



## Research paper

# Predicting thermal and thermo-oxidative stability of silane-modified clay minerals using thermogravimetry and isoconversional kinetic analysis



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## ABSTRACT

Clay minerals play an increasingly important role as functional fillers and reinforcing materials for clay polymer nanocomposites (CPN) in advanced applications. Among the prerequisites necessary for polymer improvement by clay minerals are homogeneous and stable distribution of the clay mineral throughout the CPN, good compatibility of the reinforcement with the matrix component and suitable processability. Typically, clay minerals are surface-modified with organic interface-active compounds like detergents or silanes to obtain favorable properties as filler. They are incorporated into the polymer matrix using manufacturing equipment like extruders, batch reactors or other mixing machines. In order for the surface modification to survive the stresses and strains during incorporation, the modified clay minerals must display sufficient thermal and mechanical stability to retain the compatibilizing effect. In the present study, thermogravimetry was used in combination with isoconversional kinetic analysis to determine the thermal stability of a silane-modified clay mineral based on bentonite. These findings were compared with the stability of the same clay mineral that was only surfactant-modified. It was found that silane modification leads to significantly improved thermal stability, which depends strongly on the type of silane employed.

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## 1. Introduction

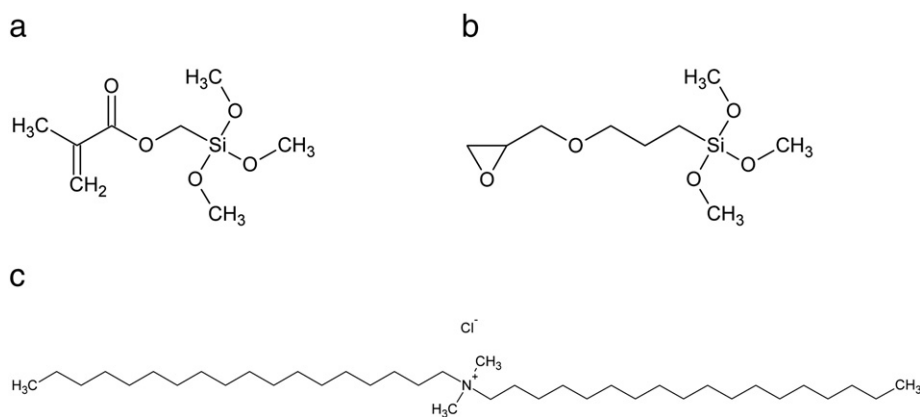
Clay minerals, often called nanoclays in specialized polymer literature, have a layered structure with a thickness layer of about 1 nm and about 50–150 nm in lateral dimensions that display large effective surface areas of about  $800 \text{ m}^2 \text{ g}^{-1}$  (Bergaya et al., 2011a, 2013; Kamena, 2005). Clay minerals are becoming increasingly important as functional fillers for polymers to improve their mechanical performance (Adewole et al., 2012; Ait Hocine et al., 2013; Alateyah et al., 2013; Bergaya and Lambert, 2013; Woo Kim and Cha, 2014), barrier properties (Bae, 2012; Bergaya and Lambert, 2013; Nah and Kader, 2010; Nazarenko et al., 2007; Pavlacky et al., 2012; Sanchez-Garcia and Lagaron, 2010) and fire resistance (Dubois, 2007; Gilman, 2006; Morgan, 2006; Schartel, 2006). Before incorporating clay minerals into a polymer, they are usually chemically adapted to improve compatibility with the organic polymer (Bergaya and Lambert, 2013). Typically, the hydrophilic nature of the native clay mineral platelets is attenuated by physical or chemical modification to increase hydrophobicity and improve miscibility with the matrix polymer (Bergaya et al., 2012). For this, in general, the clay minerals are swollen in water leading to an increase in interlayer distance. Subsequently, a typically cationic surfactant is added and attached to the silicate surface (Bergaya et al.,

2011b; Beyer et al., 2002; Kimura et al., 2000; Kurian et al., 2006; Zerda et al., 2003). A number of different modifying agents have been used for this purpose, such as a wide range of surface-active detergents as well as organosilanes (Huskić et al., 2013; Kim et al., 2011; Ogawa et al., 1998; Zhu and Wilkie, 2007). Unfortunately, when the modified clay mineral filler is introduced into the melted polymer, thermo-degradation of the organic compatibilizer may occur during the relatively long time required for swelling and exfoliation of the silicate platelets (Decker et al., 2005), which annihilates the effects of chemical modification and leads to unsatisfactory distribution and aggregation of the clay mineral. With some systems, this thermo-degradation can be avoided by applying a solvent-based approach where large amounts of volatile compounds are released, for example, when photo-polymerization of acrylate resins is performed in the presence of clay minerals to produce the CPN (Decker, 2006; Decker et al., 2004). However, in many cases, thermo-degradation plays a crucial role in CPN preparation and needs to be considered especially when dealing with hot melts during extrusion processes. Hence, it is important to predict the thermal stability of chemically modified clay minerals in order to judge their processability and to select a suitable pre-treatment regimen.

This paper summarizes a thorough thermochemical study on the thermostability of differently modified clay mineral filler intended for incorporation into polymeric matrices via extrusion of the hot melt. A bentonite (Bent) was modified with different silanes

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**Fig. 1.** Chemical structures of (a) methacryloxymethyltrimethoxysilane (MAOM-TMOS), (b) 3-glycidoxypropyltrimethoxysilane (GOP-TMOS), and (c) distearyl dimethyl ammonium chloride (DSDMAC).

