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Characterization of epoxy-asphalt binders by differential scanning calorimetry

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HIGHLIGHTS

- Curing kinetic parameters and glass transition changes were determined for epoxy polymers and epoxy-asphalt binders under different calorimetric conditions.
- The glass transition temperature was shifting to higher temperatures as cure progresses and crosslinks were formed, with the neat epoxy polymers to crosslink faster than the epoxy-asphalt binders.
- The determination of optimum curing conditions based on calorimetric measurements can assist the future material formulations and asphalt processing technologies to avoid the uncontrolled curing of epoxy-asphalt binders.

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ABSTRACT

Asphalt binders incorporating different modifiers is a common practice but empirically driven in most of the cases. Therefore, the fundamental understanding of modification mechanisms in asphalt binders is needed to design polymer modified binders in a controllable manner, especially today in which new modification technologies are proposed. Among others, epoxy-based polymers have been accepted as a promising solution for asphalt binders to develop durable and long-lasting pavement materials. Nevertheless, a relationship between processing of epoxy-asphalt binders and their properties built-up is of high importance to prevent phenomena such as over-curing during the material production. In this research, the use of standard and modulated differential calorimetric measurements is discussed by performing analyses to asphalt binders modified with two epoxy formulations in addition to a commercially available epoxy-asphalt binder as a reference. The kinetic parameters and the T_g change of various crosslinking epoxy-based binders was assessed for the different formulations. According to the results, the T_g is shifting to higher temperatures as cure progresses and crosslinks are formed, with the neat epoxy-based polymer to crosslink faster than epoxy-asphalt binders. Difference on the crosslinking performance between the two epoxy polymers was noticed as well. This research provided valuable insight into the chemical thermodynamics of crosslinking epoxy-asphalt that can help the future material designers to control reaction-induced phenomena, such as the phase separation.

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1. Introduction

Nowadays, the global demand for more durable pavement materials designed and developed to withstand the continuously increasing traffic loads and the extreme temperature fluctuations due to the climate change leads to the use of modifiers of different chemistries and various origins. Asphalt binder is a petroleum derivative product from refineries and its composition is influenced from the crude oil source and the refining techniques applied to it [1–3]. The incorporation of different modifiers in these binders is a common practice but empirically driven in most of the cases. Therefore, fundamental understanding of the kinetics and thermodynamics of modified asphalt binders and how these affect the materials properties and subsequently the pavements performance is of high importance, especially today in which new modification technologies, such as epoxy-based polymers, are proposed.

Epoxy-based polymers have been accepted as premium solution to develop durable asphaltic materials, specifically in

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countries where the demand to reduce the maintenance costs of asphalt pavements is high [4–7]. Particularly, epoxy-asphalt has been utilized mainly as surfacing solution on airfields and steel bridge decks with the San Mateo-Hayward bridge (California, the United States) to be the most notable example since this epoxy-asphalt surfacing was in service for more than 50 years without maintenance [8]. Nevertheless, the main concern that prohibits the use of epoxy-based modifiers in asphalt is the uncontrolled irreversible curing of epoxy-asphalt [9,10]. Contractors could face high risks of construction failures, because of the relatively slow curing of epoxy-asphalt in case of allowing too early traffic after construction [6].

In this study, the use of differential scanning calorimetry is discussed by performing analyses to asphalt binders modified with various types of epoxy formulations to understand the relationship between the processing (e.g., during in-plant production and in-field construction of asphalt pavements) and the properties of studied materials. The determination of optimum cure conditions based on calorimetric measurements will assist the future material formulations and asphalt processing technologies to avoid the uncontrolled over-curing of epoxy-asphalt binders and thus the negative effect of reduced material workability during construction. The procedure to predict the reaction kinetics of crosslinking epoxy-asphalt binders is discussed as well and the calorimetric measurements are introduced later on providing the influential parameters of different epoxy-asphalt binder formulations.

2. Background

The differential scanning calorimetry (DSC) is the most widely used instrument to determine the enthalpy related transitions of asphalt binders [11,12] and of polymeric materials [13]. DSC monitors the endothermic or exothermic heat flow of a sample under a controlled temperature program, considering that the heat generation and its rate is proportional to the reaction rate when crosslinking polymers are studied [14] and to thermal events, such as glass transition [15]. Especially, all polymeric materials are either in liquid or rubbery state at high temperatures and cooling of these materials demonstrates the divergency between crystalline and amorphous state. In the transition region from an amorphous to a crystalline state, material properties typical of glass are exhibited and stepwise increase of modulus, specific volume, and thus of thermal expansion coefficient, occur. Glass transition temperature (T_g) is the temperature that corresponds to this transition.

DSC analyses have been used successfully to evaluate the T_g of asphalt binders of different origins as well as the effect of various asphaltic fractions [16–18], modifiers [19–22] and rejuvenators [23,24] on their glass temperature region. The T_g can be used to interpret thermal-related defects in asphalt pavements, such as the thermal cracking. For instance, binders with high T_g accumulate less thermal stress build-up under a given thermal history and thus are more resistant to low temperature cracking. Based on past research, the T_g of asphalt binders of different performance grades and from different crude oil resources was shown to extend over the range between −60 and 0 °C [11] and between −50 and −10 °C [12] exhibiting different melting peaks. Further, the T_g depends on the degree of aging of asphalt binders [19]. An aged asphalt binder shows wider glass temperature range mainly because the new microstructure arrangement leads to weakening of association between the asphaltic molecules. A link of asphaltenes increase has been found with the T_g increase [19]. In polymer-modified binders, the compatibility of a certain polymeric formulation to asphalt binder is affected negatively when a binder has high asphaltene content [25]. Improvement of polymer-asphalt binder miscibility is reached when the aromaticity of maltenes decreased to certain values [25].

