Synthesis and characterization of new reactive polymer blends based on post-consumer glycol-modified poly(ethylene terephthalate) foils and poly(tetramethylene oxide)

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Abstract: Two series of reactive polymer blends based on post-consumer glycol-modified poly(ethylene terephthalate) (PETG) and poly(tetramethylene oxide) (PTMO) were prepared in order to investigate the possibility of utilization of waste PETG foils from the packaging industry. The resulting copolymer consisted of hard segments based on PETG and soft segments of PTMO, the latter accounted for 25, 35 or 50 percent of the total mass. The effects of the content and length of the soft segments derived from poly(oxybutylene) glycol, with molecular weights of 1000 or 2000, on the structure and thermal properties of the resulting materials were investigated.

Keywords: reactive blend, post-consumer glycol-modified poly(ethylene terephthalate) foil, glass transition temperature, thermal stability.

The progress of materials science is based on the development and implementation of new materials, which can be characterized by increasingly sophisticated functional properties [1]. Polymer plastics industry is one of the branches, which for many years has the greatest growth potential [2]. Direct mixing of appropriately selected polymers, that already exist in the market, is the fastest way of producing polymer materials with new or better mechanical properties, while maintaining a less complicated process of obtaining both materials and finished products. Nowadays, in an industrial scale one can produce lots of commercial materials, that are the polymer blends [3–5]. It is estimated that most of the existing polymers are also used as components of polymer blends intended for use in many industries, among others, mechanical engineering, packaging, and textile [6].

Poly(ethylene terephthalate) (PET) is a semicrystalline thermoplastic polyester that is widely used in the manufacture of fibers, films, and beverage containers, due to its exceptional properties, like high transparency, high dimensional stability, as well as good thermal and mechanical performance [7]. Similarly, glycol-modified poly(ethylene terephthalate) (PETG), on account...
of its transparency and clarity, can be used in medical, pharmaceutical, and cosmetic packaging. Due to the widespread use of packaging from these polymers, post-consumer waste represents a significant contribution (particularly by volume) of municipal waste. So far many ways of waste management on the basis of various types of recycling technologies have been developed, i.e.: material, chemical, or thermal [8]. One of the most interesting, although economically and ecologically unsubstantiated methods is the preparation of reactive polymer blends with excellent physical and mechanical properties based on post-consumers materials like PET or PETG [9, 10].

The aim of this study was the preparation and characterization of reactive polymer blends based on post-consumer PETG foils and poly(tetramethylene oxide) (PTMO). The influence of the soft segment length of PTMO on the morphology and thermal properties has been discussed. The essence of this work was to obtain new material and to prove that it is possible to manage post-consumer PETG foils by modifying them by material recycling and thereby obtaining new high-impact materials with unusual mechanical and thermal properties, which polymer components do not exhibit before blending.

**EXPERIMENTAL PART**

**Materials**

Glycol-modified poly(ethylene terephthalate) (PETG) post-consumer foil was granulated and vacuum dried (24 h/60 °C) before synthesis. Two kinds of poly(tetramethylene oxide) glycol were used: one with molecular weight of 1000 (PTMO1000, trade name Terathane 1000) was purchased from Du Pont (USA) and the second with molecular weight of 2000 (PTMO2000) was delivered by Sigma-Aldrich. 1,2-Ethanediol (ED) as well as two catalysts, i.e., zinc acetate [Zn(CH$_3$COO)$_2$] and antimony trioxide (Sb$_2$O$_3$), were supplied by Sigma-Aldrich. Thermal stabilizer Irganox 1010 was purchased from Ciba-Geigy (Switzerland).

**Preparation of PETG-PTMO blends**

The two series of PETG-PTMO reactive blends were synthesized in the two-step reaction in a polycondensation reactor (Autoclave Engineers, Pennsylvania, USA): glycolysis of PETG post-consumer foil and subsequently polycondensation in the presence of poly(tetramethylene oxide) glycol. The glycolysis process with ED (two-fold molar excess in relation to PETG amount) and zinc acetate (in an amount of 0.10 wt % in relation to PETG mass) as a catalyst was performed at temperature of 250 °C and under pressure of 0.5 MPa. After ca. 1 h of glycolysis process, the second stage of synthesis, being the polycondensation process, was commenced. For this purpose poly(tetramethylene oxide) glycol mixed with thermal stabilizer (Irganox 1010 in an amount of 0.5 wt % in relation to the total mass of two main substrates) along with the second portion of catalyst (antimony trioxide in an amount of 0.25 wt % in relation to PETG foil mass) were inserted. The temperature of the reaction was maintained at level of 250 °C. However, unlike the first stage which was performed under nitrogen atmosphere and elevated pressure, the polycondensation stage was carried out under reduced pressure (~20 Pa). In this case, the course of the reaction was monitored by observing the stirrer’s torque. When the polymer melt reached a high molecular weight, it was then extruded in the form of a thin wire. It was subsequently granulated and subjected to injection molding procedure.

