PET Oligomer Waste to Modify CAP Characteristics


Centro de Tecnologia, Instituto de Macromoléculas Professora Eloisa Mano-IMA, Universidade Federal do Rio de Janeiro-UFRJ, Rio de Janeiro, Brazil.
Email: *lcmendes@ima.ufrj.br

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ABSTRACT

To develop an improved method of reusing poly(ethylene terephthalate) (PET) waste in the production chain, it was chemically modified with pentaerythritol (PENTE), resulting in PET/PENTE (60/40) oligomer. This was added to petroleum asphalt cement (CAP) in different proportions—5, 10 and 20 wt%—as a modifier of bitumen characteristics. The mixture was evaluated by thermogravimetry (TG/DTG), differential scanning calorimetry (DSC), infrared spectroscopy (FT-IR), optical microscopy (OM) and the adhesion-peel test. The oligomer enhanced substantially the asphalt thermal stability—Tonset. OM images showed strong compatibility between components and PET’s amorphization. PET oligomer increased CAP’s wettability and the mixture presented cohesive fracture through the peel test. The mixture has excellent potential as paving material.

Keywords: PET Waste; Pentaerythritol; CAP; Recycling

1. Introduction

In recent years, the growing use of polymers in everyday products has generated an enormous amount of municipal solid waste. This has brought many environmental problems. In general, these wastes take long time to undergo spontaneous degradation and release toxic gases if they are burned [1,2]. The majority of discarded polymer materials are from packaging. Taking into account the huge potential of plastics and the problems caused by pollution from waste, there is a growing worldwide trend to recycle them [3]. When reused, PET packages show several advantages—lower consumption of water and energy and environmental and social benefits, among others [4]. Waste disposal is a main concern of society, prompting actions by industry and research centers [5-7]. Recently, an article on PET waste oligomerization through the action of polyfunctional alcohol—pentaerythritol was published [8].

Polymers have been studied as modifiers of asphalt mainly to overcome some deficiencies of asphalt cement and to improve its properties, such as reducing permanent thermal deformation and cracking. As modifier agents, polymers are compatible and increase asphalt degradation at high temperatures. The asphalt’s characteristics as well as the type and amount of polymer have a large influence on the appropriate asphaltic mixture [9, 10].

Asphalt cement can be formed naturally, through evaporation of surface oil deposits, but the majority comes from the heavy fraction of petroleum from distillation at refineries. Petroleum asphalt cement (CAP) consists of 90% - 95% hydrocarbons—saturated and aromatic—and 5% - 10% of structures with hetero atoms (oxygen, sulfur, nitrogen) and metals, such as vanadium, nickel and iron. Brazilian CAPs have low sulfur and metals content but high levels of nitrogen. Asphaltenes and maltenes are the main asphalt components. They are complex mixtures consisting of condensed aromatic rings, resins and saturated and aromatic compounds. The ratio between asphaltenes and maltenes has a significant effect on asphalt performance [11-14]. The reuse of plastics as additives for CAP increases the possibility of using urban plastic waste in the productive chain [15,16].

This work intended to develop a new material from plastic arising from municipal solid waste. The discarded PET was oligomerized by a polyfunctional alcohol. The PET oligomer was mixed with CAP in different proportions to evaluate its influence on the CAP’s thermal, adhesive and morphological characteristics.

2. Experimental

2.1. Materials

Flakes of poly(ethylene terephthalate) (PET) waste with 24% crystallinity degree were supplied by CPR Ltd. (Rio de Janeiro, Brazil). Commercial pentaerythritol, here
called PENTE, was provided by S. A. Degussa (São Paulo, Brazil). Commercial zinc acetate produced by J. T. Baker was used without further purification. The asphalt cement was from a refinery.

2.2. Oligomer Preparation

This measurement and others are deliberate, using specifications that anticipate your paper as one part of the entire proceedings, and not as an independent document. Please do not revise any of the current designations. The PET/PENT (60/40) blend containing 0.5 wt% zinc acetate catalyst was prepared by melt processing in an Haake Rheomix 600 internal mixer, at 250°C, 60 rpm, for 10 minutes. Before processing, PET flakes were previously dried at 120°C, for 4 hours [8].

2.3. CAP/Oligomer Mixture

The mixture of CAP with PET/PENTE oligomer in different oligomer proportions (5, 10 and 20 wt%), called CAP (95/5), CAP (90/10) and CAP (80/20), respectively, was prepared in a 500 mL glass flask, at 180°C, with mechanical stirring (600 rpm) for 2 hours.

2.4. Thermogravimetry and Derivative Thermogravimetry (TG/DTG)

The TG/DTG curves were obtained by a TA thermoanalyzer (Q500) by heating the sample from 30°C to 700°C at a heating rate of 10°C·min⁻¹ under nitrogen atmosphere. The onset temperature (Tonset), maximum degradation temperature (Tmax) and end temperature (Tend) were determined.

