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The role of thermodynamics and kinetics in rubber–bitumen systems: a theoretical overview

Haopeng Wang [a], Panos Apostolidis [a], Jiqing Zhu [b], Xueyan Liu[a], Athanasios Skarpas [c,a] and Sandra Erkens [a]

[a]Section of Pavement Engineering, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft, the Netherlands; [b]Swedish National Road and Transport Research Institute (VTI), Linköping, Sweden; [c]Department of Civil Infrastructure and Environmental Engineering, Khalifa University, Abu Dhabi, United Arab Emirates

ABSTRACT
Waste tire rubber has been incorporated into asphalt modification for decades due to its various benefits. There are two main mechanisms during bitumen–rubber interaction: rubber swelling and chemical degradation. This study surveys these two processes from the viewpoint of polymer science. The kinetics of rubber dissolution and thermodynamics of rubber swelling are discussed to provide a fundamental understanding of the interaction process and to demonstrate how optimisation of material selection and processing procedures can lead to the desired binder properties. Factors including the interaction conditions and raw material characteristics are analysed based on the previous theories and compared with experimental results.

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Crumb rubber modified bitumen; diffusion; swelling; chemical degradation; thermodynamics; solubility

1. Introduction

With the developments in transportation and the associated increase in numbers of vehicles, approximately one billion end-of-life tires (ELTs) are produced every year worldwide (WBCSD 2010). Due to the greater awareness of environmental issues and potential economic benefits, engineers are attempting to develop a more sustainable framework to dispose the ELTs (Sienkiewicz *et al.* 2012). Locally, it was estimated that the European Union (EU) produced 3.6 million tonnes of ELTs in 2013. An estimated 2.7 million tonnes of them were recovered and recycled, which represents a treatment rate of 96% and confirms the world-leading role of the EU in the waste tire management (Etrma 2016). Material recycling is the most common means of managing ELTs in the EU and has been gaining more and more attention due to the lower processing costs and additional benefits (Sienkiewicz *et al.* 2012, Torretta *et al.* 2015). In the paving industry, waste tire rubber has been successfully utilised as a modifier to improve the properties of binders (Lo Presti 2013).

Crumb rubber is recycled rubber with a granular consistency produced from ELTs through removing the steel and tire cord (fluff) and mechanical grinding. Crumb rubber modifier (CRM), whose size is usually ranging from 0.075 to 4.75 mm, is the common name used to identify the rubber particles ground from ELTs for bitumen modification (State of California Department of Transportation 2003). There are two primary methods of incorporating CRM into hot mix asphalt (HMA), which are generally referred to as dry process and wet process. In the dry process, CRM is mixed directly with the aggregate prior to introducing the required binder during the HMA production. The CRM acts as a partial replacement of stone aggregates in asphalt mixtures. Through the wet process, CRM is blended with bitumen and a predetermined reaction time is required before mixing the modified binder with aggregates. According to the different wet processing technologies (State of California Department of Transportation 2003, Lo Presti 2013, Shu and Huang 2014), rubberised asphalt has various technical terminologies, such as Asphalt Rubber (AR), Terminal Blends (TB), Crumb Rubber Modified Binder (CRMB), etc. Specifically, AR is defined as a blend of bitumen, recycled tire rubber and certain additives in which the minimum rubber content is 15% by weight of the total blend. The blend is reacted at high temperatures until sufficient swelling of rubber particles is achieved. TB is actually a preparation technique where finely ground CRMs are blended with hot bitumen at the refinery or the binder storage and distribution terminal. CRMB is a general term to identify any bituminous binder modified by CRM. Rubberised asphalt concrete has been successfully applied in paving industries for decades thanks to the development of paving technologies (Lo Presti 2013). The incorporation of CRM into HMA improves the overall pavement performance and yield also intangible benefits (Wang *et al.* 2018a). Most of these improvements are attributed to the interaction of crumb rubber and bitumen which leads to changes in binder composition and microstructure (Gawel *et al.* 2006, Attia and Abdelrahman 2009, Ghavibazoo and Abdelrahman 2013).

Previous researchers have done extensive literature reviews (Lo Presti 2013, Shu and Huang 2014, Wang *et al.* 2017a, 2017b, 2018a) of rubberised asphalt regarding the production technology, mix design methodologies, performance characterisation and specifications, storage and transport stability, construction technologies, environmental and economic impact assessment, etc. However, most of the conclusions drawn in

CONTACT Haopeng Wang haopeng.wang@tudelft.nl

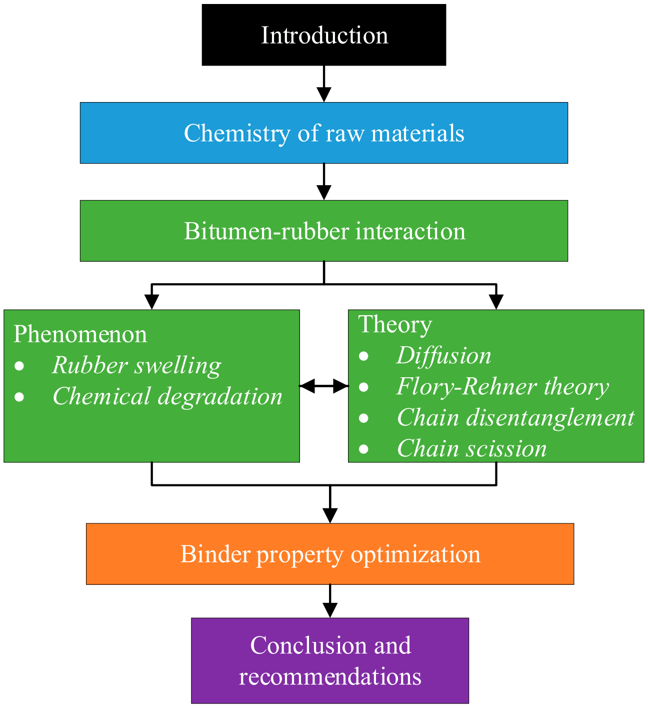

Figure 1. Framework of the article.

the previous studies were based on laboratory tests and lack of fundamental explanations, which may limit their further applications. This paper focuses on a less discussed but crucial topic, namely, the interaction mechanisms between bitumen and rubber at different conditions from the viewpoint of polymer science. It is an attempt to establish a theoretical framework for the rubber–bitumen interaction process as a tool to optimise the binder properties.

Figure 1 presents the framework of this review article. After the introduction, the chemistry of bitumen and rubber, which is most related to the interaction, is introduced. Then, the bitumen–rubber interaction is described from both phenomenal and theoretical viewpoints. The kinetic and thermodynamics aspects of the interaction will be discussed in the theoretical part. In the following section, critical factors in practice are analysed with reflections from the theories in an attempt to binder property optimisation. Conclusions and recommendations based on previous analyses are summarised in the last section.

2. Chemistry of raw materials: bitumen and crumb rubber

2.1. Composition of bitumen

Bitumen is not a polymeric material but a complex mixture consisting of hydrocarbons of different size, polarity and aromaticity. It may also contain small amounts of heteroatoms, such as sulphur (0–9 wt.%), nitrogen (0–2 wt.%), oxygen (0–2 wt.%) and traces of metals (e.g. vanadium and nickel). The number-average molecular weight of bitumen generally ranges from 600 to 1500 Da and therefore, bitumen molecules cannot be considered as macromolecules in the polymeric sense. Given the highly complex molecular structure of bitumen, it is almost impossible to conduct detailed chemical analysis. Even though bitumen consists of a continuum of similar molecules, to facilitate classification and the understanding of its properties based on dominant molecular group types, bitumen molecules are generally classified into different molecular groups depending on their size and solubility in polar, aromatic or non-polar solvents. The widely accepted SARA (saturates, aromatics, resins and asphaltenes) fractions, developed based on the selective adsorption–desorption (chromatographic) method (Lesueur 2009), are used to give the relative quantities of these components in bitumen. The physicochemical properties of bitumen and the SARA fractions are compiled in Table 1. Bitumen can be described as a colloidal dispersion of high-molecular-weight asphaltene micelles in the low-molecular-weight maltenes (saturates, aromatics, resins) (Lesueur 2009). The solubility model is also often used to describe the chemistry of bitumen where the asphaltenes are dissolved in the maltenes rather than dispersed (Redelius 2004). The key aspect of solubility model is that there is no gap in chemical properties between the fractions of bitumen which are a continuous range of molecules with respect to size, polarity and aromaticity (Redelius and Soenen 2015). The colloidal structure and solubility parameter of bitumen influences its rheology and interactions with different polymers.

2.2. Compositions of tire rubber

As mentioned before, the crumb rubber used for bitumen modification is recycled from waste tires. The composition of tires is very complex to fulfil their end-use properties. Table 2 summarises the detailed tire ingredients used in different vehicles in the EU. Normally, during the handling and shredding processes, the reinforcing wires and fibres are removed to produce a clean and highly consistent rubber material for bitumen modification. In general, truck and off-the-road (OTR) tires contain higher proportions of natural rubber (NR) than passenger car tires. NR and synthetic rubber (SR) have different interactions with bitumen at the same conditions. This explains why the tire source can have considerable influence on the properties of CRMB binders (Frantzis 2004, Artamendi and Khalid 2006). NR is industrially obtained from the latex of the tree called *Hevea brasiliensis* and it is essentially a hydrocarbon polymer. The main constituent of

Table 1. Physiochemical properties of bitumen and the SARA fractions (Daly 2017, Lesueur 2009).

