Materials Chemistry and Physics 157 (2015) 69–79

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Elucidating the catalytic effect of metal ions in montmorillonite on thermal degradation of organic modifier

Indraneel S. Zope [a], Aravind Dasari [a, *], Giovanni Camino [b]

[a] School of Materials Science & Engineering, Nanyang Technological University, Blk N4.1, 50 Nanyang Avenue, Singapore 639798, Singapore
[b] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino sede di Alessandria, INSTM Research Unit, Viale Teresa Michel 5, 15100 Alessandria, Italy

HIGHLIGHTS

- Thermo-oxidative degradation of metal ion exchanged organo montmorillonite.
- Analysis of ionic character and polarizing capacity of metal ions.
- Proposed degradation mechanisms.

ARTICLE INFO

Article history:
Received 26 July 2014
Received in revised form
2 March 2015
Accepted 7 March 2015
Available online 13 March 2015

Keywords:
Thermal properties
Oxidation
Organic compounds
Thermogravimetric analysis

ABSTRACT

A key parameter influencing ignition, heat of combustion and charring of polymer/clay (montmorillonite, MMT) nanocomposites during combustion is the catalytic activity of clay. This work explores the effect of metal ions (MIs) like Mg^{2+}, Al^{3+} and Fe^{3+} that are inherent to clay in altering the kinetics of degradation of organic modifier, hexadecyltrimethylammonium bromide (HDTMA-Br). Based on Brønsted and Lewis acid characteristics associated with these metal ions, their catalytic activity varied; Brønsted acidity affected initial stages of organic modifier degradation, while Lewis acidity influenced oxidation stability of carbonaceous residue beyond dehydration temperatures. For example, OMgMMT yielded delayed peak degradation temperature for $HDTMA^+$, while Fe^{3+} ions from OFeMMT significantly lowered the oxidation stability of carbonaceous content. Knowing the effect of each metal ion separately, correlation between clay structural chemistry and organic degradation onset has been established. Degradation mechanism for alkyl fragment (from organic modifier) was provided adding fundamental knowledge to the field that will help in the design and development of polymer/clay nanocomposites with superior fire retardancy.

1. Introduction

Polymer/clay nanocomposites, in general, exhibit lower heat release rates during combustion; but they inherently lack the resistance towards quicker ignition. Many attempts were made to understand this behavior from different (and broad) viewpoints including thermal stability of organic surfactants [1,2], 'barrier effect' as a result of collapse of nanoparticle structures [3,4], catalytic effect of clay on polymer matrix degradation [5–10], and heat transfer through cross-section by thermal conduction [11,12]. With many possible explanations put forth, general consensus is yet to be attained.

Reactivity of smectite clays (for example, MMT) is affected by replacing the relatively mobile and exchangeable cationic species like Na^+ or Ca^{2+} on their surfaces by higher valency metal ions like Mg^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+} or Fe^{3+} [13]. This ability has been widely exploited for applications like catalysis [14,15]. Depending on their locations, metal ions render inherent acidic nature to MMT in the form of Brønsted acidity and Lewis acidity [13]. For polyamide 6/MMT nanocomposite system, Davis et al. [6] argued that during processing at 300 °C, degradation of polyamide 6 possibly occurred because of peptide bond scission as a result of hydrolysis led by bound water molecules from MMT (essentially, Brønsted acidolysis). It was also proposed that free water by itself might not result in substantial degradation of polyamide 6 matrix, but the combination of clay and water is required for significant catalytic degradation. Lewis acidity has also been studied for its possible effect on catalytic degradation and carbonization of organic

---

* Corresponding author.
E-mail address: aravind@ntu.edu.sg (A. Dasari).

http://dx.doi.org/10.1016/j.matchemphys.2015.03.015

content. For example, Dong et al. reported that polystyrene/zeolite nanocomposites resulted in enhanced char when zeolite with higher Lewis acidity was used in conjunction with intumescent fillers [16]. Nonetheless, the precise role of different metal ions present in the clay structure on decomposition of organic matter is still unclear.

Further, organically modified MMT upon degradation leaves behind H^+ at exchange position following the well accepted Hoffmann degradation mechanism. Acid activated MMT could demonstrate *autotransformation* process where protons migrate and replace metal ions at structural positions in tetrahedral layers [17,18]. These “knocked-off” metal ions then assume positions at exchange sites increasing the reactivity of clay towards molten polymer matrix. Increased catalytic activity of acid treated tetra-alkyl-ammonium cation exchanged smectites has already been reported [19]. Thus, possibility of increasing concentration of metal ions like Mg^{2+}, Al^{3+} or Fe^{3+} at exchange positions beyond surfactant decomposition temperature via possible autotransformation cannot be overlooked. Although control on exact kinetics of autotransformation process may not be currently feasible, knowing the effect of each metal ion on degradation kinetics of organic matter might help answer some uncertainties. Therefore, in this work, effect of metal ions inherently present in clay on thermal degradation of organic modifier will be studied. For this, metal ion content (Mg^{2+}, Al^{3+}, Fe^{3+}) in natural sodium MMT will be amplified implementing cation exchange technique. The knowledge gained from this study will subsequently be applied towards better understanding of thermal degradation behavior of polymer/clay nanocomposites.

