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Experimental characterization of storage stability of crumb rubber modified bitumen with warm-mix additives

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HIGHLIGHTS

- A robust methodology was developed to evaluate the storage stability of CRMB binders.
- The instability mechanism was explored by the concept of dynamic asymmetry.
- It is possible to manipulate raw material properties and interaction conditions to achieve a storage-stable CRMB blend.

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ABSTRACT

One of the main drawbacks of crumb rubber modified bitumen (CRMB) is the storage stability issue. The storage instability of CRMB impedes its further application. This study aims to develop a robust methodology to evaluate the storage stability of CRMB binders using both mechanical and morphological tests. The effects of rubber contents (0, 5%, 10%, 15%, 22% by weight of bitumen) and different non-foaming warm-mix additives (wax-based and chemical-based additives) on the storage stability of CRMB were investigated. Laboratory tests were also performed on the constituents of CRMB to have a deep understanding of the mechanism of storage instability. Standard tube separation tests were conducted on different binders. Both rheological tests and X-ray computed tomography (CT) scan tests were performed on the binder samples collected from different parts of the tube test. Separation indices were developed based on the difference in mechanical property and rubber content from the tube samples respectively. Results show that CRMB with a higher rubber content is more storage stable than that with a lower rubber content. The addition of warm-mix additives is detrimental to the storage stability of the studied CRMB. Rheological tests were performed on the individual constituents of CRMB (i.e., bitumen phase and rubber phase) to understand better the dynamic asymmetry potentially existing within the unstable CRMB binder. Results show that the residual bitumen becomes stiffer while the swollen rubber becomes softer after interaction because of the preferential absorption of light components of bitumen by rubber. The dynamic asymmetry existing between the bitumen phase and the rubber phase of CRMB results in storage instability. When the bitumen phase has similar dynamic properties as the rubber phase, the resulted binder system will be stable. It is possible to manipulate raw material properties and interaction conditions to achieve the desired crossover between two phases of CRMB and hence obtain a storage-stable CRMB blend.

1. Introduction

How to appropriately treat and dispose end-of-life tires (ELTs) has been a concern for many years. A possible solution in civil engineering is to incorporate crumb rubber modifiers (CRMs) produced from ELTs into bitumen and use the modified binder as a new paving material [1,2]. The typical wet process used for bitumen modification is achieved by mixing bitumen and CRMs at 160–220 °C for a predetermined duration [3]. During this process, rubber particles are swollen to due to absorption of light fractions of bitumen. Under excessively high mixing temperatures, rubber swelling will be finished in a short time and rubber degradation starts to occur [4]. The interaction between bitumen and rubber has great effects on the property development of crumb rubber modified bitumen (CRMB). Many factors, including the raw material properties and

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interaction conditions, have been shown to influence the bitumen-rubber interaction and hence the final binder properties [5–8]. Overall performance improvement and environmental benefits of rubberized asphalt pavements using CRMB have been reported for a long time [9]. However, there are two obvious drawbacks which impede its further applications. Firstly, for traditional rubberized asphalt mixtures, their mixing and compaction temperatures are usually higher than unmodified asphalt mixtures due to the excessively high viscosity of CRMB, which increases the energy cost. To solve this issue, warm mix asphalt (WMA) technologies are innovated to effectively reduce construction temperatures as well as the emissions of volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and total suspended particles (TSP), etc. [2]. Another obvious drawback of CRMB which hinders its further application is the poor stability during storage at elevated temperatures (140–180 °C). Storage instability is a prevalent issue existing in polymer modified bitumen (PMB) but more severe in CRMB. Since WMA has been widely utilized to improve the mixture workability of rubberized asphalt pavements, its influence on the storage stability of CRMB is of great concern and has not yet been fully investigated.

Storage instability of PMB is actually a phase separation process at a microscopic scale during which polymer modifiers separate from bitumen matrix due to the different natures of polymer and bitumen [10]. If considering PMB as a binary blend which comprises a bitumen-rich phase and a polymer-rich phase, the dynamic asymmetry between these two phases directly drives the phase separation process. There are many factors controlling this dynamic asymmetry within PMB. The density difference between polymer and bitumen is believed to be one of the important causes of storage instability in three-dimensional reality [11]. More fundamental effects may come from the differences in microstructural composition, physio-chemistry (molecular weight, glass transition temperature, polarity and solubility) for polymer and bitumen which contributes to the incompatibility [12]. Solubility parameters are often used to interpret and predict the compatibility between bitumen and polymer modifiers [13]. In terms of CRMB, more specifically, raw material properties (bitumen and CRM characteristics, CRM content, additives) and the interaction conditions determine the storage stability. It is reported that CRMs of small size obtained through ambient grounding result in more storage stable CRMB binders [14]. Poor storage stability has negative influence on the overall binder properties and increases the handling difficulty of storage and transport, consequently influence the durability of asphalt pavements. It also results in difficulties for the binder system to be transported by pipelines [14]. Since storage stability directly influence the usage and performance of CRMB, understanding the mechanism and influence of other factors (e.g., rubber content and warm-mix additives) is thus of great importance for both production optimization and quality control.

Besides controlling the preparation conditions of CRMB, there are generally two types of methods to improve storage stability of CRMB. One way is to add various types of chemical compounds into CRMB to form bonds between different components of binders and/or form a polymer network structure [14]. The other way is achieved by surface treatment of CRM. Thermochemical, thermomechanical, microwave, ultrasonic, biological, and plasma methods were used to activate the CRM [15,16]. Furaldehyde or acrylic acid was also reported to activate the surface of CRM [17].

