RHEOLOGICAL AND CHEMICAL EVALUATION OF THE AGEING OF SBS MODIFIED BITUMEN AS USED IN ROOFING.

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The objectives of this paper are twofold: to evaluate rheological and chemical changes induced by the oxidative ageing of SBS modified bitumen, and to compare with changes measured by conventional methods such as softening point. In particular, in this study, three bitumen, from different crude origin, were blended with the same SBS block copolymer. After preparation, rheology as well as gel permeation chromatography (GPC) show little difference between the different blends, which also have similar softening points. After ageing, differences both in the molecular weight changes of the polymer and in the stiffening of the bitumen are found. The rheological measurements show the combined effects of bitumen stiffening and polymer network reduction, changes in softening points are still in line with the molecular weight changes of the polymer observed by GPC.

A second objective of this paper is to compare the "ageing strength" of two different ageing procedures. In particular the pressure ageing vessel (PAV), as developed by SHRP for the accelerated long-term ageing of road bitumen, was used and compared with more traditional long-term ageing procedures. In addition, measurements on recovered roofing material after different years of service life were preformed and compared with laboratory aged samples.

Evaluation des propriétés rhéologiques et chimiques après vieillissement des bitumes modifiés pour membranes d'étanchéité.

L'objet principal de ce travail consacré aux bitumes modifiés par des polymères de type SBS a été d'étudier la modification

des caractéristiques rhéologiques et chimiques après vieillissement artificiel et de les comparer à l'évolution telle que mesurée par des essais plus conventionnels tels que la température de ramollissement Bille & Anneau. Cette étude a plus particulièrement porté sur trois bitumes de d'origines différentes modifiés avec le même co-polymère SBS. Après fabrication, les caractéristiques rhéologiques ainsi que l'analyse en chromatographie par perméation de gel (GPC) des liants modifiés sont très comparables. Il en va de même de leur température Bille & Anneau. Par contre, des différences significatives, tant au niveau du durcissement que de la répartition des masses moléculaires du polymère, apparaissent après vieillissement. Les mesures rhéologiques mettent en évidence l'effet combiné de l'augmentation de rigidité du bitume de base et de la dégradation de la matrice polymère. L'évolution de la température de ramollissement Bille & Anneau semble corrélée avec la dégradation du polymère mise en évidence par l'analyse GPC.

Un deuxième objectif de l'étude a été la comparaison du degré de sévérité de différentes méthodes de vieillissement simulé en laboratoire. Plus particulièrement, l'essai PAV proposé par le programme SHRP pour la simulation du vieillissement in-situ des bitumes routiers a été comparé à des méthodes plus traditionnellements utilisés pour les produits d'étanchéité. Les caractéristiques des liants ainsi vieillis en laboratoire ont de plus été comparées à celles mesurées sur des échantillons prélevés in-situ sur des matériaux d'étanchéité présentant un nombre variable d'années de service.

Rheologische und Chemische Studie der Alterung von polymermodifizierten Bitumen fuer Abdeckungen

Die Studie verfolgt zwei Ziele: Ziel eins ist die Untersuchung von rheologischen und chemischen Veränderungen in polymermodifizierten Bitumen, die durch Alterung induziert werden. Diese Veränderungen werden am Erweichungspunk verglichen. Hierzu werden drei unterschiedliche Bitumen mit dem gleichen SBS Polymer gemischt. Vor Eintritt der Alterung können in diesen Blends fast keine Unterschiede in Rheologie und GPC gemessen werden. Auch haben diese Blends gleiche Erweichungspunkte. Nach Alterung verzeichnen sich sowohl im rheologischen Verhalten als auch in molekularen Veränderungen des Polymers Unterschiede. Das rheologische Verhalten resultiert aus dem kombinierten Effekt eines steiferen Bitumens und einem reduzierten Polymernetzwerk. Die Veränderungen der Erweichungstemperatur sind dennoch im gleichen Trend wie molekulare Veränderungen in GPC.

Ziel zwei besteht darin, die „alterungsstarke" unterschiedlichen Alterungsvorgänge labortechnisch zu vergleichen. Insbesondere die Eignung der PAV (Pressure Ageing Vessel), wie sie von SHRP entwickelt wurde für die Alterung von Strassenbaubitumen, wird untersucht und mit Ofenalterung verglichen. Zum Schluss werden auch in situ Proben von unterschiedlichen Abdeckungen untersucht und mit den labortechnisch gealterten Proben verglichen.

Valutazione reologica e chimica dell'invecchiamento del bitume modificato con polimeri SBS, utilizzato per tetti.

Gli obiettivi di questo testo sono due. In primo luogo, la valutazione dei cambiamenti reologici e chimici indotti dall'invecchiamento ossidativo del bitume modificato con polimeri SBS ed il confronto tra questi dati e quelli ottenuti ricorrendo a metodi convenzionali come la misurazione del punto di rammollimento. In particolare, in questo studio, tre bitumi di diverse origini grezze sono stati mescolati col medesimo copolimero a blocchi SBS. Per i campioni non invecchiati, sia la reologia che la cromatografia a permeazione di gel (GPC) hanno dimostrato poca differenza tra le diverse miscele, le quali presentano anche punti di rammollimento similari. Dopo l'invecchiamento, invece, sono state riscontrate differenze sia in termini di degrado del polimero che di irrigidimento del bitume. Le variazioni osservate per quanto concerne il punto di rammollimento sono in linea con il degrado del polimero constatato mediante GPC.

Il secondo obiettivo di questo testo è confrontare la "forza invecchiante" di diverse procedure di invecchiamento. In particolare, il contenitore d'invecchiamento a pressione PAV, sviluppato nell'ambito del progetto SHRP per accelerare l'invecchiamento a lungo termine del bitume stradale, è stato utilizzato e confrontato con procedure più tradizionali d'invecchiamento a lungo termine. Inoltre sono state effettuate misurazioni su materiali recuperati da rivestimenti di tetti a diversi anni dalla posa, confrontando i dati ottenuti con quelli relativi ai campioni invecchiati in laboratorio.

