Thermo-oxidative ageing of composites based on polybutylene terephthalate and a highly dispersed Fe–FeO mixture

T. A. Borukaev, N. I. Mashukov, and A. K. Mikitaev
Kabardino-Balkar State University

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At present, most polymer composites used in electronic engineering, the motor industry, and electronics undergo the action of different factors. The main destructive factor is the combined action of heat and oxygen. In this case there is a change in the properties of the composite materials with time. Such change in the main service characteristics of articles is due to ageing of the material under the action of temperature and oxygen, leading to the occurrence of different physicochemical processes in the matrix of the polymer composites [1, 2]. To retain the service properties of polymeric materials, a number of stabilisers — inhibitors of thermo-oxidative degradation — have now been developed. In particular, for polyolefins, high efficiency in this regard has been shown by highly dispersed Fe–FeO mixtures [3].

In view of this, it was of interest to study the effect of thermo-oxidative ageing on the strength, thermal, and dielectric properties of polybutylene terephthalate of grade V-305 (PBT), stabilised and modified with a highly dispersed Fe–FeO mixture (referred to below as Z) [4].

The highly dispersed Fe–FeO mixture was obtained from iron dihydrate oxalate (FeC₂O₄·2H₂O) by a known procedure [5]. Composites based on PBT and Z were prepared by the procedure given in [6].

Thermo-oxidative ageing of the initial PBT and of PBT + Z composites was carried out in an oven with good air circulation at temperatures of 120 and 260 °C. Deviation of the temperature from that prescribed amounted to ±1 K (GOST 29243–91). The heat ageing time was varied from 0.5 to 1300 h.

An important complex service characteristic reflecting the change in the physicomechanical properties of polymers and their dependence on structure is the impact strength A_p. In this context, Charpy impact tests of PBT and of PBT-based composites were carried out on a series of unnotched specimens. Each point was obtained by averaging at least five experimental results. The specimens for impact tests were produced by injection moulding at a temperature of 260°C.

The heat stability of melts of initial PBT and of PBT + Z composites was evaluated from the change in the values of the melt flow index (MFI), which was measured on an IIRT-M capillary viscometer at 230°C and a load of 5 kg. The capillary diameter was 2 mm.

The electrical properties of PBT and of PBT + Z composites subjected to heat ageing at a temperature of 120°C were assessed by means of dielectric relaxation using an R-5058 a.c. bridge at frequencies of 1 and 10 kHz in the temperature range 20–200°C.

The results of impact tests of specimens of PBT and PBT + Z composites subjected to thermo-oxidative ageing showed that the impact strength of all the specimens decreases with increase in the heat ageing time (Figure 1). However, as can be seen from Figure 1, the rate of decrease in A_p of the PBT + Z composite depends on their Z content. The lowest rate of decrease in A_p was shown by PBT + Z composites with a Z content of 0.05 and 0.1 wt.%. In this case, for all specimens, with the passage of heat ageing time, the “load–time” diagram of impact tests was transformed into the classical triangle corresponding to
The introduction of a highly dispersed Fe–FeO mixture into PBT leads, as can be seen from Figure 1, for almost all the compositions used, to a reduction in the rate of decrease in impact strength. Such behaviour of the PBT + Z composite is related to the properties of Z. Thus, the addition of Z to amorphous–crystalline PBT causes a certain decrease in the level of molecular mobility of macromolecules, especially in the amorphous phase [8], thereby inhibiting conformational transformations. Secondly, it is well known that Fe and FeO are effective inhibitors of thermo-oxidative degradation [3, 9]. It can be assumed that, as a result of modification (stabilisation), PBT + Z composites acquire a structure that is less defective at temperatures both below and above the glass transition and melting temperatures. Firstly, this entails an increase in the service life of the material by comparison with the initial polymer and, secondly, more favourable conditions are created for the reprocessing of the composite material using classical methods.

This assumption is borne out by the results of measuring the MFI of PBT and PBT + Z specimens subjected to heat ageing at a temperature of 260 °C. In this case, the period of heat stability of the polymer melt is determined by the deviation of the MFI from its original value during heat ageing by 15% and more [10]:

$$E = \frac{MFI_i - MFI_a}{MFI_i} \times 100\%$$

where MFI is the initial MFI value, and MFIa is the actual MFI value. The condition $E > 0$ corresponds to degradative processes, and $E < 0$ corresponds to processes of structure formation. The period of heat stability of the polymer melt is taken to be the time interval in which $E \leq +15\%$.

The results of investigating the heat stability by the rheological method showed the high efficiency of the developed composites at fairly high temperatures (260 °C) (Table 1).

