Construction and Building Materials 123 (2016) 847–854

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Chemical and rheological investigation of high-cured crumb rubber-modified asphalt

Naipeng Tang, Weidong Huang *, Feipeng Xiao

The Key Laboratory of Road and Traffic Engineering, Ministry of Education, Tongji University, Shanghai 201804, PR China

HIGHLIGHTS

- Active Polymer Index was defined to characterize the curing process of CRM Asphalt.
- Interaction temperature contributed more to the degradation than interaction time.
- There was linear relationship between chemical and rheological properties.
- API derived from ATR-FTIR test is a good indicator of degradation of crumb rubber.

ARTICLE INFO

Article history:
Received 28 April 2016
Received in revised form 18 June 2016
Accepted 26 July 2016

Keywords:
High-cured CRM asphalt
Degradation
ATR-FTIR
Active Polymer Index
Elastic recovery

ABSTRACT

In the production of Terminal Blend (TB) rubberized asphalt, degradation of crumb rubber in asphalt matrix can help improve the storage stability and workability of crumb rubber modified asphalt. However, degradation process of crumb rubber modified (CRM) binders was not clear from molecular components to rheological properties. This study investigated chemical and rheological perspectives of the degradation process of CRM asphalt under high interaction temperature (220–280 °C) and extended curing time (2–8 h), namely high-cured CRM asphalt. Attenuated Total Reflection (ATR) Fourier Transform Infrared (FT-IR) Spectroscopy was used to characterize the degradation behaviors of CRM binders at varying curing temperatures and times. Active Polymer Index (API) was defined as the ratio between band areas at 978–918 cm^{-1} and 850–785 cm^{-1} of FTIR tests to characterize the released active polymer from vulcanized crumb rubber. Besides, dynamic shear rheometer (DSR) was used to perform elastic recovery (ER) test, dynamic oscillatory test and multiple stress creep recovery (MSCR) test. Test results indicated that the critical degradation temperature was 260 °C in this limited study. Interaction temperature contributed more to the degradation than interaction time. Pearson correlation analysis indicated that API derived from ATR-FTIR test was a good indicator of degradation of CRM binders.

1. Introduction

Crumb rubber has been used in pavement industry over 50 years. Traditional wet-process technique, such as Asphalt Rubber, has shown disadvantages in storage stability and workability [1]. Attempts have been made to improve the storage stability or decrease the viscosity of crumb rubber modified (CRM) asphalt through various physical and chemical methods. Additives like vegetable oil, warm mix asphalt additives (Rediset and Evotherm) and bio-binder were found to effectively decrease the viscosity of CRM asphalt [2,3]. Activated or treated crumb rubber by using chemicals like furfural ($C_5H_4O_2$) and polymeric compatibilizer were proved to improve the storage stability of CRMA significantly [4,5]. Besides, storage stability of CRMA can also be improved by using high shear method or using finer powdered rubber (200 mesh) [6,7]. Most of the above studies were concerned with the partial degradation of crumb rubber in asphalt matrix.

In recent years, Terminal Blend (TB) rubberized asphalt technology arose in America has shown its potential in greatly improving storage stability of rubber/asphalt composite because crumb rubber is fully digested into the asphalt, while maintaining considerable performance in pavement practice. Full scale projects and heavy vehicle simulator testing in California indicated that fatigue performance of TB rubberized asphalt is better than that of asphalt rubber and base binder [8]. The FHWA's Accelerated Loading Facility (ALF) testing results indicated that Texas TB rubberized asphalt offer better rutting resistance than Arizona wet process asphalt rubber when the latter provide better fatigue performance [9]. It was reported that the production of TB rubberized asphalt can be

* Corresponding author.
E-mail address: hwd@tongji.edu.cn (W. Huang).

http://dx.doi.org/10.1016/j.conbuildmat.2016.07.131
0950-0618/

achieved through degradation of crumb rubber in asphalt matrix using heat and shear, meanwhile polymers might be added to the degraded rubber/asphalt composite to meet the performance grade criteria [10].

It has been confirmed by various research that degradation of CRM binders can affect rheological properties significantly [11–13]. Meanwhile, molecular weight distribution and molecular structure present remarkable change from micro perspective [12,14]. It would be better to understand the degradation mechanism through qualitative or quantitative analysis of molecular weight distribution and molecular structure in combination with rheological investigations. The current research on molecular weight distribution of CRM binders can't fully characterize the rubber/asphalt composite as some dissoluble rubber components were removed by syringe filter before Gel Permeation Chromatography (GPC) test [15]. As a rapid test method, Fourier Transform Infrared Spectroscopy (FT-IR) gains popularity and quantitative analysis using FT-IR has been successfully applied to polymer modified asphalt [16]. However, FT-IR was mostly used to qualitatively detect the released rubber components into asphalt [14,15]. The study of degradation process of crumb rubber in asphalt matrix is limited.