Introduction

Blown bitumen has been used for the production of roofing felts for many years and continues to provide satisfactory performance in a wide variety of circumstances. Nevertheless, advances in building techniques have necessitated the development of very high performance roofing felt systems incorporating carriers and coatings with a high degree of elasticity and improved durability. PMB's are used for the manufacture of high performance roofing felt and have a number of advantages over blown bitumen which include; Improved strength; Higher flexibilty at low temperatures, enabling contractors to use the material under colder weather conditions; Improved resistance to permanent deformation at higher temperatures allowing the system to be walked on during construction. And higher durability by which these systems last longer than conventional felts.

Durability describes the resistance of a material to changes caused by environmental exposure or the capacity of a material to keep its (original) properties over time. Ageing describes the process of changes a material or subject undergoes with time. The principal effects of ageing on SBS modified bitumen are a reduction in softening point, a reduction in penetration and a rise in cold bending temperature. However, the in-service performance of roofing felts is difficult to simulate in the laboratory. They may be influenced by a wide variety of environmental factors, including UV radiation, moisture, and cyclical temperature changes. The final ageing resistance of a particular roofing felt further depends on construction particulars including thickness and composition. Therefore a simulated or accelerated ageing is only indicative under a set of standard conditions. Simulated ageing methods should allow a quick screening and differentiation between binders in a way which is realistic to the actual environmental conditions. But, because of the complexity of the problem, simulated ageing tests are not a direct measure for the durability of a particular roofing membrane in a particular application.

The purpose of this work was initially to evaluate ageing by GPC (Gel Permeation Chromatography) and rheology and compare this with conventional test methods, and secondly to evaluate two accelerated ageing methods. Three SBS modified samples, containing 12 weight % of polymer were studied. These samples differed only in the type of bitumen. At first, original PMB blends and unmodified bitumen samples were investigated, using rheology, conventional methods, and GPC. In a second step, PMB blends were subjected to the dark oven procedure, 6 months and 3 months at 70°C, and were again evaluated. Additionally, blends as well as unmodified bitumen could be aged with the PAV (Pressure ageing Vessel). Finally, a large number of field-aged samples were evaluated.

Experimental.

Sample preparation:
Bitumen and polymer -12% by weight- were mixed at 185°C for three hours at low shear. The polymer was in powder form and was an SBS type of polymer with a radial butadiene part. The properties of the bitumen are described later.

Dynamic Shear Rheology (DSR):
Measurements were performed with a Rheologica Stress Tech rheometer. In the higher temperature range 30°C-160°C a 25mm plate setup with a strain of 0.01 was used. For the temperature sweeps the frequency was constant at 10 rad/second, and the heating rate was 0.5°C/min.

Gel permeation chromatography (GPC):
Three styragel columns were arranged with pore sizes of 500+1000+10000 Å. The mobile phase was THF. Calibration was performed using polystyrene standards. The detector system was a Waters differential refractometer. Before injecting the samples they were filtered (pore size: 1,0 mm) to remove insoluble components. In this respect it should be mentioned that eventually a small fraction of highly cross-linked particles would not be detected in GPC.

Laboratory ageing procedures:
Two laboratory ageing procedures were used: the dark oven ageing prEN 1296 . The second ageing method was Pressure

Ageing Vessel (PAV), as introduced by SHRP (Strategic Highway Research Program), for the simulation of long term ageing for road asphalts. The PAV was used under conditions described by SHRP (metal plates containing 50g, air pressure of 20bar) and at a middle ageing temperature of 100°C. In a second step, the ageing time was increased from normally 20 hours to 72 hours. The samples investigated here were aged without aggregates or granules.

Field-aged samples:
Field-aged samples were recovered after different service times, and from different roofs. Fillers, mineral granules and the carrier were removed by extraction, with methylene chloride prior to sample preparation. In order to evaluate this extraction procedure, an un-aged sample was extracted in a similar way from aggregates. Extracted field-aged samples were investigated using GPC, and rheology.

In addition for field-aged roofing felts and for artificially aged roofing membranes (6 months oven ageing), flow resistance limit (NS 3530:1987) which is a simplified version of prEN 1110.1999 and flexibility at low temperature (EN 1109:1999; but 10 mm mandrel instead of 30 mm) were analysed.

Flow resistance limit: is defined as that temperature at which the coating of a vertically suspended bitumen moves under specified conditions 2 mm compared to the reinforcement. Practically, the vertical displacement is measured at two temperatures, for two hours (using a new specimen at each test temperature), and the temperature at which the coating displacement has moved 2 mm is calculated.

Low temperature flexibility cold bending: In this test, the lowest temperature at which bitumen sheet test specimens can be bent around a specified mandrel without cracking is registered.

RESULTS AND DISCUSSION

Conventional measurements:

At first, samples were investigated using R&B softening points, table 1. By adding polymer to the bitumen the softening points increased by about 85°C. After ageing in the PAV, the non-modified bitumen increased their softening points, whereas PMB samples decreased their softening points. The changes in softening points suggest that sample A is less ageing resistant than sample B and C, which are very similar. After 20 hours PAV the difference between sample A and B is about the same as after 72 hours PAV.

For the dark oven ageing at 70°C only the PMB's were used, they were aged directly in R&B rings. Again sample A is less ageing resistant. Especially after shorter ageing times, the relative difference between the samples is large. After three months dark oven ageing, sample A decreased its softening point 11°C more than sample B. This difference is less after 6 months oven ageing; the difference between the samples is only 6°C

Nr	Un-aged samples		PAV (100°C)			Dark oven ageing.(70°C)	
			20hours	72 hours		3 months	6 months
	Bit.	PMB 12%	PMB 12%	Bit.	PMB 12%	PMB 12%	PMB 12%
A	33,8	+86,2	–13	+21,8	–28,5	–19	–28,5
B	38	+86,5	–5,5	+18,6	–22,5	–8	–22,5
C	36,4	+83,1	–4,5	+23,8	–24,5	N	N

Table 1. Changes in R&B softening points for the different samples after different ageing procedures.

N: not measured
(changes after ageing are relative to the R&B temperature for the non-aged sample.)

For the unmodified bitumen, SARA fractions were determined by Iatroscan before and after 72hours PAV ageing (3). Results are shown in table 2. As expected the aromatic fraction decreases, the saturates stay more or less constant, and the resins as well as asphalthenes increase.