2. Methods for characterizing storage stability of CRMB

Generally, three main techniques have been applied to characterize phase separation behaviours in bituminous binders: microscopy, chromatography/spectroscopy and mechanical testing [18]. Optical observations are usually conducted using a fluorescence microscope (FM). Images obtained from FM allows direct and rapid visualization of the relative amount and morphology of both polymer-rich phase and bitumen-rich phase based on their different UV excitation responses [10]. While FM is very popular and successful in characterizing most PMB binders (colloidal dispersion system), it is not very suitable for CRMB binders (colloidal suspension system). This is because prepared samples subjected to FM observations usually require a thickness less than 0.1 mm. However, the size of CRM particles within the bitumen matrix is usually bigger than the required sample thickness. Even though other sample preparation methods (e.g., "cooling and fracture" per EN 13632) may overcome this problem [10], a large proportion of carbon black inside CRM impedes the fluorescent effect of rubber which makes it difficult to obtain readable morphology. Gel permeation chromatography (GPC) has been adopted to obtain the information of molecular weight distributions of bitumen-rich phase and polymer-rich phase [19,20]. Through comparing different phases at a molecular level, the molecular sizes of polymer and bitumen, which is an indicator of compatibility, can be predicted and hence the storage stability. Fourier transform infrared spectroscopy (FTIR) can also be utilized to determine changes in the polymer content by measuring the change of peaks of the corresponding functional groups [21]. However, inconsistent results from FTIR are often reported [22]. The complexity of equipment, strictness of sampling procedure and difficulty in quantifying results of these techniques hinder their widespread use.

The most common way to evaluate the stability of modified binders is the cigar tube test which simulates the phase separation process in the field in the absence of continuous agitation. The mechanical properties of samples from the different tube sections after conditioning are measured and compared to give an indication of the storage stability. The actual performance of modified binders after storage or the effect of storage conditions on their properties can be directly measured through mechanical testing. In addition, since the densities of bitumen and rubber are different, it is expected to distinguish these two phases by X-ray computed tomography (CT) [23]. The obtained X-ray CT scan images can reflect the bitumen and rubber phases with different greyscale levels, which can further give insights into storage stability based on the distribution of rubber particles in different positions. This study adopted both mechanical testing method and X-ray CT visualizing technique to evaluate the storage stability of CRMB binders.

3. Objectives and approach

The present study aims to develop a robust methodology to evaluate the storage stability of CRMB with warm-mix additives using both mechanical and morphological tests. Specific objectives include:

- investigating the effects of rubber content and warm-mix additives on storage stability of CRMB binders. Both mechanical tests (dynamic shear rheometer, DSR) and morphological tests (X-ray CT scan) were conducted on the samples from different parts of the tube after conditioning; and
- having a preliminary understanding of the dynamic asymmetry between the bitumen-rich phase (BP) and the rubber-rich phase (RP). The glass transition temperature difference between bitumen and CRM was analyzed by Differential Scanning Calorimetry (DSC) test. Rheological tests were also carried out on the extracted liquid phase (i.e., BP) of CRMB and the swollen rubber phase (i.e., RP) to gain some insights into the dynamic asymmetry.

4. Materials and methods

4.1. Materials

Bitumen of Pen 70/100 was used as the base bitumen for modification. Its SARA fractions are respectively 7%, 51%, 22%, and 20%. The technical information about CRM provided by a local company is shown in Table 1.

The morphological and elemental analysis of CRM were done by Environment Scanning Electron Microscopy (ESEM) with an energy dispersive X-ray spectroscopy (EDX) in Fig. 1 [8]. It can be found rubber particles have an irregular shape and multiaperture structure. They also contain different types of chemical compounds (e.g., oxide, zinc, iron and silicon, etc.). Non-foaming warm-mix additives, including wax-based product (designated as **W**, synthetic microcrystalline wax) and chemical-based product (designated as **C**, liquid chemical cocktail including surfactants, anti-stripping agents, polymers, etc.), were added to CRMB binders.

4.2. Binder sample preparation

CRMB binders with four CRM contents (5%, 10%, 15% and 22% by weight of base bitumen) were laboratory prepared at 180 ± 2 °C and designated as CRMB-5, CRMB-10, CRMB-15 and CRMB-22. Detailed preparation procedure can be found in [8]. Two warm-mix additives were manually mixed with CRMB at 160 °C for 10 min. It is noteworthy that additives were added after the preparation of CRMB and were not participating in the bitumen-rubber interaction process. Warm-mix additives were only added to CRMB with a high rubber content in an attempt to reduce its excessively high viscosity. The resultant binders were designated as CRMB-22-W and CRMB-22-C. The dosages of additives W and C were respectively 2.0% and 0.6% based on the recommendations from the respective manufacturer.

4.3. Storage stability test

The well-known "tube test" was employed as the storage stability test. During the test, an aluminium foil tube with standard dimensions was filled with hot binder carefully to avoid bringing in air bubbles. The tubes covered with a lid were vertically placed in an oven at 163 ± 3 °C for 48 ± 1 h. After conditioning, settling tubes were moved to a freezer for 2 h. After cooling, the tubes were equally cut into three parts and samples from each part were collected by removing the metal and stored after stirring homogenously. The binder samples from different parts of the tube were subjected to both rheological tests by DSR and X-ray CT scan tests.

Table 1
Basic properties and particle size distribution of CRM.

Properties		Description or value
Source		Waste truck tyres
Processing method		Ambient grounding
Morphology		Porous
Density (g/cm^3)		1.15
Chemical composition	Rubber component (natural and synthetic)	55
	Carbon Black (%)	25
	Processing agents (%)	20
Gradation	Sieves (mm)	Passing (%)
	0.710	100
	0.500	93
	0.355	63
	0.180	21
	0.125	9
	0.063	2

4.4. Extraction of the liquid phase of CRMB

During the interaction process, the swollen rubber phase (RP) and the residual bitumen phase (BP) were formed, which are different from the original properties of rubber particle and base bitumen. Therefore, it is necessary to investigate the rheological properties of both RP and BP to have a better understanding of the dynamic asymmetry between them. The BP of CRMB was extracted by filtering out the insoluble rubber particles from the bitumen matrix through a mesh sieve (0.063 mm) in the oven at 165 ± 3 °C for 20 min [24]. The residual (drained) binder labelled as CRMB-X-BP was collected on an aluminium pan for future testing.

