

Evaluation of binder recovery methods and the influence on the properties of polymer modified bitumen.

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ABSTRACT

In hot mix asphalt, binder extraction in combination with a recovery method is commonly used to evaluate the properties of a binder embedded in an existing pavement structure. In some countries, like Germany, specifications on the softening point and elastic recovery are legally required on polymer modified binders (PmBs), after recovery from a pavement. But there are legitimate doubts whether PmBs can be completely recovered. Especially, for highly modified binders (PmB-Hs) there are more and more indications that part of the polymer fraction is lost in the recovery procedure. As expected this can lead to legal problems when specifications are required on the recovered binders. The purpose of this paper is to evaluate the effect of the recovery method on the properties of PmB-Hs. Three different highly modified binders, prepared with linear and radial SBS polymers, are recovered using three different solvents. Two extraction methods are used: centrifuge and soxhlet extraction. In addition to a recovery from hot mix asphalt, the PmB-H binder as such, and the non-modified base binder were submitted to the same extraction / recovery process. Several tests including penetration, softening point, elastic recovery, force ductility, gel permeation chromatography and fluorescence microscopy were performed on the fresh, short term aged and recovered binders. The overall purpose of the paper is to determine if, why and to what extend, the properties of highly polymer modified bitumen change in the recovery process.

Keywords: asphalt extraction, binder recovery, aging, polymer modified bitumen, linear and radial SBS,

1. INTRODUCTION

In hot mix asphalt, binder extraction in combination with a recovery method is commonly used to evaluate the properties of a binder embedded in an existing pavement structure. In some countries, like Germany, a specification on the softening point is legally required on polymer modified binders (PmBs), after recovery from a pavement. But there are legitimate doubts whether PmBs can be completely recovered, especially, for highly modified binders (PmB-Hs). If the recovery is not complete a legal requirement on the recovered binder will of course lead to problems.

PmB-Hs are specified within the German binder specification and are mainly used for open graded asphalt (OPA) mixtures. By using PmB-Hs it is secured that the necessary thick binder is not dropping off before paving the mixture. Because of the high void contents of more than 20 vol.-%, the binder requirements on aging, adhesion and cohesion are rather high. The binder course and the surface course of an OPA are made of the same PmB-H. Also the underneath the binder course laid Stress Absorbing Membrane Interlayer (SAMI) is made with the same PmB-H.

The binder used for the OPA mixtures has to be recovered after production, transportation and paving, while the PmB-H for the SAMI layer does not need to be recovered because this binder is not treated by a mixing process; the SAMI is sprayed hot on top of the wearing course. For the SAMI binder, only the values on the fresh delivered binder have to be measured for contractual reasons. The contractual requirement for R&B on the recovered PmB-H is the same as the lowest requirement for the softening point on the fresh binder, which is in most cases 65°C.

Several OPA mixtures have been laid on different Motorways in Germany. The experience from these past OPA projects has shown that there are problems because the softening points of the recovered PmB-Hs are not constant – and very often are also too low. In contrary to the softening points measured after recovery, the elastic recovery tests performed on extracted binders shows a more constant and high value. On the German Motorway A7 project, for example PmB-Hs were used in an OPA 0/8 mixture. The length of this site was below 10 km, and the recovered softening points between highest and lowest value had a range of 10°C. Under respect of the minimum value of 65°C, 26 of 30 values were under the contractual legal requirement! [1]

The observation of not constant and too low softening points of recovered PmB-Hs does not depend on the bitumen supplier, the OPA mixture (0/8 or 0/16) nor the paving system, mixing plant, etc. The phenomenon is probably not only related to the used materials and machinery for asphalt paving, it could be also related to the used test methods to recover the binder (PmB-H) out of the asphalt mixture (OPA).

The recovery procedures and technology used today, including the rotated distillation to separate the solvent, have been developed many years ago, when the asphalt industry was only using paving grade bitumen. Nowadays we are using polymer modified binders and in some cases highly modified binders which show more elastic properties at service

temperatures and also a very different viscosity profile at paving temperatures compared to standard paving bitumen. The question is if the current used recovery methods are fit for purpose for these PmB-Hs?

To evaluate this question, the authors have started an investigation to determine the effect of the recovery method on the properties of PmB-Hs. The properties that are investigated include conventional tests like penetration, softening point and elastic recovery, as well as mechanical tests like rheology, and force ductility. In addition, molecular weights are investigated using gel permeation chromatography and the morphology is investigated by fluorescence microscopy. For each sample tests are performed on the fresh (before mixing) and on the recovered binders. Some tests are also conducted after RTFOT, in order to check if properties after recovery can be evaluated by a commonly used aging procedure like RTFOT. The overall purpose of the paper is to determine where, why and to what extend, the properties of highly polymer modified bitumen are changing in the recovery process.

2. EXPERIMENTAL

2.1. Parameters of the project

To evaluate the effect of a recovery on the properties of highly modified PmBs (PmB-Hs), different parameters were varied:

- The type of polymer; three different highly modified binders were prepared, compared to the German PMB40-100/65-H specification: two times using a linear SBS and one sample was made with a radial SBS polymer. These are marked as LIN1, LIN2 and RAD respectively. The base binder and the polymer concentration (5%) was the same in all three PmB-Hs. These polymers are commercially available. The Nypol 50/100 is not included in this study.
- The recovery procedure, three different procedures are used: Soxhlet extraction is used with the solvent methylenechloride (MCL), and the extraction method by centrifuge is used with trichloroethylene (TCE), and toluene respectively. These solvents are still commonly used in Europe for extraction purposes: e.g. methylenechloride in the Netherlands, France; Trichloroethylene in Germany, although they are toxic.
- In addition to a recovery of these binders from hot mix asphalt, the PmB-H binders as such, and the non-modified base binder are also submitted to one of the extraction / recovery methods, more specific to the method using centrifuge with trichloroethylene .

2.2. Experimental Procedures

The PmB-Hs are prepared in the lab, by mixing the corresponding amounts of bitumen and SBS at 180°C for 1 hour with a Silverson high shear mixer, and then matured for 2 hours in an oven at 185°C. These 'fresh' binders are denoted as 'O' (Original). In a second step asphalt is made with these 3 PmB-Hs. The mix type is a dense asphalt concrete 0/10 with 6.2 % binder on aggregates mix. Each time 15 kg was made and divided equally in 3 parts for the 3 different recovery methods. All mixes were tested at the same time in the different extraction methods (same age of asphalt).