	Weight percentage (%)	*H/C* ratio	Molecular weight (g/mol)	Density at 20°C (g/cm^3)	Solubility parameter (MPa$^{0.5}$)	Glass transition temperature (°C)	Solvent used for separation in ASTM D4124
Bitumen	100	1.5	600–1500	1.01–1.04	17.2–18.8	−20 (−40~5)	–
Saturates	5–15	1.9	470–880	0.9	15–17	−70	*n*-heptane
Aromatics	30–45	1.5	570–980	1	17–18.5	−20	toluene and toluene/methanol
Resins	30–45	1.4	780–1400	1.07	18.5–20	–	trichloroethylene
Asphaltenes	5–20	1.1	800–3500	1.15	17.6–21.7	–	*n*-heptane insoluble

Table 2. Composition comparison of different tires in the EU, adapted from Etrma (2016).

Ingredients	Car type (%)	Truck type (%)	OTR type (%)
Rubber/elastomers	47	45	47
Carbon black	21.5	22	22
Metal	16.5	25	12
Textile	5.5	0	10
Zinc oxide	1	2	2
Sulphur	1	1	1
Additives	7.5	5	6

Note: OTR, off-the-road.

NR is the polymer *cis*-1,4-polyisoprene with a molecular weight of 10^5–10^6 Da. As can be seen in Figure 2(a), macromolecules of NR are long, regular, flexible and practically linear. In contrast, SR is any artificial rubber, synthesised from petroleum by-products through a polymerisation process. The most common SR used in tire manufacturing is styrene–butadiene rubber (SBR) shown in Figure 2(b) derived from the copolymerisation of styrene (C_8H_8) and butadiene (C_4H_6). The properties of SBR are influenced not only by the micro- and macrostructure of polymer chains, but also the styrene/butadiene ratio. NR and SBR polymers used in tire manufacturing possess similar glass transition temperatures of approximately −70°C (Burfield and Lim 1983). During the polymer production, polymers are usually heated well above the glass transition temperature to allow casting, moulding and extrusion into desired forms. Considering the typical tire moulding temperature is ~177°C in the manufacturing process (Mark *et al.* 2013), it is not uncommon to see the interaction temperature between rubber and bitumen range from 180 to 220°C. In this temperature range, the polymer chains of rubber change from rigid glassy regions to flowable melt regions. Therefore, rubber particles can be incorporated into the bitumen network establishing the inverse continuous phase due to the high chain mobility.

To improve the durability and mechanical properties of rubber, vulcanisation is applied to most rubber polymers by forming chemical crosslinks between individual polymer chains to create three-dimensional networks (Mark *et al.* 2013). The most commonly used curative during the vulcanisation process is sulphur. Figure 2(c) shows the formation of crosslink between two strands (blue and green) of NR after vulcanisation with elemental sulphur (Mark 2009). Vulcanisation

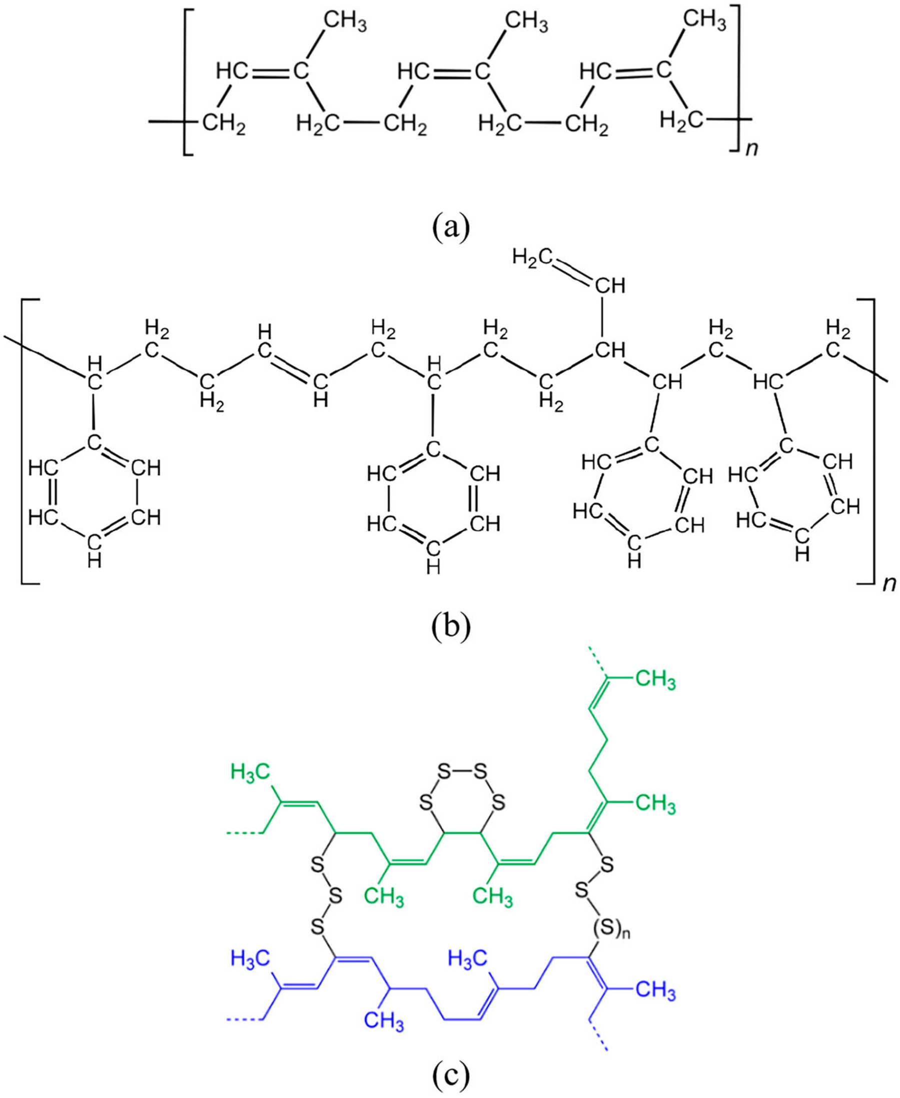

Figure 2. Chemical structure of (a) *cis*-polyisoprene, (b) copolymer SBR and (c) crosslinking after vulcanisation, adapted from Mark (2009).

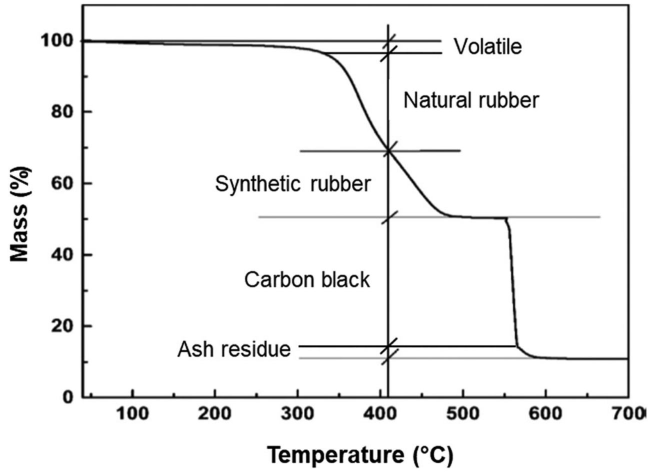

Figure 3. Typical TGA curve of crumb rubber from scrap tires.

can effectively increase the retractive force and reduce the amount of permanent deformation remaining after removal of the force. During the tire rubber manufacturing process, various additives and ancillary substances necessary for vulcanisation are added to improve the overall physical properties. Carbon black and amorphous silica are added into rubber as reinforcing fillers, which can significantly improve the anti-abrasion property and the material strength and hardness. Other additives, including activator accelerator (zinc oxide), coagulants, anti-oxidants, colour pigments, surfactants, softeners (oils), etc., are added in the tire manufacturing process to improve the tire properties and workability. Thermogravimetric analysis (TGA) is a useful and reliable tool for material composition analysis (Cui *et al.* 1999). Figure 3 presents a typical TGA curve of a tire rubber sample. It provides quantitative and/or qualitative information about the main component and their concentrations in the sample based on the decomposition temperature and mass loss (Cui *et al.* 1999). As shown in Figure 3, the main components of tire rubber include oily and volatile substances, NR and SR, inorganic fillers, carbon black and residual ash. This implies that TGA could be used for monitoring the change of rubber during the bitumen–rubber interaction process (Ghavibazoo and Abdelrahman 2013).

