

Method development for the analysis of biodegradable polymers

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Abstract. In today's modern world, plastics are used for a variety of everyday applications from plastic shopping bags to medicinal applications, but most of these plastics are resistant to environmental influences such as humidity and microbial attack. The ecological problem we now face in our landfills is the large volume of non-biodegradable plastics, which has made the development of biodegradable plastics an urgent matter. Because of this situation, the Chemical Metrology Group of NMISA (National Metrology Institute of South Africa) has embarked on a collaborative effort with the Fibre and Polymer Technology Department of KTH (Royal Institute of Technology) in Sweden to develop methods for the analysis of biodegradable polymers. During the project, commercial and research samples are analysed with various techniques, such as Pyrolysis-GC-MS, GPC, FTIR, SEM, TGA, TGA-FTIR and DSC. The aim is primarily to evaluate what information can be obtained by Pyrolysis-GC-MS and FTIR-TGA with respect to thermal properties and degradation products. Currently polylactide (PLA) is the focus of many studies and it is one of the most promising degradable polymers. One trend is to improve the properties of PLA through addition of different nanofillers. In this work polylactide nanocomposites are made by blending polylactide (PLA) with zinc oxide, titanium dioxide, halloysite (aluminosilicate) or surface modified montmorillonite (phyllosilicate). The materials are characterized by scanning electron microscopy (SEM) and DSC. The thermal stability and resulting thermal degradation products are analysed by TGA and Py-GC-MS. The results especially show the influence of nanoparticle surface modification on the degradation product pattern.

Keywords: Biodegradable polymer; plastics; analysis

1 Introduction

Degradable polymers from renewable resources are a promising solution to reduce the enormous amount of plastic waste, in particular from packaging. However, many problems still exist to ensure the safe service-life and complete degradation of the materials after disposal without leaving behind fragments or harmful compounds. Currently polylactide (PLA) is the focus of many studies and it is one of the most promising degradable polymers. The degradation of plain polylactide in different environments has been extensively studied [1,2]. In addition PLA can be produced from renewable resources. However, degradable polymers often have inadequate mechanical and barrier properties and the addition of nanoparticles could be a solution. In this work polylactide nanocomposites made from PLA and zinc oxide, titanium dioxide, halloysite (aluminosilicate) and montmorillonite (phyllosilicate) are studied. The goal of this study is to evaluate the thermal stability and mechanism of thermal degradation for these nanocomposites by using thermo-gravimetric analysis (TGA) and pyrolysis-gas chromatography mass spectrometry (Py-GC-MS).

2 Experimental step

2.1 Materials

The polymer used is amorphous PLA from NatureWorks with reference 5200D. Two kinds of TiO₂ powders are used in this work. One from Aldrich, Titanium (IV) oxide, size <100 nm (BET) and the other provided by Riedel-deHaën, the particle size is somewhat larger than for the first one. In addition zinc oxide and two nanoclays, Montmorillonite 35–45 wt.% dimethyl dialkyl (C14-C18) amine and Halloysite all from Aldrich, are used as nanofillers. Particle sizes are <100 nm. PLA films are prepared by dissolving the polymer and nanoparticles in chloroform at 45 °C followed by solution-casting into a thin film (0.1 mm) on a glass plate (3 g of polymer + 0.6 or 0.15 g of filler for 20 wt.% and 5 wt.% composites and 50 ml of chloroform). The solvent has been evaporated, and the film has been dried under reduced pressure for 1 week before analysis. Some of the films have been also ultrasonicated 30 min before the solution casting to break possible nanoparticle agglomerations.

2.2 Differential scanning calorimetry, DSC

The thermal properties of the nanocomposite films, are investigated using a DSC (Mettler Toledo DSC 820 module)

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under nitrogen atmosphere. A total of 2–8 mg of the nanocomposite has been encapsulated in a 40 μL aluminum cap without a pin. Samples are heated under a nitrogen gas flow of 80 ml/min from 25 $^{\circ}\text{C}$ to 190 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$. The melting temperatures, T_m , are noted as the maximum values of the melting peaks, and the midpoint temperature of the glass transition is determined as the glass transition temperature, T_g .

2.3 Scanning electron microscopy, SEM

The surfaces of the samples at different degradation times are studied using a Hitachi S-4800 SEM using an acceleration voltage of 0.6–1.5 kV. The samples mounted on metal studs and sputter-coated with gold-palladium using a Cressington 208HR sputter coater.

