Rheological, Spectroscopic, and Chemical Characterization of Asphalt Binders Modified with Phase Change Materials, Polymers, and Glass Powder

Haya Almutairi and Hassan Baaj *

Department of Civil and Environmental Engineering, University of Waterloo, Waterloo, ON N2L 3G1, Canada  
* Correspondence: hbaaj@uwaterloo.ca

Abstract: Recently, asphalt modifiers have increasingly gained attention for improving the mechanical and thermal characteristics of asphalt mixtures. As a result, innovative additives are being constantly developed to achieve this purpose. However, some modifiers can significantly impact the chemical and rheological properties of the asphalt binder. This paper investigates the rheological, spectroscopic, and chemical properties of asphalt binders modified with a bio-based phase change material (PCM) and phase change material mixed with glass powder (GPCM). Two binders were investigated, PG 58-28 and PG 70-28 polymer modified asphalt binder with 3% SBS. Two different percentages of GPCM (5% and 7%) were added to PG 58-28 and PG 70-28, and 5% PCM was added to PG 58-28. The results indicated that the PCMs effectively reduced the viscosity values of the asphalt binder. Moreover, testing the modified binders using differential scanning calorimetry (DSC) showed that the PCMs released the stored heat when the melting/freezing temperature was reached. However, adding glass powder with the PCMs negatively affected the thermal properties of PCMs in the asphalt mix. In addition, considerable changes in the stiffness of the binders modified with GPCM at an intermediate temperature were obtained when tested using DSR. Finally, the TGA results revealed that this specific type of PCM would not be suitable as a hot mix asphalt (HMA) modifier as its evaporation temperature is lower than the mixing temperature HMA. However, the use of PCM in warm mix asphalt (WMA) would be a more viable option. The results showed that the evaporation temperature for the PCMs was low; therefore, the PCMs cannot be used in HMA. In addition, modified binders with PCMs and GPCM showed lower viscosity compared to the control binder. The DSR rheological analysis showed that the control binder and 5%PCM, 5%GPCM, 7%GPCM, 5%GPCM, and 7%GPCM binders had similar overall properties. However, the addition of GPCM significantly decreases the stiffness at intermediate temperatures.

Keywords: asphalt binder; recycled glass powder; phase change materials; rheology; environmental scanning electron microscope; thermogravimetric analysis; differential scanning calorimetry

1. Introduction

Over the last few decades, high-performance asphalt pavement has gained more attention from designers due to inadequate maintenance and a rapid increase in traffic volumes and loads, leading to severe distress. Many researchers have pointed to the role of bitumen quality in improving the overall performance of asphalt pavement. Therefore, many innovative additives are being constantly investigated to enhance the performance of asphalt mixtures [1]. Additives such as polymers and nanomaterials have been investigated to enhance the overall performance of hot asphalt mixtures [2]. However, some additives, such as phase change materials (PCM) and glass powder (GP), are relatively new. As a result, more efforts are needed to investigate and understand the effects of these innovative additives on the performance of asphalt mixtures.
PCMs are thermal energy storage materials that can store or release a large amount of thermal energy during the phase change processes. Hence, PCMs are used in various applications in construction materials to improve their performance [3]. However, use of PCMs is argued to be significantly beneficial in improving the low-temperature performance of some materials, such as asphalt mixtures. It was reported by Ma et al. (2010) that an asphalt mix containing PCM can control the asphalt mixture temperature ranges due to the change in the ambient temperature; this can delay the extreme temperature occurrence and shorten the extreme temperature duration.

PCMs are classified based on their chemical compositions: inorganic PCMs, organic PCMs, and compounded PCMs (Eutectics) [4]. Limited studies were conducted to investigate the use of PCMs in asphalt mixtures, and these studies adopted different methods of mixture preparation. These mixtures were prepared using direct/indirect blending or the sol–gel method [5]. Ref. [6] reported that the direct blending method led to a leakage of the PCMs from the asphalt binders. As a result, there was a concern about the durability of the asphalt pavement modified with PCMs.

Another study was conducted by [7] using the direct immersion method, which involved the immersing of a porous supporting material directly into the PCM liquid to form composite phase change materials (CPCMs). The study was performed by preparing different asphalt mixtures with different composite PCM dosages (0%, 5%, 10%, and 20%) that were tested for high-temperature stability, low-temperature crack resistance, and resistance to water damage. It was concluded that using CPCMs can reduce the effect of PCMs on the saturate, aromatic, resin, and asphaltene (SARA) contents of the asphalt binder. Moreover, CPCMs solved the leakage problems resulting from adding PCMs to the asphalt mix during the high-temperature mixing process. Ref. [7] found that the CPCMs controlled the temperature fluctuations of the asphalt mixture by reducing the cooling and warming rates of the mixtures and delaying high-temperature and low-temperature extremes.

In addition, [8] studied the use of a lightweight aggregate (LWA) as a medium to incorporate the PCMs into HMA to extend the pavement life. LWA was soaked in paraffin wax PCMs, which have a phase change temperature of 6 °C, to investigate its ability to delay the freezing of infiltrated water. The thermal properties of the mixtures with different concentrations of PCMs were evaluated using a guarded longitudinal comparative calorimeter (GLCC). The results showed that the mixtures containing PCMs had a lower cooling rate than the control mixtures. The authors mentioned that some samples failed during normal handling.