Fraction Type	Before ageing (weight %)			Aft. PAV(100°C) 72 h (weight %)			% change		
	A	B	C	A	B	C	A	B	C
Saturates	14	8	7	14	7	7	0	-13	0
Aromats	46	56	54	33	36	32	-28	-36	-41
Resins	22	21	20	31	34	33	41	62	65
Asphalth.	18	15	19	22	23	28	22	53	47

Table 2. Changes in SARA fractions for the unmodified bitumen after 72 hours PAV.

Conventional test results on field-aged membranes will be discussed together with the rheological tests on field-aged samples.

GPC measurements

<u>GPC on laboratory aged samples</u>

GPC measurements were recorded for the dry polymer, the three un-aged PMB's, samples after 20 and 72 hours PAV at 100°C and samples after 3 and 6 months dark oven ageing. Some examples are shown in figure 1A to 1C. The dry polymer consists of two peaks, a larger one (triblocks) at high molecular weight and a smaller (diblocks) peak at lower molecular weight. After ageing, the response ratio of these two peaks changes, and this change from triblocks into diblocks was used to quantify the molecular weight changes, as shown in table 3.

Nr	Un-aged	PAV		Dark oven	
		20 hours	72 hours	3 months	6 months
Dry polym.	2,9	n	n	n	N
PMB-A	1,4	0,9	(1)	0,5	(1)
PMB-B	2,0	1,3	0,6	0,9	(1)
PMB-C	1,7	1,3	0,6	N	N

Table 3. Changes in polymer peak ratio, from GPC response, after accelerated ageing.
(1) only one broad polymer peak observed; N: not measured

From table 3 and from the respective graphs, we may conclude:

- In all graphs a polymer response is observed.
- Already during the preparation of the PMB's a considerable change of the polymer molecular weight takes place. After 20 hours PAV, not only molecular weight decrease but also a slight tendency for polymer cross-linking is observed. After 72 hours PAV, severe degradation is observed. After 6 months dark oven ageing, the degradation of the polymer is so severe that there is only one broad polymer signal.
- The polymer degradation after ageing is in line with the measured decrease in softening point, the relation is shown in figure 2.

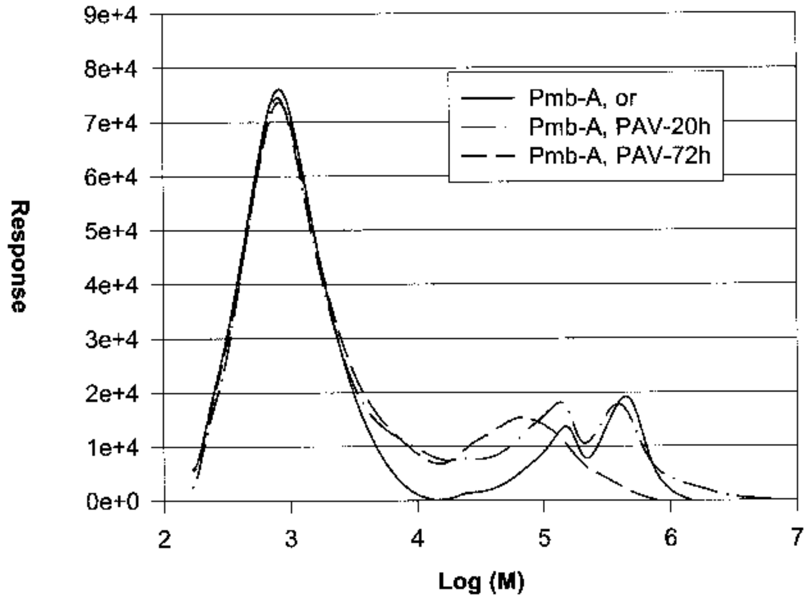

Figure 1A. GPC curves of PMB-A after different ageing times in PAV (or is un-aged).

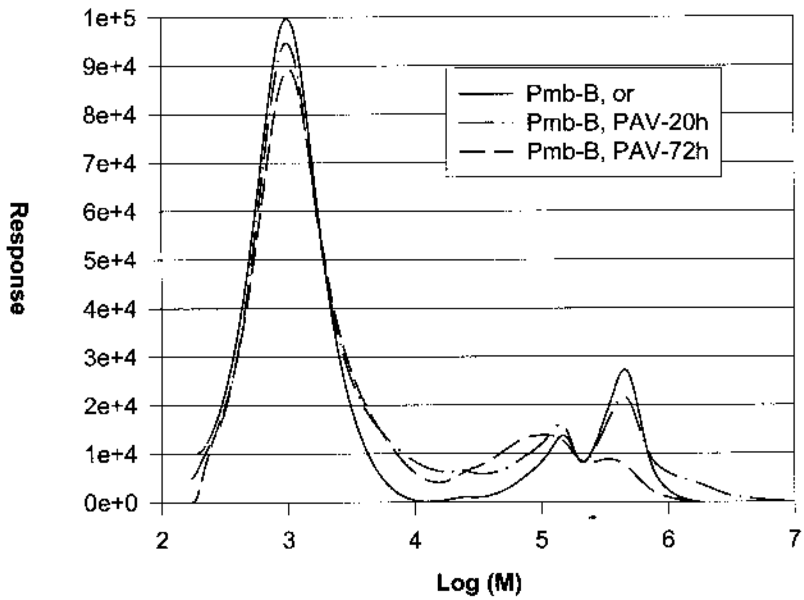

Figure 1B. GPC curves of PMB-B after different ageing times in PAV.

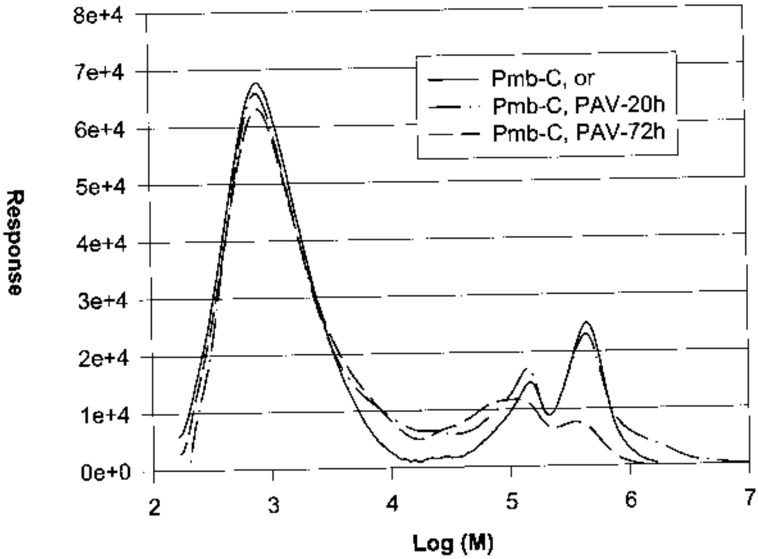

Figure 1C. GPC curves of PMB-C after different ageing times in PAV.

