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The use of solubility parameters and free energy theory for phase behaviour of polymer-modified bitumen: a review

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Advances related to the use of solubility parameters and free energy theory for the phase behaviour study of polymer-modified bitumen (PMB) are reviewed in this paper. The origin and effects of PMB phase behaviour are criticised with a focus on PMB storage stability, morphology and swelling ratio. An overview of the solubility approach for studying PMB is given regarding the historical and future developments. Free energy expressions for PMB systems are analysed, including the free energy of mixing, elastic free energy and gradient energy. The kinetic aspects are discussed with respect to the diffusion and flow processes. It is indicated that the solubility bodies in the three-dimensional Hansen space and their degree of intersection can be useful for analysing the PMB thermodynamic equilibrium and thus storage stability. But they give no indication by themselves on the PMB morphology. With solubility parameters linked to the PMB free energy, however, an integrated thermodynamic approach can assist in understanding both PMB storage stability and morphology comprehensively. Due to the chemical complexity of bitumen and certain modifiers, the solubility body centres and radiuses should be both considered for a proper expression of the polymer-bitumen interaction in PMB. A hypothetical dilution process can simplify this process, but with limitations. The introduction of elastic free energy may lead to a new and more realistic expression of free energy for PMB system. With this overview, it is expected that a preliminary foundation is established towards a comprehensive and realistic thermodynamic framework for interpreting and predicting PMB phase behaviour.

Keywords: polymer-modified bitumen; phase behaviour; free energy; thermodynamics; solubility parameters

1. Introduction

Polymer-modified bitumen (PMB) is a high-performance binder material for asphaltic road construction and maintenance. The currently common polymer modifiers for paving bitumen include polyethylene (PE), polypropylene (PP), ethylene-vinyl acetate (EVA), styrene–butadiene-styrene (SBS) and styrene-ethylene/butylene-styrene (SEBS) copolymers. It has been widely reported that these polymers can improve some properties of bitumen, e.g. increased stiffness to resist permanent deformation and better flexibility to reduce low-temperature cracking of the pavement. However, some fundamental aspects about the modification are still not fully understood

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*Corresponding author. Email: jiqing.zhu@vti.se by now and some problems remain (Polacco, Filippi, Merusi, & Stastna, 2015; Zhu, Birgisson, & Kringos, 2014). One of the areas that need to be further studied is the PMB phase behaviour, i.e. how the materials (bitumen and polymer) form the phase(s) and how the phase structure develops in PMB under different thermal conditions. PMB phase behaviour can directly and strongly affect the PMB storage stability and morphology and, furthermore, can be considerably influential on other binder properties, e.g. rheology. It is thus of great importance to investigate and understand the PMB phase behaviour.

Focusing on this topic, some previous studies (Cong, Huang, & Liao, 2008; Fawcett & McNally, 2001, 2003; Ho et al., 1997; Redelius, 2000, 2004; Yang et al., 2002, 2003) have used solubility parameters for interpreting and predicting the compatibility between bitumen and the polymer modifiers. It is believed that the Hansen solubility parameters and solubility bodies in the three-dimensional (3D) Hansen space are useful tools for analysing PMB storage stability, although no kinetic factors have been considered for this approach. Some other studies (Liang, Xin, Fan, Wang, Jiang, et al., 2019; Liang, Xin, Fan, Wang, & Sun, 2019; Masson, Collins, Robertson, Woods, & Margeson, 2003; Varma, Takeichi, Hall, Ozawa, & Kyu, 2002; Zhu, Lu, Balieu, & Kringos, 2016, 2017a, 2017b), however, adopted the thermodynamic approach and free energy theory to understand PMB phase behaviour. For example, Zhu, Balieu, Lu, and Kringos (2017b) proposed a phase-field model for predicting the PMB phase separation behaviour. This model employed a double-well potential based on the Flory-Huggins free energy of mixing for PMB system. The minimisation of free energy controls the phase equilibrium in PMB. Kinetic factors, including molecular mobility, viscosity, etc., were also integrated into the model by coupling the Cahn–Hilliard equation and the Navier-Stokes equations.

Although the thermodynamic approach has shown certain advantages over the solubility approach, it is of great complexity to obtain representative thermodynamic parameters for PMB. Practically, certain assumptions and simplifications are made for the expression of PMB free energy, which may cause limitations. In order to be more realistic, further studies still need to be conducted towards a thermodynamic framework, e.g. a new and more realistic expression of free energy for the PMB system. On the other hand, the solubility approach did provide promising results and, moreover, is very likely able to serve as a solid foundation for understanding the PMB storage stability. Further explorations might enable the calculation of PMB thermodynamic parameters based on the experimental determination of solubility parameters. In this way, the solubility approach can be integrated into a thermodynamic framework for PMB phase behaviour. Such an integrated framework has the potential to assist in the material selection process for PMB manufacture as well as the standardisation of sample preparation procedure for PMB rheology testing. According to the classic Flory-Huggins theory, the free energy of a binary system can be related to the Hansen solubility parameters of each individual components through the interaction parameter. This may provide a possible way for the integration.

To assist in enabling these promising future developments for a better understanding of PMB phase behaviour, this paper reviews the related advances and gives a comprehensive overview on the use of solubility parameters and free energy theory for modified paving bitumen research so far. In the following section, the origin and effects of PMB phase behaviour are criticised. And then, the historical and future developments of the solubility approach are analysed in the context of PMB. After this, the thermodynamic approach is reviewed with an in-depth discussion on PMB free energy expressions. Finally, the kinetic and other aspects of PMB phase separation are briefly discussed. With all these, it is expected that a preliminary foundation is established towards a comprehensive and realistic thermodynamic framework for interpreting and predicting PMB phase behaviour.

2. PMB phase behaviour: origin and effects

PMB is usually studied as a pseudo-binary blend of bitumen and the polymer modifier. Its phase behaviour originates from the chemical and physical nature of the raw materials and leads to effects on the binder microstructure and thus properties (directly and indirectly), as summarised in Figure 1. There are two aspects of behaviour for the phase(s) in a PMB, i.e. stability and separation. The former is about the thermodynamic equilibrium states of the PMB system at various polymer contents, determining if the PMB is a thermodynamically stable or unstable system at a specific polymer content. The latter regards the PMB phase evolution from a non-equilibrium state (i.e. phase separation for an unstable system) and the kinetic factors (e.g. molecular mobility, viscosity and even density in the specific case of PMB). Together they are also often referred as the polymer-bitumen "compatibility" of PMB.

The PMB system stability depends on the solubility parameters of the individual components or, alternatively, the total free energy of the system. As mentioned above, these two approaches can be interrelated with each other, e.g. via the Flory-Huggins interaction parameter. But solubility parameters do not give direct indications by themselves on the kinetic aspects of the phase evolution in PMB. This non-equilibrium and kinetic process, however, can be described by the minimisation of free energy together with the kinetic factors. In an extensive summary by Polacco, Stastna, Biondi, and Zanzotto (2006), it was claimed that an effective polymer modification of bitumen results in a thermodynamically unstable but kinetically stable system. The thermodynamic instability makes sure that the polymer modification leads to improved binder properties, yet the kinetic stability ensures that the PMB does not separate before use for construction. It is worth noting here that the PMB system stability, or thermodynamic stability in other words, is a different concept from the storage stability.