Another study by [9] showed that adding Tetradecane-PCM into the 10/20, 70/100, and 160/220 binders increased the penetration and decreased the softening temperature and the dynamic modulus of the mixture. In addition, it was found that the direct addition of the tetradecane-PCM to the binder negatively affected the rheological properties of the binder and did not store the heat energy in a latent form. Furthermore, the thermal properties of asphalt mixtures were investigated by [10] using microencapsulated PCMs. They concluded that using microencapsulated PCMs led to a slowing of the cooling rate of the mixtures below zero compared to the control mixtures. However, the results indicated that the PCMs significantly reduced the stiffness of the asphalt mixtures. A recent study has investigated the ability to use PCM and ceramsite in an asphalt mixture to decrease its high temperature [11]. The specific heat capacity and the thermal conductivity coefficient of the asphalt mixture was analyzed using the method of the insulation bucket test and thermal conductivity instrument, respectively. It was found that the addition of PCM and ceramsite reduced the thermal conductivity of the asphalt mixture as well as its specific heat capacity. Furthermore, Ref. [12] investigated the cooling effect of paraffin/SiO₂ microencapsulated phase change material (MPCM) in asphalt binders. In addition, the phase transition temperature was chosen as 53.64 °C to mitigate the urban heat island. The Fourier transform infrared spectroscopy (FT-IR) results showed no new characteristic peaks, indicating that the interaction of the blend component was only a physical interaction. In addition,
the differential scanning calorimeter (DSC) showed that the MPCM-modified asphalt binders’ melting and solidifying enthalpies were 13.76 J/g and 11.04 J/g, respectively, whereas the melting and solidifying enthalpies of the MPCM were 110.5 J/g and 108.7 J/g, respectively. Finally, they found that the modified asphalt binders possessed a lower heating rate and a higher rutting resistance than the base asphalt binders. The authors nevertheless recommended that further studies were needed to better understand the rheological properties of MPCM in asphalt pavement.

Glass is one of the most produced waste materials around the world. More than 10 million tons are produced annually [13]. In pavement construction, glass was incorporated as a replacement aggregate [14–16]. However, the use of waste glass as a filler in hot mix asphalt has still not been well evaluated. A group of researchers at École de Technologie Supérieure (ÉTS) in Quebec, Canada, reported that using recycled glass in asphalt mixtures resulted in a highly durable and environmentally friendly pavement [17].

Ref. [18] investigated the effect of blending recycled glass powder (RGP) on the mechanical properties of a polymer-modified binder with styrene-butadiene rubber (SBR). Different combinations of RGP and SBR were used to evaluate the mixture’s stability, tensile strength, moisture susceptibility, and stiffness. It was concluded that a combination of 2% RGP and 3% SBR improved the mechanical properties of the mixtures compared to the other combinations.

Moreover, Ref. [18] evaluated the fundamental rheological characterization of unmodified and polymer-modified binders with SBR and SBR-RGP using a dynamic shear rheometer (DSR). The results of the DSR test demonstrated that adding RGP has an adverse effect on the rutting resistance of the SBR-modified binder. Further studies were conducted by the same research group, Ref. [18], to investigate the rheological and mechanical properties of asphalt binders and mixtures modified with crumb rubber (CR) and RGP. The outcome of the study suggested that the best combination that improved the rheological and mechanical properties of the asphalt mixture was 5% CR and 5% RGP. Moreover, it was concluded that mixtures modified with different percentages of CR and RGP showed better resistance to the initiation and propagation of cracks, since CR and RGP exhibited a high elasticity behaviour.

Finally, most of the studies that were conducted to evaluate the performance of asphalt mixtures modified with PCM and GP did not fully address the rheological and mechanical properties of the mixes. From the authors’ point of view, only limited previously published data have been found to provide comprehensive insight on incorporating these additives in asphalt binders. Therefore, this study aims to investigate the rheological, spectroscopic, and chemical characterization of asphalt binders that are modified with GP and PCM using a viscometer, an environmental scanning electron microscope (ESEM), Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and a dynamic shear rheometer (DSR). Moreover, this study significantly contributes to advancing a better understanding of using PCM and GP in asphalt applications.

2. Materials Selection

2.1. Binder Properties

The selected asphalt binders PG for this study were the most commonly used in Canada (PG58-28 and PG70-28). The properties of the virgin asphalt binder and PG70-28 binder are shown in Tables 1 and 2, respectively.

<table>
<thead>
<tr>
<th>Index</th>
<th>Conditions (°C)</th>
<th>Unit</th>
<th>Results</th>
<th>Requirements</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>At 15</td>
<td>-</td>
<td>1.03</td>
<td>-</td>
<td>AASTHO T316</td>
</tr>
<tr>
<td>Brookfield viscosity</td>
<td>At 135</td>
<td>Pa·s</td>
<td>0.275</td>
<td>3.0 max</td>
<td>AASHTO T 48</td>
</tr>
<tr>
<td>Flash point</td>
<td>-</td>
<td>°C</td>
<td>≥230</td>
<td>230 min</td>
<td>AASTHO T 48</td>
</tr>
<tr>
<td>G*/sin(δ)</td>
<td>At 58</td>
<td>kPa</td>
<td>1.195</td>
<td>1.0 min</td>
<td>AASTHO T315</td>
</tr>
</tbody>
</table>
Table 1. Properties of the PG58-28.

<table>
<thead>
<tr>
<th>Index</th>
<th>Conditions (°C)</th>
<th>Unit</th>
<th>Results</th>
<th>Requirements</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>At 25</td>
<td></td>
<td>1.03</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Brookfield viscosity</td>
<td>At 135</td>
<td>Pa·s</td>
<td>0.90</td>
<td>3.0 max</td>
<td>AASTHO T315</td>
</tr>
<tr>
<td>Flash point</td>
<td>-</td>
<td>°C</td>
<td>≥230</td>
<td>230 min</td>
<td>AASHTO T48</td>
</tr>
<tr>
<td>G*/sin(δ)</td>
<td>At 58</td>
<td>kPa</td>
<td>3.64</td>
<td>1.0 min</td>
<td>AASTHO T315</td>
</tr>
</tbody>
</table>

2.2. Properties of Additives

2.2.1. Phase Change Materials (PCMs)

To overcome the distresses caused by fluctuations in temperature, such as thermal cracking at lower temperatures and rutting at higher temperatures, bio-based PCMs, with a melting point of −15 °C and heat storage capacity of 301 J/g, were used as modifiers for the asphalt binders with different percentages of 5% and 7%.

