Action 3.1

Characterization of asphalt rubber binders

POLITECNICO DI TORINO

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With the contribution of

Contents

PART 1 – STANDARD ASPHALT RUBBER BINDERS

Tests were carried out on bitumen-rubber mixtures obtained by employing a single reference base bitumen and CRs deriving from ambient, cryogenic and high pressure waterjet production processes. In particular, a rheological approach was adopted to derive information on the flow behaviour at high temperatures, with the corresponding identification of the possible relationships between viscosity and morphological characteristics of CRs. Results were quite encouraging and will form the basis for the future enhancement of characterization methods and of the proposed viscosity prediction model.

MATERIALS

Crumb rubber (CR)

CR samples were taken from five ELT processing plants where size-reduction operations are combined with other treatments (e.g. shredding, iron separation, granulation and sieving) in configurations which depend upon available technologies, inflow of material and desired quality of end products (Table 1).

Three of the considered plants (A, B and C) operate the so-called “ambient size reduction” by means of four consecutive processing phases consisting in shredding, iron magnetic separation, milling and sieving. However, in the case of plant B, shredding is carried out in two steps, with an extra phase of iron separation, and with an additional intermediate cold granulation treatment. This should lead to the production of CR characterized by a high degree of purity and constituted by more cubical and uniformly shaped particles.

Plant G operates in cryogenic conditions by making use of liquid nitrogen, which cools rubber granules down to -80°C under an inert atmosphere, and by employing high impact hammer mills. It is thus claimed that the resulting particles are of a cuboid-type morphology with smooth surfaces and small porosity. Moreover, as a result of the specific treatment conditions, molecular chains of rubber polymers are presumably not degraded and elastic properties are consequently fully preserved.

Plant H is a reduced-scale pilot plant which has been designed to implement the innovative High Pressure WaterJet technology. It is based on the use of high pressure (approximately 3.000 bar) water jets which may generate CR characterized by a high degree of purity.
According to owners, all the considered plants employ both car and truck tyres. The only exception is constituted by plant C, which collects exclusively ELTs coming from heavy vehicles, characterized by a higher natural rubber content.

Table 1. Configuration of ELT processing plants

	A	B	C	G	H
Primary shredding	×	×	×	×*	n.a.
Iron magnetic separation		×			n.a.
Secondary shredding		×			n.a.
Cold granulation		×			n.a.
Iron magnetic separation	×	×	×	×	n.a.
Milling	×	×	×	×*	×°
Sieving	×	×	×	×	

(*) Carried out in cryogenic conditions.
(°) Substituted by waterjet blasting.
n.a. Not applicable.

Bitumen-rubber blends

In order to compare their effectiveness as modifiers in the production of asphalt rubber binders, the different CRs were combined with the same 50/70 penetration base bitumen with a constant dosage of 15% by weight of the total binder. Mixing was carried out by operating on 500 g batches by means of a mechanical mixer, equipped with an anchor-shaped stirrer, by imposing a rotation speed of 600-700 rpm for 90 minutes. During production operations temperature was maintained at 180 ± 5°C by means of a thermostatic oil bath. The mixing protocol was adopted for all asphalt rubber binders regardless of specific reaction rates of employed CRs.

METHODS

Morphology and surface area of crumb rubber particles

CR samples taken from the processing plants were subjected to laboratory tests for the determination of particle size distribution and density. Moreover, by means of the combined use of microscopic observations, image analysis algorithms and three-dimensional analytical models, they were characterized in terms of particle morphology and surface area.

Particle size distribution analysis was performed in dry conditions by making use of sieves of the Tyler series. Density (ρ) at 25°C was evaluated with the pycnometer method by employing etilic acohol as the fluid of known density in order to prevent particles from floating to the surface. Relative density (i.e. specific gravity, SG) was calculated by referring measured density to that of water at the same temperature.