2.4 Thermo-gravimetry, TGA-FTIR

A Cahn Versa Thermo HM thermo-gravimetric analyser interfaced with Nicolet Nexus 470 Fourier Transform Infrared Spectrometer is used. A custom-made connector prevents condensation of decomposition products (temperature about 180 $^{\circ}\text{C}$). The transfer line is wrapped with heating coil and the line is controlled by a ThermoNicolet FTIR/TGA Interface and is kept at about 180 $^{\circ}\text{C}$. A small pump is used to draw the gas from TGA to the gas cell. Nitrogen is used as the purge gas. The samples weigh typically between 10 and 20 mg and the temperature has been raised from room temperature to 500 $^{\circ}\text{C}$. The heating rate is 17 $^{\circ}\text{C}$ per minute in nitrogen (Nitrogen 5.0). The gas cell is placed in the IR scanning path for the detection of the decomposition products. The gas cell is controlled by ThermoNicolet FTIR/TGA Interface and is kept at 230 $^{\circ}\text{C}$. IR detection region is between 400 and 4000 cm^{-1} . The spectra have been taken as an average 50 scans at 8 wavenumber resolution. Sampling interval is 27 s.

2.5 Pyrolysis-gas chromatography-mass spectrometry, Py-GC-MS

The pyrolysis-GC-MS system is made of CDS 100 Pyroprobe, CDS 1500 valved interface connected to Thermo Trace GC Ultra and Thermo Trace DSQ. The samples have been pyrolysed and analysed in helium (Helium 5.0) atmosphere. A Restek GC-column (part nr. 13423, 30 m, I.D. 0.25 μm) is used in this work. The column temperature is held at 40 $^{\circ}\text{C}$ for 1 min, then programmed to heat to 330 $^{\circ}\text{C}$ at a rate of 20 $^{\circ}\text{C min}^{-1}$ and finally held at 330 $^{\circ}\text{C}$ for 1 min. The temperature of the transfer line and the source is 200 $^{\circ}\text{C}$. A sample was placed in a quartz tube (heated up to 900 $^{\circ}\text{C}$ before adding sample), which is then inserted into the platinum coil of the probe. The probe is then inserted into the interface. Typically 2 to 5 min are allowed for the purging of air with helium. The temperature of the interface is 300 $^{\circ}\text{C}$. Typically samples have been pyrolysed at 750 $^{\circ}\text{C}$ for 10 s.

Table 1. Glass transition and melting temperature of PLA and PLA-titanium oxide composites.

Composite	T_g	T_m
PLA	48	111
PLA 5% TiO_2 macroparticles	44	110
PLA 20% TiO_2 macroparticles	47	110
PLA 5% TiO_2 nanoparticles	38	112
PLA 20% TiO_2 nanoparticles	36	111

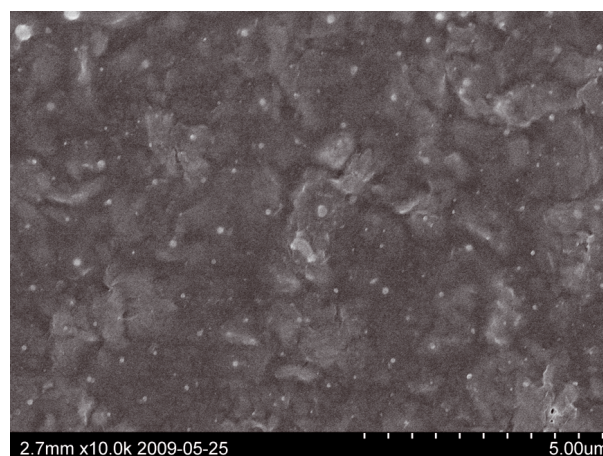


Fig. 1. SEM pictures showing the surface structure of PLA-montmorillonite.

3 Results and discussion

Several PLA nanocomposites containing 5 or 20 wt.% of different nanoparticles or nanofillers have been prepared by solution casting and characterized for the thermal properties by DSC. The distribution of nanoparticles in the polymer matrix is examined by SEM. In addition the effect of nanofillers on thermal stability and residue as well as on thermal degradation product patterns have been evaluated by TGA and Py-GC-MS. Table 1 shows the effect of titanium oxide on the glass transition and melting temperature. The addition of nano- and microparticles has not significantly affected the melting temperature. However, the nano-titanium oxide decreases the glass transition temperature of the films compared to pure PLA.