During the freezing phase of the PCMs, an extensive amount of energy is released, which can reduce the cooling rate of the asphalt mixture, leading to mitigation of the initiation and propagation of cracks at low temperatures. However, PCMs absorb a large amount of ambient heat during the melting phase. This can lead to a gradual reduction in the heating rate of the pavement, giving the asphalt pavement enough time to adjust to the ambient temperature. These properties along with its high energy absorption capacity made the bio-based PCM a potential candidate among the other PCMs. In this study, the PCM was provided by PureTemp, LLC. The physical properties of the PCM are presented in Figure 1. According to the provider, the PCM used in this study is manufactured from agricultural sources with a high heat storage capacity of 301 J/g due to the high thermal conductivity of PCM.

![Figure 1. Physical properties of PCMs (PureTemp LLC.)](image)

2.2.2. Recycled Glass Powder (GP)

In this study, recycled glass powder (GP) was collected from household waste in Quebec, Canada. The ESEM image of the GP (Figure 2) shows irregular, flaky, and angular particle shapes less than 25 μm. These observations show that GP has an intrinsic pore structure with a distribution that is not uniform.

Some early experiments were conducted to investigate the behaviour of asphalt mixtures modified with PCMs at high temperatures. The PCM, at a modification rate of 5%, was directly mixed with the asphalt binder (PG58-28) at a temperature of 150 °C. It was observed that the mixtures containing PCM had a brownish colour and demonstrated visible segregation of the aggregates (Figure 3). Even though all the mix design requirements were met during the mixing and compaction procedures, the specimen collapsed immediately after compaction, as shown in Figure 4.
It was concluded that the asphalt binder had been affected by the addition of PCMs. The modified binder apparently lost some of the cohesiveness properties needed to hold the sample together after the compaction. Similar findings were reported by [7] that the direct blending approach of PCMs to asphalt binders led to leakage issues of the asphalt binder.

We have therefore investigated the use of glass powder to tackle these challenges. Two main assumptions were behind this choice. The first is that the GP particles will absorb and retain the PCM, which reduces the risk of leakage of the PCM. The second assumption is that the mastic formed by mixing the GP with the asphalt binder will have increased stiffness due to the high stiffness of the glass and increased stability due to the amorphous morphology and frictional properties of the GP particles. Further experiments were conducted by mixing the GP with the PCM at ambient temperature to create a GPCM paste, after which the GPCM paste was added to the asphalt binder at 150 °C. It was concluded that the high-temperature stability of the binder at high temperatures was improved, and the presence of GP compensated for the loss of stiffness caused by the PCM.

Figure 2. Physical properties of PCMs (PureTemp LLC.).

Figure 3. Asphalt mix containing 5%PCM and 0%PCM.
2.3. Thermogravimetric Analysis (TGA)

The TGA test is used to determine the amount/rate of weight change in the material as a function of increasing temperature in a controlled atmosphere [19]. In this study, the TGA test was used to measure the degradation/evaporation characteristics of the PCM, GPCM, control binder, 5%PCM binder and 7%GPCM binder at a heating rate of 10 °C/min.

2.4. GPCM Preparation

Figure 5 shows the mixing procedure of GPCM paste. The paste was prepared by mixing the GP with the PCM. Different GP:PCM mixing ratios were examined; 50:50, 80:20, 70:30 and 30:70, respectively. The required ratio of GP was prepared using a weighing scale, then put into a clean beaker. After this, the PCM was gradually added with the required amount to the GP. Using a rotational mixer, the GP and PCM were mixed for 2–3 min at a speed of 1000 rph to obtain a homogenous mix. The time, temperature, and speed of mixing parameters were selected based on a trial-and-error procedure after many mixing trials to obtain the desired texture.
2.5. Asphalt Binder Preparation

Two main factors were considered when modifying the asphalt binder with PCM and GPCM at different temperatures. These factors are the nature of the additives and their evaporation temperatures obtained using a thermogravimetric analyzer (TGA). Figure 6 shows a schematic flow chart illustrating the asphalt binder modification process. Moreover, Table 3 shows the binder identifications, base binder and types of additives used in this study. According to the literature, the optimal addition dosage for glass powder was up to 10% by binder weight [20]. However, no data were recorded for the recommended amount of PCM added to asphalt binders. As a result, the two percentages selected for this study were 5% and 7%.

![Figure 6. A schematic flow chart of asphalt binder preparation.](image)

<table>
<thead>
<tr>
<th>Binder Identification</th>
<th>Base Binder</th>
<th>Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>PG 58 -28</td>
<td>-</td>
</tr>
<tr>
<td>5% PCM</td>
<td>PG 58 -28</td>
<td>3% Styrene-butadiene-styrene</td>
</tr>
<tr>
<td>5% GPCM</td>
<td>PG 58 -28</td>
<td>5% Phase Change Materials</td>
</tr>
<tr>
<td>7% GPCM</td>
<td>PG 58 -28</td>
<td>5% [Glass Powder + Phase Change Materials]</td>
</tr>
<tr>
<td>5% GPCM-SBS</td>
<td>3% SBS modified PG 58 -28</td>
<td>5% [Glass Powder + Phase Change Materials]</td>
</tr>
<tr>
<td>7% GPCM-SBS</td>
<td>3% SBS modified PG 58 -28</td>
<td>7% [Glass Powder + Phase Change Materials]</td>
</tr>
</tbody>
</table>

A total of 52 specimens were prepared: seven specimens for the environmental scanning electron microscopy (ESEM), and one was used for each binder type to evaluate its microstructure by capturing different observations. Three specimens were prepared and tested for the control, 5%PCM, and 5% GPCM binders to be tested using differential scanning calorimetry (DSC). In parallel, three specimens were prepared for each binder type to be evaluated and analyzed using a viscometer, a dynamic shear rheometer (DSR), Fourier transform infrared spectroscopy (FTIR) and a thermogravimetric analyzer (TGA).