4.5. Preparation of cylindrical swollen rubber sample

Since the remaining CRM particles on the sieve mesh from the extraction test were loose and inhomogeneous, it is difficult to prepare a disk sample to perform the DSR test. To simulate the property of the swollen rubber, cylindrical samples of rubber were cut from waste truck tire treads and were immersed in hot bitumen. The specially designed sample preparation process is shown in Fig. 2 [25]. The dimension of the rubber sample is about 2 mm in thickness and 8 mm in diameter, which is suitable to carry out the DSR tests with the traditional configuration for bitumen testing. Laboratory swelling test of rubber in bitumen was carried out by immersing the rubber cylinder into hot bitumen at 180 °C for 36 h for it to reach the swelling equilibrium [26]. The swelling equilibrium was defined as the point where the volume of rubber tended to stabilize. The swollen rubber samples were cleaned by wiping out the surface bitumen with solvents [26], which can simulate the properties of swollen CRM particles inside the bitumen matrix. Through the mixing optimization process of CRMB, the rubber particles inside the bitumen matrix were assumed to reach the swelling equilibrium [8]. The swollen samples were trimmed to 8 mm in diameter with a sharp tool to fit the DSR test. From the viewpoint of material property, the mechanical properties of swollen rubber should not be influenced by the testing sample geometry in principle. Therefore, an intact swollen rubber sample was used to represent the loose swollen rubber particles to perform DSR tests to obtain the mechanical properties.

4.6. Experimental design and methods

A detailed testing program of different binders to investigate storage stability is shown in Fig. 3. There are two testing phases for the experimental design. At Phase 1, six types of CRMB binder samples at the fresh state were subjected to the tube storage stability tests. Multiple stress creep and recovery (MSCR) tests were conducted at 64 °C on samples collected from different parts of the tube after conditioning. The high-temperature performance grade (H-PG) of the neat bitumen is 64 °C and all the H-PGs of all CRMB binders are higher than 64 °C [8]. The choice of this testing temperature for MSCR was expected to differentiate the mechanical properties of all collected samples. Storage stability index was proposed based on the MSCR parameters. X-ray CT scan tests were also conducted on the collected samples from different positions of the tube to gain more insights into the rubber particle distribution in the bitumen matrix. At Phase 2, frequency sweep tests were conducted on the liquid phase of CRMB and swollen rubber samples, which represent the bitumen phase and rubber phase respectively. The linear viscoelastic behaviours of the bitu-

Table 2
Rubber contents of binder and separation index based on CT scan test results.

Binder type	CRMB-5	CRMB-10	CRMB-15	CRMB-22	CRMB-22-W	CRMB-22-C
Top	6.36	14.37	18.35	26.19	25.37	26.25
Middle	8.38	19.46	23.74	30.46	33.35	31.53
Bottom	10.32	22.54	25.56	34.58	40.56	41.26
Average	8.35	18.79	22.55	30.41	33.09	33.01
SI_{CT}	**0.474**	**0.435**	**0.320**	**0.276**	**0.459**	**0.455**

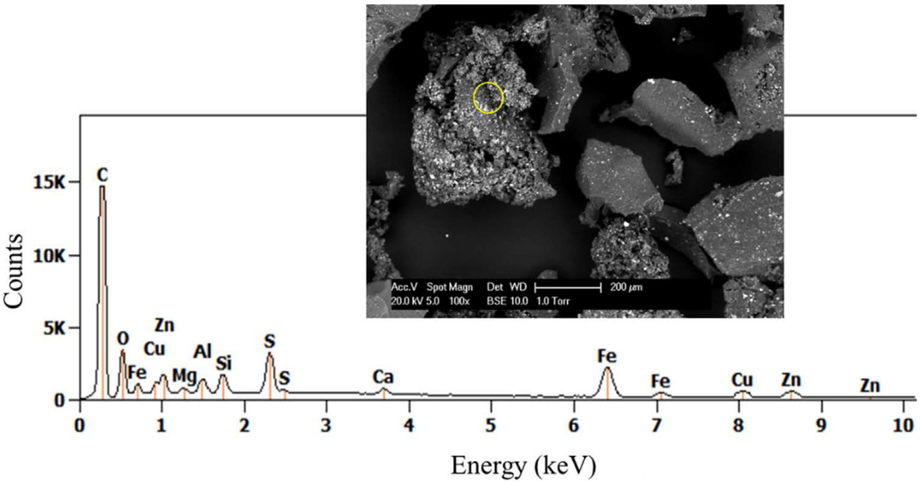


Fig. 1. Morphology and elemental compositions of CRM processed by ambient grinding.

Fig. 2. Preparation of cylindrical rubber samples for DSR tests.

men phase and rubber phase were compared in an attempt to link to the phase separation phenomena.

4.6.1. Frequency sweep test

Frequency sweep (FS) tests of binder samples were performed over a frequency range of 0.1–100 rad/s at temperatures of 10, 30, 50 and 70 °C. A strain level of 0.1% under strain-controlled mode was used for the measurement to ensure the linear viscoelastic response. FS tests of rubber samples were performed from 0.1 to 100 rad/s over a wider temperature range of −10–130 °C with an incremental step of 20 °C. The measurements were also carried out under strain-controlled mode but at a higher strain level of 1%, which is within the linear viscoelastic range of rubber as determined by strain amplitude sweep tests [25]. Before placing the rubber sample between the parallel plates of the DSR, a two-component adhesive (Evonik Rohm GmbH, Darmstadt, Germany), Plex 7742 and liquid Plexmon 801, was mixed and applied on the surface of the bottom plate and the top surface of the rubber

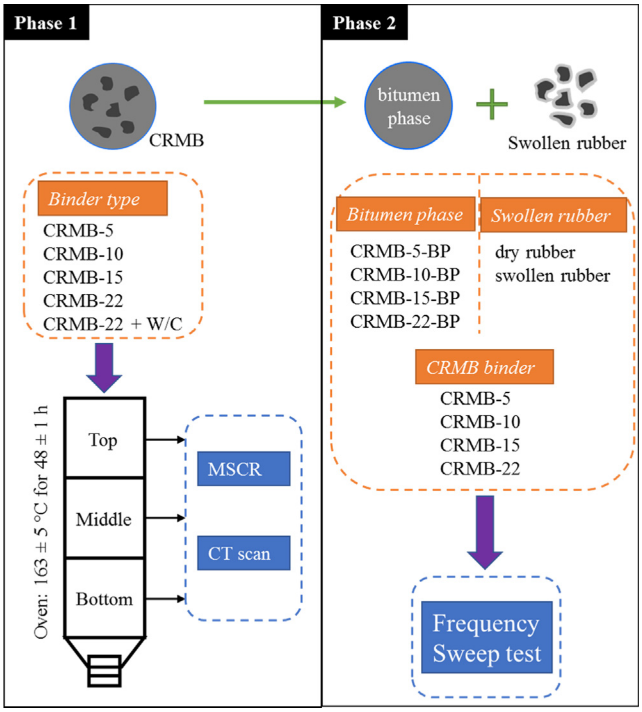


Fig. 3. Experimental testing plan for different binders.

sample to ensure sufficient bonding between rubber and plates [26]. From the technical data sheet of the adhesive, the shear strength of the cured adhesive can reach 40 MPa at room temperature, which is much higher than that of rubber. Therefore, the deformation of the glue is infinitesimal compared with that of rubber during the tests.