Table 1. TG/DTG of the materials.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Degradation temperatures (°C)</th>
<th>Tmax (°C)</th>
<th>Tend (°C)</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/PENTE 60/40</td>
<td>125</td>
<td>495</td>
<td>127/285/476</td>
<td>9.22</td>
</tr>
<tr>
<td>CAP</td>
<td>258</td>
<td>500</td>
<td>441</td>
<td>14.1</td>
</tr>
<tr>
<td>CAP (95/5)</td>
<td>238</td>
<td>488</td>
<td>448</td>
<td>0.03</td>
</tr>
<tr>
<td>CAP (90/10)</td>
<td>250</td>
<td>490</td>
<td>453</td>
<td>11.9</td>
</tr>
<tr>
<td>CAP (80/20)</td>
<td>281</td>
<td>496</td>
<td>448</td>
<td>11.3</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Thermogravimetry and Derivative Thermogravimetry (TG/DTG)

Figures 1 and 2 show the degradation and first derivative curves of the materials, respectively. Table 1 contains the Tonset, Tmax, and Tend degradation temperatures and amount of residue. The PET/PENT 60/40 blend presented three degradation steps. The first one was located at 100°C - 175°C and it was attributed to the absorbed water. The next one occurred at 250°C - 325°C, caused by the unreacted pentaerythritol. The final step, at 325°C - 525°C, was the result of the degradation process of the PET/PENTE oligomers.

The CAP’s curve shows a unique degradation step pattern. Concerning the mixture CAP/oligomer, all of them presented one stage of degradation. The Tonset and Tmax were shifted to higher temperatures, indicating a substantial increase of the CAP’s thermal stability and a higher degree of compatibility.

3.2. Differential Scanning Calorimetry (DSC)

Figure 3 shows the DSC curves of the PET/PENTE, CAP and CAP (90/10). The oligomer showed Tg around 61°C. The CAP presented a thermal transition in the vicinity of 13°C. All mixtures revealed the same transitions but that attributed to the Tg of the oligomer shifted to a lower temperature (43°C). This corroborated the high

The morphology of the matrix and dispersed phase was monitored by taking photographs.

2.7. Peel Test

The adhesive characteristic of the asphaltic mixture was evaluated based on the ASTM D1876 standard [20]. The material was poured between aluminum plates with constant thickness and the assembly was taken for peeling in an Instron machine. The force of peeling was registered and then test photos were taken to evaluate what kind of fracturing—adhesive or cohesive had occurred.
degree of compatibility observed in the TG/DTG analysis.

3.3. Units Morphological Analysis

The photomicrographs of the CAP (Figure 4) and CAP/Oligomer mixture (Figure 5) show the morphology of the materials in the solid and molten states. The CAP’s images are similar and represent a heterogeneous mixture. The crystalline phase—disperse droplets is embedded in the amorphous phase.

The CAP (95/5) photomicrographs did not reveal any phase separation. This might have occurred because of the total dissolution of CAP inside the oligomer matrix. In the mixtures with oligomer content higher than 5%, the oligomer induced the fragmentation of the crystalline domains. There is a sharp phase separation. The matrix is formed by oligomer and the CAP amorphous phase. The
crystalline phase appeared as dispersed small droplets.

3.4. Peel Test

Figure 6 shows the force required immediately before complete separation of the aluminum plates. For the mixtures, even taking into account the experimental errors, the values of the force were similar, independent on the oligomer content. The mixtures presented behavior similar to that of a ductile material.

Figure 7 shows the surface of the aluminum plates after the peel test. The CAP image revealed voids on the surface, indicating poor adhesion. For all mixtures, the oligomer improved adhesion. All surfaces were completely coated, showing cohesive fracture of the asphaltic mixture. The results indicated that the presence of the oligomer increases the resistance to disaggregation and durability of the asphaltic mixture, making it more suitable for paving.

4. Conclusion

In order to produce a new material from plastic waste, PET was oligomerized by a polyfunctional alcohol and mixed with CAP. The asphaltic mixture was characterized by several techniques. The DSC showed there is excellent compatibility between the constituents. The presence of the oligomer enhanced the CAP’s thermal stability. Morphologically, in the mixtures, PET was the matrix and the CAP crystalline phase appeared as disperse domains. The mixture presented cohesive fracture and ductile behavior from the peeling evaluation.

5. Acknowledgements

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Figure 7. Surface of the aluminum plates after the peel test: (a) CAP; (b) CAP (95/5); (c) CAP (90/10); (d) CAP (80/20).

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REFERENCES


