

## Increasing the thermal resistance of polyoxymethylene

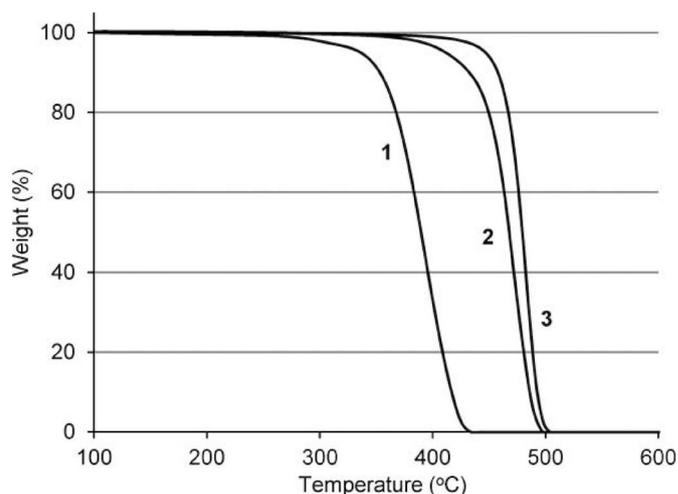
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*Simultaneous addition of polyolefin elastomer and zinc oxide to polyoxymethylene in nanocomposite samples gives rise to a synergistic thermally stabilizing effect.*

Polyoxymethylene (POM) is one of the most important polymers used in engineering, and it is being used in an increasing number of markets and applications.<sup>1</sup> Some common everyday applications of POM, for instance, include medical devices, automotive components, water and gas tubing systems, and household equipment. At high temperatures, however, toxic formaldehyde and formic acid are released from POM (because of unstable methyl oxide bonds in its macromolecular structure).<sup>2-6</sup> To further broaden the application possibilities of this polymer, it is therefore important to find a way to improve the thermal resistance of POM.

To date, various approaches have been taken to increase the thermal stability of POM. For instance, organic compounds containing an active hydrogen atom (e.g., cross-linked melamine-formaldehyde polycondensate) have been used as formaldehyde-absorbing agents.<sup>7</sup> Low-molecular-weight organic compounds such as bisphenol-A and amine have also been used to form (in situ) benzoxazines via the Mannich reaction, and to control formaldehyde generation.<sup>8</sup> Alternatively, high-molecular-weight compounds, with higher thermal stability than POM (e.g., acrylonitrile-butadiene-styrene copolymer), have been used as toughening agents,<sup>9</sup> and non-combustible inorganic minerals (such as zinc oxide) as impermeable heat-resistant barriers.<sup>10</sup> Furthermore, it is known that the simultaneous use of various additives can synergistically influence the properties of composite materials. There has only been a small amount of work conducted so far, however, on the combined effects of the different organic and inorganic compounds for increasing the thermal stability of POM. In one of the few studies, for example, it was shown that the addition of nanoclay to a POM blend (i.e., containing 25wt% acrylonitrile-butadiene-styrene copolymer) caused an additional increase in the thermal stability of the material.<sup>9</sup>

In our work,<sup>11</sup> we therefore decided to extend this direction of research and modify POM with both non-combustible zinc oxide (ZnO) and with ethylene-octene copolymer (EOC, which has a higher