The obtained copolymer samples were coded as PETG-PTMO1000 x/y or PETG-PTMO2000 x/y, where x/y was the mass ratio of PETG and corresponding poly(tetramethylene oxide) glycol, e.g., PETG-PTMO1000 75/25.

**Methods of testing**

The number-average and mass-average molecular weights (M$_n$ and M$_w$, respectively) were determined using size exclusion chromatography (SEC) on a Waters GPC instrument, equipped with a Shimadzu LC-10AD pump, a Waters 2414 differential refraction index detector (at 35 °C) and a Midas auto-injector (50 cm$^3$ injection volume) following the same procedure as described previously in [11]. Before analysis, samples were extracted in methanol on a Soxhlet apparatus for 24 h in order to remove unreacted monomers.

The amorphous structure of the samples was confirmed by differential scanning calorimeter (DSC). Measurements were carried out with a DSC 204 F1 Phoenix (Netzsch) at a heating rate of 10 °C/min in the temperature range of -100–250 °C. Then, from the second heating the glass transition temperature (T$_g$) was determined. Since all samples were found to be amorphous, the softening temperatures of the samples were determined using Boethius apparatus accordingly to the procedure described elsewhere [11].

The thermo-oxidative stability of the obtained polymer blends was evaluated by thermogravimetry (TGA 92-16.18 Setaram) using the system to measure the simultaneous TG-DSC. Measurements were carried out in an oxidizing atmosphere, i.e., dry, synthetic air (N$_2$/O$_2$ = 80/20 by volume). The study was conducted in the temperature range of 20–700 °C at the heating rate of 10 °C/min.

**RESULTS AND DISCUSSION**

Two series of reactive blends with PTMO as flexible segments and post-consumer PETG foils as rigid segments as well as a PETG reference sample were prepared by a catalyzed two-step method involving glycolysis and condensation. The variation in rigid and flexible segments contents and in the molecular weight of the PTMO
used during the synthesis affect the physical and thermal properties of the resulting materials [12]. The composition, physicochemical and thermal properties of the synthesized polymer blends are summarized in Table 1. The values of $M_n$ of the reactive blends in these series ranged from 33 000 to 43 000, while the dispersity ($\mathcal{D}$) was in the range 1.74–1.96. The increase of $M_n$ and $M_w$ values with increasing the content of PTMO segment in the copolymer chain can suggest that the obtained reactive blends exhibit comparable or higher molecular weights than PETG (ca. 29 000), synthesized at the same conditions.

In order to investigate the influence of the molecular weight of polyether segment on the phase structure of the synthesized reactive blends, DSC analysis was performed. The DSC curves of PETG-PTMO block copolymers designated during second cooling are presented in Fig. 1, while the values of $T_g$ are presented in Table 1. The $T_g$ values of related segments can provide information about microphase separated structure or the miscibility of both phases. Since the neat PTMO exhibits the glass transition at about -80 °C, the addition of polyester causes the shift in $T_g$ of the PETG-PTMO copolymers toward higher values. Additionally, for the sample PETG-PETG-PTMO2000 65/35 one can observe the melting on the first cooling cycle at the temperature of 35–40 °C. It was already confirmed [12] that PTMO2000 can crystallize, but the addition of polyester might block its crystallization. For PETG-PETG-PTMO2000 75/25 one can observe the crystallization (at $T_c$) and subsequent melting (at $T_m$). Furthermore, for both series of reactive blends the decrease of softening/flowing temperature estimated accordingly to the Boethius method ($T_f$) was observed, which was due to the presence of PTMO soft segment that affects the chain mobility. Thus summarizing the above observations one can clearly draw the conclusion about the partial miscibility of both phases depending on the rigid/flexible segment ratio and also on the rigid and flexible segment length in the PETG-PTMO copolymers.

