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TG-FTIR STUDY OF THE THERMAL DEGRADATION OF POLYOXYMETHYLENE (POM)/THERMOPLASTIC POLYURETHANE (TPU) BLENDS

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Abstract

A series of blends of polyoxymethylene (POM)/thermoplastic polyesterurethane (TPU) has been obtained by mechanical processing using a double screw extruder. The thermal stability and the thermal degradation profiles of POM/TPU blends were investigated by thermogravimetric analysis (TG) coupled on-line with Fourier transform infrared spectroscopy (FTIR). It was found that incorporation of TPU into POM matrix resulted in increase of thermal stability of blends in comparison with pristine materials. The thermal degradation of TPU in inert gas atmosphere proceeds in two steps while the thermal degradation of POM is basically a one step process with a substage in a higher temperature range. The most abundant volatile products of the thermal degradation were identified; the possibly routes of their formation have been presented.

Keywords: blends, polyoxymethylene, polyurethane, TG-FTIR, thermal stability

Introduction

Polyoxymethylene (POM) belongs to the most important engineering plastics with a unique set of mechanical, thermal, chemical and electrical properties [1, 2]. For applications where high impact material is regarded its toughness is commonly improved by blending with elastomeric compounds [3–5]. Among various POM systems with high impact resistance, blends of POM and thermoplastic polyurethanes (TPUs) are considered as very promising since TPUs, as modifiers, offer a wide range of properties resulting from their segmented structure. Furthermore, they show partial miscibility with POM based on their ability to form hydrogen bonds between urethane group in polyurethane macrochain and ether linkage in polyoxymethylene backbone [6–8]. The presence of hydrogen bonds was confirmed by FTIR data by observing characteristic shifts of absorption bands involved. Since POM/TPU blends are expected to fulfil severe requirements of engineering polymer materials their thermal behaviour needs to be carefully tested. Hence, the thermal stability of POM/TPU systems was investigated by Kumar *et al*. [9]. They found that the degra-

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dation of blends occurs at higher temperatures comparing to pure polyoxymethylene. The increase of the onset temperature of degradation was correlated with an increasing value of activation energy that was calculated by modified Freeman and Carroll method.The improvement in thermal stability of blends POM/TPU was observed also by Mehrabzadeh *et al.* who observed that the thermal characteristics of incorporated TPU was improved as well [8].

However, from the literature study it can be noticed that there were no studies performed which were focused on the determination of routes of thermal decomposition of POM/TPU blends. Therefore in this paper we present our first results of POM/TPU blends' thermal degradation studied by the hyphenated thermoanalytical method based on thermogravimetry (TG) with evolved product analysis performed with a Fourier transform infrared (FT-IR) spectrometry. A unique feature of this system is its ability to provide continuous monitoring of the IR spectra of evolving products as well as quantitative analysis of gases [10–12]. In contrast to pyrolysis GC, in which all the gases produced by heating to a given temperature are separated and analysed as a batch; TG/FT-IR offers the great advantage of sequentially identifying the gases for a comprehensive vapour-phase analysis.

Experimental

Materials

POM of a copolymer type was produced by Zaklady Azotowe in Tarnów-Moœcice S.A. (Poland). The melt flow index value was 2.5. TPU (polyester-based) was kindly provided by Jelchem S.A. in Jelenia Góra, Poland.

POM/TPU blends were melt-mixed using a laboratory double-screw extruder HAAKE (L/D = 25) with a screw speed of 50 r.p.m. at the temperature range of 175–190°C. Sample's description is presented in Table 1.

Table 1 Description of the samples

Sample	Material
1	POM
2	TPU
3	POM/TPU 90:10 *w*/*w*
4	POM/TPU 80:20 *w*/*w*

Techniques

Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy

Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TG/FTIR) was carried out using a Netzsch TG 209 thermal analyser (heating rate = 20 K min^{-1}, sample mass ~ 3 mg, nitrogen flow = 50 $\text{cm}^3\ \text{min}^{-1}$) and a Bruker IFS 66 FTIR spectrometer.

The thermogravimetric analyser and spectrometer were suitably coupled to enable the passage of evolved products from the furnace to the gas cell over a short path, to minimise secondary reaction or condensation on cell walls. Moreover, the experimental conditions have been chosen to ensure that the condensable products form a submicron aerosol mist. This size aerosol has two advantages: (*i*) the particles follow the gas streamlines, thus minimizing condensation and (*ii*) the particles produce little scattering.

