Chapter

Polypropylene Blends and Composite: Processing-Morphology-Performance Relationship of Injected Pieces

Maria Alejandra Costantino, Caren Rosales and Valeria Pettarin

Abstract

Polypropylene (PP) is a low-cost plastic commodity, which currently is in a transition zone between massive use and engineering applications due mainly to its limited mechanical properties, such as low tensile and impact resistance. That is the reason why PP is usually modified with additives and particles to improve its mechanical and thermal performance and thus meet the requirements demanded by engineering applications. Besides, PP composites are suitable materials to be processed by a simple, fast, automatic, and massive technique such as injection molding. This makes PP composites attractive for several applications. However, it is important to keep in mind that PP composites' performance depends not only on their intrinsic properties but also on processing conditions. This chapter will summarize the relationship between processing and performance of several PP composite—micro, nano, and hybrid—injected parts with the aim of generating a bridge between technologic knowledge and scientist knowledge.

Keywords: polypropylene, injection molding, microcomposites, nanocomposites, hybrid composites

1. Introduction

Polypropylene (PP) is a plastic commodity, which currently is in a transition zone between massive use and engineer applications due mainly to its limited mechanical properties, such as low tensile and impact resistance. Moreover, several years ago the replacement of conventional materials with lighter ones has attracted the attention of many industries, especially the automotive ones. Replacement of traditional materials is achieved with the development of new composite materials, which meet both the desired properties—mechanical, thermal, esthetic—and a low weight, i.e., high relative properties. These are the main reasons why PP is usually modified with additives and particles to improve its mechanical and thermal performance and thus meet the requirements demanded by engineer applications. Originally, PPs were modified with fillers as talc only to reduce their costs, but currently the purpose is focused on improving properties such as rigidity, strength, toughness, dimensional stability, and even esthetics of PP parts [1]. To achieve this purpose, several particles have been used, such as glass fibers (GF), nanoclay (NC), carbon nanotubes (CNT), and rubber. In a further step, hybrid materials formulated by two or more of these components have been proposed.

From an engineering point of view, mixing a polymer matrix with a particle is an effective low-cost way to achieve the required properties when parts are produced by injection molding. However, it is important to understand the way in which particles and processing affect the structure and properties of processed parts. It is important to keep in mind that PP composites' performance depends not only on their intrinsic properties but also on processing conditions. PP is also strongly sensitive to defects produced during manufacturing processes such as injection molding, which deteriorate and decrease a lifetime of composite parts [2]. These defects are even more pronounced in the case of composites. In recent years, a number of texts regarding properties of injection-molded reinforced polypropylenes have been published [3–5]. However, because of the continuing developments of PP composites, the achievable property values are continuing to improve. In structural and semi-structural applications, particularly, in addition to high stiffness and mechanical strength, adequate fracture toughness is often required. In order to optimize these properties, the knowledge of the relationship between morphology and deformation behavior seems to be essential. The understanding of the fracture, micro-deformation, and mechanics of failure of composites is therefore crucial for engineers. This chapter will summarize the relationship between processing and performance of several PP composite—micro, nano, and hybrid—injected parts aiming to generate a bridge between technologic knowledge and scientist knowledge.

1.1 Injection molding process

Injection molding of thermoplastic polymers is a repetitive process in which a molten polymer is forced to go through a mold cavity where it is held under low pressure until it solidifies and it is finally ejected. A scheme of injection molding machine can be observed in **Figure 1**.

First stage of injection cycle begins with the molten polymer filling the cavity mold which is closed (filling stage). During filling stage, the screw doesn't rotate but acts as a dashpot which drives the molten material into the mold. At the end of the filling stage, a lower pressure is held by the feeding system allowing a small amount of additional material to enter the mold cavity to compensate the volumetric contraction of the injected part (holding stage). Holding pressure eventually decreases to zero; this defines the beginning of the third stage known as "cooling stage." In this stage, the molten material solidifies inside the cavity, the