In this study, the soxhlet method is performed with the solvent methylenechloride. First, the asphalt is heated to 150°C in an oven for a fixed time of 2.5 h. The heated asphalt is then transferred into the soxhlet cartridges. 6 Cartridges were filled with 1300 g of material. Fresh methylenechloride is used for the recovery. Then the extraction continues for 2 days at 80°C until all binder is removed from the aggregates and the methylene chloride is clear. This is checked by closing the valves and verifying that the lower part of the cartridge is releasing solvent which isn't coloured by bitumen anymore.. Aggregates and main part of the fines remain in the cartridge. The bulb contains the solvent, the bitumen and some part of the fines. Therefore the content of the bulb is centrifuged to remove all the fines. At last, the solvent is evaporated with the rotary evaporator method according to method EN 12697-3 [2]. This recovered binder is then tested. The result is denoted as S-M (soxhlet - methylene chloride)

The fast extraction method (centrifuge - Strassentest) is performed once with trichloroethylene, and once with toluene. These two recoveries were performed by external laboratories. In this procedure, the asphalt is heated to 160°C and homogenised. Then an amount of mix is brought into the centrifuge and left to cool to 80°C before starting the extraction. Extractions are continued until aggregates are clear and no binder is remaining in the wash drum. The binder is finally also recovered in the same way with the rotary evaporator according to EN 12697-3 [2]. This recovered binder is then tested. This result is denoted as E-TC (extraction – trichloroethylene) and E-T (extraction – toluene)

In addition to a recovery from the asphalt mix, the PmB-H as such, without mixing, was also recovered with the extraction method using trichloroethylene. For these samples it was noted that there was still rest solvent ETC in the samples which was easily detected from the smell. Therefore, these samples were submitted a second time to the rotary evaporator. The respective results will be denoted as O-D-P (original – dissolved, but with rest solvent), and as O-D (original – dissolved- 2x evaporated). Finally, to complete the data, RTFOT was also performed on the 3 PmB-Hs (denoted as RT) and compared to recovered binders. An overview of the different test symbols is given in table 1.

Table 1: Description to the legends used in the graphs

Original PmB-H	O
PmB-H after RTFOT	RT
PmB-H recovered via Soxhlet with Methylenechloride (MCL)	S-M
PmB-H recovered via fast Extraction with Trichloroethylene (TCE)	E-TC
PmB-H recovered via fast Extraction with Toluene	E-T
Fresh PMB-H dissolved in TCE and not sufficiently recovered via rotary evaporator	O-D-P
Fresh PMB-H dissolved in TCE and recovered two times via rotary evaporator	O-D

2.3 Materials

In table 2 the properties of the polymers according to the manufacturers are represented. In addition, gel permeation chromatography (GPC) was conducted to have an idea of the molecular weights of the polymers and on the coupling efficiency. These tests confirm that the sample LIN2 is mainly a diblock copolymer, while sample LIN1 is mainly a triblock and the radial sample has as expected the highest molecular weight. The base binder was the same for the three PmB-Hs.

Table 2: Polymer description according to the manufacturer

Polymer structure SBS	Styrene content	Coupling efficiency	Hardness Shore A	Mp	Mw	Poly-dispersity
RAD	20	N.A.	60	339177	288074	1.199
LIN1	31	81	72	217810	218589	1.13
LIN2 (diblock)	25	N.A.	N.A.	140999	157741	1.08

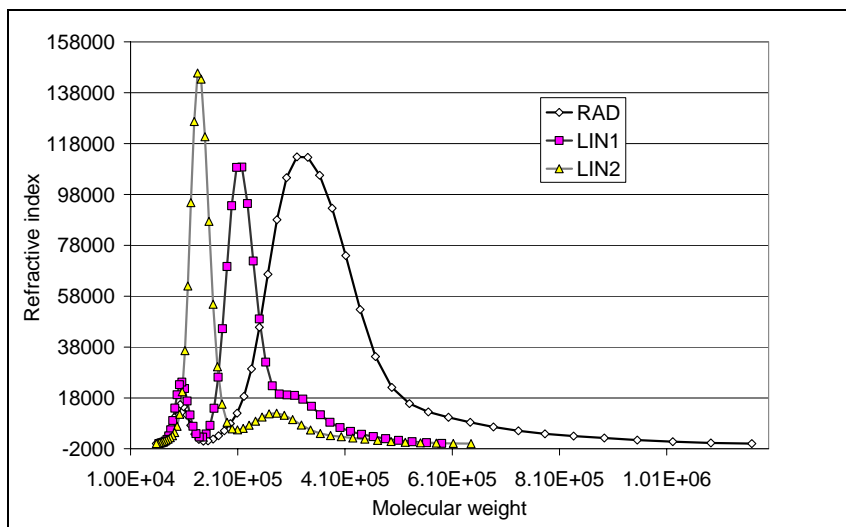


Figure 1: Gel permeation chromatography (GPC) of the pure polymers

3. RESULTS

3.1. Conventional properties

Results of conventional tests for the original and the RTFOT aged binders are given in table 2. One can already observe a difference in performance of the original binders. The 3 different polymers in the PmB-H blend, give properties that are not comparable:

- PmB-H RAD is just inside the specifications
- PmB-H LIN1 is within specification but fails for R&B after RTFOT
- PmB-H LIN2 is not fulfilling the specification for a PmB40-100/65 on softening point.

LIN2 behaves in general very poor for a high modified binder. Conventional test results like penetration at 25°C, R&B temperature and elastic recovery after the various procedures are given graphically in figure 2, 3 and 4 respectively.

Table 3: Conventional test results of the original and RTFOT aged PmB-Hs.

