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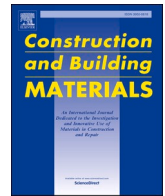
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Bio-polymer modified bitumen

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ABSTRACT

Bitumen is a key constitutive material in asphalt pavements. It binds together the rock scaffolding of a pavement. Bitumen provides asphalt pavement with flexibility and enables it to respond to traffic loading and return to its original condition after the loading, i.e. bitumen restores/repairs the damage. In Porous Asphalt (PA) or Stonemastic Asphalt Mix (SMA) asphalt mixtures, due its open graded structure, bitumen modifiers are used to improve or restore bitumen physical and mechanical performance. Traditionally bitumen modifiers are made with products of crude oil, such as: ethylene vinyl acetate (EVA) copolymers and styrene-butadiene-styrene (SBS). As crude oil production declines and the environmental and financial costs of crude oil extraction increase, there is a need to identify environmentally sustainable alternatives to use in bitumen. Bitumen modifiers generated from biological sources offer an environmentally friendly and economically viable alternative to crude oil based bitumen modifiers. This paper describes how PHBV (poly-3-hydroxybutyrate-co-3-hydroxyvalerate), a bio-based co-polymer, might be used as an alternative bitumen modifier. The effect of PHBV on 70/100pen was investigated for this paper. The chemical and physical effect of the PHBV on the bitumen performance was investigated using Gel Permeation Chromatography, Fourier Transformed Infrared Spectroscopy, Differential Scanning Calorimetry, microscopic imaging and Dynamic Shear Rheometer tests. The results indicate that PHBV has significant potential as a bitumen bio-polymer modifier.

1. Introduction

The current drive to improve the sustainability of the asphalt industry has brought researchers to assess the suitability of bio-based materials for use in road construction. Traditionally crude oil products have been used as bitumen modifiers (softeners and strengtheners) in asphalt production [1]. Recent studies [2–4] have demonstrated that plant-based products, such as vegetable oil and plant fibres can also be used as a bitumen modifier. While this offers a cheap alternative to crude oil in the production of bitumen modifiers, diverting food sources (or potential food sources) into asphalt production is unsustainable and ethically questionable, given the increased pressure on food resources globally. Biomass offers a promising alternative to crude oil in the production of bitumen and bitumen modifiers [2]. Biomass is a renewable bio-material source which uses industrial by-products and secondary materials to produce bitumen modifiers and/or rejuvenators [2,5]. Recent developments in biopolymers (polymers that originate

from the cells of living organisms) have shown promising results, where poly-3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) has been used as a replacement for crude oil based polymers [6]. PHBV is naturally produced by many micro-organisms that proliferate in wastewater treatment plants [7]. These micro-organisms can be harvested from the municipal waste water and PHBV extract extracted from the micro-organic biomass [8]. PHBV is the most studied polyester of the Polyhydroxyalkanoates (PHAs) family [9–11]. PHBV comprises of two monomers: 3-hydroxybutyrate (HB) and 3-hydroxyvalerate (HV), the chemical structure of the polymer is shown in Fig. 1 [6,11,12]. The ratio of the two monomers contained in PHBV determines the properties of the polymer. The HB mainly contributed to the stiffness of the polymer, while HV controls the flexibility and ductility. With increased HV content, the polymer becomes less crystalline, and the melting point decreases [10,11,13]. PHBVs physical properties (low melting point and low viscosity) makes it a potential bio-based material substitute for the crude oil based products currently in asphalt pavement mix design.

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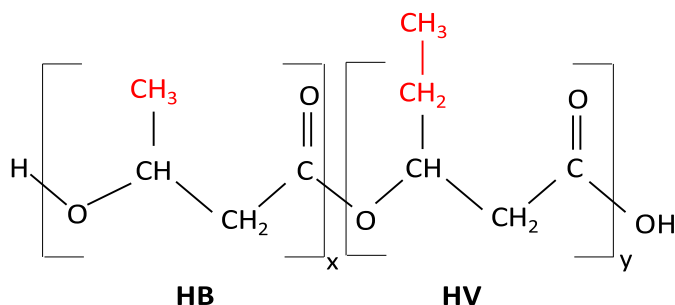


Fig. 1. Chemical Structure of PHBV.

Table 1
Bitumen 70/100pen and PHBV blends compositions.

Blend	Blend Constitutive Material	Percentage of the constituent in the blend (%)	Weight of the constituent in the blend (g)
Blend 1	Bitumen	90	100
	PHBV	10	11
Blend 2	Bitumen	80	100
	PHBV	20	25

This paper outlines an investigation into the suitability of PHBV biopolymer as bitumen polymer modifier. Bitumen 70/100pen was blended with varying amounts of PHBV (0%, 10% and 20%). Thermal Analysis, Gel Permeation Chromatography (GPC), Fourier Transformed Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Microscopic Imaging and dynamic share rheometer (DSR) testing methods were used to determine the PHBV softening point and to investigate physical and mechanical properties of PHBV and bitumen blends.

2. Materials

Poly-3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) was supplied by TU Delft Environmental Biology Group. The PHBV was extracted from the organic waste (sludge) leachate using a solvent process [14,15]. The PHBV extraction process and the recovery parameters for optimal conditions with respect to the different PHBV types was beyond scope of this project, although the authors recognise this is a central and

important principle for upscaling and to an industrial PHBV processing [15].

A blend of 70/100pen bitumen was used to investigate effect of PHBV on the performance of the bitumen.

2.1. Blending

Low shear blending was employed in order to prepare PHBV + bitumen blends. The blend preparation process began by pulverising the PHBV and then mixing it with the bitumen in varying ratios. Two blends were prepared (see Table 1 for detail on the blend composition). The blends were prepared by placing the bitumen in the oven for 1 h at 160 °C, then weighed and placed in the mixing apparatus, see Fig. 2. The PHBV was added to the bitumen in powder form, it was not preheated. It was expected that PHBV would polymerise within the bitumen caused by its heat (160 °C). Using a hot plate, the blending temperature was held constant at 160 °C and mixed for 30 min at 225 revolutions per minute (RPM). During the mixing a slight bobbling and foaming of the bitumen was observed when the PHBV was added, indicating that the PHBV still contained small amounts of moisture. The PHBV was then dried at 100 °C for a short period of time to allow the evaporation of the moisture from the PHBV sample. The blending procedure is shown in Fig. 2. To maintain constancy between the blended samples, the control sample (neat 70/100pen) was subjected to the same heating process as the blended samples. All samples were heated in the oven for 1 h and 30 min at 160 °C.

