Comparison of Carbon Black from Pyrolyzed Tires to Other Fillers as Asphalt Rheology Modifiers

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In order to dispose of old tires crumb rubber modified asphalts have been introduced. However, the research done on these products shows that they do not necessarily enhance the field applications. Since carbon black can be extracted from old tires, it might be a better way to recycle tires. This study presents carbon black (CB) from pyrolyzed tires as an asphalt modifier. CB was compared to aggregate fillers and ball clay, and mixed with asphalt to form mastics with similar weight contents (20 to 40 per cent). If the high temperature (above 65°C) stiffening effect of the fillers is highly filler dependent, the low temperature rheological behavior is similar for all fillers. At temperatures below 65°C, the same rheological model can fit all experimental data points. However, a low temperature toughening effect was only found in the case of mineral fillers. This was attributed to the aggregate/asphalt interface. This interface is too weak in the case of CB and clay to toughen the asphalt at low temperatures and to prevent particle aggregation at high temperatures. As a result CB seems to be a good rheology modifier for fillers already having a good low temperature behavior, such as polymer-modified asphalts.

In efforts to dispose of old tires, much research has been done to evaluate the performances of crumb rubber modified asphalts (1,2). Unfortunately, those studies show that crumb rubber does not necessarily improve the rheology of bitumens. An alternative to crumb rubber could be carbon black from pyrolyzed tires. When tires are heated to very high temperatures in the absence of oxygen, the polymers decompose (pyrolyze) into smaller organic molecules. The result is a combustible gas and a liquid fuel similar to diesel fuel. The carbon black originally added to stiffen the rubber remains behind as a granular char that can be easily ground to a fine powder, with 90+ percent passing the No. 325 mesh screen. Although this particle size is too large to enable the recycled carbon black to be reincorporated into new tires, it can be used effectively as a filler for asphalt concrete mixtures. One tire will yield approximately 7 to 8 lb of carbon black. Several companies are trying to commercialize the pyrolysis of tires to help dispose of used tires and to develop markets for the carbon black at a cost of 5 to 10 cents/lb.

The purpose of this study was to investigate the rheological behavior of carbon black modified asphalt. For a comparison purpose, two mineral fillers and one clay, also passing the No. 200 mesh (75 µm) screen, have been studied at similar fine contents (by weight). These fine contents were kept lower than 40 percent because of carbon black modified binders workability.

Because the Strategic Highway Research Program (SHRP) introduced new tools to evaluate the binders properties (3), the stiffening power of the fines was measured using the procedures defined by SHRP for binders. However, the purpose here was not to apply SHRP binder specifications to mastics, but rather to use SHRP procedures to compare the materials.

EXPERIMENT

Samples

Two binders were used throughout this study: AC-10 and the same asphalt modified with reacted in situ Styrene-Butadiene copolymer (Styrelf MAC-10).

Four fillers passing the No. 200 sieve (75 µm) were used throughout this study:

- Carbon Black from pyrolyzed tires (from Jarrell Group);
- Ralston Quarries (from Colorado);
- Sievers Pits crushed (from Colorado); and
- Ball Clay (Super Seal No. 2 from Kentucky–Tennessee Clay Co.)

The mastics were made with 20 and 30 percent (mass) of each fine in both binders. In the case of ball clay, only the neat asphalt was used at three clay contents (20, 30, and 40 percent). The ball clay was included in this study because clays are a "bad-acting" filler. Ball clay is a kaolin clay and is highly plastic. ASTM 242-85 limits the plasticity index of fillers. It is used as a bonding agent in fired ceramics and as an emulsifying agent in coal tar emulsions. The binders were heated up to 185°C and the fillers were then added 3 to 5 g at a time, under constant stirring. Twenty minutes were needed to obtain each mastic.

