Extraction and recovery of polymer modified bitumen

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ABSTRACT

The amount of heavy traffic is increasing continuously asking for high performance road pavements. The higher requirements in terms of stability and fatigue behavior are the main reason for the elevated use of polymer-modified bitumen (PmB). Despite the fact that PmB have been known and used for several decades, standardization is still inadequate in some parts. Only in 2012, the standards for binder extraction and has been adapted to PmB. Still, binder results obtained by the extraction with different solvents are often questioned.

In this study binder extraction and recovery was investigated in detail for five PmB available on the Swiss market and four different solvents (toluene, xylene, dichloromethane, tetrachloroethylene) from the list suggested by the European standard EN 12697-3 for binder recovery by distillation. In a first step, only the recovery process of dissolved binders was evaluated. The differences measured between virgin and recovered PmB were remarkably small for most binder and solvent combinations. In a second step, the extraction process was verified on a semi-dense asphalt concrete. Again, in most cases the properties of recovered binders showed little difference concerning penetration and elastic recovery for all four solvents. Only for some binder/solvent combinations problems were detected, in particular with dichloromethane. Examination of the residual solvent by gel permeation chromatography (GPC) showed solvent residues of lower than 0.2% by mass in the case of toluene and slightly higher residues for xylene and tetrachloroethylene. The study of the micromorphology of polymers carried out by fluorescent microscopy revealed, with the exception of one binder, little effect on the distribution and restructuring of the polymers in the bitumen.

In conclusion, it can be confirmed that the standardized extraction and recovery method works well for most cases with only small deviations from the original values. However, there are binder/solvent combinations where the extraction is not possible or where large differences between recovered and virgin binder are encountered for some rheological tests.

Keywords: Health Safety and Environment, Modified Binders, Solvents, Testing

1. INTRODUCTION

Modification of bitumen by different types of polymers is known already for a long time [1, 2]. However, the use of polymer modified binders (PmB) has increased considerably in the last years as a response to the rising amount of heavy traffic. In addition, special asphalt pavement types like open porous asphalt to reduce traffic noise has become more and more popular. These special asphalt mixes with high void contents ask for higher elasticity but in the first instance for excellent adhesion and cohesion properties, because of the weakened mineral skeleton. Generally, non-modified bitumen are not able to achieve the enhanced requirements.

However, not all polymer modified binders perform equally well and are aged to different degrees during production and construction. For this reason it is crucial to assess the binder properties in the finished pavement. Until now it is not possible to directly determine the binder characteristics from cores or other pavement specimens, as the mineral aggregates and the structure of the pavement overlap with the binder properties. Therefore, the polymer binder has first to be extracted with a suitable solvent and afterwards recovered from this solution by distillation. For non-modified binders it is known that these processes induce no major changes in the chemical, physical and rheological properties. But for polymer modified bitumen this has been questioned.

In solution the polymer network is not present anymore; the polymer molecules are not linked together, because otherwise, it would not be possible to extract them from asphalt mixes, which is actually the case for cross-linked polymers. In the recovery process the polymer network is fully rebuilt. But this deviates from the original process of PmB formation, which involves a high shear mixer at elevated temperatures. Another issue is the residual solvent left after distillation under vacuum. To which extent solvent molecules influence the PmB properties as function of polymer, solvent type and concentration is not exactly known. Nösler et. al. have shown for some SBS-modified PmB a significant decrease of the softening point by residual solvent [3].

Some studies on polymer modified binder recovery have been conducted in Europe with sometimes controversial results. In an Austrian study, no significant differences have been observed in the binder characteristics after extraction and recovery with tetrachloroethylene and toluene [4]. The Belgian Road Research Center investigated in an extensive research project the extraction and recovery process of 19 polymer binders including SBS- and EVA- modified bitumen [5]. Similar results with deviations within the limits of repeatability have been found for dichloromethane and toluene, whereas trichloroethylene resulted in higher changes. For SBS-modified bitumen different extraction methods are applicable whereas EVA modification required hot extraction. Furthermore, an influence of the mineral aggregate type has been observed. Compared to sandstone, extraction with porphyry was more difficult and resulted in higher deviations. Larger differences have been found as well by Nösler [3] in the case of trichloroethylene who related it to residual solvent in the recovered binder. The results of this limited study on three SBS-modified bitumen prepared in the laboratory are difficult to interpret, as the polymer was considerably altered during asphalt production. Still, there is some evidence, that the type of SBS used for the modification plays a significant role in the extraction and recovery process.

