Synthesis and thermal oxidative degradation of a novel amorphous polyamide/nanoclay nanocomposite

Xingui Zhang, Leslie S. Loo*

School of Chemical and Biomedical Engineering, Nanyang Technological University, N1.2 B1-12, 62 Nanyang Drive, Singapore 637459, Singapore

A B S T R A C T

A novel amorphous polyamide/montmorillonite nanocomposite based on poly(hexamethylene isophthalamide) was successfully prepared by melt intercalation. Wide angle X-ray diffraction and transmission electron microscopy showed that organoclay containing quaternary amine surfactant with phenyl groups was delaminated in the polymer matrix, resulting in well-dispersed morphologies even at high montmorillonite content. Thermal oxidation behavior of the polymer nanocomposites was studied by thermogravimetric analysis (TGA), and the chemical evolution in the solid residue was monitored by elemental analysis and Fourier transform infrared spectroscopy (FTIR). TGA results showed that the addition of well-dispersed organoclay resulted in a substantial increase (30 °C) in the onset degradation temperature of the nanocomposites as compared to the homopolymer. Elemental analysis on the solid residue indicated that the presence of nanoclay resulted in char formation with greater thermal stability. FTIR spectra showed that thermal degradation in air occurred via both oxidative and non-oxidative mechanisms simultaneously. In the homopolymer, the oxidative mechanism was more dominant. However, with the addition of well-dispersed organoclay, the non-oxidative pathway became more significant. Hence the presence of delaminated nanoclay layers could effectively retard thermo-oxidative degradation of the amorphous polymer by constraining the polymer chains and slowing down the rate of oxygen diffusion through the nanocomposites, but it was not as effective in hindering the non-oxidative degradation reaction pathway.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Polymer/nanoclay nanocomposites have been extensively studied [1–5] since the Toyota research group successfully synthesized polyamide 6 nanocomposites based on montmorillonite (MMT) in 1993 [6,7]. In many cases, the addition of a small amount (ca. 5 wt%) of nanoclay to the polymer matrix was sufficient to cause remarkable improvements in mechanical properties [8], heat distortion temperature [6], thermal stability [9,10], and flame retardance [11,12]. Blumstein first reported the improved thermal stability of a polymer/MMT nanocomposite which was based on polymethyl methacrylate (PMMA) [13].

The barrier model is a widely accepted mechanism to explain thermal property enhancement in polymer/clay nanocomposites [4,9]. However the notion of barrier effect is not limited to a silicate-enriched char layer formed on the polymer melt surface, but rather it covers the situation that the delaminated nanoclay layers spatially

constrain the molecular mobility of polymer segments and hinder the diffusion of volatile decomposition products within the nanocomposites [14,15]. More recently, Chen et al. have used the notion of "nanoconfinement", which is conceptually identical to the notion of "barrier", to study the fundamental effects of nanoclay on the enhanced thermal behavior of polymer nanocomposites [16]. Consequently, in order to enhance the barrier effect as well as the nanoconfinement effect, the clay surface was often modified with an organic surfactant to improve the interactions between the clay particles and the polymer in order to obtain a nanocomposite with well-dispersed nanofiller morphology [17–20].

Generally, it has been shown that the thermal stability of polyamide 6 or polyamide 66, as indicated by the initial temperature of decomposition in a nitrogen atmosphere, did not improve (and sometimes worsened) with the addition of nanoclay [21–25]. For example, in well-exfoliated polyamide 66 nanocomposite with 5 wt% organic MMT, Qin et al. found that the decomposition temperature of the nanocomposite was 10 °C lower than that of pure polyamide 66 (445.8 °C) in a nitrogen atmosphere, but 7 °C higher than that of the polymer matrix (440.4 °C) when the degradation took place in air [22]. They attributed this difference to

* Corresponding author. Tel.: +65 6790 6737; fax: +65 6794 7553.
E-mail address: ssloo@ntu.edu.sg (L.S. Loo).

the barrier effect of nanoclay layers in the presence of oxygen. Similar phenomena were also observed in non-charring poly-ethylene (PE) or poly(ethylene-co-vinyl acetate) (EVA)/organic MMT systems [18,26].

