of such components was of 2014 cycles, while the one of randomly aligned ones was of 1769 cycles. These properties exceed the typical industrial requirements [79].

One of the inorganic fillers that has been reported the most in the synthesis of magnetically aligned composites is alumina sheets modified with iron oxide nanoparticles. Their use has been applied in the development of more complex structures and

*Figure 8. SEM images of (a) unaligned epoxy/graphite-Fe$_3$O$_4$ composite and (b) aligned epoxy/graphite-Fe$_3$O$_4$ composite. Reproduced with permission from [75]. Copyright (2014) Elsevier.*
their behavior studied and explained, as it is described in the following sections.

2.3.2. Magnetically aligned composites with bio-inspired complex architectures

Natural composites are of interest due to their versatile properties. Nature can produce materials as diverse as seashells, exoskeletons or wood, based on limited building blocks [80]. These biological materials are composed of organic phases such as cellulose, chitin, collagen or other proteins, and inorganic phases for example phosphates and carbonates. The chemical composition as well as the orientation of such building blocks determine whether a biological material is rigid or tough, dense or porous, load-bearing or weak [81].

The advances on the spatial manipulation of fillers through magnetic fields have opened the possibility to successfully replicate some of the complex structural patterns in nature and hence their extraordinary properties [73,82]. These efforts have focused not only on the synthesis of such materials for a wide variety of applications including healthcare [80,82] but also on the physical understanding of how the alignment occurs and how it can be controlled more accurately.

A relevant research was published in 2007 [82] where orthogonal scaffolds (Figure 10) made up of collagen fibrils aligned under a magnetic field (7 T) in the presence of proteoglycans were produced. Neutralized cellulose aligned perpendicular to the direction of the field. Layers with the desired orientation could be produced by a layer-by-layer

![Figure 9. SEM images of (a, c) aligned epoxy-BN composites and (b, d) unaligned epoxy-BN composites. Reproduced with permission from [79]. Copyright (2013) American Chemical Society.](image)

![Figure 10. SEM images of collagen fibrils: (a) unaligned, (b) uniaxially aligned, and (c) orthogonally aligned on two layers. Reproduced with permission from [82]. Copyright (2007) Elsevier.](image)
approach in which the sample was rotated with respect to the field direction for each layer to mimic the twisted plywood structure of connective tissues (i.e. cornea, compact bone, intervertebral disc) [82]. In a plywood arrangement, multidirectional fibers are superimposed generating an equivalent of a cholesteric (chiral nematic) liquid crystal. When the stacking sequence completes 180°, a plywood layer is formed [83,84].

Cellulose nanocrystals (CNCs) have also been used as aligned reinforcing agents in synthetic polymer matrices. Tatsumi et al. [85] prepared poly(2-hydroxyethyl methacrylate) (PHEMA)/CNC composites using a strong (8 T) static and rotational magnetic fields to align CNCs during photopolymerization. When photopolymerized under a static magnetic field, the composites held a chiral nematic texture (plywood-like) (Figure 11a and b), while a rotating magnetic field produced a unidirectional nematic state (Figure 11c). Dynamic mechanical analysis confirmed the superior thermomechanical properties of these two aligned samples over temperatures up to 200 °C [85].

CNCs are diamagnetic which causes its longitudinal axis to lie perpendicular to the magnetic field direction. That, and the electrostatically driven self-assembly mechanism of cellulose derivatives in suspension produce a helical pattern [85,86]. In contrast, under a rotating field CNC orients parallel to the plane of rotation [85].

The use of cellulose or collagen for magnetic applications is limited because of the disadvantages of using strong magnetic fields. In this regard, there has been an interest in enhancing the biopolymers with iron oxide-based nanoparticles [87–89]. In 2016 magnetically aligned CNC-Fe₃O₄ hydrophobic polymeric composites were reported to mimic a plywood structure by combining individual layers of unidirectional oriented CNCs [90]. Poly(L-lactic acid) (PLLA)/CNC-Fe₃O₄ suspensions in chloroform were left to dry under a weak magnetic field (60 mT) at different orientations: parallel and perpendicular to the surface as illustrated in Figure 12 [90].

