ADDITION OF AN INDUSTRIAL RESIDUE TO ASPHALT: EVALUATION OF MATERIAL PROPERTIES


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ABSTRACT
Polymer waste from a button manufacturer was blended with 50/60 penetration-grade petroleum asphalt cement with the purpose of enhancing its physical properties and to obtain pavements which are more resistant to temperature gradients and permanent deformation. This polymer waste is considered as an environmental problem because it is produced in large scale and stored in sanitary landfills. First, the polymer waste was classified as unsaturated polyester. Then, the waste was blended with asphalt according to the following experimental conditions: polymer content: 2.0, 7.0, or 14.0 wt.%; mixing temperature: 140 or 180 °C; and mixing time: 20 or 60 min. The results obtained in penetration index, ring-and-ball softening point, flash point, and viscosity assays showed that the addition of polymer waste as an insoluble material to asphalt is a viable alternative to solve this environmental problem.

KEYWORDS
asphalt; polymer; button; industrial waste; environment

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doi:10.5419/bjpg2010-0018
1. INTRODUCTION

Asphalt is used since the beginning of civilization. It is a mixture of aliphatic, aromatic, and naphthenic hydrocarbons with small amounts of organic acids, bases and heterocyclic components containing oxygen, nitrogen, sulfur (O, N, S) and some trace amount of metals, mainly vanadium and nickel. Asphalt binder is a rheological, thermoplastic and viscoelastic material presenting strongly adhesive and waterproof properties. Its low price, ready availability and properties have led to its extensive use in several applications, mainly in road construction and maintenance (Al-Abdul Wahhab et al., 1998; Asphalt Institute, 2002).

Asphalt is frequently blended with polymers (Yildirim, 2007). It is well known that the addition of polymers to asphalt binders can improve its performance, producing a new material with strong viscoelastic behavior, called polymer-modified asphalt (PMA) (Vlachovicova et al., 2007). On the other hand, several manufacturing operations generate polymer wastes (PW) that can be used as asphalt modifiers, representing an attractive alternative by reducing disposal costs and potential pollution problems (Hinislioğlu and Ağar, 2004).

According to Hisislioğlu and Ağar (2004), the bitumen-polymer mixing conditions have considerable effect on the behavior of polymer-modified bitumen, taking into account the mixing temperature, mixing time, and modifier content. Attempts to improve asphalt binder quality related to its temperature susceptibility have been made by several researchers (Jin et al., 2002; Oda and Fernandes, 2001; Polacco et al., 2004, 2005, 2006; Ruan et al., 2003; Stastna et al., 2003; Vlachovicova et al., 2007; Wen et al., 2002). The use of a polymer usually starts to be significant at concentrations of about 4-6 wt.%, but the polymer amount has to be chosen very carefully because the formation of an insoluble, infusible asphalt gel can result when an excessive quantity is used (Polacco et al., 2004). According to Yildirim (2007), desirable characteristics of polymer-modified binders include a higher softening point and greater elastic recovery, viscosity, cohesive strength, and ductility.

The properties of asphalt-polymer blends depend on the concentration and the type of the polymer used. According to Stastna et al. (2003), blends of asphalt with polymers form multiphase systems, comprising a polymer-rich phase, a phase rich in asphaltenes that are not adsorbed by the polymer, and another phase formed by maltenes. These phases coexist in a micro-scale, metastable equilibrium that, from a thermodynamic point of view, always tend to separate. A kinetic condition that assumes critical importance in prolonged storage at high temperatures, due to the reduction of viscosity that propitiates phase separation, is the main driving force that dictates whether the phases separate or not (Polacco et al., 2006).

In this work a polymeric industrial waste from a button manufacturer was added to petroleum asphalt cement (CAP 50/60). The evaluation of the obtained product was made by penetration index, ring-and-ball softening point, flash point, and viscosity assays.

2. MATERIALS AND METHODS

2.1 Petroleum asphalt cement (CAP)

Petroleum asphalt cement with 50/60 penetration grade (CAP 50/60) was kindly supplied by LUBNOR/PETROBRAS (Lubrificantes e Derivados de Petróleo do Nordeste, Brazil). It is the residue (bottom product) obtained from the distillation process of crude oils from Fazenda Belém (Aracati, Ceará, Brazil).