This is evidently due to the fact that the accepting capacity of Z with respect to oxygen increases with increase in temperature [6]. This fact is an important advantage of such a stabilisation method from the viewpoint of ensuring reliable retention of the initial combination of physicochemical properties during processing of PBT from the melt.

To assess the kinetics of oxidation of polybutylene terephthalate composites, the latter, in the form of sheets of 1 mm thickness, were subjected to heat ageing in air at 120 °C with subsequent measurement of the temperature dependence of the tangent of the angle of dielectric losses $\tan \delta$. From the $\tan \delta(T)$ graphs, values of the temperature of the start of through conductivity, $T_{c}$, of the upper temperature service limit of the material were determined (Figure 2, by way of example). As can be seen from Figures 2 and 3, the dielectric properties of PBT + Z composites change ambiguously during thermal oxidation. And in terms of the absolute magnitude of $\tan \delta$ in the temperature range from room temperature to $T = T_{c}$ (Figure 2), and the values of this temperature (Figure 3), the most optimum is a composite with a Z content of 0.05 wt.%.

This means that the greatest resistance to thermo-oxidative degradation during heat ageing, as follows from the nature of change in the dielectric properties, is exhibited by a PBT + 0.05% Z composite. This seems to be due to a reduction in the oxygen diffusion rate into the polymer matrix in a composite of this composition as a result of transition of the polymer into a state with closer packing. Furthermore, the concentration of Z particles in loosely packed regions of the polymer in specimens of the above composition evidently leads to a reduction in the free volume, its redistribution in the composite, and an increase in the crosslink density of molecular entanglements [11]. As a result, the combined effect of these factors leads to weakening of diffusion of oxygen molecules, thereby lowering the oxidation rate of the PBT + Z composite.

Figure 1 Dependence of impact strength $A_{p}$ of PBT and PBT + Z composites on heat ageing time $t$. Content of Z, wt.%: 0 (1); 0.01 (2), 0.05 (3), 0.1 (4), and 0.5 (5)
Thus, the investigations carried out showed that the introduction of a highly dispersed mixture of Fe and FeO into PBT can lead to inhibition of the thermo-oxidative degradation of PBT during its heat ageing. In turn, this makes it possible to keep the combination of initial physicochemical properties of PBT during its processing from a melt at an adequate level and to increase the service life of articles manufactured from it.

The theoretical and practical significance of the results obtained prompts the present authors to carry out a more detailed study of the mechanism of interaction of highly dispersed ingredients of the Fe–FeO type with the PBT matrix.

<table>
<thead>
<tr>
<th>No.</th>
<th>Composition of composites</th>
<th>MFI, g/10 min</th>
<th>MFI/E 30 min</th>
<th>MFI/E 60 min</th>
<th>MFI/E 90 min</th>
<th>MFI/E 120 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PBT (V-305), industrial</td>
<td>36</td>
<td>28</td>
<td>-22</td>
<td>25</td>
<td>-20</td>
</tr>
<tr>
<td>2</td>
<td>PBT (V-305) + 0.01Z</td>
<td>31</td>
<td>33</td>
<td>+7</td>
<td>39</td>
<td>+26</td>
</tr>
<tr>
<td>3</td>
<td>PBT (V-305) + 0.05Z</td>
<td>27</td>
<td>33</td>
<td>+22</td>
<td>31</td>
<td>+15</td>
</tr>
<tr>
<td>4</td>
<td>PBT (V-305) + 0.1Z</td>
<td>32</td>
<td>30</td>
<td>-6</td>
<td>30</td>
<td>-6</td>
</tr>
<tr>
<td>5</td>
<td>PBT (V-305) + 0.5Z</td>
<td>28</td>
<td>29</td>
<td>+4</td>
<td>34</td>
<td>+21</td>
</tr>
<tr>
<td>6</td>
<td>PBT (V-305) + 1Z</td>
<td>31</td>
<td>31</td>
<td>0</td>
<td>28</td>
<td>-10</td>
</tr>
</tbody>
</table>

* Heat ageing temperature 260°C. The MFI was measured at 230°C and under 5 kg load

![Figure 2](image2.png)

**Figure 2** Dependence of tangent of angle of dielectric losses $tg \delta$ on temperature $T$ of PBT + Z composites. Heat ageing was carried out at 120°C for 10 h. Content of Z, wt. %: 0 (1); 0.05 (2); 0.1 (3); 0.15 (4); 0.2 (5)

![Figure 3](image3.png)

**Figure 3** Dependence of temperature of start of through conductivity, $T_{ct}$ of PBT + Z composites on heat treatment time $t$ at $T = 120^\circ C$. Content of Z, wt. %: 0 (1); 0.05 (2); 0.1 (3); 0.15 (4); 0.2 (5)

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(No date given)