Assessment of the morphological characteristics of CR particles was carried out by employing a stereomicroscope equipped with a digital camera and by processing the resulting images with a freeware software (ImageJ, version 1.45, National Institutes of Health). However, in the case of CR H it was found that due to the very high content of fine particles (passing the 0.063 mm sieve) it was necessary to perform the analyses on single-

size fractions obtained by employing the same sieve series used for size distribution evaluation.
For each CR (or CR fraction) the following parameters were derived from the plan-view image of the set of considered particles:

- average value of the shape coefficient (C_f), given by the ratio between the maximum and minimum Feret diameters (maxF and minF) of the particle;
- average value of the solidity coefficient (C_s), given by the ratio between the area of the particle ($A_{particle}$) and the minimum convex area (A_{convex}) in which it is enclosed;
- shape (ϕ_f) and roughness (ϕ_r) factors, employed to estimate surface area per unit mass (SA_m) by means of the following expression:

$$SA_m = \phi \cdot \frac{6}{\rho} \cdot \sum_i \frac{f_i}{d_{m,i}} \qquad [1]$$

where: SA_m = surface area per unit mass (in m^2/g);
ϕ = corrective factor, given by the product of the shape (ϕ_f) and roughness (ϕ_r) factors ($\phi = \phi_f \cdot \phi_r$);
ρ = density (in g/m^3);
f_i = frequency (in decimal units) of the i-th single-size fraction;
$d_{m,i}$ = mean particle diameter (in m) of the i-th fraction.

The abovementioned shape and roughness factors (ϕ_f and ϕ_r) were calculated by modeling each CR particle:

- as a sphere with a diameter (d_s) equal to the minimum Feret diameter ("S" model);
- as an ellipsoid (prolate spheroid) with an area of the maximum cross-section ($A_{ellipse}$) equal to the area of the projection of the particle on the horizontal plane ($A_{particle}$) ("E" model);
- as an ellipsoid (prolate spheroid) with area and perimeter of the maximum cross-section ($A_{ellipse}$ and $P_{ellipse}$) equal to the area and perimeter of the projection of the particle on the horizontal plane ($A_{particle}$ and $P_{particle}$) ("R" model, which takes into account particle surface roughness).

By considering the entire set of particles composing a CR (or CR fraction) sample, represented according to the above described models, surface area per unit volume (SA_v) was calculated. Consequently, shape and roughness factors to be employed for the computation of surface area by means of equation [1] were derived from the following expressions:

$$\phi_f = \frac{(SA_v)_E}{(SA_v)_S} \qquad \phi = \frac{(SA_v)_R}{(SA_v)_S} \qquad \phi_r = \frac{\phi_i}{\phi_{f,i}} \qquad [2]$$

For CR H, values of morphological parameters C_f, C_s and ϕ_f and of surface area SA_m were calculated as weighted averages of those computed for each single-size fraction. Corrective factor ϕ was thereafter obtained from the inverse of equation [1], and thereafter the roughness factor ϕ_r was computed from [2].

Viscosity of asphalt rubber binders

Asphalt rubber binders were subjected to viscosity tests carried out in a wide temperature range (125-190°C) by means of a Brookfield viscometer (DVIII-Ultra). Measurements were performed by employing a SC4-27 spindle at an imposed shear rate equal to 6.8 s^{-1} (corresponding to 20 rpm).

RESULTS

Tests on crumb rubber samples

Average values of morphological parameters and calculated surface area are listed in Tables 2 and 3. Other technical data (e.g. size distribution) were taken from action 2.5.

