

Obtention and Characterization of Polypropylene, Calcium Carbonate and Poly(ethylene-co-vinyl acetate) Composites

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Abstract: In the increasingly competitive market, the survival of the industries that manufacture components or pieces of polymer is strictly linked to the reduction of production costs. An alternative could be the use of composites of polypropylene, calcium carbonate and poly(ethylene-co-vinyl acetate) for the production of thermoplastics sheets. The thermoplastics sheets obtained by extrusion and co-extrusion processes were characterized through the chemical, physical, thermal, mechanical and morphological characteristics of materials, enabling the performance analysis of the production processes and application to the design of components or parts. The results showed that the addition of 30 wt% CaCO₃-EVA increased the thermal stability of polypropylene (PP) around 32°C, decreasing the processing temperature of composites in 15°C, also by decreasing the crystallinity of the polymer from 43% to 30% and the deflection temperature of plastics under flexural load in the edgewise position (DTUL) from 122°C to 107°C. Regarding to the mechanical tests, the yield stress of the composites obtained by extrusion and co-extrusion processes decreased with the addition of CaCO₃-EVA. According with the obtained results, we suggest that PP/CaCO₃-EVA composites could be used in the production of polymeric parts or components where tensile strengths higher than 25 MPa are not required and for service temperatures between 30°C and 70°C.

Keywords: Composites, polypropylene, CaCO₃-EVA, thermoplastics sheets.

1. INTRODUCTION

The mechanical properties of thermoplastic resins are sometimes unsuitable for certain specific applications. To overcome this, several fillers are added to impart better properties to the end material. Composite materials are manufactured to give unusual combinations of properties not found in a single material, such as strength, toughness, weight, hardness, conductivity, corrosion resistance, high temperature performance, among others [1, 2]. A wide variety of natural minerals have been introduced as fillers since 1930 in thermoplastic polymers to reduce the cost of the end product [3]. Studies have shown that filler loads play an important role in modifying the properties of polymers and found that its addition offers an effective means for improving the mechanical properties of polymeric materials. The fillers traditionally used in the industry include calcium carbonate, talc, alumina, etc., and in addition require large amounts to achieve the desired performance [3].

Polypropylene (PP) is a thermoplastic polymer whose volume utilization is growing worldwide. The annual world production of this resin is above 109 tons, with a growth rate higher than that of most plastics [4].

The PP has low cost and suitable properties to industrial and consumer products. It is a lightweight, flexible, excellent chemical resistance polymer and it has a high melting temperature. All these good properties contribute to its extensive range of applications [5]. The use of polypropylene as polymer matrix to obtain composite materials is still the subject of scientific research and technological development, due to the large attractive low cost of these composites for several different applications [5, 6]. The major advantage of introducing fillers on polypropylene is the increase in stiffness of the composites obtained, which is particularly important in applications where these materials are exposed to high temperatures. Polypropylene is transformed into articles such as bumpers for cars, bags, food packaging and containers for use in microwave ovens [7].

Calcium carbonate (CaCO₃) is one of the most used fillers to produce composites [8]. It is commonly used by manufacturers as filler in composites based on poly(vinyl chloride), while its application on polyesters and thermoplastic elastomers presents a moderate growth. The poly(ethylene-co-vinyl acetate) known as EVA can be used to improve the impact resistance of isotactic polypropylene [9]. Due to its partial polarity, acetate co-polymer also acts as compatibilizer between nanoclays and polypropylene [10].

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When fillers are added to polymeric matrices, normally they reduce the impact energy of the polymers [11]. A mineral filler may modify the characteristics of a polymer. The properties of the particles themselves (for instance its size, shape and module) can have a significant effect, especially on the mechanical properties, such as specific strain. The heterogeneous phase may also change the structure of the polymer matrix. Particles can act as a nucleating agent for crystallization or decrease the crystallinity by reducing the kinetics. The decreased mobility of the polymer chains by kinetic impediment leads to the development of small crystals and non uniform, forming a crystalline phase of low heat of fusion [12, 13]. The introduction of fillers in the polymer matrix results in a heterogeneous system, which under the effect of external load induces stress concentration with a magnitude that depends on the geometry of the particles [14]. The CaCO_3 particles can be found in the form of pellets when combined with a thermoplastic (masterbatch) and during processing, clusters need to be dispersed into primary particles in the molten polymer [2]. The effects of the aggregates on the properties of the composite are clearly detrimental, since many authors emphasize this fact, suggesting alternatively a good homogeneity of the dispersion of the particles in the polymer matrix [15].

