Binder performance and testing

Advantages of the use of selective crosslinking agents in PMB production

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Abstract

During Polymer Modified Bitumen (PMB) production it is necessary to store the material till the “digestion time” is completed, in order to achieve the optimal performance and storage stability. Crosslinking agents are used in PMB as essential additives, to ensure the chemical interaction between polymers and bitumen. They improve the storage stability as the crosslinking agent will react chemically in the matrix by forming stable bonds. Selective crosslinking additives allow improve PMB storability, but also provide more efficient, quick and stable Sulphur links, that leads to a shorter digestion time” reduction and polymer content reduction (increase productivity & cost savings). It is desirable to use non-hazardous crosslinking additives, which involve safe handily, in environmental and health terms even minimize the H2S emissions as extra characteristics. This paper presents how to evaluate in the laboratory scale the “Optimal Digestion Time” during PMB production, using selective crosslinking agents.

This paper was first published in 2020 in version 1.0 of the proceedings of the 7th E&E Congress. This second edition (version 1.1.) of the proceedings is published in June 2021. The content of this paper has not changed, but the author(s) may have provided additional information in the form of an annex.

1. INTRODUCTION

The addition of crosslinking agents to PMB enhances stability and reduces issues related to polymer separation during transportation and storage.

More advanced products contain catalysts agents which allow a stable chemical link between polymer and binder, while modify the crosslink kinetics, by reducing PMB digestion time (maturation) then rising up the productivity. The catalyst effect accelerates vulcanization reactions, cuts down the vulcanizing time, reduces the vulcanizing temperature, reduces sulphur amount and improves the physical or mechanical properties of the vulcanized PMB.

During vulcanization process, there are different steps as shown in Figure 1.

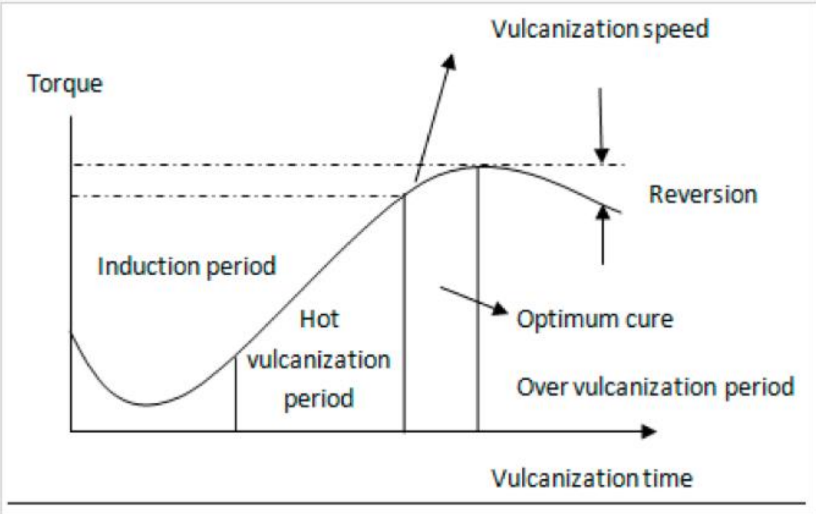

Figure 1: Vulcanization steps

Elemental sulphur is a widely used additive for polymer-modified bitumen. Sulphur vulcanization is a chemical process widely used in the rubber industry. It was moved to asphalt industry in order to improve the storage stability of some polymer modified bitumen (PMB) with unsaturated polymer modifiers such as styrene-butadiene-styrene (SBS). In this application, sulphur works in two ways: chemically crosslinking the polymer molecules via double bond of butadiene and chemically coupling polymer and bitumen through sulphide and/or polysulphide bonds. The crosslinking of polymer molecules leads to the formation of a stable polymer network in the bitumen; while the coupling between polymer and bitumen directly reduces the possibility of separation. Despite the improvements of the properties of PMB, the application of elemental sulphur presents the generation of a hazardous gas, hydrogen sulphide, especially at high temperature.