Table 2. Morphological parameters and surface area of CRs

CR	A	B	C	G	H
ρ (g/cm^3)	1.172	1.181	1.158	1.223	1.189
SG	1.174	1.183	1.160	1.226	1.192
C_f	1.84	1.89	1.75	1.65	1.65
C_s	0.845	0.844	0.849	0.899	0.872
ϕ_f	1.026	1.066	1.063	1.017	1.034
ϕ_r	1.236	1.231	1.239	1.148	1.186
ϕ	1.268	1.313	1.317	1.168	1.226
SA_m (m^2/g)	0.0126	0.0149	0.0140	0.0160	0.0376
SA_v (m^{-1})	14781	17654	15822	20107	44681

Table 3. Morphological parameters and surface area of CR H single-size fractions

Fraction (mesh #s)	12 16	20 24	24 32	32 42	60 80	80 115	115 170	170 250
C_f	1.48	1.61	1.67	1.94	1.75	1.55	1.57	1.50
C_s	0.894	0.888	0.871	0.856	0.859	0.894	0.864	0.868
ϕ_f	0.996	1.000	0.987	0.976	0.961	1.081	1.164	1.161
ϕ_r	1.218	1.207	1.230	1.212	1.154	1.091	1.118	1.103
ϕ	1.213	1.207	1.214	1.183	1.109	1.180	1.302	1.280
SA_m (m^2/g)	0.0051	0.0079	0.0101	0.0140	0.0262	0.0394	0.0617	0.0856
SA_v (m^{-1})	6041	9275	12074	16185	31522	46443	73106	104641

Tests on bitumen-rubber blends

Viscosity values measured for the asphalt rubber binders are plotted in Figure 1 as a function of temperature. Experimental data were fitted to a simple power-law model as indicated by the following equation:

$$\eta(T) = \alpha_T \cdot T^{-\beta_T} \qquad [3]$$

where: $\eta(T)$ = viscosity (in cP) at temperature T;
α_T and β_T = model parameters.

Calculated values of model parameters and coefficients of determination (R^2) are reported in Table 4, which also contains the CR percent dosages in the binders expressed both by weight ($\%CR_w$) and by volume ($\%CR_v$).

Asphalt rubber prepared with the cryogenic CR (G) exhibits the lowest viscosity values in the entire temperature range, associated to a limited temperature sensitivity (low value of β_T). Ambient CRs have the highest viscosities and temperature sensitivities. In terms of ranking, CR C, which derives only from truck tyres, is the most effective in stiffening the base bitumen, followed by CR B and CR A. The waterjet CR (H) leads to viscosities which are slightly lower than those of ambient CRs at low temperatures. However, due to its reduced temperature sensitivity (β_T equal to 5.709), the binder approaches the viscosity values of binders containing CRs A and B in the high-temperature range.

All asphalt rubber binders, with the exception of the one containing the cryogenic CR, respect ASTM standard D6114 which requires viscosity at 175°C to be comprised between 1500 and 5000 cP.

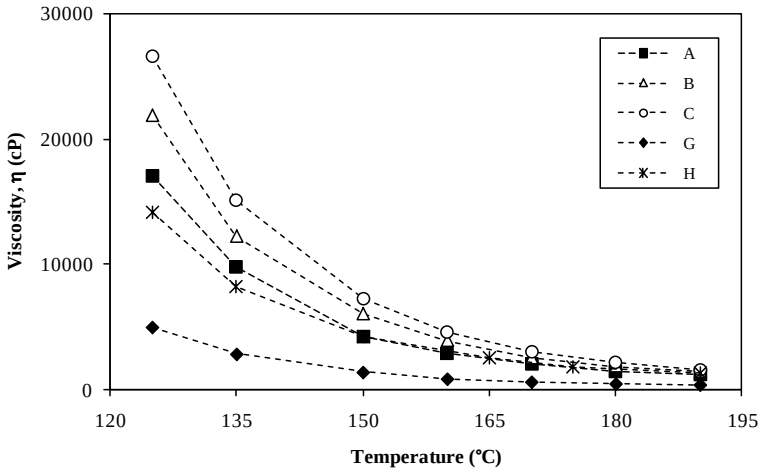

Figure 1. Temperature-viscosity curves of the asphalt rubber binders

Table 4. CR dosages and viscosity model parameters of the asphalt rubber binders

CR	A	B	C	G	H
$\%CR_w$	15.0	15.0	15.0	15.0	15.0
%CRv	15.1	15.0	15.3	14.5	14.9
α_T	6.39E+17	1.70E+18	3.91E+18	3.63E+16	1.22E+16
β_T	6.491	6.636	6.765	6.153	5.709
R^2	0.9920	0.9972	0.9981	0.9889	0.9931