2. EXPERIMENTAL PROGRAM

2.1. MATERIALS

In the European Standard EN 12697-3 [6] different solvents for binder recovery are proposed, but dichloromethane is defined as the reference (Table 1). Apart from the solvents listed in the standard, others are allowed on the condition that the recovered binder shows the same properties like after the recovery with the reference solvent.

Table 1: Proposed solvents for binder recovery according EN 12697-3 [6]

Name	Chemical notation	Density [Mg/m^3]	Boiling point [°C]	Toxicity according GHS*
Dichloromethane	CH_2Cl_2	1.33	40	Suspected human carcinogen (Cat 2)
1,1,1-Trichlorethane	$C_2H_3Cl_3$	1.34	74	Harmful by inhalation
Trichloroethylene (Tri)	C_2HCl_3	1.46	87	Known or presumed to have carcinogenic potential for humans (Cat. 1B), mutagenic
Tetrachloroethylene (Perchlorethylene)	$Cl_2C\text{-}CCl_2$	1.62	121	Suspected human carcinogen (Cat 2)
Benzene	C_6H_6	0.88	80	Known or presumed to have carcinogenic potential for humans (Cat 1), mutagenic
Toluene	$C_6H_5\text{–}CH_3$	0.86	111	Aspiration toxicity hazard
Xylene	$C_6H_4\,(\text{-}CH_3)_2$	0.86	138	Harmful by inhalation

*GHS Globally Harmonized System of Classification and Labelling of Chemicals

For the project four solvents listed in the standard have been selected based on the toxicity level and the use in Switzerland: dichloromethane, toluene, xylene and tetrachloroethylene. Chlorinated solvents are extensively used with automatic extraction machines because of their inflammability. Manual extraction is generally carried out with toluene. Although trichloroethylene is often used as well with automatic extractors, it was not considered in this project due to the high carcinogenic hazard similar to benzene. There is a general effort by the European commission to ban the use of chlorinated solvents.

Table 2: Selection of PmB available on the Swiss market

Code	Classification according to EN14023 [7]	Penetration [8] [10^{-1} mm]	Softening [9] point [°C]	Polymers, additives
A	PmB 65/105-45 (CH-C)	74	54.1	SBS
C	PmB 65/105-60 (CH-E)	78	81.0	SBS
F	PmB 10/40-70 (CH-E)	33	81.4	SBS-EVA, wax
H	PmB 25/55-65 (CH-E)	46	96.0	SBS, wax
I	PmB 45/80-65 (CH-E)	62	74.2	SBS

*CH-C: PmB with moderate requirements, CH-E: PmB with increased requirements according Swiss standard SN 670210 [10]

In a survey on commercial PmB types available in Switzerland, the most common types have been selected (Table 2). They cover hard and soft PmB, as well as binders containing wax, as some difficulties with the extraction of wax-modified binders have been reported.

2.2. METHODS

Previous studies have shown that the main influence of the extraction/recovery process is actually accounted to the hot mix fabrication, which ages the PmB in different ways and blurs the influence of the solvents [3]. Therefore, a two-step approach was envisaged in order to separate the influence of the recovery procedure from the extraction and mixing process.

