Effect of organoclays on the degradation of polyoxymethylene homopolymer during melt processing

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ABSTRACT

The improvement of Polyoxymethylene (POM) thermomechanical properties through the incorporation of nanofillers such as organoclays can be hindered by a detrimental effect of the latter on the thermal stability of the polymer. In order to be able to develop polyoxymethylene-based nanocomposites, it is necessary to assess the relation between nanofillers chemical properties and the thermal stability of POM. For this purpose, polyoxymethylene nanocomposites containing various organoclays have been processed and thoroughly characterized in this work. It is confirmed that organoclay containing nanocomposites are less thermally stable than neat polyoxymethylene. In this study, we bring evidence that the degradation of the alkylammonium ions of the organoclay is not responsible for polyoxymethylene decreased thermal stability. Moreover, it is demonstrated that the quantity of acidic sites on the organoclay surface accelerates the degradation and more surprisingly that their nature (Brönsted or Lewis) can induce different degradation mechanisms.

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1. Introduction

Polyoxymethylene (POM) is a semi-crystalline thermoplastic polymer broadly used for the manufacturing of high-precision mechanical parts, where high mechanical, thermal, chemical resistance are required [1,2]. In order to be processed, POM macromolecules need to be protected. Indeed, POM homopolymers are inherently unstable polymers. They easily degrade above 150 °C by unzipping depolymerization starting at the chain end from thermally unstable hydroxyl groups. This process is accompanied by the release of formaldehyde [3]. By the end of the 50's, these hydroxyl groups have been replaced by more stable acetyloxy or methoxy groups (end-capping process) [4,5] in order to increase the thermal stability.

Once end-capped, thermal degradation of POM starts far above its processing temperature when the methyl oxide bonds are broken under the combined action of heat and oxygen. Various degradation mechanisms have been proposed in the literature [1,5–18]. It is generally agreed that thermal degradation starts from the oxidation of the carbon atoms of the methylene groups leading to the formation of secondary hydroperoxides. These are probably thermally decomposed leading to the formation of a hydroxyl radical (able to induce hydrogen abstraction on the polymer chains) and an alkoxyl macroradical. A β-scission of the alkoxyl macroradical leads to the formation of two POM fragments with respectively a formate and an alkoxyl radical as end groups. Depending on the mechanisms proposed, the latter can either undergo the unzipping depolymerization with direct release of formaldehyde or form an unstable hydroxyl group after hydrogen abstraction from another macromolecule. Even if the reaction paths proposed in the literature may vary from an author to the other, they all agree that each hydroperoxyde decomposition induces (i) a chain scission, (ii) the formation of a formate group and (iii) at least one species able to initiate depolymerization. Other methods have been used to stabilize the polyoxymethylene such as the introduction of ethylene oxide units on the macromolecules to stop the unzipping depolymerization process [19,20], or by adding stabilizers against thermo-oxidative degradation [21].

In order to extend its application areas, the elaboration of POM based nanocomposites has been investigated in the last decade [22,23]. The increase of mechanical properties and thermo-mechanical stability of the polymer has been reported when POM

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was melt blended with various nanofillers such as silica [9], carbon nanotubes [25,26], POSS [27,28] or montmorillonite [22,29].

Among the nanofillers used, the montmorillonite is the most commonly used to improve thermomechanical properties of thermoplastic polymers. It is a 2:1 layered aluminosilicate with Na^+ or Ca^{2+} cations residing in the interlayer galleries [30]. These cations can be easily substituted by alkylammonium ions via ion-exchange reaction to help the dispersion of individual inorganic layers in a polymer matrix [31,32]. Thermomechanical properties [33,34], thermal stability [35,36], flame retardancy and barrier properties [37] can be significantly improved by addition of very low amounts montmorillonite in polymers, allowing the development of new applications in the automotive and packaging industry for instance.

However, recent studies have shown that organomodified layered silicates might have a detrimental effect on POM thermal stability. Even if Jose et al. [22] observed an increase in the degradation temperature of organomodified fluorohectorite containing POM nanocomposites, Khongkhlang et al. [29] observed that it could be decreased by 40 °C by the incorporation of only 1 wt% of organoclays. The authors suggest that POM degradation could be catalyzed by acidic sites on the clay surface such as suggested by Qin et al. regarding the photodegradation of polyethylene [38] and polypropylene [39], or by Wang et al. regarding the thermal degradation of polyamides [40]. These acidic sites could result from the Hoffman elimination that alkylammonium ions are likely to undergo above 180 °C according to Xie et al. [41]. It should however be pointed out that this latter study also states that the onset of the Hoffman elimination reaction is independent of the nature of the alkylammonium ions used to modify the layered silicate, whereas Khongkhlang et al. report some differences in the thermal stability decrease between the organoclays dispersed in the nanocomposites. Moreover, contrarily to what has been observed by Chausson et al. with alkylammonium modified titanoniobates in polyamide [36], the loss in thermal stability cannot be related to a better dispersion state, which would increase the number of polymer/acidic sites interactions either. Finally, Pielichowska [42] recently reported a 70 °C decrease in degradation temperature of POM induced by the incorporation of unmodified hydroxyapatite. This study suggests that the nanofillers surface chemistry might induce a modification in the degradation mechanism of polyoxymethylene.

