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Interaction between crumb rubber modifier (CRM) and asphalt binder in dry process

Junan Shen, Bo Li, Zhaoxing Xie

Suzhou University of Science and Technology, Suzhou, China
Georgia Southern University, Statesboro, GA, USA
Lanzhou Jiaotong University, China
Auburn University, Auburn, AL, USA

Highlights

- Interaction between CRM and asphalt binder in dry process was investigated.
- Gel Permeation Chromatography (GPC) and Fourier transform infrared spectroscopy (FTIR) were used.
- The existence of interaction between CRM and asphalt binder in dry process.
- Storage time were important parameters to influence the interaction.

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Abstract

The objective of this study is mainly to investigate the interaction between CRM and asphalt binder in asphalt mixtures added with CRM in dry process during the time period after mixing and before paving, including the storage in silo. High pressure-gel permeation chromatographic (HP-GPC) and Fourier transform infrared spectroscopy (FTIR) tests were used on extracted binders from the asphalt mixtures stored in the oven at four time phases of 0, 30, 60, 90 min at the temperature of 160 °C. The results showed that (1) the percentage of the large molecular size (LMS) from GPC test increased as the storage time of the mixtures in dry process increased, and could reach that from wet process; (2) the ratio of bonding at C=O, an aging index from FTIR, had a sharp increase from storage time 0–30 min, and kept less change for further storage; (3) increase in LMS as storage time increase could be mainly caused by the interaction of CRM with the asphalt, not by aging.

1. Introduction

Crumb rubber modifier (CRM) produced from scrap tires has been successfully utilized as an additive in Hot Mix Asphalt (HMA) with the goal of improving the hot temperature sensitivity and the durability of the asphalt pavement in addition to protecting the environment and saving resources (e.g., landfill space) [1–4]. Because of these advantages, there is an increasing interest in utilizing rubberized binders in HMA pavements in some states in the United States and other countries [5].

CRM can be incorporated into asphalt paving mixes using two different methods, which are referred to as a wet process and a dry process. The wet process has the advantage that modified binder properties can be better controlled through its mixing equipment to blend bitumen and rubber [6–11]. It is a main production method to use CRM for asphalt binders. However, the dry process has potential to consume larger quantities of recycled crumb rubber compared to the wet process resulting in greater environmental benefits. In addition, the production of CRM asphalt mixture in dry process is logistically easier than the wet process resulting in greater environmental benefits. In addition, the production of CRM asphalt mixture in dry process is logistically easier than the wet process and, therefore, the dry process would be potentially available to a larger market [12]. Up to now, the dry process is still a far less popular method. In dry process, crumb rubber is assumed to be a substitute for a small portion of the fine aggregate (usually 1–3 percent by weight of the total aggregate in the mix). The rubber particle are blended with the aggregates prior to the addition of the asphalt cement. Research into the dry process has been limited.
The interaction between bitumen and crumb rubber in the traditional dry process is negligible due to the following reasons: larger CRM particle size, higher CRM content, and no reaction additives [13,14]. Georgia DOT has been paving CRM mixes using a modified dry process since 2007: smaller size (30 or 40 mesh) and lower content of CRM (about 10% mass of asphalt binder), and a cross-link agent [transpolyoctenamer (TOR) polymer] in the rubberized mixture [15–19]. It is unknown whether the rubber-asphalt interaction could happen in the rubberized asphalt mix produced by Georgia modified dry process.

Recent researches on rubber-asphalt interaction demonstrated that during the mixing period as well as during the transportation and laydown of the mixtures, CRM particles swelled and the rate and amount of asphalt absorption by rubber particles were fairly high, resulting in a stiffer and more elastic residual. The interaction also changed the shape and rigidity of the rubber particle [20]. Due to the presence of the CRM, the rubber modified binders could not be evaluated as well as neat binders by standard Superpave binder test procedures. Several potential problems were reported during dry mix production including stiffness-related problems, plate slip, and equipment limits [8]. New method to characterize rubber asphalt binder and recycled aged rubber asphalt binder is necessary.