In order to investigate the relationship between flow behaviour of asphalt rubber binders and morphological and physical characteristics of CR, the experimental data synthesized previously were analyzed jointly and then employed for the identification of a viscosity prediction model. Given the limited set of experimental data available, emphasis of modeling was not placed on the minimization of the total prediction error, but rather on its conceptual implications. For the same reasons, the maximum number of independent variables were limited to four to reduce the possibility of selecting random regressor combinations.

It was assumed that viscosity variations have to be explained by taking into account the variations of temperature and of the parameters which are combined in equation [1] for the calculation of surface area. Therefore, the additional three independent variables related to CR characteristics and selected for the formulation of the model were the following:

– density (ρ), which is related to the composition and surface porosity of the particles and allows to take into account the effective volume occupied by different CRs with the same dosage by weight;
– corrective factor (ϕ) derived from the analytical three-dimensional modeling of surface area, which provides a quantitative measure of particle shape and roughness;
– surface area per unit volume calculated by considering spherical particles with the effective size distribution of CR ($6 \cdot \sum_i f_i / d_{m,i}$).
Based on the discussion provided above, the following model was identified and thereafter subjected to statistical evaluation:

$$\eta = 10^{a_1} \cdot T^{-a_2} \cdot \rho^{-a_3} \cdot \phi^{a_4} \cdot \left(6 \cdot \sum_i \frac{f_i}{d_{m,i}} \right)^{a_5} \qquad [4]$$

where: η = viscosity (in cP) of asphalt rubber binder;
T = temperature (in °C);
ρ = density of CR (in g/cm^3);
ϕ = corrective factor of surface area (non dimensional);
$6 \cdot \sum_i f_i / d_{m,i}$ = surface area per unit volume of spheres with the size distribution of CR (in m^{-1});
a_1, a_2, a_3, a_4 and a_5 = model parameters.

Signs attributed to the exponents of the independent variables included in equation [4] were fixed by considering the physical phenomena which are believed to explain viscosity variations. In particular, coherently with findings of previous studies (West *et al.*, 1998), it was assumed that increasing temperature and density values lead to a viscosity reduction (negative exponents). The positive exponent of corrective factor ϕ is coherent with its definition, since increasing deviations of the modeled particles from the ideal smooth spheres certainly cause a viscosity increase. Finally, no assumption was made on the sign of the last exponent since it has been well documented that viscosity can either increase or decrease as a function of surface area depending upon whether particle size or surface interaction effects become predominant in the CR-bitumen system (Shen *et al.*, 2009a,b).

Values of model parameters (a_i) obtained by fitting experimental data to the logarithmic expression of equation [4] by means of linear regression are shown in Table 6, which also contains related standard errors (se_i). Coefficients of determination R^2 and $\overline{R}^2$ (adjusted) were found to be respectively equal to 0.993 and 0.991. By calculating t-statistics of model parameters and by assuming a critical alpha level equal to 0.05, it was verified that all the variables used in the model are statistically significant in predicting viscosity.

Table 5. Parameters and standard errors of the viscosity prediction model

	i = 1	i = 2	i = 3	i = 4	i = 5
Model parameter a_i	15.65	6.36	12.62	0.443	8.93
Standard error se_i	0.45	0.12	2.18	0.05	0.94

Figure 2 shows the relationship between measured and predicted viscosity values, with data points that are well grouped around the equality line. Percent errors calculated with respect

to true measured viscosities are represented in Figure 3, where they are compared to those deriving from the use of temperature-viscosity power-law models applied to each CR type.

