A study on the oxidation kinetics of warm mix asphalt

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HIGHLIGHTS

- WMA oxidation kinetics parameters follow the same correlations for conventional binders.
- Activation energies show statistically insignificant differences between the base binder and its WMA.
- Pavement aging simulations reveal no adverse oxidative aging effects from WMA additives.

ARTICLE INFO

ABSTRACT

Warm mix asphalt (WMA) is increasingly used in pavements to reduce energy consumption and emissions, and to extend workability times. Literature reports on warm mix asphalt have addressed its usage, but its oxidation kinetics and possible effects on pavement durability are unknown. In this work, several popular types of WMAs were used in multi-temperature experiments to estimate oxidation kinetics parameters of an Arrhenius reaction model. Additionally, an example pavement aging simulation explored the potential effects of differences in activation energy on pavement aging.

Constant rate activation energies show statistically insignificant differences between the base binder and its WMAs; additionally, for each WMA material all four kinetics parameters follow the same correlations previously established for 15 non-WMA binders. These results suggest no adverse effect of WMA additives on asphalt oxidation, compared to the base binder. An example pavement binder oxidation simulation specific to Lubbock, Texas indicates that first, between a base binder and its corresponding WMAs, differences in pavement oxidation over 10 years of pavement service would be minimal and second, oxidative hardening may (or may not) slow the overall reaction rate as diffusion resistance increases, depending on the balance between diffusion and reaction rates.

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1. Introduction

Warm mix asphalt (WMA) technologies, with significantly reduced mixing and compacting temperature, have been attracting increased attention in recent years. Deploying WMA technology in the asphalt industry promises economic benefits (reduced fuel consumption and extended paving season) plus technical convenience (enhanced compaction and increased haul distances). Popular warm mix additives include emulsion based additives, chemical additives, and synthetic additives. Much effort has been made towards understanding the effects of WMA technology on pavement performance [1–5]. In particular, warm mix asphalt oxidative aging resulting in pavement fatigue failure, is now recognized as an important factor in pavement design [6–8]. It has been shown that some warm mix asphalt binders demonstrated changed rheological behavior after long-term aging [7–9]. The driving force of these rheological changes is the chemical reaction of asphalt and oxygen, i.e. asphalt oxidative aging. Thus, quantitatively understanding oxidative aging and consequent hardening, is key to predicting changes in rheological behavior. However, previous studies of warm mix asphalt focused on mechanical properties for limited aging states (e.g. one short-term aging state and one long-term aging state) with no work on WMA oxidation kinetics [10–14].

A fundamental understanding of oxidation kinetics is important because of the significant role that oxidation plays in causing changes to asphalt physical and chemical properties, changes that lead to irreversible binder embrittlement and reduced pavement life [15]. On the other hand, understanding oxidation chemistry and kinetics is complicated by the fact that the asphalt oxidative aging procedure is complex because of the diversity of molecular types and the variation of oxidation rate affected by temperature, pressure, chemical composition (specific binder), and oxygen

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diffusivity [16–19]. Because of its importance to pavement durability and complexity, the goal of understanding asphalt oxidation fundamentals has attracted significant work from researchers over several decades when many studies have been conducted to explore, describe and predict asphalt physicochemical properties and chemical reaction mechanisms [20–25]. One significant discovery is that the carbonyl area (CA), measured in the infrared spectrum as the absorbance peak area above the 1820 cm^{-1} baseline and from 1820 to 1650 cm^{-1}, has been reported to relate linearly to the amount of oxygen reacted with asphalt [26]. Furthermore, for each asphalt material, there is a specific correlation between the carbonyl area growth and rheological hardening (measured by the low shear rate viscosity or by the DSR function defined by Ruan et al. (2003), recently redefined and termed the Glover–Rowe parameter [27–29]), which links asphalt oxidation kinetics to rheological hardening. Additionally, studies showed that asphalt oxidation could be represented by two parallel reaction processes at constant temperature: a nonlinear fast-rate reaction path and a linear constant-rate path [15,26]. A theoretical model to describe both of these processes, and a method for estimating the kinetics parameters of the model has been reported [21]. The kinetics parameters can be used in a pavement oxidation model to predict asphalt aging in pavements over time and as a function of depth, for climates of choice [30]. However, previous kinetics research has focused only on hot mix asphalt materials with no reports on the oxidation kinetics of WMA materials.