Finally, 17 samples were studied (2 base binders and 15 mastics). Also, four mixes were made to evaluate the rutting resistance of the mastics, assuming the mastics were regular binders. The aggregates used for the mixes met the Michigan 4C specifications, which is close to a typical Indiana surface coarse aggregate. The binder content was 5.6 percent (mass) in each case and the air voids, 3 percent.

Testing

Specific fine testing was run on the fillers. This included:

- Particle size analysis (Figure 1), using a laser beam particle size analyzer, Microtrac II (Leeds and Northrup). Dispersion medium was water for all fillers except carbon black (2-propanol);
\begin{itemize}
  \item Rigden air voids (compacity) measurements; and
  \item Specific gravity, using a Le Chatelier flask with kerosene.
\end{itemize}

Results of these tests are gathered in Table 1.

SHRP procedure [draft 8E, see (3)] was used to characterize the filled and unmodified binders. This included dynamic mechanical analysis (DMA—Rheometrics RDA II equipped with parallel plates) at high temperatures (around 60°C) on the unaged and rolling thin film oven test (RTFOT) aged materials; Brookfield viscosity on the unaged materials at 135°C; DMA at intermediate temperatures (around 20°C) on the pressure aging (PAV)-RTFOT residues; and bending beam rheometer (BBR—Cannon) and direct tension test (DIT) on the PAV-RTFOT aged materials at low temperatures (around -15°C).

Also, the Hamburg Wheel tracking test, described elsewhere (4), has been used to evaluate the rutting performance of four mixes.

\section*{RESULTS—SHRP APPROACH}

Once again, the purpose of this study was not to apply SHRP binder specifications to the mastics. SHRP equipment was used as a tool to characterize the stiffening effect of the fines.

The temperatures where SHRP criteria (draft 8E) were met have been calculated by combining measurements at three temperatures (Figure 2 shows the temperatures where the criteria are met).

\begin{figure}
\begin{center}
\includegraphics[width=\textwidth]{figure1.png}
\end{center}
\caption{Particle size distribution of the fillers.}
\end{figure}

\begin{table}
\centering
\begin{tabular}{lccccccc}
\hline
Filler & Supplier & Specific Gravity & Fineness Modulus & Ridgen Air Voids & m value from equation (2) & \\
& & (g/cm$^3$) & (%) & & @ 55°C & @ 65°C & @ 135°C \\
\hline
Ralston Quarry & Colorado & 2.822 & 2.90 & 48.4 & 0.35 & 0.27 & 0.20 \\
Sievers Pit & Colorado & 2.717 & 2.83 & 45.9 & 0.36 & 0.19 & 0.20 \\
Carbon Black & Jarrel Group & 1.690 & 3.66 & 39.9 & 0.37 & 0.30 & 0.95 \\
Ball Clay & KY-TN Clay Co. & 2.960 & 5.59 & & 0.49 & 0.34 & 0.67 \\
\hline
\end{tabular}
\caption{Filler Properties}
\end{table}

\section*{High Temperatures}

As expected, $G'/\sin \delta$ at a given temperature and frequency (10 rad/sec) increased with the fine content. The consequence of this stiffening effect on the unaged samples was that the temperature where the criterion (1 kPa) was met increased with the fine content (Figure 2). The increase caused by 20 percent carbon black in the base AC-10 was similar to that with 30 percent mineral fillers and to that with polymer modification. The same trend was found for the RTFOT aged samples (the criterion was then 2.2 kPa). However, in the case of RTFOT aged materials, two filled samples (MAC-10 + 20% RQ and MAC-10 + 20% SP) were found to have a lower modulus than the unaged mastic. This was probably caused by a decrease of the filler content owing to a loss of filler on the RTFOT jars.

