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Low molecular weight hindered amine light stabilizers (HALS) intercalated MgAl-Layered double hydroxides: Preparation and anti-aging performance in polypropylene nanocomposites

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A low molecular weight hindered amine light stabilizer (HALS), contains 2, 2, 6, 6-tetramethyl piperidine functional group has been successfully prepared and intercalated into the interlayer region of Mg-Al layered double hydroxides (LDH) via a co-precipitation method to produce HALS-LDH. Furthermore, a series of HALS-LDH/PP nanocomposites were fabricated by dispersing HALS-LDH in poly(propylene) (PP) in a solvent casting route. Through the accelerated aging test method, the morphological properties, the thermal-oxidative degradation and photo-oxidative degradation behavior of HALS-LDH/PP composites were carefully investigated. The results show that the thermal stability of HALS in HALS-LDH was improved compared to that of HALS free of LDH dispersed into PP, and there is no negative effect on the crystallization behavior of PP after the addition of HALS-LDH. Besides, the HALS-LDH significantly enhances synergistically the thermal- and photo-stability of PP compared when LDH platelets CO_3-LDH or HALS are used separately. Under the experimental conditions, a mass loading of HALS-LDH optimized as 4 wt % in respect to PP was found to exhibit an excellent anti-aging performance for potential applications.

1. Introduction

Polypropylene (PP) with excellent comprehensive properties has been widely employed in building materials, automobile industry, household appliances, food packaging and other fields [1,2]. However, the PP products exposed to outdoor are usually suffered from the light- and thermo-oxidative degradation and then resulted in the discoloration, the cracking of the surface, stiffening, and a decrease in their mechanical properties [3,4]. Generally, various anti-aging agents are added into PP to prolong the service life, retard the light- and thermo-oxidative degradation [5]. Among them, hindered amine light stabilizers (HALSs) are mostly effective light stabilizers containing 2,2,6,6-tetramethyl piperidine functional group with anti-oxidative degradation scheme called “Denisov cycle” (see Scheme 1a, TEMPO: 2,2,6,6-Tetramethyl-1-piperidinyloxy) [6,7]. Yet, low-molecular weight HALSs (HALSs) are easy to volatilize and migrate out of PP matrix during processing or the service life, which does not only decrease the efficiency of antiaging but also leads to the pollution of environment [8].

Increasing the molecular weight of HALS is one of the important and available routes to hinder migration by polymerizing light stabilizer monomers or grafting light stabilizers to the polymer [9–12]. These HALSs with high-molecular weight exhibit higher stability, better performance and larger resistance against migration to some extent. Undoubtedly, the synthesis process of high-molecular weight HALSs is more complicated and higher cost. Therefore, it is necessary and interesting to explore more simple and environmental friendly additives. An appealing approach is to immobilize the stabilizer in order to avoid their migration out of the polymer that would be deleterious for environmental reason and subsequently their over-loading as well as for the polymer to avoid its disruptive integrity. Among the possible inorganic carriers, layered double hydroxides (LDHs), one kind of anionic clays, appear as an interesting cargo providing self-healing properties of polymer coatings [13] as well as multi-functionalities to polymer [14].

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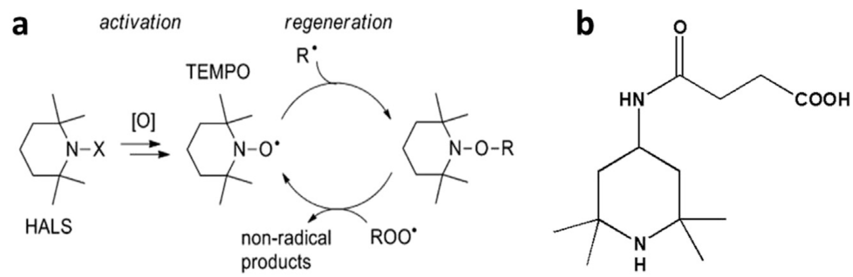

Scheme 1. (a) Denisov Cycle, (b) Molecular structures of low molecular hindered amine light stabilizers (HALS).

Indeed, LDH/polymer composites have recently drawn an increasing attention in improving the polymer properties because of their highly tunable properties [15–17]. The host-guest interaction may improve the thermal stability of guest interleaved anions and prevent their migration out of the polymer [18,19]. In that idea, it is reasonable to intercalate low-molecular weight HALSs into the interlayer region of LDH for improving their long-term light stabilizer performance once dispersed into PP.