4.6.2. X-ray CT scan test

Binder samples collected from different parts of the tube in the storage stability test were stirred uniformly and poured into special glass bottles with a volume of approximately 5 ml. Then these bottles containing the binders were scanned by a micro X-ray CT. Its resolution is 0.025 mm in all directions. The bitumen and rubber phases are distinguishable in the obtained 2D scan images based on the greyscale values (Fig. 4). It was intended to reconstruct the 3D images of the binder samples based on the slice images using specific software. However, after the interaction process, a gel-like material was formed surrounding the rubber particles, resulting in a vague boundary between bitumen and rubber phases [26,27]. Besides, the density difference between bitumen and rubber became smaller after the swelling process because of the absorption of bitumen components by rubber. It was found the resultant 3D models of binder samples were biased and cannot reflect the true amounts of rubber in bitumen. Therefore, quantitative analysis was only performed based on the 2D CT scan images.

5. Results and discussions

5.1. Storage stability

5.1.1. Storage stability index

From previous studies, it is known that the MSCR parameters are sensitive to the microstructural change of PMB and can be used to evaluate the elastic behavior of binders [28]. Phase separation of CRMB will result in significant changes of the polymer network and hence the elastic behaviors of CRMB. The non-recoverable creep compliance J_{nr} from MSCR tests is expected to be more effective than the traditional rutting parameter $G^*/\sin\delta$ to capture the microstructural change of CRMB after storage. Originally, a storage stability index is defined as the ratio between the J_{nr} of the sample taken from a given distance from the bottom of the settling tube and the same parameter measured on a unconditioned CRMB sample. To demonstrate this idea, the tubes for storing CRMB-22 with/without additives were cut into five equal parts. Samples from all parts were measured. The stability index as a function of settling tube height for three types of binders is shown in Fig. 5.

It can be found that the stability index of CRMB-22 is close to 1 over the whole range of tube heights, indicating a stable binder. For CRMB-22-W and CRMB-22-C, the storage stability index increases as the tube height increases. This implies that CRMB binders with warm-mix additives are less stable than the common CRMB. The reasons for this will be explained in the next sub-section. In addition, it is worthy to note that the stability indexes of CRMB-22 and CRMB-22-W at different positions are all lower than 1, indicating decreased J_{nr} values comparing to the unconditioned CRMB binders. This fact indicates that binders after conditioning in the oven for 48 h are stiffer than the fresh binders despite the occurrence of potential phase separation. Since the conditioning temperature is 163 °C, bitumen-rubber interaction may continue taking place and potential aging may happen, together changing the mechanical property of binders. Comparing to CRMB-22, the J_{nr} value of CRMB-22-W decreased more, which implies that the wax-based additive may promote the rubber-bitumen to improve the mechanical property.

To quantitatively compare the storage stability of different binders, a proper separation index (SI) which can address the difference between different parts of the tube needs to be developed. The above analysis demonstrates that the mechanical parameter from a fresh binder is not a suitable reference because bitumen-rubber interaction and potential aging may occur during the conditioning. Therefore, the following SI calculated by the non-recoverable creep compliance J_{nr} values of samples collected from

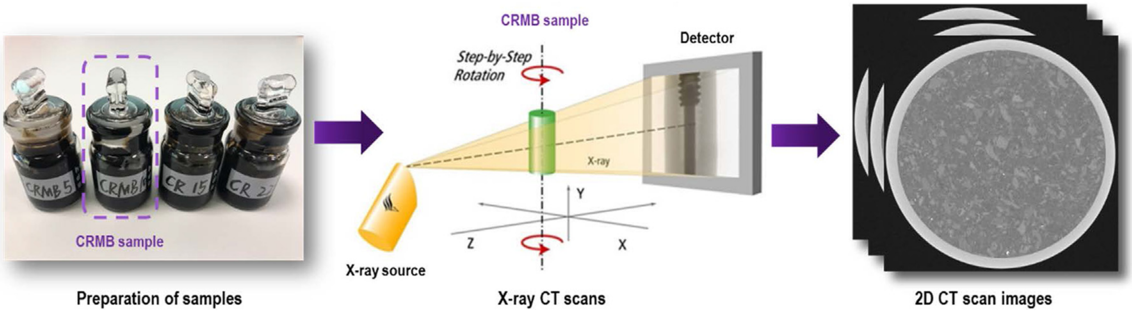


Fig. 4. X-ray CT scan test for binder samples after the storage stability test.

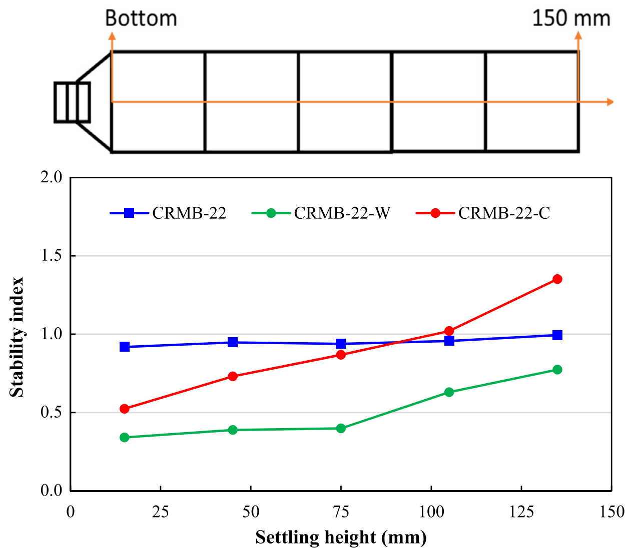


Fig. 5. Stability index as a function of tube settling height.

different parts was proposed. Standard storage stability test was used by cutting the tube into three equal parts.

$$SI = \frac{|J_{nr,t} - J_{nr,b}|}{J_{nr,avg}} \tag{1}$$

where $J_{nr,t}$ and $J_{nr,b}$ represent the values from the top and bottom sections of the tube, respectively. $J_{nr,avg}$ is the averaged J_{nr} among the samples from the three equal parts of a tube. Using $J_{nr,avg}$ of the sample after conditioning can eliminate the bias brought by sample difference due to the interaction and potential aging. A smaller SI value is preferred to achieve higher storage stability of binders.