It can be observed that the model leads to an underestimate of viscosity in the low and high temperature range, while at intermediate temperatures it overestimates true (measured) values. Percent errors are mostly comprised within ±15%, with higher absolute values generally occurring at extreme temperatures.

It should also be pointed out that errors associated to the model are comparable to those of the individual power-law equations. This clearly indicates that the main source of error relies in the choice of the type of temperature dependency and not in the selection of the prediction variables or in the overall structure of the model.

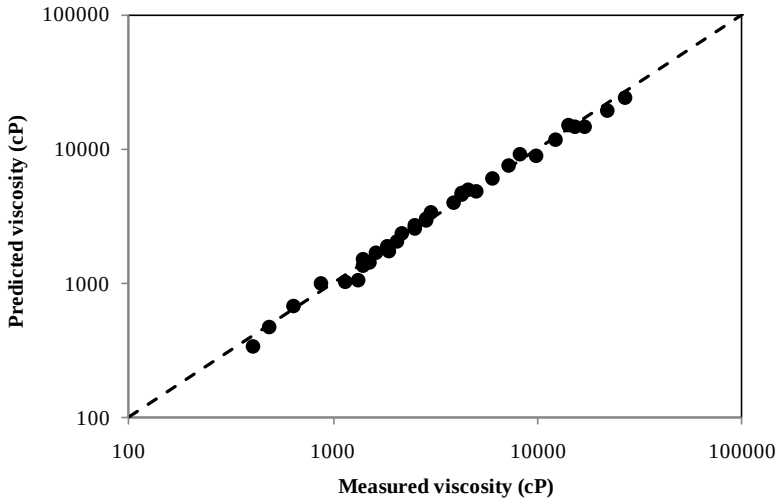

Figure 2. Comparison between measured and predicted viscosity values

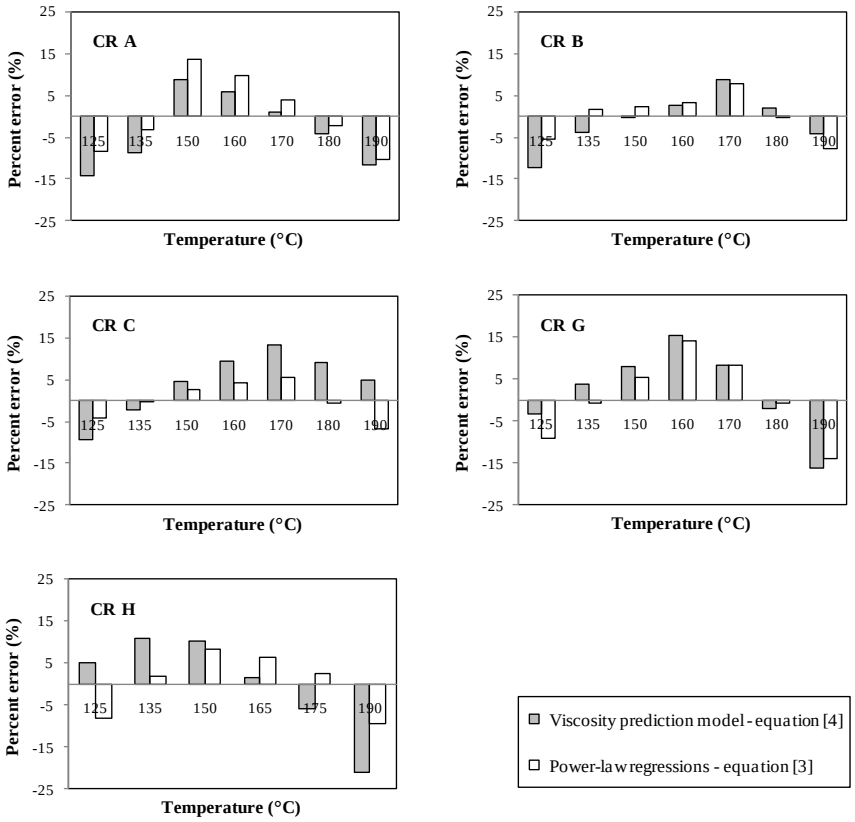

Figure 3. Percent errors of prediction model and power-law regressions

CONCLUSIONS

Experimental results obtained in the investigation of action 3.1 contribute to the general understanding of the mechanisms of interaction between crumb rubber (CR) and bitumen in asphalt rubber binders. Specific conclusions can be drawn with respect to the innovative procedures and models proposed for the evaluation of CR morphology, to the comparative evaluation of different CR types and of their corresponding asphalt rubber binders, and to the use of a prediction model for estimating binder viscosity.

Procedures and models developed for the assessment of CR morphology are based on the combined use of microscopic observations, image analysis algorithms and three-dimensional analytical models of CR particles. Validity of such an approach is confirmed by the coherency of the results with the peculiarities of CR production processes and with general information available in literature. It should be also mentioned that the tools required for characterization are simple and affordable and therefore easily accessible on a widespread basis to the research and engineering community.

CRs subjected to evaluation included products deriving from ambient, cryogenic and high pressure waterjet size-reduction processes. By making use of the abovementioned characterization techniques, it was confirmed that cryogenic products are composed of particles which are definitely smoother and more regularly shaped than those of ambient

CRs. Nevertheless, surface area was found to be higher for the cryogenic CR due to a finer size distribution. Viscosity of the binders containing ambient CRs was definitely higher than that of asphalt rubber prepared with the same dosage of cryogenic CR. Moreover, the highest viscosity values were measured for the binder prepared with the ambient CR derived exclusively from truck tyres, which contains a higher percentage of natural rubber.