Step 1: Recovery without extraction

The European method for the binder recovery consists of three phases. In phase one the major part of the solvent is distilled at elevated temperature and a slight vacuum, whereas in the second phase the residual solvent is evaporated at low pressure and high temperature in a restricted time to prevent binder aging. The second phase is the crucial step for the property of the recovered binder and directions on temperature and pressure have to be followed in order to get comparable results. The residual solvent content should be as low as possible without heating up the binder too high. Only in the case of highly viscous binders, like special polymer modified binders or hard bitumen, a third phase at higher temperature is stipulated.
A 1 liter flask was evenly covered with 150 g polymer binder. After cooling, 500 ml of solvent was added and the binder dissolved for 20 minutes at 100°C (DCM 70°C) in the rotary evaporator (without vacuum). Without cooling, the recovery of the PmB was carried out according to EN 12697-3 with slight modifications (Table 3). A research project showed, that the restriction of additional parameters, like binder amount and distillation speed, improves the precision of the method [11]. In EN 12697-3 the duration is not further specified, but a distillation speed of about 50 ml/min has been shown as both time efficient and gentle. To achieve this distillation speed, which is depending to some extent on the distillation apparatus, temperature and/or pressure are adapted in deviation to the European standard. However, the first phase is not critical as the temperature never exceeds the boiling point of the solvent.
Before the second phase started the container with the extracted solvent is replaced by an empty flask. Otherwise the target pressure cannot be reached, as there is still solvent evaporating. For the selected PmBs no third phase was necessary.

Table 3: Distillation parameters used for the recovery process

			First phase		Second phase	
Solvent	Shortcut	Boiling point [°C]	Temperature / pressure [°C] / [kPa]	Time [min]	Temperature / pressure [°C] / [kPa]	Time [min]
Dichloromethane	DCM	40	115 / 40	variable	150 / 1.3	10 ± 0.5
Tetrachloro-ethylene	TCE	121	145 / 40	variable	145 / 2.0	20 ± 0.5
Toluene	Tol	110.6	145 / 40	variable	145 / 2.0	20 ± 0.5
Xylene	Xyl	140	120 / 18	variable	180 / 2.0	20 ± 0.5

The amount of residual solvent in the binder was determined by GPC with a detection limit of 0.1% (m/m) [mh15]. No residual solvent determination was possible for Dichloromethane, as this solvent is not UV-active at wavelengths above 200 nm and therefore this method not applicable.

Step 2: Binder extraction and recovery

A semi-dense hot mix asphalt AC MR 8 according to Swiss specification SNR 640636 was chosen to study the binder recovery after extraction. This pavement type is often used as a surface layer for Swiss highways due to its higher durability compared to porous asphalt, but still good noise performance. For each binder type a batch of 65 kg was produced in the laboratory and divided afterwards into portions of 2.4 kg for extraction. Extraction was performed manually for all solvent types.

3. RESULTS AND DISCUSSION / ANALYSIS OF RESULTS

2.3. STEP 1: BINDER RECOVERY FROM SOLUTION

In the first step solely the recovery process was investigated without interfering effects of hot mix preparation and binder extraction. As depicted in Figure 1 and Figure 2, some differences in penetration values and softening point ring and ball compared to the virgin binder can be identified.

