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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	JTJ 052 T0618-1993
Aromatics (%)	54.7	
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.

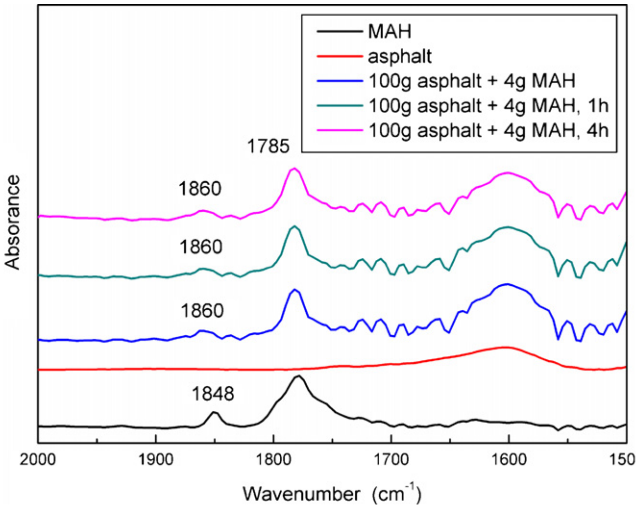

Fig. 1. Infrared spectra (offset on the absorbance axis) of MAH, asphalt, MAH–asphalt blend, and MAH–asphalt 1 h and 4 h, 150 °C, reaction mixtures (all samples were dissolved in $CHCl_3$, 0.1 g sample/100 ml $CHCl_3$).

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

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

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

Table 2
Results of DTT with various prescriptions (4 h @ 120 °C) [15].

Sample	Prescription of Component B	Rupture elongation (%)	Tensile strength (MPa)
1	4%MAH, 0.3%accelerant	281.9	2.63
2	4%SAH, 0.3%accelerant	Fail to cure	

1500–1700 cm^{-1} were ascribed to characteristic peaks of aromatic compounds. These results indicated that reactions between MAH and asphalt occurred, and the cyclic anhydride retained during the reaction.

Obviously, these results differ from that of Philip's [23]. But advanced mechanical control experiments [15] verified these FTIR results, as shown in Table 2. No. 1 sample of epoxy asphalt composite was prepared by curing epoxy resin (Component A) with curing agents system (Component B) made up of maleated asphalt (reaction mixture of asphalt and MAH), dicarboxylic acid and liquid anhydride. No. 2 sample was prepared by curing epoxy resin (Component A) with the same prescription to sample 1 except that maleated asphalt was replaced by reaction mixture of asphalt and succinic anhydride (SAH) (prepared by the same reaction procedure to maleated asphalt). The direct tensile testing (DTT) results implied that the reaction mechanism of MAH and asphaltene(s) lies not in the opening of anhydride, but in the special reaction between double bond of MAH or the whole MAH molecule and asphaltene(s).

However, by far, it is hard to conclude that the exact mechanism is Diels–Alder, alternating copolymerization or CT mechanism (as shown in Fig. 2). Luckily, we are sure that the reaction is of 2-order reaction when they reacted through Diels–Alder mechanism. Therefore, kinetics was analyzed hereafter.

3.2. Reaction kinetics

Aggregated asphaltene micelles form a colloidal dispersion in the maltenes [33,34], while MAH (120–160 °C) is a liquid incompatible with saturates in asphalt. In other words, the reaction is a liquid–liquid heterogeneous reaction. To examine intrinsic reaction kinetics of asphalt and MAH, we firstly excluded influence of external diffusion during this reaction-diffusion process by increasing stirring rate.

Table 3
Factors and levels of the L_9 (3^4) orthogonal experiments.