3. Bitumen–rubber system and interaction process

Typically, CRMB is produced by mixing bitumen and rubber at elevated temperature for a certain period. The bitumen–rubber interaction controls the property development of CRMB and has a great influence on the binder transport and storage. There are two main stages which occur during the interaction process: rubber swelling and degradation (Abdelrahman and Carpenter 1999, Wang *et al.* 2017a). Rubber swelling is a physical diffusion process while the degradation of rubber is a chemical process in which new substances are created. It is often seen in the literature that researchers use the terminology of *rubber dissolution* to describe the status of rubber particles in bitumen during the interaction. Rubber dissolution is measured by extracting the rubber particles from the binder matrix. The portion of rubber particles in CRMB that passes through a certain fine mesh (usually 75 μm), which is usually difficult recognised by eyes, is considered as the dissolved portion (Ghavibazoo *et al.* 2013b). From the definition, it can be seen that dissolution here is a vague engineering term which cannot distinguish if chemical degradation of rubber occurs or not. The dissolved portion may contain extremely fine rubber particles that are disassociated/split from coarse rubber particles. The percentage of rubber dissolution is often used to differentiate different types of CRMB, e.g. AR and TB. Swelling and complete dissolution of rubber are two opposite ends of the interaction of bitumen and rubber depending on the interaction conditions (Ghavibazoo *et al.* 2013b).

3.1. Rubber swelling

Swelling of polymers is a volume expansion process of the polymer network due to absorption of solvents. For uncrosslinked polymers (Figure 4(a)), when exposed to suitable solvents, they can be easily swollen up and eventually dissolve into the solvent. This process is called polymer dissolution which will be discussed in the following section. The dissolution of an uncrosslinked polymer into a solvent involves two phenomena, i.e. solvent diffusion-induced swelling and chain disentanglement (Tu and Ouano 1977). It should be pointed out that the definition of polymer dissolution here is different from the term ‘dissolution’ used for rubber dissolution previously in an engineering context. For crosslinked polymer systems in which links between chains or segments are established (Figure 4(b)), because of the constraints of the network structure, the network might be swollen by absorbing solvents but the dissolution will hardly occur. Limited swelling is a characteristic property of polymers with network structures (Flory and Rehner 1943). As clarified in the previous section, tire rubber contains a large portion of vulcanised/crosslinked polymer and a small portion uncrosslinked polymer. Therefore, swelling of tire rubber in organic solvents is a partial dissolution process (Stroup-Gardiner *et al.* 1993, Artamendi and Khalid 2006). Depending on the compatibility between rubber and solvents, the swelling extent and dissolution rate may vary. When mixing rubber with bitumen at high temperatures, the light fractions of bitumen will diffuse into the rubber network and cause its swelling. The volume change of rubber particles and the formation of the gel layer adjacent to the rubber–bitumen interface reduces the inter-particle distance and changes the component proportions of the remaining bitumen and, therefore, stiffens the composite material.

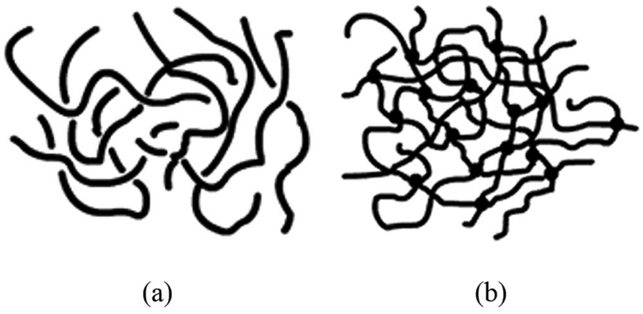

Figure 4. Schematic representation of the molecules of (a) the uncrosslinked polymer and (b) the crosslinked polymer (links are pictured as knots), adapted from Mark *et al.* (2013).

Table 3. Average bond energies of chemical bonds typically in CRMB.

Bond name	C–C	C–S	S–S
Bond energy (kJ/mol)	347	259	266

3.2. Chemical degradation

Under severe interaction conditions (excessively high mixing temperature with high shear and long mixing times), rubber network degradation occurs. Even though the network structure formed by crosslinking prevent the dissolution of rubber molecules, the high thermal energy and shearing energy induced in the mixing process will destroy the crosslinking and hence the rubber network. This process involves the scission of disulphide bond (S–S), carbon–sulphur bond (C–S) and carbon–carbon bond (C–C), which eventually results in the breakage of crosslinked bonds and backbone chain bonds reducing thus the average molecular weight of rubber (Zanzotto and Kennepohl 1996). This degradation process is referred to as devulcanisation and depolymerisation, respectively (Abdelrahman and Carpenter 1999). The average bond energies of different bonds are listed in Table 3 (Chemistry LibreTexts Library 2017). Based on the relative bond energies of S–S, C–S and C–C bonds (with the order of C–S < S–S < C–C), the S–S bond or C–S bond is less stable than C–C bond in the presence of energy perturbations, such as chemical and thermal attacks. Therefore, the scission of S–S and S–C takes place earlier and destroys the network formed by crosslinking. That is why during the mixing process of the bitumen–rubber blend at high temperatures, the acrid smell from sulfoxide may be detected. The rubber network degradation removes the constraints for the polymer chains. The free rubber polymer chains will eventually dissolve into bitumen. The mixing energy imposed by the mixer during interaction can accelerate the swelling process of rubber particles and enhance the size-reduction effects. The chemical degradation of rubber networks is adverse to the mechanical property development of binders (Tang *et al.* 2016, Yao *et al.* 2016) but beneficial to improve the binder storage stability (Lo Presti *et al.* 2018).

3.3 Other component exchange

The previous two sub-sections discussed the behaviour of rubber polymer when interacting with bitumen. However, in reality, tire rubber is a mixture of different components. During the bitumen–rubber interaction process, oily components, carbon black and some inorganic fillers bound to rubber are also released under high interaction temperatures and mixing forces. Considering the large proportion of these non-polymer components, the effects of their release into bitumen on the binder properties cannot be ignored. It was reported that these non-polymer components significantly influence the ageing and rheological properties of CRMB (Ghavibazoo *et al.* 2015, Wang *et al.* 2019c).

In summary, the interaction stages of bitumen–rubber can be divided into three steps as shown in Figure 5 (Wang *et al.* 2017a). Stage 0: initial configuration. Rubber particles are just immersed in the fluid bitumen. Stage 1: swelling phase. Rubber particles start swelling by absorbing the light fractions of bitumen and form a gel layer adjacent to the bitumen–rubber interface. Stage 2: post-swelling and beginning of degradation. The swelling of rubber particles continues happening. Meanwhile, chemical degradation takes place through the breakup of the crosslinked network and polymer chains. Swollen rubber particles are split into smaller ones due to the destruction of network structure. Stage 3: degradation and complete dissolution. The degradation of rubber particles continues progressing until they are completely dissolved into the bitumen matrix, which produces a homogenous binder. It is noteworthy that the different interaction stages may overlap. The degradation of the rubber network enhances the absorption of light components from bitumen to the remaining rubber for swelling. In turn, swelling also speeds up the degradation rate of rubber. In reality, there is a swelling gradient of rubber from the outer layer to the inner core.

4. Theoretical considerations of bitumen–rubber interaction

4.1. Relationship between bitumen–rubber interaction and polymer dissolution in solvents

Looking back to the interaction between bitumen and rubber, it has similarities as the polymer dissolution process but is not equal to each other. In the following analysis, bitumen is generally considered as the low-molecular-weight solvent, while rubber is a polymer with high molecular weight. The complex compositions of the rubber system increase the complexity of

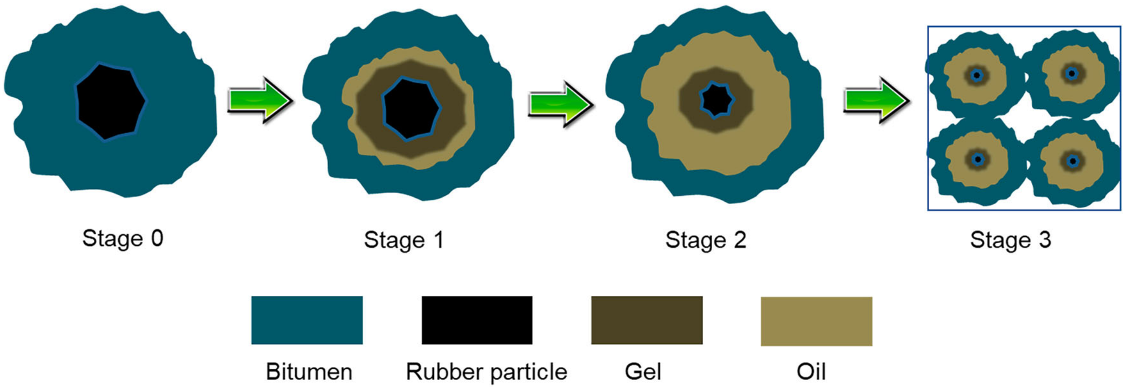

Figure 5. Interaction stages of bitumen and rubber, adapted from Wang *et al.* (2017a).