To validate SHRP results, the rutting resistance of four samples was measured by using the Hamburg wheel tracking device. The tests were run at 50°C, under water. The samples were chosen for their similar limiting high temperature. They were the unmodified MAC-10 and the same MAC-10 filled with 20 percent (mass) of each fine (except ball clay). Figure 3 shows a similar rutting resistance for all filled samples, whereas the MAC-10 failed early. Also, the carbon black filled sample exhibited very little stripping compared to the mineral fillers. Carbon black is hydrophobic, and this may explain the low stripping in an underwater rutting test.
Finally, these rutting results on the mastics confirmed the predictions of SHRP criterion: the higher $G^*/\sin \delta$ at 10 rad/s on the unaged and RTFOT aged materials, the higher the rutting resistance, although this criterion is defined for binders only.

Intermediate Temperatures

At intermediate temperatures, the effect of the fines on the PAV-RTFOT aged samples was also to increase the modulus and, to a lesser extent, to lower the phase angle. The consequence was to increase $G^*x \sin \delta$ at given temperature and frequency, and then increase the temperature where the criterion was met (Figure 2). This would mean a lower fatigue resistance if SHRP binder specifications applied to mastics.

Unfortunately, no fatigue testing was run on the mixes to find out if SHRP criterion at intermediate temperatures could predict the fatigue resistance of the mastics.

Low Temperatures

At low temperatures, for the PAV-RTFOT aged samples, the stiffening effect was still obvious for all fines: the higher the fine content, the higher the stiffness and the lower the $m$-value. In terms of paving grades, MAC-10 with 20 percent carbon black passes the
same low temperature grade as the unmodified base asphalt (AC-10). Polymer modification appears to be an easy solution to compensate for the stiffening effect of the fillers (Figure 2).

Due to lack of PAV-RTFOT aged materials, the temperature where the DTT specifications (1 percent strain at failure at 1 mm/mn) were met, could not be calculated. However, when looking at Table 2, a general trend can be observed. For carbon black modified samples, the higher the fine content, the lower the strain at failure. The increase of stiffness comes along with a lower failure resistance, which is the typical behavior of unmodified asphalt cements. Meanwhile, such an effect was not found in the case of mineral fillers. When DTTs were run on the unaged samples, a significantly higher strain to failure was found for filled samples with more than 20 percent filler (mass), although the stiffness is significantly higher (Figure 4). Therefore, the stiffening effect of mineral fillers comes along with a toughening effect at low temperatures.

Finally, at low temperatures, carbon black and mineral fillers exhibited the same stiffening effect, but a toughening effect was only found with the mineral fillers and not with carbon black and clay modified samples.

### DISCUSSION

#### Rheology of Mastics

The effect of the fillers has been quantified using experimental results from the SHRP procedure. These parameters were

- the Brookfield viscosity at 135°C;
- $G^*/\sin \delta$ at 55°C and 10 rad/sec;
- $G^*/\sin \delta$ at 65°C and 10 rad/sec;
- $G^* \times \sin \delta$ at 20 and 25°C and 10 rad/sec; and
- the BBR creep stiffness at $-15, -20, -25$°C at 60 sec.

The zero-shear viscosity at 55°C and 65°C was first chosen to calculate the stiffening ratio. However, Figure 5 shows that there was no significant difference between the stiffening ratio calculated either with the zero-shear viscosity or with the SHRP criterion ($G^*/\sin \delta$ at 10 rad/s) at these temperatures. So stiffening ratios $\eta_s$ were defined at all temperatures, as the given SHRP pa-

### TABLE 2  Direct Tension Test Results on PAV Aged and Unaged Specimens and Corresponding Creep Stiffnesses at 60 S Loading Time