Level	Factors			
	T (°C)	C_0 (g MAH/100 g asphalt)	Ss (rpm)	Error
1	120	2	200	
2	140	4	600	
3	160	6	1000	

3.2.1. External diffusion

Conversion of MAH, namely, the reacted fraction at time t, is represented by

$$\alpha = \frac{C_0 - C}{C_0} \times 100\%, \tag{2}$$

where C is concentration of MAH (g MAH/100 g asphalt); C_0 is initial concentration of MAH (g MAH/100 g asphalt). Usually, reaction temperature (T), stirring speed (Ss) and initial MAH concentration (C_0) all affect ultimate conversion of MAH (α_u); and Ss relates to external diffusion. To illuminate rate-controlling step of this process, the 4-factor, 3-level, usually noted as L_9 (3^4), orthogonal array design (OAD) experiments [35] were applied (Table 3). The effects of the above three factors on α_u were analyzed by range analysis and analysis of variance (ANOVA), as shown in Tables 4 and 5. Range analysis (Table 4) indicates that α_u was strongly depended on T in the range of experimental spaces. ANOVA (Table 5) verified results of range analysis that influences of Ss and C_0 on α_u was the same as experimental error. It is concluded that the rate-controlling step of this process is not diffusion in the experimental space.

Table 4
Results and range analysis of the L_9 (3^4) orthogonal experiments.

Order	T (°C)	C_0 (g MAH/100 g asphalt)	Ss (rpm)	Error	α_u
1	1	1	1	1	77.7
2	1	2	2	2	72.4
3	1	3	3	3	73
4	2	1	2	3	84.65
5	2	2	3	1	85.67
6	2	3	1	2	85.34
7	3	1	3	2	92.27
8	3	2	1	3	90.98
9	3	3	2	1	92.31
I/3	74.36667	84.87333	84.67333	85.22667	
II/3	85.22	83.01667	83.12	83.33667	
III/3	91.85333	83.55	83.64667	82.87667	
Range	17.48667	1.856667	1.553333	2.35	

Note: α_u is ultimate conversion of MAH, T is abbreviation of temperature, C_0 is initial MAH concentration and Ss represents stirring rate.

Table 5
ANOVA of factors on ultimate MAH conversion.

	T (°C)	C_0 (g MAH/100 g asphalt)	Ss (rpm)	Error	
Sum of variances	–	–	–	–	754.32
Average of variances	–	–	–	–	83.81333
Sum of squares of variance	155.8598	1.827622	1.248089	3.102067	–
Degree of freedom	2	2	2	2	–
Estimator of variance	77.92991	0.913811	0.624044	1.551033	–
F-value	50.24387	0.589163	0.402341	–	–
Probability	0.980485	0.370738	0.286907	–	–

