Asphalt rubber versus other modified bitumens

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ABSTRACT. Asphalt rubber and rubberized asphalt samples were produced using various available, public recipes and their properties were compared to different laboratory and bitumen terminal / refinery produced linear and radial type of styrene-butadiene-styrene block copolymer (SBS), SBS-polyphosphoric acid (PPA), ethylene-vinyl-acetate (EVA) and Elvaloy modified bitumen.

The aging characteristic of asphalt rubbers was found to be always better than the unsaturated polymer contained modified binders, however the confidence range of standards testing methods showed higher variability due to inhomogeneity of the rubber modified binders. Asphalt rubber had the highest, while Elvaloy resulted the lowest viscosity at all tested temperatures. Elasticity of SBS modified bitumens were found to be the best, while cold performance were significantly improved by rubber modified binders due to the presence of crumb rubber particles.

It was found that an appropriately designed and manufactured asphalt rubber binder can replace SBS, SBS-PPA or EVA, Elvaloy modified bitumen. However it should be considered that the main objective is probably not this but to increase utilization of rubber modified bitumen versus common non-modified bitumen.

KEYWORDS: *asphalt rubber, rubber bitumen, SBS modified bitumen, SBS-PPA modified bitumen, EVA modified bitumen, Elvaloy modified bitumen ,modified bitumen performance, comparison.*

1. Introduction

Conventionally refined bitumens have been modified by various means to extend the temperature range at which they can be used [1]. A wide variety of polymers have been used as additives in modified bitumen compositions [2].The selection of the ingredients, in particular the binder is initially influenced by climatic conditions, while the overall pavement design is highly dependent on the sub grade and traffic loading forecasts [3].

In recent years due to current shortages of styrene-butadiene-styrene block copolymer (SBS), the most widely acceptable bitumen modifier, a number of other modifiers have been recommended [4] to satisfy the continued demand for polymer modified bitumens (PmB). There are significant amount of publications [5, 6, 7] dealing with rheological properties and other scientific details on potential structure of bituminous materials, however we have seen very limited number of comparisons, where common industrial processes are followed in manufacturing modified binders, and the evaluation is done according to standard procedures.

The objective of this project was to provide a comparison of various modified bitumens produced both in laboratory and at bitumen terminals; to provide manufacturing and formulation experience gained at commercial scale.

Economical aspects were not discussed in detail, and unrealistically high priced modified bitumen (resulted by too high polymer concentration, just to obtain extremely high performance) were not manufactured and evaluated in this project.

2. Materials and methods

2.1 Materials

The modified binders were produced by using various commercially available raw materials.

2.1.1 Bitumen

A paving grade bitumen (penetration grade 50/70, performance grade PG 58-22) was chosen because of its relatively high aromatic content (*Table 1.*). High aromatic content binders are already proven to be effective in resulting homogenous polymer-bitumen dispersions [8], where the polymer contains at least one aromatic domain, such as styrene-butadiene-styrene block copolymers (SBS). This has practical importance, because majority of modified bitumen are SBS modified bitumen (PmB).

Neat bitumen	B 50/70
Saturates*, %	5
Aromatics*, %	54
Resins*, %	22
Asphaltenes*, %	19
Softening point, °C	48
Penetration at 25°C, 0.1mm	51
Elastic recovery at 25 °C, %	10
Fraass breaking point, °C	-20
Viscosity at 135°C, mPas	570
Viscosity at 180°C, mPas	90
After RTFOT, change of mass, %	+0.028
After RTFOT, G*/sin δ, kPa	5.6
Flash point (Cleveland method, open cup), °C	>250

* IATROSCAN group analysis.

Table 1. *Properties of neat bitumen.*

2.1.2 Crumb rubber

An analysis of the chosen ambient crumb rubber was performed in accordance with ASTM D 297. The chemical analysis shew common values for the chemical composition of the vulcanized passenger tire rubber (*Table 2.*). The crumb rubber was metal and cord free, and the rubber gradations always met with the criteria of asphalt rubber / rubberized bitumen formula requirements (e.g. `Arizona DOT`, `terminal blended rubberized asphalt` requirements).

Crumb rubber	CR
Specific gravity, g/cm³	1.041
Moisture content, wt%	0.5
Ash content wt%	3.6
Carbon black content, wt%	32.7
Extract content (acetone and chloroform), wt%	7.3
Sulfur content*, wt%	1.5

*determined by Inductive Connected Plasma - Atom Emission Spectroscopy (ICP-AES) method, which was found to be more accurate than regular analytical methods [9].