High pressure-gel permeation chromatography (HP-GPC) can separate an asphalt binder into fractions of various molecular sizes, thus establishing a profile of molecular size distribution (MSD) plotted with detector responses on an ordinate and elution times on an abscissa. The application of this technique to asphalt binders was systematically reviewed by the SHRP research group [21,22]. The GPC could be used for evaluating the changing of molecular size caused by any interaction of the CRM and asphalt binder.

The main objective of the study is to examine the interaction of CRM and asphalt in the mixtures with CRM added in dry process during the period of time between mixing and paving. GPC and FTIR were used to test the extracted binders from the mixtures stored at different times of 0, 30, 60, and 90 min. Two mixture gradations of PEM and SMA were used. In addition, extracted binders from rubberized PEM and SMA in wet process without storage were tested for a control.

### 2. Materials and test procedures

#### 2.1. Materials

CRM in wet process was produced by mixing 30 mesh CRM at 10% of the weight of asphalt binder with a base binder of PG 67–22 at 170 °C and 700 RMP for 45 min in the laboratory. The dry process binder used the same CRM and base binder of PG 67–22, which were introduced into aggregates together with a cross-link agent-TOR polymer at 4.5% of the weight of the CRM.

Crushed granite aggregate was utilized in all mixtures. Hydrated lime at 1.0% by the weight of the total aggregate was used for anti-stripping purpose which was recommended by GDOT. In addition, cellulose fiber at 0.35% by the weight of the total mixture was added to protect excessive drain-down.

Gradations of 12.5-mm Porous European Mix (PEM) and Stone Matrix Asphalt (SMA) showed in Fig. 1 were designed in accordance with Georgia mix design procedure (Section 828), and optimum asphalt contents (OAC) of PEM and SMA mixtures were designed according to the specifications of GDT114 and GDT 123, respectively. Both PEM and SMA gradations met the control tolerances and design criteria of Section 828 of the Standard Specifications. Table 1 presents OAC of PEM and SMA mixtures.

#### 2.2. Test procedures

The CRM was introduced into the mixer at the same time with the aggregate and asphalt binder, then were mixed at 165 °C together to produce rubberized PEM and SMA in dry process. After mixing, loose mixtures were placed on a shallow tray and aged in an oven (Fig. 2) for four storage times of 0, 30, 60, and 90 min in this study before the aged binders were recovered using Abson method. The storage temperature was set at 160 °C. The storage times were selected to consider a typical length of 1–2 h for asphalt paving from mixing to finishing paving, and simply divided into the same intervals.

For the wet process, it is assumed that rubber-asphalt has fully-reacted before rubberized mix production since crumb rubber has been blended with binder at 175–200 °C for 45–60 min. Rubberized PEM and SMA in wet were produced and there is no any storage before the recovery of aged binders.

Extraction of the aged asphalt from the stored PEM and SMA mixtures was conducted based on the ASTM D2172 procedure. The binders were recovered from the solution of trichloroethylene and asphalt (Fig. 3). Three replicates for each mixes were extracted.
and recovered, and then GPC and FTIR tests were conducted on three replicates of the recovered binders.

Waters GPC equipment with computerized software was used for chromatographic analysis of binders (Fig. 4). A differential refractive index meter (Waters 410) was used as a detector. A series of two columns (Waters HR 4E and HR 3) was used for separating constituents of asphalt binder by molecular size. For testing the samples at a constant temperature, the columns were kept at 35 °C throughout the test in a column oven. The mobile phase was THF flowing at a rate of 1 ml/min. The concentration rate used was 0.5% by weight of binder. This rate was recommended by the manufacturer of the equipment.