The objective of this study is to investigate degradation process of high-cured CRM binders in terms of their chemical and rheological properties. Attenuated Total Reflection (ATR) Fourier Transform Infrared (FT-IR) Spectroscopy is used to explore the main element components of CRM binders at varying reacting temperatures and times. Active Polymer Index (API) is employed to characterize the released active polymer content from the vulcanized crumb rubber. Dynamic Shear Rheometer (DSR) is used to perform elastic recovery (ER) test, dynamic oscillatory test and multiple stress creep recovery (MSCR) test in this study.

2. Materials and methods

2.1. Materials

One PG 64-22 base binder provided by ESSO Asphalt Company and one minus 30 mesh crumb rubber provided by China Rubber Resource Regeneration were used to prepare high-cured CRM binders. A 20% crumb rubber (by the weight of total binder) was mixed with base binder at four temperatures of 220 °C, 240 °C, 260 °C and 280 °C for 2, 4, 6 and 8 h. The blending speed was 400 rpm. The preparation of samples was reported by Abdelrahman [11], Billiter [12], Zanzotto [13] and Flanigan [17]. Besides, crumb rubber modified asphalt produced by adding 18% crumb rubber to base binder, blending for 0.5 h at 190 °C was served as a control binder in the aftermentioned FT-IR analysis. The detailed test samples are presented in Table 1. For example, for binder blended at 220 for 2 h, the produced binder is marked as E22.2 in Table 1. As storage stability is very important for engineering use, the separation test were performed for each sample through keeping an aluminium tube containing 50 ± 0.5 g binder at 163 °C for 48 h according to ASTM D7173. The top and bottom parts of the tube were collected for softening point test (ASTM D36) and the softening point difference between the top and bottom is used as an index to evaluate the storage stability. In China, if the difference is less than 2.5 °C, the binder is considered to have good storage stability. The storage stability test results are presented in Table 2. On the whole, increasing interaction temperature and extending curing time will help to improve the storage stability.

Table 1
Description of the test samples.

80% base binder + 20% crumb rubber				
Blending temperature	Blending time			
	2 h	4 h	6 h	8 h
220 °C	E22.2	E22.4	E22.6	E22.8
240 °C	E24.2	E24.4	E24.6	E24.8
260 °C	E26.2	E26.4	E26.6	E26.8
280 °C	E28.2	E28.4	E28.6	E28.8

Table 2
Storage stability test results.

Blending temperature	Softening point	Blending time			
	°C	2 h	4 h	6 h	8 h
220 °C	Up	67.3	58.3	69.6	58.9
	Bottom	68	61.9	68.2	55.7
	Difference	−0.7	−3.6	1.4	3.2
240 °C	Up	53.4	47.4	54.7	51.3
	Bottom	57.6	50.3	54.2	49.2
	Difference	−4.2	−2.9	0.5	2.1
260 °C	Up	49.1	48.2	44.8	47.3
	Bottom	52.3	49.9	46.8	48.2
	Difference	−3.2	−1.7	−2	−0.9
280 °C	Up	49.1	48.5	46.1	47.5
	Bottom	50.8	49	45.5	46.8
	Difference	−1.7	−0.5	0.6	0.7

2.2. Attenuated Total Reflection (ATR) Fourier Transform Infrared (FT-IR) Spectroscopy

The infrared spectra values were collected using a Bruker TENSOR FT-IR spectrometer equipped with a reflection diamond ATR accessory. About 1 g asphalt binder was put on the surface of ATR diamond and fixed using the steel loader. The asphalt binder completely contacted the diamond homogenously. Thirty-two scans were averaged within the wavenumber range of 4000–600 cm^{-1} for each sample and then these average spectrum values were obtained. In this study, the peak at 965 cm^{-1} attributed to C—H out of plane bending of *trans*-alkene showed a significant change during the interaction process of high-cured CRM asphalt. As FTIR peak intensities are sensitive to the concentration of components and the thickness of the sample [14], it would be better to normalize the band areas between 978 and 918 cm^{-1} to eliminate the effect of sample thickness on FTIR results. In this study, the peak at 810 cm^{-1} attributed to C-H out of plane bending of aromatics in base binder was found to vary little in terms of band areas and it has been successfully used as a reference peak in the quantitative analysis of SBS modified asphalt [18]. In this study, band areas between 978 and 918 cm^{-1} (AR_{965}) were divided by that of 850–785 cm^{-1} (AR_{810}) and the ratio is defined as Active Polymer Index (Eq. (1)).

$$\textbf{Active Polymer Index (API)} = AR_{965}/AR_{810} \quad (1)$$

The AR_{965} and AR_{810} were calculated in Thermo Scientific OMNIC™ software automatically. The integration scopes were from 978 to 918 cm^{-1} for 965 cm^{-1} and 850 to 785 cm^{-1} for 810 cm^{-1} (Fig. 1). Band areas values rather than peak absorbance were used in this study because band areas varied little within three replicates of each sample [19]. The carbonyl index was also calculated to investigate the aging status of high cured CRM binders during the preparation. The calculation method was similar to that of API and the integration scopes for carbonyl were from 1678 to 1725 cm^{-1}. The base binder