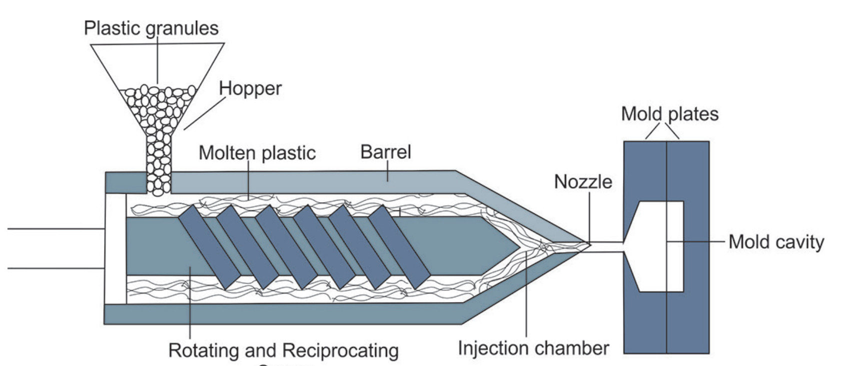

Figure 1.
Injection molding machine scheme.

mold opens, and finally the piece is ejected. The mold then closes again to start a new cycle [6].

1.2 Injection molding common defects

Although the main advantage of injection molding process is to manufacture complex parts in a single, fast, and automatic operation, there still are some processing inherent defects such as flow and weld lines which may deteriorate the mechanical performance and appearance of final injected parts. Weld lines are the result of the convergence of several flow fronts during filling stage. The origin of these flow fronts may be due to several reasons: inserts inside the mold cavity, thickness differences in the piece, or the presence of two or more injection points [7]. Weld lines are usually V-shaped as it can be seen in **Figure 2**.

Cross section of the welding plane shows two different zones within the weld line with some particular characteristics: a V-shaped zone where there is almost no molecular diffusion and unfavorable orientation and a central zone with a better molecular diffusion (see **Figure 2**). Weld line is a weak zone from a mechanical point of view and uses to present visual defects too [8, 9]. Weld line performance is determined by material nature, part complexity, and processing variables.

Another common and important injection molding defect is warping. Warping is a macro-geometric deformation of injected pieces which remains after cooling. The main causes of warping are differential contraction between different parts of pieces and released residual stresses formed during cooling stage. These deformations are mainly due to confinement of pieces in the mold cavity, orientation, crystallization, or cooling differential.

1.3 Injected polypropylene

PP performance—mechanical, thermal, and electrical—depends mainly on its morphology and crystallinity [10]; and processing affects both morphology and crystallinity of polymers. In the case of injection molding, the molten polymer is subjected to thermomechanical complex conditions characterized by high cooling speeds and stress fields. These conditions change along the flow path and mold thickness, i.e., polymer pieces present an intrinsic heterogeneous microstructure, characterized by a gradual and hierarchical variation of morphology, which evolves through the spatial domain of the piece. Injected PP particularly develops a "skin-core"

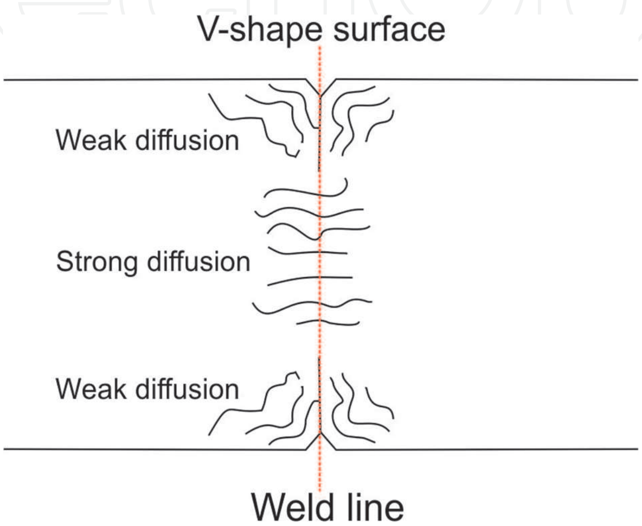

Figure 2.
Cross section of a weld line zone.

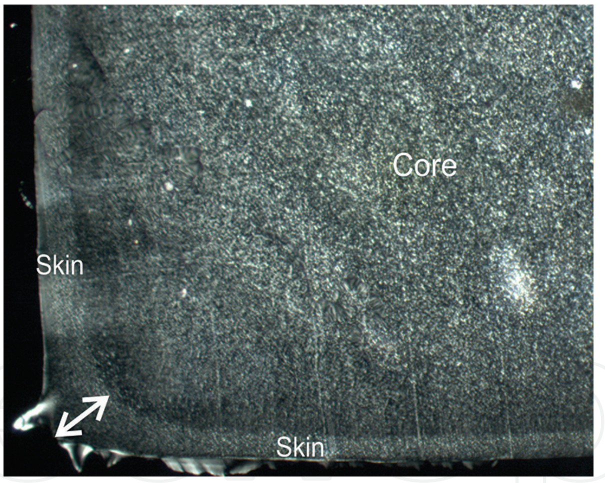

Figure 3.
Skin-core microstructure seen by polarized optical microscopy.

microstructure, which can be seen by polarized optical microscopy (PLM), as in **Figure 3**.

