MORPHOLOGICAL ASPECTS OF INJECTION-MOLDED POLYPROPYLENE WITH METALLIC PIGMENTS

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Abstract

Innovation, design freedom, cost and weight reduction are some factors for the replacement of metals by plastics. Plastics continue to offer attractive solutions for design engineers. The metallic effect obtained by incorporation of metal particles in polymers by injection molding has the advantage of eliminating post-processing techniques such as painting or metallization. Moreover, it reduces production costs and time to get a superior part quality. Nevertheless, undesired defects in the final appearance of parts are common, such as flow lines and weld lines. These defects occur due to inhomogeneous orientation and anisotropy of the metal particles. Very few studies are reporting the influence of metallic particles on the morphology development of PP parts. Therefore, this study is focused on the production of parts made of PP/metallic pigments (aluminum, bronze and copper) by injection molding in order to understand the influence of metallic particles on the aesthetic and morphological properties of the parts.

Introduction

In recent years, new materials and new technologies have been developed to eliminate the existing gaps in terms of aesthetic products. The metallic effects of the plastics came to revolutionize the automotive industry, packaging and appliances, replacing the metal by plastic in various components. Thus, attributing the quality and prestige of the metal and adding value to products [1].

Metal particles have different sizes and shapes. Those having a plate like shape promote the increase of reflected light in a specular way, increasing the luster and metallic appearance of surfaces [2]. However, the use of smaller particles or particles with a significant distribution in their size have resulted in increased light scattering (by increasing the edges, for the same surface area), so that the gloss of the part is reduced.

The defects caused by the incorporation of metallic pigments in a polymeric matrix are due to the orientation and anisotropy of the particles in the region of the weld [2, 3]. Therefore, it is essential to understand the behavior of metal particles within a polymeric matrix.

The welded line results from the meeting of two front lines, where particles tend to have a perpendicular orientation to the surface [4]. These defects can be minimized by adjusting the processing conditions. An increase of mold and injection temperatures causes the disorientation of flakes, which in turn, attenuates weld/flow lines. The changing of size and size distribution of metal particles are alternatives to minimize these defects [3, 5]. Large particle sizes ranging from 60-330 μm minimize the appearance of flow and weld lines [2]. Brightest metallic effects are also found in the aluminum pigments with large particle size, due to their highest reflectivity. Typically, 1.5-2wt% of aluminum pigments and 0.5-1wt% of bronze pigments [5, 6] is necessary to achieve a metallic look appealing by polymers.

Materials and methods

Polypropylene (PP) copolymer powder from ICORENE with specific gravity of 0.9 g/cm^3 and a melt flow index of 13 g/10 min (190ºC, 2.16 kg), was used in this study. The pigments used were: (i) aluminum with two different dimensions, (ii) bronze and (iii) copper. The pigments references are described in Table 1. The aluminum and bronze pigments were provided by Poliversal S.A.

Table 1. Metallic pigments.

Metallic pigments	Reference	Particle size
Al 75	21075 aluminum pigment (master batch)	75 microns
Al 27	Sparkle silver 880-30 (master batch)	27 microns
Bronze	Bronze powder 7600 rich pale gold (powder)	15 microns
Cu	Copper R0402 (powder)	-

A previous study [5] indicated that both Al and bronze particles had a flake like shape, whereas copper had a spherical like shape.

The injection molding test geometry was a two gated box of dimensions: 152 mm width, 73mm length, 16 mm height and 1.5 mm thick. The injection molding was carried on a Ferromatik-Milacron K85, using the processing conditions reported in Table 2.

Table 2. Processing conditions used in injection molding.

Processing conditions	
Mold temperature (ºC)	40
Melt temperature (ºC)	220
Injection speed (mm/s)	30

The mixture of metallic particles with PP was done in a rotary drum, using 2wt% of metal particles; the percentage used was based on a previous work [5].

The microstructure was evaluated using polarized and bright field microscopy techniques. For that a microscope Olympus BH-2 coupled with a digital camera Leica DFC 280 and software Leica Qwin V3, was used. The samples were cut from both the weld region and out of weld region of the part. Thin slices of 15 µm were obtained using a microtome Leitz 1401, and placed between a glass slide and cover glass after immersion in Canada balsam.