5.1.2. Effect of rubber content and warm-mix additives

Fig. 6 shows the separation index of different binders. It is interesting to notice from Fig. 6 that with the increase of rubber content, the CRMB binder has lower SI indicating higher storage stability. CRMB-22 is the most storage stable binder. In terms of warm-mix additives, the effects of both additives on the SI of CRMB are quite similar. The addition of additives significantly degrades the storage stability indicated by the higher SI values.

With respect to the phase behaviors of CRMB at high storage temperatures, it can be approximately regarded as a suspension system where rubber particles are suspended in the low-viscosity bitumen medium. According to the Stoke's law, the phase separation in CRMB is driven by the sedimentation velocity of rubber particles in the fluid bitumen. The sedimentation velocity (v) is quantified by Eq. (2) by considering the gravity force equals to the drag force (frictional force) on rubber particles in the bitumen of a Newtonian fluid state [29]:

$$v = \frac{2}{9}\frac{r^2 \Delta\rho g}{\eta} \tag{2}$$

Where r is the radius of rubber particle; $\Delta\rho$ is the difference of density between rubber particle and bitumen; η is the viscosity of bitumen; and g is the gravitational acceleration. As implied in Equation (2), the sedimentation velocity of rubber particles is proportional to the square of its radius and the density difference between rubber and bitumen, and inversely related to the viscosity of bitumen. Considering the density of rubber particles (1.15 ± 0.05 g/cm^3) is relatively higher than bitumen (1.02 g/cm^3), rubber particles tend to settle due to the gravitational force. Therefore, to reduce the sedimentation rate of rubber particles, efforts should be made to decrease the sedimentation velocity, which can be realized through: (1) using finer rubber particles; (2) decreasing the density difference between CRM and bitumen, which is difficult for supplied raw materials; (3) increasing the viscosity of bitumen or residual bitumen (liquid phase of modified bitumen).

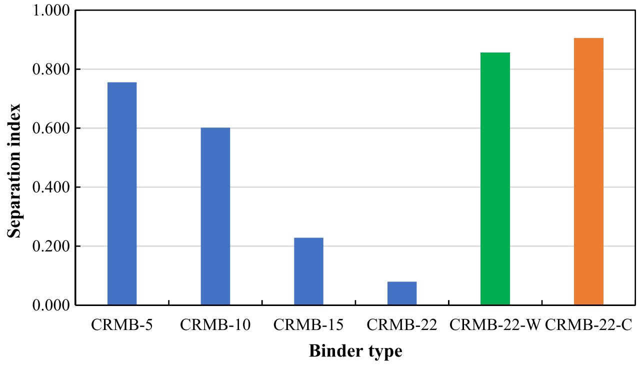


Fig. 6. Separation index of different binders.

Looking back to the storage stability test results in Fig. 6, increasing rubber content leads to more stable CRMB binders. This is because CRMB with increased volume of rubber has a higher viscosity which hinders the settling of CRM particles [30]. The states of CRM particles dispersed in bitumen were schematically shown in Fig. 7. When Rubber content is low, CRM particles absorb only small amounts of light fractions from bitumen and do not change the property of residual bitumen significantly. In addition, the stiffening effect of CRM on the improvement of binder viscosity is relatively weak because of the low content. Since the distance between particles is relatively large, the inter-particle interaction/force can be ignored. The drag force on the particles is insufficient to balance the gravitational force, so that particles will descend due to the higher density. When rubber content is higher, CRM particles significantly change the property of residual bitumen and make it more viscous. The increase of CRM particle volume in the binder after swelling reduces the inter-particle distance. With sufficient inclusions of CRM particle, a potential network can be built as shown in Fig. 7. The high viscosity of liquid bitumen and the formed polymer network restrain the movement of CRM particles. Furthermore, it is speculated that when rubber content is high enough, the liquid phase of binder has similar viscoelastic property as the swollen rubber, which is verified in the following part. This resemblance further improves the mechanical compatibility between bitumen-rich phase and rubber-rich phase and consequently increases the storage stability of binder. By contrast, the addition of warm mix additives decreased the viscosity of CRMB-22 and hence made it easier for CRM particles to descend.

5.1.3. CT scan test results

Mechanical testing is an indirect method to characterize the storage stability of binders. To have more insights into the mechanism of storage stability, CT scan tests were performed to obtain the rubber particle distribution in bitumen from different positions of the tube sample. Fig. 8 shows the processing steps of the obtained 2D CT scan images. The images were first cropped to remove the surrounding container and black background. The brighter parts in the image represent the rubber particles. Segmentation was performed based on the different greyscale values of the bitumen and rubber. A binary image was obtained in which the black islands represent the dispersed rubber particles in the white bitumen domain. Filters were also used to remove the noisy points which may be mistakenly regarded as rubber particles. After the