2.2 Polymer waste (PW)

PW (unsaturated polyester) was kindly supplied by a button manufacturer located in the State of Rio Grande do Norte (Brazil). These wastes are composed of the button chips that result from the molding process. Before their use in asphalt, they were washed, dried and ground in a ball mill to obtain a powdered product.

2.3 Polymer waste characterization

PW characterization was made by granule size distribution, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and infrared spectroscopy (IR spectroscopy).
2.3.1 Differential scanning calorimetry (DSC)

The thermal transitions of two polymer samples were obtained in a DSC 60 equipment. The analyses were made under an atmosphere of nitrogen at a heating rate of 10 °C per minute. The masses of samples 1 and 2 were 9.0 and 10.2 mg, and the final temperatures of the analyses were 550 °C and 590 °C, respectively.

2.3.2 Thermogravimetric analysis (TGA)

A Shimadzu DTG-60H was used to evaluate the thermal stability of PW. The measurements were carried out under an oxygen atmosphere using the following heating rate/mass relations: 5 °C min⁻¹/4.375 mg, 7.5 °C min⁻¹/4.254 mg, 10 °C min⁻¹/4.077, and 12.5 °C min⁻¹/4.561 mg. The final temperature of all measurements was 1200 °C. The activation energies (Eₐ) were obtained by using the Ozawa method.

2.3.3 Infrared spectroscopy

The Fourier-transform infrared spectroscopy (FTIR) was used to identify the PW. An Excalibur Series Bio Rad FTS 3000MX Spectrophotometer was used to obtain the infrared absorption spectrum.

2.4 Asphalt-polymer mixtures

Small aluminum containers were filled with CAP 50/60 and heated in a stove (Tecnal TE 394/1) during 1 hour, at 120 °C. Then, the contents were transferred to a thermoelectric heater, where the heating continued until the temperature of each experimental run was reached (140 °C or 180 °C). The polymer was gradually added to the asphalt (2, 7 or 14 wt.% of asphalt mass) at a 2000-rpm shearing speed (mixing time of 20 or 60 min). After polymer addition, the mixtures were stored in aluminum containers for characterization. For comparative purposes, the same experimental conditions were used with asphalt without polymer. A total of 16 samples were prepared, four of which without PW.

2.5 Characterization of the polymer-asphalt mixtures

2.5.1 Penetration test

Penetration tests were performed at 25 °C, with a 10-g load applied for 5 s, according to the Brazilian Association of Technical Standards ABNT - NBR6576 (2007). A Pavitest penetrometer (1/10 mm) was used for this purpose.

2.5.2 Flashing point

Technical Standards ABNT - NBR14598 (2007) using a Petrotest flash and fire test apparatus (Model 12-1660). The flash point is the temperature at which the vapor from the sample can ignite or flash. It is an important test because allows to evaluate if the asphalt is polluted with some solvent, besides indicating the maximum temperature to which a given asphalt sample can be heated, with the aim of reducing the risk of possible accidents.

2.5.3 Ring-and-Ball softening point

The experiments were performed according to the Brazilian Association of Technical Standards ABNT - NBR6560 (2000) using a Deltex – 1.586-D apparatus. The softening point is the temperature at which the specimen under consideration becomes soft enough to allow a steel ball to penetrate the sample, fall to a required distance (25.4 mm) and touch the lower reference plate.

2.5.4 Saybolt Furol viscosity

This test was performed at 135 °C according to the Brazilian Association of Technical Standards ABNT - NBR14950 (2003). It measures the time in seconds for 60 mL of sample to flow through a Furol orifice, under specified dimensions. A Pavitest Saybolt Furol viscometer was used for this purpose.