Table 2. *Properties of crumb rubber.*

2.1.3 Elvaloy

Commercially available Elvaloy 4170, the most chemically reactive grade of elastomeric terpolymer was chosen in the experiment. It had a density of 0.94 g/cm³, and melting point of 72°C.

2.1.4 Ethylene – vinyl acetate (EVA) copolymer

For this experiment an ethylene – vinyl acetate copolymer (EVA 7360M) contained 21 wt% vinylacetate monomer, having a softening point of 58°C, density of 0.941 g/cm³ --was chosen according to previous industrial practice.

2.1.5 Polyphosporic acid (PPA)

Polyphosphoric acid is an inorganic bitumen modifier, which is temperature stable and non-oxidising. The PPA was comprised of a mixture of ortho, pyro, tri, tetra and higher condensed acids, had a specific gravity of 2.05, and a boiling point range of 330-550 °C. During commercial scale manufacturing, PPA needed to be stored at elevated temperature (~60°C) to have low viscosity and be kept pumpable.

2.1.6 Styrene-butadiene-styrene block (SBS) copolymers

According to preliminary studies and experience the chosen B50/70 (PG 58-22) graded neat bitumen had good compatibility with the Calprene family of SBS.

– As linear SBS, Calprene 501C in porous pellet form was applied. It had 31% styrene content and ring & ball softening point of around 115°C.

– As radial SBS, Calprene 401 was used, which was 80/20 butadiene/styrene thermoplastic copolymer, supplied in pellet form.

2.2 Modified bitumen

Modified bitumen samples (*Table 3.*) were prepared following standard procedures used by the industry and published in various papers. All samples were prepared using the same neat bitumen source and concentration (wt%) always meant weight% of total binder (not weight% of any component).

2.2.1 Asphalt rubber binder

The asphalt rubber binder (20 wt% crumb rubber) was prepared in accordance with Arizona Department of Transportation specifications. The bitumen was heated up to 177°C and subsequently 20wt% ambient temperature crumb rubber was added. The temperature recovery was achieved relatively quickly and mixing was continued using a low shear mixer until the viscosity requirement was met.

2.2.1 Elvaloy modified bitumen

The Elvaloy modified bitumen was produced by adding 1wt% of Elvaloy 4170 reactive ethylene terpolymer to the virgin binder at a temperature of 190^{o}C. High shear mixing was applied for 2.5 hours in accordance with previous studies [10].

Manufacturer of the modifier recommends a blending method which takes 18 hours curing time, at 180-190 °C range, using a colloid mill (one pass).

2.2.1 Ethylene – vinyl acetate (EVA) modified bitumen

The EVA modified bitumen was produced by adding 6wt% ethylene – vinyl acetate (EVA 7360M) copolymer to the heated bitumen at 180^{o}C. Blending was done using Silverson type of high shear mixer for 180 minutes at a constant temperature of 180^{o}C [11].

2.2.1 Hybrid binders

The hybrid (crumb rubber - linear SBS) binders were prepared by adding linear SBS (1 or 2 wt%) to 180^{o}C bitumen, then dispersing it for 120 minutes using high shear mixer at around 4000 RPM. Upon completion crumb rubber was added at a concentration of 10 wt%. Additional 60 minutes was applied as curing time at 177-180^{o}C to complete the samples.

2.2.1 Polyphosphoric acid (PPA) and SBS modified bitumen

Both the laboratory and the terminal blended binders had the same concentration (0.25wt% PPA and 2wt% linear SBS).

First bitumen was heated in the laboratory to a temperature of 180^{o}C, then 2wt% linear SBS and 0.25wt% PPA were added together. The modifiers were blended for 180 minutes using high shear mixer.

In the bitumen terminal PPA+SBS modified bitumen was produced in 20 metric tons batch, having the same material composition in the laboratory. The PPA was stored at 60^{o}C (to keep its viscosity below pumpability level) and was introduced to the bitumen stream directly. Corrosion effects and toxic hydrogen sulphide formation was not experienced.