In this work, a low-molecular weight HALS, see Scheme 1b, which contains the functional group 2,2,6,6-tetramethyl piperidine [20] was prepared and then intercalated into the interlayer region of MgAl-LDH using a one-step coprecipitation method to produce HALS-LDH. Besides, a series of HALS-LDH/PP nanocomposites were fabricated with different mass loadings of HALS-LDH in PP and the corresponding thermo- and photostability were carefully investigated compared with CO_3-LDH/PP and HALS/PP references.

2. Experimental

2.1. Materials

All the chemicals including succinic anhydride, Tetramethylpiperidinamine (TEMP), dioxane, ether, $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, xylene, hexane were A.R. grade and directly used as received. All the water used was deionized and degassed. Polypropylene (PP) were from China Sinopec Yanshan Chemical Company. (Type: PP1300, melting index: 1.5 g/10 min, melting point: 164–170 °C, density: 0.91 g/cm^3).

2.2. Preparation of low molecular weight HALS

Succinic anhydride (15 mmol, 1.50 g) was dissolved under stirring at 80 °C into 10 mL of dioxane to produce solution I, and tetramethylpiperidinamine (TEMP, 15 mmol, 2.34 g) was dissolved into 10 mL dioxane to produce solution II. Solution II was dropwise added in solution I at 80 °C under vigorous stirring for 40 min. Then, the product was cooled down to room temperature, and individually washed using dioxane and ether three times. Finally, the powdered product HALS was collected after vacuum filtration to remove the solvent.

2.3. Preparation of HALS-LDH slurry

HALS-LDH slurry was synthesized by a one-step coprecipitation method, and furthermore the HALS-LDH nanoparticles was surface-organized in the solvent-washing route as reported by O'Hare and coauthors [21]. Typically, 1.2821 g of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.9378 g of $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 30 mL of water to form a salt solution A; 0.8000 g of NaOH was dissolved in 20 mL of water to form a base solution B. Under nitrogen atmosphere and vigorous stirring, two solutions were added dropwise into a flask, where 1.2800 g of HALS (n_{HALS}: $n_{Al3+} = 2$, mol/mol) was dissolved in 30 mL water. Then, the mixture was aged at room temperature for 24 h. Finally, the HALS-LDH slurry was first centrifuged and washed using water until pH = 7, and then using ethanol/water (1:1) three times, and subsequently with acetone three times. After washing, the obtained LDH slurry was ready for the preparation of LDH/PP nanocomposites. NO_3-LDH and CO_3-LDH slurries were prepared in a similar route.

2.4. Preparation of HALS-LDH/PP composites

The HALS-LDH/PP composites were obtained in a solvent mixing route [22]. For instance, 10.0000 g of PP and 2.3529 g of HALS-LDH slurry (Solid content: 17.0 wt%) were dispersed in 100 mL xylene. The mixture was heated to 140 °C for 3 h under vigorous stirring in a flask, and then rapidly poured into 100 mL hexane. After cooled down to room temperature, the composite sample was collected by filtration and dried at 60 °C for 24 h. Different mass loadings of HALS-LDH/PP, and references 4.0 wt% CO_3-LDH/PP (solid content: 28.4 wt%) and HALS/PP were obtained following the similar procedure. The content of HALS was equivalent to HALS moiety contained in the hybrid material HALS-LDH. The composition of the LDH/PP composites is listed in Table 1.

2.5. Characterization

Proton nuclear magnetic resonance (^{1}H NMR, 400 MHz) spectra were determined on Bruker AV400 NMR spectrometer and acquired in CD_3OD unless otherwise noted. Chemical shifts were reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, $\delta = 0.00$ ppm) and were referenced to residual solvent (CD_3OD, $\delta = 4.9$ ppm (1H)). Coupling constants (J)

Table 1
The composition of all the LDH/PP composites.

Samples	Solid content of slurry	Fillers amount in PP (g)	Composites
HALS	–	0.75	4.0 wt % HALS/PP
CO_3-LDH	28.4%	1.41	4.0 wt % CO_3-LDH/PP
HALS-LDH	17.0%	0.588	1.0 wt % HALS-LDH/PP
		1.18	2.0 wt % HALS-LDH/PP
		2.35	4.0 wt % HALS-LDH/PP