Results and discussion

The results of TG analysis of POM, TPU and their blends are shown in Fig. 1

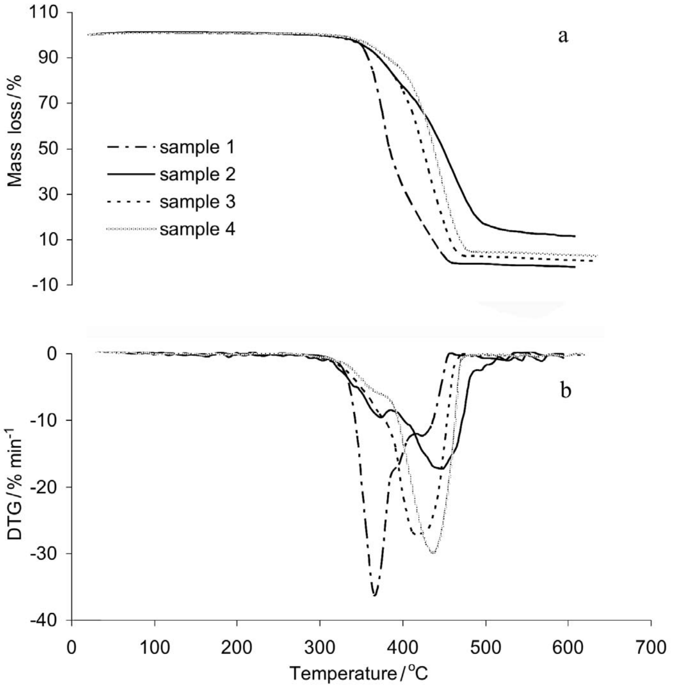

Fig. 1 TG (upper diagram) and DTG (lower diagram) profiles of POM, TPU and POM/TPU blends at 20 K min^{-1}

The onset temperature of degradation for each tested sample was approximately 310°C; it is over 100°C higher than polyoxymethylene melting point [1], making thus possible to maintain stable conditions during processing. As it can be seen from TG curve POM decomposed quite intensively up to 445°C. The main mass loss of TPU occurred from 310 to 490°C and the char yield of pristine polyurethane was considerably higher than that of POM and POM/TPU blends. POM DTG profile has a main peak with a substantial shoulder at higher temperature, while DTG curve of TPU shows a main peak with a lower temperature shoulder. The maximum rate of degradation for TPU occurred at 375 and 425°C for the first and second stage of degradation process, respectively. The DTG peak of POM displayed maximum at 365°C.

Thermal behaviour of POM/TPU blends was rather similar to POM for the investigated compositions. Decomposition reactions of blends went in one stage within temperature range of 320–460°C, but the region of maximum mass loss was shifted towards higher temperatures. This shift is indicative of changes in thermal behaviour of blends in reflection to pristine polymers. The presence of specific interactions between polymeric components (hydrogen bonds) which had been previously confirmed in this system, was probably responsible for this phenomenon [6].

The thermal stability and degradation of polyoxymethylene was previously investigated with regard to susceptibility of POM to depolymerization process upon heating [13]. Depolymerization reactions start at the hydroxyl end-groups of POM (hemi-acetal structure) and proceed as chain reactions. Since it is an important technological issue, two main industrial methods of POM stabilisation have been developed. The first one includes synthesis of POM by polymerization of formaldehyde leading to macromolecular structure with hydroxyl end groups; thermally stable acetal groups are then attached by further treatment with acetic anhydride. The second method involves synthesis of random copolymer of formaldehyde with ethylene oxide that produces long sequences of oxymethylene units separated and protected by randomly spaced oxyethylene groups. The presence of $–CH_2–CH_2–$ structures stops the progressive reaction of depolymerization. Dudina *et al*. investigated the mechanism of the thermal depolymerization of POM [14]. They found that the thermal stability of this polymer strongly depends on the chemical structure of the main chain and particularly on the kind of polymer's end groups. In the case of stabilized POM main-chain scissions were suggested as the leading mechanism responsible for degradation, causing a broad molecular mass distribution [15].

FTIR spectra of gases evolved during thermal degradation of sample 1 show main peaks at 1745 cm^{-1}, due to carbonyl group, and at 2800 cm^{-1}, originating from C–H in aldehyde group (Fig. 2).

Similar high intensity absorption bands could be observed for blends under investigation that are associated with formation of formaldehyde.