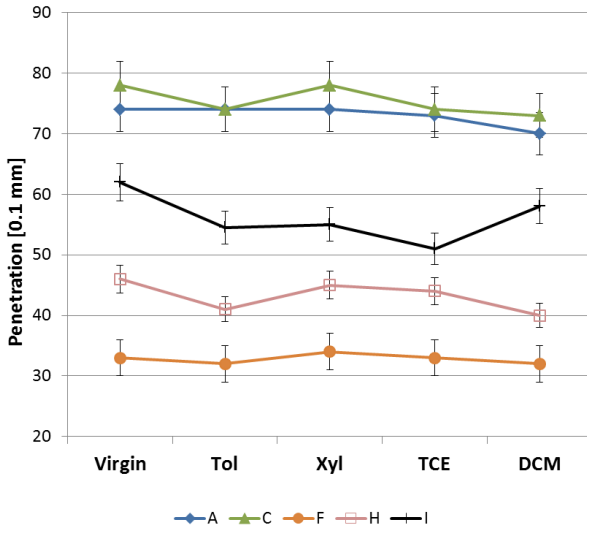

Figure 1: Comparison of penetration of recovered binder with virgin binder

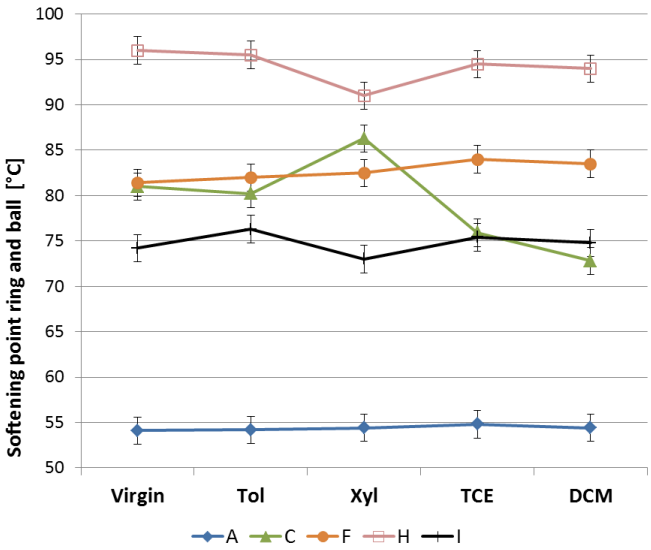

Figure 2: Comparison of softening point values of recovered binder with virgin binder

In general, the characteristics of the recovered binder is depending on PmB modification, solvent type and test method. There is common trend that after extraction with toluene and dichloromethane the penetration values are slightly lower compared to the virgin binder. Xylene showed a very good accordance for the penetration values with the exception of binder I. The analysis of the softening point ring and ball showed in general better agreement between recovered and virgin binder except with the solvent xylene, where both higher and lower results than in the virgin state were obtained. It can be seen clearly that the two tests give different results and that no correlation exists between penetration and softening point ring and ball values in contrast to non-modified bitumen. The binder type or the polymer modification respectively, was identified as the main impact factor, which is demonstrated both for penetration and softening point ring and ball. For binder A and F very similar values have been measured, whereas with the other binders larger deviations were observed. Wax modification was not identified as a general problem. Very good accordance was found for binder F, whereas for binder H slightly higher differences were measured. Overall, the differences between recovered and virgin binder were small for most binders and solvents.

2.4. STEP 2: BINDER RECOVERY AFTER EXTRACTION FROM ASPHALT MIX

Extraction of the polymer modified binder was possible for all binder and solvent combinations with one exception. In the case of binder H the extraction with dichloromethane was not possible, even after prolonged extraction time. After 3 hours residual binder was still visible in the extraction container. Therefore, no values are shown for this binder solvent combination.