Sulphur can decompose and generate sulfur free radicals at a certain temperature and in a certain time, and the sulfur free radicals have high oxidizability [1]. Therefore, in a certain condition, hydrogen atoms in the bitumen polymer chain can be captured by the generated sulfur radicals during sulfur decomposition. Sulfur free radical and hydrogen atoms can generate hydrogen sulfide in the form of gas. Free radicals are generated at the hydrogen atom-losing site of the bitumen polymer chain. Free radicals in adjacent polymer chains can be coupled with each other in cross-link form, and free radicals can also be coupled with sulfur free radicals in bridging form. Sulfur free radicals and the bitumen polymer chain can react each other.

PMB stability is highly related to the bitumen source. Depending on its colloidal stability (I_C) and Hildebrand solubility parameter, it could be easier or more difficult to stabilize the polymer in the bitumen matrix.

Additionally, the selected SBS polymer grade has a big impact in the PMB stability. During SBS manufacture, in accordance with the raw materials sequence and timing addition (styrene, butadiene, solvent, catalyst, coupling agent and finisher) it is possible to produce several SBS grades (linear, radial, di-block) with different chemical and physical properties as solubility behavior, molecular weight and therefore compatibility with the bitumen source.

The use of PMB in asphalt applications become more and more popular due it is the appropriate binder to produce Long-Life Asphalt Pavements [2]. It is important to optimize the manufacture of such kind of binder by the use of sophisticated cross-linking agents.

2. CROSS-LINKING AGENTS ADVANTAGES

The use of a crosslinking agent entails important advantages in the PMB production. In this way the most popular additives are sulphur base, which allow a vulcanization process.

To select an effective crosslinking agent it is important to check the performance advantages described in Section 2, but it is also highly recommended to analyse the safety and environmental considerations described in Section 4.

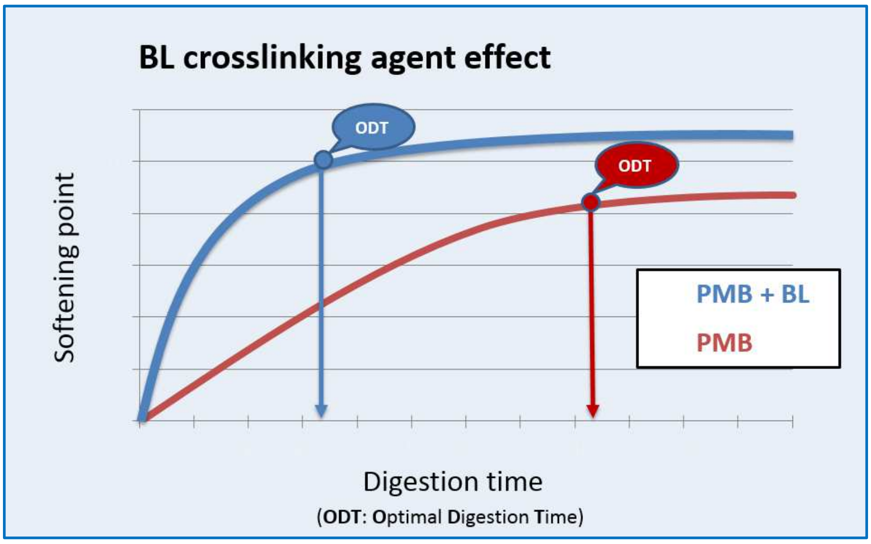

Figure 2: Cross-linking agent advantages

The results shown in this paper are the summarize of several accumulated experiences and are expressed as average trend. The vast majority of results demonstrate the huge relevance of bitumen source, polymer grade and PMB production process.

2.1. SBS dosage reduction

SBS content has an important impact in the PMB performance and costs. When SBS dosage is higher, PMB physical characteristics will improve. In addition, it is possible to improve PMB properties even more by dosing some quantity of a crosslinking agent, maintaining the SBS content or even adjusting/decreasing such polymer content. That means that the use of a crosslinking agent will optimize the PMB recipe.

Table 1 shows the required SBS dosage to achieve almost identical final PMB performance. The use of an effective crosslinking agent leads to SBS savings, even higher than sulphur.

