A Study on the Role of Eggshell Particle Size in Polypropylene Composite Properties

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ABSTRACT

Calcium carbonate was extracted from eggshell (ES) and its particle size was reduced in a three steps process resulting in three different sizes. Particles obtained were mixed with polypropylene in a Brabender mixer. The effect of particle size on thermal and mechanical properties and the use of stearic acid (SA) as a coupling agent were studied. Differential scanning calorimetry (DSC), thermogravimetrical analisys (TGA) and dynamic mechanic analysis (DMA) were employed in this research work. According to DSC results particle size and SA has a synergetic effect on crystallinity; the smaller the particle size, the higher the crystallinity, and the presence of SA also increased this property. It was needed a 20 %w of eggshell particles and SA to increased 5 °C the thermal stability of PP, for smaller ratios this property do not have significant changes. By the other hand, the coupling agent and just 0.5 %w of ES from the second attrition increased 800 MPa storage modulus of PP.

KEYWORDS: Polyprolylene, Eggshell, composites, crystallinity.

I. INTRODUCTION

Crystallization in polymers occurs when an amorphous material is turned into an ordered state or a crystalline form, it carries out in solution [1] or in the melting state [2]. In crystallization from the melting state, the polymer is heating until or near of its melting point in such a way that crystals are formed from the liquid polymer. If this process is held in a constant temperature occurs an isothermal crystallization, by the other hand, if it is used a ramp of temperatures a non-isothermal crystallization takes place.

Crystallization occurs in two steps; nucleation and crystal growth. Firstly, a series of "seed" crystals or nucleus are formed during primary nucleation; they have the commitment of start the growth in a melt polymer that contents no crystals in it. Then, nucleus magnitudes begin to increased and consequently, the crystal dimension enlarged too [3].

When nucleation happens in the presence of a foreign surface or nucleation agents an heterogeneous nucleation takes place, otherwise an homogeneous nucleation leads the crystallization [4]. Regularly, nucleation agents are solids with different shapes, sizes and origins. Natural fibers [5], synthetic fibers [6], mineral particles [7-9] and waste materials of natural origin such as eggshell [10] or shellfish shell [11] has been used to reinforced polymers and found that they also promote and enhanced crystallinity.

One of the most important polymers due to its versatility is polypropylene (PP), it is a semicrystalline thermoplastic polymer; it is obtained from the polymerization of propylene or propene. PP is part of the olefins group and it is used in a wide variety of applications such as food packing, fibers, laboratory equipment, automobile parts and films [12]. It discovered is attributed to Professor Giulio Natta in 1954 and its industrial production began in 1957 [13].

Many materials has been used in the reinforcement of polymers, recently natural origin ones, specifically natural byproducts have called attention because they are cheap, affordable and provides of certain biodegradability [14]. Among these materials eggshell is a promising resource because it is mainly composed of $CaCO_3$ [15], a ceramic compound that has been intensely studied due its ability of enhanced mechanical properties and promote crystallinity in polymers [9, 16, 17]. Deshmukh y col. en el 2010 [18] mixed polibutilentereftalate and $CaCO_3$, crystallinity inccreased 5.1% with a content of 5%w of the ceramic. Thermal stability is also another property that is affected in the presence of calcium carbonate, for example, Avella et al. (2005) [16] increased 14 °C PP degradation temperature using $CaCO_3$ emulsion-coated with a graft copolymer of isotactic polypropylene-*co*-maleic anhydride.

In this research work PP and 3 different particle sizes of eggshell were compound using a Brabender mixer; crystallinity, thermal stability and storage modulus from dynamic mechanical analysis (DMA) were studied. It was employed two mechanical attritions and an ultrasonic treatment in order to reduce particle size [19]. Stearic

acid (SA) was used as compatibilizer. It was found that SA and eggshell has a synergetic effect that increased crystallinity in PP, particle size is also a key factor that affect crystallinity.

II. MATERIALS AND METHODS

Materials

Eggshells (ES) were collected from household waste and washed with water. Acetone analytic grade was purchase from Analytyka. ES particles were suspended in distillated water during the ultrasonic process. Polypropylene (PP) with a melt flow value of 12 g/10 min and a density of 0.9 g/cm^3 was provided by INDELPRO, Altamira. Stearic acid (SA) distributed by Fermont with 50.5% purity was used to improve the interaction between PP and the $CaCO_3$ obtained from eggshell.