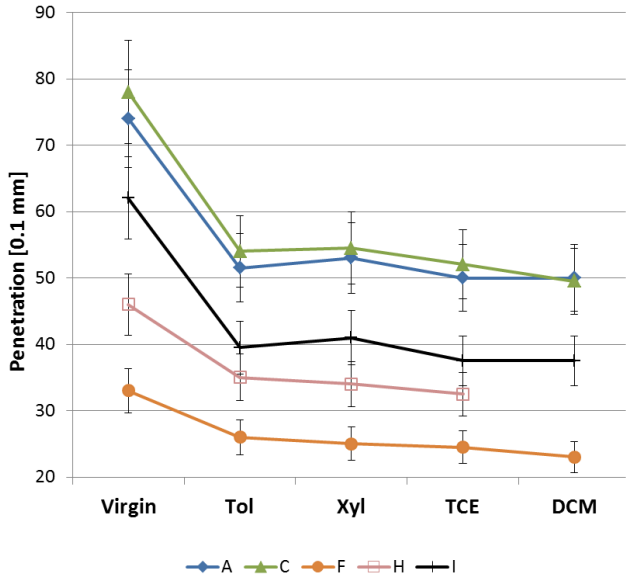

Figure 3: Penetration after extraction and recovery

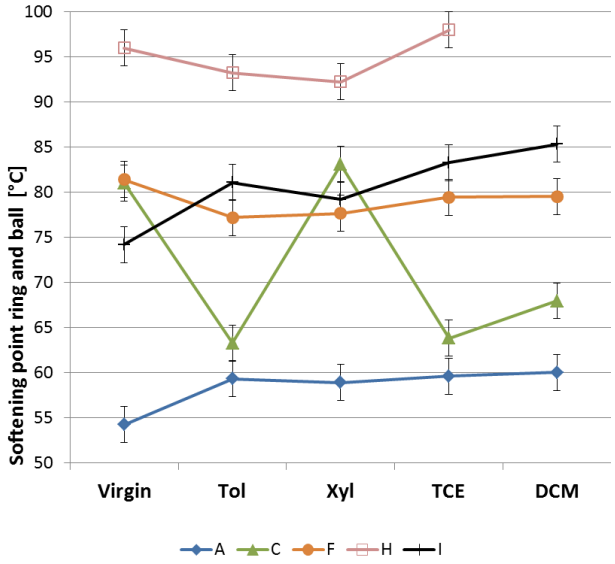

Figure 4: Softening point ring and ball after extraction and recovery

Penetration is very sensitive to aging during the mixing process as can be observed in Figure 3. In all cases the recovered binder showed a decrease in the penetration value between 9 and 20 [0.1 mm]. Surprisingly, the scattering of the penetrations values for all binders and solvents was much lower compared to step 1 without extraction from the asphalt mix. Regarding the softening point test, the aging caused not always an increase of the results as it is observed for non-modified binders (Figure 4). Three binders showed lower values after recovery. Binder C showed a very erratic behavior with large decrease in softening point for most binders, but comparable result with xylene. This cannot be explained by destruction of the SBS-polymers because the elastic recovery didn't show large changes (Figure 5).

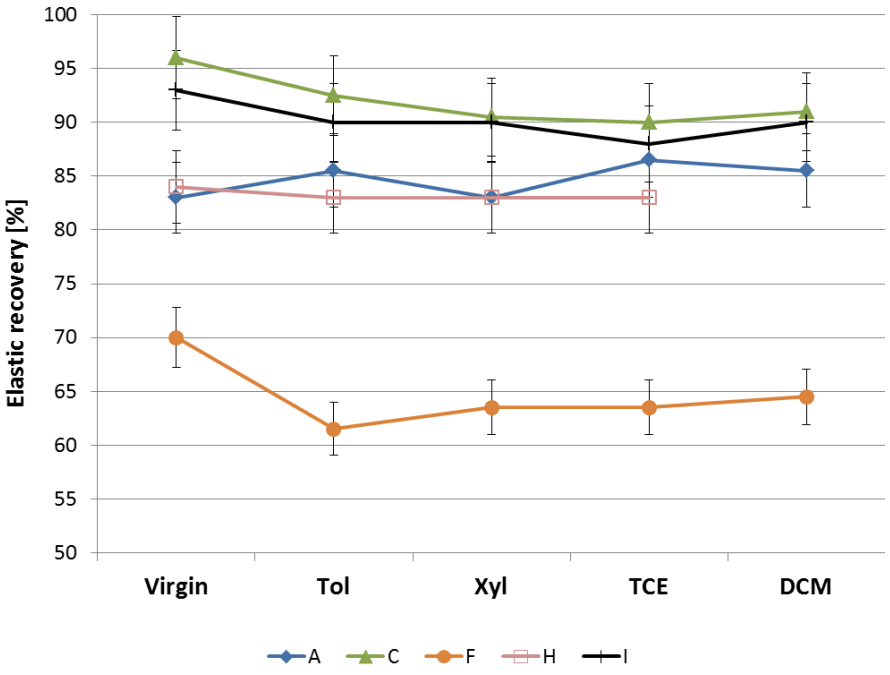

Figure 5: Elastic recovery of extracted and recovered binder

In the case of elastic recovery the influence of the extraction and recovery process is less pronounced and lies generally within the repeatability of the test method. The influence of the mixing process is in generally dominant and results in slightly lower elastic recovery values in the order of 5%. Binder A acts unexpected, it gave a slight increase of the elastic recovery by the mixing process and the scattering of the values was higher, but still within the repeatability range.