Table 1. SBS expected reduction gap when a cross-linker is used

Cross-linker	Cross-linker dosage	SBS dosage	SBS reduction
-	0,00%	4,5%	
Sulphur	0,12%	4,0 – 4,3%	5 – 10%
BL	0,12%	3,8 – 4,1%	8 – 15%

SBS content reduction also brings a positive impact in the PMB viscosity and storage stability. Viscosity is reduced at high temperature so provides a better PMB in workability terms. Storage stability is improved because lower amount of polymer is dispersed in the maltenic fraction of the bitumen matrix and because the more efficient sulphur links, as described in Section 2.3.

2.2. PMB digestion time reduction

In PMB production are involved different manufacture steps. Probably the most limited step to achieve an effective production capacity is the time and energy consumed in the digestion tanks to obtain the final PMB performance, namely the “optimal digestion time” (ODT).

The previous figure 2 symbolized two different theoretical “digestion curves” (with and without crosslinking agent).

Following Table 2 is showing an example case disclosing the ODT obtained in different scenarios.

Table 2. PMB digestion time reduction - Example cases

Cross-linker	Cross-linker dosage	Digestion time	Digestion time reduction
-	0,00%	8 hours	
Sulphur	0,12%	4 hours	50%
BL	0,12%	3 hours	62%

In the Section 3 of this article it is described a laboratory method recommendation to evaluate the ODT parameter.

2.3. PMB storage stability raise

Storage stability is a key issue when PMB have to be transported and/or stored at high temperature. The effectiveness of polymer modification in improving road performance depends on a chemical-structural modification in the binder's composition to be effective and durable [3]. The phase inversion phenomenon between bitumen components and added polymer leads the binder to assimilate the polymer characteristics. PMBs can show stability problems and separation; in fact, polymers and bitumen components can lose most of the benefits from the modification due to separation during the storage phase.

Beyond heterogeneous quality, the undesirable polymer/bitumen separation could lead to critical problem in the logistic, because the polymer phase become highly elastic and very difficult to be pumped, besides the bitumen and truck tanks removal.

The use of an effective crosslinking agent optimizes the polymer/bitumen interaction, minimizing its potential separation and improving storage stability for extended time periods.

As was described in Section 2.1 the polymer content reduction will lead to better storage stability.

Table 3 is showing an example case for PMBs storage stability (with and without different crosslinking agents) using the same polymer dosage and evaluated by EN 13399 standard test.

Table 3. PMB storage stability rise EN 13399 - Example case

Cross-linker	Cross-linker dosage	Difference in penetration (top-bottom - 0,1 mm)	Difference in softening point (top-bottom - ºC)
-	0,00%	17	9,3
Sulphur	0,12%	5	3,1
BL	0,12%	2	1,2

2.4. PMB performance improvement

As a consequence of a more effective polymer/bitumen link, PMB performances will improve when a crosslinking agent is dosed. In this case, it is obtained a lower penetration and Fraass values, higher softening point and elastic recovery values, and also rheological upgraded parameters. That is the reason why it is possible to reduce the polymer content as mentioned in the Section 2.1.

Another interesting aspect to consider is the lower reversion step during the vulcanization process, when a selective crosslinking agent is used instead of pure sulphur.

Table 4. PMB performance rise - Example cases

Cross-linker	Cross-linker dosage (%)	SBS dosage (%)	Penetration EN 1426 (0,1 mm)	Softening point EN 1427 (ºC)	Elastic Recovery EN 13398 (%)
-	0,00	3,5	57	62,0	80
Sulphur	0,12	3,5	49	67,6	88
BL	0,12	3,5	48	69,2	90

3. OPTIMAL DIGESTION TIME DETERMINATION

As described in Section 2.2 the PMB digestion step is usually linked to production plant capacity, reason why is highly recommended to analyze in advance in the laboratory. In addition, it is important to carry out such a kind of research to qualify the effect of different crosslinking agents in the PMB productivity.

The use of a selective crosslinking agent could allow reduced digestion time beyond the half, compared to same recipe with none additive.