The study, e.g. Zuiderduin *et al.* analysed composites containing polypropylene and calcium carbonate were prepared in a twin screw extruder with volumes between 0% and 32% of CaCO_3 , which we evaluated the influence of particle size (0.07 to 1.9 mm) and surface treatment (with and without stearic acid). The results of the mechanical tests showed an increase in modulus and decrease in flow stress with the amount of filler present. In the differential scanning calorimetry (DSC) test, the results showed that the particle size does not significantly influence the melting temperature (T_m) and melting enthalpy (ΔH_f) of polypropylene. Load volumes exceeding 20% favored the appearance of problems related to dispersion of the particles in the polymer matrix, lowering the toughness of the composite [16]. Only good dispersion promotes wide contact area between the load and the polymer, facilitating interaction between the polymer chains and filler particles. The scientific and technological developments of composites containing calcium carbonate suggest the use of large amounts of filler, keeping the properties of the melt flow and surface quality of the products [17]. Plates produced with thermoplastic polymers usually have a thickness

greater than 0.254 mm and can be commercially produced by extrusion [18] and co-extrusion with up to 4 m wide [19], aided by a set of calenders. The calendering process is complementary to the extrusion of films and sheets being used to produce films at high speeds and sheets loaded with fillers [20]. The co-extrusion process corresponds to the simultaneous extrusion of two or more materials out of a single array, being equipped with independent extruders for each layer formed. Through single manifold, the combination of the layers is performed before the matrix and the various materials flow in a multilayer set [21]. In most industrial applications, the plates are semi-manufactured and intended for subsequent forming processes like vacuum forming, plug-assisted pressure forming and vacuum forming snap-back [20].

The objective of this study was to evaluate the physico-chemical properties of composites of polypropylene and PP/ CaCO_3 -EVA to be used in the production of thermoplastic flat plates, as an alternative to reduce the cost of manufacture of components or parts. After obtaining the plates by thermoplastic extrusion and co-extrusion, samples have been characterized through its chemical, physical, thermal, mechanical and morphological properties, enabling the analysis of the performance of production processes in the design and use of components or parts.

2. MATERIALS AND METHODS

2.1. Materials

The commercial polymer PP (PH0141) was supplied by Braskem S.A. (Density: 0.912 ± 0.015 g/cm³; melt flow index (MFI 230°C/21.6 N): 1.8 ± 0.4 g/10 min; \overline{M}_n : $75,5 \times 10^3$ g/mol; \overline{M}_w : 395×10^3 g/mol; IP : 5.232). PH0141 is a homopolymer additivated with antioxidant, clarifying and nucleating agents, being normally used in extrusion and co-extrusion of flat plates. The masterbatch containing CaCO_3 (80 %), poly(ethylene-co-vinyl acetate) (16%) and coupling agents based on polyolefins (4%) was kindly supplied by Karina Plastic Industry Ltda (density: 2.116 ± 0.025 g/cm³, average particle size of CaCO_3 : 2.4 μm). This masterbatch act as filler and provides a good dispersion in the polypropylene matrix. To improve the visual aspect such as brightness and hue of the final product, small amount of white pigment in the form of commercial masterbatch containing titanium dioxide (80%), polyethylene (16%) and the coupling agents base polyolefin resins (4%), were used in the formulation of the composites.

Table 1: Formulation of Polymeric Composites

Layer*	PP/CaCO ₃ -EVA/Masterbatch (%, by weight)							
	A	B	C	D	E	F	G	H
One	95/0/5	85/10/5	75/20/5	65/30/5	-	-	-	-
E _s	-	-	-	-	95/0/5	95/0/5	95/0/5	95/0/5
I _T	-	-	-	-	95/0/5	85/10/5	75/20/5	65/30/5
E _i	-	-	-	-	95/0/5	95/0/5	95/0/5	95/0/5

*Layer: E_s (upper layer), I_T (middle layer) e E_i (lower layer).

2.2. Formulation and Preparation of Polymeric Composites

The composition of PP based composites obtained by extrusion (samples A, B, C and D) and co-extrusion (samples E, F, G and H) process are shown in Table 1. With the scope of keeping the surface characteristics of thermoplastics sheets, only the inner layer was modified with CaCO₃-EVA, and polypropylene and masterbatch were used in the lateral feed of the superimposed layers (samples E, F, G and H). The inner layer was codified as I_T and the side layers as E_s (upper layer) and E_i (lower layer).

The formulations were weighed and homogenized in a helical mixer for 15 min. Using the extrusion or co-extrusion, the polymer composites have been applied in the production of thermoplastic sheets, at temperatures between 195°C and 240°C. The extrusion and co-extrusion lines (Rulli Standard) are composed by one extruder (screw diameter: 130 mm) and two extruders with screw diameters of 75 mm. The screws have a L/D 34:1 and the matrix was flat-die with an overall width of 1600 mm. In the co-extrusion of thermoplastic sheets, the feed block was exclusively designed for three separate streams formed by independent extruders. The thickness of each layer of composite samples obtained by co-extrusion process were E_s (0.218 ± 0.002 mm), I_T (0.528 ± 0.002 mm) and

E_i (0.254 ± 0.002 mm). The sheets were laminated and cooled to 30 ± 5°C by calendering process (cooling rolls).