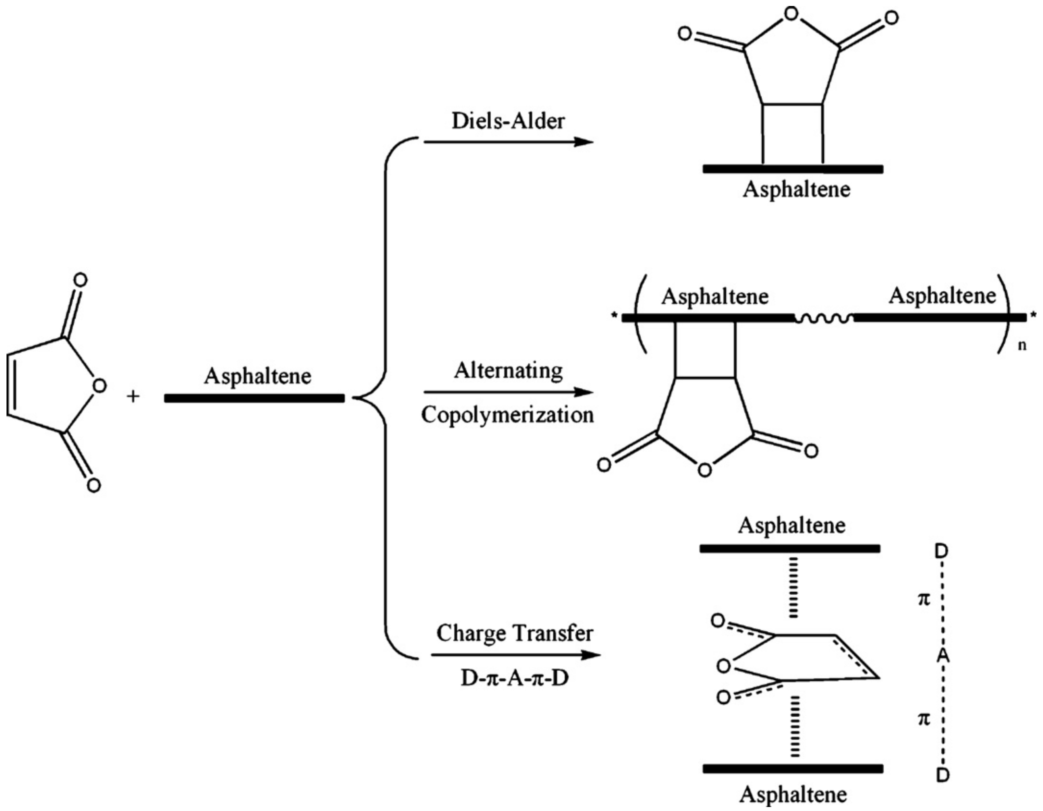

Fig. 2. Possible mechanisms of reaction between asphalt and maleic anhydride.

3.2.2. *Model fitting method*

Having excluded the influence of diffusion, the rate of a heterogeneous reaction can be expressed by means of the following general law:

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \tag{3}$$

where

$$k(T) = A\ \exp\left(-\frac{Ea}{RT}\right), \tag{4}$$

where *f*(α) is a function depending on the reaction mechanism, *Ea* the apparent activation energy, *A* the pre-exponential factor of Arrhenius, and *T* the absolute temperature. Transposing and integrating formula (3), formula (5) is yielded

$$G(\alpha) = \int_0^{\alpha} \frac{d(\alpha)}{f(\alpha)} = k(T)t. \tag{5}$$

Many attempts have been made to determine the mechanism of heterogeneous reactions by using the model fitting method [36]. Mainly, as for isothermal kinetics, plot $G(\alpha) \sim t$ (functions of $G(\alpha)$ were referred from [37]); $G(\alpha)$ with thehighest linearly dependent coefficient (intercepts were fixed to be 0) is the most possible mechanism function (MPMF).

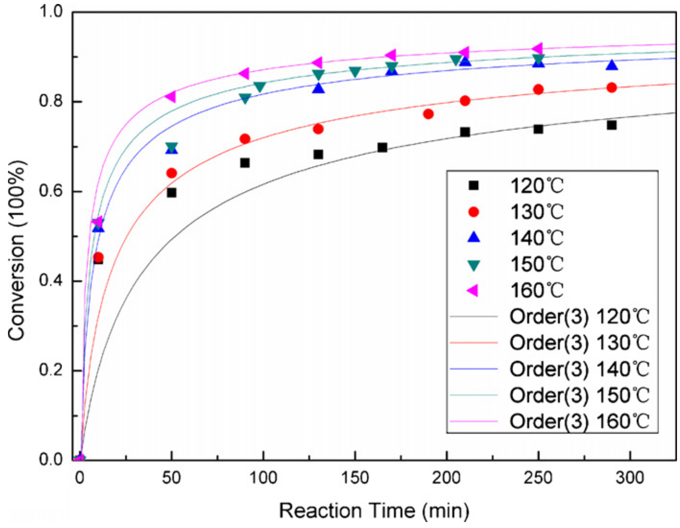

Fig. 3. Fitting results (lines, Order (3)) and experimental data (scatters).

Table 6
Results of linear fitting of JMA (1/4) ∼ *t* and Order (3) ∼ *t* (intercepts are fixed to be 0).