2.2.1 SBS modified bitumen

The SBS modified binders were produced in the laboratory by first heating the neat bitumen to 180^{o}C, then adding 8wt% linear SBS or radial SBS to form a high polymer concentrated master batch, where the polymer forms the continuous phase and the bitumen is dispersed in [12, 13]. The SBS was dispersed in the heated binder for 120 minutes at a constant temperature of 180^{o}C using high shear mixing. Upon completion of the 120 minutes, the 8% SBS concentrate modified binders were diluted with the original virgin binder to yield an overall concentration of 3% SBS in the whole blend.

One of the SBS modified binder (linSBS-t – *Table 3.*) sample was obtained from commercial scale bitumen terminal production. It was sampled from a 20 ton batch and had the same material composition as the laboratory sample (linSBS-l – *Table 3.*)

2.2.1 Rubberized bitumen

Rubberized bitumen / rubberized asphalt binder contained 10wt% and finer rubber granulates (< 0.420 mm, <40 mesh) than asphalt rubber binders. The crumb rubber was introduced to the 200-210^{o}C neat bitumen and the blend was agitated until the rubber particles dissolved in the binder and formed a homogenous product, according to industrial practice [14].

Overall, eleven types of modified bitumen were evaluated and compared in the present project (*Table 3.*)

Index	**Sample name**	**Place of production**	**Modifier**	**Concentration, wt%**
A	AR	laboratory	crumb rubber	20
B	Elvaloy	laboratory	Elvaloy	1
C	EVA	laboratory	ethyl vinyl acetate	6
D	hybrid-1	laboratory	crumb rubber + linear styrene-butadiene-styrene block copolymer	10 + 1
E	hybrid-2	laboratory	crumb rubber + linear styrene-butadiene-styrene block copolymer	10 + 2
F	linSBS-l	laboratory	linear styrene-butadiene-styrene block copolymer	3
G	linSBS-t	terminal	linear styrene-butadiene-styrene block copolymer	3
H	radSBS	laboratory	linear styrene-butadiene-styrene block copolymer	3
I	PPA-l	laboratory	polyphosphoric acid + linear styrene-butadiene-styrene block copolymer	0.25 + 2
J	PPA-t	terminal	polyphosphoric acid + linear styrene-butadiene-styrene block copolymer	0.25 + 2
K	RB	laboratory	crumb rubber	10

Table 3. *Modified bitumen.*

2.4 Testing methods

Standard bitumen testing methods were applied following the European standard procedures (EN 14023:2010).

Majority of rheological tests using dynamic shear rheometers (DSR) are still under validation, and not part of quality control standards in Europe. These tests are very informative but can be done in voluntary basis at the moment, while there are still disagreements on details (e.g. gap size for asphalt rubber DSR testing). One of the objectives of this project was to be practical, so only standardized tests were used.

At higher temperatures (135-180^{o}C), where asphalt rubber binders act mostly as Newtonian fluids [15], viscosities were measured by Brookfield viscometer (ASTM D 4402-02). Polymer modified bitumen are usually sensitive at temperatures exceeding 190^{o}C (because of more intensive depolymerisation [16], therefore 180^{o}C was the highest testing temperature used.

The aluminum cigar tube (32 mm diameter, 160 mm height) was employed to estimate phase separation / storage stability of modified bitumens since it is commonly used in practice [17]. Since there is no consensus worldwide on storage stability testing conditions, one of the strictest circumstance was applied. The cigar tube was filled with modified binder, sealed and vertically placed in the oven at 180^{o}C for 72 hours. It was taken out and instantly cooled down in a freezer at -20 °C. Afterwards, the frozen tube from the freezer was cut into three equal sections. The samples obtained from the top and bottom sections were used to evaluate storage stability status by measuring their ring & ball softening points. Separation was attained from the difference of softening points. When the difference is lower than 5^{o}C, the binder should be considered storage stable.

3. Results

The presented findings herein mostly serve practical and comparison purposes. It is well known that chemical composition of binders have significant impact on final product properties. Because of the compatibility issue, the choice of a polymer modifier for bitumen is restricted to a few chemical families. Each bitumen having its own particular chemical composition, ways to predict whether a particular polymer will be compatible with a given bitumen are not well defined and the formulator usually relies on laboratory experiments rather than on theoretical predictions [18]. In all cases, and even if the polymer has a potentially compatible chemistry, the formulation of PMBs requires a good selection of the initial bitumen. For example:

– high asphaltenes content decreases polymer/bitumen compatibility,

– the aromaticity of the maltenes needs to fall between certain values to reach a good level of compatibility.

In this project one bitumen source was used, so the property changes caused by the chemical composition of bitumen did not play a role.