2.6. Viscosity

The flow properties of asphalt binders before and after modifications were tested using a Brookfield rotational viscometer at various temperatures ranging from 90 °C to 165 °C. The kinematic viscosity of asphalt binders was measured according to AASHTO T 201 (ASTM D 2170) standards. This test was mainly performed to ensure that the asphalt workability is suitable for road construction, i.e., pumping and mixing.
2.7. Environmental Scanning Electron Microscopy (ESEM)

Several studies were conducted to evaluate the microstructure of asphalt binders using ESEM [21]. In this test, one specimen was prepared and evaluated for each asphalt binder: control, PG70-28, 5%PCM, 5%GPCM, 7%GPCM, 5%GPCM-SBS, and 5%PCM-SBS.

The specimens were put and softened in the oven at 110 °C for approximately 30 min in covered containers to avoid their oxidization or contamination during the softening process. For the 5%PCM binder, the specimen was softened at a lower temperature of 80 °C to avoid the evaporation of the PCM during the softening process. Then, approximately 0.1 g of the specimen was poured into steel moulds to prevent the spilling of the asphalt binder during the vacuum process, as shown in Figure 7. The moulds were then placed in the ESEM chamber (FEI Quanta 250 FEG). The microscope was set at an acceleration voltage of 20 keV and a chamber pressure of 0.8 mbar.

![ESEM Image](image)

**Figure 7.** ESEM (FEI Quanta 250 FEG).

2.8. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a method used to characterize the chemical functional groups within the material. When the molecules of asphalt binders are exposed to infrared radiation, they absorb parts of it. The plot of this absorption against the wavelength represents a spectrum graph that shows chemical functional groups of asphalt binder. FTIR was conducted for all samples described in Table 3. Furthermore, 5%GPCM was tested under FTIR immediately after mixing and stored in a small metal container at room temperature for one month. This was undertaken to investigate the effect of storage on the chemical functional groups of the asphalt binders.

2.9. Differential Scanning Calorimetry (DSC)

The main objective of using DSC was to measure the energy absorbed or released by the samples as a function of temperature. As explained earlier, the TGA test was conducted first for all the samples before running the DSC tests to determine their thermal stability and volatile content. This step was crucial to set the maximum temperature of the DSC tests as any decomposition/evaporation in the sample would highly affect the DSC measurements.

In this study, DSC was performed between −90 and 100 °C using a TA Instruments DSC Q2000 on 5–10 mg samples, in a sealed aluminum container, at a heating/cooling rate of 10 °C/min. The heat flow measurements were used to compare the thermal behaviours of the modified asphalt binders.

2.10. Dynamic Shear Rheometer (DSR)

The dynamic shear rheometer (DSR) was used to determine the binders’ performance grade (PG) and to study the impact of the different modifiers and modification rates of their rheological behaviour in the viscoelastic domain. This test measured the dynamic shear modulus (G’) and phase angle (δ) at different temperatures according to AASHTO T315-09. According to the AASHTO standard, when treating the unaged binder at high temperature, the rutting index (G’/sinδ) for the unaged binder should not be less than 1.0 kPa, at which
the critical temperature occurs. The test was conducted in a strain-controlled mode and at a constant frequency of 10 rad/s, using 25 mm plates with a 1 mm gap. In addition, the rutting index of \( G^*/\sin \delta \) was used to evaluate the rutting performance of the binders. The testing temperatures range from 52 °C to 64 °C at an increment of 6 °C.

Moreover, the DSR conducted frequency sweep tests at various temperatures and directly measured \( G^* \) and phase angle to investigate the rheological properties of the control and modified asphalt binders at intermediate and high temperatures. The master curve is used to predict the viscoelastic properties of the binder at any temperature and over a wide frequency range.

Two different temperature ranges were used to generate the master curve for all binders. Two disc-shaped silicon moulds with diameters of 8 mm and 25 mm were used to fabricate the specimens to be tested at low and high temperatures. The 8 mm diameter specimens with a 2 mm gap were used for the temperature range −10 °C to +40 °C, whereas the 25 mm diameter specimens with 1 mm gap was used for the temperature range +40 °C to +80 °C. For each temperature, the test was conducted in strain-controlled mode with frequencies ranging from 0.1 to 20 Hz. Furthermore, a sigmoidal model was selected to generate the master curves with a reference temperature (\( T_{ref} \)) of 20 °C.

In addition, a Black Space curve was developed for the control, PG70-28, 5%PCM, 5%GPCM, 7%GPCM, 5%GPCM-SBS, and 5%PCM-SBS binders. The curve represents the relationship between phase angle (\( \delta \)) and dynamic modulus (\( G^* \)) at each of the temperatures and loading frequencies at which these parameters are measured. This relationship gives an easy visualization of the tested binder’s response in terms of its stiffness, relaxation capabilities, and the relationship between them at any given loading frequency or temperature [22].