For the tensile tests, the sample specimens were prepared by extrusion and co-extrusion with a thickness of 1.00 mm and 10.00 mm wide. The specimens were cut with metal knives and sent to the tensile tests (Figure 1). The other properties were measured using only the samples of the extrusion process.

2.3. Characterization

The MFI experiments were carried out according with ASTM D1238-04c [22] in an automatic plastometer (Gottfert, temperature of 230°C and load of 21.6 N).

The Fourier transform infrared spectra (FTIR) were recorded using attenuated total reflection (ATR) regime using a Perkin-Elmer spectrometer with a resolution of 4 cm⁻¹. The spectra were obtained in wave number region of 4000-650 cm⁻¹ using 16 scans. Before film analysis, an open beam background spectrum of clean crystal was recorded.

The thermogravimetric experiments (TGA) were performed with a Shimadzu instrument (model TGA 50). Samples were heated from 20°C to 900°C at a



Figure 1: Specimens obtained by extrusion and co-extrusion used in tensile tests.

heating rate of 10°C/min, under nitrogen atmosphere (50 mL/min). Thermal transitions were determined using DSC. DSC measurements were carried out on a DSC Q200 (TA Instruments). Samples were heated from room temperature up to 200°C at 10°C/min, under nitrogen atmosphere and quenched (fast cooling) from 200°C up to 30°C. The DSC data were obtained from the first heating.

In the deflection temperature experiment (DTUL), the deflection temperature of plastics under load is measured. It is a measure of a polymer's ability to bear a given load at elevated temperatures. The sample, initially at 23°C and under a load of 1.28 MPa in the center of the specimen, was heated in a bath at a heating rate of 2.0 ± 0.02 °C/min. The DTUL was measured when the deformation of sample achieved 0.254 mm.

Density measurements were carried out according with ASTM D792-00 [23]. The liquid used in the experiments was ethanol up to the density limit of 1.0 g/cm³, after this limit, water was used.

Tensile tests were performed in an Emic tensile machine (model 2000) with the separation grips of 100 mm. A load cell TRD-26 of 20 kN was used. The flat plate specimens were conditioned at 23 ± 2 °C, RH of 50 % for 5 days and the speed was 25 mm/min.

The morphology of samples was evaluated through scanning electron microscopy (SEM) in a microscope Philips (model XL 30). The morphology of samples obtained from cryogenic fracture was assessed.