CaCO3 particles size reduction

Eggshells were grinded using a blender (**B**), ES powder was soaked in acetone for 2 h in order to separate the $CaCO_3$ from organic compounds. A second size reduction of $CaCO_3$ particles (**M_{10}**) was performed in a SPEX 8000M high energy ball mill for 10 h using distillated water as lubricant. Finally the particles were suspended in distillated water for 5 h for further size reduction (***US***) [19] in an UP200Ht Hielscher ultrasonic horn, with 26 KHz frequency, a wave amplitude of 100% and a tip diameter of 7 mm. The pulse was set in 100% for a continuous operation. The ratio mass/volume of suspension during sonication was fixed in 5%.

Composites preparation

Composites were prepared in a Brabender Intellitorque mixer with roller blades, using 100 rpm and a mixing temperature of 190 °C during 10 minutes. The formulations of PP-ES were: 4, 6, 10 and 20% by weight (w) for particles **(B)**, 0.5, 1, 2, 4, and 6%w for particles **M_{10}** and **US**. It was used 0.5%w of SA in relation of the total amount of material in the chamber, and it was incorporated during the mixing, some samples did not were mixed with SA with the aim to evaluate the effect of SA on composites.

Particles and composites characterization

Particle size was measured in a Malvern Nano ZS Nano ZS, using the dynamic light scattering (DLS) technic, distilled water was utilized as a suspension media.

The crystallization percentage $(\boldsymbol{x})$ was obtained by differential scanning calorimetry (DSC) using a Perkin Elmer Pyris 1 DSC. First, samples were heating from 50 to 200 °C, and then cooling from 200 to 0 °C using a 10 °C/min heating and cooling rate, in order to eliminate the thermal history and then a second heating was carried out from 0 to 200 °C with a heating rate of 10 °C/min. Crystallization was calculated using the next equation:

$$(\boldsymbol{x}) = \frac{\Delta H_f}{\Delta H_f^{\circ}(PP\ mass\ fraction)} \times \mathbf{100} \qquad \textbf{Eq. 1}$$

Where ΔH_f° is the heat of fusion for 100% crystalline PP. In this case ΔH_f°=137.9 J/g [20].

Thermal behavior of all samples was studied by means of a SDT Q600 analyzer, from ambient temperature until 1000 °C, with a heat rate of 10 °C/min, in a nitrogen atmosphere.

Rectangular specimens were elaborated by compression at a temperature of 240 °C and 10 ton according to ASTM-D638 standard. DMA analysis was carried out in a TA instruments model Q800, from -40 to 150 °C with a heating rate of 5 °C/min and a frequency of 1 Hz, in order to evaluate the thermomechanical behavior.

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III. RESULTS AND DISCUSSION

Particle Size

After each step of the mechanical size reduction process, particle size is reduced as it was expected. Table 1 shows that after the use of the blender the particle size is 59.5 µm, when particles are ball milled its size diminish 92.6% until 4.4 µm, finally after the use of ultrasound the size reach 329 nm. Again, the size reduction from sample M_{10} to sample US is 92.5%. Even when the total size reduction is 99%, particles do not reach the nanoparticle category. In 2013 Hassan et al [19], developed the size reduction method used in this article, they observed agglomerates of ES nanoparticles by microscopy, and confirm the size reduction by an increased in surface area.

Table 1. Particle size determinated by means DLS

Sample	Particle size (µm)
B	**595**
M_{10}	**4.4**
US_a	**0.329**

Crystallinity

The table 2 shows crystallinity of PP and all samples. PP/ESB composites do not show in increase of $\boldsymbol{x}$, compared with PP PP. The addition of SA reduces PP crystallinity in 15%, however SA produces a sinergetic effect whit particles **B** as it can be observed in composites 6 and 20% B, they practically equal the crystallinity of PP. It has

been proved that calcium carbonate with the aid of a surfactant can increased the PP crystallinity as they act as nucleating agents. As an example Pradittham et al. in 2014 [21] increased this parameter in 7% with 1.5%w of this ceramic material and palmitic acid.

For composites with $\mathbf{M_{10}}$ particles, the behavior is different; at lower concentrations composites shows a similar crystallinity of that of PP, but for 2 and 4% $\mathbf{M_{10}}$ composites $\boldsymbol{x}$ is lower. However when concentration of $\mathbf{M_{10}}$ particles is 6% crystallinity increases to 16.5%. This behavior is attributed to a good dispersion of particles in PP matrix, this behavior was reported previuosly[21]. Composites crystallinity is higher than PP $\boldsymbol{x}$ when SA is mixed with $\mathbf{M_{10}}$ particles. For this materials, composite 2% $\mathbf{M_{10}}$ has the highest value, it reached an increase of 10.8% compared to composite 6% $\mathbf{M_{10}}$ without SA. It can be highligth that the concentration of particles needed to increase $\boldsymbol{x}$ is considerably lower.