A PERKIN-ELMER DSC-7 was used to determine the degree of crystallinity of the composites. Tests were run at the temperature range between 30ºC to 200ºC, at 20ºC/min, with nitrogen as purging gas. The degree of crystallinity was determined considering the heat of fusion of 100% crystalline (ΔH_f^0) PP to be 148 J/g [7].

Metallic appearance

Metallic pigments offer exceptional effects on the polymeric matrix, as depicted in Figure 1. It is observed a silver color offered by PP/Al, a golden color for PP/Bronze and a dark brown color for PP/Cu parts. It can also be distinguished a difference between PP/Al 27 and PP/Al 75 as a result of their differences in particle size. While PP/Al 75 has the traditional metallic effect awarded to plastics by other techniques such as painting or metallization, PP/Al 27 has a metallic look which resembles the appearance of pure metal, such brushed aluminum or polished steel. All composites have metallic color, with the exception of PP/Cu. This result may be due to the spherical like shape of the Cu pigment [5], which greatly diminishes the reflectance of light.

The analysis of defects is of extreme importance to the quality of parts. The most frequent defects on the injection molded boxes with metallic particles are: weld lines, flow lines and warpage (see Figure 1). The visual defects occur from the junction of two flow fronts, such as weld lines and flow lines. They occur in PP and in PP/metallic pigments. However the orientation of the particles and its anisotropic character in terms of reflection of light causes the appearance of a dark line at the surface of the part [8]. The PP/Al 75 has less pronounced defects in comparison to PP/Al 27, as expect from the fact that larger particles have less edges to reflect diffusive light in comparison to smaller particles (for the same surface area) [8]. These defects are already reported in the literature [5, 9]. The appearance of these defects is dependent of the metallic particle, its content and size/shape of the particles used.

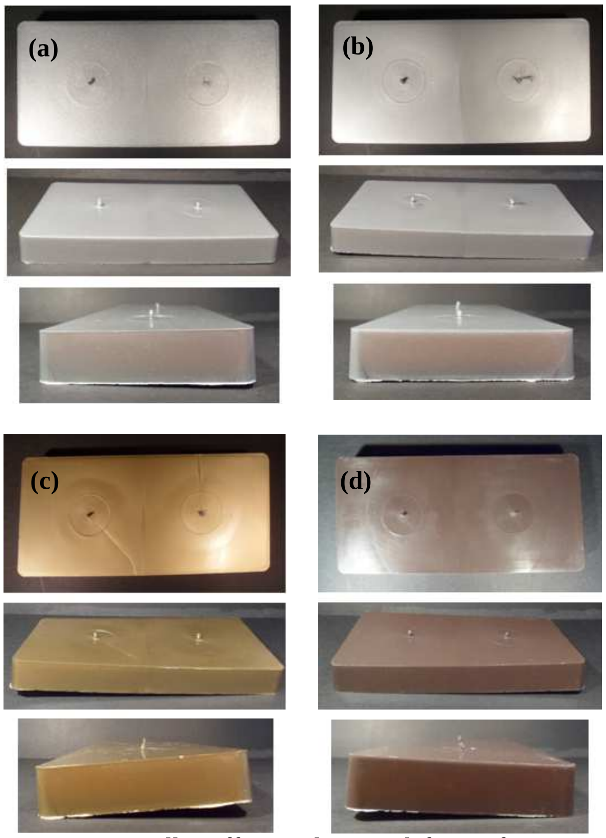

Figure 1. Metallic effect and main defects of injection moldings of: (a) PP/Al 75; (b) PP/Al 27; (c) PP/Bronze and (d) PP/Cu.

Figure 2 depicts the reflectance curves of injection moldings.

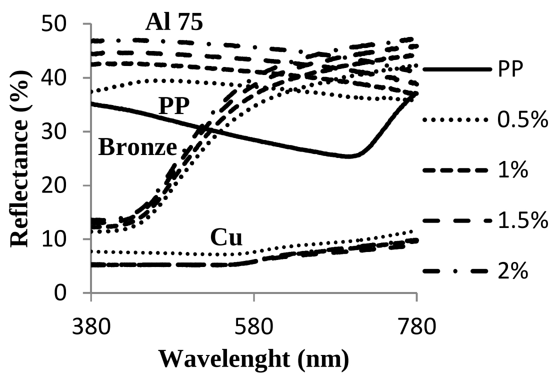

Figure 2. Reflectance curves of injection molded PP/metallic pigments.