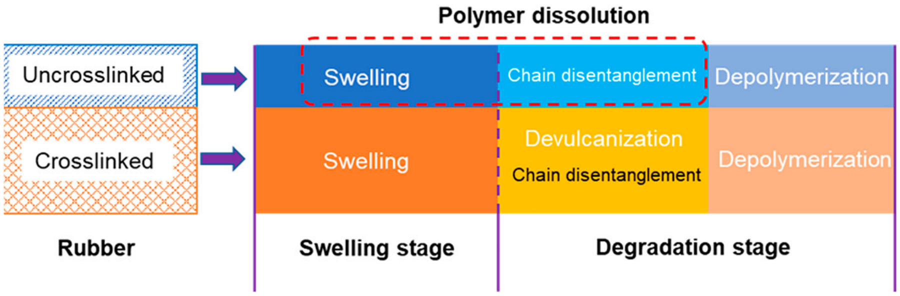

Figure 6. Interaction stages of rubber when mixed with bitumen.

the interaction mechanism with bitumen. The uncrosslinked and crosslinked parts in rubber have different behaviours when interacting with bitumen. Combining the experimental findings in bitumen–rubber interactions and the knowledge of polymer dissolution, Figure 6 summarises the interaction mechanisms of rubber with bitumen at different stages. The devulcanisation process will break the crosslinks and make chain disentanglement happen. It should be emphasised that each interaction step does not necessarily follow the exact sequence as shown in Figure 6. In most instances, rubber swelling and degradation occur simultaneously because of the diversity of rubber particle size. Fine particles finish the swelling stage in no time and start the degradation stage. Similarly, chain disentanglement, devulcanisation and depolymerisation can also overlap. The theoretical aspects of rubber swelling and degradation stages will be described as follows.

As illustrated in Figure 6, polymer dissolution in solvents is actually a two-step process, which consists of: (a) diffusion-induced swelling of the polymer network and (b) chain disentanglement of the swollen polymer. The dissolution of a polymer in a solvent is usually a very slow process depending on the microstructure and chemical composition of a given polymer as well as the surrounding environment. Figure 7 shows the dissolution process of an uncrosslinked polymer. Polymer molecules consist of long chains with large numbers of segments, forming tightly folded coils which are entangled to each other. When the polymer is just added into a thermodynamically miscible solvent, the coils still hold together as a solid due to the cohesive and attractive intra- and intermolecular forces, Figure 7(a). Later on, due to polymer–solvent interactions, segments with polymer chains start to imbibe solvent molecules, increasing the volume of the polymeric network and forming a swollen polymeric gel, Figure 7(b). The swollen gel exhibits elastic rather than plastic properties. Once the swelling reaches a critical point, which means all segments are solvated but remaining in contact due to strong polymer interactions, the polymer chains start disentangling from the bulk. The whole loosen/unfolded coils will slowly diffuse out of the swollen polymer gel and eventually disperse into the solution. When all the chain segments are dispersed into the solvent, the solvent molecules will fill the empty space between the loose segments, occupying a spherical or ellipsoidal volume, Figure 7(c). This apparent volume occupied by the swollen polymer coil with the absorbed solvent is called hydrodynamic volume. Therefore, there are two transport mechanisms in this dissolution process as shown in Figure 8, i.e. solvent diffusion and chain disentanglement. The rubbery–solvent interface moves towards the solvent, while the glassy–rubbery interface moves towards the glassy part of the polymer (Narasimhan 2001).

To have more insights into the microstructural changes of the polymer during dissolution, Figure 9 displays the evolution of polymer chains from a spatial viewpoint. It can be found polymer chains are distributed in different states at different positions, implying different microstructures of the polymer. Many researchers have proved the formation of a multilayer structure during the polymer dissolution process (Miller-Chou and Koenig 2003). The structure of the surface layer between the pure polymer and the pure solvent is summarised as follows: the infiltration layer, the solid swollen layer, the gel layer and the liquid layer (Figure 10). This structure classification is based on the glassy polymers. However, some of the

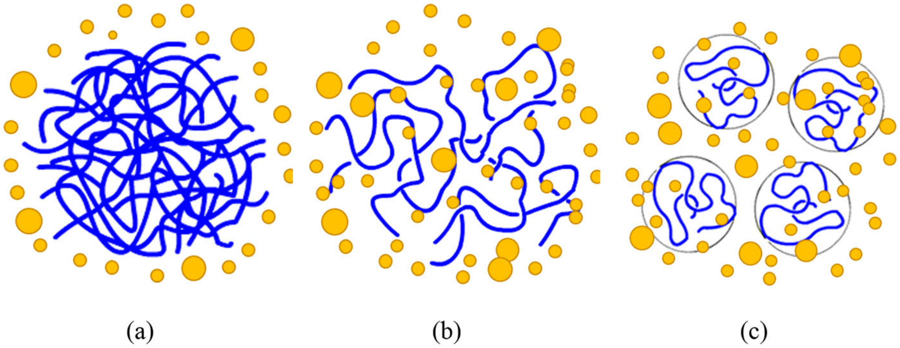

Figure 7. Schematic representation of the dissolution process for polymer molecules, blue lines represent polymer chains and yellow dots represent solvent molecules. (a) polymer molecules in solid state just after being added to a solvent; (b) a swollen polymeric gel; (c) solvated polymer molecules dispersed into a solution.

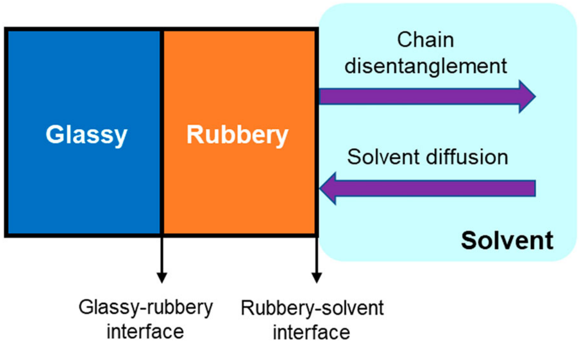

Figure 8. A schematic diagram of a one-dimensional solvent diffusion and polymer dissolution process, adapted from Narasimhan (2001).

layers may not be formed during dissolution depending on the polymer and solvent properties as well as the interaction conditions. Adjacent to the core of pure polymer is the infiltration layer. The solid swollen layer is established for the polymer–solvent system in the glassy state. When swelling equilibrium achieves, the penetrated solvent molecules start to push the polymer molecules into the solvent. During this transport process of polymer substance, chain disentanglement may happen as shown in Figure 8. In the gel layer, polymer chains start disentangling when the solvent concentration inside the polymer chain reaches the critical gel concentration (Peppas *et al.* 1994). At this moment, the two interfaces (polymer–gel and gel–solvent) proceed at the same velocity. As time passes, a more dilute upper layer called the liquid layer is formed to the direction of the pure solvent. As the glassy–rubbery interface continues to move inward (to the direction of polymer core) in Figure 8, the glassy core gradually disappear. As a result, the rubbery–solvent interface keeps moving outward until the complete polymer dissolution is achieved (Vrentas and Vrentas 1998). Above is the schematic description of the polymer dissolution process. Several other models were also developed to explain the polymer dissolution behaviours: phenomenological models with diffusion equations (Tu and Ouano 1977), external mass transfer models (Lee and Peppas 1987), stress relaxation models with the reptation theory (Brochard and Degennes 1983), anomalous transport models and scaling laws (Peppas *et al.* 1994), continuum framework models (Narasimhan and Peppas 1996b).

Therefore, an entire bitumen–rubber interaction involves polymer dissolution and many other reactions. The kinetics and thermodynamics framework of bitumen–rubber systems is discussed in the next sub-sections following the sequence of the aforementioned phenomena.

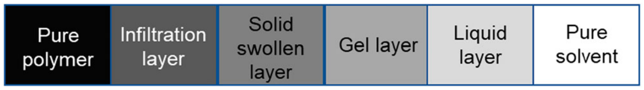

Figure 10. Schematic representation of the surface layer structure, adapted from Miller-Chou and Koenig (2003).

4.2. Diffusion of bitumen into rubber

When rubber networks are exposed to bitumen, certain fractions of the bitumen (mostly the low-molecular-weight maltenes) diffuse into and are imbibed by the polymer network, causing its swelling. This diffusion process continues until the solvent concentrations inside and outside the polymer are equal to each other. Previous studies have shown that the Fickian model is most appropriate for describing the swelling of rubbery polymers (Papanu *et al.* 1989). The kinetics of bitumen diffusion into rubber is usually described by Fick's laws of diffusion (Artamendi and Khalid 2006, Wang *et al.* 2019a). Fick's second law predicts the evolution of bitumen concentration with time due to the progress of diffusion into rubber as

$$\frac{\partial C}{\partial t} = \nabla \cdot D \nabla C \tag{1}$$

where C is the concentration of diffusing substance; t is time; and D is the diffusion coefficient. For the Fickian diffusion, it is obvious that the concentration gradient is the driving force for the diffusion process. However, for non-ideal systems including CRMB, the diffusion is often driven by the gradient of chemical potential, which can be described by the Cahn–Hilliard equation

$$\frac{\partial \phi}{\partial t} = \nabla \cdot M \nabla \left(\frac{\partial F}{\partial \phi} \right) \tag{2}$$

where ϕ is the local polymer fraction; M is the mobility coefficient; and F is the total free energy of the system. The chemical potential is defined as $\partial F / \partial \phi$. The Cahn–Hilliard equation has a similar form to Fick's second law. In the system, the diffusion rate is positively correlated to the mobility coefficient. The Cahn–Hilliard equation is useful when considering the thermodynamics of swelling equilibrium.