T (°C)	Slope		Error of slope		R^2	
	JMA (1/4)	Order (3)	JMA (1/4)	Order (3)	JMA (1/4)	Order (3)
120	0.01313	0.05792	2.9795E−4	3.38E−03	0.99539	0.97009
130	0.03294	0.11761	0.00165	0.00393	0.97779	0.99006
140	0.08498	0.28963	0.00615	0.02061	0.95963	0.96087
150	0.11359	0.39169	0.00432	0.01325	0.98573	0.98867
160	0.16445	0.59853	0.00333	0.0071	0.99672	0.99888

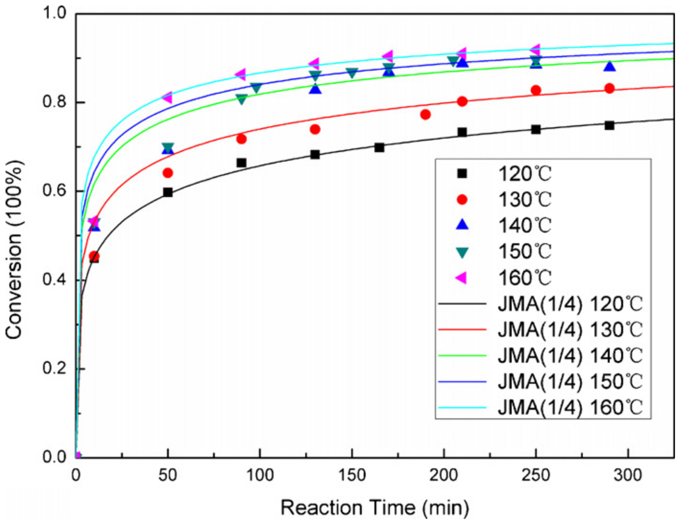

Fig. 4. Fitting results (lines, JMA (1/4)) and experimental data (scatters).

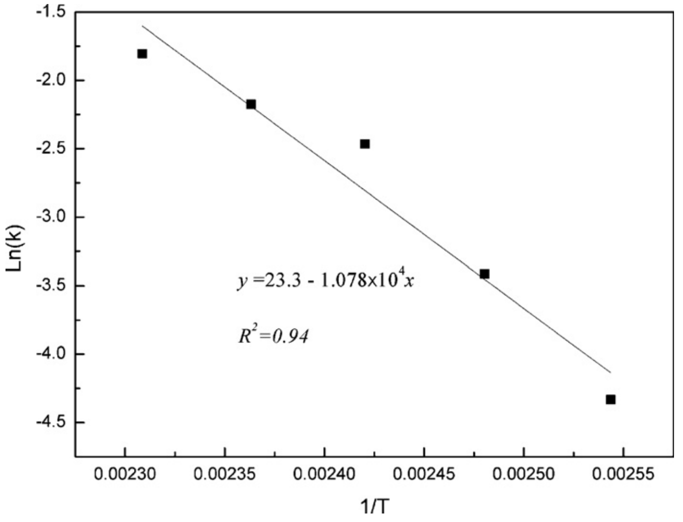

Fig. 5. Function of Ln(k) ~ 1/T of JMA (1/4).

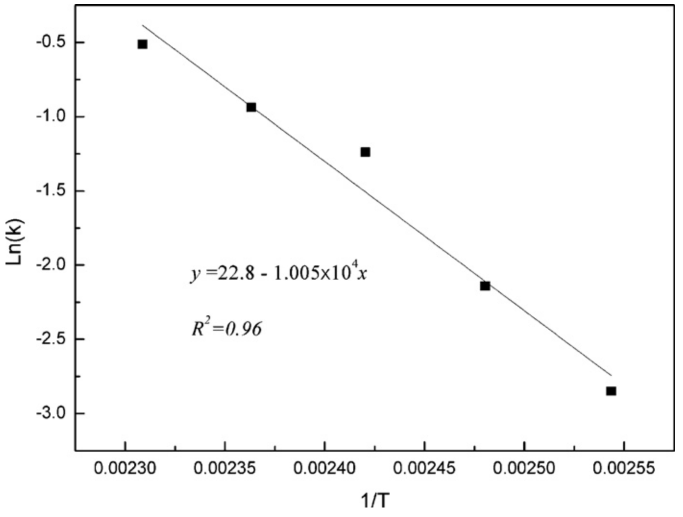

Fig. 6. Function of Ln(k) ~ 1/T of Order (3).