<table>
<thead>
<tr>
<th>Aging Temperature (°C)</th>
<th>Measurements</th>
<th>Units</th>
<th>Base Asphalt : AC-10</th>
<th>Base Asphalt : MAC-10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0% Filler 20% CB 30% CB 20% RQ 30% RQ 20% SP 30% SP</td>
<td>0% Filler 20% CB 30% CB 20% RQ</td>
</tr>
<tr>
<td>PAV -6</td>
<td>Load at Failure</td>
<td>N</td>
<td>&gt;50.0 71.3 83.1 71.3 102.0 92.8</td>
<td></td>
</tr>
<tr>
<td>PAV -6</td>
<td>Strain at Failure</td>
<td>%</td>
<td>&gt;2.00 1.06 0.56 3.16 4.26 1.93</td>
<td></td>
</tr>
<tr>
<td>PAV -12</td>
<td>Load at Failure</td>
<td>N</td>
<td>49.8 74.6 72.7 81.1 94.1 88.5 83.7 79.7 76.8 121.2</td>
<td></td>
</tr>
<tr>
<td>PAV -12</td>
<td>Strain at Failure</td>
<td>%</td>
<td>0.33 0.34 0.45 0.27 0.42 0.41 1.91 1.10 0.38 2.06</td>
<td></td>
</tr>
<tr>
<td>No -15</td>
<td>BBR Stiffness</td>
<td>MPa</td>
<td>80 103 126 105 137</td>
<td></td>
</tr>
<tr>
<td>No -15</td>
<td>BBR Slope</td>
<td></td>
<td>0.49 0.48 0.47 0.48 0.48</td>
<td></td>
</tr>
<tr>
<td>No -18</td>
<td>Load at Failure</td>
<td>N</td>
<td>43.9 70.3 93.6 54.8 107.3</td>
<td></td>
</tr>
<tr>
<td>No -18</td>
<td>Strain at Failure</td>
<td>%</td>
<td>0.19 0.22 0.40 0.12 0.25</td>
<td></td>
</tr>
</tbody>
</table>
rameter of the mastic divided by the same SHRP parameter of the base binder.

**Free Asphalt Theory**

Mineral fillers in asphalt have been studied for years, and Anderson thoroughly overviewed the subject in 1982 (5–10).

Rigden found that the critical parameter to describe the stiffening effect of the mineral fillers was the solid phase volume fraction (5). Many studies confirmed this approach (6–9).

Rigden's theory is based on the fixed asphalt concept. The fixed asphalt is the fraction of the asphalt needed to fill the air voids of the filler. Hence, a minimal amount of asphalt is required to obtain a fluid when blending fillers with asphalt. The liquid phase is called free asphalt. The free asphalt volume fraction is then directly related to the stiffening effect of the filler. In order to calculate the free asphalt volume fraction ($\phi_{fa}$), Rigden developed a test (used in this study) to measure the percent air voids volume in the fillers ($\phi_{av}$). Knowing the fine/asphalt ratio with respect to the volume ($F/A$), the free asphalt volume fraction can be calculated as follows:

$$\phi_{fa} = \frac{F/A - \phi_{av}}{1 - \phi_{av}}$$

**FIGURE 4** DTT results on the unaged samples at $-18^\circ$C.

**FIGURE 5** Stiffening ratios from $G^*/\sin\delta$ versus stiffening ratios from zero-shear viscosities.
Although Rigden's theory gives good predictions at a given temperature, it does not explain the temperature and shear rate dependency of filled asphalts. The free asphalt fraction was calculated using equation (1) for all high temperature measurements. Then stiffening ratios were plotted versus free asphalt fraction at each temperature (Figure 6). Although one single curve can fit all experimental data points at 55°C and 65°C regardless of the filler, different curves per filler are needed at 135°C. At this temperature, neither carbon black nor ball clay behave like the mineral fillers and the free asphalt concept underestimates the stiffening effect of carbon black and ball clay.

The fines used in this study have similar Rigden air void indices (Table 1). The free asphalt fraction is rather similar from one sample to another, at a given (F/A), ratio. So, looking at the (F/A), ratio instead of the free asphalt fraction gives the same results. In terms of SHRP results, this effect is highlighted by the fact that 20 percent (mass) carbon black is equivalent to 30 percent of each mineral filler.