Tensile strength increased by 70 and 58%, and elongation at break by 240% and 172% for the parallel and perpendicular PLLA composite films with 1 wt% CNC-Fe₃O₄, respectively, compared to the unoriented samples [90]. The storage modulus and glass transition temperature of the samples also increased with alignment. These ordered structures also produced anisotropic electrical and magnetic properties, which could find application in self-biased electronic products. They could also be...
further processed through hot-press lamination to produce bilayer structures with orthogonal orientations [90].

Taking advantage of two dimensional fillers, Erb et al. [71] applied previous observations on the alignment of CNTs coated with magnetic nanoparticles [91] and translated them into the coating of alumina sheets. Their polyurethane (PU)/magnetic alumina composites (shown in Figure 13) presented various microstructures according to the direction and type of the applied magnetic field during the synthesis [71]. Furthermore, it was possible to produce composites resembling a prismatic pattern through a layer-by-layer approach [71]. A prismatic pattern is common in the outermost layer of mollusks, teeth and fish scales [92] which enhances a material’s hardness and flexural modulus [71]. Their flexibility improves in relation to the content of organic matter [93]. The tensile yield strength of the PU composites containing 20 vol% magnetic alumina in the direction of alignment showed an increase of 86% and 63% compared to pristine polymer and the same composite tested in the direction perpendicular to alignment, respectively [71]. Similarly, the Young’s modulus parallel to alignment displayed a 2.8-fold increase, compared to the pristine polymer, while compared to that in the perpendicular direction, it increased by a factor of 2.5.

One of the main advantages of using magnetic fields to control the orientation of reinforcement elements is that it allows the fabrication of complex composite architectures, for example, with locally reinforced regions [71]. For example, in bone there are channels with various diameters creating high-stress regions. Collagen fibers and mineral sheets arrange themselves concentrically around these areas to create a local reinforcement. Such structures have also been reported, as well as composites where the orientation of sheets changes gradually across the sample due to the multiple magnetic domain patterns produced by certain magnets (i.e. refrigerator magnets) [71,94].

Magnetic control of the dispersed phase in composites has also been applied in 3D printing. Using surface modified alumina and an epoxy resin ink, specially developed for this application, microarranged structures have been fabricated to mimic abalone shell, shrimp cuticle and cortical bone [95]. The 3D printer was modified with electromagnetic selenoids around the resin container to produce the desired magnetic field while photopolymerization occurred selectively with the use of a digital light processor. The resulting materials showed prismatic and plywood structures and a concentric reinforcement, and are shown in Figure 14 [95]. Tensile tests were performed on monolithic and bone-like 3D printed samples. When the load was applied, the osteon structure had a higher relative tensile strength than samples with alumina sheets oriented at 30°, 60°, and 90° from the load axis, but did not out-perform the sample with alignment at 0° [95]. A similar research can be found in [96] with oriented magnetic alumina in a poly(urethane acrylate)-HEMA matrix prepared by 3D printing.

Another interesting research on microstructural organization used high volume fractions of alumina sheets coated with magnetic nanoparticles [100]. In this study, the authors created complex-shaped composites based on polymer, metal and ceramic matrices (poly(methyl methacrylate) (PMMA) with 60 vol% modified alumina, cooper with 90 vol% modified alumina and silica with 95.5 vol% modified alumina) with nacre-like and periodic orientations of the alumina sheets through slip casting method under a rotating magnetic field (Figure 15) [100].

In general, the presence of alumina sheets, which are stiff and strong, increased the fracture strength, elastic modulus and crack growth resistance [100]. The alignment of sheets contributes to the crack deflection by inducing a tortuous path for failure to develop. Specifically, the magnetic alumina/PMMA material was a lamellar composite with elastic modulus varying in the microscale, which made it useful for damping applications. PMMA-based composites increased their fracture toughness by 7–10 times and their fracture strength by 3–4 folds, compared to the pristine polymer matrix [100].

