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# Recycling of polypropylene/montmorillonite nanocomposites by pyrolysis

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#### ABSTRACT

The recycling of polymer/montmorillonite (MMT) nanocomposites, upon the end of their life cycle, has attracted so far less attention than its production. In this work, polypropylene/organophilized montmorillonite (PP/OMMT) nanocomposites were prepared by melt blending and then pyrolysed to produce pyrolysed filler which can be useful to fabricate new composites. XRD and SEM methods were employed to investigate the structure and morphology of the PP materials, as well as the pyrolysed OMMT. We show that OMMT, a thermal cracking catalyst, influences pyrolysis products distribution, promoting formation of light hydrocarbons instead of wax-like olefins. The pyrolysate obtained has been confirmed to be re-usable as filler in PP composites which showed mechanical properties similar to nanocomposites containing pristine montmorillonite.

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#### 1. Introduction

Filled polypropylenes are commercial materials widely used in large quantities in different application fields [1–3]. Addition of fillers like bentonites enhances many of the mechanical and thermal characteristics of polypropylene, including stiffness, heat deflection temperature or shrinkage. On the other hand, the presence of fillers usually deteriorates strength and toughness. Bentonites or montmorillonites derive from naturally occurring clay mineral (Smectites), purified and processed in order to obtain a nanoclay suitable for the production of a nanocomposite material [3–7].

Polypropylene is also a significant component of mixed plastic waste from which fuels and chemicals can be recovered via thermal or catalytic degradation. Pyrolysis of polypropylene matrix was investigated at a temperature of 420 °C with reaction times ranging from 10 to 180 min reaching total conversion of approximately 60%. Thermal cracking of the polymers towards low molecular weight materials is attractive, but, unfortunately, it gives a very broad

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http://dx.doi.org/10.1016/j.jaap.2016.04.005 0165-2370/© 2016 Elsevier B.V. All rights reserved. range of products. It also requires high temperatures typically more than 500 °C and even up to 900 °C [8–10]. Catalytic pyrolysis is being investigated as a viable solution to these problems [11–13]. The catalytic degradation of polymers have been studied by contacting melted polymer with a catalyst in fixed bed reactors [14–16], heating mixtures of polymer and catalyst powders in reaction vessels [17], and passing the products of polymer pyrolysis through fixed bed reactors containing cracking catalysts [18,19].

Catalytic effect of both organically modified montmorillonite (OMMT) and Ni(2)O(3) on the carbonization of polypropylene (PP) during pyrolysis was studied by Song et al. [20]. The authors found that Brønsted acid sites on the surface of degraded OMMT layers and the carbenium ions play an important role in the carbonization of PP and the high-yield formation of multi-walled carbon nanotubes (MWNTs). These ions are active intermediates that promote the growth of MWNTs from the degradation products with higher carbon numbers through hydride-transfer reactions. The catalytic effect of Ni was also confirmed during synthesis of carbon nanotubes with diameter of about 160 nm through catalytic decomposition of polypropylene and maleated polypropylene in an autoclave at 700 °C [21].

Pyrolysis of PP waste has been also carried out in a fixed bed reactor at 500 °C and basic salts, bases and Lewis acids were used as additives [22]. It was found that thermal pyrolysis and the pyrolysis of the waste PP with Lewis acids and basic salts result in liquid products, while the use of bases lead to formation of wax products [23].

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### Table 1 Composition of the initial PP/OMMT samples.

Name of sample	Matrix (wt%)	Compatibilizer (wt%)	Filler (wt%)
PP	100	-	-
PP/OMMT	97	_	3
PP/PP-g-MA/OMMT	90	7	3

Current research on polymer nanocomposites tends towards recycling [24,25]. The majority of the research work focuses on recycling of the polymer matrices rather than the fillers as this process is cheaper and less energy consuming. In general, mechanical properties of composites of recycled polypropylene with montmorillonite worsen with a processing time. Moreover, the crystallisation temperature and crystallisation time of PP in the composite decrease with each extrusion cycle, what is directly linked with the mechanical properties of these materials [29,30].

Only a few studies deal with the pyrolysis of montmorillonite filler, and describe the process of pyrolysis of different types of clays to yield pyrolysed montmorillonite [26–28].

Hence, in this work we propose a novel method of polypropylene/montmorillonite nanocomposites recycling by pyrolysis to produce pyrolysed montmorillonite that can be re-used in the preparation of polymer composites. Previous works mainly focus on pyrolysing polymer nanocomposites in order to recover monomer during high temperature decomposition; solid residues after pyrolysis of polymer nanocomposites are treated as useless wastes. Hence, we developed this method to overcome the problem with residues after pyrolysis process. These residues still include layer silicates which can be re-used as suitable fillers for melt intercalation with polymer matrices. In this work we prepared polypropylene/montmorillonite nanocomposites by melt intercalation method. Then we pyrolysed these nanocomposites and re-used solid residue to produce new types of PP composites (Fig. 1) which have still improved properties compared to the neat polymer.

#### 2. Experimental

#### 2.1. Materials

The polypropylene matrix (PP) with the trade name *Moplen*<sup>®</sup> HP500 N was purchased by Lyondell Basell Polymers. Maleic anhydride grafted polypropylene (PP-g-MA, *Polybond*<sup>®</sup> 3200), which was used as a compatibilizer, was supplied by Chemtura Corporation. Montmorillonite modified with a quaternary ammonium salt *Dellite*<sup>®</sup> 72T (OMMT), was delivered by Laviosa Chimica Mineraria S.p.A.

#### 2.2. Sample preparation

In order to produce the initial nanocomposites, the polypropylene and the compatibilizer were dried before extrusion in a vacuum oven at 80 °C for 12 h, and montmorillonite was dried at 100 °C for 12 h. Then, the components were pre-mixed in a barrel-shape mixer at 60 rpm for 2 h. Two nanocomposites where prepared: one with compatibilizer (PP/PP-g-MA/OMMT), and one without (PP/OMMT). Batches of 500 g were prepared. The polypropylene matrix (PP) was also extruded in the same manner as the nanocomposites for comparison. Table 1 contains the composition of the three samples.

Polypropylene/montmorillonite nanocomposites were obtained by melt intercalation method, using the procedure described in our previous works [31–33]. A mini processing line consisting of a Brabender DR20 feeder, twin screw extruder Haake Rheomex OS PTW 16/25, cooling bath Zamak W1500 and pel-



Fig. 1. Scheme of research.

letizer Zamak G-16/325, was applied. The processing parameters that govern the structure and morphology of polymer/OMMT nanocomposites were optimized [33].

#### 2.3. Pyrolysis process

The initially prepared PP/OMMT and PP/PP-g-MA/OMMT nanocomposites were pyrolysed to produce pyrolysed MMT (PMMT). The pyrolysis was carried out in an in-house designed apparatus [34,35] equipped with a furnace able to heat up to 600 °C, with an optional mechanical stirrer, a section for condensation of volatile products (a set of four condensers in a sequence: steel and glass-made air condensers followed by two reflux condensers), a

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