Finally, the free asphalt concept was in good agreement with the stiffening effect of the fines at 55°C and 65°C, but underestimated the stiffening effect of carbon black and ball clay at 135°C.
Suspension Approach

Heukelom and Wijga developed a semi-empirical approach to describe the increase of viscosity of dispersions, including fillers in asphalt (10). They proposed the following equation to calculate the viscosity of the blends, for \( \eta_r < 100 \):

\[
\eta_r = [1 - 1.28 \times (1 + m) \times \phi]^{-2}
\]  

where \( \eta_r \) is the relative viscosity (the viscosity of mastic divided by the viscosity of the base asphalt), \( m \), a parameter describing the virtual increase of concentration due to a poor peptization of the particles and/or the nonsphericity of these particles, and \( \phi \), the volume fraction of the filler. This latter parameter being related to the fine/asphalt ratio:

\[
(F/A)_r = 1 / [(1/\phi) - 1]
\]  

Although the peptization is certainly temperature-dependent, Heukelom and Wijga did not look at the variation of \( m \) versus temperature.

Linear plots of \( (\eta_r)^2 \) versus \( \phi \), at a given temperature, led to the \( m \)-values, using the method described by Heukelom. This consists in evaluating \( \phi_{\text{max}} \), the volume concentration where \( 1/\eta_r \), equals 0. Therefore \( \phi_{\text{max}} \) represents the compacity of the filler and correlates well with Rigden Air Voids Index for most fillers (10). Knowing \( \phi_{\text{max}} \), the following equation was applied to calculate \( m \):

\[
m = (0.78/\phi_{\text{max}}) - 1
\]

The constant (0.78) corresponds to an ideal case where the particles are fully peptized spheres with distributed sizes, as measured by Heukelom for a regular asphalt emulsion.

So, \( m \) values in equation (4) were calculated from experimental results. Figure 7 shows the validity of Heukelom’s law in the 55°C to 135°C temperature range. Table 1 shows the variation of \( m \) versus temperature for each fine. Whereas the \( m \)-values for carbon black, ball clay, and both mineral fillers were rather similar to 55°C and 65°C, results at 135°C were clearly different. Although the trend for the mineral fillers was a slight decrease, \( m \) for carbon black and ball clay increased at 135°C. This increase of the \( m \)-value means that the peptization of carbon black and ball clay is better at 65°C than at 135°C. A reasonable explanation is that carbon black and ball clay aggregate easily at high temperatures, creating clusters between the solid particles. Some asphalt is then entrapped inside the aggregates so that the apparent volume fraction of the filler increases. Thus the viscosity and, consequently, \( m \) increase. This behavior also explains why Rigden Air Voids indices do not correlate with \( \phi_{\text{max}} \) in the case of carbon black at 135°C. However, this result does not occur at 65°C because the viscosity of the asphalt is still high and prevents this aggregation from happening during the measurements.

Finally, Heukelom’s law was found to give a good prediction of the rheological behavior of filled samples at high temperatures. Heukelom’s law was then generalized for every SHRP measurement, including \( G^* \times \sin\delta \) after PAV at intermediate temperatures and creep stiffness at low temperatures. The same model was used (\( m = 0.238 \)) to fit all experimental results, for all aging levels (unaged, RTFOT, and PAV aged samples). Finally, the model used to fit the experimental results reduces to a Maron & Pierce law (11):

\[
\eta_r = [1 - \phi/A]^{-2}
\]

where \( A = 0.630 \) (which is rather similar to the compacity as measured by the Rigden Air Void index).

The comparison of the samples at any aging level can be made assuming the stiffening effect is not aging dependent. In other
words, it means that the aging of the asphalt is not modified by the fillers. Figure 8 shows that the stiffening effect is fairly constant versus aging.

The correlation between calculated and experimental results (using Heukelom's law) was found to be highly significant, \( r^2 = 0.95 \) (Figure 9). The average error was found to be 12.7 percent and 80 percent of the data are within 20 percent error. The data points out of this range were either high temperatures measurements (for carbon black and ball clay) or aged samples. In the former case, the difference can be explained by an underestimated \( m \)-value (cf. previous section). In the latter case, a reasonable explanation is that the actual filler content was lower than the expected one (due to experimental problems such as pouring the RTFOT aged samples from the RTFOT jars).