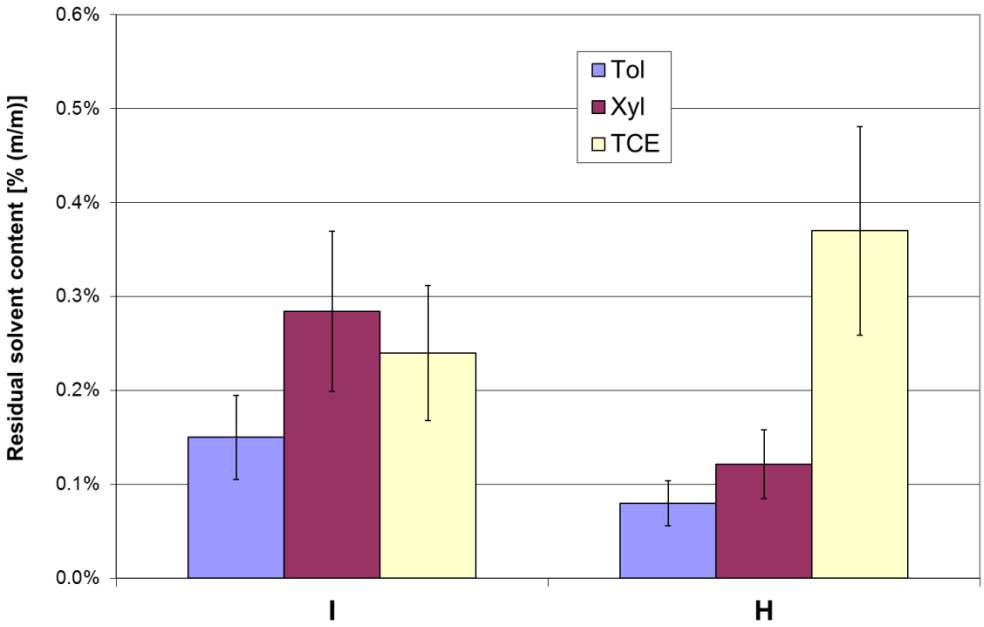

Figure 6: Residual solvent content after recovery of binder H and I

The solvent content was determined by GPC using UV-detection at 215 nm. This detection was not suitable for DCM as this solvent doesn't absorb sufficiently at this wavelength. For the two binders investigated, toluene residues were the lowest with values around 0.1 % (Figure 6). There is a significant influence of the binder on the amount of solvent remaining in the binder. This could explain some of the unexpected results in the case of softening point ring and ball results after extraction. However, in most cases the residue is around 0.2% or below which will decrease the ring and ball by 1°C according to by Nösler et.al. [3] who investigated it for trichloroethylene. However, it hasn't yet been verified, whether the softening effect is the same for all solvents.

The polymer dispersion was investigated by fluorescence microscopy before and after extraction/recovery [12]. The dispersion of the polymers in the virgin binder is mostly fine in a homogeneous bitumen phase, with sometimes larger agglomeration of polymers (Figure 7). Only binder A is different, showing a homogeneous polymer phase without separated bitumen and polymer regions. This is typical for grafted PmB, where the polymer is chemically linked to the bitumen.