The reflectance curves of PP/Al 75 follow in the grey scale (although not depicted, PP/Al 27 shows the same type of curve), PP/Bronze follows yellow color, whereas PP/Cu follows brown color. There is an increase in reflectance with increasing load percentage in PP/Al and PP/Bronze, in opposition to PP/Cu.

Morphological analysis

Figure 3 depicts the optical microscopy images of 2wt% PP/metallic pigments in the weld zone. All of them have a good distribution of the metallic pigments in the matrix. However, with the exception of PP/Cu, a denser population of particles is observed in the weld region. The PP/Al 27 has a higher amount of particles in the sample than PP/Al 75 for the same pigment content, as a result of the smaller particle size of the PP/Al 27.

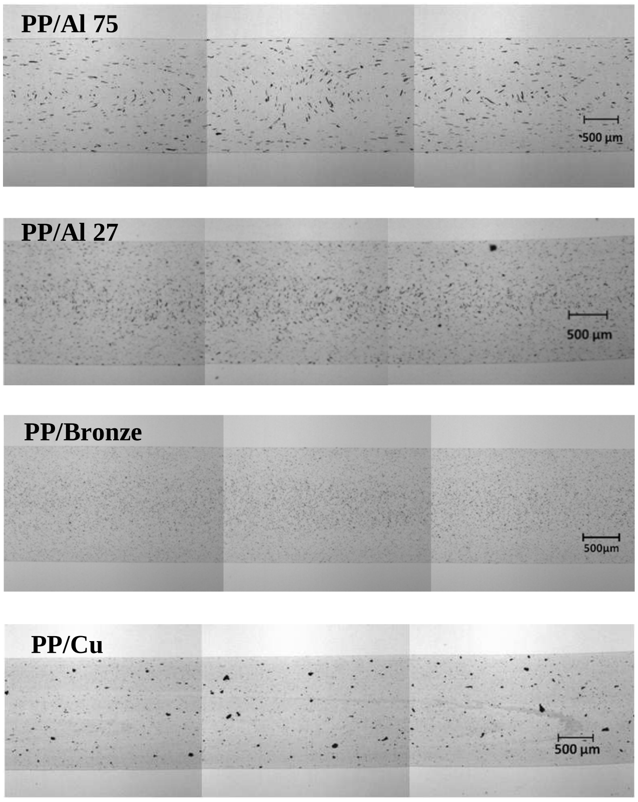

Figure 3. Transmitted optical microscopy images of PP/metallic pigments in weld zone.

In the weld region the particles flake adopt the orientation imposed by the flow lines. Therefore, when two flow fronts meat each other a weld line is formed. The rapid solidification of the melt due to the contact with the mold does not allow the reorientation of the particles at that location. Thus particles remain perpendicular to the plane of the surface, and a dark line appears [3, 5].

The behavior of metal particles outside the weld line differs from the region of weld line. As observed in Figure 4, there is a good distribution of the pigments; however they tend to accumulate in the central region of the core. The metal particles are randomly oriented in the core whereas in the skin they tend to orient themselves parallel to the surface. This is the major difference between the two regions – out of the weld and in the weld that results in the absence (out of the weld) or appearance (at the weld) of dark lines.

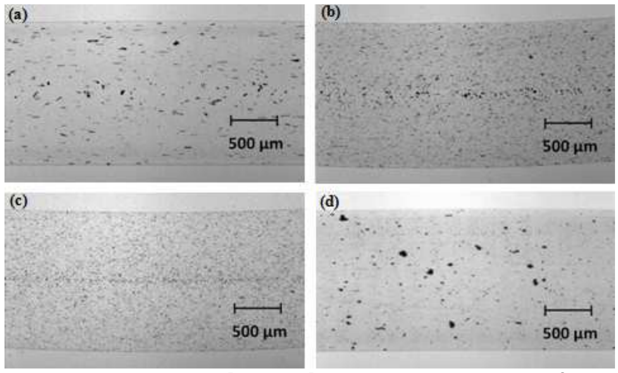

Figure 4. Transmitted optical microscopy images of: (a) PP/Al 75; (b) PP/Al 27, **(c)** PP/Bronze and (d) PP/Cu pigments outside weld zone.