Find below some recommendations on how to determine the "optimal digestion time" (ODT) in the laboratory:

General suggestions:

- PMB lab production temperature has to be run between 175°C and 195°C.
- Never exceed 195°C to avoid bitumen oxidation and polymer degradation.
- Lower is the temperature, longer will be the process time (exponentially).

Lab procedure:

- Step 1: Place neat bitumen into the oven at 185°C, the time required to achieve the proper production temperature.
- Step 2: Weigh the required quantity of binder, sufficient to perform later programmed tests. Proceed to tare the empty container and then weigh the binder until it reaches the required mass (Figure 3 -1).
- Step 3: Calculate and weigh the quantity of polymer amount needed.
- Step 4: Calculate and weigh the quantity of crosslinking needed.
- Step 5: Take out neat binder from the oven and keep it stirred at indicated production temperature.
  It is important pay attention to maintain production temperature during manufacture process hereby described:
- Step 6: Add the polymer gradually to the binder while keeping on mixing (Figure 3 -2).
- Step 7: Once the entire polymer has been added, continue mixing it for 30 minutes at least.
- Step 8: At this time, add the crosslinking agent (Figure 3 -3) and keep on mixing, up to optimum digestion time (ODT).

Figure 3: Lab modification steps

In order to determine the ODT, a PMB sample must be seized every 30 min / 1 hour during mixing process (after crosslinking agent addition). Ring and Ball softening point parameter has to be evaluated to analyze performance progression. It is considered already obtained when softening point temperature vs digestion time curve begins to be asymptotic (Figure 4).

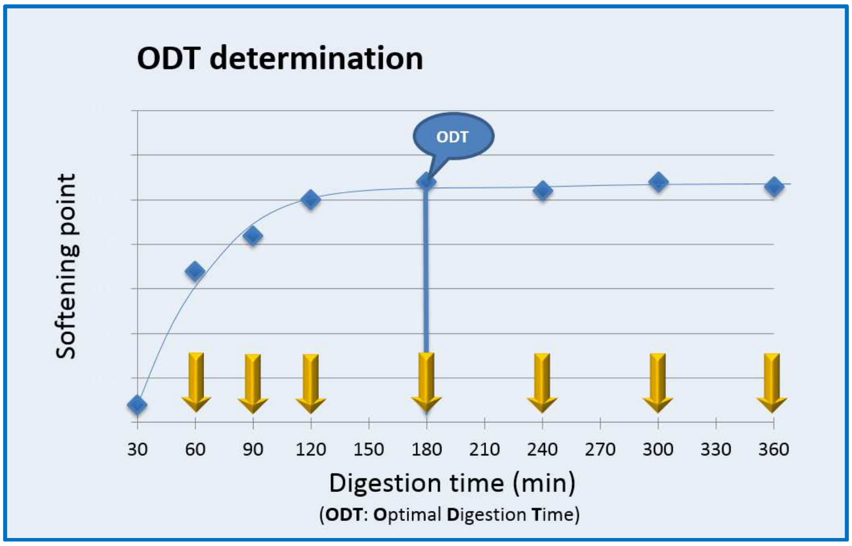

Figure 4: ODT determination

In some cases, there is a final drop in the softening point due to the reversion phase (described in Figure 1). Therefore, it is also important to re-check the final softening point value after 24 hours digestion time. The use of an appropriate cross-linking agent can also help to minimize the reversion phase process.

The laboratory study provides a reference for the optimal digestion time, but it is always necessary to check again during the production, since industrial manufacture settings could vary from lab conditions.

4. CROSS-LINKING AGENT SAFETY AND ENVIRONMENTAL CONSIDERATION DURING PMB PRODUCTION

Other strongly suggested important factors for a cross-linking agent choice are safety and environmental aspects. From market analysis it is possible to identify important differences between cross-linking agents.

4.1. Cross-linking agent handling

When a crosslinking agent is dosed during the PMB production, some operators could be in contact with it. As sulphur molecules are involved in this kind of additives, skin irritation may appear. The use of pure sulphur is a challenge due to own hazard classification, even worst when it is dosed in powder form, but also when the granular or prill form is used.

In several special crosslinking agents, the presence of catalyst molecules may also present a risk for the human safety and the environment.