There are many methods for measuring the diffusion of materials in polymers, such as optical method, gravimetric method, vapour sorption, employing radioactive trace materials and interferometer procedures (Buckley *et al.* 1962, Buckley and Berger 1962). However, because of the complexity and particularity of the combination of rubber and bitumen, the conventional gravimetric method is often used to monitor

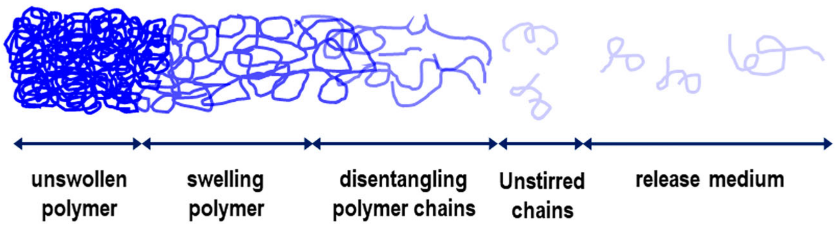

Figure 9. Polymer dissolution process from a molecular scale.

the diffusion process. Laboratory swelling tests with a rectangular rubber block have been done to obtain this parameter (Frantzis 2004, Artamendi and Khalid 2006, Feng *et al.* 2015). Following the initial linear region, it was found a clearly defined equilibrium plateau region occurred. For other geometrical rubber specimens, for instance, cylindrical specimens, the diffusion coefficient can be obtained through the analytical solutions of one-, two- and three-dimensional diffusion models (Luo *et al.* 2017, Luo and Huang 2018).

4.3. Equilibrium swelling of rubber in bitumen

4.3.1. The Flory–Rehner theory

The classical benchmark theory for describing the swelling process in polymer gels is the Flory–Rehner theory (Quesada-Pérez *et al.* 2011). Based on this theory, the thermodynamic force of mixing (osmotic force) and the retractive force of the polymer chains (elastic force) are the two opposing forces competing to determine the swelling behaviour in gels. On swelling, each polymer network strand is stretched, and the crosslink junctions move further apart. Against the osmotic force, there is an opposite elastic force, which balances the stretching of the network and opposes its deformation. When the osmotic pressure is balanced by the elastic restraint, swelling reaches its equilibrium state (Ganji *et al.* 2010). According to the Flory–Rehner theory, the thermodynamic equilibrium of a gel is reached when the chemical potential of the solvent (designated by μ_b) is equal inside and outside the gel

$$\mu_b^{\mathrm{in}} = \mu_b^{\mathrm{out}} \tag{3}$$

Using the concept of osmotic pressure (Π), Equation (3) can be rewritten in the following form

$$\Pi = -\frac{\mu_{\mathrm{b}}^{\mathrm{in}} - \mu_{\mathrm{b}}^{\mathrm{out}}}{\nu_{\mathrm{b}}} \tag{4}$$

ν_b is the molar volume of bitumen. The osmotic pressure, defined as the rate of change of the total free energy of the polymer–solvent system, can be calculated using the following equation:

$$\Pi = -\frac{N_{\mathrm{A}}}{\nu_{\mathrm{b}}}\frac{\partial \Delta F}{\partial n_{\mathrm{b}}} \tag{5}$$

where N_{A} is Avogadro's number; n_{b} is the number of bitumen molecules; ΔF is the change of Helmholtz free energy since the rubber–bitumen system is theoretically incompressible. The free energy change during the swelling process in the case of incompressible system is

$$\Delta F_{\mathrm{total}} = \Delta F_{\mathrm{mix}} + \Delta F_{\mathrm{el}} \tag{6}$$

where $\Delta F_{\mathrm{total}}$ is the change of total free energy in the gel, ΔF_{mix} is the change of free energy of mixing and ΔF_{el} is the change of elastic free energy. Equilibrium swelling is achieved by minimisation of the Helmholtz free energy. In the Flory–Rehner theory, the mixing free energy is formulated with the Flory–Huggins equation

$$\Delta F_{\mathrm{mix}} = n_{\mathrm{b}} k_{\mathrm{B}} T[\ln \phi_{\mathrm{b}} + \chi \phi_{\mathrm{r}}] \tag{7}$$

where k_{B} is the Boltzmann constant; T is the temperature; ϕ_{b} is the local volume fraction of solvent (bitumen); ϕ_{r} is the local volume fraction of rubber in a swollen state, defined by Equation (8); χ is the interaction parameter between the bitumen and rubber; n_{b} is the number of bitumen molecules

$$\phi_{\mathrm{r}} = \frac{V_0}{V} \tag{8}$$

Here V is the volume of the rubber gel (including the absorbed solvent within it) at a given state and V_0 is the volume of the dry rubber. The simplest model that captures the idea of rubber elasticity is the affine network model (Flory 1950, 1985), which assumes an affine deformation: the relative deformation of each network strand and the macroscopic relative deformation of the whole network are the same. The free energy required to deform a network mainly arises from the change of entropy associated with an isotropic deformation

$$\Delta F_{\mathrm{el}} = -\frac{3}{2}\nu_{\mathrm{e}} k_{\mathrm{B}} T(\ln \alpha_{\mathrm{s}} - \alpha_{\mathrm{s}}^2 + 1) \tag{9}$$

where ν_{e} is the number of effective chains in the network; α_{s} is the linear swelling ratio, which can be computed with the following equation by involving the molar volume of the solvent φ_{b}

$$\alpha_{\mathrm{s}}^3 = \frac{V}{V_0} = \left(V_0 + \frac{\varphi_{\mathrm{b}} n_{\mathrm{b}}}{N_{\mathrm{A}}}\right)/V_0 \tag{10}$$

The chemical potential (Rubinstein and Colby 2003) of the bitumen in the rubber gel is defined as

$$\mu_{\mathrm{b}}^{\mathrm{in}} - \mu_{\mathrm{b}}^{\mathrm{out}} = N_{\mathrm{A}}\left(\frac{\partial \Delta F_{\mathrm{mix}}}{\partial n_{\mathrm{b}}}\right)_{T,P} + N_{\mathrm{A}}\left(\frac{\partial \Delta F_{\mathrm{el}}}{\partial \alpha_{\mathrm{s}}}\right)_{T,P}\left(\frac{\partial \alpha_{\mathrm{s}}}{\partial n_1}\right) \tag{11}$$

Incorporating Equations (7), (9) and (10) into Equation (11) yields

$$\begin{aligned}\mu_{\mathrm{b}}^{\mathrm{in}} - \mu_{\mathrm{b}}^{\mathrm{out}} \\ = RT\left[\ln(1-\phi_{\mathrm{r}}) + \phi_{\mathrm{r}} + \chi\phi_{\mathrm{r}}^2 + \varphi_{\mathrm{b}}\frac{\nu_{\mathrm{e}}}{V_0}\left(\phi_{\mathrm{r}}^{\frac{1}{3}} - \frac{1}{2}\phi_{\mathrm{r}}\right)\right]\end{aligned} \tag{12}$$

When reaching equilibrium, the chemical potential of the solvent inside and outside the swollen polymer will be equal to each other, which means the left side of Equation (12) will be cancelled. Rearranging Equation (12) gives

$$-\ln(1-\phi_{\mathrm{r}}) + \phi_{\mathrm{r}} + \chi\phi_{\mathrm{r}}^2 = \varphi_{\mathrm{b}}\frac{\nu_{\mathrm{e}}}{V_0}\left(\phi_{\mathrm{r}}^{\frac{1}{3}} - \frac{1}{2}\phi_{\mathrm{r}}\right) \tag{13}$$

The number of effective chains per unit volume can be linked with the specific volume of rubber $\bar{v}$ and the molecular weight between crosslinks M_{c} as follows:

$$\frac{\nu_{\mathrm{e}}}{V_0} = \frac{1}{\bar{v} M_{\mathrm{c}}} \tag{14}$$

Recalling the definition of crosslink density ν_x (Ganji *et al.* 2010), which is a measure of crosslinked points per unit volume (mol/cm^3), gives the final expression through further rearrangement

$$v_x = \frac{1}{\bar{v}M_c} = \frac{v_e}{V_0} = -\frac{\ln(1-\phi_r) + \phi_r + \chi\phi_r^2}{\varphi_b\left(\phi_r^{\frac{1}{3}} - \frac{1}{2}\phi_r\right)} \tag{15}$$

The term $2M_c/M$ in common equation for calculating the crosslink density is eliminated due to the fact that the molecular weight of the rubber is much higher than M_c. It should be noted that the previous equations are derived for the crosslinked polymer system. For the polymer system with only entanglements, the number of moles of crosslinks can be replaced by the number of moles of entanglements (Papanu *et al.* 1989, Narasimhan and Peppas 1996a). Then, similar calculations can be performed. Ideally, through laboratory experiments, the swelling ratio of rubber ($q = V_0/V = 1/\phi_r$) in certain solvents can be measured by different methods. In addition, with known values of the Flory interaction parameter, both crosslink density and a molecular weight between crosslinks can be further derived through Equation (17) when the solvent is determined. On the other hand, if the crosslink density of rubber and the Flory interaction parameter between rubber and bitumen are known in advance, the equilibrium swelling ratio of rubber in bitumen can be predicted.