3. Results and Discussion

3.1. TGA Observations

Figure 8 shows the evaporation curves of the PCM and GPCM, respectively. The examination of the PCM’s and GPCM’s respective TGA curves shows that the two curves behaved very differently. The slope (\( dw/dt \)) of each curve indicates the material’s weight loss rate. For the PCM curve, the evaporation took place immediately, and almost 3% of the mass was lost at a temperature of 50 °C. As the temperature increased, the weight loss increased. It is clearly shown that the rate of weight loss was almost constant after 50 wt% losses till it completely evaporated at about 150 °C. For the GPCM paste, three phases were observed in the evaporation curve. In the first stage, there was a steady stage, at which there was no weight loss as the temperature increased to 125 °C (in other words, the slope of \( dw/dt = 0 \)). In the second phase, the weight loss started at 125 °C and reached 50 wt% losses at 250 \( dw/dt \). However, the final phase was similar to the first phase, where almost no weight loss was observed till the end of the test.

It is worth mentioning that when GP was added to PCM (GPCM) in a ratio of 50:50, the maximum weight loss of the PCM occurred at about 250 °C. However, when the ratio of the GP:PCM was 0:100 (PCM only), the maximum weight loss of the PCM took place at 150 °C. The delay in the maximum evaporation temperature was attributed to the ability of the GP material (powder form) to absorb PCM (liquid form). The explanation of this mechanism is that the pores in the GP were able to form in a semi-shell-like shape, delaying the evaporation process of the PCM. The fact that glass has a relatively low thermal conductivity has most likely also contributed to delaying the evaporation of the PCM retained in PG particles.

In addition, the TGA test was conducted on the control, 5%PCM, and 7%GPCM binders. Table 4 summarizes the initial, medium, and maximum evaporation temperatures of these binders.
3. Results and Discussion

3.1. TGA Observations

Figure 8 shows the TGA spectrum of PCM and GPCM.

Table 4. Initial, medium, and maximum evaporation temperatures obtained from TGA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Evaporation Temperature (°C)</th>
<th>Mass Losses (%)</th>
<th>Medium Evaporation Temperature (°C)</th>
<th>Mass Losses (%)</th>
<th>Maximum Evaporation Temperature (°C)</th>
<th>Mass Losses (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>200 °C</td>
<td>0.5%</td>
<td>400 °C</td>
<td>25%</td>
<td>&gt;700</td>
<td>&gt;70%</td>
</tr>
<tr>
<td>5%PCM</td>
<td>225 °C</td>
<td>3%</td>
<td>460 °C</td>
<td>45%</td>
<td>&gt;700</td>
<td>&gt;70%</td>
</tr>
<tr>
<td>7%GPCM</td>
<td>260 °C</td>
<td>3%</td>
<td>455 °C</td>
<td>50%</td>
<td>590 °C</td>
<td>10%</td>
</tr>
</tbody>
</table>

TGA results showed that the evaporation temperature of the PCMs alone was relatively low. This low gradation temperature created a challenge in maintaining the mass of PCMs in the asphalt mixture to achieve its anticipated benefits. For this reason, use of PCMs in hot mix asphalt cannot be evaluated. Moreover, to mitigate the risk of PCM evaporation during the production process, it is recommended to use PCMs with warm or half-warm mix asphalt (WMA and HWMA), as the production temperature of these mixes is typically lower than 150 °C. The PCMs can also help reduce the viscosity of the binder during the mixing and compaction, which can facilitate the conduction of these operations at lower temperatures.

TGA analysis indicated that the PCMs had a thermal decomposing temperature significantly lower than the mixing temperature of the PG70-28 binder. It is reported that SBS-modified binders have higher mixing and compaction temperatures than straight-run binders, as the SBS increases the viscosity and reduces the pummability of the binder [23]. As a result, using this type of PCM is not compatible with polymer-modified binder as it is expected that severe evaporation can happen to the PCM during the production of the asphalt mix.

3.2. GPCM Preparation

As mentioned in Section 2.4, different mixing ratios of GP:PCMs were examined; 50:50, 80:20, 70:30, and 30:70, respectively. It was found that a 50:50 ratio resulted in a heterogeneous mix, as the PCM leakage was visible. In addition, the 80:20 ratio resulted in a dry and hard mix due to the high amount of GP. The mixing ratio of GP:PCMs selected to produce the GPCM paste was 70:30, as it provided a homogenous mix. After the ratio was selected, the GPCM paste was analyzed using TGA, DSC, and ESEM.

3.3. Asphalt Binder Preparation

Based on the TGA results, the initial evaporation temperatures of the PCMs and GPCM were relatively low compared to the base binders (PG58-28 and PG70-28). As a result, the recommended temperatures for the binder preparation using PCM and GPCM
should not exceed 90 °C and 110 °C, respectively. However, the GPCM was added to the PG70-28 binder at a temperature range of 130 °C to 150 °C, as the PG70-28 binder needed a higher mixing temperature to ensure the binder was fluid enough to obtain a homogenous mix. It is worth mentioning that approximately 2.5% mass loss in the GPCM occurred when the mixing temperature reached 150 °C. Therefore, three different temperature ranges were selected to produce the 5%PCM, 5%GPCM, 7%GPCM, 5%GPCM-SBS, and 7%GPCM-SBS binders, as presented in Table 5. Moreover, after different trials, it was found that a mixing time of 20 min was sufficient to provide a homogenous mixture and well-distributed additives.

Table 5. Binder preparation temperatures/mixing time for different additives.

<table>
<thead>
<tr>
<th>Base Binder</th>
<th>Additive</th>
<th>Mixing Temperature °C</th>
<th>Mixing Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG 58-28</td>
<td>PCM</td>
<td>80–90 °C</td>
<td>20 min</td>
</tr>
<tr>
<td>PG 58-28</td>
<td>GPCM</td>
<td>90–110 °C</td>
<td>20 min</td>
</tr>
<tr>
<td>PG70-28</td>
<td>GPCM</td>
<td>130–150 °C</td>
<td>20 min</td>
</tr>
</tbody>
</table>

To prepare the modified binders, the base binders were heated to the desired temperature ranges, the additives then were added gradually and mixed using a rotational mixer at 2500 rpm for 20 min in a heating mantle to ensure that the mixing temperature of the binder remained constant.