3. Methods

3.1. Thermal stability

A thermal method was used to investigate the melting point of PHBV. Three separate test samples of 0.5 g in weight were placed on a glass plate and subjected to thermal heating within a fan oven. Testing was conducted at 3 temperatures. Temperature 1: 130 °C for 60 min – observations were made at 10mins, 30mins and 60mins. Temperature 2: 160 °C for 60 min – observations were made at 10mins, 30mins and 60mins. Temperature 3: 180 °C as sample softened rapidly, the sample was only heated for 30 min and one observation was made at 30 min.

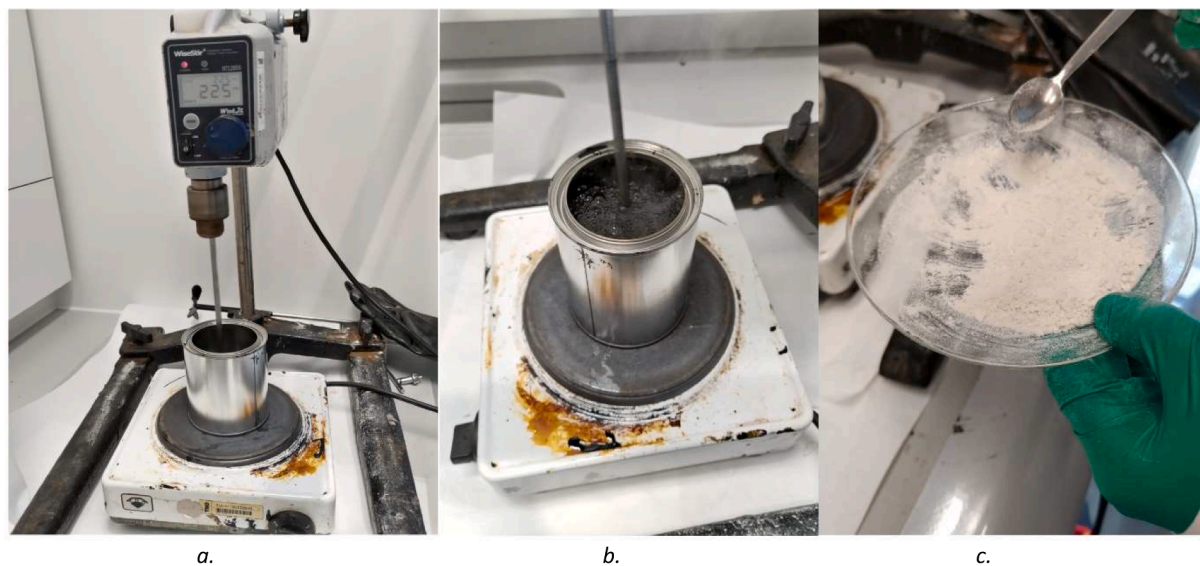


Fig. 2. Blending of 70/100pen bitumen with 10% PHBV; a) Low-shear blending (225RPM at 160 °C) b) swelling of the 70/100pen bitumen containing 10% PHBV blend during the blending process and c) PHBV in powder form.

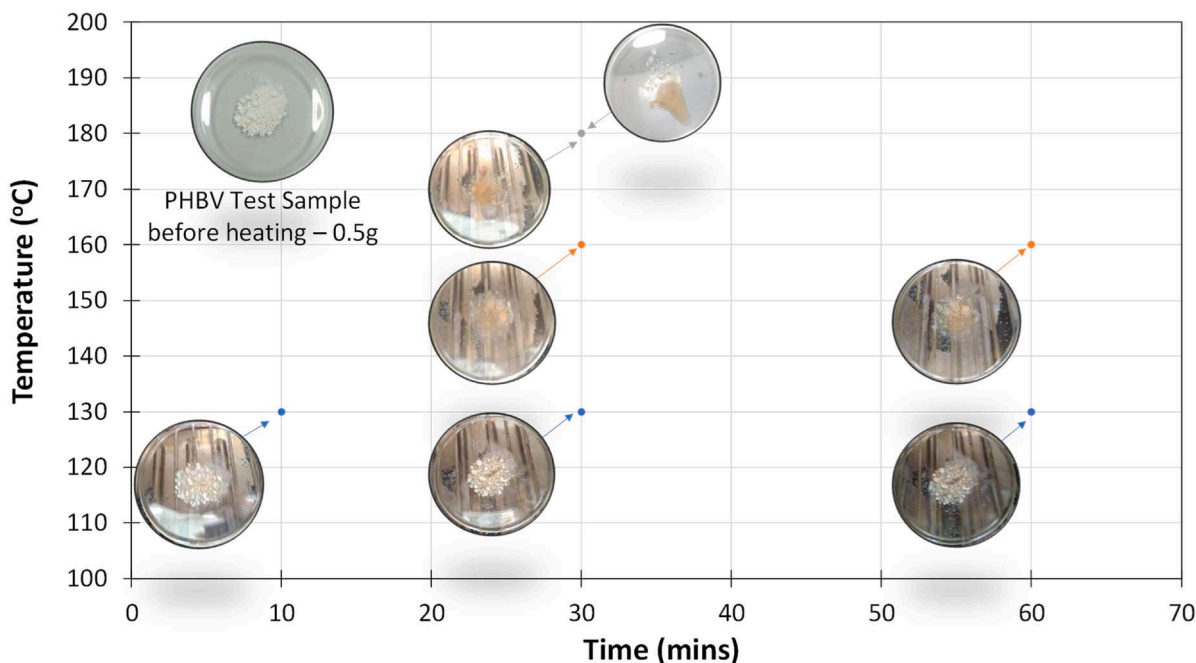


Fig. 3. PHBV softening point test.