In epoxy-asphalt binders, a T_g range from −8 to 50 °C for fully cured epoxy-asphalt binders was reported in [22]. It has been found as well that the bisphenol A diglycidyl ether (DGEBA), main compound of epoxy resins, is immiscible with asphalt binders [25–27]. Nevertheless, improved miscibility between epoxy-based polymers and asphalt binder is possible by applying specific formulations. Certain epoxy formulations may result miscible polymeric systems with asphalt binders and thus it is of high importance to evaluate their impact on the curing (crosslinking) behaviour of epoxy-asphalt binders.

2.1. Polymerization reaction kinetics

As a crosslinking (polymerizing) material turns irreversibly into networked microstructures, like epoxy-asphalt binder, and thus it cures, heat releases proportionally to the consumption rate of reactive elements as

$$[C_A] + [C_B] \xrightarrow{K} [C_{AB}] + \Delta H_T \tag{1}$$

where C_A and C_B are the concentrations of the two reactive components of epoxy-asphalt binders before reaction, C_{AB} is the concentration of the newly produced material after curing, K is the rate of reaction and ΔH_T is the exothermic heat of chemical transition.

The exothermic heat of reaction ΔH up to time t can be calculated by

$$\Delta H(t) = \int_0^t \left(\frac{dQ}{dt}\right) dt \tag{2}$$

where dQ/dt is the rate of exothermic heat generation.

Non-isothermal measurements of reaction heat of binders as a function of time and temperature yield information about the degree of curing. The conversion data is derived from the measured exothermic heating rates by dividing the rates by the total exothermic heat. Particularly, the total area under the calorimetric scans, based on the extrapolated base line at the end of reaction, was used to calculate the total heat of reaction (ΔH_T).

The degree of cure or conversion x is given as

$$x = \frac{\Delta H(t)}{\Delta H_T} \tag{3}$$

where $\Delta H(t)$ is the partial area under a calorimetric measurement up to time t.

The total exothermic heat ΔH_T up to t_T is defined as

$$\Delta H_T = \int_0^{t_T} \left(\frac{dQ}{dt}\right) dt \tag{4}$$

where t_T is the time required to complete the reaction and ΔH_T is the amount of heat generated during the measurement until the completion of cure.

The rate of cure is a parameter proportional to the rate of heat release defined as

$$\frac{dx}{dt} = \frac{1}{\Delta H_T}\left(\frac{dQ}{dt}\right) \tag{5}$$

where dQ/dt is the rate of heat generation and is provided by the measurements.

The determination of reaction kinetics is crucial to develop a prediction scheme for physico-mechanical properties of crosslinking materials [9,10]. The kinetic model allows to predict the cure degree and the reaction rate as a function of time and temperature of crosslinking binders as

$$\frac{dx}{dt} = K(T) f(x) \tag{6}$$

where $K(T)$ is a temperature-dependent parameter, which is described by an Arrhenius equation, and $f(x)$ is a function of conversion.

In the n^{th} order model, no diffusion controlled factor need to be applied and thus the reaction rate is defined as

$$\frac{dx}{dt} = K(T)(1-x)^n \tag{7}$$

$$K(T) = K_0 \exp(-\frac{E_a}{RT}) \tag{8}$$

and hence

$$\frac{dx}{dt} = K_0 \exp\left(-\frac{E_a}{RT}\right) \cdot (1-x)^n \tag{9}$$

where K_0 is the pre-exponential kinetic factor, E_α is the activation energy or the energy barrier to be overtaken to begin the reaction, R is the universal gas constant and n is the reaction order upon the crosslinking. The crosslinked, or fully cured, molecules do not flow easily when the conditioning temperature of epoxy modifier becomes the full cure temperature and, thus, their mobility lowers. Hence, the Eq. (8) is not always valid for modelling the epoxy-based polymers. Nevertheless, in the case of epoxy-asphalt, it is a sufficient function to describe the reactions of these materials.

During the non-isothermal calorimetric analysis in DSC, temperature varies linearly with time as

$$T - T(0) = \beta t \tag{10}$$

and

$$\beta = \frac{dT}{dt} \tag{11}$$

where T is the current temperature, $T(0)$ is the initial temperature, t is time, and β is the calorimetric scanning rate. By combining Eq. (9) with Eq. (11) yields Eq. (12), which represents the theoretical shape of a calorimetric scan, as

$$\beta\frac{dx}{dt} = K_0 exp\left(-\frac{E_a}{RT}\right)(1-x)^n \tag{12}$$

Eq. (12) can be reduced to a linear form by taking the natural logarithm of both sides of the equation as

$$\ln\left(\beta\frac{dx}{dt}\right) = \ln K_0 - \frac{E_a}{RT} + n\ln(1-x) \tag{13}$$

A multi-linear regression is performed using $\ln[\beta(dx/dt)]$, $-1/RT$, and $\ln(1-x)$ as variables derived from DSC data to solve for K_0, E_a, and n.

When the degree of curing reaches a high level, a quantitative measurement of the residual heat is very difficult due to the small exotherm. In that case, measuring the T_g is a more sensitive way to determine the degree of cure. It is well accepted that for many crosslinking polymers there is a unique relationship between the T_g and the degree of cure [14]. Therefore, the evolution of T_g is examined in this research as well.

3. Materials and methods

3.1. Materials and preparation

Epoxy-based polymers for asphalt binders are normally binary reactive systems able to form co-polymerized networks when epoxy monomers react chemically with specially terminated pre-polymers under certain energy conditions. In this research, two polymers were selected and their components used as received without any further purification. The two studied epoxy-based polymers, named KD-HDP and KD-HYP, were supplied by Kindaikasei Corp, Japan, and both polymers were formulated by two liquid components; (i) the epoxy and (ii) the hardener. Especially, the component used as hardener (i.e., B-KD) was an acrylonitrile-butadiene pre-polymer for both KD-HDP and KD-HYP, and the mix of epoxy monomers of KD-HDP and KD-HYP were named A-HDP and A-HYP, respectively.