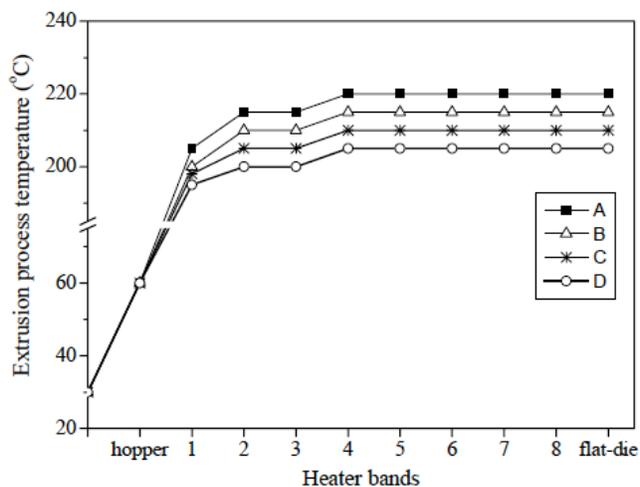
3. RESULTS AND DISCUSSION

3.1. Production of Thermoplastic Plates and MFI Analysis

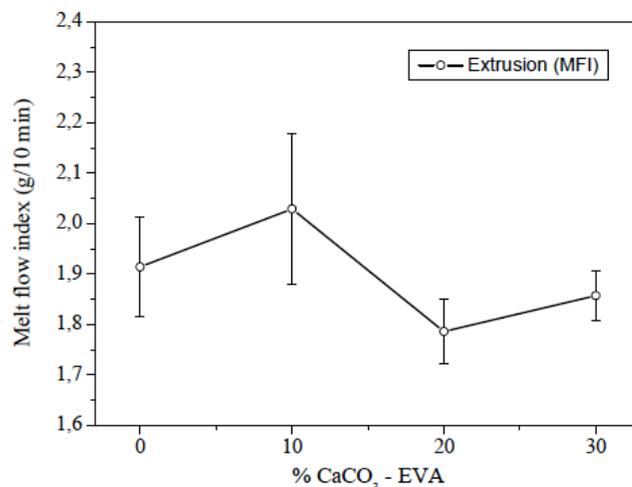
The flat plates were fabricated with dimensions of 1080 mm width and 1 mm thickness. The temperatures of extrusion processing and MFI measurements are shown in Figure 2a and 2b, respectively. It can be seen that by adding CaCO₃-EVA the processing temperature of the polypropylene composites gradually decreased 5°C per each 10 % addition of CaCO₃-EVA, probably due to the different heat capacities of the components of test sample A. In co-extrusion experiments, (samples E, F, G, H), the layers E_S and E_I showed temperatures equivalent to the processing by extrusion. In tests E, F, G, H; the I_T layer showed temperatures equivalent to the tests A, B, C and D. Through the co-extrusion process it was possible to preserve the surface characteristics of thermoplastic flat plates conferred by the polymer without the presence of CaCO₃-EVA. Figure 2b shows the MFI as a function of CaCO₃-EVA amount. The results show that the MFI of the polypropylene did not change considerably with the addition of 10% to 30% CaCO₃-EVA. The non-linear variation of MFI of PP composites with the increasing addition of CaCO₃-EVA is observed in function the commercial polymer PP (PH0141) has melt flow index of 1.8 ± 0.4 g/10 min for the same manufacturing batch.

3.2. Composition and Chemical Structure

The FTIR spectra of polypropylene composites are shown in Figure 3a and 3b. Through the FTIR analysis it was possible to identify the groups characteristics of



(a)



(b)

Figure 2: (a, b) Processing temperatures of extrusion (a) and MFI (b).

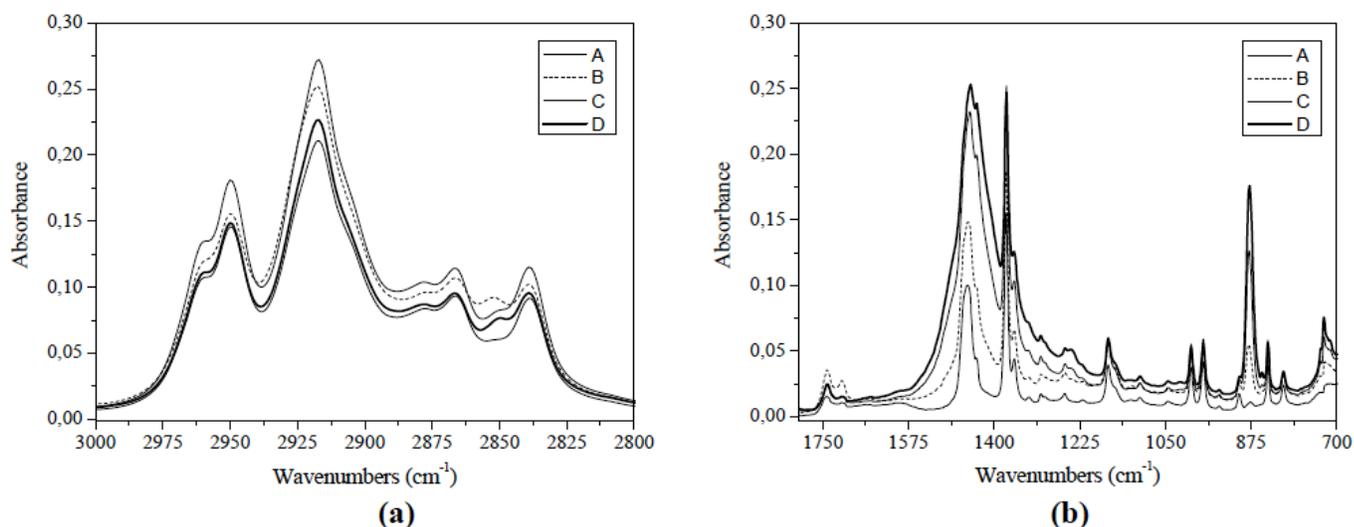


Figure 3: (a, b) FTIR spectra of PP/CaCO₃-EVA composites.

isotactic PP used in the formulations. The spectra showed the presence of four bands located between 3000 cm⁻¹ e 2800 cm⁻¹ (2956 cm⁻¹, 2921 cm⁻¹, 2875 cm⁻¹, 2840 cm⁻¹). Another band common for all materials was in 1371 cm⁻¹.

The FTIR technique allows quantitative and qualitative analysis to identify, for instance, the presence and concentration of fillers, impurities and other ingredients. Through the overlap of the spectra (Figure 3a and 3b) the major changes in polypropylene composites were analyzed.