3.2. Gel permeation chromatography (GPC)

The GPC test was performed in order to obtain the molecular weight and size distributions of the various samples and carried out in accordance with EN ISO 13885-1:2020 guidelines. A column tightly packed with rigid particles which contain micropores of uniform size was used as the stationary phase. An eluent was used as a mobile phase which flows through the column together with the specimen. The separation of different components with different molecular size arises as the smaller molecules penetrate deeper into the pores, are thus immobilised and spend more time in the column. The retention time is a measure for molecule size and by extension molecular weight, as the two are closely linked [16].

Three columns, APC XT 45, 1.7 μm , APC XT 200, 2.5 μm and APC XT 450, 2.5 μm were used to separate the various components by molecular size. Tetrahydrofuran (THF) was used as both the eluent and as the solvent to create solutions of specific concentration (about 1.2 g/l), which were then filtered with the help of a Millex FH syringe microfilter (with a diameter of 13 mm and a pore size of 0.45 μm to remove any insoluble parts). Pure PHBV did not dissolve sufficiently in the Tetrahydrofuran (THF) solvent. In order to overcome this problem, the polymer (PHBV) was first dissolved in chloroform and then transfer to THF. The test was performed at a constant column temperature of 35 $^{\circ}\text{C}$ at a constant flow rate of the isocratic solvent of 0.5 ml/min. To detect components a combination of a Photodiode Array Detector (PDA) over a range from 190 to 450 nm and a Refractive Index Detector (RI) was used. To determine the molecular weight, the UV-detector (PDA) was used at a wavelength of 254 nm.

3.3. Fourier transformed infrared spectroscopy (FTIR)

Fourier Transformed Infrared Spectroscopy (FTIR) was used to study the prevalence of chemical functional groups and possible differences between the pure and blended bitumen samples. FTIR is generally used to identify bitumen ageing behaviour and polymer content of bitumen [17–19]. Infrared radiation is used. As the bonds in different functional groups absorb infrared radiation with a specific wavelength to a different extent. The Identification of functional groups was achieved by using a Perkin Elmer Universal ATR Sampling Accessory for both the

pure bitumen and blended samples, as well as a pure PHBV sample. The spectra were recorded in absorbance within a wavenumber range of 4000 – 600 cm^{-1} , a resolution of 4 cm^{-1} and 24 scans. A background spectrum of the empty, clean ATR crystal was recorded prior to each measurement. The binder specimen was applied to the ATR crystal within 1 min after recording the background.

3.4. Differential scanning calorimetry (DSC)

To further analyse the blends, Differential Scanning Calorimetry was used as a thermoanalytical technique to investigate the thermal events within the blends, such as: glass transition (T_g) and melting (T_m). The DSC controlled temperature program was used to accurately measure and record heat flow into and out of the test sample. This data was used to determine the transition temperatures of the material [20]. Glass transitions (T_g) are the main focus, since these indicate a change in the bitumen blends from a relatively hard and brittle 'glassy' state into a more rubbery or viscous state. A DSC 6000 from Perkin Elmer was used for a temperature scan range from -75°C to 180°C at a rate of $10^{\circ}\text{C}/\text{min}$. Firstly, specimens were weighed (~ 12 mg) and placed in small aluminium pans, which were sealed before placing them in the DSC. The specimens were then given a thermal history by heating them slowly to 80°C , then cooled down to -75°C and heated up to 180°C at a constant heat flow.

3.5. Microscopic imaging

To elucidate the microstructure characteristics of the blends, a Keyence digital microscope was used, with a VHX-E100 lens and a magnification of 300 times. The goal was to map the dispersion of the PHBV throughout the blends and to link possible changes in physical properties to changes in the microstructure due to chemical interactions within the blends.

3.6. Dynamic share rheometer (DSR)

The dynamic share rheometer (DSR) test was conducted in accordance with EN 14770:2012. The DSR approach was employed to investigate bitumen stiffness change at range of temperatures between