The two components of KD-HDP were oven-heated for 1 h at 50 °C, and then mixed together at weight ratio 61:39 (A-HDP:B-KD), according to the supplier. In similar way, the two components of KD-HYP polymer (weight ratio 50:50 of A-HYP and B-KD) were heated for 1 h at 30 °C in the oven, and immediately afterwards mixed together. In both cases, the two components were mixed together for approximately 20 s to minimize the chemical reactions during mixing. The freshly prepared mixes were immediately placed in a refrigerator at −10 °C to freeze the reactions. The uncured mixes were directly used for calorimetric measurements.

For the formulation of an epoxy-asphalt binder with equivalent amount of epoxy (20% wt resin of component A) for all studied cases, the uncured KD-HDP and KD-HYP polymers were mixed with an already pre-heated asphalt binder of 70/100 pengrade for 60 s at 170 °C. The weight ratio of epoxy-asphalt binders (epoxy:hardener:asphalt) based on the before mentioned chemistries were 20:13:67 and 20:20:60, respectively.

To compare the material behaviour of newly formed epoxy-asphalt binders, extra samples prepared using a commercial available epoxy-asphalt binder (EA_{ref}) formulated with equivalent amount of epoxy resin. This product formulated from two liquid components as well; (i) the component A, which includes epichlorohydrin-bisphenol-A (DGEBA), and (ii) component B, which consists of a mix of a 70 pengrade petroleum asphalt binder with heavy naphthenic distillates and extracts. Nevertheless, the exact incorporating chemistry of component B is proprietary protected by the supplier and thus its chemical formulation is unknown. All the samples were prepared by mixing component A and B at weight ratio of 20:80. Unless otherwise stated, the two components were oven-heated separately for 1 h, to 85 and 110 °C, respectively, and after that mixed together for 20 s.

The compositions of studied formulations in this research are collected in Table 1.

3.2. Calorimetric measurements

The standard and modulated calorimetric measurements were performed on Perkin-Elmer DSC 4000. Enthalpy calibration in the instrument was conducted using indium standard and dry nitrogen was used as purge gas. After the formulation of samples, they were sealed in aluminium pans with sample weights between 15 and

Table 1
Name and composition of studied materials.

	Epoxy (% wt)	Hardener (% wt)	Bitumen (% wt)
KD-HDP	61[1]	39[2]	0
KD-HYP	50[3]	50[2]	0
EA-HDP	20[1]	13[2]	67
EA-HYP	20[3]	20[2]	60
EA_{ref}	20	80	

[1] Component A-HDP consists of (a) bisphenol A – epichlorohydrin, dimer fatty acid polymer (M_W = 320.814 g mol^{-1}), and (b) 4-*tert*-butylphenyl glycidyl ether (M_W = 1.038 g mol^{-1}).

[2] Component B-KD consists of (a) 2-propenitrile polymer with 1.3butadiene, 1-cyano-1-methyl-4-oxo-4-[(2-(1-piperazinyl)ethyl)]amino]butyl-terminated (M_W = 107.155 g mol^{-1}), (b) 9.12-octadecadienenoic(9Z,12Z)-dimer polymer, with 3.3-[oxybis(2.1-ethanediyloxy)]bis[1-propaneamine] (M_W = 560.904 g mol^{-1}), and (c) phenyl-1-(3,4-dimethyl)phenylethane (M_W = 210.32 g mol^{-1}).

[3] Component A-HYP consists of (a) 2.2-[hexane-1.6-diylbis(oximethylene)]bis (oxirane) (M_W = 230.152 g mol^{-1}), and (b) 4-*tert*-butylphenyl glycidyl ether (M_W = 1.038 g mol^{-1}).

20 mg. Three scans per sample were performed for standard calorimetric measurements. During measurements, the DSC monitors the heat flow of the samples under controlled conditions by having an empty aluminium pan as reference.

The total heat flow (dQ/dt) as function of enthalpic (constant pressure) heat capacity of material (C_p), the rate of temperature change (dT/dt) and a kinetic component, which is provided as a function of time (t) and temperature (T), is defined as

$$\frac{dQ}{dt} = C_P \frac{dT}{dt} + f(t,T) \tag{14}$$

To study the reaction kinetics of previously described binders, the non-isothermal behaviour of materials in an inert nitrogen environment was investigated using heating rates of 5, 10, 20 and 40 °C/min in a temperature range from 0 to 300 °C. Moreover, non-isothermal measurements performed to determine the T_g evolution at different times over curing of studied materials (two replicates per material). Specifically, all samples were oven-conditioned at 130 °C for different time intervals; from 0 to 3 h with time step of 0.5 h and scanned from 0 to 300 °C with 40 °C/min heating rate.

In addition to standard non-isothermal mode of DSC, modulated calorimetric analyses were conducted for the same purpose for all newly formed systems. In modulated studies, samples after placing them in aluminium pans were cooled to −50 °C for 5 min and then were heated to 200 °C at a rate of 5 °C/min. The modulated temperature signal was 1 °C at a modulation period of 120 s. After reaching the goal temperature, the samples were equilibrated for 5 min at 150 °C. A sample was modulated tested for each formulated binder.

4. Results

4.1. Standard calorimetric measurements

Fig. 1 shows the standard non-isothermal calorimetric scans of EA_{ref} for a temperature range from 30 to 300 °C. As shown in these scans, a single exothermic peak is demonstrated for all applied heating rates, something which happens for the other studied materials as well. Based on these scans, the total exothermic reaction heat (ΔH_T) of different binders was determined by integration of DSC non-isothermal signal at different heating rates. The shape of exothermic heat was almost the same for all binders independently on the implementing epoxy formulation. The kinetics parameters of occurring reactions can be calculated based on the theory discussed earlier and thus the effect of different formulations in curing of neat epoxy polymers and epoxy-asphalt binders is determined (see Fig. 2). The kinetics data of curing of studied materials are listed in Table 2, which includes also the calorimetric information obtained from both standard and modulated measurements. The later will be discussed in the next sub-section.

