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Stabilization of polypropylene using dye modified layered double hydroxides

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ABSTRACT

Layered double hydroxide (LDH) was successfully modified with a common azo dye, 3-(4-anilinophenylazo) benzenesulfonic acid. Thermal stability of dye was increased with LDH shielding and the prepared mLDH/polypropylene (PP) nanocomposite maintained the dye derived UV-absorption property, whereas the dye/PP compound shows very weak UV-absorption. LDH based composites of polypropylene were applied to artificial aging and the tensile strength alteration of composites during aging was monitored. mLDH/PP samples endured 4 times longer than neat polypropylene under accelerated weathering conditions.

1. Introduction

The idea of dye-stabilization through clays has its origin from thousands of years back. Mayans were using a natural clay palygorskite to stabilize indigo blue, which remains its color then for centuries [1]. The interest on clay–dye co-operation was ever since remained and especially a smectite type of clay, montmorillonite, was intensively investigated by many researchers regarding their dye applications [2–5]. However, the negative charge loading of montmorillonite layers shows selectivity toward cationic dyes, which limits intercalation molecule selection.

Layered double hydroxides are a rather new subgroup of clays and differ from other clays with their positively charged layers and interlayer anions. The general molecular formula of layered double hydroxide (LDH) is usually shown as $[M^{2+}_{(1-x)}\ M^{3+}_{x}\ (OH)_2]^{x+}\ [A_{x/n}^{n-}]^{x-}\cdot yH_2O$, where M^{2+} and M^{3+} represent divalent and trivalent cations, A is the interlayer ion and x is $M^{2+}/(M^{2+}+M^{3+})$. The opposite charge of LDHs and their interlayer ion exchange capability make them good candidates as host for anionic dyes. Moreover, this host can act as a shielding agent and can provide thermo- and photostability as well as color stability to dyes [5,6].

Polymer degradation through solar radiation, on the other hand, is an important problem causing material failures and one of the factors determining lifetime of polymers. Addition of nanoclays such as montmorillonite and their photodegradation mechanisms were previously studied and found out that addition of clay does not alter the degradation mechanism but reduces the oxygen induction time compared to neat polymer [7,8]. The similar studies were also performed for LDHs and reduction in the oxygen induction time as well as increase in the photodegradation rate was observed [9,10]. Very recently it was also reported that modification of LDH alters the catalyzer effect of LDH on polymer photodegradation and UV-absorber modified LDH can act as a UV-shield in polybutylene succinate and poly(ethylene terephthalate) nanocomposites [11,12].

Anionic dyes also show UV-absorption properties combined with the lack of thermostability. These dyes can be hosted by LDHs and the thermally stabilized nanofillers might act in the polymer as a UV-stabilizer. This makes the prepared nanocomposites multifunctional together with the already existing properties of the filler such as having selected color in combination with color stability, being gas barrier, reinforced, and flame retardant. In the presented work, MgAl LDH was modified with an anionic dye, 3-(4-anilinophenylazo) benzenesulfonic acid (metanil yellow). Dye, LDH, dye modified LDH (mLDH) and their prepared composites

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with polypropylene were characterized via thermogravimetric analysis, UV–vis spectroscopy, and tensile testing.

2. Experimental

2.1. Materials

All chemicals used for the synthesis and modification of LDHs, magnesium chloride hexahydrate, aluminum chloride hexahydrate, urea, 3-(4-anilinophenylazo) benzenesulfonic acid (70% dye content), were provided by Sigma–Aldrich. Maleic anhydride functionalized homopolypropylene (PP-g-MA), Exxelor PO 1020, was supplied by ExxonMobil Chemical and polypropylene HD120MO was delivered by Borealis.

2.2. Preparation of the nanofiller

MgAl LDH was synthesized from its metal chloride salts, $MgCl_2 \cdot 6H_2O$ and $AlCl_3 \cdot 9H_2O$, with a Mg:Al ratio of 2 as described elsewhere [13]. In a typical synthesis, 0.5 M solution of magnesium and aluminum chloride salts in required ratio is mixed with excess urea and LDH is precipitated at reflux temperature. The synthesized LDH was modified with 3-(4-anilinophenylazo) benzenesulfonic acid (metanil yellow) using anion-exchange intercalation method similar to described in the literature [14]. Anionic dye was used in stoichiometric ratio for the substitution with interlayer carbonate ions. The modified LDH was washed then with distilled water to remove the residuals of unreacted chemicals and dried till constant weight.

2.3. Nanocomposite preparation

LDH, dye, and mLDH were first melt-compounded with PP-g-MA in a microcompounder (DSM Xplore 15, The Netherlands). PP-g-MA:Filler ratio was kept to be 2 and in the following step this masterbatch was diluted with polypropylene (PP) in the desired concentration using the same instrument. The processing conditions were 100 rpm screw speed, 10 min mixing time and 190 °C mixing temperature. Thus, one should notice that the presented polypropylene composites contain also PP-g-MA in a limited range.