Storage stability is likely the most significantly affected binder property by the PMB phase behaviour. It is a well-known fact that some combinations of bitumen and polymer modifiers result in the preferred storage-stable PMBs but some others may have the instability issue during

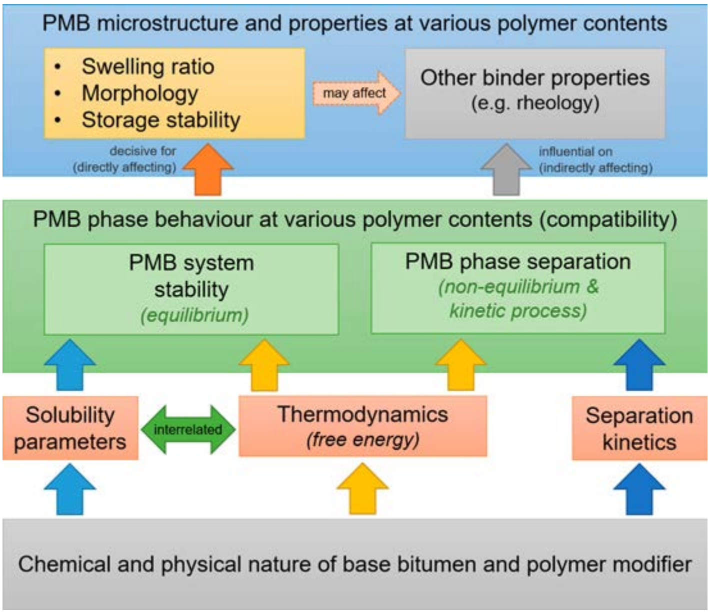


Figure 1. The origin and effects of PMB phase behaviour.

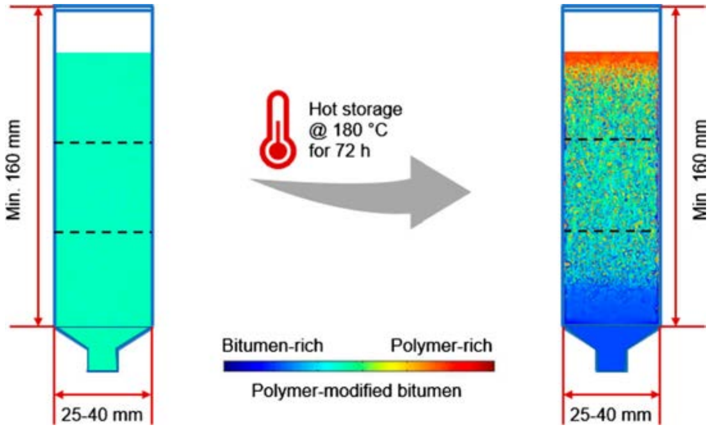
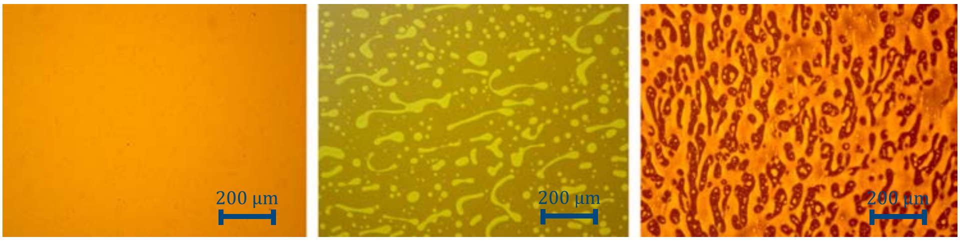


Figure 2. Schematic representation of the hot storage process for determination of PMB storage stability by EN 13399.

PMB storage and transport. In an unstable PMB, the polymer-rich phase eventually separates from the bitumen-rich phase, if no stirring or other measure is applied. The common method for characterising PMB storage stability is the so-called “tube test” (the European standard EN 13399 and the American ASTM D7173). By EN 13399, the PMB sample is poured into hot storage tubes and stored in an oven at 180°C for 3 days. This hot storage process is schematically presented in Figure 2. After the hot storage, a common practice is to measure the softening point difference between the PMB in the top part and in the bottom part of the tube. According to the European specification EN 14023, a PMB product is determined as unstable if its softening point difference by the tube test is greater than 5°C.

The tube test is believed to be reliable for most PMB products, although it may give misleading results in some highly-modified cases. It directly measures the overall results caused by both the thermodynamic and kinetic instability, i.e. the actual PMB phase separation. In this test, a thermodynamically unstable PMB starts to separate into two phases by diffusion, due to the non-equilibrium initial state. Once the density difference between the two phases becomes sufficiently significant, the gravity starts to drive the flow of the two phases and accelerates the separation in the vertical direction. As the PMB sample is stored at a sufficiently high temperature for a sufficiently long time, it is probable that the level of thermodynamic instability has very high relevance with the tube test result. In other words, the test conditions give rise to a high molecular mobility, low viscosity and likely enough time for the PMB sample to complete all the possible kinetic phase evolution processes. This is plausibly the reason why the solubility approach can give good indications on PMB storage stability without considering the kinetic factors.

Morphology is another binder property that is significantly affected by the PMB phase behaviour. PMB morphology is usually observed by microscopy (Isacsson & Lu, 1995; Polacco et al., 2015). There are many previous studies (Adedeji et al., 1996; Airey, 2002, 2003; Brûlé, Brion, & Tanguy, 1988; Hernández, Medina, Sánchez, & Mendoza, 2006; Lu & Isacsson, 1997; Lu, Isacsson, & Ekblad, 1999; Lu, Redelius, & Soenen, 2010; Masson et al., 2003; Oliver, Khoo, & Waldron, 2012; Pérez-Lepe, Martínez-Boza, & Gallegos, 2007; Sengoz & Isikyakar, 2008a, 2008b; Sengoz, Topal, & Isikyakar, 2009; Soenen, Lu, & Redelius, 2008, 2009; Sun & Lu, 2006; Varma et al., 2002; Zhu, Lu, & Kringos, 2018) that employed microscopy to investigate the PMB two-dimensional (2D) morphology. Some of them discussed the relationship of PMB morphology with the polymer-bitumen compatibility and PMB storage stability. Typical microscopy



(a) Homogeneous PMB (b) Binary PMB I (c) Binary PMB II

Figure 3. Microscopy images showing different PMB morphological structures at 180°C.

Table 1. Storage stability and estimated swelling ratio of the three SBS-modified bitumen binders.

Samples		Homogeneous PMB	Binary PMB I	Binary PMB II
Storage stability by EN 13399	Softening point (°C) – Top, ring & ball	86.5	84.2	94.5
	Softening point (°C) – Bottom, ring & ball	86.5	52.2	69.0
	Difference $\Delta T_{\mathrm{Top-Bottom}}$ (°C)	0.0	32.0	25.5
Estimated swelling ratio		–	3.8	12.2

images of SBS-modified bitumen binders are shown in Figure 3, where the lighter phase is SBS-rich and the darker phase is bitumen-rich. In Figure 3, the images are based on the materials studied by Zhu et al. (2018). All the three PMBs contain 5% the same SBS copolymer by weight of the blend but different base bitumen types from various crude oil sources.

It can be seen in the images that PMBs can have an either homogeneous or binary structure, depending on the specific combination of bitumen and polymer (and temperature). Although there is no clear criterion, it is commonly believed that a homogeneous structure at the storage temperature qualifies a stable PMB while a binary structure indicates the potential of instability. Referring to Zhu et al. (2018), Table 1 lists the storage stability results by EN 13399 for the three SBS-modified bitumen binders in Figure 3. The homogeneous PMB (Figure 3(a)) is storage-stable while the binary PMBs (Figure 3(b) and 3(c)) are unstable. For the binary structures, the patterns can vary from case to case, leading to the different morphological microstructures of the PMBs. These observation results are controlled by the PMB phase behaviour, i.e. (1) if the PMB separates into two phases and (2) how the phases behave under certain thermal condition.