4.3.2. The Flory–Huggins parameter

The Flory interaction parameter χ in the Flory–Huggins equation for polymer solutions is of prime importance since it describes the thermodynamic state of polymer–solvent interaction in a given mixture. This parameter is defined to characterise the difference of interaction energies in the mixture. If there is a net attraction between species from polymer and solvent (i.e. they like each other better than they like themselves), $\chi < 0$ and a single-phase mixture is favourable for all compositions. However, the most often situation is that a net repulsion exists between species (i.e. they like themselves more than each other) and this will oppose the mixing process. Therefore, the sign of the interaction parameter χ determines the energetic tropism for mixing, that is positive for opposing mixing, zero for ideal mixtures and negative for promoting mixing (Rubinstein and Colby 2003).

Several methods (Liu and Shi 2008), such as vapour pressure lowering, osmometry, light scattering and inverse gas chromatography, were proposed to estimate the value of χ. However, these tests are generally time-consuming and need cautious operations. With the help of solubility parameters, the interaction parameter can be rapidly estimated. The solubility parameter is a good indicator of solubility of a specific solvent. It is very useful to predict miscibility and compatibility of polymers. Liquids with similar solubility parameters will be miscible, and polymers will dissolve into solvents whose solubility parameters are close to their own (Rubinstein and Colby 2003). For non-polar, non-associating polymer–solvent system with species interacting mainly by dispersion forces, the interaction parameter χ can be estimated from the Hildebrand solubility parameters as (Hansen 2002)

$$\chi = \frac{v_1(\delta_1 - \delta_2)^2}{RT} + \beta \tag{16}$$

where v_1 is the molar volume of the solvent; δ_1 and δ_2 are the Hildebrand solubility parameters for the solvent and polymer, respectively; R is the universal gas constant; T is the absolute temperature; β is the empirical constant. However, for complex polymer systems, the Hansen solubility parameters (HSP), which consider the non-polar/dispersion forces, the polar forces and hydrogen bonding forces, usually provides a better approximation. Previous studies have successfully applied the HSP to express the solubility and internal stability of bitumen (Redelius 2004). A similar equation to estimate the interaction parameter based on the HSP can be obtained (Hansen 2002)

$$\chi = \frac{v_1}{RT}\left[(\delta_{D1} - \delta_{D2})^2 + \frac{(\delta_{P1} - \delta_{P2})^2}{4} + \frac{(\delta_{H1} - \delta_{H2})^2}{4}\right] \tag{17}$$

where δ_D, δ_P and δ_H are, respectively, the dispersive, polar and hydrogen bonding components of the HSP. Because polymers are not volatile, δ is often obtained through an indirect method in which polymers are mixed with a series of solvents of varying but known solubility parameters. The solubility parameter of the polymer is taken as the δ value of the solvent which enables the maximum extent of swelling (Redelius 2000, 2004). Comparing to the average solubility parameter values, the solubility body of a material in the three-dimensional Hansen space is more realistic and useful (Zhu *et al.* 2019).

4.4. Disentanglement of rubber polymer chains

As discussed previously, polymer chains will disentangle if contacted with thermodynamically compatible solvents. Disentanglement occurs in a form of diffusional motions of chains out of the swollen polymer gel. The disentanglement of polymer chains can be described by the famous reptation model (De Gennes 1971). In the reptation model, an entangled chain diffuses along its confining tube as shown in Figure 11. The time needed for the chain to diffuse out of its original tube is the reptation time τ_{rep}. It is predicted to be proportional to the square of the chain size (radius of gyration) R_g divided by the reptation diffusion coefficient D_{rep} (Equation (20))

$$\tau_{rep} \sim \frac{R_g^2}{D_{rep}} \tag{18}$$

In the context of CRMB system, it is important to know the rubber dissolution rate in bitumen to control the binder

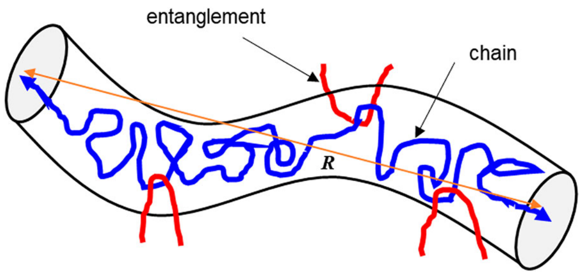

Figure 11. Reptation model for entangled polymer chains.

properties. The dissolution rate is related to the disentanglement rate r_{dis} of the polymer chain, which is taken to be proportional to the chain size divided by the reptation time. Thus

$$r_{\mathrm{dis}} \sim \frac{R_{\mathrm{g}}}{\tau_{\mathrm{rep}}} \sim \frac{D_{\mathrm{rep}}}{R_{\mathrm{g}}} \tag{19}$$

It is reported that R_{g} and D_{rep} can be related to polymer molecular weight and concentration (Papanu *et al.* 1989). Therefore, the disentanglement rate of rubber in bitumen can be expressed as

$$r_{\mathrm{dis}} = \frac{A}{M_{\mathrm{r}}^{a}\phi_{\mathrm{r}}^{b}} \tag{20}$$

where A is an empirical constant; M_{r} is the molecular weight of rubber; a is related to the rubber molecular weight distribution and b is related to rubber concentration. Both a and b are larger than 1.

4.5. Chain scission of rubber network

As mentioned before, during the degradation process of rubber into bitumen, crosslinked bonds and main chain bonds will break up successively based on the interaction condition. For three-dimensional crosslinked network of rubber, the chain scission reaction has three limiting cases: (a) chain scission at random; (b) cleavage of crosslinks and (c) directed scission. It was found that the soluble fraction of a network that has undergone scission can be linked to the effective number of chains in the gel fraction using a simple relationship (Horikx 1956). Specifically, the number of scissions can be measured by the soluble fraction of in the degraded network. This offers an opportunity to monitor the rubber network degradation process in bitumen by measuring the dissolving fraction of rubber. The effective number of chains can be determined by swelling measurements (Flory and Rehner 1943).

For the case of chain scission at random, the total number of crosslinks is assumed to be constant during the degradation reaction. Therefore, the following relationship in a rubber can be established

$$1 - \frac{\nu_{e2}}{\nu_{e1}} = 1 - \frac{\left(1-\sqrt{s_2}\right)^2}{\left(1-\sqrt{s_1}\right)^2} \tag{21}$$

where s is the soluble fraction in the crosslinked rubber and ν_e is the effective number of chains in the gel fraction (De Sousa *et al.* 2017). In the above equations, subscript '1' and '2', respectively, indicates the states before and after the degradation (chain scission reaction).

The soluble fraction in a polymer is given by (Charlesby 1953)

$$s = \frac{(2+\gamma)+\sqrt{\gamma^2+4\gamma}}{2\gamma} \tag{22}$$

where γ is the crosslinking index of the whole polymer (average number of crosslinks per original chain). The crosslinking index can be calculated by

$$\gamma = \frac{\nu_{\mathrm{e}}}{N} + 2 \tag{23}$$

where N is the number of primary molecules of polymer. Therefore, the number of chain scissions (n) of polymer is given by

$$n = N_2 - N_1 = (\nu_{\mathrm{e}} + 2N)\left(\frac{1}{\gamma_2} - \frac{1}{\gamma_1}\right) \tag{24}$$

For the case of crosslinking scission, no chain scission but only severance of crosslinks happens. Equation (21) becomes as follows:

$$1 - \frac{\nu_{e2}}{\nu_{e1}} = 1 - \frac{\gamma_2\left(1-\sqrt{s_2}\right)^2}{\gamma_1\left(1-\sqrt{s_1}\right)^2} \tag{25}$$

The number of scissions is equal to the number of severed crosslinks given by

$$n = N_2 - N_1 = \frac{1}{2}N(\gamma_1 - \gamma_2) \tag{26}$$

For the case of directed scission, only qualitative conclusions can be drawn because of the invalidity of the interchange of the crosslinking and scission reactions. To sum up, the number of scissions can be computed from the soluble fraction of a degraded network, as determined by the effective number of chains in the gel fraction with the help of swelling measurements.

5. Critical factors in practice and their theoretical bases

Similar to polymer modified bituminous binders, the interaction conditions and raw material characteristics will have a great impact on the rubber swelling and degradation process and consequently the binder properties. A thorough understanding of these factors will guide the material selection and process optimisation to obtain the desired properties from the modification.