Due to the novelty of the production process, conclusions regarding the waterjet CR are of great interest in the light of its possible use in asphalt rubber. It was found that its morphological properties are intermediate between ambient and cryogenic CRs, while flow properties of the corresponding asphalt rubber binder are comparable, at high temperatures, to those of binders containing ambient CRs.

Based on the available experimental data, a prediction model was developed for binder viscosity in order to highlight its dependency upon the physical and morphological properties of CR. Even though the database was quite limited, the model proved to be statistically sound and coherent with interaction phenomena which occur within asphalt rubber binders.

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PART 2 – LOW-VISCOSITY ASPHALT RUBBER BINDERS

MATERIALS

The materials used in the experimental research, the characteristics of which will be explained in the next paragraphs, are the following:

- Bitumen, TotalErg Azalt 35/50
- Bitumen, TotalErg Azalt 70/100
- Bitumen, class 50/70, obtained by mixing the two previous
- Crumb rubber from ELTs, supplied by Tritogom
- Low viscosity additive, called Sasobit, supplied by German company Sasol Wax

Bitumen

The first two types of bitumen, used in all laboratory tests, are the following: TotalErg Azalt 35/50 and TotalErg Azalt 70/100, produced precisely by the TotalErg SpA. The third type of bitumen, however, was produced by the mixing of the two mentioned above. This new obtained is of class 50/70 (penetration index at 25ºC between 50 and 70 dmm). The mixing was done considering the following dosages: 50% of bitumen 35/50 and 50% bitumen 70/100.

In Table 1, three of the most important parameters of any bitumen are showed. These are the penetration grade, the softening temperature (calculated with the ring & ball test) and the viscosity at a temperature of 175ºC.

Table 1. Penetration grade, softening temperature and viscosity of virgin binders

	Penetration grade at 25ºC [0,1mm]	**Softening Temperature [TºC]**	**Viscosity (η) at 175ºC [mPa·s]**
B 35/50	44	52,2	103
B 50/70	59	48,8	87
B 70/100	85	43,6	73

Crumb rubber from ELTs

The crumb rubber used in the investigation presents granules of a size mostly comprised between 0.5 and 0.8 mm (Table 2).