2. Experimental section

2.1. Materials and synthesis procedure

Metal ion exchanged MMT clays (MI-clays) were prepared by standard cation exchange technique. Na^+ MMT clay, commercially named *Cloisite Na*$^+$, was obtained from Southern Clay Products. It has a mean formula unit of $Na_{0.65}[Al,Fe]_4Si_8O_{20}(OH)_2$ and cation exchange capacity (CEC) of 92 meq/100 g. In a typical procedure, 20 g of Na^+ MMT clay was suspended in 1 L deionized water under mechanical stirring for 24 h. Metal salt solutions (Mg^{2+}, Al^{3+}, Fe^{3+}) with 20% excess of CEC value were dissolved separately in 500 mL deionized water. MMT suspensions were heated to 80 °C to which metal salt solutions were added drop-wise over a period of 30 min while stirring mechanically. The suspensions were stirred for 24 h to get maximum cation exchange. Each suspension was then filtered and thoroughly washed with deionized water. Silver nitrate test for halides was conducted to confirm the thoroughness of washing. Finally, MI-clays were dried at 110 °C and ground to fine powder (200 mesh).

MI-clays were further modified using HDTMA-Br obtained from Sigma Aldrich. MI-clays (20 g each) were separately suspended in 1 L deionized water at 80 °C for 24 h. Surfactant solutions were made by dissolving HDTMA-Br in 200 mL deionized water. HDTMA-Br solution was then added drop-wise to each MI-clay suspension over a period of 10 min with mechanical stirring. The suspensions were stirred for 24 h. Each suspension was then filtered and washed thoroughly with deionized water. Silver nitrate test for bromide was conducted to confirm the thoroughness of washing. Subsequently, these modified organo MI-clays (OMI-clays) were dried at 110 °C and ground to fine powder (200 mesh). Overall process is schematically represented in Fig. 1.

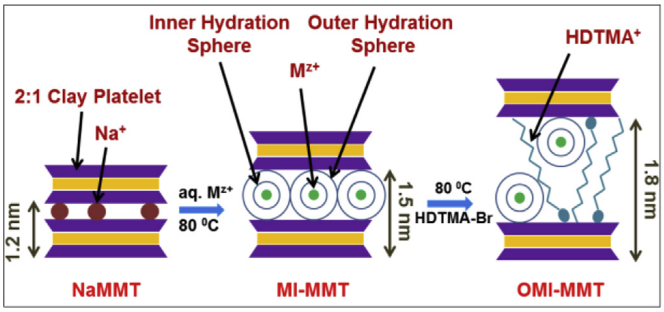

Fig. 1. Schematic representation of modification of NaMMT clay to obtain MI-clays and subsequently OMI-clays. Aq. M^{z+} denotes aqueous solution of metal salts (Mg^{2+}, Al^{3+} or Fe^{3+}).

2.2. Characterization

To study dehydration and degradation behaviors of MI- and OMI-clays, thermogravimetric (TG) analysis was carried out using TA Instruments 2950 under air and nitrogen atmospheres. All samples were dried at 110 °C for 24 h in a convection oven before the test. Test was carried out from room temperature to 750 °C employing a heating rate of 20 °C/min. X-ray diffraction (XRD) measurements were performed on Shimadzhu XRD6000 (40 kV, 30 mA, Cu kα) with scan speed of 1°/min, scan range of 3–45° and step size of 0.02°. Structural chemistry of clays and their residues were analyzed from respective Fourier Transform Infrared (FT-IR) spectra that were collected using PerkinElmer SpectrumGX spectrometer and KBr disks. All spectra were acquired using 64 scans and 4 cm^{-1} resolution.

Elemental concentrations in different metal-ion exchanged clays were determined using PerkinElmer Optima2000 inductively coupled plasma optical emission spectrometry (ICP-OES) with detectors analyzing for Na, Mg, Al and Fe. For sample preparation, accurately weighed 0.2 g of MI-clay (or OMI-clay) was dissolved in 30 mL of 1.0 M HCl for 3 h using ultrasonic bath. The suspension was subsequently centrifuged at 6000 rpm for 5 min. Supernatant was collected into a 100 mL volumetric flask while settled clay was re-suspended into 30 mL of 1.0 M HCl and procedure was repeated. Upon centrifugation, the supernatant was added to earlier solution, thereafter, solution was diluted to 100 mL mark. 15 mL from this solution was used for quantifying respective ion content. Same procedure was employed to prepare test samples for all clays. PerkinElmer Series II 2400 CHNS Elementary Analyzer was used to determine carbon content in OMI-clays and their residues. All samples tested were pre-dried at 110 °C for 30 min. Carbon content values reported are averaged based on triplicate results.

3. Results and discussions

3.1. Structural aspects of MI-clays

Exchanged metal cations are known to have a profound effect on various structural aspects of MMT including changes in their basal spacing (d_{001}), interlayer water structures and their dehydration behaviors [20,21]. Their ability to form thermodynamically stable hydration complexes in the presence of water has been widely reported [20]. Such hydration complexes are formed as a result of cations surrounded by coordinately bonded water molecules (schematically shown in Fig. 2). They are represented as $[M^{z+}(H_2O)_6]^{z+}$ where *z* is the valence of cation *M*. Strength of these hydration complexes is governed by charge density of the cations present at the core position (i.e., in terms of their ionic character –