The thermal stability of the synthesized polymers is an important parameter that can limit their application. The thermo-oxidative stability of the synthesized PETG-PETG-PTMO copolymers was studied under oxidative (air) atmosphere. The mass loss (TG) and derivative of mass loss (DTG) curves for the samples with different contents of flexible PTMO segments are shown in Fig. 2. Characteristic temperatures corresponding to mass losses of

### Table 1. Characterization of PETG-PTMO copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$\mathcal{D} = \frac{M_w}{M_n}$</th>
<th>$T_g$, °C</th>
<th>$T_m$ a) = 124 ± 2</th>
<th>$T_m$ b) = 140 ± 3</th>
<th>$T_{5%}$, °C</th>
<th>$T_{50%}$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETG</td>
<td>29 175</td>
<td>53 888</td>
<td>1.84</td>
<td>70</td>
<td></td>
<td></td>
<td>367</td>
<td>435</td>
</tr>
<tr>
<td>PETG-PTMO1000 75/25</td>
<td>33 830</td>
<td>62 396</td>
<td>1.84</td>
<td>5</td>
<td>135 ± 2</td>
<td></td>
<td>360</td>
<td>428</td>
</tr>
<tr>
<td>PETG-PTMO1000 65/35</td>
<td>43 352</td>
<td>75 489</td>
<td>1.74</td>
<td>-22</td>
<td>126 ± 1</td>
<td></td>
<td>342</td>
<td>417</td>
</tr>
<tr>
<td>PETG-PTMO1000 50/50</td>
<td>34 828</td>
<td>63 931</td>
<td>1.84</td>
<td>-40</td>
<td>118 ± 2</td>
<td></td>
<td>344</td>
<td>421</td>
</tr>
<tr>
<td>PETG-PETG-PTMO2000 75/25</td>
<td>33 782</td>
<td>66 213</td>
<td>1.96</td>
<td>20</td>
<td>133 ± 2</td>
<td></td>
<td>345</td>
<td>416</td>
</tr>
<tr>
<td>PETG-PETG-PTMO2000 65/35</td>
<td>36 544</td>
<td>70 895</td>
<td>1.94</td>
<td>-33</td>
<td>122 ± 2</td>
<td></td>
<td>338</td>
<td>412</td>
</tr>
<tr>
<td>PETG-PETG-PTMO2000 50/50</td>
<td>39 822</td>
<td>74 467</td>
<td>1.87</td>
<td>-45</td>
<td>113 ± 3</td>
<td></td>
<td>319</td>
<td>406</td>
</tr>
</tbody>
</table>

\[ a) T_m – melting temperature. \]
\[ b) T_f – flowing temperature. \]
5 % ($T_{5\%}$) and 50 % ($T_{50\%}$) are given in Table 1. The value of $T_{5\%}$ is considered to represent the beginning of thermal degradation.

The PETG and its copolymer exhibit two stages of degradation on air, which appear at 350–450 and 450–545 °C. The TG and DTG curves for PETG-PTMO copolymers reveal comparable profiles. The first stage is attributed to the decomposition of flexible and rigid segments. The second stage in the temperature range of 450–550 °C is attributed to the decomposition of residue. It is known, that the oxygen attack on poly(ether-ester) block copolymers is initiated in the flexible segment and, in most cases, it occurs at the α-carbon atom to the ether oxygen atom [13] and results in the formation of volatiles. The values of $T_{5\%}$ and $T_{50\%}$ in the series decreased with increasing content of flexible PTMO segments.

CONCLUSIONS

Two series of high molecular weight PETG-PTMO copolymers were synthesized by a two-step method involving catalyzed glycolysis and condensation in the melt. The PTMO molecular weights varied from 1000 to 2000. For most of the samples, the partial miscible structure was observed with only one value of $T_g$. However, by changing the length and content of flexible and rigid segment in the copolymer one can affect the phase structure and thus the physical properties of the resulting materials. Moreover, it was found that, along with an increase of flexible segment content, the softening/flowing temperature of the blend decreases. Similarly, the thermo-oxidative stability of PETG-PTMO copolymers was lower in comparison to the neat PETG post-consumer foils, which resulted from the influence of PTMO length and content.

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REFERENCES