Table 2. Sieve analysis of crumb rubber

Diameter [mm]	**% Passing material**
1,000	100,00
0,833	99,79
0,710	94,78
0,589	69,52
0,500	32,92
0,417	9,39
0,250	0,35
0,125	0,14

LV additive

The LV additive used in the study was a long-chain aliphatic hydrocarbon wax presented in solid form in the form of spheres of white colour and with a diameter between 1 and 5 mm.

Bitume-rubber blends

Bitumen-rubber blends were prepared by employing the above mentioned three base bitumens combined with 18.5% crumb rubber (on total weight of asphalt rubber binder). Additional binders were prepared by employing the low-viscosity additive with a dosage of 3% by weight on base bitumen. Thus, the investigation considered the following six binders:

- AR35/50
- AR35/50 + 3.0% Sasobit
- AR50/70
- AR50/70 + 3.0% Sasobit
- AR70/100
- AR70/100 + 3.0% Sasobit

Preparation of the blends was carried out in the following conditions:

- Temperature: 190ºC
- Time: 6 hours (360 min)
- Rotating impeller
- Rotation speed of the impeller: 600 RPM

VISCOSITY TESTS

During the mixing process samples were taken after 5, 30, 60, 90, 120, 150, 180, 210, 240, 300 and 360 min. They were then subjected to viscosity tests at 175°C.

Time-viscosity plots for each binder were subjected to analysis for the evaluation of the following characteristic parameters:

- Maximum viscosity μ_p: maximum value of the viscosity (peak value).
- Peak time $T_{\mu,p}$: time at which the viscosity achieves the maximum value.
- Swelling rate (SR): velocity of swelling phenomenon, expressed by:

$$SR = \frac{\mu_p - \mu_i}{T_{\mu,p}}$$

- Degradation rate (DR): velocity of depolymerisation of the rubber, expressed by:

$$DR = \frac{\mu_p - \mu_{2t,p}}{T_{\mu,p}}$$

where $\mu_{2t,p}$ can be understood like the viscosity value achieved after a time that is equal to the double of the peak time.

RESULTS

Results are synthesized in Table 3, which lists the values of the 4 characteristic parameters extracted from time-viscosity curves.

Table 3 Characteristic time-viscosity parameters (Units: viscosity [mPa·s], time [min])

	μ_p	$T_{\mu,p}$	SR	DR
AR 35/50	5662	71	40	25
AR 50/70	6357	74	75	50
AR 70/100	5776	85	48	25
AR 35/50+Sasobit	5769	60	58	28
AR 50/70+Sasobit	5891	61	60	30
AR 70/100+Sasobit	5823	79	69	17

CONCLUSIONS

The results when working with the asphalt rubber binders without LV additives (AR 35/50, AR 50/70 and AR 70/100) show that viscosity evolution during the time of mixing follows a typical trend. At first, viscosity increases (during the first hour or one and a half hour) as a consequence of the swelling process, by which the oil fraction of bitumen is absorbed by rubber granules. In the second phase of mixing, depolymerisation or devulcanization occur, thus leading to a progressive reduction of viscosity which tends to an asymptotic value.

When the LV additive is added to the blends, the same trends in the time-viscosity plots are observed, but with an obvious reduction of viscosity during all the degradation process.

Peak viscosity values are reached after 60-90 minutes of mixing for the standard binders. However, when the LV additive is employed, the time corresponding to the maximum value of viscosity is in most cases of the order of 60 minutes.

In general terms, the AR 70/100 blends are the last ones to reach the peak viscosity value, while the AR 50/70 blends are those that have the higher value of viscosity.

Finally it can be stated that the obtained results show that the use of LV additives may actually lead to the production of asphalt rubber binders with reduced viscosity. However, viscosity changes are bound to be influenced by the type of base bitumen base and by the percentage of employed crumb rubber.

For more info, please contact:

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