# Empirical Property of Asphaltic Binder PA 50/70 Modified with Mixture of Industrial Waste

Denes C. S. da Graça, Michelle G. Mothé, and Gisélia Cardoso

***Abstract* — The incorporation, by wet, of 10% w/w from the mixture of two solid wastes, rubber from waste tires and oily petroleum sludge, in proportions 15/85% w/w (M1) and 85/15% w/w (M2) on asphalt binder CAP 50/70 (PA-M1-10 and PA-M2-10) was evaluated against the unmodified binder, regarding the empirical properties: apparent viscosity, flux activation energy, penetration, softening point, specific mass, adhesion to stone aggregates, machining, and compaction temperature, and indirect tensile strength test (ITS) of its hot asphalt mixture (HMA). Test results showed that the modifiers do not significantly change the values of empirical properties under analysis, except the flow activation energy. Modified samples had a lower value when compared to the binder PA 50/70, and the penetration of modified binder PA-M2-10, which for having a higher concentration of rubber tire made it harder, changed to binder class 40-50, according to standard ASTM D946-09A. The ITS behavior of HMA's processed with modified binders showed compatible values with the unmodified binder, meeting the standard ASTM D6931-12.**

***Keywords* — asphalt mixture, empirical properties, HMA, industrial waste, modified asphalt binder.**

## I. Introduction

The quality of the asphalt coating road pavement bearing layer is directly related to its ability to withstand climatic actions and traffic density, agents that cause defects, such as wheel tracks, the appearance of thermal cracks, and fatigue [1]-[4]. Thus, the construction and maintenance of highways require strategies that meet the technological requirements imposed and sustainability, as these are engineering actions that involve high consumption of natural, non-renewable resources, which raise an alert about their availability on the planet [5].

Nowadays, the diversity and increase of industrial production place the study about the use of by-products from industrial processes and solid waste as alternatives to replacement of non-renewable resources, making use of solid waste in road infrastructure works, through the development of sustainable technology, in addition to mitigating costs with its disposal [3]-[10].

Whatever the application of the material in road paving, it is necessary to understand the behavior of its chemical, physicochemical and mechanical properties so that it is possible to dimension and optimize its potential use [11]-[20].

It is important to emphasize that the use of residues as asphalt binder modifiers allows rationality in binder used in road pavement coating works. However, the qualification and acceptance of asphalt binders depend on the performance of numerous empirical tests based on probabilistic calculations, following recommended conditions that must be strictly followed, which justifies and motivates studies on empirical properties and HMA processing with modified asphalt binders [4]-[15].

The empirical properties of asphalt binders (apparent viscosity, penetration, softening point, and density) are susceptible to temperature, whose heat intensity comes from the contribution of vibrations and molecular rotations of saturated, aromatic, resins, and asphaltenes compound present in its composition [14]-[20].

Tire waste has been used as a modifying agent of asphalt binder modifier because it has a good dispersion history, providing satisfactory performance. Some studies had been adding amounts from 3 to 10% w/w. There were changes in empirical properties, such as viscosity, thermal stability during the modification of the binder, and mechanical properties of asphalt concrete [3], [4], [6]-[9], [16]-[19].

The oily sludge, residue generated throughout the production chain of the oil industry [7]-[9], [21], from a physical-chemical point of view, is a water/oil emulsion, and those arising from the bottom of a primary treatment tank oil have siliceous fragments [21]-[25]. However, due to its chemical composition, it is difficult to disperse in an asphalt binder, which makes the use of a dispersion facilitating substance necessary when applying it as a modifier of an asphalt binder [4], [8], [9].

Analyze how much the physical, physicochemical, and/or mechanical properties of asphalt binder are sensitive to temperature variation means evaluating its thermal susceptibility. Asphalt binders with high thermal susceptibility to temperature variations are not desirable for use in pavement construction works and/or concrete processing for pavement coating, as they are exposed to thermal cycles during service. Currently, there are several methods to assess the thermal susceptibility of binders and asphalt concretes [8], [9], [26].