In order to be able to develop organoclay containing POM nanocomposites, the issues regarding a possible modification of its thermal stability need to be assessed. The purpose of the present work is to evaluate the extent of the decrease of POM thermal stability during processing and to relate it to the surface properties of various organically modified-montmorillonite. Three organoclays, which are widely used to develop thermoplastic based nanocomposites, have been compared. The thermal stability of POM nanocomposites has been investigated by thermogravimetric analyses. For a better understanding of the mechanisms involved during degradation, the degradation study has also been followed using temperature controlled Fourier Transform Infrared Spectroscopy in Attenuated Total Reflection mode (FTIR-ATR). Eventually the organoclay surface properties have been characterized using pyridine as a probe molecule in order to quantify Lewis and/ or Brønsted acidic sites types [43—45] and the relationships between the nature of the organoclay and the thermal stability of nanocomposites have been established.

2. Experimental section

2.1. Materials

Polyoxymethylene (POM) homopolymer Delrin 100 was supplied by DuPont de Nemours (Puteaux, France) and used after drying 1 night at 60 °C under vacuum. Organically modified montmorillonites (Cloisite® 20, 30B, 93A) with different surfactants (Table 1) were supplied by Rockwood Additives (Wessel, Germany). These organoclays will be referred to as C20, C30, and C93 in the rest of the paper. Organoclays have also been dried overnight before processing at 60 °C under vacuum. Absence of residual water was verified by thermogravimetric analyses.

2.2. Nanocomposites processing

Nanocomposites were processed by melt blending organoclay (5 wt% inorganic content) with POM using a twin screw 15 cc Xplore microcompounder (DSM, Geleen, Netherlands). The mixture was sheared for 1 min with a 100 rpm screw speed at 200 °C and injected with a 12 cc Xplore molding device (DSM, Geleen, Netherlands) at 90 °C to obtain 5A dumb-bell-shaped specimens. X-Ray diffraction analyses allowed measuring the average distance between two clay platelets (d_{001}) for the various organoclays before and after incorporation in the POM matrix. The values reported in Table 2, suggest that the organoclay has not been exfoliated in the polymer matrix during processing. The increase in d_{001} obtained with C20 suggests that polymer melt intercalation between the clay platelets occured. With C30 and C93, if any polymer intercalation took place it did not increase d_{001}. Since significant polymer degradation took place during processing with formaldehyde release, the structure of these nanocomposites has not been further investigated.

2.3. Analyses

2.3.1. Thermogravimetric analyses (TGA)

A Pyris 1 thermogravimetric analyzer (Perkin Elmer, Waltham, MA, USA) was used. Sample mass was comprised between 5 and 10 mg. Analyses were performed under 20 mL/min Nitrogen flow with a heating rate of 20 °C/min. Degradation temperatures reported correspond to the onset of degradation and have been measured when the sample lost 5% of its initial weight.

2.3.2. Infrared spectroscopy in Attenuated Total reflectance mode (FTIR-ATR)

After cryomilling and sieving POM pellets into fine powders with particles size < 30 μm, POM were dried at 60 °C under vacuum for 1 night and the absence of residual water verified by TGA. Dry blends of POM and organoclay 95/5 w/w were prepared and disposed on the temperature controlled Ge ATR crystal. The FTIR-ATR spectra were recorded by a Nicolet 5700 spectrometer equipped with a MCT (Mercury-Cadmium-Tellurium) detector. Measurements were carried out with 128 scans in the 600—4000 cm^{-1} range with a 2 cm^{-1} resolution, while maintaining the ATR crystal at 200 °C. An infrared spectrum was acquired every 75 s. Spectra were processed to subtract the contribution of atmospheric water and CO_2 which can act as interferences due variations in the atmosphere during acquisition.

2.3.3. In situ infrared analyses (in situ IR)

In order to study the pyridine interaction with the organoclay surface and calculate the acidic sites content, in situ IR analyses of surface acidity were performed by monitoring the adsorption of pyridine [46,47]. The in-situ IR cell allows controlled adsorption of probe molecules on a thin disk shaped solid sample.

Organoclays were ground in an agate mortar then pressed between two highly polished steel mirrors with a 0.5 bar pressure into self-supported disk-shaped samples with a 20 mm diameter and >0,1 mm thickness. The sample was then activated at 200 °C under