

Antioxidant intercalated hydrocalumite as multifunction nanofiller for Poly(propylene): Synthesis, thermal stability, light stability, and anti-migration property



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ABSTRACT

One of the major issues for poly(propylene) PP concerns its protection towards oxidative phenomena resulting in polymer failure. Using known anti-oxidant (AO), Irganox 1425, an original approach is taking advantage of the counterion, cations Ca^{2+} , in building hydrocalumite inorganic sheets, and concomitantly providing the AO anions to be immobilized within an inorganic host structure. Through the classical co-precipitation method, the hybrid assembly composed of AO molecules interleaved between hydrocalumite layered structure is successfully elaborated in one-step process free of contamination. Hydrocalumite (Ca_2Al) belongs to the family of layered double hydroxides (LDH). The structure of the AO-LDH hybrid material is determined by means of XRD, FT-IR, while the radical-scavenging activity of AO-LDH is investigated using DPPH[•] (1,1-Diphenyl-2-picryl-hydrazyl) radical concentration variation. A series of AO-LDH/PP composites is then obtained by dispersing AO-LDH into PP at different loading ratios, and addressing the thermal stability, light stability and anti-migration of the resulting composites. The use of hydrocalumite vessel in confining AO molecules helps to increase the thermal stability and resistance against the photo oxidation while providing a barrier effect against organic species migration. An optimized of 4 wt% AO-LDH into PP results in the best radical-scavenging activity, 1 wt% is preferred to stabilize PP under light, the former formulation is the best compromise of all the series.

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1. Introduction

Since 1937 when the first antioxidant agent with the structure of hindered phenol, BHT ($\text{C}_{15}\text{H}_{24}\text{O}$, 2,6-Di-tert-butyl-4-methylphenol) was disclosed, phenolic antioxidant agents are still widely used in polymer processing and manufacturing. One major drawback in using organic AO molecules is their possible migration out of the polymer creating defect/porosity highly deleterious in time as well as their high reactivity that may provoke chain scission/degradation. In order to solve such issue related to the migration of small phenolic molecules [1], the antioxidants are usually extended toward higher molecular weight to gain

antioxidant efficiency in time [2–4]. A study has shown that phenolic-based antioxidant associated to a hyper-branched structure with a molecular weight between 1000 and 3000 g mol^{-1} can not only prevent antioxidants migration, but also provide a suitable compatibility with polymers [5]. In order to overcome such complex chemical and time-consuming process related to the generation of AO of high molecular weight as well as to avoid the by-products, inorganic vessels constitute a breakthrough [6,7]. In this view, the versatile layered double hydroxides (LDH) used to improve the thermal, mechanical properties and flame retardant properties of the polymer have gradually been developed [8–10].

In the particular case of hydrocalumite $[\text{Ca}_2\text{M}^{3+}(\text{OH})_6]^+ (\text{A}_{1/n})^{n-} \cdot m\text{H}_2\text{O}$ with the inorganic sheets composed of $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$, the LDH sheets are adjustable in terms of cations ($\text{M}^{3+} = \text{Al}^{3+}, \text{Fe}^{3+}, \text{Ga}^{3+} \dots$) but not respectively to the proportion $\text{Ca}^{2+}/\text{M}^{3+}$ fixed at 2 as well as highly tunable in terms of the guest anions A to be interleaved [11–15]. Such a variety in the cation composition in

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association with the functional anions results in a large number of adapted hybrid structures. Mostly present in cement-type application because hydrocalumite is a structure produced during the cement hydration and may be used as container for cement additives such as superplasticizers [16,17], hydrocalumite has been scarcely reported so far as hybrid filler and even more so as filler for polymer. However early works have proven to be of great advantage in the field of polymer nanocomposites [18–20]. This prompts us to revisit the hydrocalumite host structure associated to specific anions to endow the polymer with potential performances [21,22]. Using benzoate-modified LDH with Ca, Zn or Mg as divalent metals, LDH could not be completely dispersed in polymer however the composites were found to enhance the polymer thermal stability prominently [23]. As far as Ca_2Al -hydrocalumite potential use as additive is concerned, the intercalation of sulfonate [24], UV absorber [25] and other functional anions were successfully reported, this in some cases to enhance heat and flame retardant properties of polymer [26,27]. Indeed an additional role of using intercalated LDH platelets was to promote the residue formation (i.e. ceramic) covering the surface of polymer and thus achieving the effect of flame retardant during combustion. Interestingly, any physical cross-linking network between LDH sheet and polymer chains can significantly improve the mechanical properties of polymer [28,29]. The content of LDH will also influence the polymer performance, as well as having an effect on its degree of crystallinity and on its glass transition temperature [30]. These performances may vary linearly as a function of LDH loading or may present optimized compositions [31]. At the same time, efforts were paid to blend LDH and polymer better, using a variety of methods, such as co-rotating twin-screw micro-extruder [32,33], or solvent extraction method applied in laboratory [34].

