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A comparative study of the effect of different rigid fillers on the fracture and failure behavior of polypropylene based composites

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ABSTRACT

Polypropylene (PP) composites with 5 wt% of different rigid particles (Al_2O_3 nanoparticles, SiO_2 nanoparticles, Clay (Cloisite 20A) nanoparticles or $CaCO_3$ microparticles) were obtained by melt mixing. Composites with different $CaCO_3$ content were also prepared. The effect of fillers, filler content and addition of maleic anhydride grafted PP (MAPP) on the composites fracture and failure behavior was investigated. For PP/$CaCO_3$ composites, an increasing trend of stiffness with filler loading was found while a decreasing trend of strength, ductility and fracture toughness was observed. The addition of MAPP was beneficial and detrimental to strength and ductility, respectively mainly as a result of improved interfacial adhesion. For the composites with 5 wt% of $CaCO_3$ or Al_2O_3, no significant changes in tensile properties were found due to the presence of agglomerated particles. However, the PP/$CaCO_3$ composite exhibited the best tensile behavior: the highest ductility while keeping the strength and stiffness of neat PP. In general, the composites with SiO_2 or Clay, on the other hand, displayed worse tensile strength and ductility. These behaviors could be probably related to the filler ability as nucleating agent. In addition, although the incorporation of MAPP led to improved filler dispersion, it was damaging to the material fracture behavior for the composites with $CaCO_3$, Al_2O_3 or Clay, as a result of a higher interfacial adhesion, the retardant effect of MAPP on PP nucleation and the lower molecular weight of the PP/MAPP blend. The PP/MAPP/SiO_2 composite, on the other hand, showed slightly increased toughness respect to the composite without MAPP due to the beneficial concomitant effects of the presence of some amount of the β crystalline phase of PP and the better filler dispersion promoted by the coupling agent which favor multiple crazing. From modeling of strength, the effect of MAPP on filler dispersion and interfacial adhesion in the PP/$CaCO_3$ composites was confirmed.

1. Introduction

Polypropylene (PP), its blends and composites find wide applications in home appliances, automotive parts, extruded profiles, packaging industry, construction, etc. [1,2]. Although PP is relatively ductile at room temperature, it has the disadvantage of having insufficient toughness at low temperatures and in the presence of notches. Therefore, its use is still limited in many engineering applications. An efficient way to increase the toughness of PP is by blending it with rubber but this approach has the drawback to significantly decrease the material stiffness and tensile strength.

The incorporation of rigid particles into PP may induce enhancements in mechanical properties such as stiffness, strength, fracture resistance, impact toughness, wear resistance, hardness, among others [3,4]. In particular, this is a promising approach to improve simultaneously the material stiffness and toughness [2,5–11].

It is well known that the mechanical properties of composites are determined by component properties, composition, structure and interfacial interactions [12]. In particular, they are strongly related to type, size and shape, content and surface treatment of the fillers [12,13]. Generally, commercial fillers present a relatively broad particle size distribution hence, most of them are expected to form aggregates in some extent.

In addition, interfacial adhesion between inorganic fillers and polymers is often rather poor and this can be detrimental to several material properties. Therefore, different additives able to react

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with the filler are frequently added in the formulations. They have reactive groups compatible with the chemical nature of the polymer and the filler [14,15].

Interfacial adhesion and dispersion of fillers into polymer matrices has been successfully improved by using polymeric coupling agents such as grafted polyolefins. While stiffness is independent of coupling, strength and fracture toughness are expected to be greatly affected by it. It has been established in the literature [9] that changes in interfacial interactions between filler and matrix influence the debonding process, the material failure behavior and hence, the overall performance of composites. Uniform dispersion of the filler in the polymer matrix, on the other side, avoids the creation of crack-initiating large agglomerates [8] thus, it is critical to the material impact toughness [16]. In principle, an ideal modifier to simultaneously optimize the material tensile and fracture properties seems to be one able to improve filler dispersion as well as to increase interfacial adhesion but not to a level as high as to suppress debonding.

In this work, polypropylene (PP) based composites with different rigid fillers (Al_2O_3 nanoparticles, SiO_2 nanoparticles, Clay (Cloisite 20A) nanoparticles or $CaCO_3$ microparticles) were prepared with and without MAPP as a coupling agent. The aim of this work was to study the effect of the incorporation of the different fillers and the coupling agent on the materials fracture and failure behavior. The effect of filler loading in the case of the PP/$CaCO_3$ composites was also analyzed. The fracture behavior was studied not only by developing a quantitative calculation of fracture toughness values by fracture mechanics, but also by identifying the fracture mechanisms operative in the composites. The identification of the most promising filler among those investigated for improving toughness was also a goal of this work.