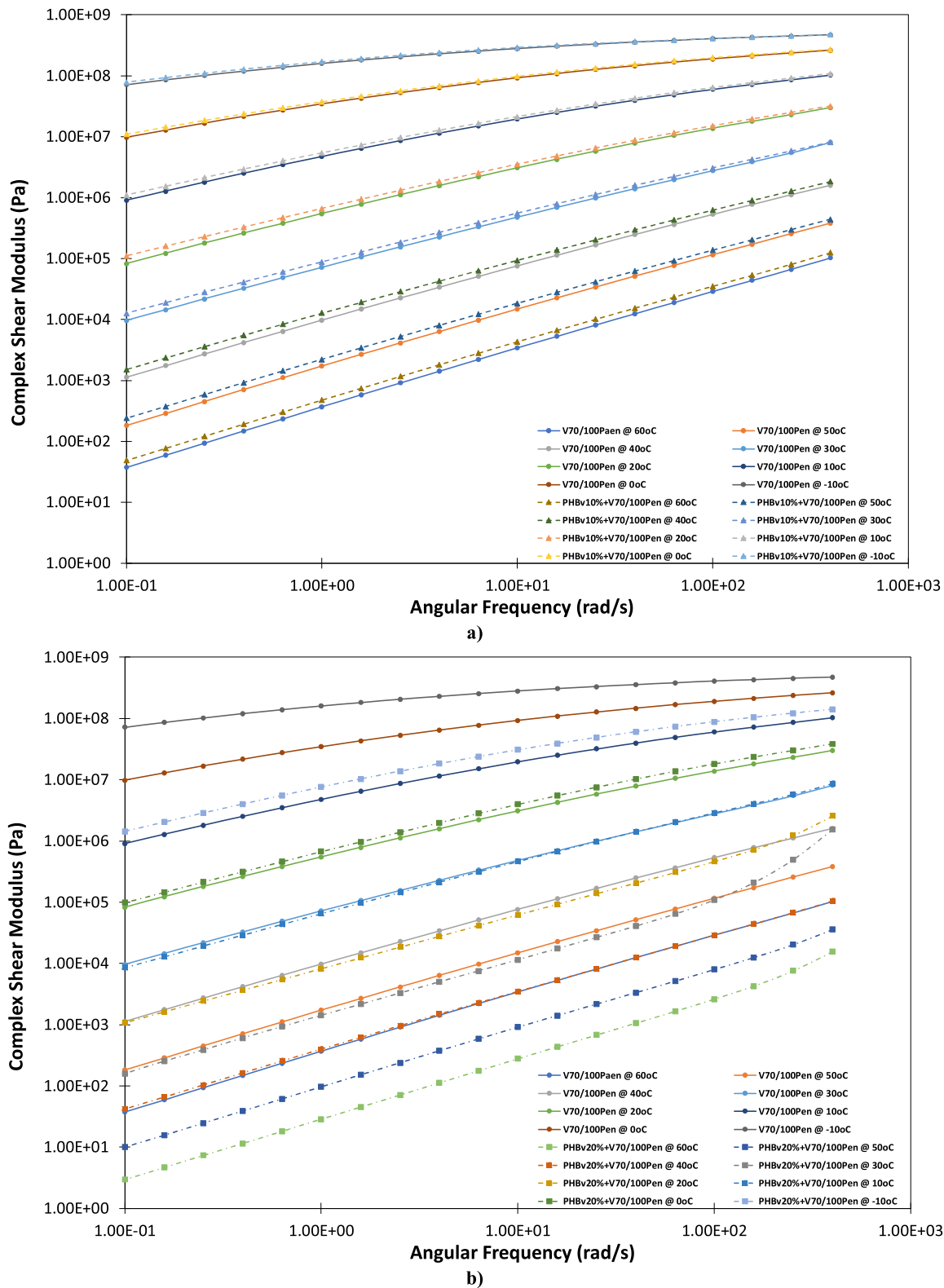


Fig. 4. DSR data for 70/100pen bitumen and PHBV blends; a) Complex Shear Modulus Vs Angular Frequency for 70/100pen bitumen neat and for 70/100pen bitumen + 10% PHBV and b) Complex Shear Modulus Vs Angular Frequency for 70/100pen bitumen neat and for 70/100pen bitumen + 20% PHBV.

–10 °C and 60 °C at 10 °C increments. The first test was conducted at temperature range of between –10 °C and 30 °C using an 8 mm diameter plate; the second test was carried out at temperature range between 30 °C and 60 °C using an 25 mm diameter plate. All tests were carried out at a frequency rate of 0.1 – 400 rad/sec (0.02 – 64 Hz). The complex

shear modulus and phase angle were recorded. Three bitumen blends for each bitumen, containing 0%, 10% and 20% PHBV were prepared and tested. A sample made up of 100% PHBV was also tested.

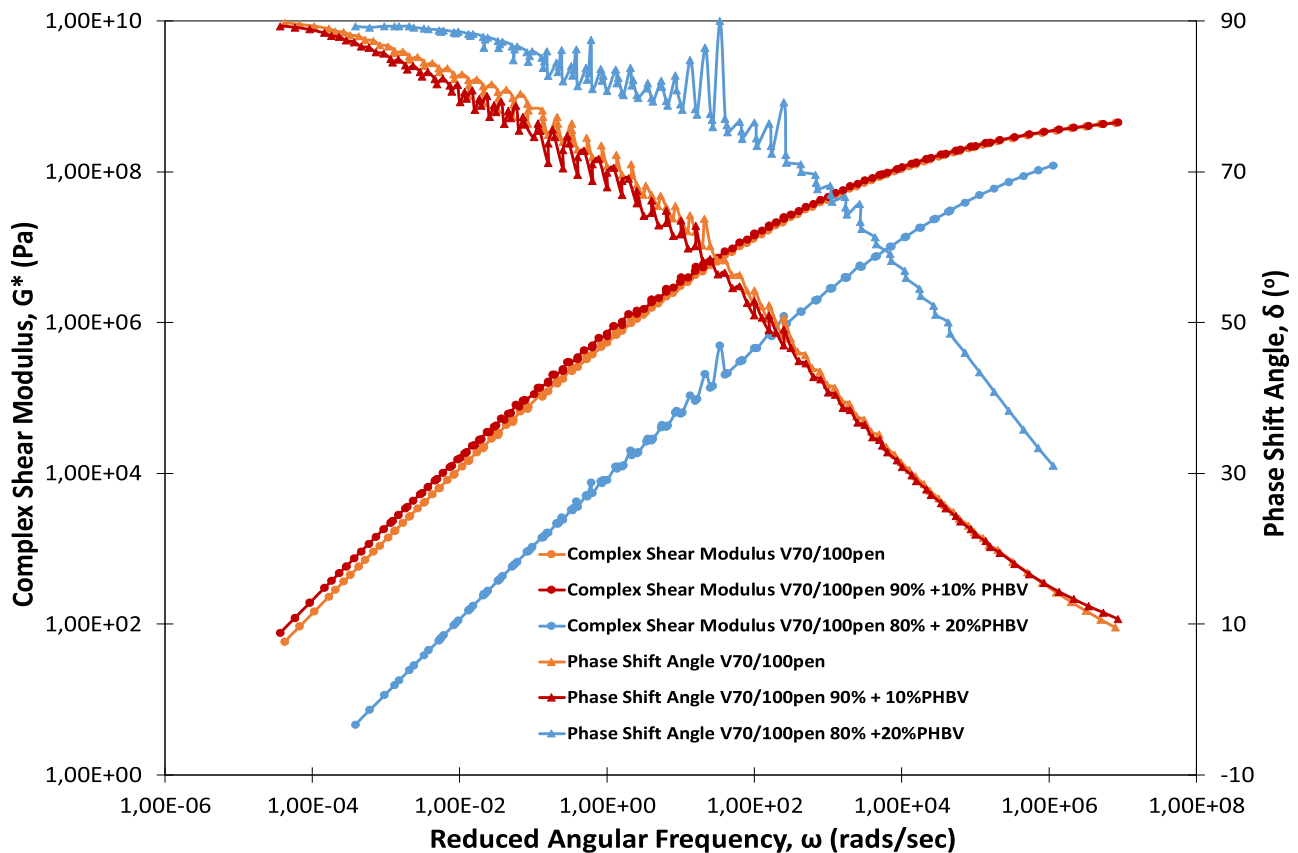


Fig. 5. DSR master curve for 70/100pen bitumen and PHBV blends.