GPC on field-aged samples:

Samples aged on different roofs have been collected and were tested using GPC, examples are shown in figure 3A and B. However, before analyzing these data, one should mention that the bitumen origin of these samples is not exactly known, but is similar to the ones studied with laboratory ageing methods. In all cases the polymer type which was used is similar.

Again the ratio of both peak positions of the polymer response is calculated to quantify the effect of ageing on the polymer molecular weight as was done for the laboratory aged samples, table 4.

In service time (years)	Peak ratio	Average per service time
3	1,47	1,68
3	1,89	
9	1,57	1,49
9	1,41	
8	0.86	
11	1,05	
14	0,72	0,78
14	0,70	
14	0,92	

Table 4. Changes in polymer peak ratio, from GPC response after in-service ageing.

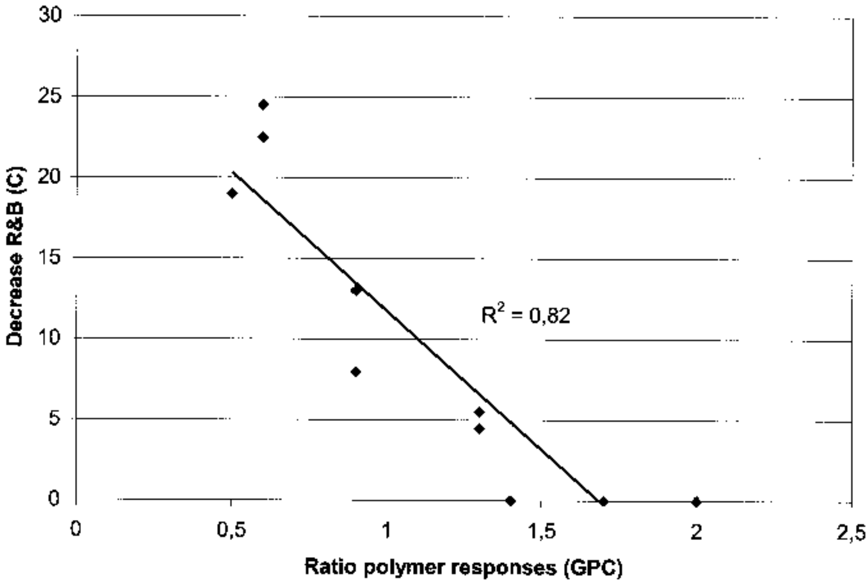

Figure 2. Relation between softening point decrease and polymer response in GPC.

Even after 14 years of service life the polymer is still apparent from the GPC curves. With service life the polymer molecular weight is reduced more and more, although the oldest field-aged samples (14 years) may indicate a slight cross-linking of the polymer.

It is very difficult to relate accelerated ageing tests to a certain lifetime on the roof, since the lifetime varies with climatic conditions, and also in the same climate it varies individually with construction particulars. In addition, correlations based on GPC measurements, as summarized in tables 3 and 4, only relate to the change of triblocks into diblocks. However, from these numbers we may conclude that the polymer degradation in PAV at 100°C for 72 hours and the dark oven ageing for 6 months is very severe and relates definitely to more than 14 years of service life. By reducing the time of the accelerated ageing tests, as was done with the dark oven ageing for 3 months and the PAV ageing at 100°C for 20 hours, the polymer degradation is somewhat reduced. Another possibility to make the accelerated tests less severe, which may be more realistic but which was not further investigated in this study, would be to reduce the ageing temperature.