For the binary PMBs in Figure 3(b) and 3(c), it can be observed that the area fraction of the SBS-rich phase is much higher than the actual polymer content 5%. This is due to the swelling of the modifier by absorbing certain components of the bitumen, as shown in Figure 4. This swelling process starts during the PMB manufacture, after the dispersion of modifier into pre-heated bitumen by low shear stirring or high shear milling. It can also be described as the partial dissolution of polymer in bitumen. Sufficient swelling of the modifier is technically required in order to ensure good quality of PMB products. The degree of swelling can be characterised by the swelling ratio of the polymer-rich phase in PMB, which is defined as the ratio of the swollen volume to the initial volume. According to Cavaliere, Da Via, and Diani (1996), the polymer modifier usually swells significantly in PMB and the swelling ratio can be up to 9. Meanwhile, some other measurements (Sengoz et al., 2009; Zhu & Kringos, 2015) indicated that PMB swelling ratio can be even more than 10 at certain stages of the phase evolution. Assuming uniform thickness of the phases through the whole thin film sample for morphology observation, the PMB swelling ratio can be estimated by analysing the area fractions of the phases in a microscopy image. The analysis results for the above-mentioned binary PMBs are listed

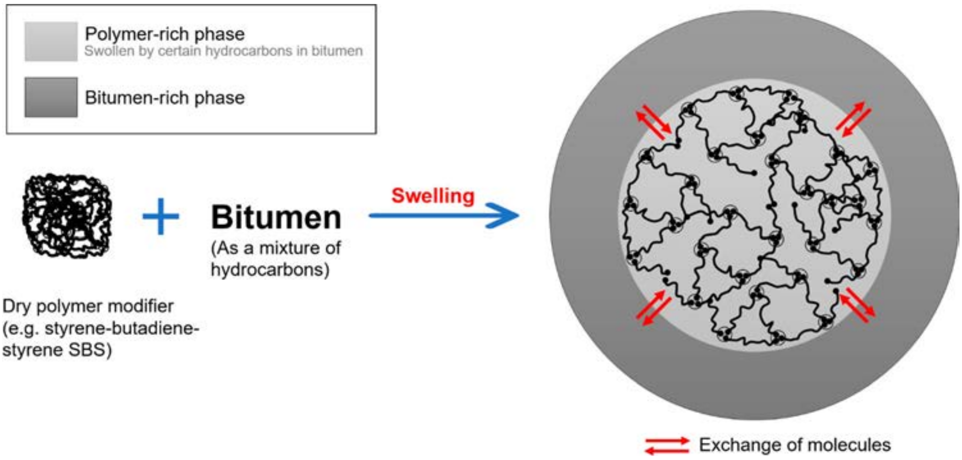


Figure 4. Swelling of polymer modifier in bitumen.

in Table 1, indicating that the different base bitumen types can result in significantly different swelling ratios even with the same modifier.

To some extent, synthetic polymer swelling in bitumen shares common mechanisms with the crumb rubber swelling. But the swelling ratio of crumb rubber in bitumen is usually lower, up to 3 according to Sienkiewicz, Borzędowska-Labuda, Wojtkiewicz, and Janik (2017), Wang, Apostolidis, Liu, and Scarpas (2018) and Wang, Liu, Apostolidis, Erkens, and Scarpas (2019). The common swelling mechanisms include mass diffusion and volume expansion (mechanical deformation). After the dispersion of modifier into bitumen, certain hydrocarbons in bitumen with favourable solubility parameters (possibly aromatic species slightly condensed and substituted by linear chains), towards a uniform chemical potential, start diffusing into the polymer network through the interface (Miller-Chou & Koenig, 2003; Mouillet, Lamontagne, Durrieu, Planche, & Lapalu, 2008; Wang, Cheng, & Xiao, 2017). The presence of new molecules in the network leads to rearrangement and disentanglement of polymer chains (Artamendi & Khalid, 2006; Narasimhan & Peppas, 1996), which may expand the volume (deform the network). Before the polymer becomes uniformly swollen, some interface layers may form at the initial stage (Ueberreiter, 1968). On the other hand, the polymer network tends to keep its original form, generating internal stresses to resist the expansion (deformation). A preliminary equilibrium (zero net flux of molecule exchange) may be reached in certain time, if the network does not break down. After this, however, the stress relaxation of the polymer network (amorphous portion) starts to dominate the swelling afterwards (Schott, 1992a, 1992b). The rate of the whole swelling process can likely be represented by a second-order kinetics. The swelling reaches its equilibrium at the end and this brings about the formation of a polymer-rich phase. The actual polymer content in the polymer-rich phase depends on the swelling ratio and Mouillet et al. (2008) reported typical values around 10%. It was also reported that the bitumen-rich phase usually consists of the residual molecules of the bitumen and less than 1% polymer.

The swelling equilibrium can in fact vary significantly from case to case, depending on the specific combination of the bitumen and polymer modifier as well as the thermal condition (Wang, Liu, et al., 2018). Extremely extensive swelling, often along with the degradation of the polymer network, may lead to the dissolution of modifier in bitumen. The total dissolution of polymer causes a limited extent of binder property improvement while a partial dissolution (but sufficient swelling) usually results in good modification effects for paving bitumen (Redelius, 2004). Due to the stirring and milling operations during manufacture, the sufficiently swollen polymer-rich phase is often well-dispersed in PMB. Once these operations are discontinued, however, some PMBs may go through a coarsening (self-similar growth) process (Soenen et al., 2008; Zhu et al., 2018). This means that the PMB microstructure evolves until it reaches an interfacial equilibrium between the two phases. The equilibrium at the interface depends on the chemical composition and physical characteristics of the phases as well as the thermal condition. It is this equilibrium, together with the kinetic factors, that defines the post-swelling phase behaviour of the PMB (i.e. morphology evolution).

3. Solubility model for PMB

3.1. *Hildebrand solubility parameter*

It has long been a widely accepted concept that a compound is most readily dissolved in a substance that is similar to it (Hagen, Jones, Hofener, Randolph, & Johnson, 1984). The solubility theory is based on such a concept that solvents with similar solubility parameters as the solute are usually good solvents for the solute, known as the “like dissolves like” principle. The Hildebrand solubility parameter (δ) was proposed on a thermodynamic basis to estimate the enthalpy change of mixing (Hildebrand, 1981; Hildebrand & Scott, 1950). It is defined as the square root of the cohesive energy density (CED) of a material by

$$\delta = (E/V)^{1/2}, \tag{1}$$

where E is the cohesive energy and V is the molar volume. E represents the increase in internal energy per mole of the material when all the intermolecular forces are eliminated, i.e.

$$E = \Delta H_{vap} - RT. \tag{2}$$

In Equation (2), ΔH_{vap} is the enthalpy of vaporisation; R is the universal gas constant; and T is the temperature. Thus, the CED, i.e. E/V, represents the energy required to break all intermolecular physical links in a unit volume of the material (Bicerano, 1993). According to this theory, the solubility parameter difference between two materials must be small enough to lead to a relatively low enthalpy change due to mixing them and thus the miscibility.