Figure 1 shows an example of scanning electron micrographs of the PLA montmorillonite nanocomposite. In most cases the nanoparticles are evenly distributed in the PLA matrix as shown for PLA-Montmorillonite in Figure 1. However, halloysite is distributed rather unevenly and there are rather large differences in the particle size, which can influence the results as well as their reproducibility.

Table 2 summarises the prepared nano- and microcomposites and their compositions. Table 3 compares the thermal stability of the prepared composites. In some cases addition of nano- or microparticles results in increased thermal stability, while in other cases thermal stability decreases. Zinc Oxide is the nanoparticle that most severely decreases the thermal stability. Films that have

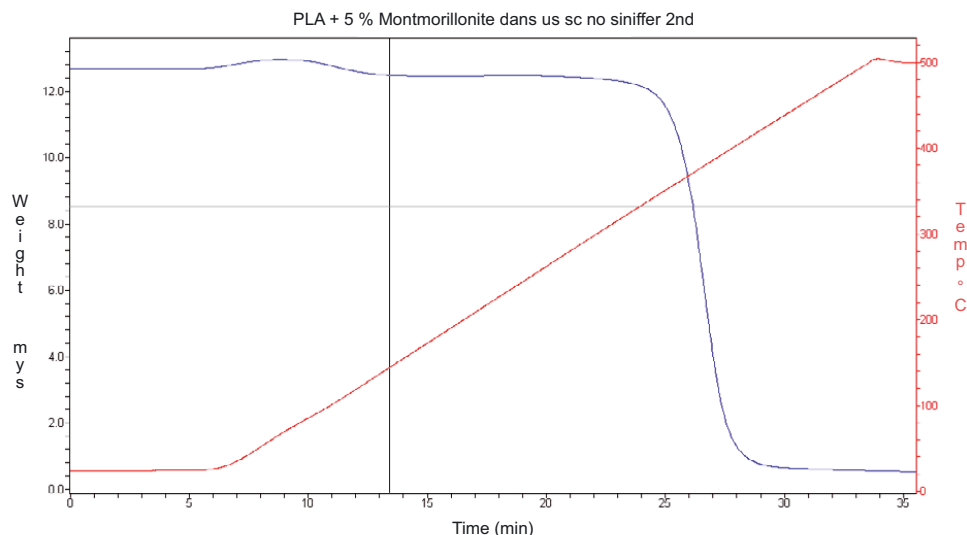


Fig. 2. TGA thermogram of PLA + 5% montmorillonite.

Table 2. Prepared composites, their composition and method of preparation.

Sample	Method of preparation	Nano-Composite
PLA	–	–
PLA + 5% ZnO	ultrasonication	yes
PLA + 5% TiO ₂	ultrasonication + solution casting	yes
PLA + 5% TiO ₂	ultrasonication + solution casting	no
PLA + 5% TiO ₂	heating + solution casting	yes
PLA + 20% TiO ₂	ultrasonication + solution casting	no
PLA + 20% TiO ₂	heating + solution casting	yes
PLA + 20% TiO ₂	heating + solution casting	no
PLA + 5% Halloysite	ultrasonication + solution casting	yes
PLA + 20% Halloysite	ultrasonication + solution casting	yes
PLA + 5% Montmorillonite	ultrasonication + solution casting	yes
PLA + 20% Montmorillonite	ultrasonication + solution casting	yes

been both heated and ultrasonicated have lower thermal stability than films that have been dissolved only by heating. Addition of 20% titanium oxide leads to increased degradation onset, while 20% halloysite or montmorillonite leads to lower degradation onset compared to pure PLA. Transparent films are obtained when using 5% loading of halloysite or montmorillonite. In all other cases the

Table 3. TGA results of polylactide composite.