Previous researches indicate that hydrotalcite-based compounds offer great potential in the development prospect regarding applications of polymer combined with antioxidants, such as hydrolysate from Irganox 1010 [35–37]. The results proved that intercalated LDH improved the PP thermal oxygen aging resistance and that similar performance as Irganox 1010 was obtained after migration tests. In order to develop further this approach, Irganox 1425 [$\text{Ca}(\text{C}_{17}\text{H}_{28}\text{O}_4\text{P})_2$, 694.84 g mol⁻¹] as guest species is selected. Indeed, Irganox 1425 presents a standard feature of phenolic antioxidants as well as bearing phosphonic acid ethyl ester groups as present in Fig. 1. Irganox 1425 exhibits good performance as light stabilizer and antioxidant for composite polymer in industry [38]. Considering such interesting properties of Irganox 1425, the

synthetic steps are customized accordingly to this AO molecular structure and affinity with LDH sheets. Through structural characterization and thermal aging resistance, light stability and migration testing of composite materials, the leitmotiv is here to demonstrate that the mobility of small molecules can be drastically reduced while keeping or even improving the AO efficiency through constructing intercalated hybrid filler as well as to provide a new concept for the development of antioxidants.

2. Experimental section

2.1. Preparation of Ca_2Al -LDH

Synthesis of Ca_2Al -AO-LDH slurry. On the basis that the cations Ca^{2+} were provided from Irganox 1425, AO-LDH was directly prepared by co-precipitation method. Typically, 20 mL of salt solution containing 0.75 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 20 mL of base solution containing 0.64 g NaOH were added dropwise into a flask with 240 mL solution of 4.17 g Irganox 1425. The pH was maintained at 12 until complete addition of the salt solution, and the resulting suspension was aged under N_2 atmosphere at 45 °C for another 48 h. Subsequently, centrifuged products were washed three times with 60% ethanol aqueous solution and dried for structural analysis, while another washing using acetone three times was performed for surface modification [34]. Finally, the final slurry was used for the preparation of AO-LDH/PP. All the deionized water used was boiled to remove the carbon dioxide. Ca_2Al - NO_3 -LDH and Ca_2Al - CO_3 -LDH used as reference were prepared according to the literature [39,40].

Synthesis of AO-LDH/PP Composites. AO-LDH/PP composites were synthesized according to an aqueous miscible organic solvent treatment published by Wang et al. [34]. A mixture 20 g of PP and a fixed amount of AO-LDH slurry was stirred in 200 mL xylene, during 3 h at 140 °C. After cooling, the precipitation was performed in 200 mL hexane, AO-LDH/PP composites were further dried at 80 °C for 24 h. The intercalated structure of AO-LDH was mixed with PP as functionalized filler and compared with the reference composites.

2.2. Antioxidant activity test of AO-LDH

The radical-scavenging activity of AO was detected by DPPH[•] (1,1-Diphenyl-2-picryl-hydrazyl) ethanol solution with the corresponding changes in the absorption peak at 517 nm by UV detection. Experimentally, various amounts of AO-LDH 2, 4, 6, 8, 10 mg, (calculated from the molecular formula of AO-LDH corresponding to a given quantity of AO), were added to DPPH[•] solution with a concentration of 100 μM. After the corresponding solution was placed in the dark for a given time, UV detection was then carried out.

2.3. Thermal stability test of LDH/PP composites

The thermal stability of the composites was investigated by two methods: TG-DTA analysis and accelerated thermal aging test. For the former, the decomposition temperature of the composite materials was analyzed under heating condition at 5 °C/min with different amounts of AO-LDH. For the latter, the composites were hot-pressed into a thin film with a thickness of 0.1 mm at 170 °C, and then the accelerated thermal aging test was performed at 150 °C, using FT-IR detection. Based on the increase of carbonyl group during the thermal process, the evolution of the carbonyl peak in 1810–1660 cm⁻¹ range was used to reflect the aging degree.

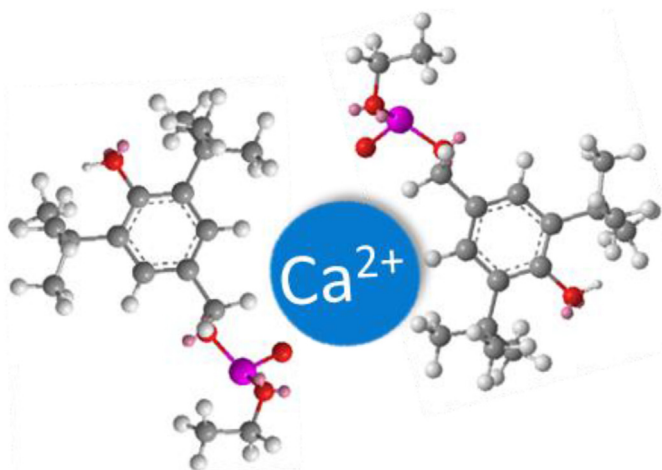


Fig. 1. Chemical structure of Irganox 1425 antioxidant.

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