It should be also pointed out, that there is a huge number of papers regarding the mechanical behavior of PP based composites reinforced with rigid particles. However, most of them consider the effect of the incorporation of only one rigid particle into different kinds of PP. For this reason, it is really hard to compare the results reported in the literature and sometimes they appear contradictory [1–4,10–13].

In this work the effect of different fillers on the mechanical and fracture performance of PP based composites is directly compared.

2. Experimental

2.1. Materials and sample preparation

A commercial Polypropylene (PP) (CUYOLEN 1100N) kindly provided by Petroquímica Cuyo, Mendoza, Argentina, with a melt flow index of 11 g/10 min and a density of 0.9 g/ml was used as the matrix of the composites.

Four different commercially available additives: Silica oxide (SiO_2), organo-modified Clay (Cloisite 20A), Aluminum oxide (Al_2O_3) and Calcium carbonate ($CaCO_3$) (Sigma–Aldrich) were employed as fillers. They were used as received. Their main characteristics are listed in Table 1.

Particle size distributions of the different fillers were determined from SEM micrographs of cryo-fractured surfaces of the composites obtained at liquid nitrogen temperature. Quantitative image analysis was performed with the help of the image processing software *Image J*. To ensure statistical validity of the analysis, a minimum of 200 particles was measured.

Table 1
Main characteristics of the different fillers used as provided by the supplier.

Filler	Mean particle size (nm)	Specific density (g/cm^3)
$CaCO_3$	10,000–30,000	2.93
Al_2O_3	<50	4.00
SiO_2	10	2.33
Clay	$d_{001} = 2.44$	1.77

Composites of PP with 5 wt% of Al_2O_3, SiO_2 or Clay particles and composites with 5, 10, 20, 30, 40 wt% of $CaCO_3$ particles were prepared.

The components were mixed in an intensive mixer at 190 °C and 50 r.p.m for 10 min. Then, composite sheets (nominal thickness $B = 0.5$ mm) were compression molded in a hydraulic press at 180 °C under a pressure of 100 kPa for 10 min. Finally, the sheets were rapidly cooled by circulating water within the press plates under a pressure of 100 kPa.

In order to improve the dispersion of the fillers in the PP matrix, modified composites with 10 wt% of maleic anhydride grafted PP (PP-g-MA) (Epolene E-43 wax, Eastman Chemical Company, USA) were also prepared in a similar manner.

2.2. Mechanical characterization

Uniaxial tensile tests were performed in an Interactive Instruments 10 K universal testing machine at a crosshead speed of 5 mm/min for neat PP, the blend of PP and MAPP and the different composites by following ASTM D882-02 standard recommendations. From these tests, stress–strain curves were obtained and from these curves, Young's modulus (E), tensile strength (σ_u) (maximum stress) and strain at break (ε_b) were determined.

Quasi-static fracture tests on deeply double edge-notched (DENT) specimens were also carried out at 1 mm/min for all materials in the testing machine [17]. Sample dimensions were: length (L) = 50 mm and depth (W) = 20 mm. The distance between grips was 30 mm. Two properly aligned sharp notches of 5 mm were introduced by sliding a fresh razor blade into machined slots with the help of a specially designed device. The *J*-Integral approach was adopted to characterize fracture toughness. It was obtained from the whole area under the load–displacement curve (U_{tot}) as follows:

$$J_c = \frac{\eta U_{tot}}{B(W-a)}, \tag{1}$$

where U_{tot} is the overall fracture energy, B is the thickness and η is a geometrical factor defined by [18]:

$$\eta = -0.06 + 5.99\left(\frac{a}{W}\right) - 7.42\left(\frac{a}{W}\right)^2 + 3.29\left(\frac{a}{W}\right)^3 \tag{2}$$

All mechanical tests were performed at room temperature. A minimum of five replicates were tested for each system and the average values with their deviations were reported.

2.3. Fracture surface analysis

Fracture surfaces of cryo-fractured specimens and of specimens broken in tensile tests were analyzed by Scanning Electron Microscopy (SEM) after they had been coated with a thin layer of gold.

2.4. X-ray diffraction analysis

X-ray diffraction (XRD) analysis was carried out for the different materials investigated. A Phillips PW 1050/25 difractometer operating in a 2θ range between 5° and 70° was used. The scattering angle was varied in 1°/min steps. Cu Kα radiation was used as source.

2.5. Investigation of the fracture mechanisms

To study the fracture mechanisms on micro-deformational level, side surfaces of specimens broken in fracture tests were