The bands near 2920 cm⁻¹ and 2850 cm⁻¹ indicate the vibrations of asymmetric and symmetric stretching of the grouping (CH₂), respectively, being characteristic of polyethylene. For polyethylene, it is also evident the deformation of the swing type (CH₂) at 727 cm⁻¹. It was also possible to note the band of (C—O) group of vinyl acetate at 1020 cm⁻¹. According with the literature [24], the spectrum of poly (ethylene-co-vinyl acetate) with 20% vinyl acetate presented the stretching vibrations of the type (C—O) at 1020 cm⁻¹ and type balance (CH₂) at a wave number of 720 cm⁻¹, with absorbance values of 0.253 and 0.138 respectively. Through the analysis of

spectrum of Figure 3b, the absorbance values at 1020 cm⁻¹ and 727 cm⁻¹ were respectively 0.157 and 0.327, which indicates the presence of approximately 5.24% of vinyl acetate in the composition of copolymer. The band identified at approximately 1740 cm⁻¹ is the frequency of vibration of carbonyl group (C=O). While the region in the infrared spectrum between 1750 cm⁻¹ and 1725 cm⁻¹ is characteristic of the ester functional group [25].

Other two specific bands, located throughout the overlapping of the spectra (Figure 3b) were near 1415 cm⁻¹ and 872 cm⁻¹. These bands characterize the presence of the inorganic functional group carbonate ion (CO₃)⁻², which is in agreement with literature data [25]. These studies clearly showed that the first absorption between 1490 cm⁻¹ and 1410 cm⁻¹ is intense and broad, being characteristic of carbonate ion (CO₃)⁻² functional group. The second absorption between 880 cm⁻¹ and 860 cm⁻¹, also from carbonate group ion is narrow and has a low to medium intensity [25].

3.3. Thermal Properties

The thermal stability of composites were evaluated by TGA (Table 2). The onset temperature of sample D

Table 2: TGA Data of PP/CaCO₃-EVA Composites (Under Air Flow, 10 °C/min)

Sample	PP/CaCO ₃ -EVA/Masterbatch (% , by weight)	Onset temperature (°C)	Endset temperature (°C)	Maximum temperature (°C)
A	95/0/5	429	494	474
B	85/10/5	445	500	481
C	75/20/5	453	504	486
D	65/30/5	461	506	494

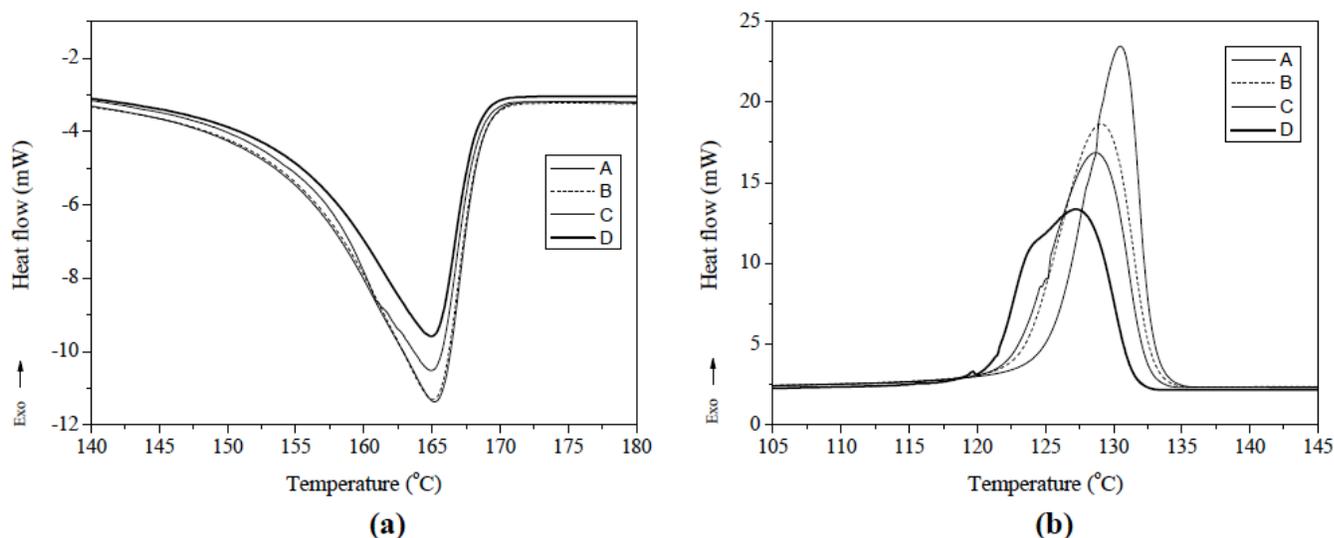


Figure 4: (a, b) DSC scans for PP/CaCO₃-EVA composites: thermal parameters T_m (a) and T_c (b).