The proportion of epoxy (i.e., 20% wt) and asphalt binder together with hardener (i.e., 80% wt) is fixed for all modified binders, but only the formulation of epoxy polymer was changed. It was expected that on changing the epoxy formulation, significant differences observed in the kinetic parameters of binders (i.e., E_a, K_0, n). As shown in Fig. 2, the activation energy (E_a), which is the energy barrier to be overtaken to initiate the curing reaction [9], is higher for EA_{ref} than EA-HDP and EA-HYP. Thus, the reference epoxy-asphalt binder demands higher applied energy levels to form crosslinks and to be cured. However, once this binder overtakes this energy barrier, it cures faster than the other binders. This observation is contradictory with previous studies on the topic shown marginally lower activation energy values for epoxy-asphalt binder (46–49 kJ/mol [27] and 65 kJ/mol [28]) than of their

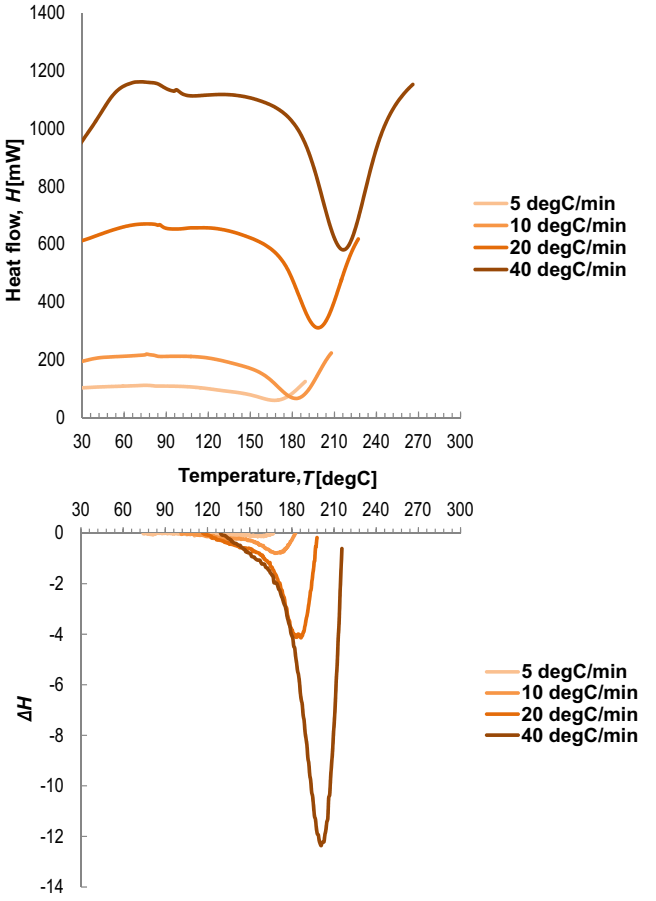


Fig. 1. Standard non-isothermal calorimetric scans at different heating rates of EA_{ref}; (top) heat flow and (bottom) derivative of heat flow over temperature.

neat epoxy polymers (50 kJ/mol [27] and 78 kJ/mol [28]). In [27,28], the curing kinetic parameters have been determined using the same formulas discussed earlier in the paper. In general, the contact opportunities between the reactive components of epoxy polymers are reduced by adding the asphalt binder and the cure reactions are inhibited leading to higher energy needs [9].

In addition to kinetic parameters, the T_g changes due to the cure of different crosslinking binders is examined. The T_g is shifting to higher temperatures as cure progresses and crosslinks are formed, and thus a higher T_g corresponds to a greater degree of cure. In other words, the T_g values rise with material crosslinking until achieving an ultimate value corresponding to the ultimate conversion at a given temperature. Fig. 3 shows how the T_g changes as cure progresses by the standard non-isothermal scanning of EA_{ref} at different time intervals. Further, the evolution of T_g over curing time (in the oven) of different epoxy-based polymers (i.e., KD-HDP and KD-HYP) is shown in Fig. 4(a). Similarly, the T_g increase due to the cure of epoxy-asphalt binders (i.e., EA-HDP, EA-HYP and EA_{ref}) is demonstrated in Fig. 4(b) as well. The T_g studies after non-isothermal curing demonstrates significant difference between the epoxy-based polymers and modified binders. By comparing Fig. 4(a) and (b), it is obvious that the epoxy cure faster than epoxy-asphalt binders showing that the asphalt binder prohibits the interaction between the reactive components of polymers and thus slows down the crosslinking process. Moreover, difference on the extent of the T_g is observed when different polymers are cured. During cure, the KD-HYP demonstrates higher extent of the T_g than KD-HDP (see Fig. 4(a)). Overall, the T_g was very sensitive to small changes in the degree of cure by performing stan-