RESULT		RAD	LIN1	LIN2	Specifications TL-PmB 2001 PMB40-100/65H
Pen @25 °C	dmm	73	65	90	40-100
R&B	°C	65.5	72.5	52.2	> 65
Elastic recovery	%	95	97	67	> 50
After RTFOT					
Pen @ 25°C	dmm	52	52	66	
Retained Pen @ 25°C	%	71	80	73	60 % (or 10% increase)
R&B	°C	61.5	65.1	55.7	
Delta R&B	°C	- 4	- 7.4	+ 3.5	+ 8°C / -5°C

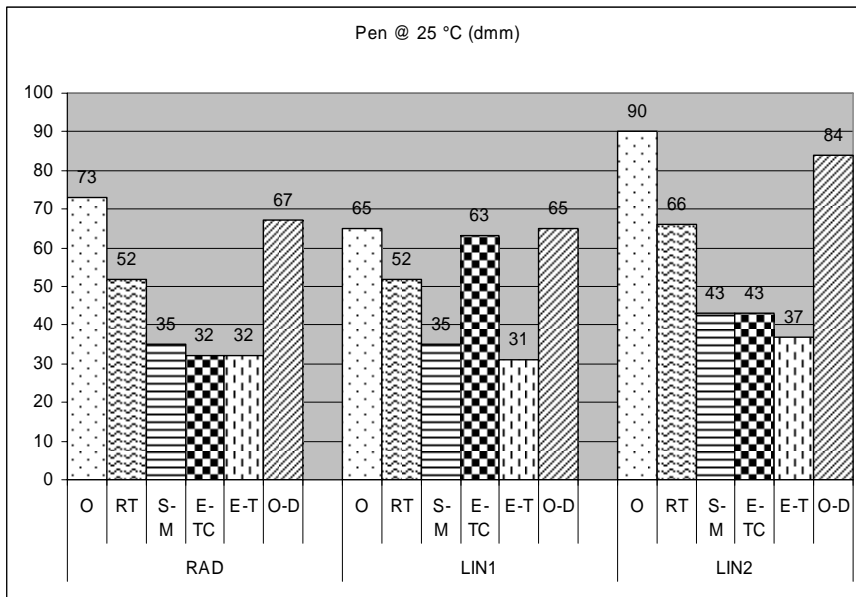


Figure 2: Penetration of the three PmB-Hs after several procedures (procedures are explained in table 1)

In figure 2, penetration levels after the different recovery procedures are presented. If we assume that the type of recovery process does not influence the binder properties, then all the physical test results for a given binder type, performed with the three recovery methods, should give the same test result, since the asphalt mixture used for the three recovery methods was the same and was performed at about the same time after mix preparation. For RAD and LIN2, the extraction method or the solvent does indeed not have a large influence, the results are almost the same, independent of the method; penetration levels are reduced by half. For the sample LIN1 the extraction with trichloroethylene gives penetration values that are higher compared to the extraction with MCL or toluene. So in this case there is an influence which is not expected.

Dissolving the PmB-H in the solvent trichloroethylene, O-D samples, should, if the recovery procedure as such has no influence, give the same properties as for the original binders. In figure 2, we can observe that the O-D procedure indeed results in only a small decrease in penetration. But, it should be noted that this were the tests results obtained after having the samples two times in the rotary evaporator equipment. And finally, the decrease in penetration observed after RTFOT, the RT samples, is less pronounced compared to the decrease after extraction, and this is observed for the three binders.

The observations for the R&B temperature, from figure 3, show also that the results after mixing and extraction are rather independent of the solvent or extraction procedure, and again LIN1 with TCE seems to be an exception, with a lower softening point temperature than the other two extraction methods for this binder. But the results for R&B are strongly dependent on the binder type; for the radial sample there is a decrease in softening point, after aging and also after mixing and recovery, the decrease is limited to less than 5°C. For the sample Pmb-H LIN1, the decreases in R&B temperature are much larger. And for the sample LIN2 the effects are opposite, there is an increase in R&B

temperature. In figure 3, the recovery of the binder as such, the samples O-D, has influenced the R&B softening points for two binder types RAD and LIN1, with respectively about 4°C and about 8°C. For the LIN2 sample there is no effect, and again it should be noted that this was tested on samples that were dried in the rotary evaporator test twice. After RTFOT there is also an effect on the R&B softening points; for RAD and LIN1 the R&B temperature decreases while it increases for RAD.

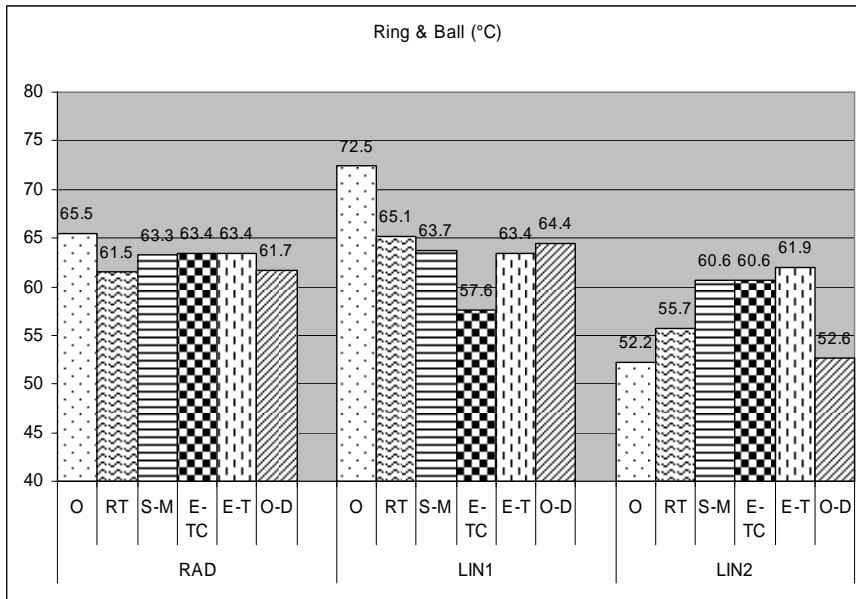


Figure 3: Softening points of the three PmB-Hs after several procedures (procedures are explained in table 1)

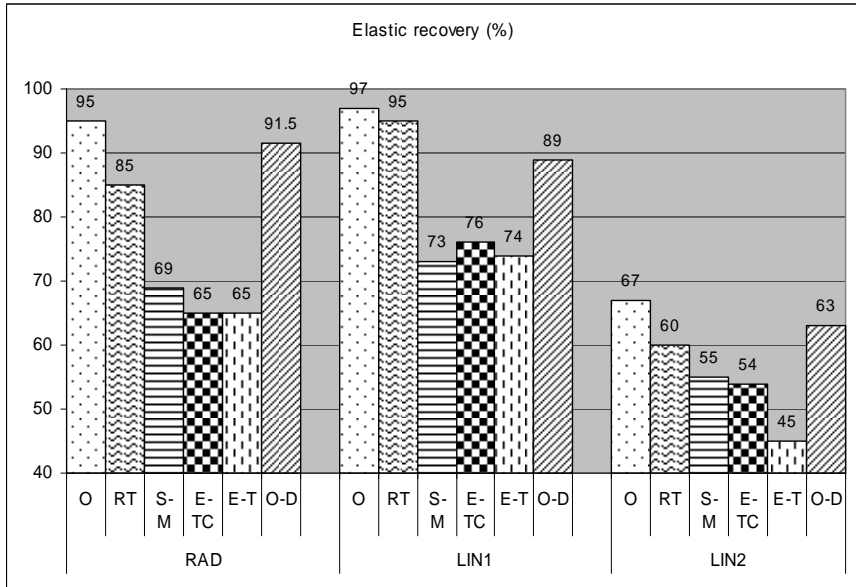


Figure 4: Elastic recovery of the three PmB-Hs after several procedures (procedures are explained in table 1)