The principle objective of this work was to study the oxidation kinetics of warm mix asphalt materials by aging a PG 70-22 base binder with and without warm mix additives and to assess the potential impact of differences on pavement oxidation using a pavement oxidation model. Changes in CA under multiple time/temperature combinations provided kinetics parameters to be used in a pavement oxidation kinetics model.

2. Materials and methods

2.1. Materials

An unaged polymer modified PG 70-22 binder was blended with three typical WMA additives (emulsion, chemical and synthetic zeolite) used in Evotherm, Rediset and Advera WMA products. For binder preparation, the base binder was pre-heated in a 140 °C oven for 30 min and distributed into 1 L cylindrical metal containers. During the heating process, nitrogen was purged in to the oven to prevent binder oxidation. WMA additives were then blended for 5 min at recommended concentrations, as shown in Table 1. The same base binder was also included in all the following experiments as a control.

CA_{tank} values, representing initial aging states, are summarized in Table 1. The values of CA_{tank} ranged from 0.541 arbitrary units (a.u.) to 0.598 a.u., a much tighter range than has been previously reported for different base binders (and not unexpected considering that all materials in this study used the same base binder) [21].

Table 1
Asphalt sample preparation.

Asphalt	WMA additives	WMA additive concentration (weight percent of asphalt)	CA_{tank}
PG 70-22	N/A*	N/A*	0.559
PG 70-22	Emulsion	0.50%	0.583
PG 70-22	Zeolite	0.25%	0.552
PG 70-22	Chemical	0.25%	0.541

Note: *Base binder control without warm mix additives.

2.2. Aging procedure

Asphalt oxidation was conducted in pressure oxygen vessels (POV) designed for more precise temperature control than conventional ovens. Asphalt binders were poured into 4 cm × 7 cm aluminum trays so that the mass of the binders on each tray was 2.4 ± 0.05 g. The average thickness of the binder was close to 0.8 mm. It has been shown that this thickness adequately reduces oxygen diffusion resistance for kinetics measurements at constant temperature [26]. Samples were kept on racks in four different POVs with 1 atm air, each at at a different temperature (333–371 K) for up to 90 days. Each POV was immersed in a continuously stirred triethylene glycol (TEG)/water constant-temperature bath, at 333, 346, 359 or 371 K, with temperature fluctuations of ±0.6 K. Moreover, fresh preheated air was purged into the vessel to maintain the oxygen concentration of fresh air. As the binders in the POVs aged at different rates corresponding to their temperatures, samples were collected for testing according to the schedule in Table 2.

2.3. Characterization

A Thermo Scientific Nicolet 6700 Fourier-Transform Infrared (FTIR) spectrometer with an attenuated total reflectance (ATR) zinc selenide prism was used to measure carbonyl (C=O) area. In this procedure, the asphalt sample was softened by heating on a hot-plate and then applied to the prism. The CA (arbitrary units), defined as the peak area above the 1820 cm^{-1} baseline and from 1820 to 1650 cm^{-1}, has been used as a direct indicator of asphalt oxidation that relates directly to changes in binder rheology [24,31,32].

3. Results and discussion

3.1. Carbonyl area and asphalt oxidation

CA values, were measured for asphalt samples aged to different times at different temperatures. Fig. 1 shows the CA growth over time of the base binder and WMA binders. The CA growth for 15 asphalt binders at constant temperature has been characterized as a non-linear fast-rate reaction in parallel with a linear constant-rate reaction. CA growth of a PG 70-22 binder selected for this study, either with or without warm mix additives, was consistent with this fast-rate, constant-rate model. These CA values, together with the aging time and temperature, provided the necessary data for estimating the kinetics parameters for this kinetics model, described below.

3.2. Kinetics model optimization

According to the fast-rate, constant-rate oxidation kinetics model [21], asphalt oxidation, represented by carbonyl area (CA) growth, can be described by the following equations reflecting the combined fast-rate, constant-rate parallel reaction processes:

$$CA = CA_{tank} + M(1 - e^{-k_f t}) + k_c t \tag{1}$$

Table 2
Sampling timeline for asphalt at different aging temperatures.

Aging temperature (K)	Aging time (days)
333	2, 5, 10, 20, 35, 55, 90*
346	1, 3, 5, 8, 15, 30, 50
359	1, 2, 4, 6, 10, 20, 30
371	1, 2, 4, 6, 10, 20

Note: *90 day test only performed on base binder and one warm mix asphalt binder.