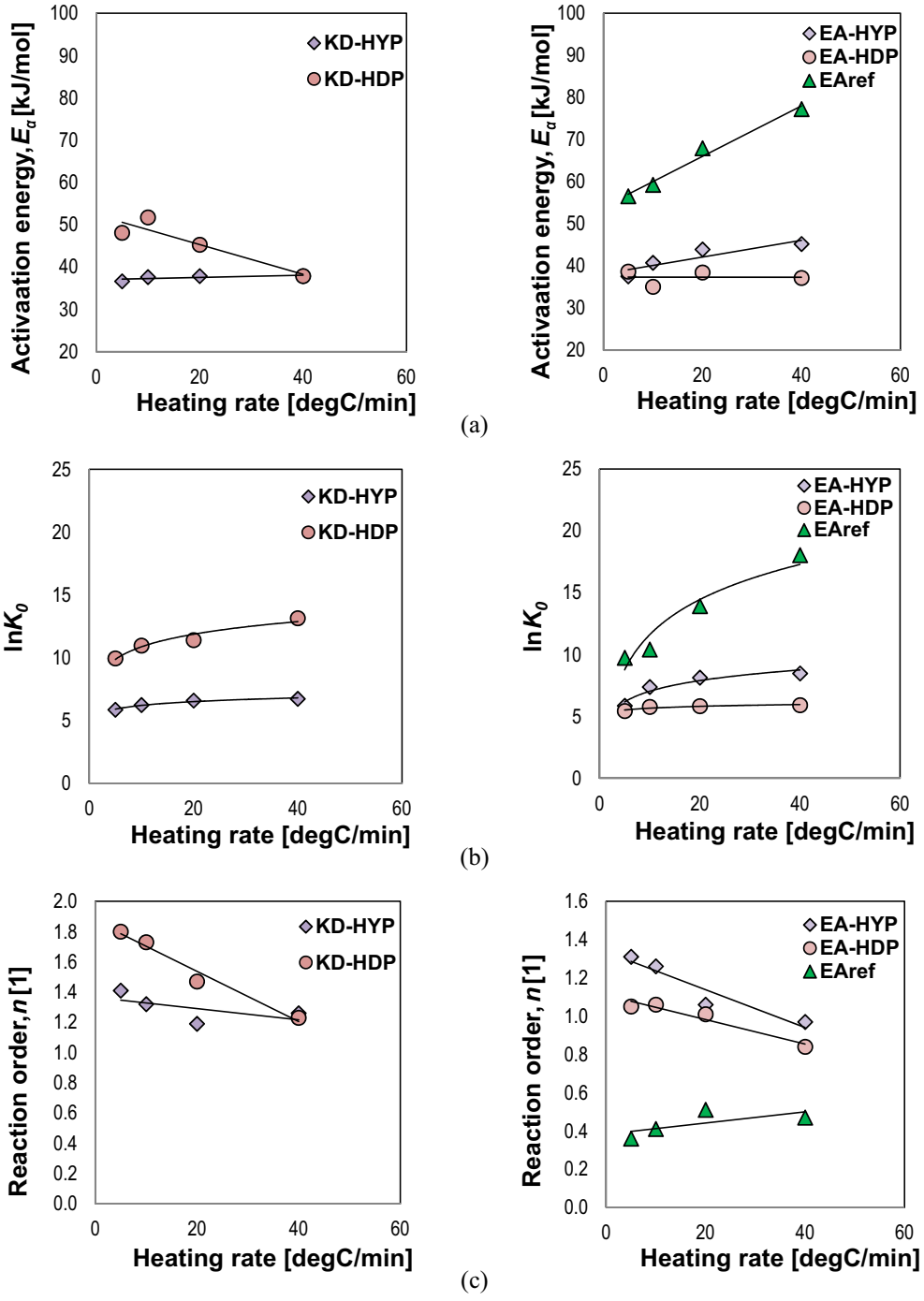


Fig. 2. Kinetic parameters; (a) activation energy, (b) reaction rate and (c) reaction order corresponding to standard DSC curve of each studied material.

dard calorimetric measurements in crosslinking epoxy-asphalt binder and thus it can be used as alternative method to monitor the cure progress.

4.2. Modulated calorimetric measurements

As mentioned before, the modulated calorimetric measurements offer higher precision in the determination of the T_g by isolating scans from other thermal-driven events as crystallization and melting. In case of reacting systems as crosslinking epoxy-asphalt binders, the modulated function can offer kinetic curves as shown in Fig. 5 reflecting the exothermic heat flow unaffected by the heat flow effect of change in C_p. In this study, the underlying heating rate was 5 °C/min with 120 sec modulation period and 1 °C modulation amplitude. Especially, modulated calorimetric scans track the difference in heat flow between a sample and an inert reference pan as function of time and temperature, as in standard calorimetric scans. However, a sinusoidal modulation (oscillation) is applied on a linear heating (or cooling) ramp as shown in Fig. 5. In this figure, the sinusoidal heat flow data is represented with red line and their time-based derivative with blue line. Therefore, Fig. 5 shows the heat flow (red line) and its derivative (blue line) together with the specific heat capacity and kinetic curves of EA_{ref} after performing calculation in the Pyris software of DSC.

Table 2
Kinetic parameters corresponding to calorimetric measurements of studied materials.