Finally, elastic recovery was investigated, this property is a measure for the elasticity of the PmB-H, at large elongations. The original PmB-H with RAD and LIN1 SBS have a very high elastic recovery; while LIN2 original already starts with a low elastic recovery. This can be expected since LIN2 is mainly a diblock copolymer. After RTFOT (RT), there is a slight decrease in elastic recovery for all 3 PmB-Hs, but the values for RAD and LIN1 are still high, while LIN2 stays at a much lower level. After extraction, there is clearly a drop in elastic recovery in all cases (all extractions and solvents): the largest drop is for the radial SBS (RAD), the lowest drop is for LIN2, which is the sample that started with a poor initial elastic recovery. The loss in elastic recovery is rather independent of the recovery method

for the 3 PmB-Hs, except for the sample LIN2 recovered with toluene which shows a somewhat larger drop compared to the other two recoveries. The value for LIN2 extracted with toluene would be out of the specification if one follows the same limits for recovery as for RTFOT (min 50%) Dissolving and recovering the PmB-Hs without performing the mixing, has some influence but the decreases are limited to a maximum of 11% of the initial values.

Based on only these 3 conventional properties, some observations can be made:

- The original PmB-Hs have different properties, due to the different types of polymers (see table 2 and figure 1).
- Dissolving a PmB-H and recovering this binder, without performing the mixing process with aggregates, should if the methods are perfect have no influence on the properties. In fact there are some influences on all three properties, there is a slight decrease in penetration and in elastic recovery and there is also a decrease in the R&B temperature, but the changes are within or very close to 10% of the original binder. However if this just happens on a sample that is borderline on R&B, this sample would after the recovery treatment be out of specification.
- After the recovery process from the asphalt mixtures, conventional properties have changed, and the changes are quite independent of the recovery method or solvent used, this is also what is expected. But it is not clear what has caused the changes, since the PmB-Hs have undergone multiple steps and each step may contribute to the observed changes: the changes may have happened because of aging during the mixing with aggregates, or because of aging in the extraction / recovery process, or due to an incomplete recovery, polymer is left on the aggregates, or because of an incomplete evaporation of the solvent, rest solvent that is still present in the samples. Since these questions could not be answered it was necessary to use other measurement techniques.

3.2. The influence of solvent remaining in the binder:

As discussed before, the PmB-H O-D samples, which are recovered without the mixing step, using trichloroethylene still contained solvent, when they were received from the external laboratory where the tests were done. It was necessary to submit these samples again to the rotary evaporator test. In table 4, the tests performed before and after the second rotary evaporator treatment are shown. It is quite clear that there is a large effect of this second rotary evaporator treatment on the penetration level and also on the R&B temperature.

Table 4: Comparison of penetration and R&B of samples before and after the second rotary evaporation test.

	RAD		LIN1		LIN2	
	O-D-P	O-D	O-D-P	O-D	O-D-P	O-D
Pen @ 25°C (dmm)	122	67	145	65	170	84
R&B (°C)	55.8	61.7	57.7	64.4	46.3	52.6

In order to quantify these effects some additional tests were performed: The concentration of trichloroethylene was determined for some selected samples using ASTM method D 5808-03 [3], these results are shown in table 5

Table 5: The rest concentration of TCE in various samples after extraction with TCE and drying through the rotary vapour procedure, the O-D samples were dried twice in the rotary vapour procedure.

Sample	Base O-D	RAD E-TC	LIN1 E-TC	LIN2 E-TC	RAD O-D	LIN1 O-D	LIN2 O-D
w% TCE ASTM D 5808-03	0.40	0.32	0.91	0.34	0.21	0.13	0.10

From table 5 we can clearly see that there is a rest concentration of TCE present in all the samples that have been in contact with this solvent. The sample LIN1 E-TC has the highest rest concentration of TCE, which is nearly 1 %. This explains why this sample showed a much lower R&B softening point compared to the other recovered samples, and also showed a higher penetration value, in the previous section. Since we can assume that all the recovered binders from one mix type, should have the same value of R&B, this would mean that the R&B temperature of LIN1 has decreased by 6°C because of the presence of 0.9% rest solvent.

The samples that have been through the rotary evaporator twice have in general lower concentration of TCE, with one exception, the recovered base binder. It is not clear why this sample is deviating, this was also not further investigated.

In general, the data indicate that recovering the binder is not so easy. Removing all the solvent to a low level is very important in order to get correct results on the recovered binders and is certainly a prerequisite if one wants to put specifications on some of these values.

3.3 Other binder tests

Rheology:

Rheological tests were performed, over a large temperature range (-10°C to +90°C) to evaluate the properties of PMB-Hs before and after recovery. In figure 5, black curves of the 3 original PMB-Hs are visualized. As was already observed in section 3.1, the original samples are very different: LIN1 shows a very elastic typical “PmB” behaviour, for RAD this is somewhat less pronounced, while LIN2 is not really demonstrating the elastic behaviour of a PmB-H.

The behaviour after recovery gives a completely different picture. In figure 6 and 7 black curves after recovery with respectively methylenechloride and trichloroethylene are shown for the 3 mixes, the black curves after recovery with toluene are not shown but they are very similar to the graphs in figure 6 and 7. All the samples behave now in the same way irrespective of the recovery method but also irrespective of the original binder! After recovery, the PmB (RAD and LIN1) have lost their elasticity, and have become similar to the PmB-H LIN2, which was already not very elastic from the beginning. For one binder type, LIN1, all the steps are summarized in figure 8. This PmB was originally the best, and therefore changed more than the others.