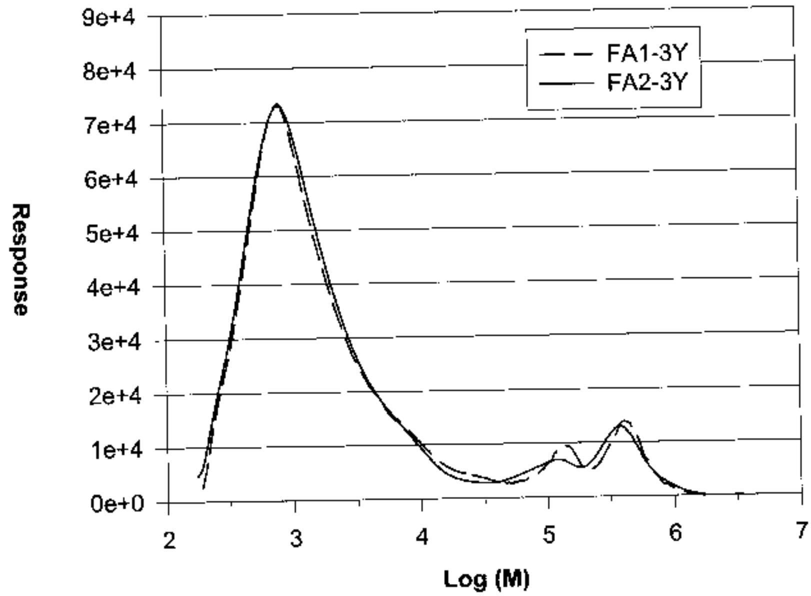

Figure 3A. *GPC curves of samples after 3 years on a roof.*

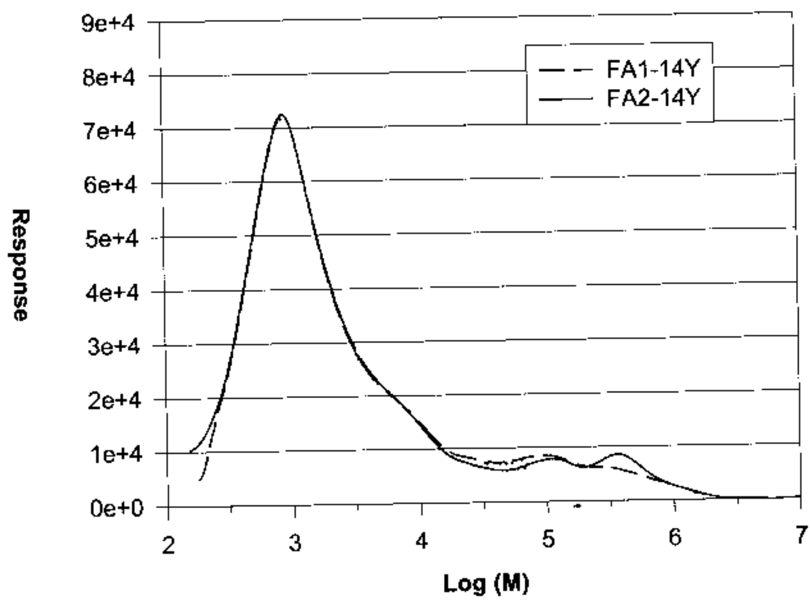

Figure 3B. *GPC curves of samples after 14 years on a roof.*

Rheological observations:

Upon adding polymer to bitumen, the properties of the material change drastically, as can be observed in the rheological temperature sweeps, figures 4A and 4B.

- ❑ At higher temperatures, gradually the elasticity increases, and the stiffness-temperature curve shows a plateau modulus between 1.10^3 Pa and 1.10^4Pa. A plateau in the stiffness modulus is typical for polymer modified systems, in which the polymer has formed a network structure, which in this case is not permanent, and will finally, drop off again at higher temperatures. The rubbery plateau modulus and the related minimum in the phase angle originate from the existence of entanglements in the polymer, and is referred to as rubbery plateau region (2). The shape and size of the plateau region is very sensitive to changes in molecular weight and molecular weight distribution. For dry polymers the rubbery plateau modulus is close to 10^6 Pa. Here this plateau modulus is lower which indicates that the polymer phase is swollen with components from the bitumen (4).
- ❑ Also at low temperature, although not so obvious, properties change by adding polymer to the bitumen. The stiffness of the PMB gradually becomes lower as compared to the original bitumen. This has been reported occasionally in literature, but the reasons are still unclear. A possible explanation could be that at low temperatures the swollen polymer phase is softer than the bitumen phase. Especially, if this polymer phase forms a continuous matrix this softer phase will reduce the overall stiffness of the PMB blend.

For the three un-aged SBS bitumen containing 12% of polymer but differing in the crude origin of the bitumen temperature sweeps were recorded. The curves were very similar, and in each case a continuous polymer network is formed. Compared to literature reports (1) this observation may be strange. It is generally accepted that the bitumen type has a strong influence on the polymer concentration needed to form a polymer network in which the polymer is the continuous phase. This in turn should have a strong influence on the rheological behavior. In this case, the polymer concentration is probably so high that a network is formed anyway (7), or the difference between these bitumen compositions is too small.

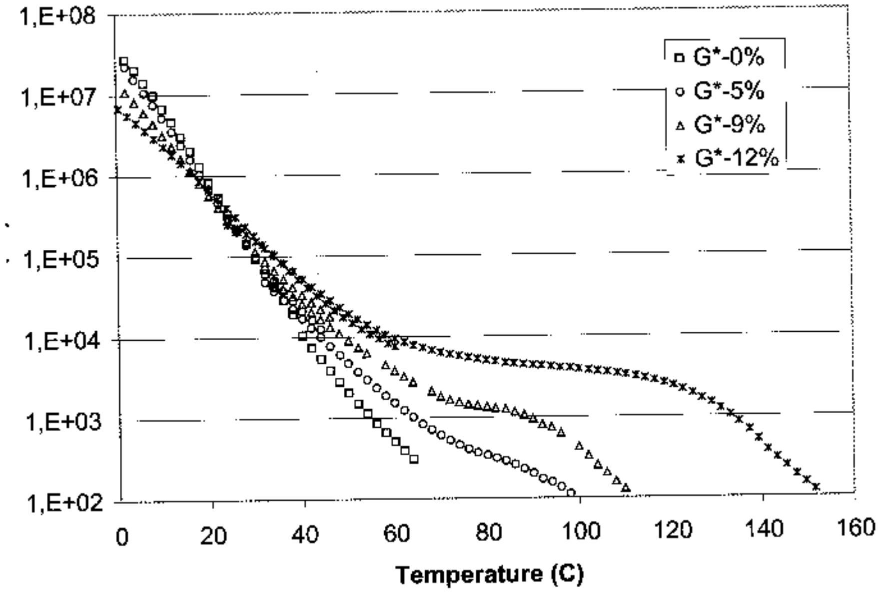

Figure 4A. *Temperature sweeps of sample B with different concentration of SBS polymer (rate; 0,5°C/min., 1,59Hz, G* is shown)*

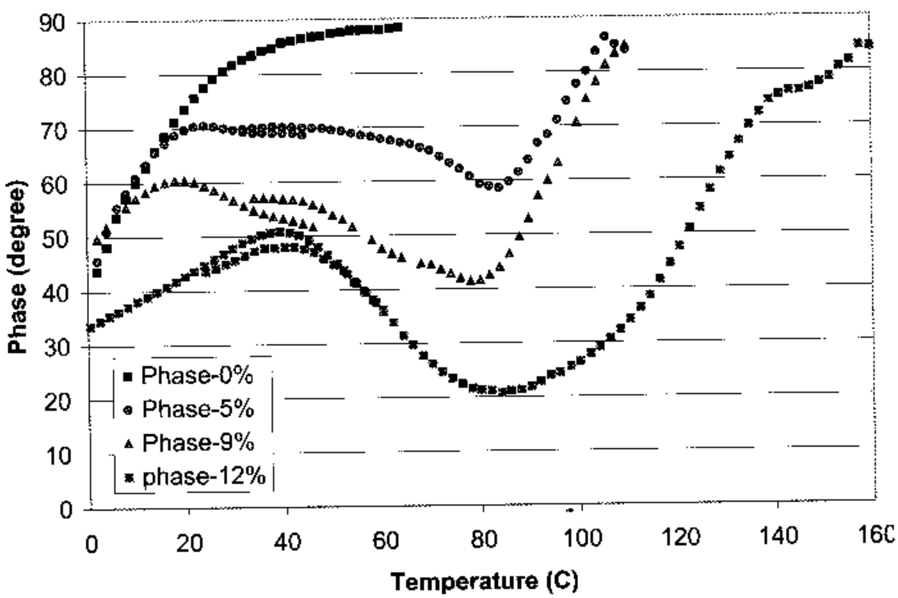

Figure 4B. *Temperature sweeps of sample B with different concentration of SBS polymer (rate; 0,5°C/min., 1,59Hz, Phase angle is shown)*