3.4. Viscosity

A Brookfield viscometer measured the dynamic viscosities under six different temperature levels. As mentioned earlier, this characteristic is essential in pavement production and application. It is most likely that the PCM evaporated completely at 150 °C. It was noted that when the evaporation temperature of the PCM was exceeded, the binder started to smell pungent. As for the 5%PCM binder, the test was conducted at different temperatures ranging from 85 °C to 135 °C. Moreover, to explore the evaporation impact on the viscosity of all other binders (PG 58-28, PG 70-28, 5%GPCM, 7%GPCM, 5%GPCM-SBS, and 7%GPCM-SBS), the test was conducted under all temperatures, which ranged from 90 °C to 165 °C with an increment of 5 °C.

Figure 9 shows the measured viscosity results (log scale) drawn versus temperatures. It was noted that for the 5%PCM binder at 90 °C, approx. 25% of the PCM evaporated as explored in the TGA test, with only a 10.6% reduction in the viscosity compared to the control binder. It is worth mentioning that, when testing the 5%PCM binder at temperatures above 90 °C, there was no effect on the viscosity of the 5%PCM binder compared to the control binder. This increase can be attributed to the fact that 100% of the PCM evaporated.

On the other hand, adding 5% and 7% GPCM to the base binders, PG 58-28 and PG 70-28, led to a significant decrease in the viscosities at 105 °C and above, as shown in Figure 9, which can meet the temperature requirements to produce warm mix asphalt (WMA). For higher temperatures, the viscosity of the modified binders was lower than that of the base binder. For example, the viscosity of the 7%GPCM binder at 150 °C was recorded at 0.152 Pa·s, whereas the control binder at the same temperature was 0.214 Pa·s. From a designer’s point of view, further attention should be drawn to the reduction in the viscosity of the binders, since it can negatively affect asphalt mixture properties and performance at high temperatures, i.e., rutting resistance.
3.4. Viscosity

A Brookfield viscometer measured the dynamic viscosities under six different temperature levels. As mentioned earlier, this characteristic is essential in pavement production and application. It is most likely that the PCM evaporated completely at 150°C. It was noted that when the evaporation temperature of the PCM was exceeded, the binder started to smell pungent. As for the 5%PCM binder, the test was conducted at different temperatures ranging from 85°C to 135°C. Moreover, to explore the evaporation impact on the viscosity of all other binders (PG 58-28, PG 70-28, 5%GPCM, 7%GPCM, 5%GPCM-SBS, and 7%GPCM-SBS), the test was conducted under all temperatures, which ranged from 90°C to 165°C with an increment of 5°C.

Figure 9 shows the measured viscosity results (log scale) drawn versus temperatures. It was noted that for the 5%PCM binder at 90°C, approx. 25% of the PCM evaporated as explored in the TGA test, with only a 10.6% reduction in the viscosity compared to the control binder. It is worth mentioning that, when testing the 5%PCM binder at temperatures above 90°C, there was no effect on the viscosity of the 5%PCM binder compared to the control binder. This increase can be attributed to the fact that 100% of the PCM evaporated.

Figure 9. Viscosity results for all binders.

3.5. ESEM Observations

Table 6 shows the ESEM observations of the microstructure of the GPCM and the asphalt binders. The homogeneity of the GPCM was assessed using ESEM. The GPCM observations in Table 6a show that the GP particles were well dispersed in the mastic.

Previous studies on binder microstructure using ESEM show that its fibril structure can be correlated to fundamental changes in the physical and chemical properties of the binder [24]. Thus, visual comparisons were conducted on the different binders based on their relative fibril sizes and abundance. ESEM observations were obtained at three different magnifications of 10, 40, and 50µm for a more detailed view of the microstructure. It can be noted from the 5%PCM pictures in Table 6e–g that the PCM modification of the asphalt binder had a visible impact on the microstructure of the binder. The 5%PCM’s fibril size was relatively large with a sparser structure than the control binder shown in Table 6b–d.

Similarly, with GPCM modifications, the size of the fibrils became larger than the control binder and yet were smaller than the %PCM binder. The addition of glass powder was found to improve the high-temperature stability of the binder. The GP morphology, shown in Table 6a, and its physical characteristics would improve the stability of the mastic at high temperatures.

A denser and more connected fibril was noticed when observing the PG70-28 binder under ESEM, as shown in Table 6n. Adding GPCM to the PG70-28 binder caused the loss of the interconnected network of the fibrils obtained on the PG70-28 binder. To summarize, GPCM and PCM modifiers significantly impacted the binder’s microstructure by making the fibril size wider with a less patterned microstructure. These observations were reasonably consistent with the previous research findings on the softer binder observations [21].
Table 6. ESEM observations for all tested binders.

<table>
<thead>
<tr>
<th>GPCM</th>
<th>Control</th>
<th>5% PCM</th>
<th>5% GPCM</th>
<th>7% GPCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>(b)</td>
<td>(c)</td>
<td>(d)</td>
<td>(e)</td>
</tr>
<tr>
<td></td>
<td>(f)</td>
<td>(g)</td>
<td>(h)</td>
<td>(i)</td>
</tr>
<tr>
<td></td>
<td>(j)</td>
<td>(k)</td>
<td>(l)</td>
<td>(m)</td>
</tr>
</tbody>
</table>

Remarks: Observations for all tested binders.
Table 6. Cont.