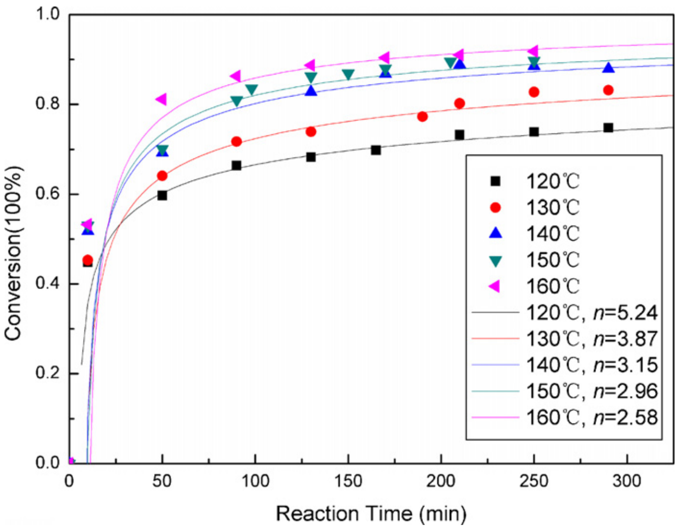

Fig. 7. Refitting in the form of n order reaction and the regression of order n.

Unexpectedly, not 2-order, but both of JMA (1/4) and of Order (3) are qualified to be MPMFs of this process. Figs. 3 and 4 show the fitting results of Order (3), JMA (1/4) and experimental data points at different temperatures, respectively. Table 6 tabulates the ANOVA results of JMA (1/4) and Order (3). These results, especially the 3-order reaction mechanism, do not support the singular Diels–Alder mechanism proposal.

3.2.3. Avrami exponent

JMA (1/4) is

$$G(\alpha) = [-\ln(1-\alpha)]^4. \tag{6}$$

Then, function of $\alpha \sim t$ is described by

$$\alpha = 1 - \exp[-(kt)^{(1/4)}]. \tag{7}$$

Thus, overall reaction rate equation is

$$\frac{d\alpha}{dt} = k(T)\frac{1}{4}(1-\alpha)[-\ln(1-\alpha)]^{-3}, \tag{8}$$

where $k(T)$ was the regressive slope of line $[-\ln(1-\alpha)]^{1/4} \sim t$ (Table 6, JMA (1/4)). And, Ea and A were obtained from linear regression of [ln(k) ~ 1/T] (Fig. 5); that is, $Ea = 89.66\ \mathrm{kJ\,mol^{-1}}$; $A = 7.92 \times 10^{11}\ \mathrm{s^{-1}}$.

Also, from JMA equation

$$G(\alpha) = [-\ln(1-\alpha)]^{1/n} = kt, \tag{9}$$

$$\ln[-\ln(1-\alpha)] = n\ \ln k + n \ln t \tag{10}$$

was deduced, and Avrami exponent n can be achieved from the regressive slope of line $[\ln[-\ln(1-\alpha)] \sim \ln t]$ (as shown in Table 7).

JMA equation is a formal theory used to study solid state reaction processes of random nucleation and growth of nuclei. Here, it was introduced to investigate the reaction of asphaltenes and MAH from the viewpoint of reaction products' dimension enlargement. The value of n, ranging from 0.25084 to 0.39176 (Table 7, slope), tends to rise with the reaction temperature, which suggests that the mechanism of the reaction between asphalt and MAH depends on the reaction temperatures, and moreover, the increasing Avrami exponent n usually means the relative increase of dimensions of new nuclei [38]. Generally, the relative increase of dimensions may be attributed to disassociation of asphaltene, or reaction of asphaltene with multiple MAH molecules simultaneously, or both of them. However, from the perspective of chemistry, repulsive interactions of polar MAH molecules reduce the possibility of reaction between asphaltene with multiple MAH molecules at one time. On the other hand, the higher the reaction temperature, the more energy the molecules have. Thus, asphaltenes have the ability to overcome