	Heating rate [°C/min]	Activation energy, E_a [kJ/mol]	Reaction rate, K_0 [1/s]	Reaction order, n [1]	Total heat flow, ΔH_T [J/g]
KD-HDP	5	48,08 ± 0,51	2,1E04 ± 3,0E03	1,80 ± 0,01	−73,13 ± 1,54
	10	51,74 ± 0,60	5,8E04 ± 3,1E03	1,73 ± 0,01	−127,70 ± 5,08
	20	45,28 ± 3,22	9,0E04 ± 5,2E03	1,47 ± 0,02	−131,70 ± 8,38
	40	37,86 ± 3,45	5,1E05 ± 2,3E05	1,23 ± 0,05	−55,17 ± 0,52
				MDSC	−100,95
KD-HYP	5	36,63 ± 0,34	3,5E02 ± 3,9E01	1,41 ± 0,00	−47,10 ± 3,98
	10	37,63 ± 0,41	5,1E02 ± 1,3E01	1,32 ± 0,01	−47,23 ± 0,64
	20	37,87 ± 1,17	7,3E02 ± 3,1E01	1,19 ± 0,01	−47,52 ± 0,34
	40	37,86 ± 2,12	8,4E02 ± 2,8E01	1,26 ± 0,01	−41,56 ± 0,67
				MDSC	−20,37
EA-HDP	5	38,66 ± 1,03	2,3E02 ± 4,2E01	1,05 ± 0,03	−60,99 ± 2,94
	10	35,05 ± 1,15	3,2E02 ± 1,3E01	1,06 ± 0,03	−39,57 ± 0,23
	20	38,47 ± 1,37	3,4E02 ± 1,2E01	1,01 ± 0,04	−37,12 ± 0,29
	40	37,16 ± 2,30	3,7E02 ± 1,1E02	0,84 ± 0,05	−25,03 ± 2,16
				MDSC	−38,84
EA-HYP	5	37,53 ± 1,38	3,5E02 ± 1,2E02	1,31 ± 0,04	−28,39 ± 1,60
	10	40,76 ± 1,63	1,6E03 ± 8,4E02	1,26 ± 0,06	−30,83 ± 1,56
	20	43,92 ± 1,87	3,4E03 ± 8,9E02	1,06 ± 0,08	−12,38 ± 6,84
	40	45,22 ± 3,16	4,8E03 ± 4,7E02	0,97 ± 0,09	−11,15 ± 0,30
				MDSC	−23,60
EA_{ref}	5	56,54 ± 2,19	1,7E04 ± 9,6E03	0,36 ± 0,01	−27,86 ± 2,25
	10	59,27 ± 1,65	3,3E04 ± 1,5E04	0,41 ± 0,01	−48,94 ± 3,33
	20	67,95 ± 7,52	1,1E06 ± 1.0E06	0,51 ± 0,02	−51,58 ± 3,18
	40	77,24 ± 14,39	6,8E07 ± 6,5E07	0,47 ± 0,16	−38,91 ± 3,60
				MDSC	−48,95

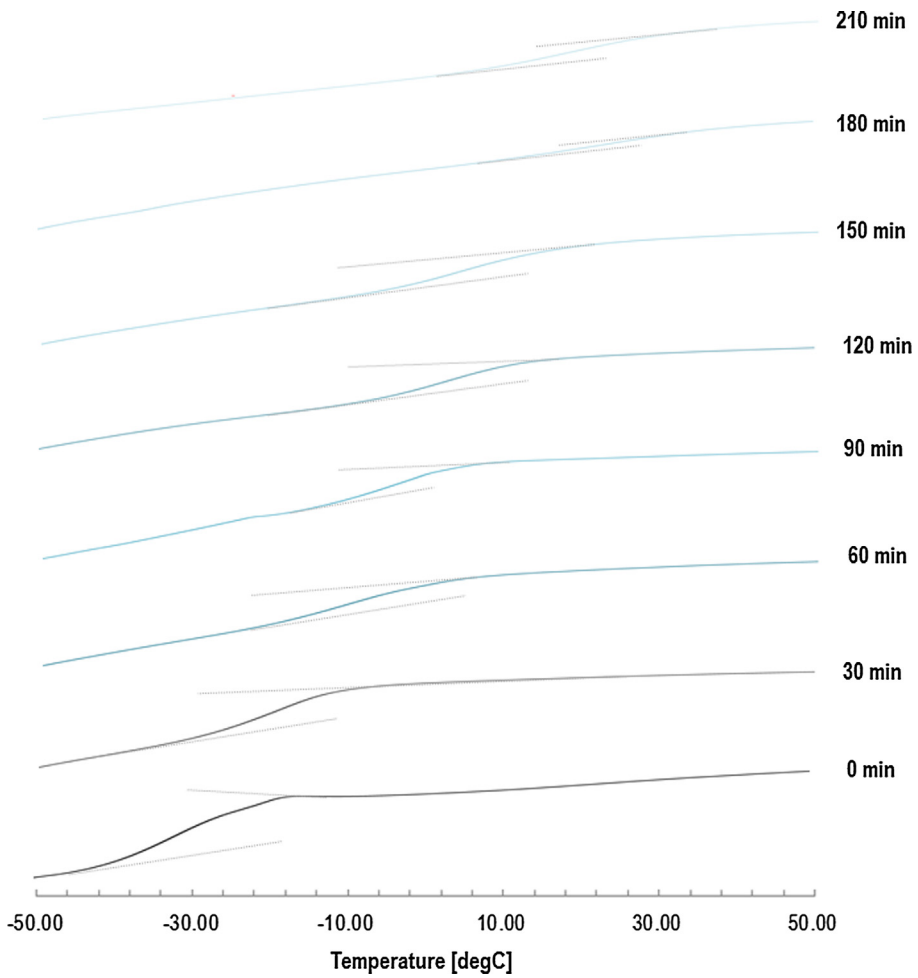
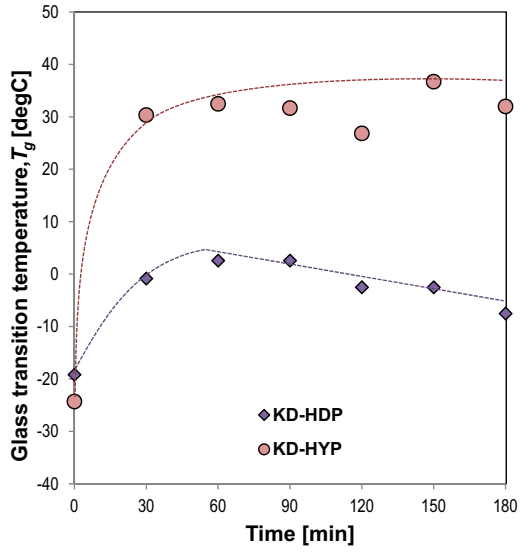
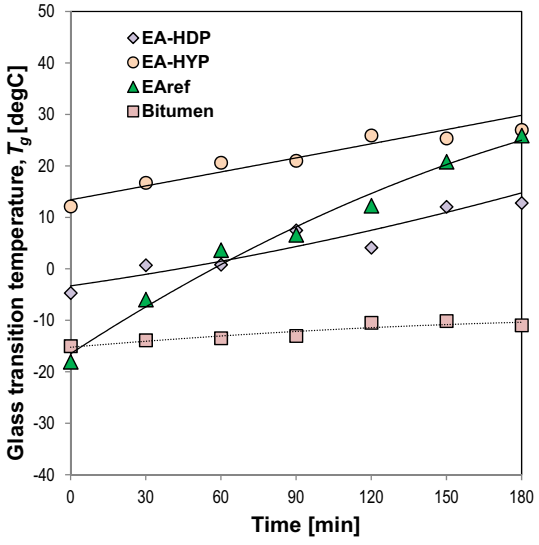


Fig. 3. The T_g of EA_{ref} at different time intervals after standard non-isothermal calorimetric scans.