For the PMB samples it was not possible to construct master curves, frequency sweeps recorded at different temperatures differed too much in shape and an overlap could not be obtained. This indicates that molecular motions recorded at different frequencies cannot be shifted with the same temperature dependency. Or, in this case, the swelling of the polymer, the polymer network morphology, and the polymer bitumen interactions are temperature dependent. Therefore, PMB samples are evaluated using temperature sweeps, at which only one frequency is used.

Rheology after PAV ageing

Similar rheological measurements were performed after ageing: (the lowest service temperatures were not investigated) In figure 5A and B curves of sample PMB-A and PMB–B after different PAV ageing times are shown. With ageing, the blends in the lower temperature region, below 80°C, become stiffer and more elastic, a similar behavior was observed for the unmodified aged bitumen samples. At higher temperatures the plateau modulus starts to be less pronounced, and after long ageing times, nearly becomes undistinguishable. In addition, the phase angle minimum becomes less pronounced, and its position shifts to higher temperatures. Similar observations were made before in literature (1). However, care is needed to find the reasons for these changes in rheology, because different processes take place simultaneously, as explained below, and can have opposite effects on the rheological properties:

- ❑ Regarding the changes in the polymer, most of its molecular weight is decreased and its polydispersity is increased, as seen in the GPC curves. This effect alone, would reduce the flatness of the entanglement plateau region. A degradation alone would shift the plateau to lower temperatures, whereas an, even slight, cross-linking shifts it to higher temperatures. In case of a very strong polymer degradation, the rubbery region would finally disappear.

- ❑ Upon ageing, the bitumen phase becomes more elastic and stiffer at corresponding frequencies and temperatures. This effect is seen in the low temperature region, but it also has its influence on the appearance of the polymer rubbery plateau region, because part of this region is covered by the stiffer bitumen phase. Therefore the onset of the polymer rubbery region is not related to changes in the polymer phase, and the polymer degradation should be estimated from the end temperatures of the rubbery plateau region, in the temperature region above 110°C. The overall stiffening also changes the phase angle minimum and shifts it to higher temperatures. Therefore, the phase angle will not be used to compare the aged samples.

- Another interaction which is influenced by ageing is the compatibility between the now aged polymer and the aged bitumen: the fraction of aromats is decreased, and the concentration of asphalthenes and resins is increased. This sharpens the competition between polymer and asphaltenes for aromats, and influences the swelling and concentration of polymer in the polymer phase. If there is less swelling, the rubbery plateau region is first shifted to higher temperatures and the plateau modulus is higher, provided the volume of the polymer phase is still high enough so that it can form a network structure.

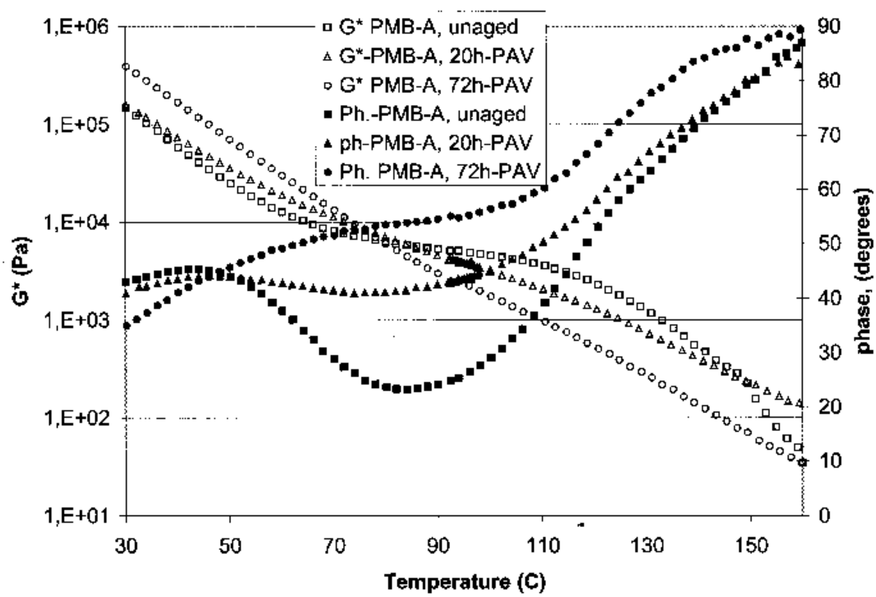

Figure 5A Temperature sweeps of PMB-A after different ageing times in the PAV.
(rate; 0,5°C/min., 1,59Hz)