[methacryloxymethyltrimethoxysilane, MAOM-TMOS (Fig. 1a) and 3-glycidoxypropyltrimethoxysilane, GOP-TMOS (Fig. 1b)] at different concentrations of the silane. The organobentonite (OBent) modified with surfactant [distearyl dimethyl ammonium chloride, DSDMAC (Fig. 1c)] was used as a reference. The modified Bent samples were investigated by thermogravimetry (TGA) and the thermal data were further analyzed with model-free kinetic analysis using the approach developed by Vyazovkin (Vyazovkin, 2001a; Vyazovkin and Dollimore, 1996) to obtain quantitative predictive models of the kinetics of thermal degradation of the organomodification.

## 2. Experimental

### 2.1. Chemicals

Nanofil® 5, which was used for all experiments, is an organobentonite (OBent) modified with distearyl dimethyl ammonium chloride (DSDMAC, 586.5 g.mol<sup>-1</sup>) supplied by Rockwood Clay Additives GmbH (Moosburg, Germany). To further modify the clay surface, either methacryloxymethyltrimethoxysilane (MAOM-TMOS, trade name Geniosil® XL33, 220.3 g.mol<sup>-1</sup>) or 3-glycidoxypropyltrimethoxysilane (GOP-TMOS, trade name Geniosil® GF80, 236.3 g.mol<sup>-1</sup>) purchased from Wacker Chemie AG (Munich, Germany) were applied as-received in a purity of 98%. The swelling agent for the Bent was dimethylformamide (DMF), which was procured from Th. Geyer GmbH (Renningen, Germany).

### 2.2. Methods

#### 2.2.1. Modification of bentonite

The Bent was modified by two different silanes MAOM-TMOS and GOP-TMOS as follows. Initially, 1 g of the Bent was pre-treated for 1 hour with a Sonotrode HD 2200 VS 70 T (Bandelin Electronic, Berlin, Germany) in 40 ml DMF at 20 °C to improve the swelling properties. Subsequently, each suspension of Bent was treated with either 40, 70 or 100 mmol of the respective silane. The samples were stirred for 16 hours, and then washed exhaustively at 20 °C in a Büchner funnel with 300 ml ethanol and 300 ml water, filtered off and dried under vacuum at 80 °C overnight.

#### 2.2.2. Thermogravimetric measurements of modified bentonite

Dynamic as well as isothermal thermogravimetry experiments were carried out on a TGA/DSC1 from Mettler-Toledo GmbH (Gießen, Germany) equipped with the module 835 with SDTA sensor, furnace LF110 and MX5 balance. For model-free kinetic analysis, each sample was measured with 5 dynamic heating rates (10 °C, 15 °C, 20 °C, 25 °C, and 30 °C min<sup>-1</sup>) from 25 °C to 1000 °C under nitrogen atmosphere or under synthetic air. Each 10 mg sample was measured in

70 µl Al<sub>2</sub>O<sub>3</sub> crucibles. From the dynamic TGA profiles, isothermal kinetic profiles of degradation were calculated as described below. To check the validity of the calculated kinetic parameters, isothermal experiments under synthetic air were conducted at 3 selected temperatures, covering the whole temperature range of each model. Isothermal experiments with the MAOM-TMOS-treated samples were carried out at 415 °C, 425 °C, and 435 °C, whereas for GOP-TMOS- and DSDMAC-treated samples, isothermal conditions were 290 °C, 310 °C, and 330 °C. Peak integrals and degradation degree versus temperature profiles were calculated from the thermogravimetric raw data using the STARE Software 9.30 (Mettler-Toledo GmbH, Gießen, Germany). For better determination of onset and endset temperatures of each dynamic measurement, the differential thermogravimetric trace (dTGA) was calculated. The degradation degree,  $\alpha(t)$ , at time  $t$  was calculated as the ratio of the lost mass until time  $t$  and the total loss of mass (Eq. (1)):

$$\alpha(t) = \frac{\Delta m_t}{\Delta m_{\text{tot}}} \quad (1)$$

Selected dynamic and isothermal experiments under nitrogen were performed with all samples to check how thermal degradation in the presence of oxygen altered the thermal degradation behavior.

#### 2.2.3. Model-free kinetic analysis of thermogravimetric data

Model-free kinetic analysis (MFK) was performed using MATLAB 7.12.0.635 (Mathworks, Ismaning, Germany) and the kinetic parameters describing the thermal degradation of the organic modification of the nanoclay was calculated using the method proposed by Vyazovkin (2001a).

To quantitatively describe the kinetics of thermal decay in terms of the degradation degree  $\alpha$  in dependence of time  $t$  and temperature  $T$ , knowledge of the kinetic triplet  $E_a$ , activation energy (J.mol<sup>-1</sup>),  $f(\alpha)$ , reaction model and  $A$ , pre-exponential factor (s<sup>-1</sup>) is required, so that the basic rate equation can be formulated (Eq. (2)):

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha) \quad (2)$$

In Eq. (2),  $A \exp\left(-\frac{E_a}{RT}\right)$  is the temperature-dependent rate constant (Arrhenius equation).

Due to the complexity of most processes, it is often not possible to provide an adequate description  $f(\alpha)$  of the reaction mechanism. Therefore, several model-free approaches were developed under the assumption of the isoconversional principle (Vyazovkin and Sbirrazzuoli, 2006). The isoconversional principle states that at a constant extent of conversion, the reaction rate is a function only of the temperature (Vyazovkin and Sbirrazzuoli, 2006). Therefore, arbitrary isothermal degradation profiles can be derived from a set of dynamic thermal

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