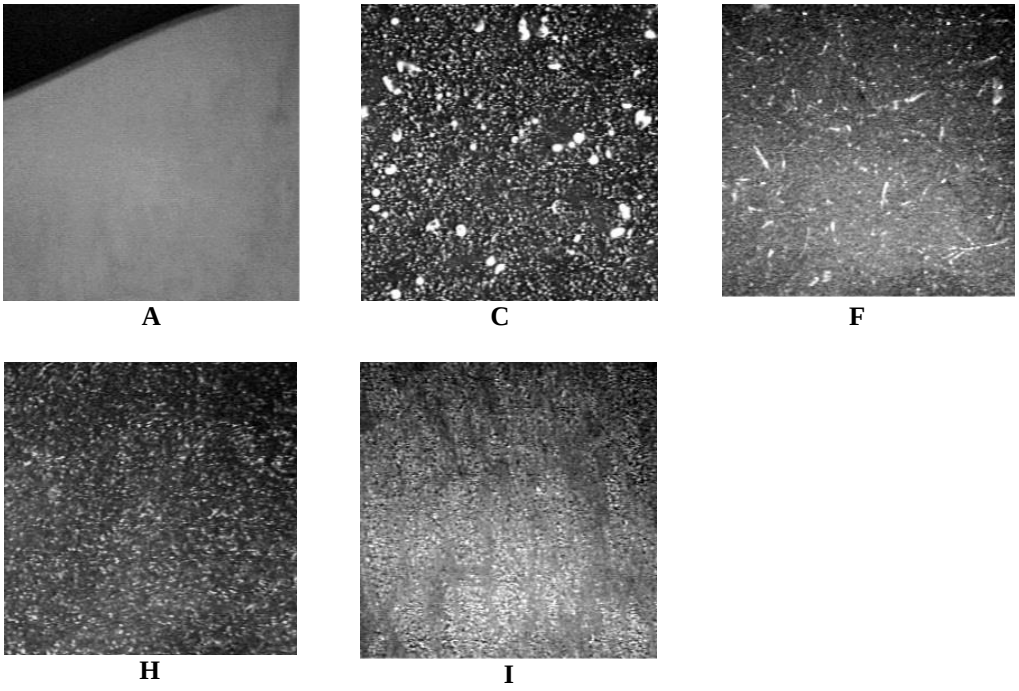

Figure 7: Polymer dispersion in the virgin binder (magnification factor 200)

In the case of most binders like PmB F (Figure 8), no significant changes before and after recovery can be recognized by fluorescence microscopy. Only PmB I shows a different behavior (Figure 9), with mixed phases after recovery from toluene, DCM and xylene compared to the continuous bitumen phase of virgin binder or after recovery from TCM. However, these changes cannot be correlated to differences in penetration, softening point or elastic recovery results. Vice versa, the large deviations encountered in some rheological tests are not reflected by a specific polymer distribution.