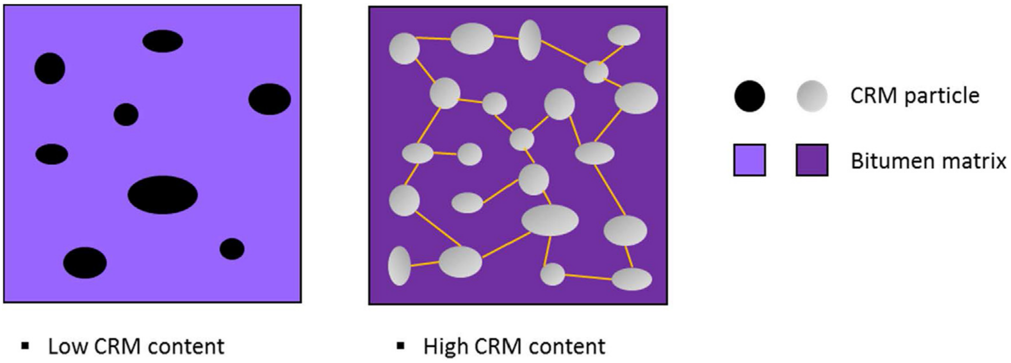
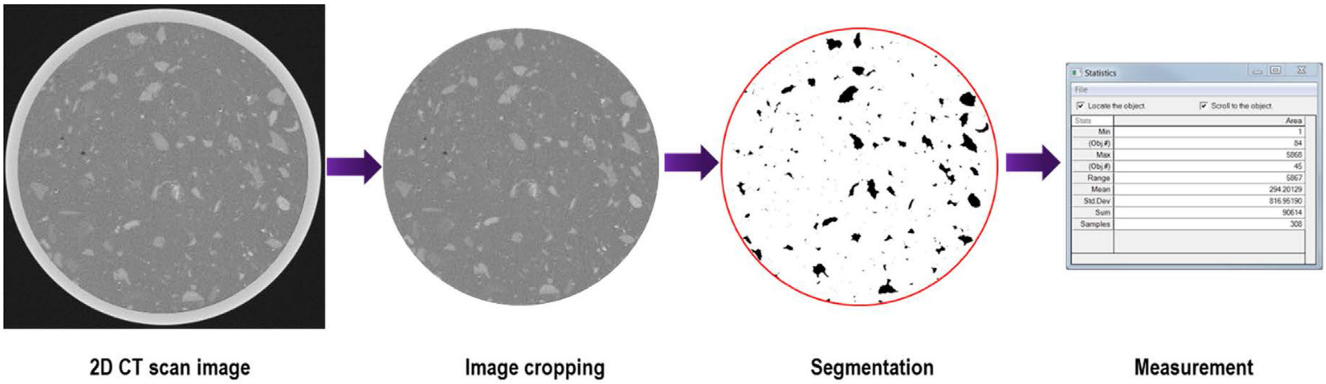


Fig. 7. Schematic representation of CRM particles suspended in bitumen matrix. (Note: Different colours represent different states of CRM particle and bitumen; The lines connecting rubber particles were imagined for illustration purpose).



Stats	Area
Min	1
(Obj.#)	84
Max	5868
(Obj.#)	45
Range	5867
Mean	294.20129
Std.Dev	816.95190
Sum	90614
Samples	308

Fig. 8. CT scan image processing procedure.

segmentation, the measurement function was applied to calculate the area occupied by rubber particles. The rubber content was further calculated by dividing the total area as displayed by the red circle. The rubber content in different parts of the tube sample was determined by averaging the results from 200 scan images through batch processing using the above procedure. The calculated rubber content varied from different scan images and fluctuated around the averaged value. The obtained rubber content from 2D images maybe deviate from the reality but it is reasonable to compare the values from different samples since a consistent procedure was used.

Another separation index SI_{CT} based on the CT scan results is defined in Equation (3).

$$SI_{CT} = \frac{|\phi_t - \phi_b|}{\phi_{avg}} \tag{3}$$

where ϕ_t and ϕ_b represent the rubber volume contents of the sample taken from the top and bottom parts, respectively. ϕ_{avg} is the averaged rubber volume content of samples from the three equal parts. The reason for using ϕ_{avg} rather than the original rubber volume content of each binder is because swelling of rubber particles occurring during bitumen-rubber interaction significantly increase the volume of rubber particles. Similar to the previous separation index, a smaller value of the separation index represents higher storage stability of the binder.

Based on the initial dosages of CRM and the densities of CRM and bitumen, the original volume contents of rubber in CRMB-5, CRMB-10, CRMB-15, CRMB-22 are 4.29%, 8.22%, 11.84% and 16.46% respectively. Table 3 summarizes volume fractions of rubber in the binder from different parts and the resulted separation indices. It can be seen clearly that the rubber contents in different parts of the tube are different due to the inhomogeneity of CRMB binders. Because the density of rubber particles is larger than bitumen, rubber particles settle down in the tube during the storage stability test. That is why the rubber content in the bottom is higher. The varying degree of rubber content varies with the type of binder. The average volume fraction of rubber for each binder is approximated twice as high as the original dosage. This confirms the occurrence of rubber particle swelling in the bitumen matrix [31]. From the SI_{CT} in Table 2, it gives similar findings as the previous SI based on the mechanical properties (J_{nr}). The SI_{CT} value decreases with the increase of rubber content, indicating a more storage stable binder. The addition of warm-mix additives has adverse effects on the storage stability of CRMB binder as reflected by the increased SI_{CT} value.

Fig. 9 compares the separation index from the mechanical test and the CT scan test. There is a high correlation between these two separation indices, which confirms that the mechanical testing (MSCR in this study) is an effective method to differentiate the difference between different parts of the sample to characterize the storage stability. It is noteworthy that the separation indices from CT scan test are closer to each comparing to those from mechanical tests. This means J_{nr} from the MSCR test is more sensitive to the change of rubber content in CRMB binders. In addition, Fig. 10 shows the CT scan images of CRMB binders with different rubber contents. It verifies the previous assumption of the status of rubber particles in the bitumen matrix as shown in Fig. 7. When increasing the rubber content, a potential rubber network can be established due to the interparticle interactions

Table 3
Glass transition temperatures of bitumen and CRM.