The number of observed "layers" in the microstructure depends on the resolution of the experimental technique used. A simple analysis considers a three-layer model (two external skins and an inner core) [11–13], but other layers may be also observed (two external skins, two sub-skin regions, two shear zones, and an inner core). The intrinsic molecular nature of the polymer together with this layer morphology determines the mechanical performance of injected PP parts.

Besides, adding a second component—particles or additives—into a PP matrix may also change its crystalline structure, i.e., may produce changes in injected piece performance.

Through this chapter, the relationship between processing and performance is reviewed for injected PP composites. The combined effect of the molding process and the fillers on the properties of the polymer composites is reviewed. Also, the effects of the occurrence of inhomogeneities, such as weld lines or flow lines in microstructure and therefore in performance, are summarized.

2. Injected PP microcomposites

The first attempt to obtain a good composite is to add a microparticle to the polymer matrix. Among PP microcomposites, fiber-reinforced plastics are a popular type of composites used in many engineering applications mainly because of their excellent capability to form complex shapes. These fibers—glass or carbon, stiff and elastic—generally increase both stiffness and strength of PP matrixes. Even though injection molding is currently the most used technique to process this kind of composites, there are some issues that directly link the processing with a nonuniform orientation of fibers and their breakage. In fact, there is a strong heterogeneity of the microstructure in terms of fiber orientation of injected parts: short-glass fibers use to tend parallel to the injection flow direction in the skin zones and highly angled with respect to flow direction in the core layer. Fiber orientation depends also on location along the piece (e.g., distance from injection points). There is a strong dependence of the macroscopic mechanical behavior on fiber orientation. In fact, when the average angle of fiber orientation varies in only a few degrees with respect to loading direction—corresponding with a change in the average value of the component of fiber orientation matrix with respect to loading direction of only a few hundredths—the composite tensile strength varies by approximately 7.5% [14]. In addition to orientation, fiber length also dominates the tensile strength of injection-molded composites. In general, fiber breakage results in a decrease in tensile strength, so it is important to know how injection molding affects fiber breakage. An increase in shear (injection velocity, shear components, etc.) may cause an enhanced fiber and matrix orientation which would lead to higher tensile performance along the flow direction. However, it also causes a remarkable fiber breakage [15]. Experimental results indicate that an increase in injection velocity results in a decrease in ultimate tensile stress, due to the high fiber breakage. This effect is partly attenuated at low mold temperature, due to an increase of fiber orientation [3]. In case of complex parts that contain weld lines, the situation is even more complicated. The fibers are nonuniformly distributed in the regions around the defects, and there is also a distribution of glass fiber densities. All these features modify fracture behavior of injected pieces changing failure patterns, with crack pathways that follow stress concentrators developed during processing [4].

As it was stated before, not only all modifications are done to obtain a nanocomposite with improved mechanical performance, but also esthetic features are searched for some special applications. Composites of thermoplastic polymers with metallic fillers are an important group of engineering materials with a wide range of properties including electric and thermal conduction, high mechanical properties, and improved esthetic quality. Currently, metallic looking plastics replace metals by plastic in many applications, trying to achieve the quality and prestige of metals and adding value to products [16]. It is possible to obtain a metallic looking plastic part by adding metallic pigments. In this way, it is possible to eliminate post-processing operations such as painting. Metallic pigments have different shapes and sizes. Particles with a flake shape promote the reflected light in a specular way increasing the metallic appearance of part surfaces [17]. In spite of the injection defects—as weld or flow lines—being known to affect pieces of esthetics, this could be improved by adjusting processing conditions [18, 19]. Melt temperature is one of the processing parameter that more influences esthetic of injected parts: higher melt temperatures decrease shrinkage and make weld lines wider and more diffuse [20]. In case of PP/aluminum composites, the presence of aluminum that increases thermal conductivity plus the inherent temperature gradient and shear stresses of the injection molding induces β-polymorph formation. This effect also depends on processing conditions; a higher melt temperature induces a higher β-phase content. At the same time, the mechanical performance of parts shows to be dependent on PP morphology, i.e., processing conditions. Quasi-static fracture performance also depends on the location of the samples. At weld line zone, PP/aluminum composite failed in a brittle way following the weld line. Fracture toughness of both PP and PP/aluminum is similar, indicating that weld lines are a predominant weak defect inside the injected parts. Away from weld lines, PP and PP/aluminum show a