In the context of PMB, some previous studies (Cong et al., 2008; Yang et al., 2002) estimated a single solubility parameter for base bitumen while some others determined the δ values for different compositional fractions of bitumen. The latter seems more realistic, as bitumen is not a single compound but a complex mixture consisting of a continuum of relatively large hydrocarbons (Redelius & Soenen, 2015). It is common to divide bitumen into four fractions (i.e. SARA: saturates, aromatics, resins and asphaltenes) according to the solubility in different solvents (D’Melo & Taylor, 2015). Table 2 lists the δ values of these bitumen fractions reported in literature. Although there is a variation between studies (possibly due to the various separation approaches, determination methods, conditions and bitumen types), an increase in solubility parameter can be seen from saturates through all fractions to asphaltenes. Meanwhile, some other studies (Kamiya et al., 2001; Yang et al., 2003) divided bitumen into two fractions, i.e. maltenes (including saturates, aromatics and resins) and asphaltenes. They reported the δ value of maltenes at < 16.4 $(\mathrm{J/cm^3})^{0.5}$ and 14.95–17.61 $(\mathrm{J/cm^3})^{0.5}$ respectively. It should be noted that the compositional fractions of bitumen are still mixtures of various hydrocarbons despite certain common characteristics for each fraction. There are studies (Liu, Xuan, Zhao, Cong, & Liao, 2003; Masson, Polomark, & Collins, 2005) claiming that certain bitumen fractions may have higher relevance with the polymer-bitumen compatibility.

For the most common polymer modifiers, the δ values can be found in literature, as listed in Table 3. A general rule is that the higher the molecular weight of a polymer, the closer the δ

Table 2. Hildebrand solubility parameter values of bitumen fractions reported in literature.

Bitumen fraction	Hildebrand solubility parameter	Reference
Saturates	17.4–20.0 $(\mathrm{J/cm^3})^{0.5}$	Hagen et al. (1984)
	14.3 $(\mathrm{J/cm^3})^{0.5}$	Wloczysiak, Vidal, and Papirer (1997)
Aromatics	19.0–22.5 $(\mathrm{J/cm^3})^{0.5}$	Hagen et al. (1984)
	17.8 $(\mathrm{J/cm^3})^{0.5}$	Wloczysiak et al. (1997)
Resins	21.9–26.6 $(\mathrm{J/cm^3})^{0.5}$	Hagen et al. (1984)
	19.4–20.1 $(\mathrm{J/cm^3})^{0.5}$	Wloczysiak et al. (1997)
Asphaltenes	24.9–32.9 $(\mathrm{J/cm^3})^{0.5}$	Hagen et al. (1984)[a]
	19.6–26 $(\mathrm{J/cm^3})^{0.5}$	Wloczysiak et al. (1997)[b]
	16.4–20.4 $(\mathrm{J/cm^3})^{0.5}$	Kamiya, Tasaka, Zhang, Dong, and Inagaki (2001)[c]
	16.16–19.50 $(\mathrm{J/cm^3})^{0.5}$	Yang, Cong, and Liao (2003)[d]

[a] Approximation based on the solubility distribution of selected functional groups.
[b] Overall estimation based on several studies with different asphaltene separation approaches.
[c] Asphaltenes separated with *n*-heptane.
[d] Asphaltenes separated with *n*-pentane.

Table 3. Hildebrand solubility parameter values of polymer modifiers/segments/blocks reported in literature.

Polymer modifier/segment/block	Hildebrand solubility parameter	Reference
Polyethylene, PE	15.76–17.99 $(\mathrm{J/cm^3})^{0.5}$	González, Muñoz, and Santamaría (2006)
	16.2–16.4 $(\mathrm{J/cm^3})^{0.5}$	Pérez-Lepe, Martínez-Boza, Attané, and Gallegos (2006)
Polypropylene, PP	16.8–18.8 $(\mathrm{J/cm^3})^{0.5}$	Rojo et al. (2004)
Poly(vinyl acetate), *P*(VA)	19.2 $(\mathrm{J/cm^3})^{0.5}$	Small (1953)
	17.9 $(\mathrm{J/cm^3})^{0.5}$	Merk, Lichtenthaler, and Prausnitz (1980)
Polystyrene, PS	18.6–19.8 $(\mathrm{J/cm^3})^{0.5}$	Ho et al. (1997)
	18.7 ± 0.5 $(\mathrm{J/cm^3})^{0.5}$	Fawcett and McNally (2001)
Polybutadiene, PB	16.6–17.6 $(\mathrm{J/cm^3})^{0.5}$	Ho et al. (1997)
	17.4 ± 0.5 $(\mathrm{J/cm^3})^{0.5}$	Fawcett and McNally (2001)
Poly(ethylene/butylene), *P*(EB)	16.0–16.6 $(\mathrm{J/cm^3})^{0.5}$	Ho et al. (1997)

values of the bitumen fractions need to be to reach a good compatibility. Some of the common modifiers are copolymers, e.g. EVA, SBS and SEBS. They contain different segments or blocks in the polymeric chains. These segments/blocks may have different solubility and play different roles for the modification (Kamiya et al., 2001; Masson et al., 2005). Some studies (Cong et al., 2008; Machado, Lucas, & González, 2001; Yang et al., 2002) tried to estimate a single solubility parameter for copolymers, but it is more realistic to analyse the δ values of each segment/block, e.g. the poly(vinyl acetate) segment, polystyrene (PS) block, polybutadiene (PB) block and poly(ethylene/butylene) block listed in Table 3.

3.2. *Hansen solubility parameters*

The Hildebrand solubility parameter was intended for non-polar, non-associating systems without any specific interactions (Miller-Chou & Koenig, 2003). To account for specific and various interactions, the Hansen solubility parameters with three components were introduced (Hansen, 1969), with the total cohesive energy as

$$E = E_D + E_P + E_H. \tag{3}$$

The three components represent respectively the contributions from the dispersion force (E_D), the polar force (E_P) and the hydrogen bonding (E_H), leading to the three-component Hansen solubility parameters δ_D, δ_P and δ_H. They can be related back to the Hildebrand solubility parameter (δ) by

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2. \tag{4}$$

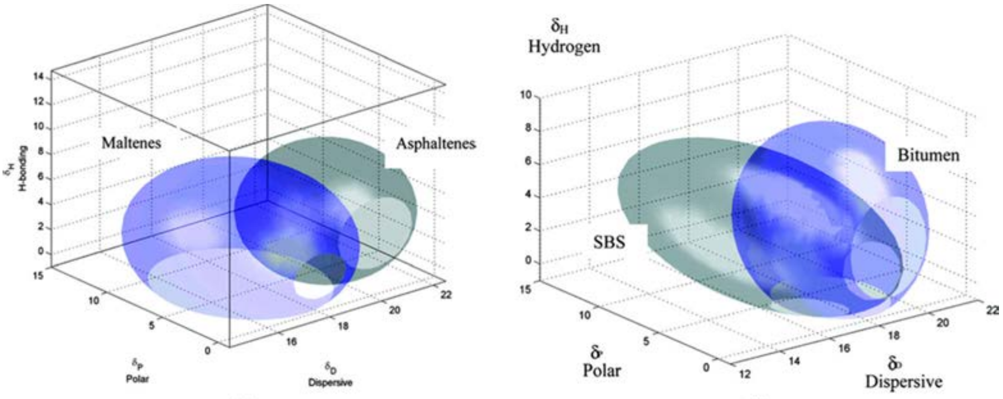
The Hansen solubility parameters have been believed to provide a better approximation than the Hildebrand solubility parameter in the context of bituminous materials (Redelius, 2000, 2004). However, the challenge is the indirect determination of solubility parameters for bitumen, due to its complex chemical composition. Solubility parameters can be directly calculated for pure liquids and two- or three-component mixtures of them. But for solid materials and more complex mixtures, it is usually not possible to directly measure or calculate the solubility parameters. Bitumen is a complex mixture consisting of a continuum of relatively large hydrocarbons. The molecules in bitumen might show a continuous range of solubility parameters, instead of a single value. An average solubility parameter may be not enough to properly describe the solubility property of the bitumen. The same can also happen to the polymer modifier in PMB, for example copolymers or if the modifier has a too large variation in degree of polymerisation. Although an estimation of the Hansen solubility parameters for a Venezuelan bitumen was reported by Redelius (2004), i.e. $\delta_D = 18.4$ (J/cm^3)$^{0.5}$, $\delta_P = 3.9$ (J/cm^3)$^{0.5}$, and $\delta_H = 3.6$ (J/cm^3)$^{0.5}$, it was also claimed that the solubility body in the 3D Hansen space is more realistic and useful.

