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# Reaction of asphalt and maleic anhydride: Kinetics and mechanism

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ABSTRACT

Reaction of asphalt and maleic anhydride (MAH) was investigated by FTIR and chemical titration. FTIR results indicated that chemical reaction between asphalt and MAH did occur, and the cyclic anhydride band in MAH retained during the reaction. Kinetics of the reaction was analyzed by model fitting method when the influence of diffusion was excluded by $L_9$ ($3^4$) orthogonal array design. Consequently, models of 3-order reaction and John–Mehl–Avrami (JMA, 1/4) were both justified to be the most possible mechanism functions (MPMFs) of this reaction. The two MPMFs could be understood from diverse viewpoints. Apparently, since the molecular dimension of reaction product enlarged during the reaction, JMA equation was introduced to simulate the process, and Avrami exponent exhibited the disassociation of asphaltenes with temperature. Essentially, from the viewpoint of chemical reaction, 3-order reaction model demonstrated that the reaction occurred not through the single mechanism of Diels–Alder, alternating copolymerization or charge transfer (CT) but through the compound of them; besides, CT mechanism was the basic one. These results provide a new approach to improve the performances of asphalt by CT mechanism and a kind of novel reactive asphalt useful for advanced researches and technologies.



## 1. Introduction

Asphalt is the most widely used road paving materials. To reduce its thermal susceptibility and permanent deformation, kinds of polymer modifiers for asphalt have been developed. Usually, these polymer modifiers include SBS (styrene–butadiene–styrene block copolymer) [1–3], PE (polyethylene) [4,5], EVA (ethylene–vinyl acetate) [6], EBA (ethylene–butyl acrylate) random copolymers [7], etc. Due to its high strength and stiffness, the orthotropic steel deck system has been widely used in the construction of long-span steel bridges. Unfortunately, its pavement has not been well solved for the stresses and deformations of the steel deck bridges are much more complex than those of the highways. Asphalt composites paved on steel deck bridges should provide a high resistance to extreme ambient temperature from −20 °C (winter) to 70 °C (summer), wear and the wide variety of solvents that come into contact with such surfaces, and a flexibility with the vibration of steel decks. Moreover, they must meet all the foregoing requirements without adversely affecting the skid properties, traction strength and final hardness of the surfaces. Although the above-mentioned modifiers results in somewhat improvement of the properties of the asphalt concrete, they cannot satisfy the rigorous demands of the steel deck bridge surface paving for their thermoplastic natures.

Recently, thermosetting epoxy resin modified asphalt (named epoxy asphalt) has attracted much attentions [8,9] for its predominant performances paved on the demands-rigorous orthotropic steel deck bridges [10]. Epoxy asphalt [11–14] has been broadly investigated in last four decades. Nevertheless, asphalt and epoxy resin, asphalt and curing agents of epoxy resins tend to separate from each other due to their poor compatibility which reduced the stability of their performances.

Stable and high performances epoxy asphalt composites have been prepared by curing epoxy resin with curing agents system made up of maleated asphalt (reaction mixture of asphalt and MAH), dicarboxylic acid and liquid anhydride [15–18]. It is believed that maleated asphalt could be cured by epoxy resin so as to improve the compatibility of asphalt and epoxy resin, moreover, maleated asphalt could present many short chains that would enhance the cured composites' intensity, according to the bimodal networks theory [19–21].

Although the reaction of asphalt and MAH has been studied to obtain better paving performances [15–18,22], the reaction mechanism is still unclear. Philip et al. [23] reported that the reaction of asphaltene and MAH probably underwent a Diels–Alder mechanism, while Boucher et al. [24] suggested that MAH likely formed alternating copolymers with bitumen species. However, there was no persuasive evidence to prove the existence of alternating copolymers or Diels–Alder products because of the complexities of asphalt species and their structures. According to the often-cited Yen model of asphaltene [25,26], asphaltenes form almost

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**Table 1**
Asphalt properties and test method.

| Asphalt properties | | Method |
|---|---|---|
| *Crude source: Saudi Arabia* | | |
| Density @ 15 °C/g cm$^{-3}$ | 1.034 | JTJ 052 T0603-1993 |
| Penetration @ 25 °C/0.1 mm | 68.0 | JTJ 052 T0604-2000 |
| Softening point (°C) | 48.5 | JTJ 052 T0606-2000 |
| Viscosity at 60 °C/Pa s | 218.2 | JTJ 052 T0625-2000 |
| Ductility @ 15 °C/cm | >150 | JTJ 052 T0624-1993 |
| Flash point (°C) | 328 | JTJ 052 T0611-1993 |
| Fraass brittle point (°C) | −17.5 | JTJ 052 T0613-1993 |
| SARA fractions | | |
| Saturates (%) | 12.6 | |
| Aromatics (%) | 54.7 | JTJ 052 T0618-1993 |
| Resins (%) | 22.1 | |
| Asphaltenes (%) | 10.6 | |

planar molecules that can associate through π–π bonding to form graphite-like stacks, and polynuclear aromatics behave as donors (D) in charge transfer (CT) processes owing to the presence of the substituted alkyl groups. Also, the latest research shows that asphaltene forms π–π charge transfer complexes (CTCs) with kinds of charge acceptors (A), such as *o*- and *p*-chloranils [27], pyromellitic acid, nitrobenzoic acid [28]. Usually, MAH reacts through two special mechanisms, one is Diels–Alder mechanism and the other is π–π CT mechanism. The electron cloud of C=C in MAH is largely shifted to its two electron-withdrawing O atoms of C=O, which made MAH act as π-electron acceptor (A) [29]. Thus, the reaction is probably underdone by CT mechanism. Moreover, in the reaction of asphaltenes and MAH, compared with Diels–Alder products and alternating copolymers, CTCs form more likely and easily because they are non-bonding interacted, relatively simple composites. Therefore, we propose that asphalt and MAH reacted, at least in part, through CT mechanism.