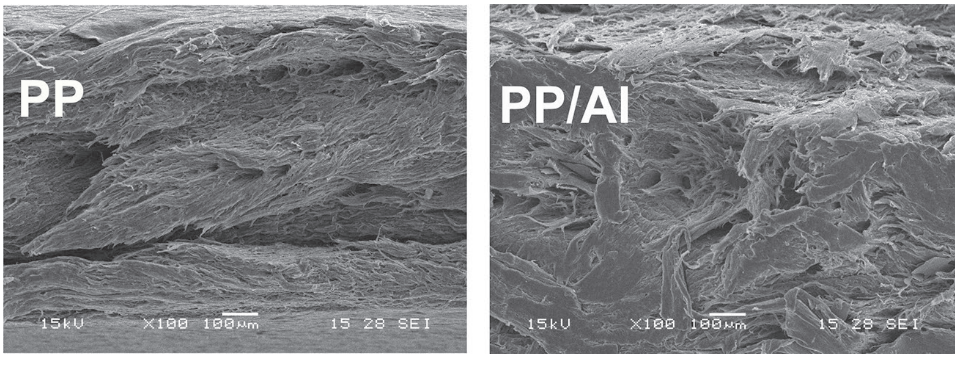

Figure 4.
SEM pictures of PP and PP/Al fracture surfaces.

similar fracture behavior characterized by a nonlinearity of stress vs. strain curves with a crack stable propagation and large plastic deformation. However, differences in the propagation mode between PP and PP/aluminum parts were found. In fact, specific plastic work w_p (specific energy absorption per unit volume) is equal to 4.51 MJ/m^3 for neat PP and 16.01 MJ/m^3 for the PP of PP/Al composite. These values indicate that much more energy is involved in the propagation of a crack in the PP of PP/Al samples than in the PP of neat PP samples. The occurrence of β-phase in the composite promotes matrix fibrillation and makes PP of PP/aluminum parts to consume more energy before break than pure PP injected parts (**Figure 4**).

3. Injected PP nanocomposites

In the last three decades, a large interest in nanocomposites was seen in both academic and industry fields [21], due to their potential improvement of properties with a low content of the second phase. In the case of nanocomposites, nanofiller dispersion and orientation are very determinant of mechanical and thermal properties. In theory, only well-dispersed and exfoliated (nanoclays) nanoparticles could lead to an effective improvement of composite performance. Most of commercial nanoparticles, such as nanoclay, are hydrophilic and have weak adhesion or interaction with a hydrophobic matrix as PP, leading to a nanocomposite with a poor dispersion. As a solution to this problem, some producers recommend using masterbatches (MBs), which include all compatibilizers needed to promote nanoclay dispersion and have the additional advantage of being easy to process and compatible with standard processing as injection molding. In fact, some authors have reported nanocomposite preparation by using MB [22–25]. However, these studies indicate that nanoparticles were not exfoliated but intercalated. The influence of the flow pattern during injection molding on the fracture and impact properties of complex injected PP/clay nanocomposites has been studied [22, 23]. Nanoparticles were mostly intercalated—even though they were chemically modified and compatibilized—and both fracture parameters (KIC and G) and impact toughness were determined by molecular and nanoparticle orientation induced by the flow pattern. Toughness mechanisms—as particle delamination or separation—were active only in certain loading directions. It was stated before that nanoclay delamination or splitting is an effective toughness mechanism in nanocomposites [26]. In PP, craze-like bands are one of the main mechanisms responsible for matrix energy absorption during deformation. To activate this mechanism, free surfaces are necessary for craze bands to initiate and nanoclay delamination produces those surfaces. However, these crazes can initiate only at the pole of clay particles, i.e., only particles oriented at 45° or more to load direction can induce multiple crazing in tensile-loaded samples and subsequently act as a toughening mechanism. Besides, weld and flow lines produced during filling acted as defects in the presence of nanoparticles [22, 23]. For PP/nanoclay composites under tensile conditions, the amount of absorbed energy was lower at the weld line than away from it and in the flow direction. This is a clear example of how injection molding flow pattern affects the piece performance of injected nanocomposites.