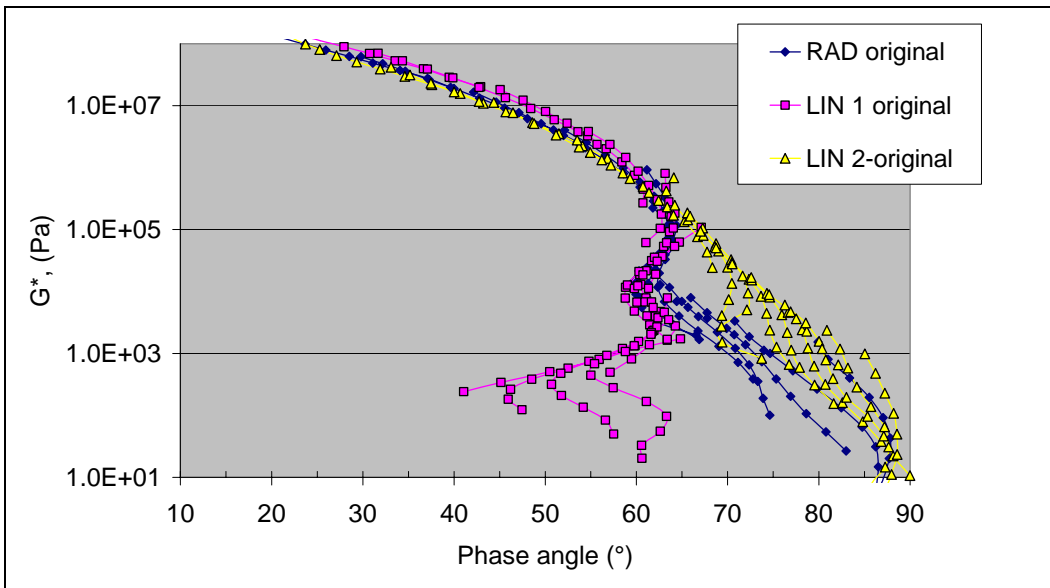


Figure 5: Black curves of the three original PMB-Hs.

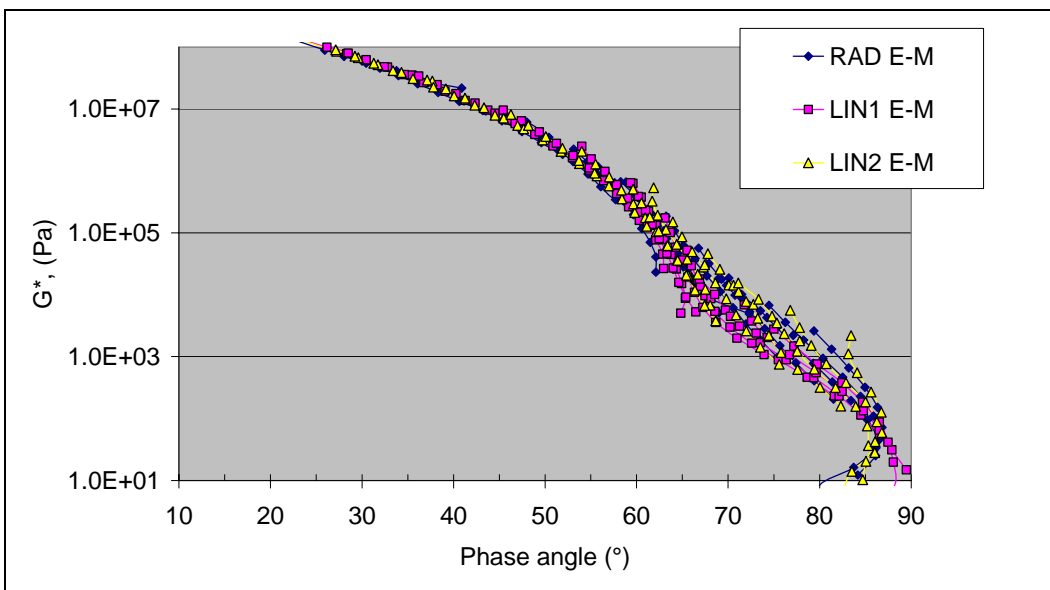


Figure 6: Black curves of the three PMB-Hs after recovery with soxhlet and methylenechloride.

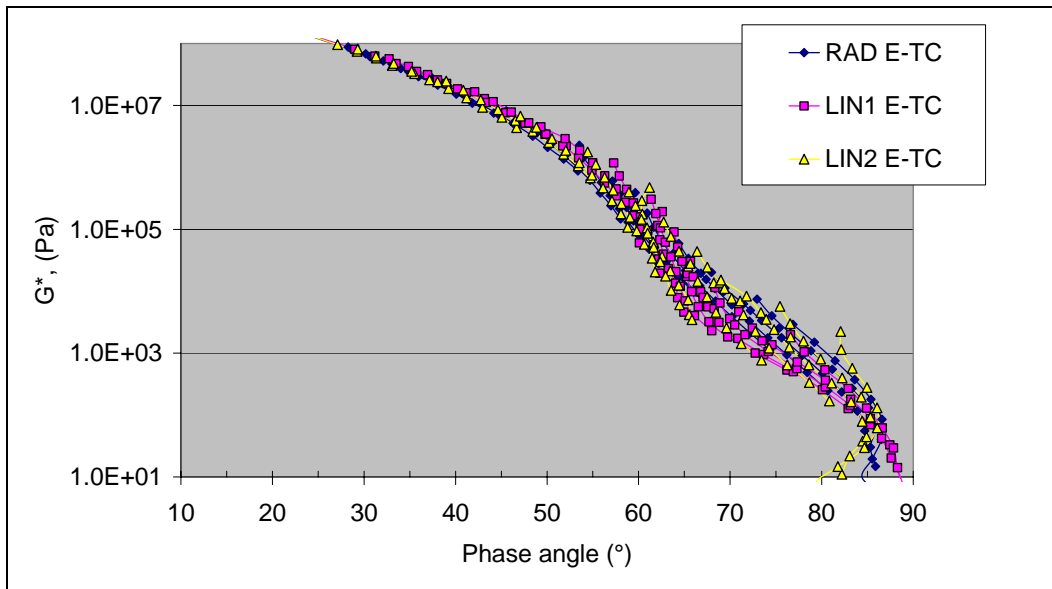


Figure 7: Black curves for the three PMB-Hs after extraction with trichloroethylene