<table>
<thead>
<tr>
<th>Magnification</th>
<th>PG70 -28</th>
<th>5% GPCM-SBS</th>
<th>7% GPCM-SBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 µm</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
</tr>
<tr>
<td>40 µm</td>
<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
<tr>
<td>50 µm</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
<td><img src="image9" alt="Image" /></td>
</tr>
</tbody>
</table>

3.6. FTIR Results

Figure 10 shows FTIR spectra for all the tested binders (PG 58-28, PG 70-28, 5%PCM, 5%GPCM, 7%GPCM, 5%GPCM-SBS, and 7%GPCM-SBS). The figure was used to qualify the variation of the chemical functional groups for each binder. Generally, the PG 58-28, PG70-28, and 5% GPCM-SBS samples had relatively similar peak values with no visible differences for most of the spectrum. However, for the 5%PCM, 5%GPCM, 7%GPCM, and 7%GPCM-SBS, there were visible differences in the polyaromatic group (wavenumber of 1700 cm\(^{-1}\)) and the sulfoxide group (wavenumber of 1030 cm\(^{-1}\)).

At a low wavenumber area below 800 cm\(^{-1}\), it can be noticed that 7%GPCM-SBS, 5%PCM, and 5% GPCM had higher peak values. In other words, the peak values in the carbonyl area are lower for the 5%PCM, 7%GPCM-SBS, and 5%GPCM compared to other binders (PG 58-28, PG 70-28, 7%GPCMNS, and 5%GPCM-SBS). As expected, samples that contained SBS showed higher peak values at 700 cm\(^{-1}\) due to the presence of polystyrene in the polymer.

Figure 11 illustrates the spectrum of the 5%PCM binder under different storage conditions: immediately after mixing and one month later. Both samples were stored in a small metal container at room temperature (23 °C). The figure shows that the storage conditions had almost no effect on the chemical functional groups of the modified samples with GPCM.
3.7. DSC Characterization

Figure 12 presents the relationship between the heat flow normalized per unit weight of the samples (Y-axis) versus temperature (X-axis) for the control, 5%PCM, and 5%GPCM binders. The purpose of using DSC was to measure the heat flow of the binders during the heat/cooling cycles.

For each binder, the bottom curve represents the heating phase of the cycle, whereas the top curve represents the cooling phase of the cycle, as shown in Figure 12. Two main components were considered on the heating/cooling curves: the temperature at which the peaks occurred (phase transition) and its corresponding heat flow.

It was found that the PCMs and GPCM had a visible effect on the thermal behaviour of the modified binders. As shown in Figure 12, the heat flow released from the 5%PCM was 0.335 W/g at −15 °C. However, it was noticed that the released heat flow by the 5%GPCM binder was 0.175 W/g at −20 °C. It was also found that the released heat flow from the 5%PCM binder was much higher than that of the 5%GPCM binder. The use of
GP could therefore have negatively affected the ability of the PCMs to employ its latent heat of fusion to release heat. A possible explanation is that when the PCM is trapped in the pores of the GP particles, the PCM has less tendency to release heat due to the low thermal conductivity of the GP. These findings indicated that PCM/GPCM would enhance the mechanical properties of the asphalt binder at low temperatures.

![Figure 12. DSC diagram for control, 5%PCM, and 5%GPCM binders.](image)

**Figure 12.** DSC diagram for control, 5%PCM, and 5%GPCM binders.

### 3.8. DSR Grading

Table 7 represents the high PG temperatures (HH) for all asphalt binders, which are the minimum temperatures corresponding to \((G^* / \sin \delta) \geq 1\) kPa, AASHTO T315-09 (2000), obtained from the DSR test. The results showed that the values of \(G^* / \sin \delta\) for 5%GPCM and the control binder were similar. \(G^* / \sin \delta\) values for the control binder and 5%GPCM were recorded at 1.9880 and 1.9472, respectively. For the 5%PCM and 7%GPCM, the \(G^* / \sin \delta\) values were reduced by 12.6% and 42.3% compared to the control binder, respectively. However, it was observed that the corresponding temperature for the 5%PCM was similar to that of the control binder (57.6 °C), as shown in Table 6. The reduction in the \(G^* / \sin \delta\) values can negatively affect the rutting resistance of the asphalt binder due to the decrease in the elastic response of the materials.

<table>
<thead>
<tr>
<th>Binder Name</th>
<th>Minimum Temperature (°C) Corresponding to ((G^*/\sin \delta) \geq 1) kPa</th>
<th>(G^*/\sin \delta)</th>
<th>Continuous PG Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>58</td>
<td>1.9880</td>
<td>PG 63.6-XX</td>
</tr>
<tr>
<td>PG70-28</td>
<td>64</td>
<td>1.8770</td>
<td>PG 69.9-XX</td>
</tr>
<tr>
<td>5% PCM</td>
<td>58</td>
<td>1.7363</td>
<td>PG 62.3-XX</td>
</tr>
<tr>
<td>5% GPCM</td>
<td>52</td>
<td>1.9472</td>
<td>PG 57.6-XX</td>
</tr>
<tr>
<td>7% GPCM</td>
<td>52</td>
<td>1.1452</td>
<td>PG 53.9-XX</td>
</tr>
<tr>
<td>5%GPCM-SBS</td>
<td>58</td>
<td>1.8505</td>
<td>PG 63.7-XX</td>
</tr>
<tr>
<td>7%GPCM-SBS</td>
<td>58</td>
<td>1.4316</td>
<td>PG 61.5-XX</td>
</tr>
</tbody>
</table>

Moreover, for the PG70-28, the \(G^*/\sin \delta\) value and the corresponding temperature were documented at 1.8770 and 69.9 °C, respectively. The addition of the 5% and 7%GPCM to the
PG70-28 binder resulted in a reduction in both the $G^*/\sin \delta$ values and their corresponding temperatures. The $G^*/\sin \delta$ values for the 5%GPCM-SBS and 7%GPCM-SBS were recorded at 1.8505 and 1.4316, respectively, and the corresponding temperature was 63.7 °C and 61.5 °C, respectively.