As nanofiller dispersion and exfoliation are crucial, a great effort has been made to improve them by adding additives. However, it is also possible to improve dispersion and exfoliation by changing their processing characteristics. An example of this is shear-controlled orientation in injection molding (SCORIM), which is a not conventional injection molding technique based on a shear-controlled application to the molten polymer during holding stage. SCORIM involves the use of a conventional injection molding machine with a special device with two

Skin orientation (A_{110} index)	Percentage of crystallinity (%)	J integral (N/mm)
0.15	31	94.6
0.165	37	83.8
0.17	40	73
0.189	37.5	40.6
0.19	41	51.4
0.195	39	29.8
0.20	42	8.6

Table 1.
Orientation, percentage of crystallinity, and fracture energy values [34].

pistons that generate the shear stresses. It was reported that SCORIM improves the performance of injected parts by controlling their morphology [27, 28]. Significant improvements were found in both stiffness and tensile resistance, molecular and filler orientation, dimensional tolerance, esthetic appearance, and weld line elimination in PP [29] and in its nanocomposites [30–32]. It was demonstrated that SCORIM changes the morphology of PP nanocomposites, not only in terms of molecular and nanoclay orientation but also in crystal phases present in PP matrix: the shear stresses driven by SCORIM process induce the formation of γ phase in PP nanocomposites [24, 33]. SCORIM induces a thicker skin in nanocomposites, i.e., a larger proportion of orientated molecules and clay particles, which favors the sliding of macromolecules, improving the deformation capability. Meanwhile, γ polymorph induces a larger-scale plastic deformation compared with the common α phase. γ phase promotes tearing of PP ligaments leading to fibrillation which is a toughness mechanism [34]. All these morphology features—better molecular and particle orientation and γ polymorph presence—improved PP/nanoclay toughness (**Table 1**).

In case of carbon nanotubes (CNTs), it is important not only to attain a good dispersion but also to obtain an interconnected network morphology (above the percolation threshold) to lead an improvement in composites' performance. This morphology depends on nanotube orientation, dispersion, and distribution [35]. It is known that injection-molded parts have a higher percolation threshold than compressed ones due to the morphology and orientation induced by processing [36–38]. Moreover, weld lines could make particle dispersion and orientation even more complex for this kind of materials. It was reported that PP-/CNT-injected parts presented also agglomerates and an isotropic morphology induced by flow pattern during injection [39]. Also, an orientation profile of CNT trough molding thickness has been seen near to the injection point. CNT particles in the skin zone are oriented parallel to the flow front, while they tend to align transversally in the core zone. This has also been observed for fiber-reinforced polymers [40, 41]. In weld line region particularly, it was reported that agglomerates are more diffuse with a random orientation of CNT in both skin and core zones [42]. This heterogeneous orientation induces different fracture mechanisms in the pieces, weld line zone being the weakest part of injected pieces. Agglomerates act also as defects diminishing fracture energy of nanocomposites, when compared with pure PP. As a result of this particle orientation, electrical conductivity—both AC and DC—also changes along injected pieces: at the weld line region, there is an increase in conductivity values due to the more efficient conductive filler distribution. In this example, it can be clearly seen that morphology developed during injection molding is a crucial feature which

	Electrical resistivity (Ohm/cm)	e-Painting efficiency	G_C (kJ/m^2)
PP/CNT weld line	1.10^9	0.7	3.3
PP/CNT bulk	1.10^{10}	0.6	8.4
Neat PP	1.10^{14}	0.1	18.1

Table 2.
Electrical, e-painting efficiency, and fracture energy values [42].

determines piece performance. A 3D interconnected CNT network is optimal to obtain good electrical conductivity values, but it is not favorable for obtaining a good fracture performance (since it inhibits alternative toughness mechanisms to occur) (**Table 2**).