Open cup flash point test (EN ISO 2592) results are not reported here, because all samples met the criteria (>250^{o}C).

3.1. Consistency

According to penetration (EN 1426) and softening point (EN 1427) test results (*Table 4.*), not surprisingly, all modifier had increased softening points and decreased penetration values.

– High rubber concentration (20 wt%) resulted the highest softening point, while the lowest penetration as well.

– Elvaloy resulted a relatively high penetration and low softening point compared to other modifiers. The applied concentration should be increased to obtain higher performance.

– EVA showed similar performance to the linear SBS modified bitumen. According to previous findings [19] performance of plastomer modified bitumens are comparable on hot and medium temperatures.

– Excellent correlation was found between laboratory and terminal blended PPA+SBS samples, which makes scale up easy during binder formulation. The exact same was observed in case of linear SBS modified binders (laboratory versus terminal blended).

– The rubberized bitumen had similar softening point to the laboratory lin-SBS modified bitumen but the penetration was significantly lower. If SBS needs to be replaced this might need to be taken into consideration.

– Radial SBS resulted in similar performance regarding consistency to linear SBS modified bitumen.

Index	Sample	Penetration at 25^{o}C, 0.1mm	Softening point, ^{o}C
A	AR	29	75
B	Elvaloy	54	58
C	EVA	45	67
D	hybrid-1	52	67
E	hybrid-2	46	72
F	linSBS-l	47	64
G	linSBS-t	45	63
H	radSBS	44	73
I	PPA-l	45	65
J	PPA-t	42	65
K	RB	37	64

Table 4. *Penetration and softening point results.*

3.2. Aging characteristic

There is continuous development in reliable simulation of short term aging of various modified and non-modified bitumen [20], since the rolling thin-film oven (RTFO) test method was mostly developed for low viscosity, non-modified bitumens. When the neat bitumen meet aging criteria, it is a relatively easy meet with the actual aging standard testing specifications (e.g. ASTM D2872 - 04, EN 12607-1) when polymers are used. The followings were experienced:

– All crumb rubber containing samples (especially asphalt rubber) exhibited superior aging performance compared to other modified bitumens. The reason is the significant carbon black content (*Table 2.*) of the rubber crumbs. These samples would be more resistant to fatigue cracking according to findings of other researchers as well [21].

– Since the ethylene backbone is saturated (in Elvaloy), it is relatively resistant to oxidation or aging versus butadiene-based materials (like SBS).

– EVA showed slightly worse aging performance than Elvaloy.

– Polyphosphoric acid did not adversely affect aging, the samples showed similar results to linear SBS modified bitumens (both laboratory and terminal blended). This data correlates with other research, where non modified bitumen was modified with PPA [22].

– Radial SBS resulted very similar aging characteristic compared to linear SBS modified bitumen. Since the molecular chains of both SBS are not fully saturated they were more sensitive to oxygenation / aging than the crumb rubber containing samples.

3.3. Cold performance

Europe Standards still do not require cold performance testing using a bending beam rheometer, but the common Fraass breaking point test (EN 12593). The following observations were made (*Table 5.*):

– The reproducibility of testing in case of asphalt rubber was found to be poor (± 4°C), which is caused by inhomogeneity of the binder. In practice these particles provide excellent cold performance as they absorb stress.

– All crumb rubber containing binders (asphalt rubber, rubberized bitumen, hybrid-1, hybrid-2) resulted a very high cold performance. The reason is definitely connected to elastic rubber particles.

– Elvaloy and EVA did not result better Fraass breaking points. The reasons can be found in their plastomer nature.

– Similar results were obtained in case of linear and radial SBS modifiers.

– Additional 0.25 wt% PPA together with linear SBS resulted slightly lower cold performance compared to purely SBS modified bitumen, but since modifier concentrations should be taken into considerations, overall PPA improved cold properties (purely linear SBS samples has higher SBS content than PPA+SBS samples).

Index	**Sample**	**Fraass breaking point, °C**
A	AR	-25
B	Elvaloy	-10
C	EVA	-11
D	hybrid-1	-23
E	hybrid-2	-24
F	linSBS-l	-17
G	linSBS-t	-17
H	radSBS	-16
I	PPA-l	-16
J	PPA-t	-15
K	RB	-22

Table 5. *Fraass breaking point test results.*

3.4 Elasticity

The ability of the modified binder to recover after stretching is related to the type of modification agent used. For evaluation the standardized elastic recovery (EN 13398) test was used (*Table 6.*) Although it is not as sophisticated as multiple stress creep recovery test, where previously different elasticity related results were found with similar samples [23].