3.3. *Solubility body in the 3D Hansen space*

Redelius (2000) employed turbidimetric titrations (with three titrants) to estimate the bitumen solubility body in the 3D Hansen space. When a solvent has a solubility parameter inside the bitumen solubility body, the bitumen is completely soluble in the solvent in all concentrations. On the other hand, if a solvent locates outside the bitumen solubility body, the bitumen could be still soluble but partially or in limited concentrations in the solvent. Forty-eight solvents were used by Redelius (2004) to determine solubility bodies of the maltenes, asphaltenes and total bitumen with respect to a given concentration. The solubility body of SBS copolymer was also constructed, representing the space where the PS and PB blocks are both completely soluble. The results are reprinted in Figure 5. It was claimed that the partial solubility of the polymer in bitumen fulfils the requirement for the effective modification by certain amounts of SBS.

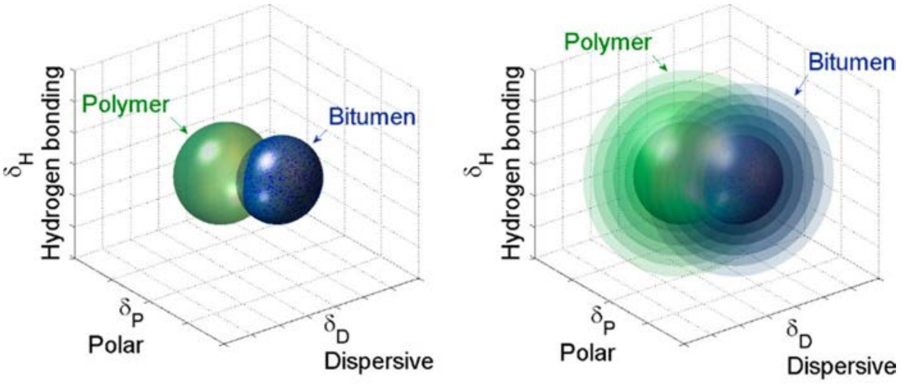
A question that often arises, about the use of solubility parameters for bitumen (including PMB), is how the temperature affects the determination. The concern is usually regarding the use of solubility parameters determined at one temperature (typically ambient temperature) to interpret or predict the bitumen performance at another temperature (e.g. PMB hot storage temperature). According to Hansen (2007), the effect of temperature on solubility relations is most significant for systems with a high hydrogen bonding character. Bitumen is probably not such a system. It was also claimed that using solubility parameters established at ambient temperature generally leads to satisfactory results even for addressing phenomena at higher temperatures. Although there are no relevant bitumen data found in literature, it is believed to be fair to use bitumen solubility parameters determined at ambient temperature, even for interpreting and predicting properties at higher temperatures.

Assuming that the solubility bodies of bitumen and polymer are to be spheres in the 3D Hansen space, the centre of the sphere represents the simply averaged solubility parameters for all the



(a) (b)

Figure 5. (a) The Hansen solubility bodies of maltenes and asphaltenes separated from a Venezuelan bitumen. (b) The Hansen solubility bodies of SBS and the Venezuelan bitumen. Reprinted from Redelius (2004) with permission from American Chemical Society.



(a) (b)

Figure 6. Schematic PMB solubility body in the 3D Hansen space: (a) the all-concentration complete solubility body and (b) the full solubility body with both complete and partial solubility.

molecules or chains, although the materials might not behave as the average solubility parameters indicate. The radius of the sphere means the diversity of solubility parameters within the material. A bigger sphere reveals a wider distribution of solubility parameters (soluble in more solvents); and a smaller sphere shows that the solubility parameters are more concentrated in certain area (soluble in limited solvents). Based on the results by Redelius (2004), Figure 6(a) non-quantitatively illustrates an example of the intersecting solubility bodies of bitumen and polymer in the 3D Hansen space, denoting the partial solubility of the polymer in bitumen for PMB.

However, it is very important to distinguish the solubility body for complete solubility in all concentrations like in Figure 6(a) from the space for complete solubility in limited concentrations, namely partial solubility in the other concentrations like the gradient spherical shells in Figure 6(b). A critical concentration exists for every point outside the all-concentration complete solubility body in the 3D Hansen space, indicating the transition from complete to partial solubility. This critical concentration decreases as the point moves away from the surface of the all-concentration complete solubility body. For fixed concentration and temperature, the construction of the complete solubility body is to find the surface with the critical concentration at the given concentration. Outside the complete solubility body, the solubility gradually decreases as solubility parameter differences become larger.

Furthermore, in the context of PMB, the solubility body should have a concentration property, representing the polymer content of the discussed PMB. The comparison of solubility should be performed between two bodies with matching concentration properties, the sum of which is 1. With this, the intersection of the solubility bodies of bitumen and polymer, as in Figure 6, shows that a part of the polymer solubility parameters are inside the bitumen solubility body. The other parts of the polymer solubility parameters are outside. In this sense, the degree of intersection between the two solubility bodies can represent the polymer-bitumen compatibility. This determines if the PMB separates into two phases, i.e. the system stability in Figure 1. But it gives no indication on how the phases behave towards the equilibrium and afterwards in the kinetic separation process (no indication on the morphology). In order to reach a better understanding of PMB phase behaviour, the thermodynamic basis of solubility theory must be linked to the free energy of the PMB system for a comprehensive framework.

4. Free energy of PMB system: the thermodynamic approach

4.1. *Phase diagram and free energy*

In the context of PMB as a pseudo-binary blend, the temperature-composition phase diagram is the basis for phase behaviour studies. It serves as a 2D map that shows the equilibrium states of the blend under given conditions. Soenen et al. (2008) and Varma et al. (2002) observed that SBS-modified bitumen separates upon cooling and presents an upper critical solution temperature (UCST) on the phase diagram. In a typical binary phase diagram with UCST, as Figure 7(a), exist three state regimes divided by two curves. The one-phase regime is the area above the bimodal curve. The unstable regime is the area below the spinodal curve. The metastable regime is in between. The separation of blends with different composition and/or at different temperatures may be governed by different mechanisms. Blends located in the unstable regime separate by spinodal decomposition while blends located in the metastable regime separate by nucleation and growth. The spinodal decomposition leads to a bi-continuous pattern when the two phases both have a volume fraction around 50%. Otherwise, a droplet-in-matrix pattern is displayed. The equilibrium states on the phase diagram of a PMB determine the composition (concentration) of the polymer-rich phase and bitumen-rich phase, as well as the swelling ratio of the polymer modifier.