Sample	T_g(°C)	Onset (°C)	End (°C)	Delta C_p (J/g*°C)
70/100	−17.18	−26.81	−9.23	0.118
CRM	−58.37	−61.77	−55.45	0.244

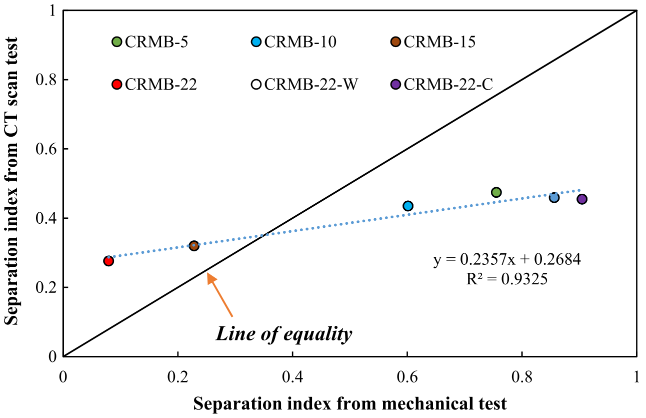


Fig. 9. Comparison between the separation indices from different tests.

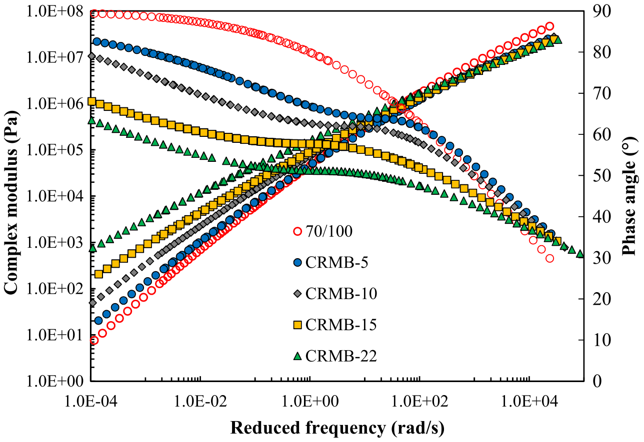


Fig. 11. Viscoelastic master curves of CRMB binders with different rubber contents.

with the bitumen, which restrains the movement of the dissociative rubber particles.

5.2. Dynamic asymmetry between the components of CRMB

As mentioned earlier, if considering PMB as a binary blend consisting of a bitumen-rich phase and a polymer-rich phase, the dynamic asymmetry between these two phases directly drives the phase separation process. Considering CRMB as a blend of two viscoelastic materials, to better understand the effects of the viscoelasticity of individual component on phase separation dynamics, two questions need to be answered: (1) if there is indeed a dynamic asymmetry between bitumen and rubber within CRMB; and (2) to what extent the dynamic asymmetry affects the phase separation in CRMB. The first question was addressed by investigating the viscoelasticity of CRMB and by analyzing the glass transition temperature (T_g) difference between bitumen and rubber.

5.2.1. Viscoelastic master curves of CRMB binders

A modified CAM model associated with the WLF equation were used to establish the master curves of complex modulus and phase angle of CRMB binders (Fig. 11) [32]. Rubber modification improves the viscoelastic response of bitumen. CRMB binder is and more elastic stiffer than neat bitumen at lower frequencies while softer at high frequencies. In addition, all CRMB binders exhibit a characteristic plateau zone in the intermediate-frequency range. Therefore, in the CRMB system, rubber is presumably a slower phase while bitumen is a faster phase. The stiffening or softening effect is more pronounced as the rubber content increases. This peculiar feature of CRMB explains why CRMB has both better high and low-temperature performances. CRMB with a higher rubber content has a wider relaxation spectrum, which means a more gradual transition from the elastic behaviour to viscous behaviour due to the presence of rubber. A gradual elastic-viscous transition means the system can be more stable when encountering temperature changes.

5.2.2. Glass transition temperature

Both neat bitumen and CRM samples are prepared for DSC tests to determine the glass transition temperatures. Approximately 15 mg of bitumen or CRM is placed in a DSC cup. The cup is sealed with a lid using a special tool to ensure a proper contact between the sample and the bottom surface. The cup containing testing materials was placed in the apparatus and conditioned at 25 °C for 5 min. Then temperature was decreased from 25 °C to −60 °C. The measurement started after the isothermal conditioning at −60 °C for 5 min, with temperature ramping from −60 to 140 °C at a rate of 20 °C /min [33]. The heat flows of testing sam-

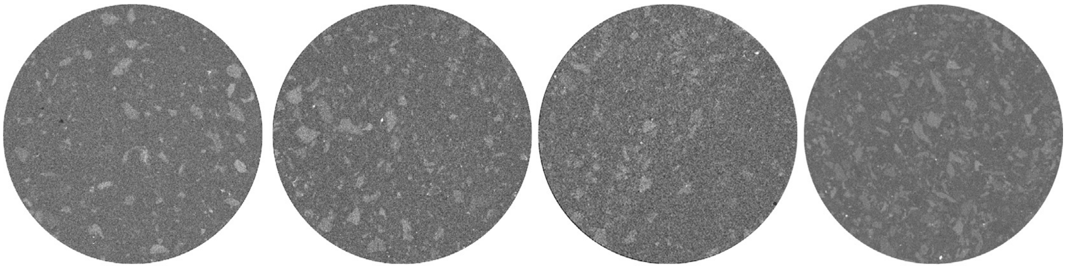

(a) (b) (c) (d)

Fig. 10. CT scan images of (a) CRMB-5, (b) CRMB-10, (c) CRMB-15 and (d) CRMB-22.

ples were monitored and compared to those of the reference sample (an empty aluminium pan in this study) for further derivations.

The T_g and related thermal parameters of bitumen and CRM are shown in Table 3. The Delta C_p parameter reflects the change of heat capacity after glass transition. It is obvious that bitumen and CRM have quite different glass transition temperatures. However, since the large variation of CRM source and complex glass transition phenomena of bitumen, it is difficult to quantitatively characterize the dynamic asymmetry between bitumen and CRM based on their T_gs. Bearing this in mind, the fundamental viscoelastic properties of these two components were investigated in the following part to see what is the direct contribution to a dynamic symmetry or dynamic asymmetry.

5.2.3. Rheological properties of bitumen phase and rubber phase

The bitumen-rubber interaction process alters the volume fractions of rubber and the mechanical properties of both bitumen and rubber. To investigate whether this interaction process has effects on the dynamic asymmetry between BP and RP, FS tests were performed on the extracted liquid bitumen phase and the swollen rubber phases. It is assumed the rubber particles in CRMB binders with different rubber contents have similar mechanical properties as simulated by the swollen rubber sample. This is because there is a sufficient amount of bitumen in the binder to allow swelling to occur [5]. The master curves of bitumen and rubber before and after swelling were developed in Fig. 12.