– Asphalt rubber exhibited relatively low elastic recovery (compared to other modifiers), due to its inhomogeneity. This finding did not correlate with previous research data where asphalt rubber showed the best elasticity [24]. Since elasticity in pavements usually means recovery after various shear stresses we incline to recommend multiple stress creep recovery tests to include for evaluation.

– Based on our experiment Elvaloy acted like a plastomer, probably because of the dominant effect of ethylene in the molecular chain.

– Little improvement was found in case of the plastomer EVA modified binder compared the elastomer modified bitumens.

– The elastic recovery of hybrid binders were between the purely SBS modified and crumb rubber modified samples. SBS had significant impact on performance.

– radial SBS and lin SBS exhibited the highest elastic recovery compared to any other modified bitumens. The sample from the commercial scale batch showed further improvement, which can be caused by better dispersion because of the multiple passes through the colloid mill, and longer curing times used in the industry.

– PPA modified binder exhibited lower elastic recovery compared to linear SBS modified binders, which can be the result of lower SBS concentration. The commercially produced PPA+SBS blend showed a slightly worse elastic characteristic.

– Due to improved homogeneity the rubberized bitumen had slightly better elasticity than EVA or Elvaloy modified bitumen, better than asphalt rubber, but lower than the SBS containing samples.

Index	**Sample**	**Elastic recovery at 25°C, %**
A	AR	40
B	Elvaloy	45
C	EVA	35
D	hybrid-1	62
E	hybrid-2	75
F	linSBS-l	77
G	linSBS-t	85
L	radSBS	81
I	PPA-l	72
J	PPA-t	68
K	RB	47

Table 6. *Elastic recovery results.*

3.5. Flow properties

Viscosity temperature susceptibility was studied (Figure 1.) and the following observations were made:

– Crumb rubber at 20wt% (asphalt rubber binder) resulted extremely high viscosity compared to other modified bitumen. According to real life experience this is the reason why the pavements are durable and the aggregate coating is thicker than in case of other binders [29].

– Elvaloy resulted the lowest viscosity at all tested temperatures compared to other modified bitumens, which could be a significant advantage during applications.

– EVA caused minimal viscosity changes compared to competitive products except asphalt rubber and radial SBS modified bitumen, however the viscosity significantly increased compared to the B50/70 non modified bitumen.

– The flow properties of hybrids fell between the viscosities of linear SBS and asphalt rubber samples, while rubberized bitumen showed the lowest viscosities over various temperatures. Depending on the concentration and particle size distribution the crumb rubber has significant viscosity increasing effect.

– The use of PPA addition with SBS decreased the overall viscosity of SBS modified bitumen.

– Radial SBS resulted much higher viscosity compared to linear SBS modified binders including PPA containing modified bitumens.

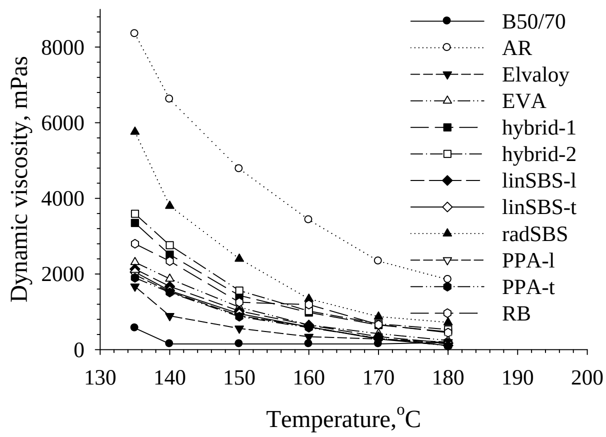

Figure 1. *Viscosity-temperature susceptibility of various modified bitumen.*

3.6. Storage stability

Testing of storage stability is a recommended option by the European Committee for Standardization (EN 14023:2010), and could be critical in refinery or bitumen terminal production where extensive storage and transportation is required. During this project special emphasis was laid on evaluation of phase separation of various modified bitumen (Table 7.). However there are numerous ways to calculate the rate of phase separation [16, 26, 27], to be practical one of the simplest was chosen. The following observations were made:

– Asphalt rubber is sensitive for phase separation (as it was found before as well [27, 28], but the industry easily overcame on this problem by recommending field blended manufacturing next to the hot mix plant.