In the present paper, to understand the reaction of asphalt and MAH better, it was investigated by FTIR and kinetic analyses. Kinetics of this reaction was analyzed by "master plot" method when the influence of the diffusion was excluded by $L_9$ ($3^4$) orthogonal array design. John–Mehl–Avrami equation and 3-order reaction model were selected to interpret the heterogeneous reaction of asphalt and MAH, and kinetic parameters, such as apparent reaction active energy (*Ea*), and exponent factor (*A*) and order of reaction (*n*) or the Avrami exponent (*n*), were obtained.

## 2. Experimental

### 2.1. Materials

Maleic anhydride (Shanghai Chemical Reagent Co., Ltd., 99.9% purity) was used as received. Properties of Saudi Arabia asphalt used are given in Table 1.

### 2.2. Reaction procedure

Reactions were carried out in a $N_2$ protected wide-mouthed glass flask fitted with a mechanical stirrer, reflux condenser (75–85 °C warm water refluxing) and thermocouple. Asphalt was heated to reaction temperature (120–160 °C) and MAH added at one time and reacted for a period of time (4–6 h) with the given constant stirring rate. The specimens were removed at intervals up to 5 h when MAH added and stored in airtight containers at ambient temperature. Control experiments were carried out as above procedure with the omission of MAH.

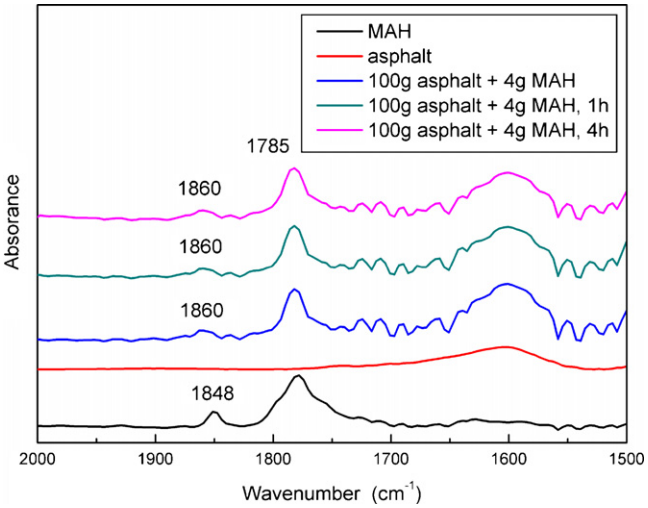


**Fig. 1.** Infrared spectra (offset on the absorbance axis) of MAH, asphalt, MAH–asphalt blend, and MAH–asphalt 1 h and 4 h, 150 °C, reaction mixtures (all samples were dissolved in $CHCl_3$, 0.1 g sample/100 ml $CHCl_3$).

### 2.3. Titration of MAH conversion

MAH is perfectly soluble in the mixture of water and ethanol (volume ratio, 1:1), thus the free MAH could be extracted from a petroleum ether (boiling range, 90–120 °C) solution of the reaction mixture. (To increase the separation efficiency, separatory funnels should be warmed in a 45–55 °C water bath.) The extract was titrated with aqueous KOH to a phenolphthalein end point [30,31]. Then, the content of free MAH could be counted by

$$\%\mathrm{MAH} = \frac{\mathrm{ml\ KOH} \times \mathrm{N\ KOH} \times 4.90}{\mathrm{Sample\ weight,\ g}}, \quad (1)$$

where N represents molar concentration of KOH (mol/L). Control titrations of the neat asphalt and the aged neat asphalt were carried out as above procedure.

### 2.4. Infrared spectra

Infrared spectra were recorded using a dry $CO_2$-free air purged Avartar 360 FTIR Spectrometer (Nicolet). About 0.1 g of sample was dissolved in 100 ml $CHCl_3$ to attain a sample solution. Thin films of asphalt were prepared by dropping fixed quantity with microliter syringe on KBr plates. Band assignments were made on the basis of values tabulated in the literature [32].

## 3. Results and discussion

### 3.1. Infrared spectra

The bands of C=C (900–1000 cm$^{-1}$) were covered by the asphalt vibration bands, so IR spectra of MAH, asphalt, MAH–asphalt blend, and the reaction mixture of MAH–asphalt 1 h and 4 h (150 °C, 0.1 g/100 ml $CHCl_3$) are presented from 1500 cm$^{-1}$ to 2000 cm$^{-1}$ in Fig. 1. MAH shows characteristic cyclic anhydride peaks at 1785 cm$^{-1}$ and 1848 cm$^{-1}$, and asphalt has no peak from 2000 cm$^{-1}$ to 1700 cm$^{-1}$. When MAH and asphalt were blended (at room temperature) and dissolved in $CHCl_3$, peak of 1785 cm$^{-1}$ has almost no change, but peak of 1848 cm$^{-1}$ has a 12 cm$^{-1}$ red shift to 1860 cm$^{-1}$. However, when they were heated for 1–4 h at 150 °C, the IR spectra are almost the same as that of MAH–asphalt blend in room temperature. The shape of peaks has no change between co-blend and two reaction products. Also, several peaks of MAH–asphalt blend and the two reaction mixtures were observed in the bands of 1500–1700 cm$^{-1}$. Generally, bands of