The thermal susceptibility index (IST) or Pfeiffer and Van Doormaal index is one of the evaluation methods through penetration and softening point data, calculated by the empirical equation (1):

$$\mathrm{IST} = \frac{(500.\log \mathrm{Pen}) + (20.\mathrm{PA}) - 1951}{120 - (50.\log \mathrm{Pen}) + \mathrm{PA}} \tag{1}$$

Submitted on February 02, 2022.
Published on March 22, 2022.
D. C. S. da Graça, Federal University of Rio de Janeiro (EQ/UFRJ), Brazil.
(e-mail: dagracadcs@yahoo.com.br)
M. G. Mothé, Federal University of Rio de Janeiro (EQ/UFRJ), Brazil.
(e-mail: michelle@eq.ufrj.br)
G. Cardoso, Federal University of Sergipe (DEQ/UFS), Brazil.
(e-mail: giselia@academico.ufs.br)

where: IST = IP = thermal susceptibility index or penetration index (dimensionless); PA = softening point of binder (°C, ring and ball); and Pen = penetration (0,1 mm, 25°C, 5 s.).

In general, asphalt binders of interest for use in pavement coating have IST between -2 and +1. Asphalt binders with IST < - 2 have high sensitivity to temperature variations but are brittle at low temperatures and quickly soften at high temperatures. Those with IST > + 2 are few sensitive to high temperatures and also brittle at low temperatures [26]. The National Agency for Petroleum, Natural Gas and Biofuels (ANP) of Brazil establishes, for the processing of HMA, asphalt binders with an IST between -1.5 to +0.7 [26].

The temperature effect on the behavior of apparent viscosity in asphalt binder and its modifieds can be evaluated by the Arrhenius equation, (2):

$$\eta=\eta_{\infty}.e^{(-\frac{E_f}{RT})} \tag{2}$$

where $E_f$ = flow activation energy; R = ideal gas constant; T = absolute temperature; η = viscosity at study temperature and $\eta_\infty$ = viscosity when the temperature tends to infinity.

Articles available in the literature show that the analysis of the thermal behavior of modified asphalt binder with a mixture of waste tire rubber and oil sludge presents a thermal degradation temperature at 270 °C, a temperature higher than the processing temperature for conventional HMA (160 °C) [8].

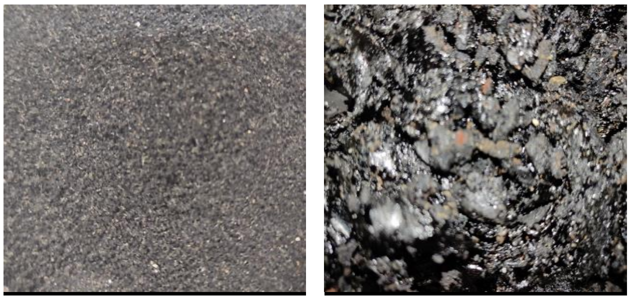
This study aims to comparatively analyze the behavior of empirical properties of the asphalt binder PA 50/70 with its modified ones, by wet method, with 10% m/m of a mixture of waste rubber from waste tires and oily sludge from the bottom of a primary treatment tank oil, respectively, in the proportions 15/85% m/m (M1) and 85/15% m/m (M2) and the tensile strength by diametrical compression (ITS) of HMA.

## II. Experimental

The modified PA 50/70 binder with the industrial waste mixture was evaluated by: characterization of the asphalt binder (apparent viscosity, flow activation energy, penetration, softening point, specific mass). Regarding the processing, it was analyzed: HMA (granular distribution and surface strength of stone aggregates, binding of the binder to stone aggregates, machining temperature (TU) and compaction temperature (TC), content of asphalt binder by the Marshall method) and indirect tensile strength test (ITS) of your HMA's.

### A. *Materials*

Petroleum asphalt binder (PA) with penetration 50-70 (0.1 mm, 5 s., 100 g, 25 °C), granitic stone aggregates supplied by Municipal Urban Planning Company (EMURB) of the Aracaju city/ Sergipe-Brazil, waste tire from tire retreading unit from Itabaiana city/ Sergipe - Brazil and oily sludge from the bottom of primary treatment tank oil supplied by Petrobras / UN-SEAL. The Fig. 1 shows photographs of residues studied: (a) rubber from useless tires and (b) oily sludge from the bottom of a tank from primary oil treatment like collected for study, and Table I shows the codes and their respective descriptions referring to the materials studied.