Figure 5 shows the microstructure of PP part along the thickness direction. It is possible to observe a typical structure of an injection-molded part consisting of skin, shear layer and core. Due to the sudden cooling of the part in the cold mold walls, the skin is characterized by very high chain orientation. The shear layer appears between the skin and the core and is characterized by having an undeveloped spherulitic structure. Finally, in the core, well developed spherulitic structure is observed.

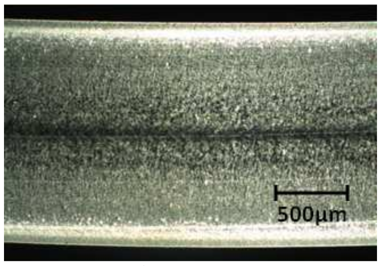

Figure 5. Microstructure of the PP part.

Figure 6 illustrates the microstructure of the PP/metallic pigments. PP/Al 75 shows an increased size of skin compared to the PP. This is due to the higher thermal conductivity of aluminum which provides a faster cooling rate and consequently an increase of the skin thickness. In the shear layer it is observed the formation of transcrystalline structures around the particles. The transcrystalline structures are characterized by having a high density of crystals formed at the surface of the metal particles, inhibiting the normal spherulitic growth. However, this particles are not working as nucleating agents, since that is only observed in the shear layers of the molding and not on the skin or in the core region.

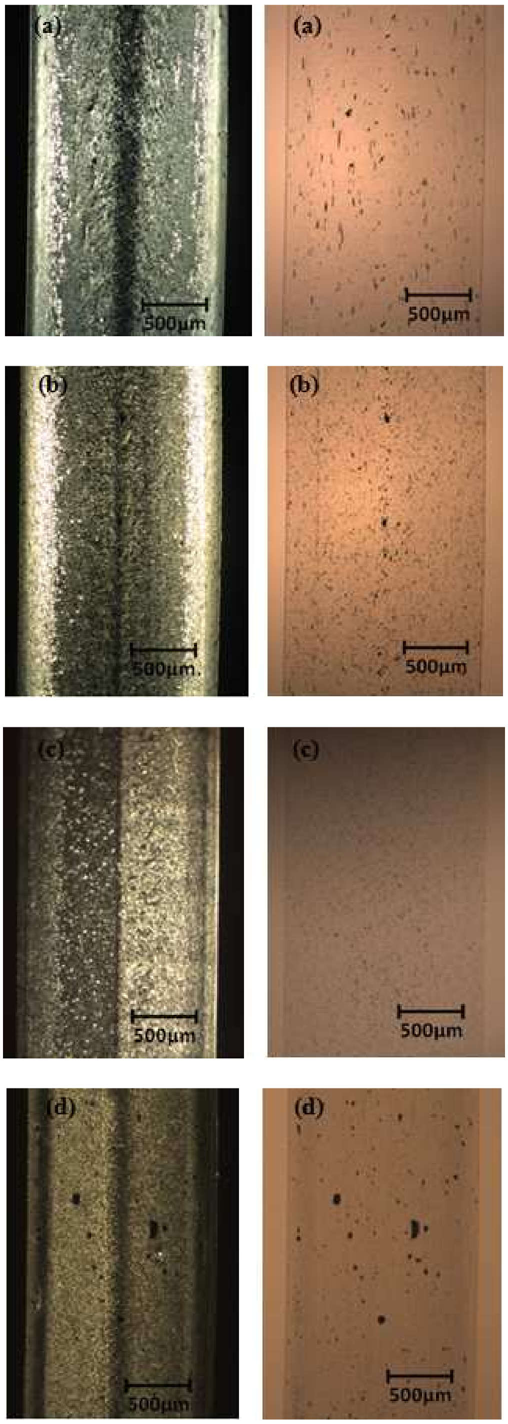

Figure 6. Microstructure of: (a) PP/Al 75; (b) PP/Al 27, (c) PP/Bronze and (d) PP/Cu.

For PP/Al 27 it is again observed a skin thickness increase relative to the PP part. Metal particles in the core are perpendicular to the plane of the surface, while the particles in the skin are parallel to the surface. This is due to the lower shear rate in the core and the symmetric velocity profile in the midplane, thereby enabling the particles to orient in the plane direction. In PP/Al 27 are also seen transcrystalline structures in the shear layer.