Each binder sample dissolved into THF was filtered through a 0.45 μm syringe filter prior to injection into the injection module. A sample volume of 50 μl was injected into GPC injector for each test. One test took 30 min and elution started at approximately 11 min from injection and ended at approximately 21 min, as shown in Fig. 5. Testing for each sample was repeated three times and then the average value of the large molecular size (LMS) portion was reported.

A typical chromatogram of a typical virgin asphalt binder is illustrated in Fig. 4. The area under the curve represents 100% of the binder molecules injected into the GPC system. The asphalt binder constituents are generally classified into several groups. In this study, a chromatogram was partitioned into 13 slices and three parts: large molecular size (LMS; slices 1–5), medium molecular size (MMS; 6 to 9) and small molecular size (SMS; 10–13) (Fig. 5). Only the front part, the LMS value, in the quantitative data of the chromatogram was used to characterize the binder properties. Research has shown that the large molecular size (LMS) of binder had better correlations with asphalt binder properties than other sizes [11,23].

FTIR spectrum were recorded by NICOLET iD7 ATR FTIR spectrometer, whose resolution is 4 cm⁻¹, scanning frequency is 16 times and test range was from 500 to 4000 cm⁻¹. It was selected that the main result range was 500–2000 cm⁻¹ in order to observe the change of the characteristic index (C=O). The FTIR-obtained spectrum possessed absorption bands characteristic of asphalt binders. The functional and structural indexes were calculated from the band areas measured from valley to valley. The choice was set on the areas rather than the band heights because several vibrations of the same type were simultaneously taken into account (for example the C=O ester, acid and ketone vibrations between 1753 and 1635 cm⁻¹). According to the band of bonding, the ratio change of chemical bonding will be calculated for the sake of avoiding the samples thick effect [24]. Based on Eqs. (1) and (2), the ratio changes in the asphalt binders after storage were calculated.

\[
I_{1,0} = \frac{\text{Area of the carbonyl band centered around 1030 ester cm}^{-1}}{\sum \text{Area of the spectral bands between 2000 cm}^{-1} \text{and } 600 \text{ cm}^{-1}}
\]

\[
I_{C=O} = \frac{\text{Area of the carbonyl band centered around 1690 ester cm}^{-1}}{\sum \text{Area of the spectral bands between 2000 cm}^{-1} \text{and } 600 \text{ cm}^{-1}}
\]

### 3. Results and discussions

Fig. 6 showed the LMS values obtained from GPC tests of the binders extracted from PEM mixtures with different storage times.
In general, the LMS values increased as the storage time increased. A larger increase in LMS was found from 9.3% for 0 min to 14.2% for 30 min; then a steady increase in LMS was continuing to 16.0% for 90 min. The LMS from wet process was 14.8% much higher than that of 9.3% from dry process without storage (0 min case). This is because the fact that the modified binder with CRM in wet process was completely mixed for 45 min and the binder experienced the interaction of CRM and binder, as well as some aging. The LMS value of the binder in dry process with a storage 45 min researched that of in wet process, indicating that there will be no difference between the CRM asphalt binder in dry process after aging 45 min and the CRM asphalt binder in wet process regarding the molecular size distribution. The results indicated that the CRM particles in mixtures with dry process absorbed low molecular weight maleness and left the residual asphalt binder containing a higher proportion of asphaltenes as other researcher previously reported. This change may be attributed from both the interaction and aging effect.

Fig. 7 showed the LMS values of the binders extracted from rubberized SMA mixtures in dry process, which were from the GPC test at different storage times. Overall, as found for the PEM in Fig. 5, the LMS values increased from 9.3% for 0 min to 12.5% for 90 min as the storage time increased except that case for 60 min. Again, the LMS from wet process without storage, 11.8%, is much higher than that from the dry process without storage, indicating a complete reaction of CRM and binder as well as aging occurred for mixing CRM modified binder in wet process. Also, the LMS value from dry process reached the similar level to that of wet process at 90-min storage.