3. RESULTS AND DISCUSSION

3.1 Polymer residue

3.1.1 Granule size distribution

Figure 1 shows the size distribution of the polymer sample “as received” (Fig. 1a) and “after grinding” (Fig. 1b). With regard to the polymer “as received”, it can be observed that approximately 90 wt.% is between 1.40 and 4.00 mm. For asphalt incorporation, the polymer was ground in a mill containing porcelain balls (Fig. 1b), resulting that the particle sizes of 75 wt.% of the material ranged...
between 0.106 and 0.425 mm. The granulometry of the material used in the experiments (powdered form) was in the range 0.038 – 0.850 mm.

3.1.2 Infrared spectroscopy

Figure 2 shows the FTIR spectrum of the polymer waste. As can be observed, the main absorptions are at 1278 cm\(^{-1}\) (C–O, ester), 1452 – 1500 – 1580 – 1600 cm\(^{-1}\) (C=C, aromatic), 1732 cm\(^{-1}\) (C = O, ester carbonyl), and 2983 cm\(^{-1}\) (C–H stretching). From the analyses of the results it can be concluded that PW is an unsaturated polyester resin.

3.1.3 Differential scanning calorimetry (DSC)

The DSC of the PW was carried out (in duplicate) to determine its glass transition temperature (T\(_{g}\)). As can be observed in Fig. 3, the T\(_{g}\) is around 75 °C.

3.1.4 Thermogravimetry

Figure 4 shows the thermal degradation behavior of PW (weight loss vs. temperature curves) using the following heating rates (T\(_{a}\)): 5 °C/min, 7.5 °C/min, 10 °C/min, and 12.5 °C/min.
It can be observed in Fig. 4 that the shape of the thermogravimetric curves were almost the same for all heating rates, that is, the decomposition of all samples started around 240 °C. With these data, the activation energies (E\text{/R}) could be obtained using the Ozawa method (Tonbul and Yurdakoç, 2001). In Fig. 5, it can be observed that the activation energy (represented by the ratio E\text{/R}) increases with increasing polymer degradation, varying from 6,979.58 to 28,288.78 K between 0.05 and 0.85 fractional weight losses (α).

### 3.2 Polymer-asphalt mixture

The techniques used to prepare and characterize the polymer-asphalt mixtures were described in sections 2.4 and 2.5. Table 1 presents the results. Assays 1 to 12 were made with polymer addition, whilst assays 13 to 16 were carried out without polymer addition, for comparison.

#### 3.2.1 Penetration test

According to the literature, the addition of polymer or crumb rubber increases the consistency of the asphalt, decreasing the penetration value (Oda and Fernandes, 2001). This reduction indicates an improvement in the stiffness of the product, generating pavements that are more resistant to changes in temperature and traffic loads. From Table 1 it can be observed that only samples with 7 wt.% polymer presented a significant decrease in the penetration value. When 2 wt.% polymer are added, this material probably acts as a disperse phase only. With 7 wt.% polymer it is believed that the small particles of the polymeric residue are “swollen” into the asphalt binder, resulting in a network whose structure remains preserved. With 14 wt.% polymer no significant decrease in the penetration value was detected. This can be attributed to the high amount of PW, indicating that part of the material was not incorporated by the asphalt binder (CAP 50/60), acting only as a fine aggregate (filler). When mixing was stopped and temperature was decreased, part of the PW was deposited in the base of the sample. Regarding temperature and mixing time, the best values were obtained at 180 °C and 20 minutes. The expected behavior was a decrease in the penetration index with increasing mixing time due to the extended contact between asphalt and polymer.

#### 3.2.2 Flash point

The determination of the flash point is related to worker’s safety during transport and handling. According to the results presented in Table 1 it can be observed that the flash point decreased with increasing polymer addition. The decrease in the flash point is due to the presence of volatile compounds from the thermal degradation of the asphalt and polymer.