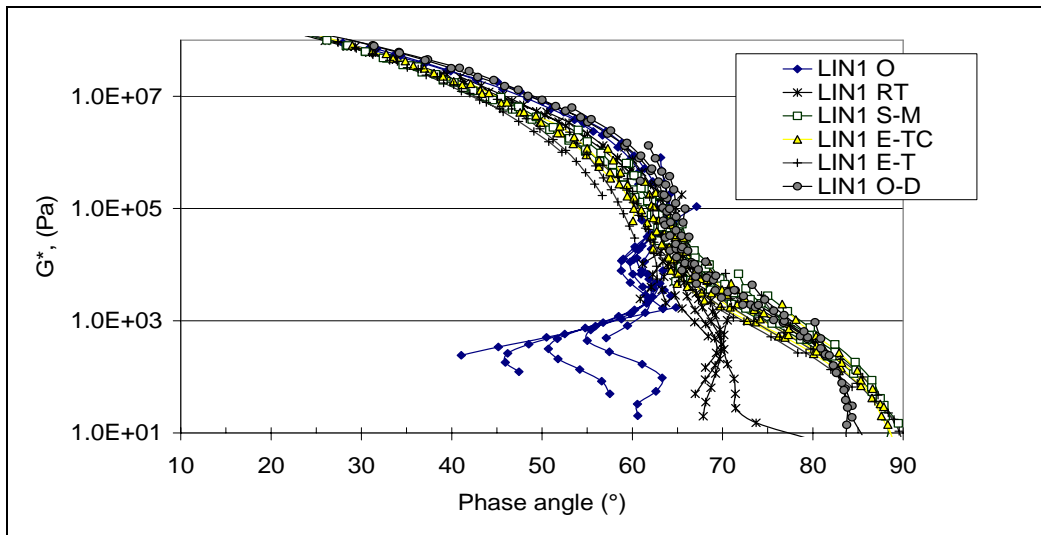


Figure 8: Black curves for the PMB-H LIN1 after several procedures.

Figure 8 also includes the sample after RTFOT and the sample recovered as such, without asphalt mix. The behaviour after RTFOT is still showing more elasticity than the samples recovered from the mix, which corresponds to the conventional properties. However, the sample recovered from the binder, without mix, also shows a reduction in elasticity, and is rather similar to the binders recovered from the mixture. This is not expected since this sample was still good with regard to elastic recovery and penetration in section 3.1. It is at this moment not clear why this happened. It seems that rheology is not able to discriminate between the different binder types, at least not after recovery, and that the extraction as such without mixture has a large effect on the rheological low-strain behaviour.

Microscopy:

The morphology and compatibility of the polymer modified binders, before and after recovery, was investigated with a UV-microscope. Some selected photographs are shown in figure 9. These binders were investigated by taking a drop of sample at a temperature of 180°C, and by looking at this drop through the bottom plate. Since the drop cools very quickly this is in fact almost an instantaneous record of the morphology as it is at 180°C. An overview of different sample preparation techniques for microscopy investigations is given in ref 4. The magnification is the same for all the graphs.

From figure 9 we can see that in the original sample, polymer and bitumen phases can still be distinguished from each other, while this distinction is less after RTFOT, and no distinction can be made for the recovered samples. The sample that is recovered without mixing (LIN1 O-D) shows a morphology in between the one after RTFOT and that seen in the original sample. There can be several reasons why the interconnectivity between polymer and bitumen phases changes:

- A decrease in the molecular weight of the polymer will improve its compatibility; shorter chains are easier to blend than larger molecules.
- A decrease in the polymer content will also improve its compatibility (at least in the concentrations used in these binders).
- A change in the bitumen phase for example through aging can also change the compatibility with the polymer (5).
- And the presence of rest solvent will most likely also have an influence on the compatibility.

Further tests will show which of these possibilities applies.

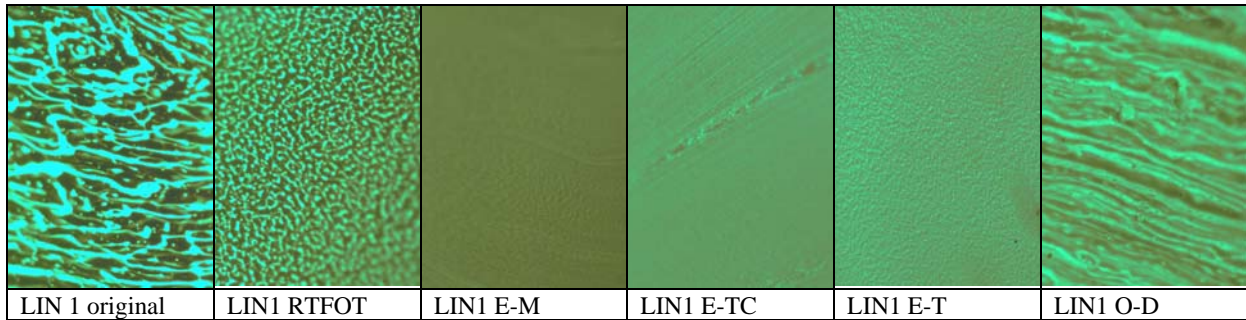


Figure 9: Morphology of PmB-H LIN1 by UV-microscopy after different recovery procedures (a drop is poured on a glass plate taken from 180°C)

Force ductility:

Another property that was investigated was force ductility. This test was used since it can demonstrate very clearly if there is a polymer network present in the sample, and also how this reacts at high elongations. On all binders and at the different stages, force ductility tests were performed at 10 and 25°C. In figure 10A, B and C, force ductility curves at 10°C are shown. The binders recovered with toluene are not shown but the results were very similar to the tests done with methylene chloride, results of the binders that still contained a lot of rest solvent are also shown (O-D-P samples). As an illustration of the effect of the polymer, a force ductility curve of the unmodified base binder is included in figure 10A.