There was some difference in the LMS values between from PEM and from SMA. This difference may be caused by difference of aging between the two mixtures since the two mixtures have difference in asphalt thickness.

Fig. 8 showed the Fourier transform infrared spectra (FTIR) of asphalt binders extracted from PEM asphalt mixtures. For the dry process, it can be seen that the storage time changed the chemical bonding: the infrared spectra curve presented below that of the wet process and C=O absorbance peak at 1700 cm\(^{-1}\) was not obvious at 0 min, while IR curves at 30-, 60-, and 90-min storage were close to that of the wet process and C=O absorbance peaks were observed. The following reasons could result into the above results: 1) small molecular group with little C=O was absorbed into crumb rubber, and the percentage of large molecular group with some C=O increase in the binder, 2) the binder was oxidized with oxygen during storages, resulting into more C=O in the binder.

Fig. 9 showed that the ratio changes, as defined in Eq. (2), of the carbonyl index (C=O) in the CRM after different storage process. Generally, the ratio increased from around 0.01 for 0 min in dry process to around 0.02 at 90 min. The ratio for wet process was around 0.02, higher than that of dry process. This is again due to the aging occurred during mixing of CRM and binder in the wet process. There was a huge increase from 0 min to 30 min. The change in the ratio between 60 and 90 min was minor.

Fig. 10 showed the Fourier transform infrared spectra (FTIR) results of four asphalt binders extracted from SMA. Overall, the trend that he absorbance at characteristic wave number with the storage time was very similar from PEM binders to that from SMA binders, especially, at 1700 cm\(^{-1}\), 1600 cm\(^{-1}\) and 1065 cm\(^{-1}\). It indicated that asphalt have aged in the storage process.
Fig. 11 presented the ratio of bonding, as defined in question (2), of extracted binders from SMA mixtures with different storage times. Overall, the ratios increased from 0.01 from 0 min to 0.025 for 60 min. The change of the ratio from 60 min to 90 min was minor. The ratio from the wet process was much higher than that from 0 min in dry process, and was almost to that for 30 min in dry process. The increase in the ratio with the storage time increase was caused mainly by aging.

The change of the values of LMS obtained from GPC was observed for the extracted binders from the PEM and SMA stored from 0 to 90 min. This change in the LMS is partially caused by the heat aging and interaction between CRM and asphalt. The ratio of bonding from FTIR was increased also for the PEM and SMA during the storage time discussed, indicating the aging was occurred. However, the ratio of bonding changed very minor from the late storage time, but the LMS kept increase regardless of the type of mixtures. This fact suggested that interaction of CRM and binder exist and the main reason causing the increase in LMS.

4. Summary and conclusions

This project was to exam if there is interaction between CRM and asphalt binder for rubberized mixtures in dry process and to see if the binder properties from dry process can reach to those in wet process. Two types of hot mix asphalt with CRM in dry process were mixed and stored in oven for 0, 30, 60 and 90 min. Binders were extracted from the mixtures and tested using GPC and FTIR. Some conclusions are drawn as follows:

1. The LMS of extracted asphalt binders from the rubberized PEM and SMA in dry process, increased as the storage time increased. This trend was found for both rubberized PEM and SMA. After 90-min storage, the extracted binders from mixes with dry process showed a similar LMS to that from the wet process.
2. The ratio of bonding, carbonyl index (C=O) of the binders extracted from rubberized PEM in dry process increased as the storage time increased, but increased much quicker in the early than the late storage times.
3. There was interaction of CRM and binders, especially in the late storage time, when the aging index kept minor increased and the LMS still increased steadily. In other words, partial of the reasons that LMS increased was the interaction of the CRM and binders.
4. The GPC and FTIR test results on the extracted binders in dry after 45 min storage were similar to those of CRM binders in wet process. The extracted binders from PEM and SMA in dry process could perform the same as those from wet process after storage with regarding to GPC and FTIR.

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