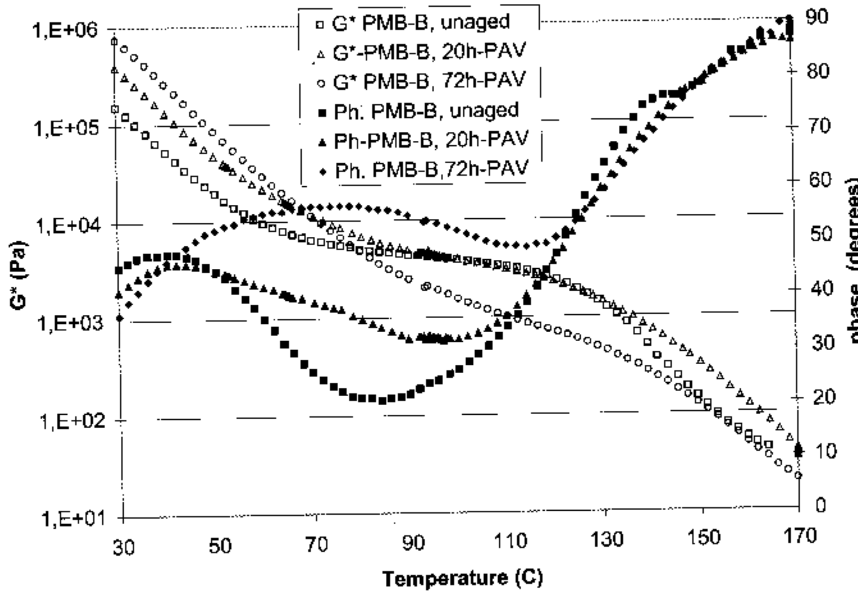

Figure 5B. Temperature sweeps of PMB-B after different ageing times in the PAV. (rate; 0,5°C/min., 1,59Hz)

On comparing the higher temperature region of these SBS samples, figure 5, the differences between the samples after PAV ageing are rather small. The plateau modulus region in PMB-A is decreased somewhat more, PMB-B and -C (PMB-C is not shown) are very similar.

<u>Rheology after 6 months dark oven ageing:</u>

This type of ageing was performed on two of the samples, PMB-A and PMB-B, and temperature sweeps were recorded after 6 months oven ageing, figure 6.

If we compare the higher temperature region, a decrease in networking ability is observed, which is even more severe as after 72 hours PAV ageing, and the difference between both samples is very small. Based on the high temperature region results, the time needed in PAV to have a similar network degradation as after 6 months dark oven should be somewhat more as the 72 hours that were actually used.

If the lower temperature region however, (30°-90°) is analysed, the ageing of the bitumen after 6 months dark oven ageing is different from what happened during 72hours PAV-ageing. PMB-B has become significantly more elastic and stiffer, although PMB-A has about the same stiffness and elasticity as after PAV ageing. This indicates that even by changing the time used in PAV, the ageing of the PMB samples would still be different from what happens during 6 months dark oven ageing. Based on literature information, the difference in ageing temperature could be responsible for the observed changes (5).

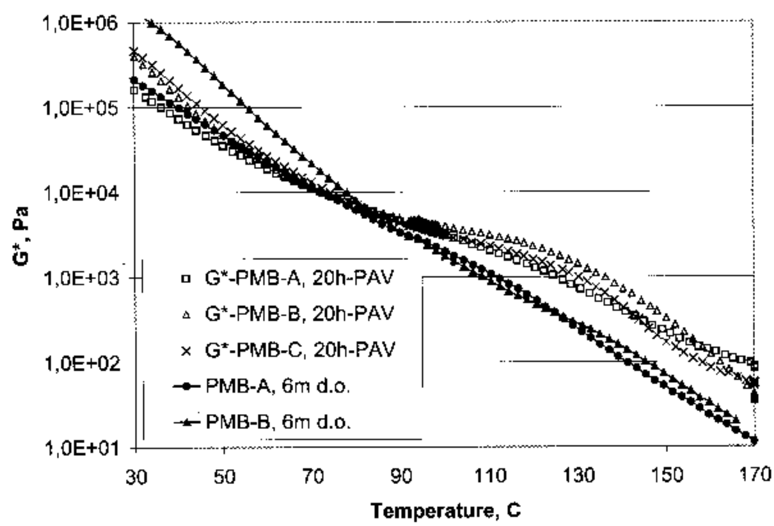

Figure 6. Temperature sweeps of the different samples after 20 hours in the PAV (100°C) and after 6 months dark oven ageing. (rate; 0,5°C/min., 1,59Hz)

Rheology after field ageing:

For some field-aged samples temperature sweeps after different years of service life were recorded figure 7. These samples were extracted prior to measurement, and in order to evaluate the influences of the extraction procedure an un-aged, but also extracted sample was included. Due to the extraction procedure itself the PMB sample becomes stiffer and the polymer entanglement region is somewhat less pronounced.

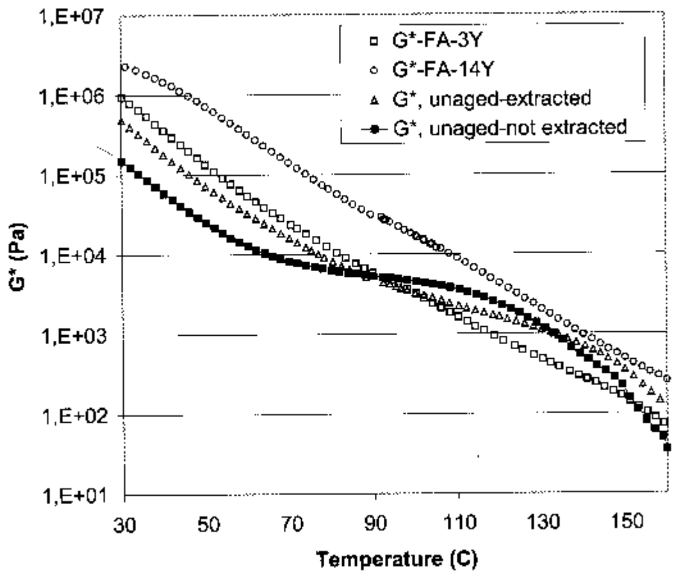

Figure 7. *Temperature sweeps after different years of service life, for an un-aged unextracted PMB sample and for an un-aged extracted sample. (rate; 0,5°C/min., 1,59Hz)*

In the lower investigated temperature region, already after 3 years service life there is some increase in stiffness of the bitumen phase. With ageing time, the stiffness of the bitumen increases more and the samples become very elastic at the lower investigated temperature region. In the higher temperature region, the 3 year aged sample shows changes in the polymer rubbery region, which certainly indicate some decrease in the polymer molecular weight. At all investigated temperatures the modulus of the 14 year aged sample is higher as for the original PMB, the rubbery plateau region is no longer visible with this type of test, and is probably covered under the large increased overall stiffness.