The phase diagram of a binary blend can be constructed by analysing its free energy. For a given blend, the free energy of the pure components keeps constant at a fixed temperature while the free energy of mixing forms a single or double well as shown in Figure 7(b). In the case of double well, the free energy curve has two minimum points and two inflection points. The minimum points decide the composition of the equilibrium phases (bitumen-rich phase and polymer-rich phase for PMB), due to the free energy minimisation. The location of binodal points at that temperature can thus be determined on the phase diagram. At the binodal points, a double tangent can be constructed to the free energy curve. This shows the homogenisation of chemical potential throughout the whole equilibrium system. The plot of all binodal points at different temperatures leads to the binodal curve on phase diagram of the blend (Figure 7). Similarly, the spinodal curve can be constructed by plotting all the inflection points of the free energy curves at different temperatures.

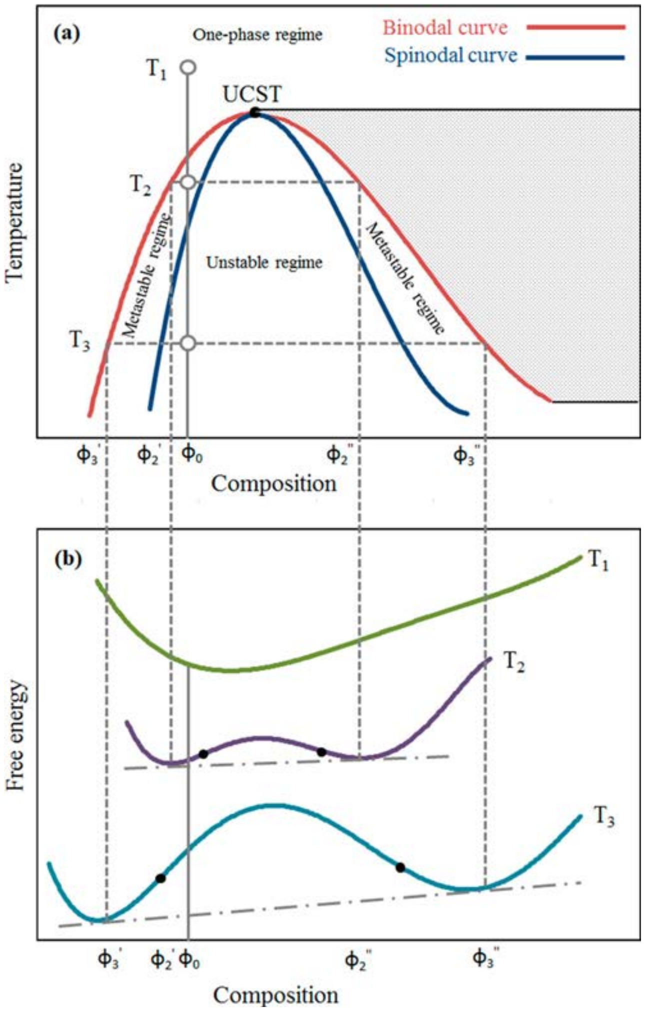


Figure 7. Phase diagram (a) and free energy curves (b). The ϕ_0 represents the initial composition; ϕ_2' and ϕ_2'' represent the equilibrium phase composition at temperature T_2; and ϕ_3' and ϕ_3'' represent the equilibrium phase composition at temperature T_3. Reprinted from Zhu et al. (2016) with permission from Elsevier.

In Figure 7, when the temperature is high enough (T_1), the chemical potential can be homogeneous throughout the whole system at any composition. With a specific composition (ϕ_0), the blend may go through a metastable state (T_2) and finally reach an unstable state (T_3) as the temperature decreases. At a fixed temperature, the composition of a blend certainly affects its phase behaviour. However, the very-high-ϕ-value area (ϕ for polymer friction) in a PMB phase diagram, like the shaded area in Figure 7(a), is not of practical interest regarding the common application of PMB (low polymer content) as binder for road paving.

4.2. *Flory-Huggins theory*

The analysis in the previous section indicates that the free energy of PMB system determines its thermodynamic stability and phase behaviour towards the equilibrium. To express PMB free energy, the Flory-Huggins theory was employed as a basis (Liang, Xin, Fan, Wang, Jiang, et al., 2019; Liang, Xin, Fan, Wang, & Sun, 2019; Zhu et al., 2016, 2017a, 2017b). The Flory-Huggins theory was originally proposed for polymer solutions and blends with dominating weak interactions, i.e. dispersion and weak polar forces (Flory, 1942, 1953; Huggins, 1942a, 1942b). For a binary polymer blend, the molar free energy of mixing can be expressed by

$$\Delta f_m = RT\left[\frac{\phi_1}{N_1}\ln(\phi_1) + \frac{\phi_2}{N_2}\ln(\phi_2) + \phi_1\phi_2\chi\right], \tag{5}$$

where Δf_m is the molar free energy of mixing of the blend (per mole of segments); ϕ_1 and ϕ_2 are local volume fractions of the two polymers; χ is the interaction parameter between the two polymers; N_1 and N_2 are segment numbers of the two polymer chains in the Flory-Huggins lattice.

According to this theory, the interaction parameter χ characterises the degree of interaction between the two polymers and can be calculated with the Hansen solubility parameters (Emerson, Toolan, Howse, Furst, & Epps, 2013; Lindvig, Michelsen, & Kontogeorgis, 2002; Painter, 1993) of the two polymers (subscripts 1 and 2) by

$$\chi = \frac{V_s}{RT}\left[(\delta_{D1} - \delta_{D2})^2 + \frac{(\delta_{P1} - \delta_{P2})^2}{4} + \frac{(\delta_{H1} - \delta_{H2})^2}{4}\right], \tag{6}$$

where V_s is the molar volume of the segments in the Flory-Huggins lattice; δ_D, δ_P and δ_H are respectively the dispersive, polar and hydrogen bonding components of the Hansen solubility parameters of the two polymers. Equation (6) indicates that a smaller difference in solubility parameters between two materials normally results in a lower χ value that stands for a higher degree of interaction. This equation gives good approximations only if the weak interactions are dominant in the blend. The constructed solubility bodies by Redelius (2004), as shown in Figure 5(b), confirms the feasibility of using Flory-Huggins theory and Equation (6) in the context of PMB.

4.3. *Polymer-bitumen interaction parameter for PMB*

Considering PMB as a pseudo-binary blend, Equation (6) shows that the solubility parameter difference between bitumen and polymer determines the PMB interaction parameter, i.e. the degree of interaction between the bitumen and polymer. This is consistent with the degree of intersection criterion for solubility bodies discussed above. For example, Figure 8 non-quantitatively demonstrates the influence of solubility body centre distance on the interaction of bitumen with a given polymer. In Figure 8(a), the solubility body of the bitumen is relatively far away from that of the polymer, without any intersection. This may represent a poor polymer-bitumen compatibility and low level of interaction (high χ value). As in Figure 8(b), the solubility parameter difference becomes smaller and the solubility bodies intersect, indicating a higher degree of polymer-bitumen interaction in the PMB (lower χ value). In this sense, the solubility body centre distance affects the polymer-bitumen interaction in PMB.