Particle size and the use of a compatibilizer play a key role in the increased of crystallinity; data presented in table 2 demonstrate that the lower the particle size the higher $\boldsymbol{x}$, this is also true for PP/ES-US composites. It was expected that US particles increased even more this property because of the lower particle size that these materials have, but is just slaigthly higher for this particles compared with PP/ES-M_{10} composites. In 2006, Shentu et al. [22] reports a x value similar that obtained for PP/ES-4% **US** + SA composite prepared in this investigation. They employed 1% by mass of $CaCO_3$ nanoparticles (80 nm), and oleic acid as compatibilizer. They attributed the increment of this property to a heterogeneus crystalization. It is clear that the smaller the particle size the less amount of filler is needed to increased crystallinity.

Table 2 Crystallinity of PP and composites with (SA) and without (wSA) stearic acid.

	Crystallnity (%)	
Sample	**w/AE**	**AE**
PP	43.1	27.3
4% B	43.7	35.9
6% B	29.4	41.4
10% B	38.3	34.7
20% B	32.8	43.7
0.5%M10	47.8	49.8
1% M10	44.5	51.3
2% M10	39.9	53.9
4% M10	38.8	45.1
6% M10	59.6	46.4
0.5 % US	43.9	46.1
1% US	43.1	50.7
2% US	51.1	43.4
4% US	45.9	55.8
6% US	48.2	51.3

*w/AE: without stearic acid, AE with stearic acid

Themogravimetric Analysis

In regard of thermal degradation temperature (T_d) there is a slightly increased between 3 and 4 °C when $CaCO_3$ is added to PP matrix and this behavior is similar for all composites without compatibilizer, In table 3 are presented the results obtained from TGA. The addition of the organic acid increased T_d, and $\mathbf{M_{10}}$ particles are the ones that record the highest temperatures.

There is not a clear tendency between particle size and T_d because temperatures are very similar among all composites. However the amount of filler and the surfactant have an influence on this property. This was observed in sample 20% **B** in which there is 5 °C of difference between this material and PP. Boronat et al in 2015 [23], used 25 µm ES particles to prepared bio-polyethylene composites they also found that 20%w of ES plus the aid of a coupling agent increase this property. Hence, the amount of $CaCO_3$ it does have an influence in polypropylene thermal stability.

Table 3 Thermal degradation temperature of PP and composites

	Decomposition temperature (Td), ºC	
Sample	**w/AE**	**AE**
PP	458	460
4% B	461	461
6% B	462	461
10% B	461	462
20% B	462	463
0.5%M10	462	463
1% M10	462	462
2% M10	461	462

4% M10	462	463
6% M10	462	460
0.5 % US	462	462
1% US	462	462
2% US	461	462
4% US	463	461
6% US	463	462

*w/AE: without stearic acid, AE with stearic acid

Dynamic Mechanical Analysis (DMA)

According to Figure 1a, **B** particles increased storage modulus (E') in PP matrix; for composites 4, 6 and 10%w E' is practically the same, but for composite 20% **B** is 460 MPa bigger than PP. The addition of stearic acid ~~to PP~~ (Figure 1b) increased E', but in this case, it seems that no synergetic effect is done with $CaCO_3$, except for composite 20% **B** + SA, in which E' is slightly smaller than its homologous without SA.

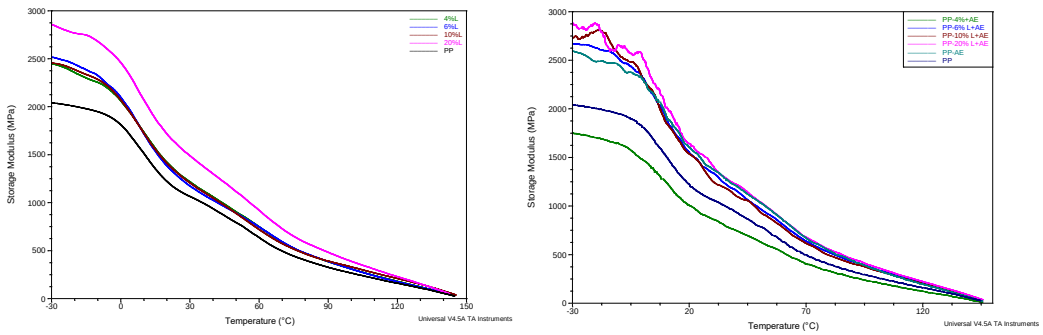

Figure 1. Storage modulus versus temperature for PP/ES B composites: a) without stearic acid and b) with stearic acid.