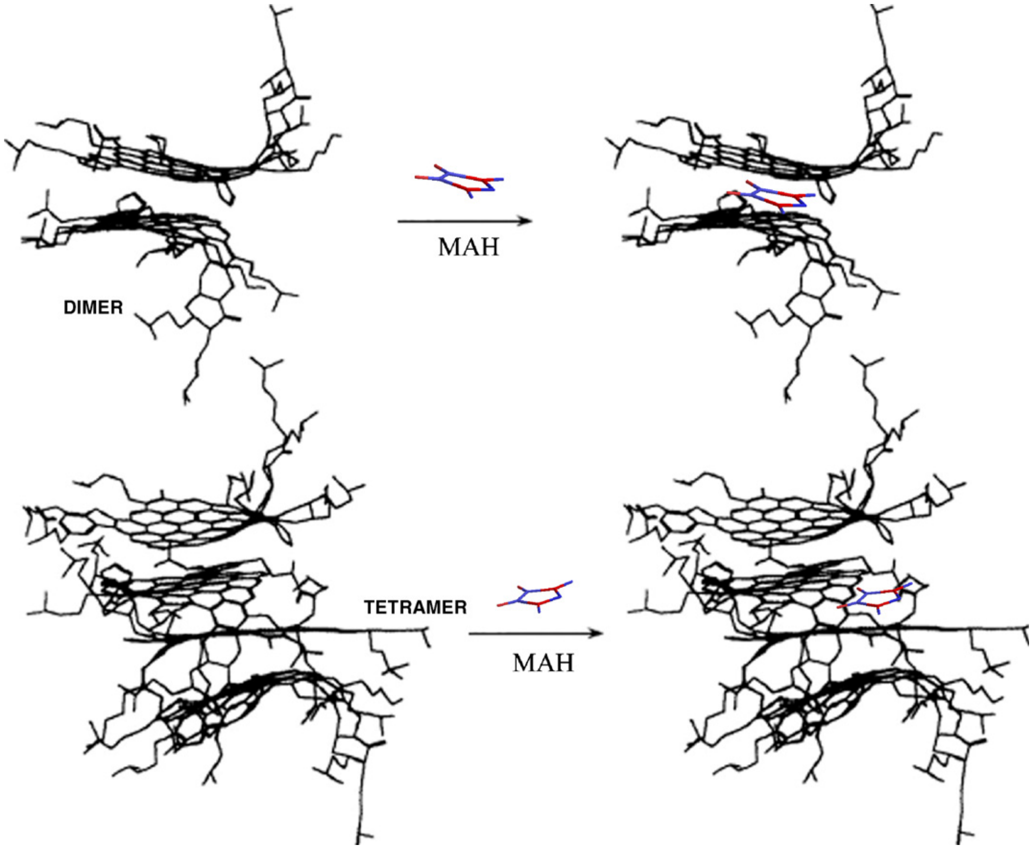

Fig. 8. Formation of π–π charge transfer complexes (D–π–A–π–D) between asphaltene dimer, asphaltene tetramer and MAH. (Models of asphaltene dimmer and asphaltene tetramer were reprinted from Ref. [34].)