Magnetic alignment has also been applied in the development of self-shaping composites with bio-inspired structures. This type of materials is capable of adapting their shape and properties in response
Figure 14. (a) Abalone shell, scale bar = 5 μm. Reproduced with permission from [97]. Copyright (2014) Wiley-VCH. (b) Schematic representation of the prismatic structure. (c) SEM image of the printed prismatic architecture, scale bar = 25 μm. (d) Shrimp cuticle, scale bar = 15 μm. Reproduced with permission from [98]. Copyright (2014) Elsevier. (e) Schematic representation of the plywood structure. (f) SEM image of the printed plywood architecture, scale bar = 50 μm (black) and 20 μm (white). (g) Cortical bone, scale bar = 200 μm. Reproduced with permission from [99]. Copyright (2006) Elsevier. (h) Schematic representation of the concentric structure. (i) SEM image of the printed concentric architecture, scale bar = 5 mm (black) and 25 μm (white). Reproduced with permission from [95], Springer Nature Limited under Creative Commons Attribution 4.0 International License, 2015.

Figure 15. (a) SEM images of magnetic alumina-SiO₂ composites under a rotating magnetic field displaying a periodic orientation pattern. (b) Layer-by-layer growth of an enamel-dentin-like interface and their microstructures. Reproduced with permission from [100]. Copyright (2015) Springer Nature Limited.
to environmental changes. Self-shaping mechanisms are common in plants, which possess heterogeneous, hierarchical structures that are responsible for their adaptive behavior. Biological systems such as seed dispersal units (i.e. seedpods, pinecones, awns), tendrils or the Venus flytrap exhibit specific architectures characterized by layers with fibers at different orientations [101,102]. A change in their environment (e.g. light, humidity) produces swelling or shrinking of the matrix leading to a change of shape.

Iron oxide-coated alumina sheets within a gelatin matrix have been used to produce composites that mimic the bending and twisting deformations of pinecones, wheat awns and seedpods when dry or hydrated [101]. Pinecone-inspired materials consisted of a layer of vertically aligned sheets and one with horizontally aligned. Wheat awn-like composites consisted of a randomly aligned and a horizontally reinforced layer. Upon hydration, samples bent towards the layer with reinforcement orientation parallel to the bilayers long axis. Both of them were produced through rotating magnetic fields, which ensured both long axes of the sheets were aligned in direction of the magnetic field and on the plane of rotation [101]. The resulting materials are shown in Figure 16a–f [101].

In contrast, seedpod-inspired composites displayed a twisting deformation [101]. They consisted of two layers with orthogonal vertically aligned sheets. This was achieved through a vertical rotating magnetic field at 0 and $\pi/2$ angles for each layer. Interestingly, it was possible to control the direction and degree of twisting in relation to the angle at which the samples were cut. When both layers expand in perpendicular directions when hydrated the system is driven to a chiral twist. Aligned hydrogel composites display anisotropic swelling; it is this difference in preferential swelling direction that defines the way in which the specimen deforms [101]. Figure 16g–i [101] shows these composites.

Venus flytrap-inspired composites made up of magnetic alumina sheets in an epoxy were reported in 2017 [102]. It was based on aligned reinforced layers and on the pre-stresses generated by curved orientation patterns. These composites had an arc-like shape that mimicked the shape of the flytrap with two layers displaying radial and tangential alignment, respectively. The snapping action was triggered by the repelling force between two magnets on the leaf’s edges and an external magnetic field [102].

2.3.3. Magnetic alignment mechanism

To successfully design and produce magnetically aligned composites as the ones reviewed in the previous sections, a physical and mathematical description of fillers under magnetic fields has been developed. Erb et al. [71] first reported a theoretical description on how alumina sheets behave under a static magnetic field when surface modified with magnetic iron oxide. Since then, their model has been applied by other research groups and other polymer-filler systems [75]. The importance of such theory is that it provides an overview of whether alignment is possible or not depending on the physical properties of the polymer-filler system. The following section summarizes the mathematical representation of what occurs when a 2D filler in dispersion is exposed to a magnetic field.