For $\mathbf{M_{10}}$ composites (Figure 2a) the storage modulus stay around the PP E' value, but when SA (figure 2b) is added this property increased around 2000 MPa with 0.05%w of this particles, even bigger than the value found for composite 20% **B**. In these materials, ES and SA have a better performance as reinforcement, and the amount of filler needed is less because the particle size is smaller (4.4 µm). Commonly, particle size determines the quantity of material that fills a polymer matrix. When particle size is bigger, on the order of microns, the load can be between 10 and 60%w [24-26]. This is because a bigger particle size reduces the number of particles content in a certain amount of filler, this makes that the quantity of filler requires for covering the entire matrix surface be more than that needs for a smaller particle size. The correct amount and a good dispersion of fillers in the matrix entail a good interface. This explains why in composites B was needed more filler to increase E'.

As composites with **US** particles are composed of the smaller particle size it was expected a similar behavior as $\mathbf{M_{10}}$ composites, however in these materials SA do not increased the storage modulus (see Figure 3b). The addition of US particles keeps E' similar than that found in B composites with SA.

An increase in storage modulus reflects an increase in stiffness [25], hence the addition of ES to PP matrix rises the stiffness of the polymer.

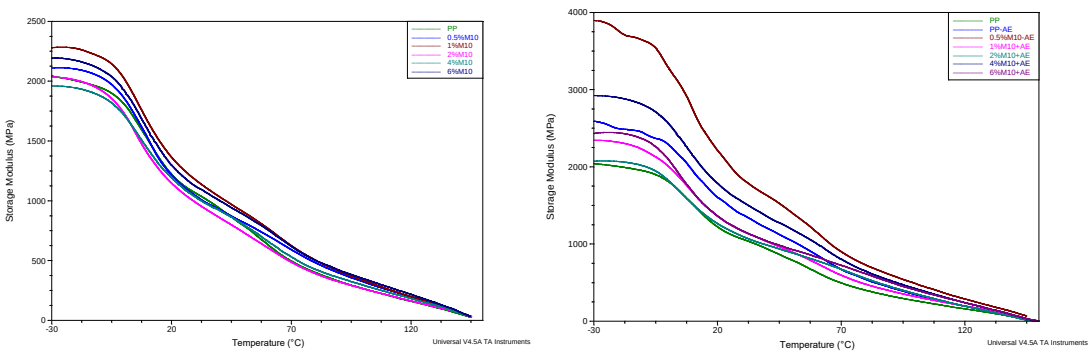

Figure 2. Storage modulus versus temperature for PP/ES M_{10} composites: a) without stearic acid and b) with stearic acid.

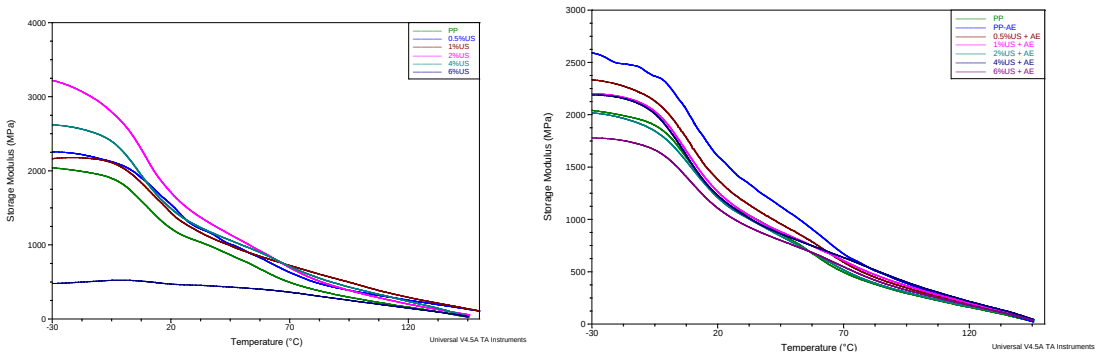

Figure 3. Storage modulus versus temperature for PP/ES US composites: a) without stearic acid and b) with stearic acid.

IV. CONCLUSION

In this research work $CaCO_3$ from eggshell was successfully used in the preparation of PP-calcium carbonate composites. This ceramic material acts as a nucleating agent and promotes a heterogeneous crystallization in the polymer matrix. It was found that particle size and stearic acid has positive influence in crystallinity; the smaller the particle size plus the addition of SA increased crystallinity as the amount of $CaCO_3$ is higher. The presence of calcium carbonate and stearic acid has an effect on thermal degradation behavior, they increased T_d, however it was needed a 20%w of $CaCO_3$ to rise 5 °C the degradation temperature of PP. The highest E' values were found for $\mathbf{M_{10}}$ composites. There is a synergetic effect between $CaCO_3$ and SA that increase the stiffness of PP in $\mathbf{M_{10}}$ composites and in some of **B** composites, however for **US** composites SA decrease this property. It is clear that for thermal stability large quantities of eggshell are needed in order to increase it, but for storage modulus small amounts are enough. By the other hand crystallinity is more related to particle size.

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