(30 wt% CaCO₃-EVA) showed an increase in the thermal stability (around 32°C) when compared to sample A. The degradation temperature increased with an increasing in the concentration of CaCO₃-EVA and eventually in the function to the amount of inorganic particles of calcium carbonate contained in the composites.

DSC of PP/CaCO₃-EVA composites (Figure 4a and 4b) revealed that the polymer matrix undergoes cold crystallization upon heating. The effect of CaCO₃-EVA addition on polypropylene that melt-blending by extrusion process does not lead to significant modification of thermal parameters such as the melting temperature (T_m) and cold crystallization temperature (T_c).

The peak of cold crystallization temperature (T_c) was recorded for CaCO₃-EVA composites at lower values when compared to PP (sample A), which attests the reduction of nucleation effects conferred by the microfiller. Table 3 shows the decrease in PP (sample A) melting enthalpy (ΔH_f) and in the crystalline values from 43% to 30%, which was triggered by the CaCO₃-EVA addition in the extrusion process. For higher

amounts of CaCO₃-EVA (30 wt%), the level of crystallinity decreased, a behaviour that can be attributed to possible aggregation and poorer dispersion. According the study, e.g. Zuiderduin *et al.* investigated crystallization exotherms of calcium carbonate were measured as a function of CaCO₃-EVA content. Untreated particles, however, interfere with the crystallization process of the polypropylene phase and the melting enthalpy (ΔH_f) is lowered when the particle content is increased. The CaCO₃ particles do not act as a nucleating agent in polypropylene since the crystallinity is not increased.

3.4. Deflection Temperature Under Load (DTUL) and Density Analysis

The deflection temperature test results are a useful measure of relative service temperature for a polymer when used in load-bearing parts. Figure 5 shows the DTUL and density of de CaCO₃-EVA composites. DTUL of PP composites decreases with the increase of CaCO₃-EVA weight content. The highest filler concentration (30 wt% the CaCO₃-EVA) reduced the DTUL values around 15°C, and this may be due to a lowering of the mobility of the polymer chains at this

Table 3: T_m , T_c , ΔH_f and Crystallinity as Function of CaCO₃-EVA Content

Sample	PP/CaCO ₃ -EVA/Masterbatch (%, by weight)	T_m (°C)	T_c (°C)	ΔH_f (J/g)	Crystallinity (%)
A	95/0/5	168	130	81	43
B	85/10/5	165	130	73	39
C	75/20/5	165	129	65	35
D	65/30/5	164	127	57	30

high filler load. We suggest that PP/CaCO₃-EVA composites could be used in the production of polymeric parts or components where the thermal resistance of polypropylene required is between 30°C and 70°C.

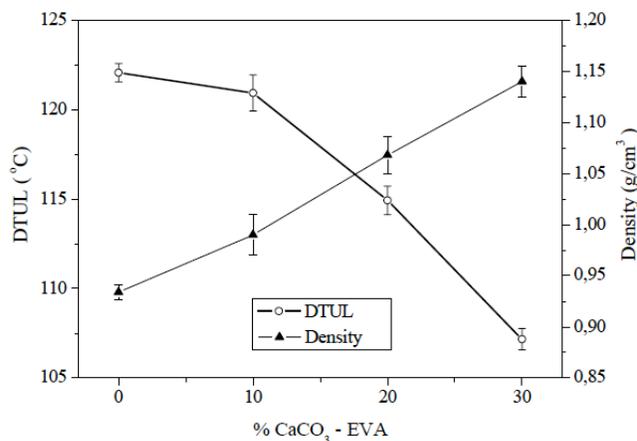
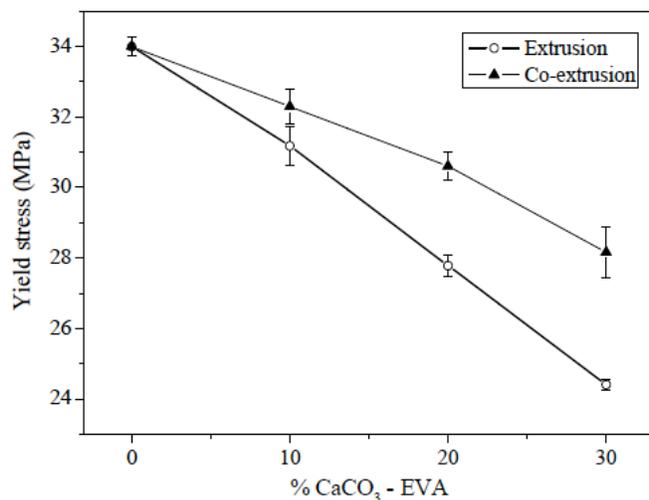


Figure 5: DTUL and density of PP/CaCO₃-EVA composites.