Sample	Onset (°C)	Residue % weight	Film
PLA	361.2	5.81	transparent
PLA + 5% ZnO	295.8	16.25	opaque
PLA + 5% TiO ₂	356.6	11.55	opaque
PLA + 5% TiO ₂	371.7	11.50	opaque
PLA + 5% TiO ₂	381.8	14.16	opaque
PLA + 20% TiO ₂	350.8	23.80	white
PLA + 20% TiO ₂	375.5	31.04	opaque
PLA + 20% TiO ₂	380.4	23.42	white
PLA + 5% Halloysite	371.7	9.51	transparent
PLA + 20% Halloysite	356.7	20.47	slightly opaque
PLA + 5% Montmorillonite	361.3	4.87	transparent
PLA + 20% Montmorillonite	350.3	12.26	slightly opaque

prepared films are opaque or white. In Figure 2 the TGA curve for polylactide with 5% montmorillonite is shown.

In Figure 3 pyrolysis GC-MS chromatographs of polylactide and polylactide-20wt.% montmorillonite nanocomposite are shown. When a nanocomposite containing polylactide and 20% montmorillonite is analysed in pyrolysis-GC-MS, several additional peaks that may result from degradation of dimethyl dialkyl (C14–C18) amine used for surface modification of montmorillonite nanoclay have been observed (Fig. 3b). The other nano- and microcomposites show similar degradation product patterns to pure PLA, where lactide monomers can be identified as main degradation products.

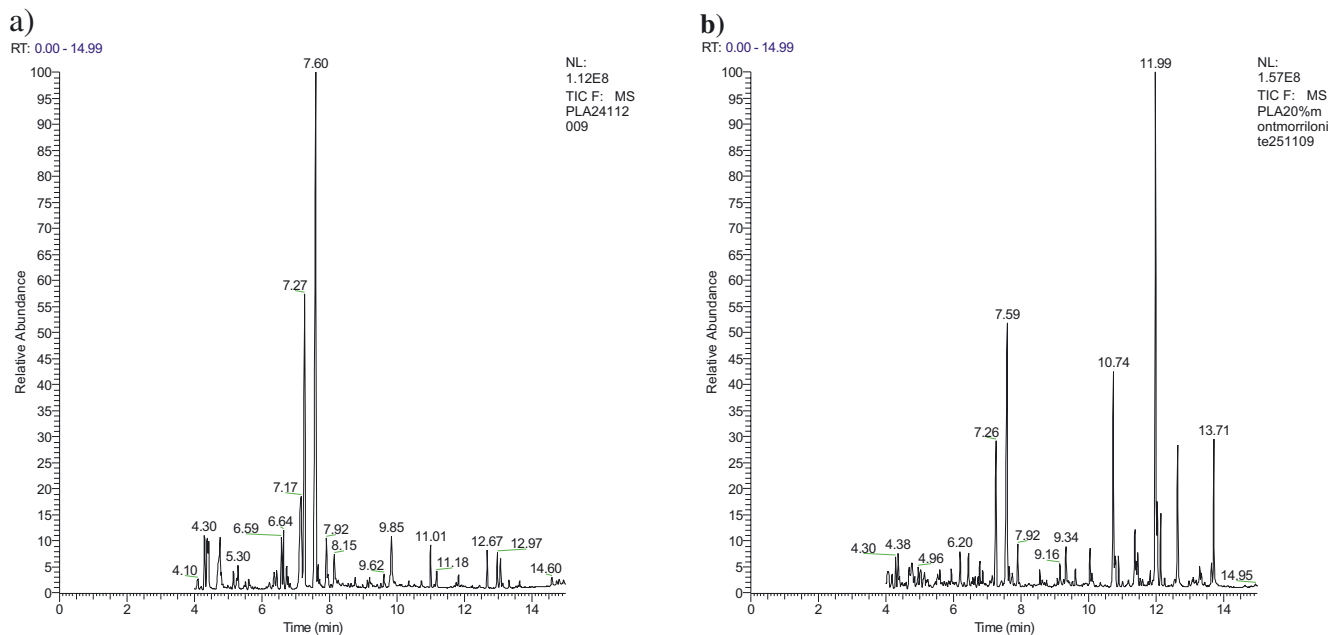


Fig. 3. Pyrolysis-GC-MS chromatograph of (a) PLA and (b) PLA with 20% montmorillonite.

4 Conclusion

Depending on the type of nano- or microparticle the thermal stability is increased or decreased. In most cases the nanoparticles do not affect the degradation product patterns. However, the surface modification of montmorillonite nanoclay results in several new pyrolysis products.

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