4. Results

4.1. Thermal stability

The goal of the thermal test was to examine melting point of the PHBV and as such its ability to blend with a bitumen. The PHBV is a thermal polymer [21] and similarly as crude oil derived polymers eg. SBS, it changes its state when heated. Fig. 3 illustrates the PHBV thermal test results. At the 130 °C PHBV is softened but it is not changing state from soft powder to the liquid, increasing the temperature to 160 °C within 30 min of heating the material melts and completely turns into the viscous form. Increasing the temperature further to 180 °C melted and similarly as for 160 °C it was more viscous and very soft to touch. The results show that the softening point of PHBV (160 °C) is much higher than 70/100pen bitumen (47 °C – 52 °C) which was expected, however it is compatible with asphalt mixing temperature of 140–180 °C [EN 13,108 and IS 844]. As PHBV softens, its physical appearance resembles bitumen, i.e. the material turns into a viscous liquid after it has melted; while it is soft to the touch and hardens with temperature decrease. These initial observations are promising when considering the suitability of PHBV as a bitumen polymer modifier.

4.2. Dynamic shear rheometer (DSR)

Fig. 4 shows the results from the DSR test programme which was carried out using 70/100pen binder. The results show that blend containing 10% PHBV followed the same behaviour as neat binder, see Fig. 4a. However, by increasing the PHBV content to 20% bitumen shear modulus dropped by two temp points, see Fig. 4b. The shear modulus results at –10 °C blend containing 20% PHBV responds to other two blends at 10 °C. As illustrated in Fig. 5, the master curve, confirmed the bitumen softening trend and clearly shows a drop in the complex shear

Table 2

Mass distribution, in daltons, of the 70/100pen bitumen with PHBV.

Bitumen Blend	Mn	Mw	PDI
70/100pen + 0% PHBV	676	1785	2.64
70/100pen + 10% PHBV	693	1896	2.73
70/100pen + 20% PHBV	679	1790	2.63
100% PHBV	38,194	91,592	2.34

modulus. This indicates that the bitumen stiffness has reduced and increased in the Phase Shift Angle indicating that the modified bitumen is becoming more viscous. These findings indicate that PHBV material can be used as a bitumen replacement, modifier and, at certain level, as a bitumen softener. One of the reasons for such a response is that PHBV is a 3-hydroxyvalerate (HV) monomer. The authors believe that drop in the bitumen stiffness (complex shear modulus) is due to the high content of the HV monomer in the sample [11], which indicates the importance of PHBV production quality control. Another potential reason is the mixing process because low shear mixing the polymer was not fully blended with the mix, and high shear mixing process was suggested. This will be the focus of future studies.

4.3. Gel permeation chromatography (GPC)

Table 2 summarises GPC test results. The number average molecular weight (Mn) and weight average molecular weight (Mw) were recorded calculated for all bitumen blends and pure PHBV. The initial most obvious observation is that pure PHBV samples molecular weight is significantly higher in comparison to the bitumen blends. This is expected as PHBV is a polymer contains longer and heavier molecules [22]. However, the GPC results show that adding the PHBV to the 70/100pen bitumen did not significantly affect the blends molecular

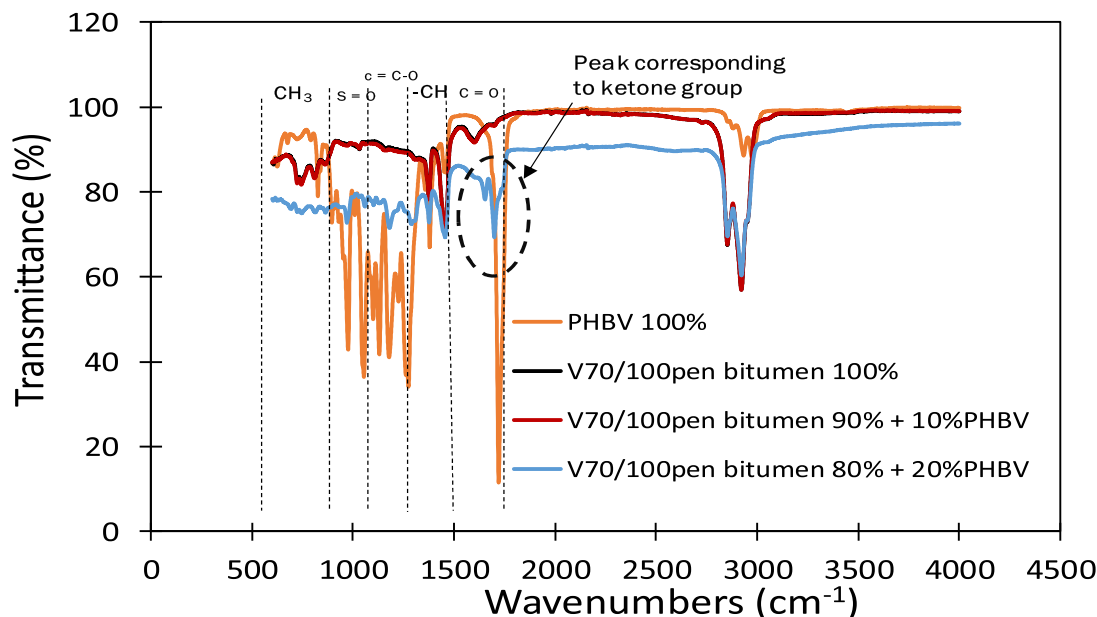


Fig. 6. IR-spectra of 70/100pen bitumen with 0, 10 and 20% PHBV blends and pure PHBV.

weight. The result show that for the 70/100pen bitumen the mass distribution shifts first towards the heavier molecules for the 10% in comparison to the neat 70/100pen bitumen (blend without PHBV). The sample with 20% added PHBV shows an opposite result where the mass distribution shifts towards the lighter molecules. The 0% and 20% mass distributions almost overlap, especially concerning the lighter molecules. Authors suspect that reason for this is that the sample of the PHBV added to the 70/100pen + 20 %PHBV blend had high level of the HV monomer. This would cause shift towards the lighter molecules in the blend and also increase blends ductility. However, it was expected that due to the material mechanical response, as shown by the DSR test results (see Fig. 5), and the blend physical appearance (very low viscosity and sticky), molecular weight of the blend 70/100pen bitumen and PHBV will reduce below the neat 70/100pen bitumen. Nevertheless, the results indicate that PHBV affected the blend chemical structure.