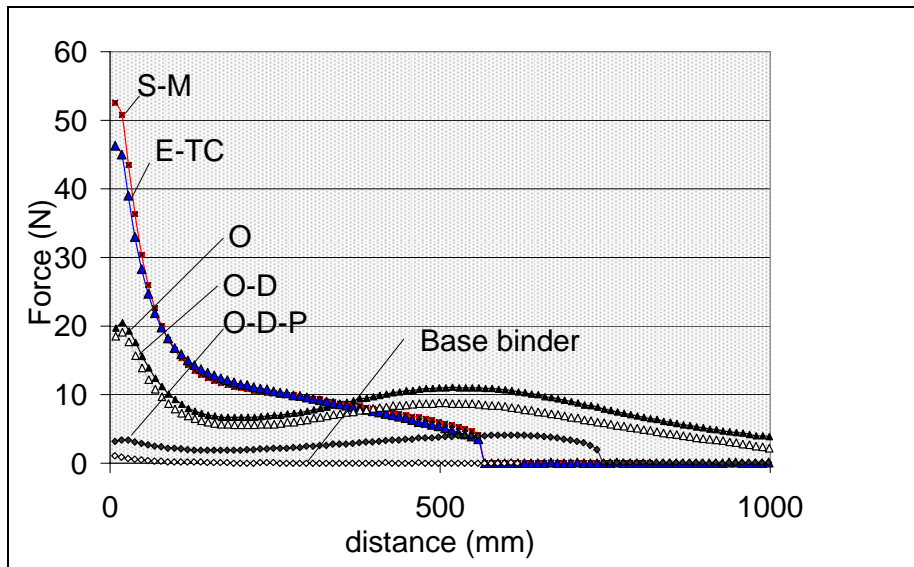


Figure 10A: Force ductility curves at 10°C, binder RAD

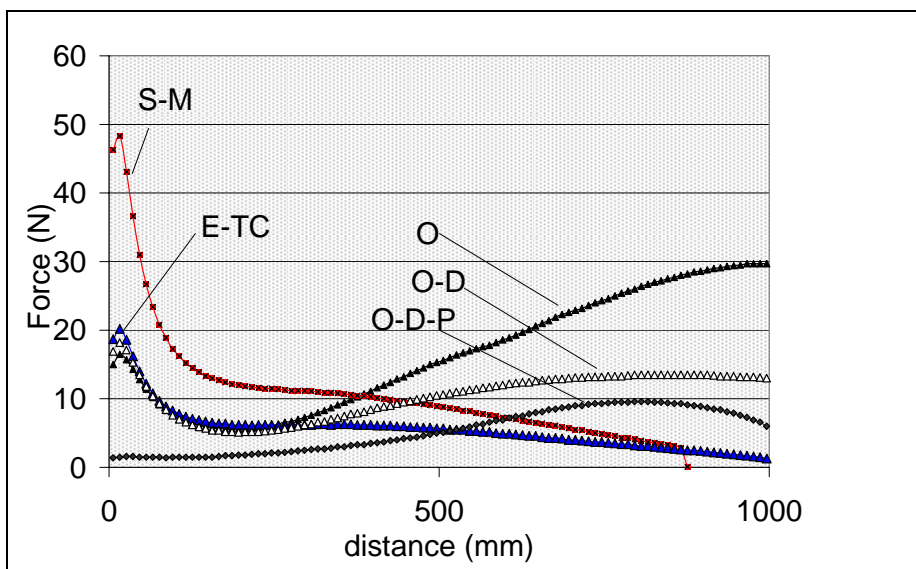


Figure 10B: Force ductility curves at 10°C, binder LIN1

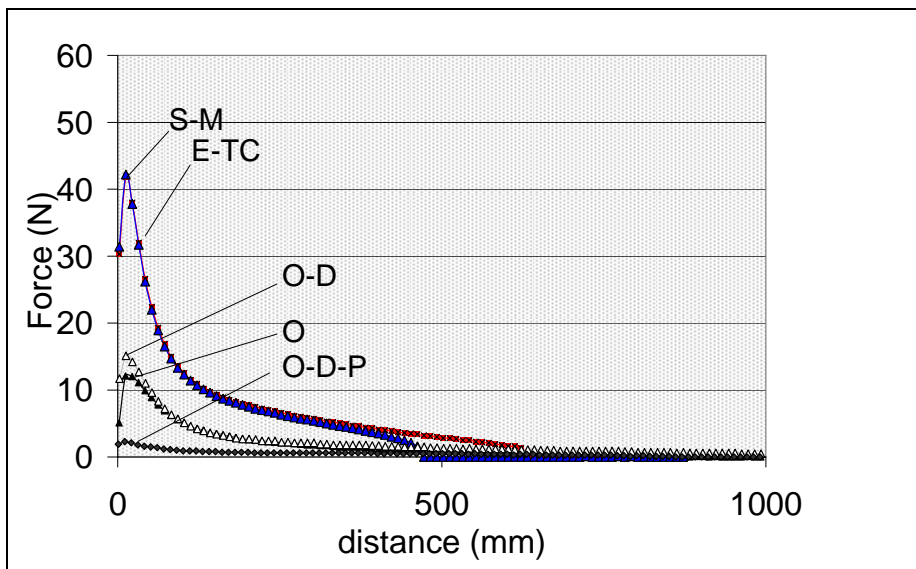


Figure 10C: Force ductility curves at 10°C Binder LIN2

From Figure 10 we can see that the original binders are distinguished in this test, for the LIN1 the force increases with elongation, for RAD it is more or less constant and for LIN2 the force decreases to a very low value. After recovery from the mix, shown for two procedures S-M and E-TC, we see that the initial force is much larger, due to the increased stiffness, with one exception, LIN1 extracted with E-TC. But as we saw in section 3.2 this sample still contained rest solvent (0.9%) and therefore it was not as stiff as the other recovered binders. There are, in the tests after recovery from the mix, differences between the different binder types, but these differences are small. For the RAD and the LIN2 sample the recovery without mixing (O-D) does not have a large influence on the properties, but there is some effect for the LIN1 sample, although the difference is only observed at large elongations. For all the samples, the presence of solvent, (O-D-P) samples, has a large effect on the initial force but even in the samples with solvent the evolution of force with elongation is similar to the samples dried further (O-D).

Gel Permeation chromatography (GPC)

In order to look directly at the molecular weights of the polymer before and after recovery GPC curves were taken after several procedures and the graphs are shown for the sample LIN1 in figure 11. In this figure the part where the polymer molecular weights are detected is enlarged, the bitumen signal is not completely on the graph.