PP/Bronze does not show the appearance of transcrystalline structures. The size of the skin is similar to the PP because the thermal conductivity of the bronze is relatively low in relation to other metal particles (aluminum and copper), not affecting the cooling of melt in the mold and consequently the size of the skin.

In PP/Cu there is a very homogenous structure, with the decrease of spherulitic size from the skin to the core. A thicker skin thickness is found in comparison to that of PP. No change in crystalline structure around the particle is observed as seen in the composites of PP/Al 27 and PP/Al 75.

Figure 7 shows the crystallinity degree of PP/metallic pigments. All of them exhibit a degree of crystallinity near that of PP of about 57%. There is no significant influence on the crystallinity of the part by using different pigments.

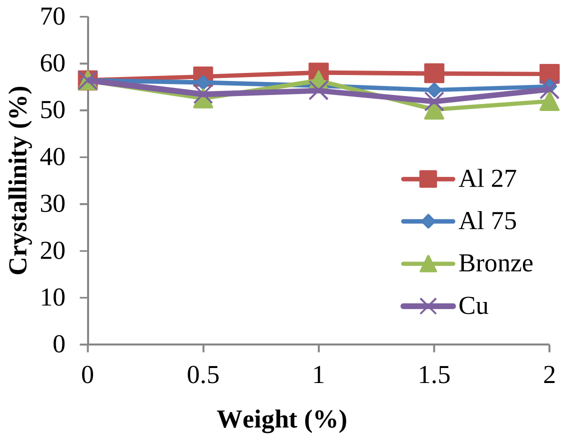

Figure 7. Effect of metallic particle on the crystallinity degree of PP.

Conclusions

The addition of metallic pigments in PP matrix has influence on the aesthetical and morphological properties of injection molded parts. Regarding the aesthetic effect, all of the pigments attribute the metallic color and appearance to the part, corresponding to the pigment used. The exception is observed for PP/Cu which has a non-metallic brown color. As regard the defects, the most common are the weld lines present in PP/Al and flow lines in PP/Bronze. In the PP/Cu the weld lines and flow lines are not visible, possibly due to the spherical shape of the Cu particles.

The optical micrographs show the orientation of the particles on weld line resulting from the joining of two flow fronts. The particles are aligned perpendicularly to the surface causing a dark line in the region of the weld line. Through the polarized light microscopy it is concluded that the metallic particles affect the microstructure of the PP. It is observed a change in the skin thickness and appearance of transcrystalline structures in the shear zones of the injection molded part, especially in the case of Al pigments. The degree of crystallinity of PP is not affected by the type of metallic pigment used.

Acknowledgments

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References

1. I. Wheeler, *Metallic Pigments in Polymers*. UK: Rapra Technology Limited. ISSN 1-85957-166-2 (1999).
2. H. Bunge, *Metallic looking plastics with new silver and colored aluminum pigments*. *SPE ANTEC Tech. Papers*, 3, 2586-2588 (1998).
3. M. J. Park, J. S. Jeong and J. S. Park. *Flake orientation in injection molding of pigmented thermoplastics.* Journal of Manufacturing Science and Engineering, Transactions of the ASME, 134 (**1**), (2012).
4. Y. Kobayashi et al. *The unique flow of polypropylene at the weld line behind an obstacle in injection molding*. Journal of Polymer Engineering and Science, 51 (**3**): 526-531 (2011).
5. C.I. Martins, I. Santos and A.J. Pontes, *On the effect of metallic particles on the performance of injection moulded PP plastic parts.* Conference on Polymer and Mold Innovations, 375-382 (2012).
6. R. A. Charvat, *Coloring of Plastics – Fundamentals*. 2ªed. John Wiley & Sons, New Jersey. ISSN 0-471-13906-8 (2004).
7. Monasse, B. and Haudin, J. M. *Growth transition and morphology change in polypropylene.* Colloid & Polymer Science, 263(**10**), 822–831(1985).
8. R. M. Harris, *Coloring Technology for Plastics*. Plastics Design Librar, New York. ISSN 1-884207-78-2 (1999).
9. K. Rawson et al, *Controlled orientation of reflective pigment and optical property characterization of injection-molded polypropylene*. Journal of Polymer Enginnering and Science 39**(1)**:177-189 (1999).