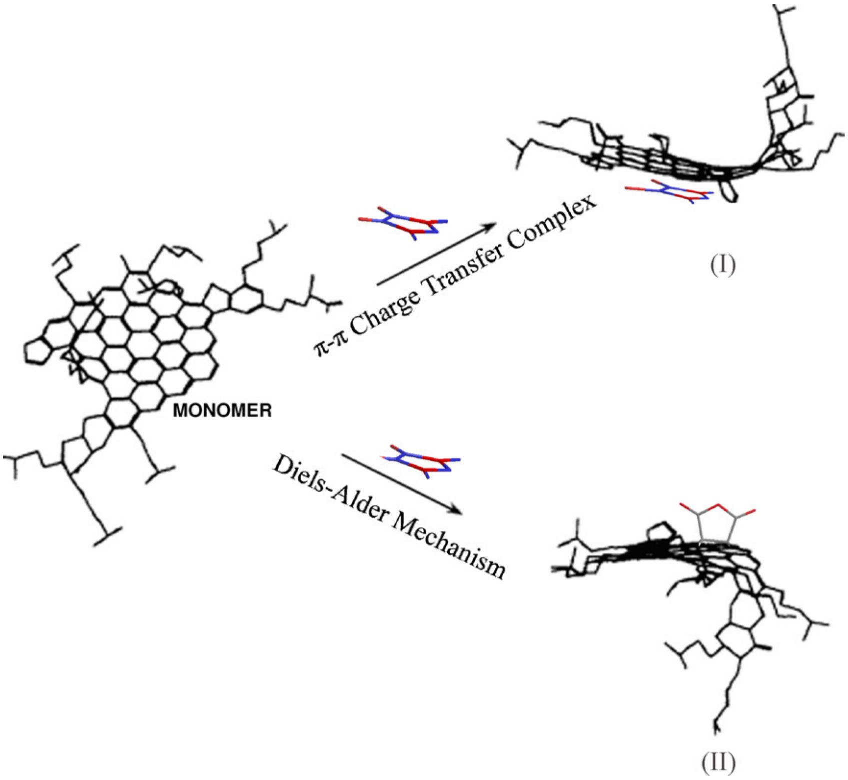

Fig. 9. Reaction of asphaltene monomer and MAH. (Models except MAH were reprinted from Ref. [34].)

Table 7
Linear fitting results of $\ln[-\ln(1-\alpha)] \sim \ln t$.

T (°C)	Slope	Error of slope	Intercept	Error	R^2
120	0.25084	0.00734	−1.08E+00	0.03567	0.99908
130	0.31923	0.00948	−1.23654	0.04789	0.99883
140	0.34649	0.01691	−1.12153	0.09986	0.99746
150	0.36944	0.0182	−1.14506	0.08957	0.99681
160	0.39176	0.02616	−1.04405	0.13664	0.99588

the π–π interaction between their stacks to disassociation [39], which means the relative dimension of asphaltene to MAH drops. Namely, the dimension of "new nuclei" increases with temperature. Hereby, the relative increase of dimensions is, in all probability, a consequence of the disassociation of asphaltenes. Thus, the disassociation of asphaltenes increased the aromaticity of reaction system which enhanced the FTIR peaks of 1500–1700 cm^{-1}, as shown in Fig. 1.

3.2.4. *Reaction order*

The integral format of 3-order (Order (3)) is

$$G(\alpha) = (1-\alpha)^{-2} - 1 = k(T)t. \tag{11}$$

$$\text{Thus,} \quad \alpha = 1 - [1 + k(T)t]^{-1/2}. \tag{12}$$

Then, overall reaction rate equation is

$$\frac{d\alpha}{dt} = \frac{1}{2}k(T)(1-\alpha)^3, \tag{13}$$

where $k(T)$ was the regressive slope of line $[(1-\alpha)^{-2} - 1 \sim t]$ (Table 6, Order (3)). Thus, Ea and A were obtained from linear regression of $[\ln(k) \sim 1/T]$ (Fig. 6). That is, $Ea = 83.52$ kJ mol^{-1}; $A = 4.84 \times 10^{11}$ s^{-1}. Luckily, the values of Ea and A are close to those of model JMA (1/4).

However, Fig. 3 manifestly fitted unsatisfactorily, especially in the initial stage of reaction at lower reaction temperature, i.e. 120 °C and 130 °C. Therefore, they were refitted in general order form of

$$\frac{d\alpha}{dt} = k(T)(1-\alpha)^n. \tag{14}$$

Then, the integral formal of Eq. (14) is

$$G(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n} = k(T)t. \tag{15}$$

$$\text{That is,} \quad \alpha = 1 - [1-(1-n)k(T)t]^{1/(1-n)}. \tag{16}$$

Refitting results, shown in Fig. 7, are better than Order (3) as expected. However, the variable reaction order, increasing from 2.58 to 5.24 with the decrease of reaction temperature, is unusually big.