Field-aged membranes were further investigated using two other methods; flow resistance limit and low temperature flexibility, figure 8A and B, also reported in reference 6. In these graphs the temperature changes compared to the un-aged membranes are shown. The flow resistance limit after field ageing decreases slightly with time, most likely due to the molecular weight reduction of the polymer, as was also found in the GPC curves. However, for the 6 months dark oven aged sample the temperature at which flow resistance limit is reached is decreased much more, again indicating that the oven ageing is a very severe test, which is not observed in field ageing.

In addition, for the field-aged samples there is hardly any change in the low temperature flexibility test. The temperatures in this test are much lower than the lowest investigated temperatures in the rheological measurements, and therefore the observed increased stiffness in the rheological temperature sweeps is not in contradiction with these observations. The reduction in flow resistance is very little after field ageing, but much larger after the accelerated dark oven ageing. One reason for this relates to the high temperature used in the dark oven ageing and to the high polymer degradation in the oven ageing. During the 6 months artificial ageing of a membrane, granules from the surface sink down to the bottom, because the viscosity is reduced, and in the cold bending test these granules initiate cracks. In the field-aged samples, granules stay at the top and do not interfere with the cold bending test.

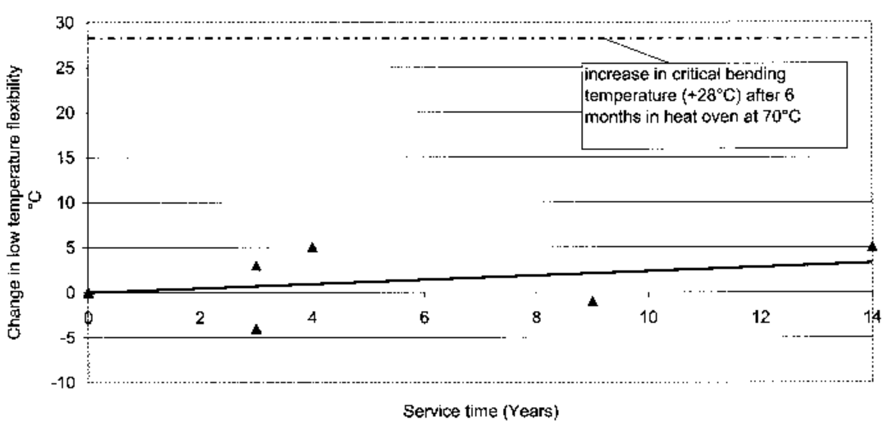

Figure 8A. Change in low temperature flexibility after different years of field service, and after artificial dark oven ageing for 6 months.

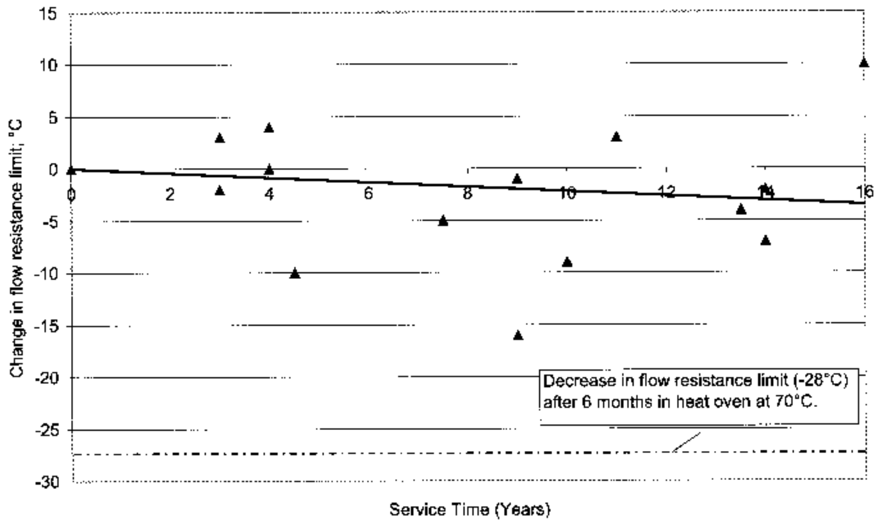

Figure 8B. Change in flow resistance limit after different years of field service, and after artificial dark oven ageing for 6 months.

Finally, it should also be noted that there has been a continuous development in both production techniques and formulation since the oldest roofing felts in this study were made. It is therefore reasonable to assume that the roofing felts of today will perform even better than those included here.

Conclusions

- The bitumen composition has an influence on the polymer degradation in PMB's.
- Already during the preparation of PMB's the polymer molecular weight is reduced considerably.
- The changes that occur by both types of laboratory ageing, PAV as well as dark oven ageing, are very similar in a GPC analysis. The polymer mainly shows a degradation although at short ageing times, as observed after 20 hours PAV, a polymer cross-linking may occur. However, these ageing tests are not similar from a rheological observation, because the stiffening of the bitumen phase is different. The most obvious reason for this is the difference in ageing temperature (5). (100°C for PAV and 70°C for dark oven)
- On comparing laboratory ageing with field-aged samples, we can conclude that the changes in molecular weight of

the polymer can be simulated in the laboratory by adapting the ageing time of the test. In this respect are the 6 months dark oven ageing and 72 hours of PAV ageing very severe tests, and the polymer degradation observed in these tests was not observed in any of the field-aged samples. However, even if the polymer molecular weight changes are correctly simulated, the overall stiffening of the blends in accelerated tests is still different from the stiffening observed in the field-aged samples.

- Although not further investigated here, it is known that the ageing temperature has a very important role in the stiffening of the bitumen (5). Therefore it may be rational to adapt at least the ageing temperature as much as possible to the actual climatic conditions. This is also partly done by SHRP for the evaluation of road bitumen.
- Upon ageing many factors are changed simultaneously, and to find the reason(s) for the rheological observations a combination with other techniques is advisable. For example, due to ageing, the bitumen increases its stiffness and elasticity, the interaction between aged polymer and aged bitumen is different from the un-aged state, and the polymer is changing its molecular weight and molecular weight distribution. In some cases the bitumen phase may become so stiff, that at least in the temperature sweeps presented here, the polymer rubbery plateau region is completely covered.
- Severe laboratory ageing tests do not seem to be necessary, on the contrary, if an accelerated ageing test is too severe the differences between different samples are (again) leveled off. This effect was obvious in dark oven ageing tests and less obvious from (the less severe) PAV ageing tests.

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