(a)



(b)

Fig. 4. The T_g evolution during cure at 130 °C of (a) epoxy-based polymers KD-HDP and KD-HYP and (b) epoxy-asphalt binders EA-HDP, EA-HYP, EA_{ref}, and bitumen, after standard non-isothermal calorimetric scans.

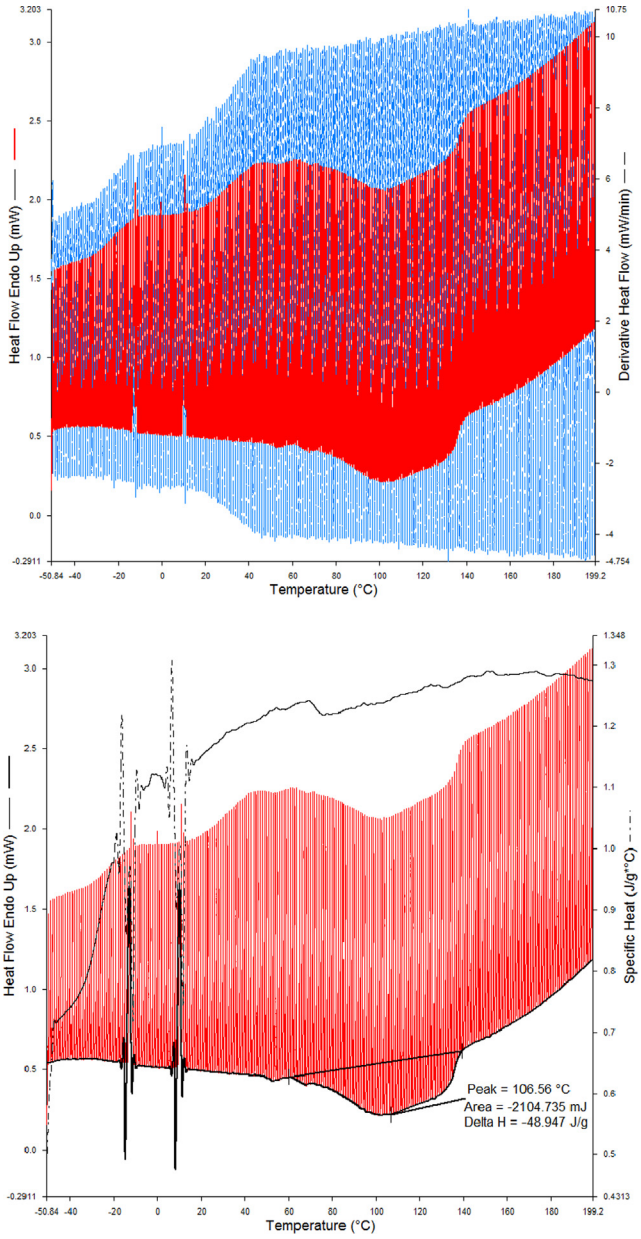


Fig. 5. Modulated calorimetric scans of EA_{ref} including the heat flow and the derivative heat flow (top) and analysed exothermic heat flow (bottom).

The specific heat capacity signal was calculated by the software based on Discrete Fourier Transformation where the measured amplitudes of the sample temperature and heat flow modulation compared to a reference sinusoidal wave of the same frequency (see black line in Fig. 5). The raw data and the enthalpic calculation for neat epoxy polymers and newly developed epoxy-asphalt binders are provided in Fig. 6.

Regarding the scan of EA_{ref} in Fig. 5, it is obvious the thermal history effect in the heat flow data since irregular peaks appeared. These irregular peaks affect the precise positioning of the baseline tangents and thus the individual T_g values of epoxy and asphalt binder cannot be given. This issue is difficult to be resolved for the uncured binders because they should be pre-heated at high temperatures and then cooled down with modulation before any measurement to remove any extraneous thermal effect. This pre-treatment before cure will result crosslinks in the studied binders and thus the accuracy of kinetics will be lost. Therefore, it is hard to determine the exact evolution of the T_g during curing for binder of thermosetting nature by performing modulated measurements. Therefore, the unmodulated measurements of thermosetting binders through curing studies are more reliable than of modulated ones. This explains the change of the T_g position as the cure progresses and thus a broader glass transition region appeared. In Figs. 5 and 6, the broad glass transition region is shown having T_g values closer to those of fully cured binders. Finally, the total exothermic heat flow determined from the two performed calorimetric methods demonstrated similar values. For example, the total heat released from the crosslinking EA_{ref} was −50,04 and −51,58 J/gr for the modulated and standard analysis (heating rate of 20 °C/min), respectively.