Since the bitumen and polymer have a continuum of solubility parameters, furthermore, their interaction parameters should be also a continuous range of values (instead of a single one). Thus, the solubility body centre by itself might not be enough to properly describe the solubility property of the bitumen and polymer. In the case of Figure 8(a), the solubility body centre may give a good approximation by itself, since there is no intersection of the solubility bodies. But the intersection indeed brings in more effects. For example, Figure 9 non-quantitatively demonstrates the influence of solubility body radius on the polymer-bitumen interaction with

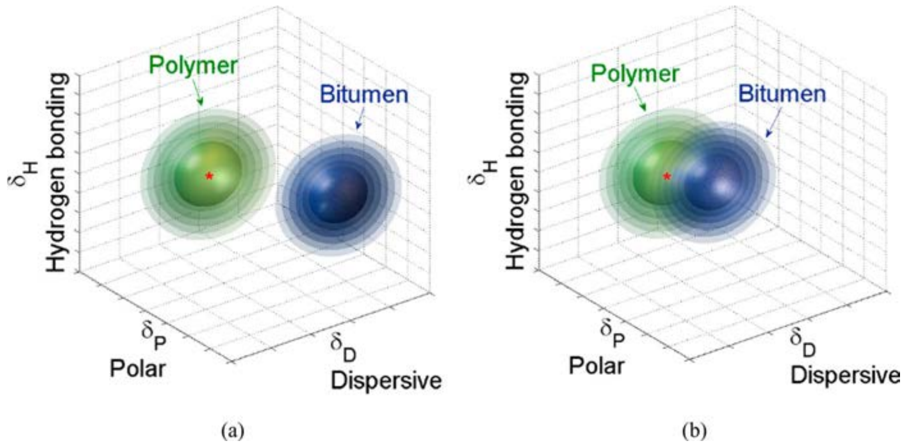


Figure 8. Influence of solubility body centre distance on polymer-bitumen interaction: (a) and (b) show spheres of the same size; the red star indicates the same location in the 3D Hansen space.

a fixed centre distance (thus fixed χ value by Equation 6). In Figure 9(a), the bitumen solubility body is relatively small (smaller than the previous cases). There is no intersection of the all-concentration complete solubility bodies. This means that the bitumen is soluble only in limited solvents. No part of the polymer chains is completely soluble in the bitumen. The entire polymer is partially soluble or completely insoluble. In addition to Figure 8(a), this may also represent a poor polymer-bitumen compatibility and low level of interaction. As in Figure 9(b), the bitumen solubility body becomes larger, although the centre distance keeps the same. The two all-concentration complete solubility bodies get intersecting, showing a better polymer-bitumen compatibility and higher degree of polymer-bitumen interaction in the PMB. This indicates that the solubility body radius also has its impact on the polymer-bitumen interaction. To properly characterise the polymer-bitumen interaction in a PMB system, the effects of both solubility body centre and radius must be considered. As a note, it should be mentioned that 8 and 9 represent extreme cases of the effects for a better visual clarity. In normal cases, the effects should be mostly in between.

4.4. *Proposed free energy for PMB: hypothetical dilution*

Based on the Flory-Huggins free energy of mixing, Zhu et al. (2016) proposed an expression for PMB free energy with a hypothetical dilution process as a simplification. Some other researchers recently adopted this expression and investigated the phase behaviour of polymer composites as well as PE- and SBS-modified bitumen (Ding, Yao, Gong, Chen, & Ren, 2019; Liang, Xin, Fan, Wang, Jiang, et al., 2019; Liang, Xin, Fan, Wang, & Sun, 2019). This dilution simplification can be interpreted by solubility bodies. As mentioned above, the Flory-Huggins theory can give good approximations to the PMB free energy when there is no intersection between the solubility bodies of bitumen and polymer, like in Figure 8(a). This represents a very-high-polymer-content interaction in the PMB, which may lie out of the practical range for real PMBs but make great sense for studying the polymer-bitumen interaction. With higher polymer content, it is more difficult to dissolve the polymer in solvents. For a very-high-polymer-content PMB, the radius of the polymer solubility body can thus be very small. But the size of the bitumen solubility body might have only a limited difference with that for a normal polymer content, due to the presence of n-heptane insoluble (asphaltenes). When the polymer content is sufficiently high, there can be no intersection between the solubility bodies of bitumen and polymer. In this case, the free

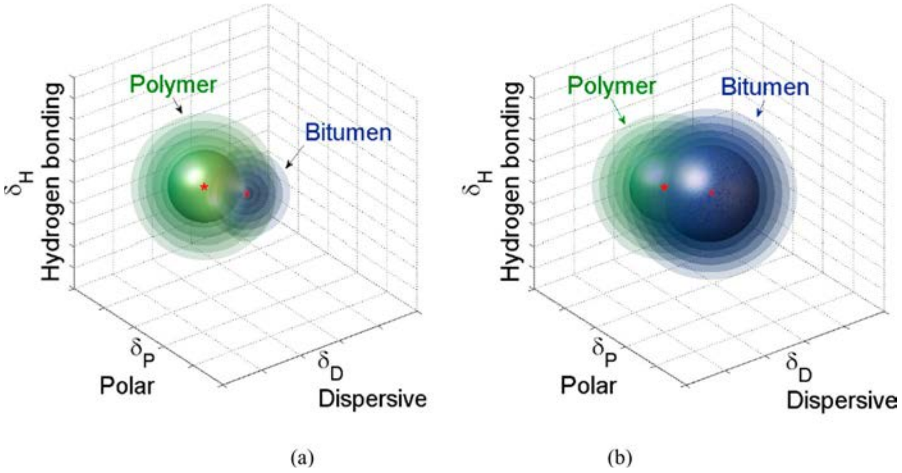


Figure 9. Influence of solubility body radius on polymer-bitumen interaction: polymer sphere is the same size in (a) and (b); the red star and cross indicate the same locations in the 3D Hansen space.

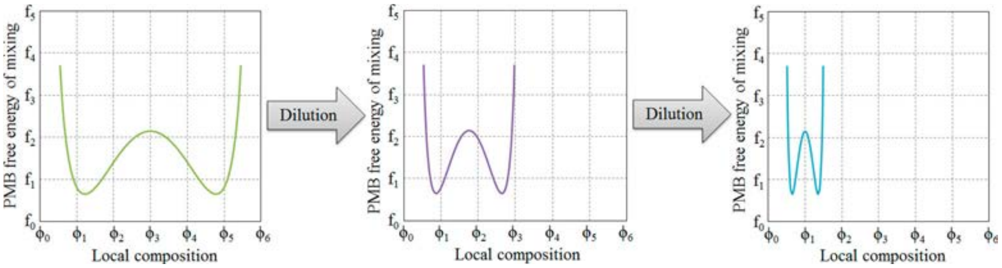


Figure 10. Hypothetical dilution process as a simplification for PMB free energy.

energy of the PMB system can be represented by the Flory-Huggins free energy of mixing with respect to a χ value. For lower polymer contents, the PMB free energy can be approximated by diluting the blend as a simplification, as in Figure 10. As the solubility body radius determines the no-intersection polymer content, the hypothetical dilution process can thus reflect the influence of the solubility body radius.

4.5. *Elastic free energy for polymer swelling in PMB*

The dilution assumption simplified the modelling of polymer swelling in PMB but also caused limitations. For improvements, the free energy expression for swelling needs to be discussed. The Flory–Rehner theory has been employed as a basis for rubber swelling in modified bitumen with crumb rubber (Wang, Apostolidis, Zhu, Liu, & Scarpas, 2019). This theory was originally proposed for the swelling of polymer network structures, e.g. gel (Flory, 1950, 1953; Flory & Rehner, 1943). It considers the local free energy (of mixing) and certain long-range free energy, e.g. elastic free energy and electrostatic free energy (Quesada-Pérez, Maroto-Centeno, Forcada, & Hidalgo-Alvarez, 2011). The swelling reaches its equilibrium when the net osmotic pressure becomes zero, i.e. homogenous chemical potential throughout the whole system.