The polydispersity index (PDI) is used as a measure of the broadness of a molecular weight. And is calculated using following formula:

$$PDI = \frac{M_w}{M_n}$$

The larger the polydispersity index, the broader the molecular weight. A monodisperse polymer where all the chain lengths are equal (such as a protein) has an $M_w/M_n = 1$. The best controlled synthetic polymers (narrow polymers used for calibrations) have M_w/M_n of 1.02 to 1.10. Step polymerization reactions typically yield values of M_w/M_n of around 2.0, whereas chain reactions yield M_w/M_n values between 1.5 and 20.. The polydispersity index (PDI) for all fours blends, even for neat bitumen, indicate that blends have broad molecular dispersity (>2.0). Nevertheless, results show that all blends have very similar molecular dispersity in range of 2.34 – 2.73 indicating high molecular dispersion including pure PHBV.

4.4. Fourier transformed infrared spectroscopy (FTIR)

The spectra of the 70/100pen bitumen do show considerable variation. The 0 and 10% blend show roughly the same spectrum. While the 70/100pen bitumen with 20% added PHBV has a different spectrum, see Fig. 6. Again, of particular interest is the peak that appears at 1680 cm^{-1} , which is absent for the other bitumen blends. The peak indicates increase in the Carboxylic ($\text{C} = \text{O}$) molecular groups and corresponds to the ketone groups. This peak is also present, at much greater intensity, in

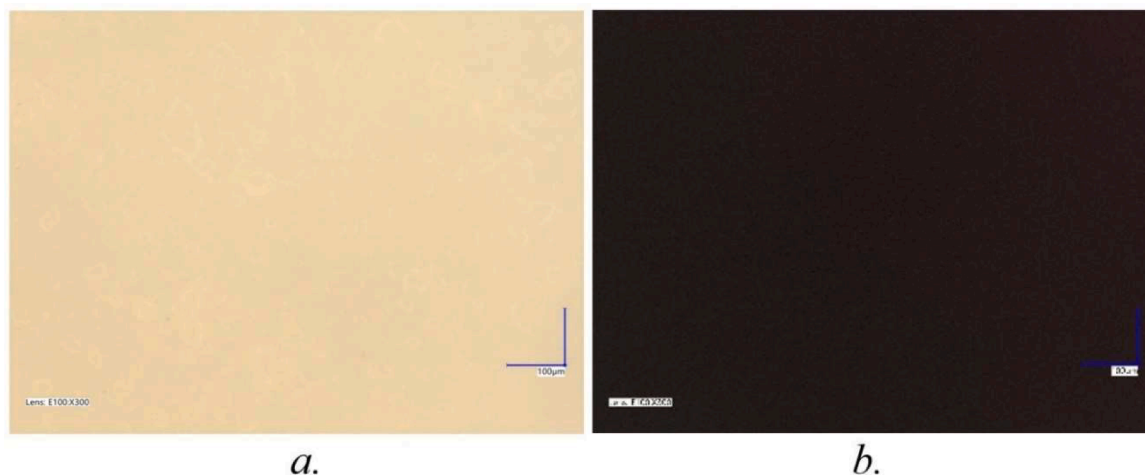


Fig. 7. Microscopic images of a) pure PHBV, b) 70/100pen bitumen, both at a magnification of 300x.

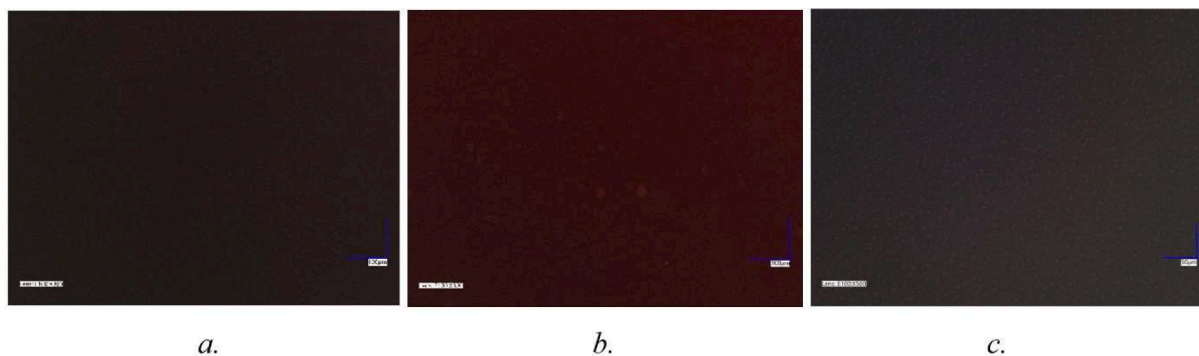


Fig. 8. Microscopic images of 70/100pen bitumen, with a) 0% PHBV, b) 10% PHBV and c) 20% PHBV added, all at a magnification of 300x.