Both the TG results and the changes in characteristic absorption bands (CO_2 2356 and 2329 cm^{-1}, C–O–C – 1139 cm^{-1}) with increasing temperature observed in case of sample 2 confirm the two-step degradation of the TPU. These results are in agreement with previous studies on thermal degradation of thermoplastic polyurethane elastomers based on MDI and polyether diol [16–18]. During the first stage of TPU degradation carbon dioxide was produced as a main volatile product, as displayed in Fig. 2 and in Table 2.

The FTIR spectra collected for sample 2 at maximum rate of mass loss during the second stage of degradation show additional peaks characteristic for ethers. Taking into account the chemical structure of sample 2 it can be assumed that evolving low molecular mass compound was butyl ether.

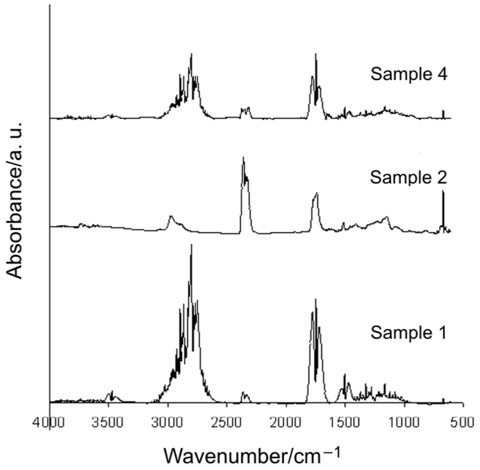

Fig. 2 FTIR spectra of volatile degradation products at maximum rate of degradation of sample 1 (at 365°C), sample 2 (at 450°C) and sample 4 (at 440°C)

Table 2 IR absorption bands of volatile products (groups) formed during the thermal degradation of samples 1, 2 and 4

Sample number	Wavenumber/cm^{-1}	Group
Sample 1	2800	C–H$_{(str)}$ in CHO
	1745	C=O$_{(str)}$
Sample 2	2356	CO$_{2(str)}$
	2322	CO$_{2(str)}$
	667	CO$_2$
	2952	C–H$_{(str)}$
	1139	C–O–C$_{(str)}$
Sample 4	2349	CO$_{2(str)}$
	2306	CO$_2$
	669	CO$_2$
	2800	C–H$_{(str)}$ in CHO
	1745	C=O$_{(str)}$

The intensity of absorption peak at 2800 cm^{-1}, due to emission of formaldehyde, *vs*. temperature is presented in Fig. 3. The enhanced thermal stability of POM/TPU blends can also be confirmed by characteristic temperatures of volatile products evolution – the maximum rate of formaldehyde emission occurs at temperature about 60°C higher than for pure POM and the intensities of formaldehyde emissions for

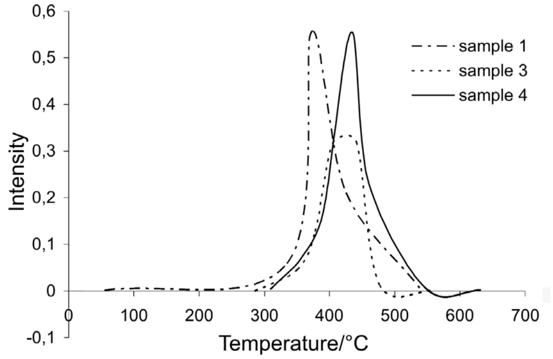

Fig. 3 Intensity changes of 2800 cm^{-1} during thermal degradation of sample 1, 2 and 4

blends are lower or comparable with pristine POM. Simultaneously, the formation of formaldehyde during the thermal decomposition is unfavourable in terms of flammability (it is providing fuel for combustion).

Petrovic *et al*. indicated that the degradation of PU in the first stage occurs mainly in hard segments and depends on their content and composition [19]. The soft segments degradation takes part during the second step. There are three possible ways of thermal decomposition of urethane linkage: dissociation to isocyanate and alcohol, dissociation to primary amine, olefin and carbon dioxide as well as the formation of a secondary amine with the elimination of carbon dioxide [20, 21]. In the case of blends the two-stage process of degradation might be not clearly displayed because of relatively small contents of TPU compound. The exact mechanism of thermal degradation process of POM/TPU blends is still under detailed research.

Conclusions

POM/TPU blends show increased thermal stability in comparison to pristine polymers and their degradation temperatures are high enough to enable advanced processing of these promising polymer engineering materials. Application of TG-FTIR method made it possible to identify low molecular mass volatile products (e.g. formaldehyde and carbon dioxide) formed during the thermal degradation process. Complex multiphased morphology governed by weak specific interactions (hydrogen bonding) strongly influences the course of decomposition and requires further detailed studies, including kinetic analysis.

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