Magnetic fields drive the orientation of anisotropic particles into configurations of minimal magnetic energy. When subjected to a magnetic field, these high aspect ratio particles exhibit a magnetic moment that will attempt to align itself in direction of the magnetic field (Figure 17) [71,103]. The synergetic effect of individual magnetic domains generates magnetic energy or torque ($U_m$) that aligns the
anisotropic particle towards the field as long as the produced magnetic energy overcomes the gravitational energy \(U_g\).

In various publications \cite{71,75,103,104}, a method has been proposed to theoretically describe the behavior of magnetic anisotropic particles (i.e. sheets and rods) in suspension. It allows for the prediction of the minimum static magnetic field strength that is needed to align particles. The magnetic energy is given by Equation 1 \cite{71,75,103,104}, which assumes an ellipsoidal geometry where \(\mu_0\) is the magnetic permeability of free space, \(X_{ps}\) is the magnetic susceptibility given by the product between the iron oxide fraction on the surface of the sheets and the susceptibility of iron oxide, \(a\) is half the average thickness of the sheets, \(b\) is the average radius of the sheets, \(\bar{d}\) is the average diameter of the iron oxide nanoparticles, \(\Psi\) is the angle between the magnetic field and the long axis of the sheets, and \(H_o\) is the minimum magnetic field required to observe alignment. This magnetic energy will act on one of the long axes of the particles guiding it towards the direction of the field \cite{71}.

\[
U_m = \frac{2\pi \mu_0 X_{ps}}{3(\chi_{ps} + 1)} \left[(a + \bar{d})(\bar{b} + \bar{d})^2 - ab^2\right]H_o^2 \sin^2 \Psi
\tag{1}
\]

The gravitational energy of a sheet using the ellipsoidal shell model can be calculated with Equation 2 \cite{71,75,101,103} where \(V_p\) is the volume of the sheet, \(g\) is the gravitational constant, \(\rho_0\) is the density of the particle, \(\rho_1\) is the density of the fluid, and \(\theta\) is the angle between the horizontal plane and the sheet long axis. This gravitational energy increases with the size of the particle, driving its orientation towards the surface.

\[
U_g = V_p(\rho_p - \rho_f)gb\sin \theta
\tag{2}
\]

However, thermal fluctuations also have an effect on alignment as thermal energy favors the randomization of the orientation of particles. To consider this energy contribution, Boltzmann statistics are applied by calculating the sum of the Boltzmann factors for the energy of each of the states (possible orientations) with Equation 3 \cite{71,75,101,103} and then establishing the probability of a sheet displaying a range of orientational states using Equation 4. For example, if one considers the case where \(\theta_1 = 75^\circ\) and \(\theta_2 = 90^\circ\) and a probability of 0.9 this would mean that 90% of the sheets will exhibit \(\theta\) within that range. This condition is only fulfilled provided that \(H_o\) is applied.

\[
Z = \int_0^{90^\circ} e^{-\left(U_m - U_g\right)/k_BT} d\theta
\tag{3}
\]

\[
P_{\theta_1 \rightarrow \theta_2} = \int_{\theta_1}^{\theta_2} e^{-\left(U_m - U_g\right)/k_BT} d\theta/Z
\tag{4}
\]

More interestingly, it has been demonstrated that when a magnetic field rotates above a critical frequency, sheets will not only be aligned in direction of the field but also parallel to the plane of rotation \cite{71,104,105}. This is explained by the fact that at low frequencies, particles will rotate in synchronicity with the field but once they reach a threshold, the viscous torque dominates and the particles immobilize. Frictional energy \(U_f\) is calculated with Equation 5 \cite{75,101,103} where \(\eta\) is the viscosity of the fluid, \(V_p\) is the volume of the particle, \(\dot{\phi}/\dot{f}_0\) (with \(\phi = 90^\circ + \theta\)) is the sheet angular frequency, and \(f/f_0\) is the Perrin factor (Equation 6).