2.4. Techniques

X-ray diffraction (XRD) patterns were recorded by XRD 3003 θ/θ, Seifert-FPM Freiberg/Sa. (now: GE Inspection Technologies GmbH). Fourier transform infrared (FTIR) investigation was carried out over the wave number range 4000–400 cm^{-1} using Equinox 55 FTIR spectrometer. Elementary analyses were performed by vario MICRO CHNOS analyzer. Transmission electron microscopy (TEM) images were recorded by Zeiss Libra 200MS and UV–vis spectroscopy was carried out by Lambda 800 from Perkin Elmer for compression molded samples with a thickness of 0.1 mm. Thermogravimetric analysis (TGA) was performed using TGA Q 5000 of TA Instruments, coupled with FTIR spectrometer Nicolet 380 of Thermo Electron under nitrogen and tensile tests were performed using a Zwick universal test machine. The specimens for tensile tests were compression molded and prepared according to DIN EN ISO 527-3 with a thickness of 0.2 mm. The accelerated weathering of the samples were carried out using Xenotest Alpha from Atlas according to DIN EN ISO U4892-2, which includes constant UV-light exposure, controlled temperature, 108 min dry phase cycle with controlled humidity and 12 min wet phase cycle.

3. Results and discussion

3.1. LDH synthesis and modification

In X-ray scattering, typically (001) reflections of LDH crystals are observed. In Fig. 1 the reflections of synthesized LDH corresponding to (003), (006) and (009) planes are found indicating good crystallinity. The reflection peak for (003) plane represents the repeating unit of LDH, which is the sum of thickness of one metal hydroxide layer and the spacing between two adjacent layers. This peak appears at a 2θ of 11.6° corresponding to an interlayer distance of 0.76 nm due to Bragg's law. Modification of LDH with metanil yellow molecules increased the LDH interlayer distance from 0.76 nm to 2.55 nm. The modified LDH also shows a quite ordered crystal structure and up to third order of reflections were detected. This strongly indicates that metanil yellow was intercalated into LDH galleries.

FTIR spectra of LDH (Fig. 2) give further useful information about the success of the modifications. Pristine LDH shows typical vibration bands of carbonates under LDH constraint, which appear for the synthesized LDH at 1366, 870, and 678 cm^{-1} due to asymmetric stretching mode, non-planar, and bending angular stretching modes, respectively. These bands disappear after modification of LDH. This was attributed to the exchange of the carbonate ions with the selected metanil yellow molecules. Strong vibration bands at 1594 cm^{-1} and a doublet at 1517 and 1497 cm^{-1} were associated to C=C vibrations of the metanil yellow [15]. S=O stretchings of dye appear at 1188 and 1035 cm^{-1} [15].

Table 1 shows the elementary analysis of the modified LDH. These experimental values were used to calculate the degree of intercalation. Each calculation was carried out based on either N-content or S-content from experimental data and compared with observed data. The degree of intercalation varied depending on selected experimental value for the calculations. The calculations might vary due to several different reasons. Mg:Al ratio was taken as 2 during the calculations but end-product LDH might show a different metal ratio than aimed. The coefficient of crystal water was set to be 0.48 due to the literature value [10]. This value, however, might also vary due to synthesis conditions. Metanil yellow in use shows 70% purity. The remaining dye sub-structures might also affect the elementary analysis results. XRD and FTIR results, on the other hand, show almost no traces of carbon dioxide.

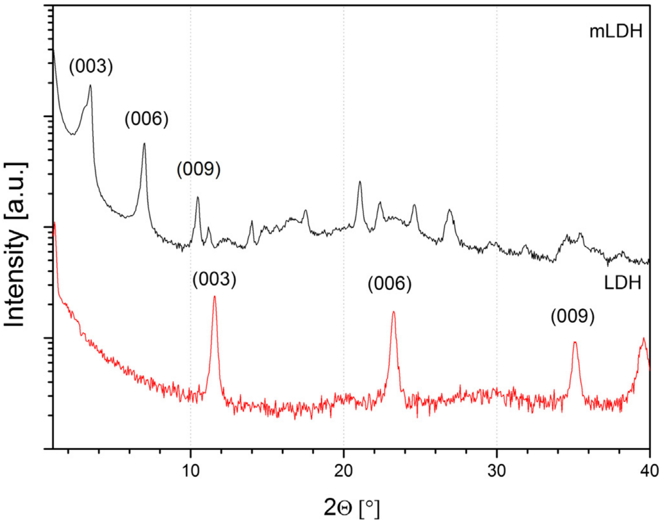

Fig. 1. X-ray diffractograms of pristine LDH and modified LDH.