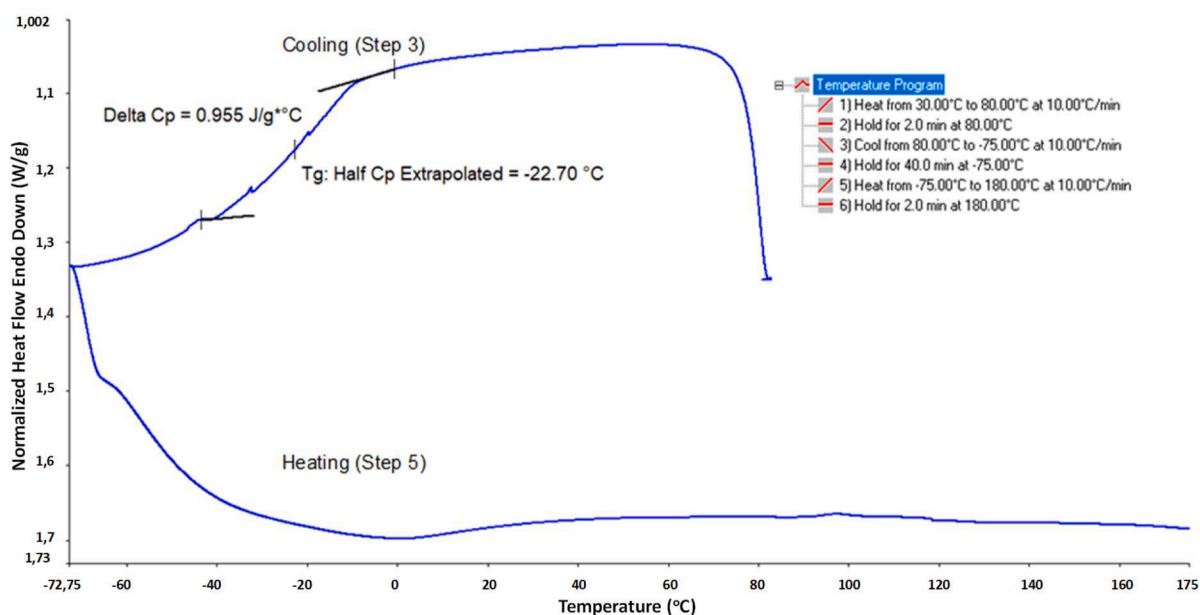


Fig. 9. 70/100pen neat bitumen, DSC test - heat flow response.

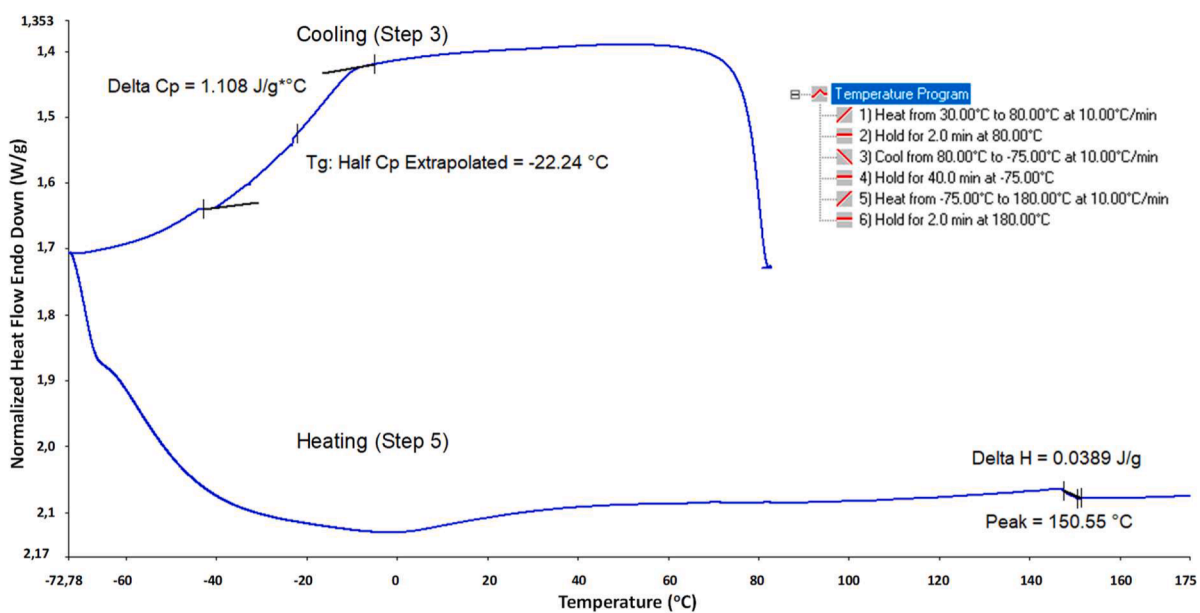


Fig. 10. 70/100pen bitumen blend containing 10 %PHBV, DSC test - heat flow response.

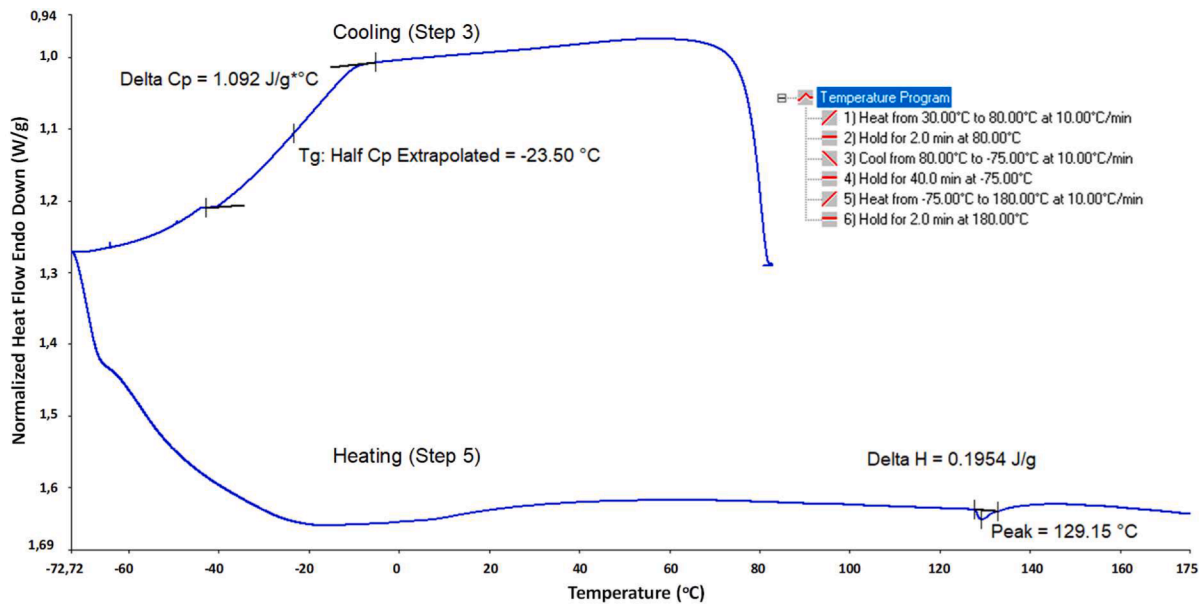


Fig. 11. 70/100pen bitumen blend containing 20 %PHBV, DSC test - heat flow response.