(a) (b)

Fig. 1. Photograph of the tailings studied: (a) particulate waste tire rubber and (b) oily sludge from the primary oil treatment tank.

TABLE I: Code Name and Description of Materials

| Code | Description |
|---|---|
| M1 | Mixture 15% tire rubber and 85% of oily sludge |
| M2 | Mixture 85% tire rubber and 15% of oily sludge |
| PA-M1-10 | Petroleum asphalt with penetration in the range of 50-70 with 10% of M1 |
| PA-M2-10 | Petroleum asphalt with penetration in the range of 50-70 with 10% of M2 |

### A. *Methods*

#### 1) *Modification of binder PA 50/70*

For the modification of the PA 50/70 binder, premixes of particulate tire rubber (diameter less than 0.6 mm) and oil sludge, in the proportions of 15/85% m/m and 85/15% called M1 and M2, respectively, were carried out, at a temperature of 120±5°C, by means of a mechanical mixer, using an inclined paddle impeller, at a speed of 100±2 rpm, for 40 minutes. Then, 10% m/m of M1 and M2 were added, respectively, to the PA 50/70, at a temperature of 160±5°C, under mechanical agitation, at the same speed as the premix M1 and M2, for 90 minutes, thus obtaining the modified ligands PA-M1-10 and PA-M2-10, respectively.

#### 2) *Characterization of the modified asphaltic binder*

*Apparent viscosity and flow activation energy* - The apparent viscosity of binder PA-50/70 and modified PA-M1-10 and PA-M2-10 was measured using a Brookfield rotational viscometer, model DV-III Ultra, Spindle 21, at 20 rpm, heated by a thermal cell resistive, at temperatures of 135 °C, 150 °C and 170 °C, after isotherms of 10 minutes, on each temperature, to ensure thermal equilibrium, following the procedure established by the ASTM D 4402 standard. The flow activation energy was calculated from the slope of the ln curve of the apparent viscosity as a function of 1/T(K), measured at the temperatures of 135 °C, 150 °C and 170 °C for each binder sample in study, using the Arrhenius equation (2).

#### 3) *Penetration, Softening Point and Specific Gravity*

The penetration tests of the binder PA 50/70 and of the modified PA-M1-10 and PA-M2-10 were carried out in triplicate, at a temperature of 25 °C, applying a load of 100 g, in samples contained in a cylindrical metallic container of 55 mm in internal diameter and 35 mm in height, by means of a universal analog penetrometer, brand Contenco, model 426, following the procedure established by the ASTM D5 standard. The softening temperature of the binder PA 50/70 and of the modified PA-M1-10 and PA-M2-10 was determined by means of ring and ball equipment, brand Pavitest/Contenco, following the ASTM D36 standard. The specific mass of the binder PA 50/70 and of the modified PA-M1-10 and PA-M2-10 was determined using a 25 mL pycnometer, calibrated at a temperature of 25 °C. The asphalt binder was heated to 100 °C and inserted into the pycnometer until it filled approximately ¾ of its volume. After cooling for 30 minutes at room temperature, the pycnometer with the sample was placed in a water bath at 25 °C, during the same cooling period. After thermal equilibrium, the mass of the pycnometer-sample set was measured. Then, the volume of the pycnometer-sample set was completed with distilled water and again measured the mass of the set; calculations were carried out to determine the specific mass, using the equations (3) and (4). Procedure performed, following the AASHTO T228 standard.

$$D_{Rel.} = \frac{(C - A)}{(B - A) - (D - C)} \tag{3}$$

$$D = D_{Rel.} * W_{25°C} \tag{4}$$

where A = mass of pycnometer (plus stopper); B = mass of pycnometer filled with water (plus stopper); C = mass of pycnometer partially filled with asphalt binder (plus stopper); D = mass of pycnometer, asphalt, and water (plus stopper); $W_{25°C}$ = density of water at the 25 °C.