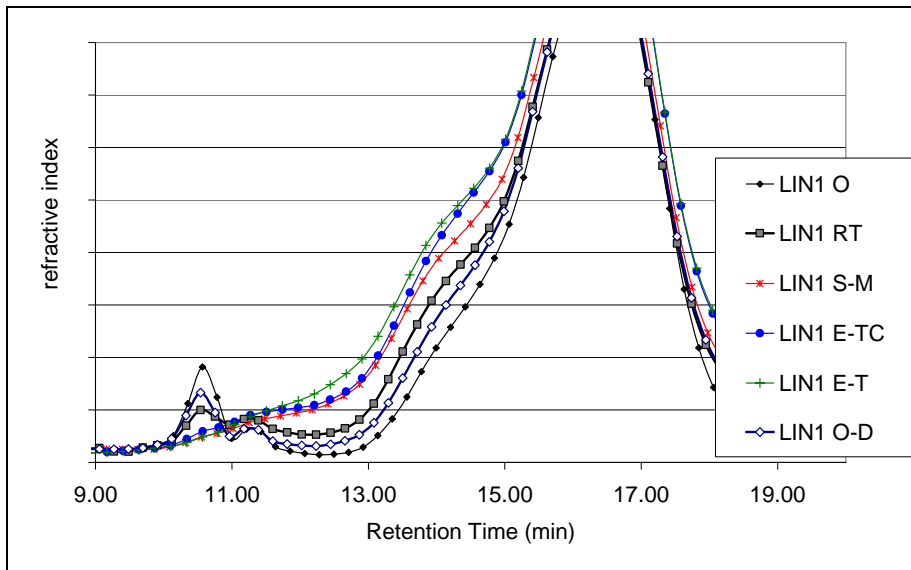


Figure 11: GPC curves for LIN1 after several recovery procedures

In figure 11 there is a clear change for the samples after recovery from the mix. Only the original binder, the dissolved PmB, and the sample after RTFOT show two separate polymer peaks followed by a bitumen peak. But even by just dissolving and recovering the PmB-H, some slight changes have occurred in the molecular weight of the polymer, also after RTFOT, polymer peaks are present, but smaller. However, after the extractions from the mix, these peaks disappear and the curves show a bigger bump in the bitumen peak. These GPC results confirm the trends found in the force ductility tests, in the conventional properties and in rheology, that after extraction the typical PMB properties have decreased.

Infra Red spectroscopy

Finally, FT-IR measurements were performed in order to have an idea whether the polymer concentration was the same in all the samples. FT-IR was measured in attenuated reflectance mode on the bitumen samples directly. Two IR absorption bands were followed: the absorption band at 699cm^{-1} which corresponds to the C-H out of plane bending in monoalkylated aromatics (styrene), and a band at 966cm^{-1} corresponding to the C-H out of plane bending of trans-alkene (butadiene). For the IR measurement it appears that all samples have approximately the same content of polystyrene and polybutadiene. In this project there was no time to work via a calibration curve, so these tests should be used as a semi-quantitative indication. Some data are shown in table 6.

Table 6: IR measurements for the binder LIN1

		LIN1 O	LIN1 RT	LIN1 O-D	LIN1 E-T	LIN1 E-TC	LIN1 S-M
Peak at 699cm^{-1}	Height (A)	1.83	1.8	1.94	1.84	1.79	1.83
	Area (cm-1)	0.119	0.119	0.127	0.124	0.122	0.125
Peak at 966cm^{-1}	Height (A)	1.43	1.46	1.5	1.48	1.49	1.53
	Area (cm-1)	0.167	0.173	0.177	0.173	0.173	0.179

4. DISCUSSION

The FT-IR method and the GPC method give some clear answers, it seems that for the 3 binders investigated in this project, the SBS polymers could be extracted almost completely and it is also clear from the GPC test that in the extracted samples from the mixture the polymer chains have degraded to a large extent. This degradation, to this extent, is not because of the recovery process itself since the samples O-D do not show this effect, so the degradation must have occurred in the mixing step. And we also see that a short term aging test (like RTFOT) does not simulate the observed polymer degradation. Since the polymer chains are degraded after recovery this also explains why the interconnectivity of the polymer bitumen phases has improved, seen in UV-microscopy. The trends seen in force ductility tests and in elastic recovery are similar to the ones observed from GPC combined with FT-IR. The samples O-D keep their good properties, they show a behaviour that is similar to the behaviour of the original binders, with a slight

deterioration in properties, while the binders recovered from the mix show a clear deterioration in the capability to resist large elongations, which is expected if the polymer chains are reduced in molecular weight. If we look at the penetration levels, they are also in agreement with these findings, the O-D samples do not change much, the RTFOT samples are in between and the samples after recovery from the mix have changed most. There was one sample however that formed an exception, but it was shown that this sample contained about 1% of rest solvent and penetration data are strongly influenced by the presence of rest solvent. Rheology tests show that the low strain visco-elastic properties are changing a lot after recovery, but these tests also show that the recovery as such changes these properties, it is still not clear why this is, maybe rheology is very sensitive to the presence of small amounts of solvent.

Regarding the R&B softening points, the trends found correspond to the observations made with other techniques, but also in these tests dissolution and recovery of the binder as such has an influence, more specifically, two of the three binders lost respectively about 4°C and about 8°C on the R&B softening point. And these numbers can make a large difference if they are set by a specification. It has also been shown that there is always some rest solvent present in the binders after a recovery procedure, at least for the solvent E-TC. And that the concentration of rest solvent varies and can have a large effect on some test results.

Regarding the polymer degradation observed in this study, it is not clear yet if and how this degradation is dependent on the type of laboratory mixer used, and if it would also occur, to the same extent, if the samples were to be mixed in an asphalt plant.

5. CONCLUSIONS

The conclusions from this study are listed below:

- The tests indicate that there is always some rest solvent present in the samples after recovery; this was shown for the solvent trichloroethylene, according to ASTM D 5808-03 [3]. The presence of rest solvent has a lot of consequences; it decreases the R&B temperature, it increases penetration, and it influences the force ductility.
- It seems that different recovery methods can give comparable results, but only when care is taken to decrease the solvent content to a very low level. In particular, those tests for which the presence of rest solvent has an influence should be treated carefully. Even without smell, chlorines are still detectable in the recovered samples.
- The action of dissolving and recovering the PmB-H as such (without prior mixing process with aggregate material) has only a slight impact on the polymer molecular weight, and on most other physical properties, but even though the influences are small they can become important when there is a specification limit.
- The PmB-Hs, in this particular study, degraded to a large extent during the mixing with aggregates, this was observed as a decrease in molecular weight of the polymer part, but still the properties of these PmBs were much better compared to unmodified base bitumen. Future tests will have to show if this polymer degradation is related to a particular laboratory mixing device and if it would also occur in samples mixed in an asphalt plant.
- The results indicate that in this particular study, the RTFOT aging is not simulating the degradation of the polymer chains during mixing, but as noted before it is at this moment not clear if the polymer degradation observed in this study is representative for an asphalt mixing process, as it takes place in an asphalt plant.
- Demanding legal requirements for the softening point on a recovered binder becomes rather problematic since these tests have demonstrated that there is always according to ASTM D 5808-03 rest solvent in the sample, and that sometimes the concentration of rest solvent can be around 1.0w% and even more. In addition, it was shown that the presence of rest solvent has a large impact on the R&B softening point (0.9w% corresponded to 6°C decrease). The presence of rest solvent and the variation in its concentration are certainly, at least already two causes for the often large fluctuations in softening points found on job sites.

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