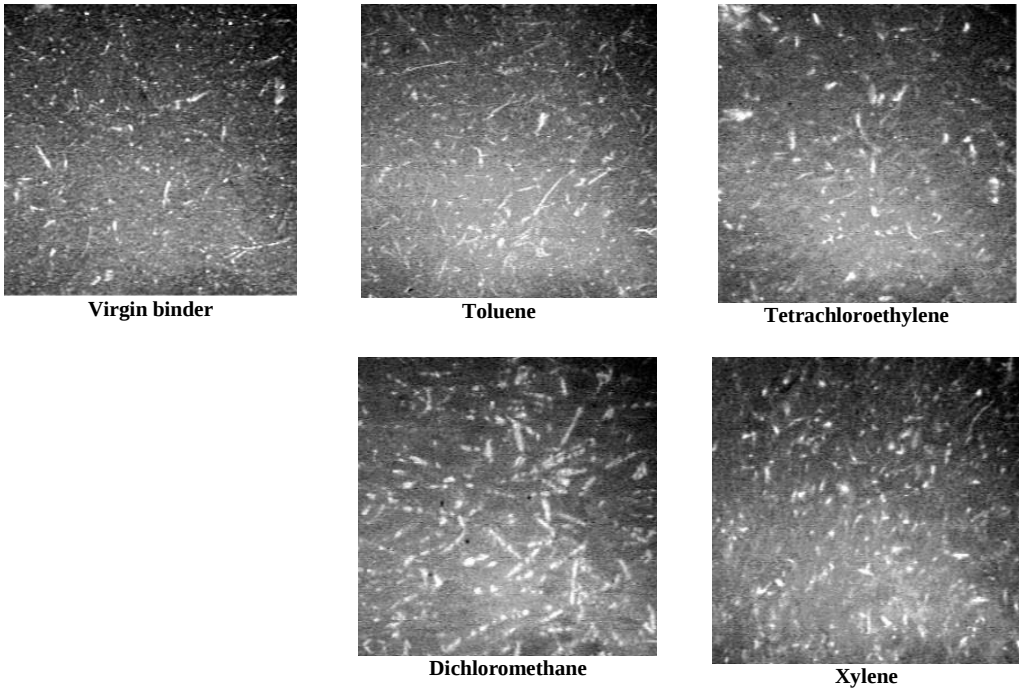

Figure 8: Polymer dispersion of PmB F (magnification factor 200)

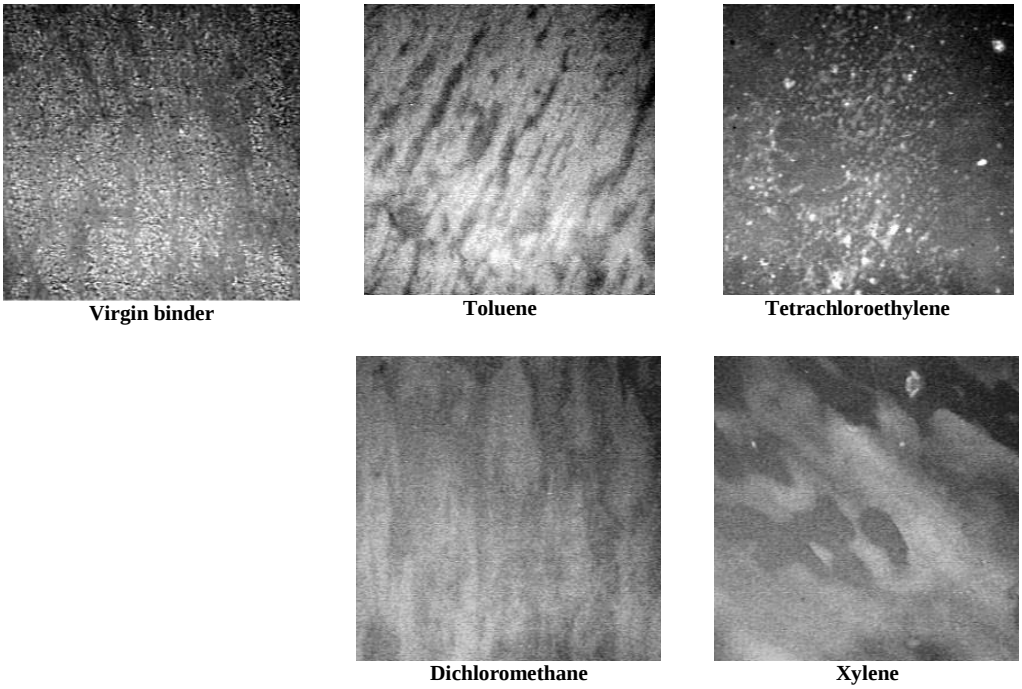

Figure 9: Polymer dispersion of PmB I (magnification factor 200)

4. CONCLUSIONS

- Although the extraction process was possible with all four solvents with the exception of one binder solvent combination involving dichloromethane, it cannot be granted that the extraction of every PmB is possible with all solvent types.
- If only the binder recovery from the solution is considered, the values of the recovered binder are in most cases close to the virgin binder. However, in some cases larger differences were encountered
- After extraction and recovery the aging effect dominates the results of the penetration, resulting in lower values. The aging is less pronounced for elastic recovery and softening point ring and ball, where both decreased and increased values were measured for the recovered PmB
- No general difficulties have been encountered with viscosity reduced PmB containing wax
- Solvent residues after recovery were below 0.2 % (m/m) for toluene and slightly higher for tetrachloroethylene and xylene
- Fluorescence microscopy indicated no correlation between polymer dispersion and rheological properties
- The number of PmB investigated in this project is not sufficient to draw final conclusions, which solvent PmB combination is possible or not

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