### Table 1. Properties of asphalt samples.

<table>
<thead>
<tr>
<th>Assay</th>
<th>Mixing temperature (°C)</th>
<th>Polymer (wt.%)</th>
<th>Mixing time (min)</th>
<th>Saybolt Furol viscosity (SSF)</th>
<th>Flash point (°C)</th>
<th>Penetration (25 °C-1/10mm)</th>
<th>Softening point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>140</td>
<td>2</td>
<td>20</td>
<td>246.00</td>
<td>250.8</td>
<td>45.66</td>
<td>52.90</td>
</tr>
<tr>
<td>2</td>
<td>140</td>
<td>2</td>
<td>60</td>
<td>261.66</td>
<td>262.9</td>
<td>51.66</td>
<td>53.50</td>
</tr>
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<td>180</td>
<td>2</td>
<td>20</td>
<td>232.00</td>
<td>258.9</td>
<td>42.66</td>
<td>51.50</td>
</tr>
<tr>
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<td>244.6</td>
<td>50.33</td>
<td>51.60</td>
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<tr>
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<td>52.50</td>
</tr>
<tr>
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<td>7</td>
<td>60</td>
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<td>237.0</td>
<td>45.50</td>
<td>51.90</td>
</tr>
<tr>
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<td>180</td>
<td>7</td>
<td>20</td>
<td>279.00</td>
<td>235.0</td>
<td>36.66</td>
<td>53.00</td>
</tr>
<tr>
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<td>7</td>
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<td>235.0</td>
<td>40.87</td>
<td>54.50</td>
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<td>140</td>
<td>14</td>
<td>20</td>
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<td>224.8</td>
<td>51.75</td>
<td>51.45</td>
</tr>
<tr>
<td>10</td>
<td>140</td>
<td>14</td>
<td>60</td>
<td>519.66</td>
<td>214.9</td>
<td>52.33</td>
<td>50.85</td>
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<td>11</td>
<td>180</td>
<td>14</td>
<td>20</td>
<td>472.33</td>
<td>234.6</td>
<td>49.60</td>
<td>50.85</td>
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<tr>
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<td>180</td>
<td>14</td>
<td>60</td>
<td>565.66</td>
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<td>60</td>
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<td>282.9</td>
<td>52.16</td>
<td>55.75</td>
</tr>
<tr>
<td>15</td>
<td>180</td>
<td>0</td>
<td>20</td>
<td>241.50</td>
<td>265.0</td>
<td>51.66</td>
<td>55.75</td>
</tr>
<tr>
<td>16</td>
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<td>0</td>
<td>60</td>
<td>229.00</td>
<td>264.7</td>
<td>52.33</td>
<td>55.85</td>
</tr>
</tbody>
</table>
polymer residue (polyester resin). This decrease in flash point does not impair the use of the obtained asphalt because the heating temperature in field applications is around 135 °C, and the lowest flash point obtained in our experiments was 214.9 °C. In a general way, it can be concluded that polymer amount and mixing temperature presented significant influence in the flash point.

3.2.3 Saybolt Furol viscosity

Viscosity is an important property to evaluate the behavior of bituminous material for paving operations, such as mixing, spreading and compaction. Modified asphalts with high viscosity can form thicker films coated over the aggregate, avoiding its displacement and, consequently, increasing the durability of the obtained pavement. From the results shown in Table 1, as expected, it can be noticed that the viscosity increases with increasing PW addition. This increase was more significant with 14 wt.% polymer. It is important to point out that no significant changes were observed between the high and low levels of mixing time and temperature, suggesting that the amount of polymer is the factor that actually interferes in the viscosity value.

3.2.4 Ring-and-ball softening point

The ring-and-ball test evaluates the behavior of asphalt with temperature and can be correlated with material hardness and, consequently, its resistance to rutting (permanent deformation). This test can also be used to obtain the reference temperature for field application. High values of softening point indicate that the asphalt can be used in paving operations because it will not soften in hot days. However, a great amount of heat will be necessary for application in paving operations, therefore offering risks for workers.

From the results shown in Table 1, a small decrease can be observed in the softening point after polymer incorporation, with temperatures varying from 55.85 °C for the base asphalt (0 wt.% polymer) to 50.85 °C, with 14 wt.% polymer residue. It is important to notice that the desired behavior would be an increase in the softening point with polymer addition, but this variation is not significant because the softening point is always considered within a temperature interval.