As is known, reaction order n represents the molecule(s) taking part in the reaction, i.e. 2-order reaction usually means two molecules interact (collide) and react. Generally, since the possibility of three molecules collision together at one time is very small, the order of reaction is less than 3. Even, some reaction, which is 3-order reaction from the molecule level, is still apparent 2-order reaction because the concentration of the third molecule is fixed or inert. Namely, provided that five molecules collided together at one time to approach "one time" interaction, order of the reaction is 5, though possibility of this process is very few. Fortunately, this happens in the reaction of asphalt and MAH.

Considering the hypothesis of CT mechanism between MAH and asphaltenes, it is possible that the reaction order is as big as 5 or even bigger. P4, P2 and P1 are different D–π–A–π–D CTCs products (as shown in Figs. 8 and 9, and as abstracted in Eqs. (17), (20) and (22)).

To construct such CTCs, 2, 3 or 5 molecules (including MAH molecule) have to interact at one time, respectively. For example, ([A] represents mole concentration of A)

$$\text{MAH} + 4\text{asohaltenemolecule(tetramer)} \rightarrow \text{P4}, \tag{17}$$

$$r = -\frac{d[\text{MAH}]}{dt} = [\text{MAH}][\text{asphaltene molecule}]^4. \tag{18}$$

If [asphaltene molecule] = [MAH], then

$$r = -\frac{d[\text{MAH}]}{dt} = [\text{MAH}]^5. \tag{19}$$

Also,

$$\text{MAH} + 2\text{asohaltenemolecule(dimer)} \rightarrow \text{P2}, \tag{20}$$

$$r = -\frac{d[\text{MAH}]}{dt} = [\text{MAH}]^3. \tag{21}$$

As for

$$\text{MAH} + 1\text{asohaltenemolecule(monomer)} \rightarrow \text{P1}, \tag{22}$$

$$r = -\frac{d[\text{MAH}]}{dt} = [\text{MAH}]^2. \tag{23}$$

As a result, the unusual reaction orders (n) are easy to be explained. The total reaction of asphalt and MAH may be attributable to the hybrid of reactions (19), (21) and (23). With the reaction temperature, molecule motion speeds up, which results in lower association degree of asphaltenes (as analyzed by Avravi exponent), so the reaction order reduces. Evidently, the higher order of reaction implies the higher association degree of asphaltene molecules (see: Eqs. (17), (19) and (23)). In other words, the experimental results demonstrated the reasonableness of the hypothesis that CTCs between asphaltene and MAH formed. Although the formed structures of Fig. 9(I) and (II) were hard to be distinguished through present experiments, the mechanism of reaction (22) is likely to be CT mechanism for the easily occurred non-bonding interaction of CT mechanism. Moreover, the Diels–Alder product was much easier sterically hindered than CTCs when they formed. Therefore, reaction of asphalt and MAH was at least mainly undergone through CT mechanism.

4. Conclusions

The liquid–liquid heterogeneous reaction of asphalt and MAH, whose rate-controlling step was not external diffusion in the experimental space, occurred with the anhydride cyclic retained during the reaction. Kinetic analyses reveal 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. Moreover, with the reaction temperature increase, association degree of asphaltenes reduces, and the reaction order lowers. In practice, reaction of asphalt and MAH could be dealt with 3-order reaction or JMA (1/4) under the condition of stirring speed over 200 rpm, initial MAH concentration in the range of 2–6 (g MAH/100 g asphalt) and temperature ranging from 120 °C to 160 °C.

Reaction of MAH and asphalt, which is readily to prepare a reactive asphalt, is useful for advanced researches and technologies, i.e.

we have been inspired by the reaction and prepared a kind of bi-component rubber-like epoxy asphalt composites (REACs) [15–18] with better uniformity and much better performances than previous modified asphalts, which have been widely used in China. Also, CT mechanism could be used to modify asphalt, which provides a new method to improve the performances of asphalt.

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