5.1. Effect of interaction conditions

5.1.1. Temperature

The temperature has a great influence on both bitumen and rubber as they are both temperature-sensitive materials. When the temperature increases, both the mobility of bitumen molecules and rubber polymer chains increase, which enhances the diffusion process of bitumen into the rubber (Rubinstein and Colby 2003). The mobility and diffusion coefficients are highly dependent on temperature. From Equations (1) and (2), it can be found that at higher temperatures, the diffusion speed of bitumen into rubber and associated swelling rate of rubber greatly increase, which are also verified by experimental results (Green and Tolonen 1977, Artamendi and Khalid 2006, Wang *et al.* 2020). Table 4 summarises the diffusion coefficients and equilibrium swelling data from different researchers. Theoretically, as the temperature increases, the equilibrium swelling extent of rubber decreases because the rubber network is harder to expand due to the entropy-driven retractive forces as the temperature increases (Mark 1981). However, experimental data usually show an increase in swelling with temperature, indicating other reactions which decrease the crosslink density may occur (i.e. chain disentanglement, devulcanisation etc.) (Green and Tolonen 1977). Moreover, the main

Table 4. Diffusion coefficients and equilibrium mass uptake of bitumen into rubber.

Bitumen type	Temperature (°C)	Rubber type	Diffusion coefficient, $D \times 10^{-6}$ (mm^2/s)	Equilibrium mass uptake (%)	Reference
100KSR*	180	Car tire	0.759	75	Frantzis (2004)
		Truck tire	0.764	125	
50KSR		Car tire	0.742	75	
		Truck tire	0.746	95	
100VEN		Car tire	2.243	90	
		Truck tire	3.647	150	
50VEN*		Car tire	1.28	80	
		Truck tire	2.784	100	
100KSR	150	Car tire	3.80	70	Artamendi and Khalid (2006)
		Truck tire	2.69	120	
	180	Car tire	5.30	75	
		Truck tire	4.15	120	
	210	Car tire	16.98	70	
		Truck tire	10.75	120	
50KSR	180	Car tire	5.30	75	
		Truck tire	4.52	95	
100VEN		Car tire	15.90	90	
		Truck tire	9.62	140	
50VEN		Car tire	8.55	80	
		Truck tire	8.04	95	
Pen 60/70	190	Natural rubber	5.96	165	Feng *et al.* (2015)
Pen 70/100	160	Truck tire	2.54	115	Wang *et al.* (2020)
	180		4.91	140	
	200		10.75	170	

*KSR means Kuwaiti origin; VEN means Venezuelan origin; 100 and 50 means the penetration grade.

conditioning parameter that influences the bitumen–rubber interaction is the temperature while interaction duration and mixing speed contribute significantly as well but with minor effects on the rubber dissolution mechanism (Ghavibazoo *et al.* 2013b). Only when reaching certain temperatures, the chemical degradation of rubber occurs. Depending on the CRM composition, the chemical degradation starts at different temperatures. At an intermediate interaction temperature (e.g. 190°C), rubber dissolution in bitumen can happen with the help of high-speed mixing, which generates a more homogenous blend (Ghavibazoo *et al.* 2013b). On the other hand, a lower interaction temperature (e.g. 160°C) was not sufficient to trigger the formation of the three-dimensional network even at high mixing speeds. Also, a higher interaction temperature (e.g. 220–240°C) led to the dramatic degradation of rubber in bitumen, hence the degradation of rheological properties of the modified blend (Ragab *et al.* 2013, Yao *et al.* 2016, Wang *et al.* 2018b).

5.1.2. Time

The interaction between bitumen and rubber is a continuous process which needs a certain time to achieve desired properties. The properties of CRMB developed significantly during the early stage of interaction (e.g. the first 30 min). This coincides with the results of the diffusion process in which solvent diffuses into polymer faster at the early stage and slows down later until reaches the diffusion equilibrium. Through simulated swelling of rubber particles with SBR sheets, the swelling process increases enormously in the beginning and then reaches an equilibrium. However, as the swelling time increases, the crosslinking network of rubber is destroyed resulting in a decrease in crosslink density and an increase in the glass transition temperature of rubber (Frantzis 2004, Artamendi and Khalid 2006, Dong *et al.* 2012). A decrease in apparent viscosity of the bitumen–rubber system is noticed. Later, continuing extending the interaction time has a minor effect on the physical properties of CRMB (Abdelrahman 2006). To sum up, Figure 12 schematically plots the viscosity evolution curves of CRMB over time at different interaction temperatures (Abdelrahman 2006, Lo Presti and Airey 2013). At low interaction temperatures (∼160°C), rubber swelling is dominating the interaction process, the viscosity keep increasing until reach a plateau. At intermediate interaction temperatures (∼180°C), the rubber in bitumen first experiences the swelling stage and then starts the chemical degradation stage, which is reflected by the decreased viscosity. At high interaction temperatures (>200°C), rubber swelling finishes in a very short time and chemical degradation plays a dominant role during the interaction. Different interaction temperatures correspond to different types of

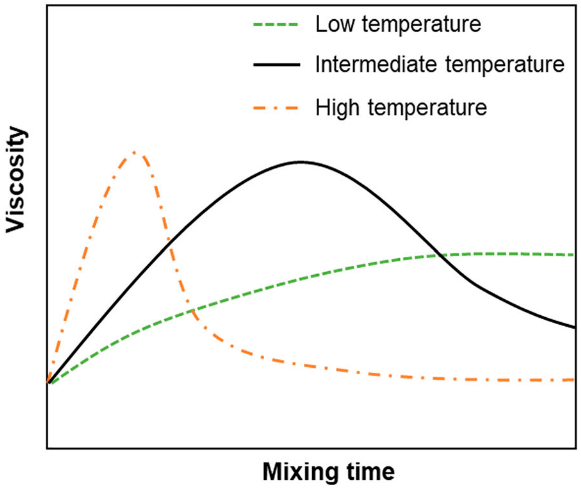

Figure 12. Viscosity evolution of CRMB over time at different interaction temperatures.

rubberised binder products, which can be determined based on the user requirements.

In addition, increasing the mixing speed has an equivalent effect of extending mixing time. However, the effect of interaction time and mixing speed is highly dependent on the interaction temperature which has dominant effects during the processing. The other two parameters can only facilitate the interaction process when the temperature meets the critical value (Ghavibazoo *et al.* 2013b). An ambiguous time–temperature superposition principle may exist, meaning increasing the interaction temperature can decrease the required mixing time to achieve comparable results.

5.1.3. Mixer type

The mixer type also influences the property development of CRMB. Conventionally, there are two types of mixers that exert the mechanical mixing energy during the bitumen modification process: the common blade type mixer and the high shear mixer. The mixing head varies with different application scenarios. The main difference is whether shearing energy is applied or not. Using high shear mixing can significantly reduce the rubber particle size, accelerating the interaction process. In addition, the exerted mixing energy can break the bonding between rubber particles and contribute to reducing the agglomeration (Celauro *et al.* 2012). Furthermore, carbon black and inorganic fillers attached on the rubber network are released into the bitumen under the high shear force (Abdelrahman 2006, Attia and Abdelrahman 2009). It was reported that carbon black also tends to absorb the lightweight fraction of bitumen. The existence of carbon black in bitumen improves the anti-ageing, high-temperature performance and thermal conductivity (Cong *et al.* 2014, Wang *et al.* 2019c).

5.2. Effect of rubber particle characteristics

5.2.1. Tire type

The main difference between truck tires and car tires is the different proportions of NR, SR and other ingredients they consist of. Truck tire rubber consists mainly of NR, whereas car tire rubber consists of more SR. From the chemical structure of different rubbers shown before, it can be found that SR with a more complex network is less susceptible to degradation than NR. In addition, it is easier for NR to swell in bitumen due to the relatively simple long-chain structure with less network constraints. Therefore, under the same interaction conditions, bitumen diffusion into truck tire rubber is usually faster than into car tire rubber and the equilibrium swelling extent of truck tire rubber is also higher than car tire rubber as reflected by the experimental data in Table 4 (Artamendi and Khalid 2006). From Equation (20), it can be found that polymers with higher molecular weight have a lower dissolution rate (Miller-Chou and Koenig 2003). This indicates that NR is also easier to be dissolved into hot bitumen than SR.

5.2.2. Morphology and processing method

There are two conventional methods of processing scrap tires: ambient grinding and cryogenic grinding. Ambient ground tire rubber particles usually have irregular shapes and porous appearance. In contrast, rubber particles produced through the cryogenic process are found to be more angular with a smooth cracked surface. The surface area of ambient ground rubber particles is about twice larger than the cryogenic counterpart (Shen *et al.* 2009). The large specific surface area of rubber particles increases the chances of contact with bitumen, hence promoting the interaction with bitumen. The resulted faster absorption of light fractions from bitumen into rubber causes more swelling and enhances the binder properties (Billiter *et al.* 1997). Other studies also suggested that CRMB binders prepared with ambient ground crumb rubber exhibited higher viscosity and higher elasticity with higher complex modulus and lower phase angle (Shen and Amirkhanian 2007, Lee *et al.* 2008).