\[
U_f = -6\eta V_p \frac{\dot{\phi}}{\dot{f}_0}
\tag{5}
\]

\[
\frac{\dot{f}}{\dot{f}_0} = \frac{4}{3} \left(2 - p^2\right)^{-1}
\]

\[
S = \left(\frac{2}{a}\right)^{2(1-p^2)} \left(2^{1/2} \arctan\left[p(1-p^{1/2})\right]\right)
\tag{6}
\]

If the gravitational energy is smaller enough compared to the magnetic energy, it can be disregarded to simplify calculations. Assuming that is the case, \(U_m + U_g = 0\) is true as there must be a balance of energies. Substituting Equations 1 and 5 in this expression, Equation 7 \cite{103} is obtained:

\[
\frac{d\psi}{dt} = \omega - \omega_c \sin 2\Psi
\tag{7}
\]

\[
\omega_c = \frac{\mu_0 X_{ps} H_0^2}{18 (f/f_0) \eta (\chi_{ps} + 1)} \left[(a + \bar{d})(\bar{b} + \bar{d})^2 - 1 \right]
\]

This frequency \(\omega\) is in fact the magnetic field frequency. When \(\omega < \omega_c\) the sheet rotates with the
magnetic field \((d\Psi/dt =0)\). When \(\omega\) reaches \(\omega_c\), the sheets stop rotating. This behavior is fundamental to achieve control over two axes of the sheet as proven by several publications \([71,96,101–104]\).

The effectiveness of the alignment relies not only on the strength of the magnetic field and the magnetic susceptibility of the particles, but also on the inherent anisotropy of them that is given by their aspect ratio \([71]\). The main challenge for nanocomposites prepared through this process is to overcome thermal randomization \([71]\). Based on the dynamic model given by Equations 1–7, it is possible to predict how a pre-polymerized system will behave in terms of the physical properties of particles and fluid. The information needed to perform these calculations can be obtained through conventional characterization techniques: electron microscopy, densitometry, viscometry, and magnetic measurements. A similar model for rod-like particles has been described by Erb et al. \([71]\) and differs on the volume-dependent parameters.

3. Conclusions

The development of polymer composites, including polymer nanocomposites, capable of fulfilling more demanding requirements has been pinpointed by the needs in a wide range of industries, from automobiles to medicine. The concept of anisotropy plays an important role as it is related to advanced thermal, electrical, mechanical, magnetic, and even self-shaping properties. Linking these two notions, it has become clear that anisotropy can be achieved and tuned by the precise control of the position and orientation of the dispersed phase in polymer composites.

Since decades ago, flow-related processing has proven to be capable of generating the alignment of fibers, tubes and sheets towards the flow direction. More recently, the alignment of particles under electric fields was also reported and studied. However, these approaches are limited mainly due to the type of polymer matrix and fillers that can be used, and to the restrictions to create complex structural patterns.

The use of magnetic fields to control the alignment of fillers in polymer composites has emerged as a promising alternative. Based on this approach, a variety of magnetically aligned polymer composites has been reported in literature. Although most materials used as fillers require strong magnetic fields to display alignment, this can be overcome through their surface modification with iron oxide species for example. Moreover, the use of magnetic fields that rotate or change direction as a function of time, and layer-by-layer preparation processes enable the production of composites displaying structures inspired by the natural patterns observed in biological materials.

Further studies remain to be done by applying the reported methodologies and findings, upon adaptions where necessary, to new systems that could improve the performance of current materials. Besides, there is a need to address issues such as the limited scalability, and the layer-by-layer preparation approach, which is time consuming and may lead to decreased mechanical properties. Until now research has been well developed, both theoretical and practical, for the manipulation of the orientation of microsheets in polymer composites. However, polymer nanocomposites with complex structures will be advantageous for the development of next-generation devices and technologies such as novel functional electronic devices and medical devices as well as smart structures. Furthermore, studying how nanostructures behave under magnetic fields will broaden the understanding of the mechanisms behind the synthesis of polymer nanocomposites with aligned dispersed phase.

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