Comparing the dry rubber with the swollen rubber, it can be found that dry rubber exhibits obvious elastic behaviors while the swollen rubber shows obvious viscoelasticity and becomes softer than the dry rubber. The complex moduli of swollen rubber are all lower than that of the dry rubber at low frequencies. At high frequencies, the moduli of different samples merges together. In terms of the liquid phases of different CRMB binders, they are stiffer than the neat bitumen because of the loss of light fractions to rubber. Since the mechanical properties of both bitumen phase and rubber phase are changed after interaction, it is of more interest to analyze the relative relationship between these two phases. Comparing the bitumen phase with swollen rubber phase, the swollen rubber sample has lower moduli in the high-frequency region and higher moduli in the low-frequency region. This explains the peculiar viscoelastic response of CRMB as shown in Fig. 11. It is important to notice that the crossing points of the master curves of bitumen phase and swollen rubber phase are located in the relatively low-frequency region. When increasing the rubber content, the crossing point shifts to the lower frequency side. Considering the reference temperature to build master curve is 30 °C, the crossing point in the low-frequency region corresponds to high temperatures. This means the two phases have similar mechanical properties in the high-temperature region. CRMB with a low rubber content may be stable at lower temperatures (e.g., ambient temperatures) because of the similarity between the bitumen phase and rubber phase as reflected by the crossing over at a relatively high frequency. It may be unstable at higher temperatures (e.g., storage temperatures) because of the dissimilarity between BP and RP. At a fixed low frequency (approximately corresponding to the storage temperature) as indicated by the green arrow in Fig. 12, no crossing point is reached when the Rubber content is low, which means the dynamic asymmetry remains. When increasing the Rubber content to a certain value, the crossing point appears and the dynamic asymmetry between the two phases disappears. At this moment, the CRMB binder exhibits as a stable blend during high-temperature storage. This dynamic symmetry between bitumen phase and rubber phase is the fundamental reason why CRMB-22 is more storage stable. Since the crossing point of the master curves of two phases is highly dependent on the constituents of CRMB and interaction conditions, it is possible to manipulate these factors to achieve the desired crossover between two phases and hence obtain a storage-stable CRMB blend. In general, bitumen-rubber interaction (mainly swelling) changes both the mechanical properties of bitumen matrix and rubber due to the swelling of rubber by absorbing light fractions of bitumen [31]. Therefore, by controlling the interaction conditions and selecting the proper raw materials (bitumen and rubber), it is possible to achieve a resemblance between bitumen and rubber phases after the interaction.

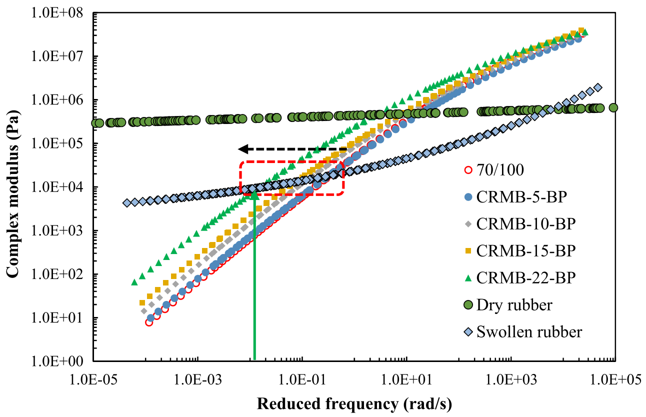


Fig. 12. Complex modulus master curves of liquid bitumen phase and swollen rubber phase.

6. Conclusions and recommendations

This study investigated the effects of rubber content and warm-mix additives on the storage stability of CRMB binders and explored the dynamic asymmetry between the bitumen-rich phase and the rubber-rich phase. Various tests on the constituents of CRMB were done to understand the mechanism of storage stability. The main findings are as follows:

- The viscoelastic response of CRMB improves with the increase of rubber content (i.e., higher complex modulus and lower phase angle). CRMB with a higher rubber content has a wider relaxation spectrum, which means a more gradual transition from the elastic behaviour to the viscous behaviour. A gradual elastic-viscous transition is beneficial for the system stability when encountering temperature changes.
- The mechanical (or other) parameters of fresh CRMB binders cannot be used as a reference in the separation index to evaluate the stability after storage because bitumen-rubber interaction and aging may continue occurring during the storage period. Instead, a parameter taken from the stored samples can serve this purpose.
- Separation indices developed from both MSCR test and CT scan test results reveal that CRMB with a higher rubber content is more storage stable than CRMB with a lower rubber content. The incorporation of both warm mix additives is detrimental to the storage stability of CRMB-22. Based on the results in this study, it is not suggested to add warm mix additives into CRMB during the storage or transport stage.
- When the bitumen-rich phase and rubber-rich phase of CRMB exhibit similar mechanical behaviours, which can be called dynamic symmetry, CRMB will be storage stable. The dynamic asymmetry between binder components drives the phase separation behaviour of CRMB. It is possible to manipulate raw

material properties and interaction conditions to achieve the desired crossover between two phases of CRMB and hence obtain a storage-stable CRMB blend.

For future studies, more systematic DSC analyses on CRMB and its constituents can be carried out. The effect of warm-mix additives on the storage stability can be extended to CRMB with different rubber contents. The theory of solubility parameter can be used on the constituents of CRMB (rubber and bitumen) to investigate the compatibility between rubber and bitumen, which can provide a more fundamental understanding of the phase separation behaviours. Practical methods (e.g., adding chemical compounds and surface treatment of CRM) can be applied to further improve storage stability of CRMB after considering the findings in this study.

CRediT authorship contribution statement

Haopeng Wang: Conceptualization, Investigation, Methodology, Writing - original draft, Writing - review & editing. **Xueyan Liu:** Investigation, Supervision. **Sandra Erkens:** Funding acquisition, Project administration, Supervision. **Athanasios Skarpas:** Funding acquisition, Project administration, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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