Unlike thermal degradation in the absence of oxygen, where bond scission occurs randomly, oxidative degradation is character-ized by random scission of the polymer backbone [27]. The key issues in the thermal oxidative degradation of polymer systems are: (a) the sites where oxidation occurs, (b) the type of structural fragments which is most vulnerable to degradation, (c) the means by which the polymer matrix should be protected against thermal degradation, and (d) the main principle behind the protection [27]. Studies in the thermal oxidation of polymer/clay nanocomoposites are important because many such materials are required in appli-cations which involve prolonged service in air at high temperatures. Hence, knowledge of the onset degradation temperature, the resulting degradation products, and the polymer degradation mechanism in the presence of nanoclay and oxygen are critical in order to design polymer nanocomposites with superior thermal properties [23]. Currently, much of the research on the thermal or thermo-oxidative degradation of polymer/nanoclay nano-composites have focused on analyzing the gaseous decomposition products evolved during the degradation process. Such analysis was accomplished through the use of hyphenated techniques such as TGA combined with mass spectrometry and FTIR (TGA/MS and TGA/FTIR), as well as pyrolysis-gas chromatography combined with MS (pyrolysis-GC/MS) [11,16,24,27,28]. Although these studies revealed valuable indirect information on the chemistry of the degradation process, they were not able to provide direct information on the chemical changes undergone by the solid materials upon thermal degradation [24,26,29]. In fact, drawing conclusions from such indirect evidence alone could lead to contradictory and sometimes erroneous conclusions. For instance, during thermal decomposition in nitrogen, Pramoda et al. found that the functionalities of the evolved products analyzed by TGA/FTIR were similar for both polyamide 6 and its nanoclay nanocomposites. Hence they concluded that the presence of nanoclay would not affect the degradation pathway of polyamide 6 [30]. However, in another similar study, Jang and Wilkie used GC/MS to analyze the evolved condensable products of polyamide 6 and its nanoclay nano-composites and found some differences. Hence they conjectured that the degradation pathway of polyamide 6 had been modified in the presence of clay [24]. They then tried to confirm their hypothesis by analyzing the solid residue of pure polyamide 6 and its nano-composites at 40 wt% mass loss using FTIR, but the infrared spectra did not present sufficient information to indicate that chemical changes had occurred in the residue during the degradation process. Jang and Wilkie, however, did not examine the residue at other mass losses. Hence, in order to fully ascertain the role of nanoclay during thermal decomposition, it is also important to study the changes in the chemical composition and structure of the solid residue formed at various temperatures [27]. Recently, Chen and Vyazovkin repor-ted the FTIR analysis of the gas-phase and condensed-phase degradation products of polystyrene (PS) and its nanocomposites, and concluded that the PS/clay nanocomposites exhibited greater stability under thermal oxidation than PS [31]. To the author's knowledge, however, very little investigation of this nature has been carried out, particularly for polyamide systems [24,26].

In this paper, the thermo-oxidative stability of a novel melt pro-cessed nanocomposite based on an amorphous semi-aromatic polyamide, poly(hexamethylene isophthalamide), is presented. This polymer is commonly known as polyamide 6I. Very little research has been carried out on amorphous polyamide/nanoclay nano-composites, although there exists quite a large literature for melt processed nanocomposites based on aliphatic semicrystalline

polyamides, including studies on their thermal stability [24,30,32,33]. At first glance, it may seem unusual to choose this inherently complex amorphous polyamide for the study, but it must be emphasized that this was a deliberate choice. First, using a fully amorphous polyamide would remove the complications that would arise due to the presence of a crystalline phase or nanoclay-induced crystalline phase transitions (which is common in semicrystalline polyamides) [34,35]. Second, as discussed later, the FTIR spectrum of the amorphous polyamide is remarkably straightforward and easy to interpret [36]. In many applications, poly(hexamethylene isophthal-amide) is advantageous over semicrystalline polyamides because of its optical transparency, good electrical insulation properties, good chemical resistance and low moisture absorption [37–39]. This high-performance material is used as transparent covers and panes in the electrical industry and as packaging materials in polymer blends [40–42]. Therefore, successful synthesis of a novel amorphous polyamide/clay nanocomposite with enhanced thermal properties could broaden the scope of applications of this polymer.

The objective of this work is to gain insight into the chemical transformations and decomposition process of this polymer nano-composite during thermal oxidation. Thermal analysis (TGA/DTG) was used to identify the different stages of degradation. Elemental analysis (EA) and FTIR were performed on the solid residue obtained at various temperatures in order to provide direct information about the chemical changes occurring in the material. Finally, an expla-nation to account for the improved thermal stability in such poly-mer nanocomposites is proposed in light of these results.

2. Experimental

2.1. Materials

The materials used in this study are listed in Table 1. The polymer was obtained from Lanxess under the product trade name Durethan T40. Fig. 1a shows the repeat unit of the amorphous polyamide (aPA). Pristine sodium montmorillonite (MMT) nanoclay and one type of MMT-based organoclay, abbreviated as NaMMT and 10AMMT respectively, were supplied by Southern Clay Products. 10AMMT contains a surfactant with a phenyl ring. The chemical structure of this surfactant is shown in Fig. 1b, where "HT" stands for hydrogenated tallow. Prior to blending, the polymer and nanoclay were first dried in a vacuum oven at 80 °C for at least 12 h. GC grade 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 99.8% purity) and GC grade 2,2,2-trifluoroethanol (TFE, 99.9% purity) were purchased from Aldrich Chemical Company and used as-received.

2.2. Melt processing

The aPA/nanoclay nanocomposites were made via a two-step process in a nitrogen atmosphere. First, a 50 g master batch of aPA containing 12 wt% MMT (wt% excludes surfactants) was prepared by melt blending the dried polymer pellets and nanoclay in a Haake

Table 1
Materials used in this study.

Material (designation used in this paper)	Supplier designation	Specifications
aPA	Durethan T40	Poly(hexamethylene isophthalamide)
NaMMT	Cloisite® Na+	92.6 CEC,[a] d_{001} spacing = 1.05 nm
10AMMT	Cloisite® 10A:dimethyl, benzyl, hydrogenated tallow quaternary ammonium chloride organoclay	125 CEC, organic content = 36.9 wt%, d_{001} spacing = 1.95 nm

[a] CEC: cation exchange capacity, mequiv/100 g.