Table 3
DSC results of the binders.

Binder blend	Glass Transition (T_g) (°C)	Melting temperature (T_m) (°C)
70/100pen	-22.70	–
70/100pen + 10% PHBV	-22.24	150.55
70/100pen + 20% PHBV	-23.79	129.15

the spectrum of the pure (100%) PHBV (see Fig. 6), highlighting the effect of the modifier (PHBV) on the bitumen blend.

4.5. Microscopic imaging

The structure of the various bitumen blends was further analysed using microscopic imaging.

Fig. 7 shows the PHBV and the neat bitumen sample, with a smooth and homogeneous structure.

Fig. 8 a) shows a homogeneous structure for the neat bitumen – 0% PHBV. The blend with 10% PHBV does not show any visual noticeable changes. A number of small polymer specks are noticeable in the blend containing 10% PHBV (see Fig. 8 b). The 20% blend on the other hand shows a change in physical appearance (see Fig. 8 c). The PHBV appears to be dispersed throughout the bitumen and forms small specs of near uniform size, indicating that the polymer has dispersed well with the bitumen but blend is still two phase material PHBV and bitumen.

4.6. Differential scanning calorimetry (DSC)

Fig. 9, Fig. 10 and Fig. 11 illustrates the DSC test results for 70/100pen bitumen blends with and without PHBV. Thermal events like glass transition (T_g) is observed in all the samples where PHBV modified blends show a melting event. In these samples, during glass transition, the amorphous phase of bitumen and modifier (PHBV) change from a brittle-glassy state to a flexible rubbery state. Below the T_g , the binder is at glassy state where the bitumen and bio-polymer PHBV are rigid with limited molecular motion. Table 3 summarises the DSC test data results, T_g and T_m , for the 70/100pen bitumen blends containing 0%, 10% and 20% of the PHBV bio-polymer. The results show that PHBV has a

minimal effect on the T_g values of the blends. The T_g values for 70/100pen all blends range from -22.4 °C – 23.5 °C. The blend containing 10% PHBV the T_g was not affected by the modification (inclusion of the PHBV into the blend). A slight decrease in T_g values, -23.5 °C, for the blend with 20% PHBV can be observed (see Fig. 11). However, a melting event is observed for both blends containing PHBV (see Table 3) where the melting temperature (T_m) for the blend containing 10% PHBV was at 150.55 °C and 129.15 °C for blend containing 20% PHBV.

The results further demonstrate that for the blend containing 20% PHBV, the T_m dropped, indicating a reduction in that blends softening point and viscosity. This is consistent with previous results which showed that 70/100 pen blend containing 20% PHBV achieved better blending (Fig. 8) and reduced the Complex Shear modulus (Fig. 4 and Fig. 5).

5. Conclusions

The test results presented in this paper indicate that PHBV can be an effective bitumen modifier. However, the results also revealed that PHBV effects the bitumen blends differently and that highlights the need for further research. The inclusion of 10% PHBV in the 70/100pen bitumen blend slightly increased the Complex Modulus of the blend, however with further addition of 20% of PHBV to the mix, the complex modulus decreased dramatically. The same findings were evident in the e FTIR showing the molecular weight drop indagating increase in lighter molecules and for GPC increase in C = O molecules, which is also observed in pure PHBV. The DSC test showed T_m temperature dropped by 20 °C. Initially authors suspected that these findings were caused by sub-optimal blending for some of the studied blends. It is suspected that low shear blending process prevented the blend constituents (bitumen and PHBV) to mix well enough. However, this theory was dismissed because the optical imaging showed good blending of the PHBV and bitumen in the 10% PHBV blends. Furthermore the 20% PHBV mixed at same conditions have resulted in the softening of the bitumen blend containing 20% PHBV. Second possible explanation is the higher content of 3-hydroxyvalerate (HV) monomer in the PHBV sample added to the mix. As mentioned in the introduction, 3-hydroxyvalerate (HV) controls the flexibility and ductility of the PHBV [9,11,22]. This indicates the importance of strong quality control in the PHBV production. Interestingly these findings also show that if we can control the monomers (HB and HV) content in PHBV we can adjust the PHBV samples to

be used as bitumen polymer modifiers, to strengthen the bitumen, or bitumen softeners/rejuvenators, to soften hard bitumen or rejuvenate aged bitumen. This will be the focus of our research going forward. Overall, the findings of this initial exploratory study demonstrates that PHBV has significant potential for use in asphalt mix production, paving the way for more sustainable and economically viable asphalt pavement.

CRediT authorship contribution statement

Amir Tabaković: Writing – review & editing, Visualization, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Jeremy Lemmens:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **Jelmer Tamis:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Conceptualization. **Dave van Vliet:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Formal analysis, Conceptualization. **Sayed Nahar:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Willem Suitela:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Mark van Loosdrecht:** Writing – review & editing, Writing – original draft, Supervision, Conceptualization. **Greet Leegwater:** Writing – review & editing, Writing – original draft, Supervision, Project administration.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Amir Tabakovic reports financial support was provided by European Commission. Amir Tabakovic has patent #BIOPOLYMER BITUMEN SUBSTITUTE (P135324EP00) pending to Organisatie voor Toegepast Wetenschappelijk Onderzoek (TNO). There are no additional relationships or activities to declare.

Data availability

The authors do not have permission to share data.

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