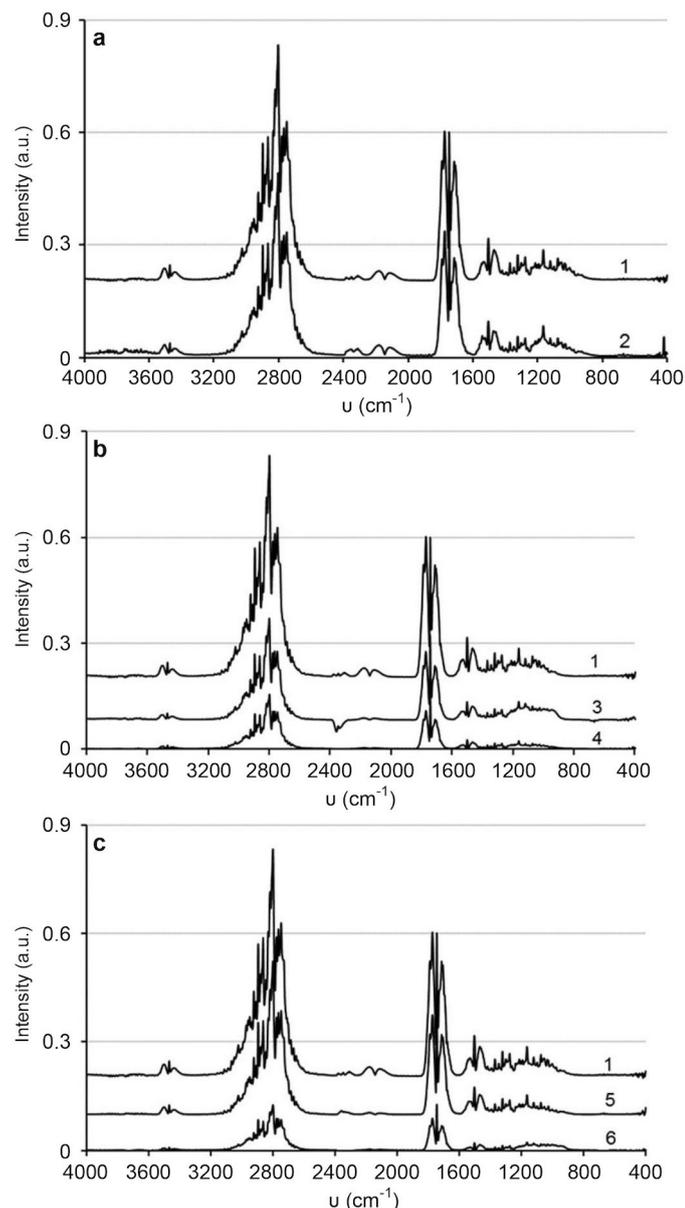


**Figure 1.** Experimentally obtained thermogravimetric analysis results for (1) neat polyoxymethylene (POM) and POM/ethylene-octene copolymer (EOC) composite samples. Results are given for composites containing (2) 38wt% and (3) 17wt% EOC. Compared with the POM sample, degradation of the composite samples occurs at higher temperatures (i.e., the thermal stability of POM is increased by addition of EOC).

thermal stability than POM and can act as a toughening agent). To prepare our samples we thus modified the POM matrix via thermoplastic compounding with an EOC, and a high-purity (99.7%) nanostructured ZnO filler (which was synthesized at Riga Technical University's Institute of Inorganic Chemistry). For our experiments we used two different commercially available EOCs, each of which has a distinct alpha-octene (1-octene) content (i.e., EOC17 and EOC38 with octene co-monomer contents of 17 and 38%, respectively). In the main part of our work, we then conducted a thermogravimetric analysis (TGA), coupled with Fourier-Transform IR (FTIR) spectroscopy, to evaluate the effect of adding either of the EOCs (at concentrations of up to 50wt%), and of ZnO addition (up to 2wt%), on the thermal behavior of POM.

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Our TGA results confirm that addition of the elastomers causes an increase in the thermal stability of POM (see Figure 1). We also find that the addition of only 2wt% ZnO improves the thermal stability of POM,



**Figure 2.** Fourier-Transform IR spectra of the evolved gases from the degraded POM regions for (1) the neat POM sample, (2) POM with 2wt% zinc oxide (ZnO), (3) POM with 10wt% EOC17, (4) POM with 10wt% EOC17 and 2wt% ZnO, (5) POM with 50wt% EOC17, and (6) POM with 50wt% EOC17 and 2wt% ZnO.  $\nu$ : Wavenumber. a.u.: Arbitrary units.

by delaying the onset of the polymer's degradation processes. Furthermore, we observe a somewhat stronger thermal stabilizing effect for the systems containing EOC38 below about 400°C (i.e., before destruction of the POM phase). In contrast, at higher temperatures (when the POM matrix is partially or completely degraded), the thermal destruction behavior is increasingly influenced by thermal resistance of the remaining elastomer phase. This effect is slightly stronger for the EOC17 samples because of the smaller number of tertiary carbon atoms in the macromolecular chain.

We show TGA/FTIR spectra of the gases that evolved from the degraded region of the POM phase of our samples in Figure 2. These results indicate that the addition of ZnO to the POM matrix causes a decrease in the intensity of the evolved gas spectral peaks (particularly for formaldehyde). For the systems containing EOC, we also see a decrease in the formaldehyde peak intensities. Moreover, we measure even greater decreases in the formaldehyde peak intensities upon addition of 2wt% ZnO into the respective polymer blend matrices (especially for the POM blend containing 50wt% EOC17). This result is evidence of the synergetic effect, with respect to thermal stability, of our POM modifications.

In summary, we have addressed the thermal instability of POM at elevated temperatures in this work. The results of our TGA/FTIR analyses illustrate that the thermal resistance of POM can be improved by the addition of EOC elastomers (with differing 1-octene concentrations). In addition, we observed a synergistic effect upon the simultaneous addition of EOC and ZnO to the POM matrix, i.e., there is an efficient decrease in the gas exchange rate and inert gases (e.g., carbon dioxide) tend to stay in the zone of thermal destruction. In the next stages of our research, we plan to continue these investigations and to study the origin of the apparent synergism in the POM/EOC/ZnO system for a wider ZnO content range. In this way, we hope to identify new material formulations for prospective engineering applications.

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