4. Injected PP hybrids

The use of two different reinforcements at the same time may expand the application field of PP composites by combining their properties. Hybrid nanocomposites made by a rigid filler and soft particles have attracted attention due to incorporation of both stiffness and higher energy absorption and elongation at break. The goal is to obtain an optimal balance between rigidity and impact resistance [43–45]. An example of these kinds of hybrid composites is a rubber/nanoclay/polypropylene nanocomposite, which may increase simultaneously stiffness and toughness of PP. A study about how injection molding flow pattern and inhomogeneities affect the morphology and performance of this hybrid nanocomposite at different locations in injected intricate moldings was reported in literature [46]. A noticeable morphological feature was found: rubber particles appear to be more elongated and oriented in flow direction in the skin of injected pieces, while they appear spherical shaped in the core. Regarding nanoclay, an orientation profile was found: there is a strong orientation of nanoparticles in flow direction in skin zone, while they are randomly distributed in the core. A scheme of these morphology features is shown in **Figure 5**. Surprisingly, there are no significant morphological differences between the zone near the injection point and the zone of the weld line. These morphological features have an important influence in mechanical performance of injected pieces. In fact, fracture features showed to be dependent on the morphology developed during processing: in the core—with spherical-shaped rubber particles and randomly oriented nanoclay—a cavitation process was seen accompanied by shear yielding; in the skin, with elongated-shaped rubber particles and strongly orientated nanoclay particles in flow direction, there were no signs of cavitation, and fracture surface was slightly rugged. It is known that size and shape of rubber particles play a key role in

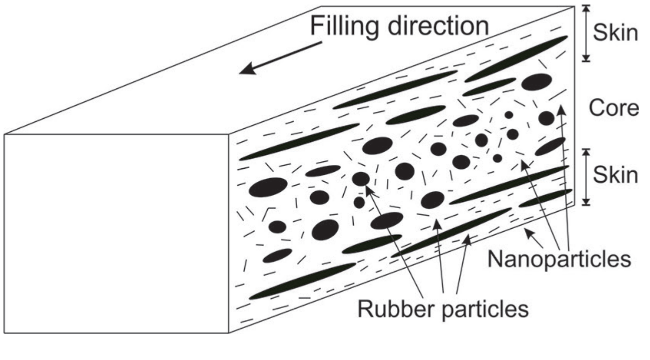

Figure 5.
Particle morphology feature scheme.

toughness mechanisms [47–50]. Spherical particles favor stress concentration which induces several absorption mechanisms—craze, shear yielding—while elongated ones are not able to produce stress fields needed to promote toughness mechanisms [50]. The non-visibility of the weld line seen previously in the morphological analysis is in concordance with fracture results: weld lines did not act as stress raisers and did not introduce an alternative crack path.

Another kind of a hybrid composite which combines both reinforcement and energy consumption promotion is composites reinforced with both glass and cellulose fibers. Kahl et al. studied the synergetic effect of those two fibers in hybrid injected PP-based composites. They found that fiber orientation depends not only on the flow pattern but also on the amount of cellulose fibers present in the hybrid composite. There is a general trend of both kinds of fibers to orientate parallel to flow direction. A higher cellulose fiber content in the hybrid composite decreases the orientation of both fibers. Besides, short fibers tend to align following flow direction much more than longer ones [51]. There are some other examples of works in which fiber interactions govern the morphology of hybrid injected pieces. Gamze et al. found that mechanical performance of injected carbon nanotubes/glass fiber PP hybrid composites depends on fiber interaction in the matrix. The simultaneous usage of carbon nanotubes and glass fibers increases the system polarity, leading to a better dispersion of carbon nanotubes, with the subsequent effect in the final performance of pieces [52].

In summary, there are several evidences indicating that not only the developed morphology during processing but also the interaction between reinforcements is crucial in the final performance of injected pieces.

5. Conclusions

Through this chapter, it has been shown that PP composites' performance depends not only on their intrinsic properties but also on processing conditions. Processing of a two- or three-phase PP-based composite induces distinct morphologies and microstructures that depend on both processing conditions and phase interaction, i.e.:

- The same composite would develop different morphologies or microstructures if processed with different conditions.
- Different composites processed with the same conditions would also develop different morphologies or microstructures.

These induced characteristics, such as crystallinity, crystalline phase, or phase morphology, will definitely affect final performance of processed pieces, including thermal, mechanical, and fracture behaviors. Moreover, if different types of reinforcements are added in a composite, it has been observed that not only the developed morphology during processing but also the interaction between reinforcements is crucial in the final performance of pieces.

All these features should be kept in mind when trying to use a composite, knowing that laboratory results should not be directly extrapolated to final processed pieces.

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