More generally, all SHRP measurements can be estimated using equation (5). The only parameter needed is the volume fraction of the fines. As long as the asphalt matrix is too viscous to allow particle aggregation (i.e., at temperatures below 65°C), predictions from equation (5) are accurate (20 percent average error).

However, at temperatures above 65°C, the behavior of the fines becomes highly filler dependent. Particle aggregation becomes more probable, and another parameter, describing the peptization degree of the suspension, is needed to give a better prediction of their stiffening effect.

Toughening Effect of Mineral Fillers

A better fracture resistance was found with the mineral fillers but not with carbon black nor with ball clay. This toughening effect of mineral fillers resembles the enhanced fracture properties of materials reinforced with rigid particles (glass beads in epoxy resins, for example). Strong interactions between the fillers and the asphalt are needed for such a behavior to occur. In the case of ball clay and carbon black, the asphalt/particle interactions are weak, as shown by the high temperature aggregation of the dispersed particles. This explains why no toughening effect was found with them.

Also, fracture mechanics measurements made by Salam and Monismith (12) showed that the finer the aggregate, the higher the fracture toughness. These results were in good agreement with those presented herein.

This toughening effect could explain the better thermal cracking resistance of stone mastic asphalt (SMA), which is usually attributed to the high binder content (around 15 percent) (13). Since the thermal crack propagates through the brittle asphalt matrix, no big difference on the thermal cracking resistance should appear when considering varying binder contents. So the better thermal cracking resistance of SMA is more likely due to the high fine content. Furthermore, the asphalt layer surrounding the rocks is thick in SMA mixes. This toughening effect should be more pronounced in this particular case.

However, this qualitative result needs to be confirmed by specific experiments to quantify and understand the toughening effect of the fillers.

CONCLUSIONS

The effect of the fines passing the No. 200 mesh sieve has a considerable effect on the performance of a bituminous mix. It has been shown that both the amount of fines and their characteristics are important factors. Some of the important fine properties are compaction, density, and chemical composition. For example, if 20 percent (weight) carbon black is added to a mix, some of the naturally occurring fines must be removed or the mix will probably become too stiff. Also, the same amount of carbon black, ball clay, and natural fines will not produce the same results.
This study showed that

- The new procedures introduced by SHRP can be used to investigate the effect of fillers.
- The rheology of mastics is mainly governed by the volume content of the fillers at temperatures less than 65°C, but other parameters such as the m-value in Heukelom’s law are needed to predict the high temperature behavior of the filled asphalts. As a result, a Maron and Pierce law with \( A = 0.630 \) was found to be reliable in order to predict any SHRP measurement, knowing the volume content of the filler and the value of this measurement for the base asphalt. However, those results are only proposed in case of low filler concentrations (up to 40 percent weight) and stiffening ratios less than 100.
- Carbon black from pyrolized tires, and mineral fillers as well, were found to greatly improve the rutting resistance of the binders.
- A toughening effect occurred with mineral fillers at low temperatures, but not with carbon black nor with ball clay. Consequently, carbon black will be an efficient rheology modifier for a base asphalt having good low temperature properties, such as polymer-modified asphalts. Also, it would not be worth substituting carbon black for mineral fillers in specific applications (such as SMA) where a good thermal cracking resistance is necessary.
- Fracture mechanics experiments are needed to understand and quantify the low temperature toughening effect of the fines.

The binder and some of the fines combine to produce a mastic that binds the asphalt concrete together. The percentages of fines in this mastic may be as high as 40 percent. Therefore, the characteristics of these fines and the effect they have on this mastic should be carefully studied before a mix is placed on the road. The type and amount of No. 200 fines must be carefully selected to produce asphalt concrete with the desired properties.

**REFERENCES**


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