–Phase separation was experienced in case of Elvaloy even at 1wt%.

– Compatibility of EVA with the chosen bitumen was found to be acceptable (5^{o}C – which is recommended option in EN 14023 standard), however previously we found that in some cases even 3wt% can result bad storage stability. The reason should be definitely found at the chemical composition of the bitumen.

– Storage stability of both hybrid binders fell between the asphalt rubber and linear SBS modified bitumen.

– 3wt% linear SBS resulted good stability, while the same radial SBS concentration fell out of the criteria level. At certain climates, where the SBS concentration needs to be increased, this might not be enough. The practical solution is usually adding a few percentages of crosslinker agents.

– PPA improved the storage stability and lower SBS concentration had to be applied to reach similar performance to the purely linear SBS modified binders.

– Rubberized bitumen with 10wt% rubber concentrate and finer particles resulted good storage stability.

Index	Sample	Stability, softening point of upper part, ^{o}C	Stability, softening point of lower part, ^{o}C	Stability, ΔT,^{o}C
A	AR	72	81	9
B	Elvaloy	60	54	6
C	EVA	70	65	5
D	hybrid-1	65	72	7
E	hybrid-2	70	78	8
F	linSBS-l	66	63	3
G	linSBS-t	65	62	3
H	radSBS	76	67	9
I	PPA-l	65	64	1
J	PPA-t	64	63	1
K	RB	62	67	5

Table 7. *Storage stability of various modified bitumen.*

3.7. Reproducibility and manufacturing experiences

– The technical parameters during asphalt rubber production are mild, temperature is not high enough (S-S, S-C bonds break around 230^{o}C) so rubber particles are usually not partially devulcanized. The result is a heterogeneous binder where rubber is mainly acting as flexible filler. This gives a lot of performance advantage over other modified bitumen. Since the recommended manufacturing method continuously monitors the viscosity changes, the reproducibility of manufacturing is excellent [30].

– In case of Elvaloy modified bitumen manufacturing a polymer rich surface appeared during blending (at 180^{o}C) which became a little thicker during storage. This was found to be a consequence of bitumen-polymer incompatibility.

– The reproducibility of both PPA+SBS modified bitumen and linear SBS modified binders (laboratory versus bitumen terminal) was found to be excellent.

4. Conclusion

Polymer-bitumen compositions were manufactured both in the laboratory and in bitumen terminals. The objective was to be practical and evaluate the samples according to standard procedures. This project has provided some insight in the performance of modified binders, and the following main conclusions were made:

– The rubberized bitumen (10wt% fine rubber) had similar softening point to the laboratory lin-SBS modified bitumen but the penetration was significantly lower. If SBS needs to be replaced this might need to be taken into consideration.

– Polyphosphoric acid did not affect aging, the samples showed similar results to linear SBS modified bitumen (both laboratory and terminal blended).

– The reproducibility of testing in case of asphalt rubber was found to be poor (± 4°C), which is caused by inhomogeneity of the binder. However, in practice these particles provide excellent cold performance as they absorb stress. Instead of Fraass breaking point testing the bending beam rheometer is recommended.

– All crumb rubber containing binders (asphalt rubber, rubberized bitumen, hybrid-1, hybrid-2) resulted in very high cold performance. The reason is definitely connected to elastic rubber particles.

– All crumb rubber containing samples (especially asphalt rubber) exhibited superior aging performance compared to other modified bitumens.

– Linear and radial SBS resulted very similar aging characteristic. Since the molecular chains of both SBS are not fully saturated they were more sensitive to oxygenation / aging than the crumb rubber containing samples.

– Asphalt rubber exhibited relatively low elastic recovery (compared to other modifiers), due to its inhomogeneity. Since elasticity in pavements usually means recovery after various shear stresses we incline to recommend multiple stress creep recovery tests to include for evaluation.

– The flow properties of hybrids fell between the viscosities of linear SBS and asphalt rubber samples, while rubberized bitumen showed the lowest viscosities over various temperatures. Depending on the concentration and particle size distribution the crumb rubber has significant viscosity increasing effect.

– Excellent correlation was found between laboratory and terminal blended PPA+SBS samples, which makes scale up easy during binder formulation. The exact same was observed in case of linear SBS modified binders (laboratory versus terminal blended).

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