### Table 2. Penetration Index (PI) obtained using the data of penetration test and the ring-and-ball softening temperature.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>PI</th>
<th>Exp.</th>
<th>PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>−0.7031</td>
<td>9</td>
<td>−0.7585</td>
</tr>
<tr>
<td>2</td>
<td>−0.2780</td>
<td>10</td>
<td>−0.8788</td>
</tr>
<tr>
<td>3</td>
<td>−1.1776</td>
<td>11</td>
<td>−1.0021</td>
</tr>
<tr>
<td>4</td>
<td>−0.7870</td>
<td>12</td>
<td>0.5692</td>
</tr>
<tr>
<td>5</td>
<td>−0.8592</td>
<td>13</td>
<td>0.0049</td>
</tr>
<tr>
<td>6</td>
<td>−0.9437</td>
<td>14</td>
<td>0.2522</td>
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<tr>
<td>7</td>
<td>−1.1488</td>
<td>15</td>
<td>0.2284</td>
</tr>
<tr>
<td>8</td>
<td>−0.5887</td>
<td>16</td>
<td>0.2822</td>
</tr>
</tbody>
</table>

3.2.5 Temperature susceptibility

The Penetration Index (PI) was defined by Pfeiffer and van Doormal, and correlates the needle penetration test and the ring-and-ball softening temperature (Zhang et al., 2008). It is used to evaluate temperature susceptibility of a given asphalt, being also a powerful indicator for classifying bitumen rheological behavior. The penetration index at 25 °C is given by Equation 1.

\[
\text{Penetration Index (PI) }_{25^\circ C} = \frac{500 \cdot \log P + 20 \cdot T_{R&B} - 1951}{120 - 50 \cdot \log P + T_{R&B}} \tag{1}
\]

where \(T_{R&B}\) is the ring-and-ball softening point and \(P\) is the penetration value.

For paving-grade bitumen, the PI typically lies between −2 and +2 (Kok and Yilmaz, 2009). In Brazil, the National Fuel Department (DNC, 1993), in its technical specifications for petroleum asphalt cement, establishes the following limits: \(-1.5 < PI < +1.0\). In this research, the PI of all 16 samples are shown in Table 2. It can be observed that the values lie between −1.18 and 0.60 (more precisely, \(-1.1776 < PI < +0.5692\)), indicating that the obtained asphalt is appropriate for paving applications.

4. CONCLUSIONS

From the findings of the present work, the following conclusions can be listed:

- The PW is an unsaturated polyester resin that can be added to asphalt only after a grinding process;
The amount of polymer added to the asphalt matrix was the main parameter affecting the properties of the polymer-asphalt mixture. The addition of PW resulted in modifications in the CAP 50/60 physical properties, generating a material with enhanced properties;

The results of Penetration Index showed that all prepared samples can be used in paving operations;

The results obtained in this research showed that the addition of PW into asphalt is a viable alternative to solve an environmental problem due to generation of polymer residues, and to develop novel alternatives to paving operations.

ACKNOWLEDGMENTS

The authors would like to thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico – Brazilian National Council of Technological and Scientific Development) and ANP (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis – Brazilian National Agency of Petroleum, Natural Gas and Biofuels) for financial support.

NOMENCLATURE

ABNT – Brazilian Association of Technical Standards
ASTM – American Society for Testing and Materials
CAP – Petroleum asphalt cement
DSC – Differential scanning calorimetry
$E_a$ – Activation energy
FTIR spectroscopy – Fourier transform infrared spectroscopy
N – Nitrogen
O – Oxygen
$P$ – Penetration value
$PI$ – Penetration Index
PW – Polymer waste
R – Universal gas constant
S – Sulfur
SSF – Saybolt Seconds Furol
$T_s$ – Heating rate
$T_g$ – Glass transition temperature
TGA – Thermogravimetric analysis
$T_{R&B}$ – Ring-and-ball softening point
$\alpha$ – Fractional weight loss

5. REFERENCES


DNC. Brazilian National Fuel Department – Technical Regulation for Petroleum Asphalt Cement DNC Nº 01/92 - Rev. 02, Governmental Decree nº 05, 1993. (in Portuguese)