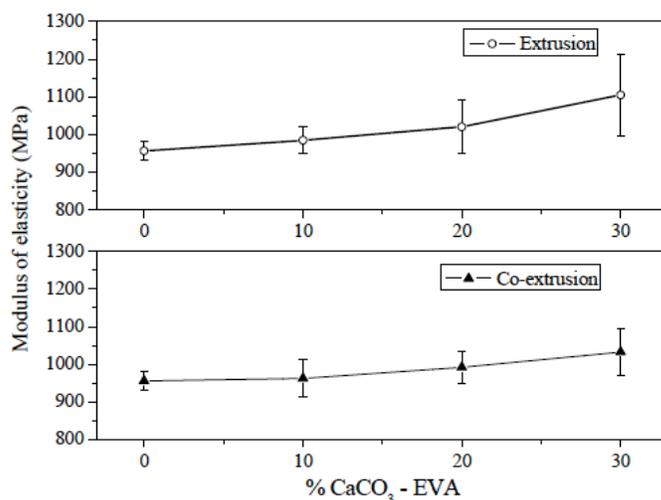
The density of PP composites increases with the increase of CaCO₃-EVA weight content. The densities of the CaCO₃-EVA and polypropylene are: 2.116 g/cm³ and 0.912 g/cm³, respectively. Therefore, the thermoplastic sheet thickness must be changed to maintain the weight of the polymer components or parts.

3.5. Mechanical Properties

The material tensile properties are shown as a function of yield stress and modulus of elasticity. The yield stress (Figure 6a) is plotted as a function of CaCO₃-EVA concentration. It should be noted that the



(a)



(b)

Figure 6: (a, b) Yield stress (a) and modulus of elasticity (b) as function of CaCO₃-EVA content.

yield stress decreased upon addition of the CaCO₃ filler. CaCO₃ modified PP composites showed a decrease of the yield stress, which must be probably due to the debonding of the filler particles from the polypropylene polymer matrix. The modulus of elasticity (Figure 6b) is increases with CaCO₃-EVA content. The stiffness have increased from 956 to 1105 MPa (extrusion process) and from 956 to 1032 MPa (co-extrusion process) by adding 30 wt% of CaCO₃-EVA. It should be noted that the results of yield stress and modulus the materials composites are a function of the cross-section depends of the manufacturing process applied to produce the samples (extrusion or co-extrusion process). Others materials, such as ethylene in the structure of poly(ethylene-co-vinyl acetate) and titanium dioxide, should also have contributed, in a small scale, to reduce the yield stress and to increase the modulus of elasticity of the composites.

3.6. Morphology

The morphology of cryogenic fracture of PP/CaCO₃-EVA composites obtained by extrusion process is shown in Figure 7. The morphology of the compounds up to a concentration of 20 wt% CaCO₃-EVA (sample C) shows that the aggregates have been well distributed in the polypropylene matrix during the extrusion process. It is not clear from SEM images, shown sample D, that the aggregates have been broken up to the primary particles.

Figure 8 shows the morphology of cryogenic fracture of PP/CaCO₃-EVA composites obtained by co-extrusion process. The morphology of the samples