The addition of 5% and 7%GPCM reduced the service temperature compared to the control binder. For example, the service temperatures of 5%GPCM and 7%GPCM dropped to 57.6 °C and 53.9 °C, respectively, compared to that of the control binder (63.6 °C). Similarly, adding 5% and 7%GPCM to the PG70-28 binder reduced the service temperatures of the modified binder to 63.7 °C and 61.5 °C, respectively, compared to the PG70-28 binder (69.9 °C).

Generally, it can be concluded that, as the GPCM content increased in the binder, the $G^*/\sin \delta$ values and the service temperature decreased. Thus, the rutting resistance decreased.

### 3.9. Master Curve

Figure 13 shows master curves for the control, PG 70-28, 5%PCM, 5%GPCM, 7%GPCM, 5%GPCM-SBS, and 7%GPCM-SBS binders at a reference temperature of 25 °C. The data for both axes were plotted on logarithmic scales of dynamic modulus versus reduced frequency. As shown in Figure 13, the master curves of the 5%PCM, 5%GPCM, and 7%GPCM binders had a similar trend to that of the control binder. At intermediate frequencies, a slight increase in the stiffness of the 5%PCM binder was observed compared to the control binder, yet there was a slight decrease in the stiffness of the 7%GPCM binder. On the contrary, the dynamic modulus of the PG70-28 binder increased at intermediate frequencies due to the presence of SBS in the asphalt binder matrix. The SBS polymers are usually added to the asphalt binder to mitigate high temperatures and traffic-related issues, since the SBS polymers contribute to increasing the stiffness.

![Figure 13. Master curves for all binders.](image-url)

As shown in Figure 13, the dynamic modulus of the 5% and 7%GPCM-SBS binders decreased as GPCM contents increased. The reduction in the dynamic modulus was more important at intermediate frequencies due to the softening effect of the GPCM. As a result, the intermediate stiffness (stiffness at intermediate temperature) was reduced compared to that of the PG70-28 binder. Moreover, the reduction in the intermediate stiffness can negatively affect the fatigue cracking resistance of binders since the initiation of the fatigue cracking is usually associated with the intermediate stiffness. Moreover, the 5% and 7%GPCM-SBS binders showed a similar evolutionary trend to the control binder throughout the test.
3.10. Black Space curve

Figure 14 shows the Black Space curves for the control, PG 70-28, 5%PCM, 5%GPCM, 7%GPCM, 5%GPCM-SBS, and 7%GPCM-SBS binders. As can be seen, the Black Space curves were diverse for all the tested binders, especially at low frequencies. It was noticed that the viscous behaviour for the control binder was dominant at low frequencies and high temperatures, at which the phase angle reaches 90°. The 5%PCM, 5%GPCM, and 7%GPCM binders exhibited the same viscous behaviour as the control binder at the same temperatures and frequencies.

![Black Space curves for all binders](image)

Figure 14. Black Space curves for all binders.

On the other hand, the PG70-28 binder showed lower phase angles throughout the test, indicating that the elastic behaviour of the binder was dominant. However, adding 5% and 7%GPCM in the PG70-28 binder increased the phase angle values, leading to a decrease in the elastic behaviour of the binder.

4. Conclusions

This paper presented a laboratory study on the rheological, spectroscopic, and chemical characterization of asphalt binders modified with GP and PCM. Different binders—control, PG 70-28, 5%PCM, 5%GPCM, 7%GPCM, 5%GPCM-SBS, and 7%GPCM-SBS binders—were assessed using a viscometer, a dynamic shear rheometer (DSR), Fourier transform infrared spectroscopy (FTIR), environmental scanning electron microscopy (ESEM), a thermogravimetric analyzer (TGA), and differential scanning calorimetry (DSC). A few conclusions and recommendations were drawn from the experimental results:

- The maximum evaporation temperature of the PCM obtained from the TGA analysis was low, which made it difficult to maintain the quantity of PCM in the asphalt mix to achieve its anticipated benefits. Adding PCM to HMA was not applicable. Alternatively, to mitigate the risk of evaporation of the PCM during the production of asphalt mixes, it would be more beneficial to use the PCM with warm and half-warm mix asphalts (WMA and HWMA) or cold mix asphalt (CMA).
- The evaporation temperature for the GPCM was higher than the PCM. Hence, the GPCM could be used in HMA.
- The viscosity analysis showed that the viscosity of PCM- and GPCM- modified binders significantly decreased compared to the control binder. This reduction indicated that PCM and GPCM additives have a softening effect on the asphalt binder.
- The observations obtained from the ESEM indicated that adding PCM and GPCM resulted in an increase in the width of the fibril sizes of the modified binders, which indicated that the additives had a softening effect on the asphalt binders.
• The DSC results showed that the 7%GPCM binder released heat flow less than that of the 5%PCM binder, which could negatively impact the thermal properties of the PCM in the asphalt binder. This could be attributed to the low thermal conductivity of the GP.

• For the DSR rheological test analysis, it was concluded that 5%PCM, 5%GPCM, 7%GPCM, 5%GPCM, and 7%GPCM exhibited similar overall properties to the control binder. However, the results demonstrated that the GPCM significantly impacted the stiffness of the modified binder at intermediate temperatures.

Author Contributions: Conceptualization, H.A. and H.B.; methodology, H.A. and H.B.; formal analysis, H.A.; investigation, H.A.; resources, H.B.; data curation, H.A.; writing—original draft preparation, H.A.; writing—review and editing, H.B.; visualization, H.A.; supervision, H.B.; project administration, H.B.; funding acquisition, H.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC) [NSERC Discovery Grant—RGPIN-2022-03743].

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References


Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.