5.2.3. Rubber particle size

Regarding the size of crumb rubber particles, it has a significant influence on its swelling kinetics and degradation into the bitumen, considering also that swelling is a Fickian diffusion process. For one-dimensional diffusion, the following relationship can be derived from Equation (1)

$$\frac{M_t}{M_\infty} = \frac{4}{d}\sqrt{\frac{Dt}{\pi}} \tag{27}$$

where M_t and M_∞ represent the total mass of the diffused substance at time t and at equilibrium, respectively; d is the sample thickness and D is the diffusion coefficient. Therefore, the required interaction time for rubber with bitumen to achieve the same swelling ratio increases with the square of the particle size (Buckley and Berger 1962). Figure 13 shows the swelling ratio change of different size rubber particles (from 0.2 to 1.0 mm) with time based on the numerical simulation. Fine rubber particles require less time to react and thus swell faster and achieve the swelling equilibrium earlier than coarse rubber particles (Wang *et al.* 2019a). Consequently, fine rubber particles also degrade faster, affecting the properties of the binder liquid phase. However, coarse rubber particles need more time

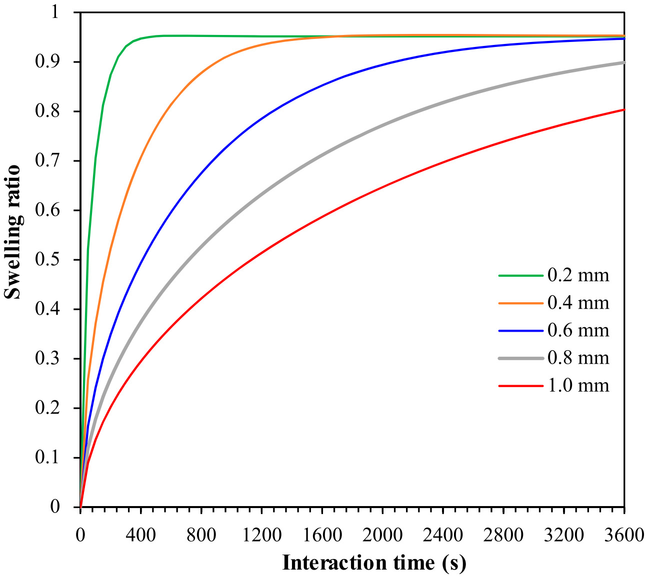

Figure 13. Swelling ratios of rubber particles of different sizes over the course of time.

to reach the swelling equilibrium. They have more influence on the binder instead of the liquid phase because of their higher swelling volume and less degradation rate (Abdelrahman and Carpenter 1999). They also yield higher complex modulus/viscosity and lower phase angle values of CRMB than finer particles do under the same interaction conditions (Attia and Abdelrahman 2009, Shen *et al.* 2009). Reducing crumb rubber size can produce a more homogenous bitumen–rubber blend and improve the storage stability of binders (Ghavibazoo *et al.* 2013a). However, CRM with finer sizes significantly increases the cost because of the required additional grinding.

5.2.4. Rubber particle content

From the micromechanical theory of particulate-filled composite materials, the particulate content is always of great importance to the mechanical properties of the composite system. Many studies have confirmed that the rheological properties and performance-related parameters of CRMB are functions of the rubber content (Huang 2008, Lee *et al.* 2008). Unlike the common aggregate fillers which primarily have stiffening effects in bituminous binders, CRM particles also result in physiochemical interactions with bitumen which will alter both the bitumen composition and the rubber microstructure. From the multilayer structure of swollen rubber in Figure 10, the mechanical properties of rubber after swelling will be changed. Results show that swollen rubber is softer than dry rubber due to the absorption of bitumen and exhibit noteworthy viscoelasticity (Wang *et al.* 2020). Based on the micromechanical models, the reinforcing effect of CRM on the binders will be enhanced with the increasing rubber content (Huang 2008, Medina and Underwood 2017, Wang *et al.* 2020).

5.2.5. Pre-treatment of CRM

The pre-treatment of CRM particles influences the interaction efficiency between rubber and bitumen. As mentioned before, the crosslinks in rubber formed by vulcanisation can significantly prevent the rubber from swelling by absorbing organic solvents. The concept of devulcanisation is introduced as selective scission of crosslinks with negligible main chain scission. Therefore, CRM pre-treated with devulcanisation can have a better interaction (swelling) with bitumen. Various devulcanisation processes have been developed by the rubber industry, including thermochemical, thermo-mechanical, microwave, ultrasonic, biotechnological devulcanisation (Joseph *et al.* 2016). Microwave (Ma *et al.* 2015) and ultrasonic methods (Xu *et al.* 2015) were reported to activate crumb rubber and promote the miscibility between bitumen and crumb rubber. CRMB prepared with activated crumb rubber exhibited superior storage stability and low-temperature performance. It is also common to use organic solvents to pretreat CRM to improve the miscibility (Subhy *et al.* 2015). Besides the physical treatment of CRM, chemical modification of CRMB was also achieved by adding activators or other chemicals. For instance, trans-polyoctenamer rubber (TOR) can promote the interaction between the sulphur in the rubber network and the sulphur within the asphaltenes (Liang *et al.* 2017). Polyphosphoric acid (PPA) can react with many functional groups in bitumen. It breaks the asphaltenes agglomerates and creates the possibility for better dispersion of asphaltenes in the maltenes phase, which allows for better interactions with rubber (Yadollahi and Mollahosseini 2011). This either enhances the performance of CRMB or increases the storage stability of CRMB.

5.3. Effect of bitumen characteristics

Bitumen from different crude oil sources usually has varying chemistry, with different SARA fractions. This will influence the compatibility with crumb rubber thereof the swelling of rubber. It is reported that the total solubility parameters of NR and SBR are around 16.9 and 18.1 MPa$^{0.5}$, respectively (Mark *et al.* 2013). In addition, solubility parameters for bitumens are in the range 17.2–18.8 MPa$^{0.5}$ (Zhu *et al.* 2019). Thus, the similarity between the solubility parameters of bitumen and natural and SR indicates that bitumen is a swelling agent of both rubbers. Recalling the solubility parameters of different fractions of bitumen, then, theoretically, aromatics with a solubility parameter of 17–18.5 MPa$^{0.5}$ should have the highest miscibility with crumb rubber from scrap tires based on the classical ‘like dissolve like’ compatibility principle. Therefore, in general, softer bituminous binders with lower molecular weight are more prone to diffuse into and absorbed within the rubber network (Artamendi and Khalid 2006). Various laboratory tests of preparing CRMBs have validated the above statement. Among the same graded bitumens, the one with a higher fractions of maltenes yields a higher swelling extent of crumb rubber particles, leading to faster dissolution during the later interactions (Airey *et al.* 2004).

6. Conclusions and recommendations

The interaction between rubber and bitumen plays a very important role in controlling the properties of rubberised bituminous binders. From the viewpoint of polymer science, in the binary binder system, bitumen can be regarded as the low-molecular-weight solvent, while rubber can be regarded as the polymer with high molecular weight. The bitumen–rubber interaction at high temperatures is generally a rubber dissolution process (which consists of swelling and chain disentanglement) and a chemical degradation process. In principle, the rubber swelling process can be systematically modelled by the Flory–Rehner theory in combination with the diffusion theory. The chain disentanglement of the swollen polymer network is a subsequent process to swelling. The chemical degradation of rubber in bitumen mainly includes the chain scission reactions which are observed as devulcanisation and depolymerisation. Admittedly, it is of great difficulty to do quantitative analysis on the model in the context of rubber swelling in bitumen since both rubber and bitumen are very complex systems instead of pure matters. However, the fundamental knowledge in polymer–solvent interaction is still of great importance to understand the interaction process and guide the material selection and process optimisation to obtain desired binder properties.

The effects of interaction conditions (temperature, time and mixing energy) and raw material characteristics (rubber type, particle size, particle content, pre-treatment, etc.) were analysed based on the proposed theoretical framework. These critical factors can fundamentally alter the bitumen–rubber interaction parameters, and consequently the binder properties. In view of the diversity of raw materials (bitumen and rubber) and varying demands of binder properties, it is difficult to draw any universal conclusion. However, the following recommendations are made in terms of specific application scenarios.

- Temperature is the dominant factor that determines the product type of rubberised binders. Different CRMB products can be produced by manipulating the interaction temperature ranges which correspond to different interaction mechanisms.
- To maximise the swelling effect of rubber in bitumen, bitumen with more maltenes (soft grade bitumen) and tire rubber high NR components should be chosen to create resemblance in solubility parameters.
- Devulcanised rubber is encouraged to be used in bitumen modification to eliminate the acrid smell and to improve the mechanical property and storage stability of rubberised binders.

For future research, the following points are recommended to enhance the understanding of this type of material and use it in a more rational way.

- The volumetric, chemical and mechanical properties of rubber in the blend during interaction should be monitored. The rubber in the blend undergoes multiple effects, including thermal ageing, diffusion of bitumen, mechanical energy from mixing. It is useful to know the nature of rubber before and after the interaction to control the binder property and to predict its behaviour in the long-term service.
- More dedicated laboratory tests should be done to establish a database for different bitumen and rubber systems, for instance, solubility parameter, diffusion coefficient, swelling coefficient, dissolution rate, etc.

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ORCID

Haopeng Wang http://orcid.org/0000-0002-5008-7322
Panos Apostolidis http://orcid.org/0000-0001-5635-4391
Jiqing Zhu http://orcid.org/0000-0003-1779-1710
Athanasios Skarpas http://orcid.org/0000-0002-3478-8807
Sandra Erkens http://orcid.org/0000-0002-2465-7643

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