There are two main formats for crosslinking agents:

- Powder format: more risky incidence because presents some hazard classification.
- Granular format: less risky incidence but not exempt of hazard classification.

Most commercial crosslinking agents are hazardous and only few of them, more sophisticated, do not show any health and environment hazard classification.

It is highly recommended to check these products MSDS in order to evaluate which hazards are exposed to the operators (production process) but to the drivers as well (delivery process).

4.2. H_2S emissions

All the refined bitumen grades (standard) contain sulphur by itself, due the own acidity of the crude oil source (sour or sweet) but also due the refining process, which unquestionably brings different H_2S emission levels.

Therefore, during PMB production, the hydrogen sulfide emissions will be linked to their bitumen source, but also even more linked to the process temperature. So H_2S emissions will depend on the bitumen temperature, bitumen sulphur content by itself and the sulphur dosed by the crosslinking agent addition.

H_2S emissions are responsible for the associated odours, which generate some issues in indoor facilities and those production sites located nearby residential areas.

European market provides few crosslinking agents formulated compounds with low sulphur content and catalysts. This combination has a positive impact by reducing the free sulphur capable to form hydrogen sulphide.

In addition to the above, even more sophisticated compounds are also available. This new crosslinking agents generation is formulated with more complex additives including scavengers, in order to minimize H_2S emissions drastically.

Table 5 shows an example case with some H_2S values for different crosslinking agents. These results are the average values during the 15 first minutes after additive addition at 180ºC, registered in a lab PMB production. H_2S analyser sensor was located at 10 cm far from the hot bitumen surface.

Table 5. PMB H_2S emissions - Example case

Cross-linker	Cross-linker dosage	SBS dosage	H_2S emissions in lab	H_2S emissions reduction
Sulphur	0,15%	4,0%	16 ppm	reference
BL	0,15%	4,0%	8 ppm	-50%
BL-S3	0,15%	4,0%	3 ppm	-81%

No doubt, that pure sulphur dosed as a crosslinking additive for the PMB production is the worst option as hazardous additive that penalize with a negative charge to the environment or to the operators health.

More sophisticated crosslinking agents are capable to reduce H_2S fumes over 80% facing to pure sulphur, which is a strong reduction. Its chemistry reduces hydrogen sulfide emissions and associated odors, which makes its use pretty proper in those production sites located close to residential areas.

As an observation of our experiences, the highest H_2S measures are registered from 15 first minutes, after the crosslinking agent dosage. Then the emissions decrease and two hours after would achieve similar values than a neat bitumen.

These measures can be used as a reference to evaluate and compare different crosslinking agents in laboratory scale, but it is highly recommended to check the final emission in the PMB plant installation. Emissions values are totally dependent on the gas analyser sensor location, that should be located where the measurement is required.

According to European legislation, following safety limits are established:

- 8 hours TWA: 5 ppm (7 mg/m^3)
- STEL (15 min): 10 ppm (14 mg/m^3)

Beyond the benefit in H_2S reduction though the use of sophisticated crosslinking agent, it should be also considered that the substantial reduction of the digestion time will leads a much lower H_2S impact per PMB production batch.

5. CONCLUSIONS

- Crosslinking agents improve polymers (SBR/SBS) and bitumen compatibility during Polymer Modified Bitumen production. They enhance stability and reduces issues related to polymer separation during transportation and storage, thus provide regular and homogenous PMB quality.
- Some of them contain catalysts additives, which favour a stable chemical link between polymer and binder, modifying the vulcanization kinetics, reducing PMB digestion time and rising up the PMB productivity.
- In addition, they improve PMB physical performance and let a polymer content reduction.
- This paper presents how to evaluate the "Optimal Digestion Time" (ODT) during PMB production in laboratory scale.
- It is highly recommended to check the crosslinking agents MSDS in order to evaluate potential hazards for the operators safety health and environment.
- During PMB production, some H_2S emissions are produced. The highest H_2S measures are registered from 0 to 15 minutes after the crosslinking agent addition.
- A new generation of more sophisticated crosslinking agents are capable to reduce H_2S fumes over 80% facing to pure sulphur, which is a strong reduction.

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