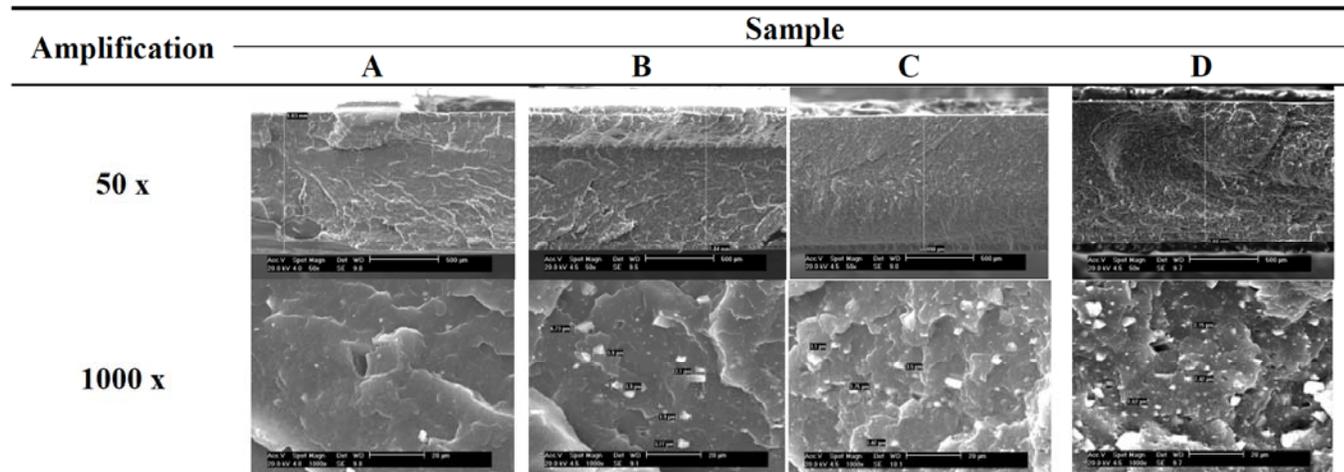
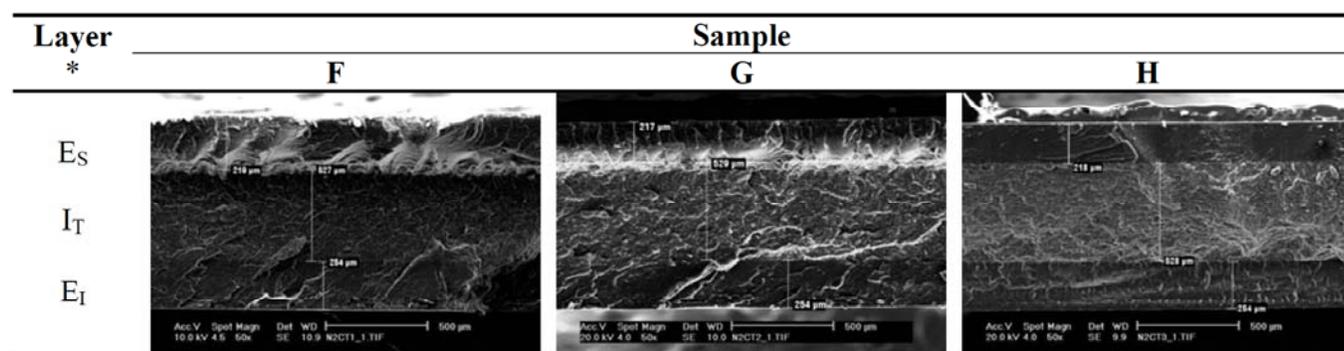


Figure 7: Scanning electron microscope images of morphology of PP/CaCO₃-EVA composites.



*Layer: E_S (upper layer), I_T (middle layer) e E_I (lower layer).

Figure 8: SEM images of PP/CaCO₃-EVA composites of co-extrusion process (50x).

shows fine interaction between E_S, I_T, and E_I layers. The thickness of each E_S, I_T, and E_I layers of composites obtained by co-extrusion process were respectively for samples F (0.219; 0.527 and 0.254 mm), G (0.217; 0.529 and 0.254 mm) and H (0.218; 0.528 and 0.254 mm).

The dispersion of the filler is critical in the compounds when a concentration of 30 wt% CaCO₃-EVA (sample D) is used. Complementary results show that the mechanical properties (yield stress and modulus of elasticity) the later depends strongly of the dispersion of particles in polypropylene matrix by manufacturing process.

4. CONCLUSIONS

The processing temperature of the polymer composites was gradually reduced by 5°C with the addition of CaCO₃-EVA. Through the co-extrusion process it was possible to preserve the surface characteristics of thermoplastic flat plates. The results show that the MFI of the polypropylene was stable.

Through the FTIR spectra analysis it was possible to identify isotactic polypropylene, which exhibits the configuration constituted by the atomic arrangement responsible for the best commercial properties to the polymer. The values for the absorbances at 1020 cm⁻¹ and 727 cm⁻¹ indicate the presence of approximately 5.24% of vinyl acetate in the copolymer composition. Other two specific bands located near 1415 cm⁻¹ and 872 cm⁻¹ were observed, characterizing the presence of inorganic functional group of carbonate ion (CO₃)²⁻.

Results showed that the addition of 30 wt% CaCO₃-EVA increases the thermal stability of polypropylene around 32°C and decreases the crystallinity of the polymer from 43% to 30%. The highest filler concentration (30 wt% the CaCO₃-EVA) reduced DTUL values around 15°C and this may be due to a lowering of the mobility of the polymer chains at this high filler load. The yield stress is decreased upon addition of the CaCO₃ particles and the modulus of elasticity of composites is increased.

Morphology of the compounds up to a concentration of 20 wt% CaCO₃-EVA (sample C) showed that the

aggregates have been well distributed in the polypropylene matrix however the dispersion of the filler is critical in the compounds when a concentration of 30 wt% CaCO₃-EVA (sample D) is used.

We suggest that PP/CaCO₃-EVA composites could be used in the production of polymeric parts or components where tensile strengths higher than 25 MPa are not required and for service temperatures between 30°C and 70°C. Furthermore, as the density of PP composites increases with the increase of CaCO₃-EVA weight content, therefore, thickness of the thermoplastic flat plates must be changed to maintain the weight of the polymer components or parts.

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