In the context of modified bitumen, the net osmotic pressure for swelling is controlled by the competition between the free energy change due to mixing and the free energy change due to elastic strain (deformation). In other words, the swelling equilibrium of modifiers is governed by the balance between the thermodynamic osmosis and the elastic retraction (Ganji, Vasheghani-Farahani, & Vasheghani-Farahani, 2010; Van der Sman, 2015). As discussed above, the free energy of mixing can be expressed by the Flory-Huggins theory. For elastic free energy, the Flory–Rehner theory assumes an affine network and yields the expression for isotropic strains as

$$\Delta f_{el} = (3/2)RT(\alpha^2 - 1 - \ln\alpha), \tag{7}$$

where Δf_{el} is the elastic free energy per mole of chains in the network and α is the linear swelling ratio. It is defined by

$$\alpha^3 = V_s/V_0, \tag{8}$$

where V_s is the volume in a swollen state and V_0 is the initial (reference) volume. The introduction of elastic free energy provides a solid thermodynamic basis for modelling the polymer swelling in PMB. It seems promising that further investigations on this may lead to a new and more realistic expression of free energy for PMB system.

5. Kinetic and other aspects of phase separation in PMB

Besides the free energy of mixing and elastic free energy, another essential aspect for a PMB system is to define the interfaces between different phases for the thermodynamically unstable cases. A common expression of gradient (interfacial) energy (Tanaka & Araki, 1997; Ubachs, Schreurs, & Geers, 2004; Zhou, Zhang, & Weinan, 2006) with respect to the local polymer fraction (ϕ) in the PMB can be written as

$$f_{gr} = (1/2)\kappa|\nabla\phi|^2, \tag{9}$$

where f_{gr} is gradient (interfacial) energy density; κ is the gradient energy coefficient; ∇ is the Nabla operator. κ is a positive parameter related to the interfacial tension and thickness between the phases (Moelans, Blanpain, & Wollants, 2008). A lower gradient energy coefficient usually results in a finer PMB structure and sharper interfaces.

As for the kinetics, some previous studies (Artamendi & Khalid, 2006; Wang, Apostolidis, et al., 2018; Wang, Liu, et al., 2019; Wang, Apostolidis, et al., 2019) used Fick's second law to describe the diffusion of molecules from bitumen into crumb rubber as

$$\partial c/\partial t = \nabla \cdot D\nabla c. \tag{10}$$

In this equation, c is the concentration of the diffusing substance; t is time; and D is the diffusion coefficient. For non-ideal systems including PMB, however, the driving force for diffusion is the gradient of chemical potential instead of concentration. With respect to the local polymer fraction (ϕ) in the PMB, the Cahn–Hilliard equation can thus represent the diffusion process by

$$\partial\phi/\partial t = \nabla \cdot M\nabla(\partial F/\partial\phi), \tag{11}$$

where M is the mobility coefficient and F is the total free energy of the system. The term $\partial F/\partial\phi$ is defined as the chemical potential. The mobility coefficient controls the diffusion rate. It is related to the interdiffusion (or chemical diffusion) coefficient between the two phases while the interdiffusion coefficient is determined by the self-diffusion (or tracer diffusion) coefficient of each individual phase. A lower mobility coefficient usually leads to a slower diffusion process.

Furthermore, to describe the flow-induced separation in PMB, the incompressible Navier-Stokes equations can be coupled with the above-mentioned diffusion process. For laminar flow of Newtonian fluids, the equations of motion in vector notation can be written as

$$\rho(\partial \boldsymbol{u}/\partial t) + \rho(\boldsymbol{u}\cdot\nabla)\boldsymbol{u} = -\nabla p + \mu\nabla^2\boldsymbol{u} + \boldsymbol{F}, \tag{12}$$

where ρ is the density; $\boldsymbol{u}$ is the velocity vector; p is the pressure; μ is the dynamic viscosity; $\boldsymbol{F}$ is the force vector. The density ρ and dynamic viscosity μ of a phase is dependent on the local composition as well as the properties of the individual components (polymer and base bitumen). The force term $\boldsymbol{F}$ can represent gravity, surface tension and/or other external forces. With a velocity vector involved, the complete form of the Cahn–Hilliard equation (Cahn & Hilliard, 1959; Yue, Feng, Liu, & Shen, 1999, 2006; Zhou, Yue, Feng, Ollivier-Gooch, & Hu, 2010) can be written as

$$\partial\phi/\partial t + \nabla\cdot\boldsymbol{u}\phi = \nabla\cdot M\nabla(\partial F/\partial\phi). \tag{13}$$

Additionally, some previous studies (Ouyang, Wang, Zhang, & Zhang, 2005; Shu & Huang, 2014; Sienkiewicz et al., 2017; Zapién-Castillo, Rivera-Armenta, Chávez-Cinco, Salazar-Cruz, & Mendoza-Martínez, 2016; Zhang, Wang, Wu, Wang, & Wang, 2009) considered certain types of modified bitumen as suspension systems (suspended particles in fluid medium) and used Stokes' law to interpret their separation as

$$v_t = 2r^2(\varDelta\rho)g/(9\mu_m). \tag{14}$$

In this equation, v_t is the terminal velocity of the suspended particles; r is the particle radius; $\varDelta\rho$ is the density difference between particles and the medium; g is the gravitational acceleration; and μ_m is the dynamic viscosity of the medium. It represents the small-Reynolds-number case of the Navier-Stokes equations. Stokes' law might works well for the separation kinetics of certain particle modifiers, e.g. highly crystalline materials and less swollen rubber. Its applicability, however, must be justified when it is used for other cases.

6. Summary and future perspective

This paper reviews the related advances on the use of solubility parameters and free energy theory for the phase behaviour study of modified paving bitumen. The origin and effects of PMB phase behaviour are criticised in terms of the solubility and free energy. The historical and future developments of the solubility approach are analysed in the context of PMB. The PMB free energy expressions and kinetic aspects are discussed. Based on this overview, the following can be summarised:

- PMB phase behaviour originates from the chemical and physical nature of the raw materials and leads to effects on binder properties. Depending on the specific combination of bitumen and polymer, the storage stability, morphology and swelling ratio of PMBs can vary from case to case. These properties are controlled by the phase behaviour of the PMB, i.e. (1) if the PMB separates into two phases and (2) how the phases behave under certain thermal condition.
- The solubility bodies in the 3D Hansen space and their degree of intersection can be useful for analysing the PMB thermodynamic equilibrium and thus storage stability. But they give no indication on how the phase(s) behave towards the equilibrium and afterwards in the kinetic separation process, i.e. no indication on PMB morphology. For a comprehensive

framework, the thermodynamic basis of solubility theory must be linked to the free energy of PMB systems.

- The thermodynamic approach, integrated with kinetic factors (diffusion and flow), can describe all aspects of the PMB phase behaviour and can thus assist in understanding both PMB storage stability and morphology. The Flory-Huggins interaction parameter can serve as a link between solubility parameters and the PMB free energy. Due to the chemical complexity of bitumen and certain modifiers, however, both the solubility body centre distance and radiuses should be considered for a proper expression of the polymer-bitumen interaction in PMB.
- A hypothetical dilution process can simplify the polymer-bitumen interaction (swelling) process, but with limitations. The introduction of elastic free energy may provide a thermodynamic basis for modelling the polymer swelling in PMB. It seems promising that further investigations on this might lead to a new and more realistic expression of free energy for PMB system.
- With all the discussed in this paper, it is expected that a preliminary foundation is established towards a comprehensive and realistic thermodynamic framework for interpreting and predicting PMB phase behaviour. Such a framework may have significant impacts on new material design, construction process control as well as test method standardisation.

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