5. Summary and future challenges

In this study, two different formulations of epoxy-based polymers were used as modifiers for asphalt binder by having a com-

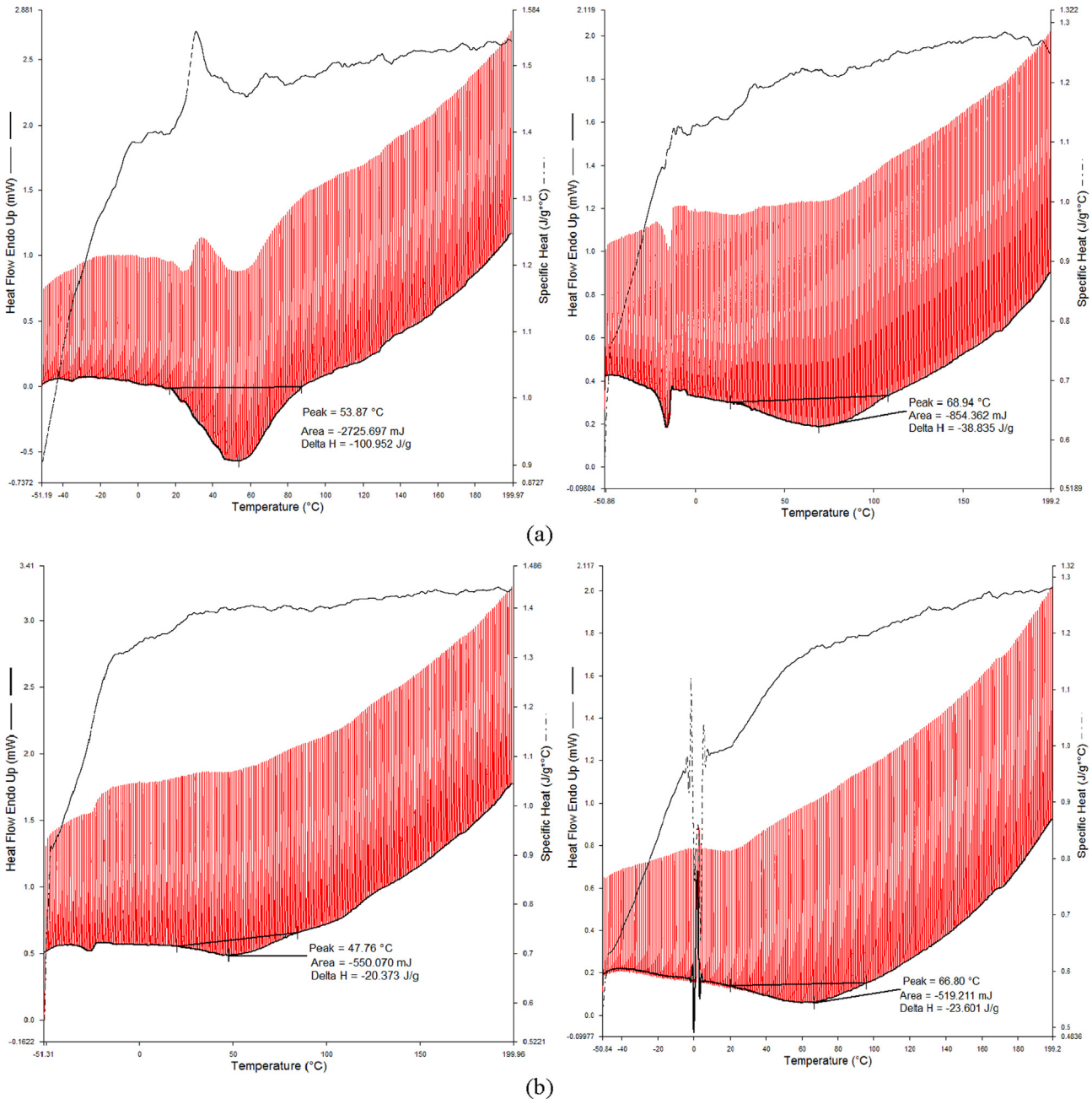


Fig. 6. Modulated calorimetric scans of (a) KD-HDP (left) and EA-HDP (right) and (b) KD-HYP (left) and EA-HYP (right) including the heat flow.

mercial available epoxy-asphalt binder as reference, and their thermal behaviour under standard and modulated calorimetric measurements was observed. These measurements performed in a DSC provided insight information about the processing parameters, such as T_g, by considering the release of heat during the calorimetric measurements proportional to the progress of chemical reactions. Kinetic parameters (i.e., the activation energy, reaction order and rate) and the T_g change were determined for the epoxy polymers and epoxy-asphalt binders under different calorimetric conditions.

Difference on the crosslinking performance between the two epoxy polymers was noticed. Particularly, the T_g is shifting to higher temperatures as cure progresses and crosslinks are formed, with the neat epoxy polymers to crosslink faster than epoxy-asphalt binders. The asphalt binder prohibits the interaction between the two reacting epoxy components and thus the reduction of the T_g evolution rate obtained. The effect of applied energy on crosslinking of studied materials was more pronounced on the neat epoxy compared to the asphalt binders modified with those polymers.

The insight information provided by the standard measurements in DSC were compared those obtained from the calorimetric measurements under modulated temperatures as well. As known the modulated calorimetric measurements offer higher precision in the determination of the T_g by isolating the scans from other thermal-driven events. Nevertheless, the exact evolution of the T_g of crosslinking materials by performing those measurements was hard to obtained. A broad glass transition region was provided with T_g values closer to those of fully cured binders. During the modulated calorimetric measurements, the multi-phase binders developed in the research were crosslinking and hence the glass transition regions were shifting over scanning.

Overall, the determination of optimum curing conditions based on calorimetric measurements as performed in this study can assist the future material formulations and asphalt processing technologies to avoid the uncontrolled over-cure of epoxy-asphalt binders and thus the negative effect of reduced mix workability during construction. In combination with the in-depth understanding of the chemical thermodynamics of binders with thermosetting nature, the material designers would be able to control various reaction-induced phenomena, such as the phase separation, after obtaining appropriate calorimetric information. Thus, the microstructure of cured epoxy-asphalt binders is possible to be predicted and desired miscibility of various incorporating phases to be achieved.

6. Author contribution statement

The authors confirm contribution to the paper as follows: study conception and design: PA, AS; data collection: PA; analysis and interpretation of results: PA, XL, SE, AS; draft manuscript preparation: PA. All authors reviewed the results and approved the final version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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