### *B. The Processing of Hot Asphaltic Mixture (HMA)*

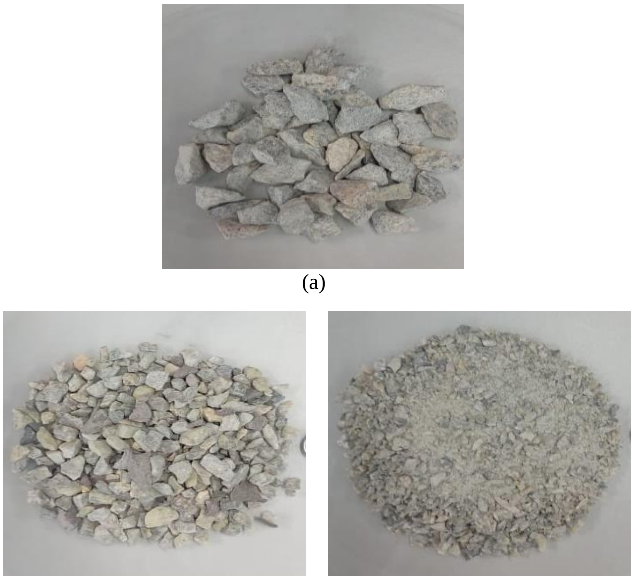
The processing of the HMA's took place with the asphalt binders at TU temperatures and the predefined binder project content, added to the stone aggregates at a temperature 10 °C above the TU, which were previously characterized in terms of particle size distribution and resistance to abrasion Los Angeles.

The asphalt concrete specimens were obtained in a metallic mold with dimensions 101.5±0.5 mm in diameter and 63.5±1.3 mm in height, which after cooling on a laboratory bench at room temperature, unmolded, characterized in terms of volumetric parameters, and subjected to test mechanics of indirect tensile strength test (ITS).

### *C. Particle size distribution of stone aggregates*

Stone aggregates were characterized in terms of their particle size distribution, following procedures standardized by ASTM C136, using a set of standardized sieves (AASHTO T-027-14-UL, ASTM C 136-06), with mesh opening ranging from 19,000 to 0.075mm. The Fig. 2 (a, b, c) show, respectively, photographs of the stone aggregates used: coarse, intermediate, and fine, both of a granitic nature, conveniently fractionated, to compose the granulometric curve for HMA under study, whose filling material (filer) will be the fraction of stone powder passing through the 0.075 mm opening sieve.

It is observed that the aggregates intentionally present high irregularity and smooth angularity. These intend to process HMA with high resistance to permanent deformation and fatigue cracking, with reduced rigidity and high bond strength between the aggregate surfaces and the asphalt binder film. It makes the HMA less susceptible to disaggregation (stripping) and consequent tearing off the coating pieces.



(a) (b) (c)

Fig. 2. Photography of the stone aggregates used: (a) coarse, (b) medium and (c) fine.

Table II shows the granulometric percentage distribution of the stone aggregates: 12 mm gravel, 9.5 mm gravel and stone dust with a diameter of less than 0.075 mm, which favors the adequacy of the granulometric distributions of the stone aggregates, to fit the chosen range, the C one of the National Department of Infrastructure and Transport (DNIT 031/2006-ES).

The knowledge of the individual influence of each aggregate in the constitution of the final granulometry of the HMA guarantees the best adjustment of the composition of the aggregates for its adequacy to the design limits of the chosen particle size range, in this research the C Range of the DNIT. The granulometric composition of HMA is responsible for the behavior of properties related to rigidity, permeability, resistance to fatigue and permanent deformation, workability, stability, and durability [27].

Fig. 3 and 4 show the profiles of the characteristic particle size distribution curves of the individual and mixed stone aggregates, respectively, referring to the percentage of the passing size distribution in the series of sieves referred to in Table II.

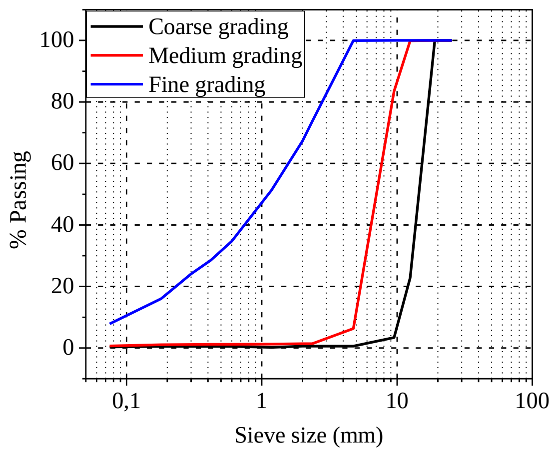



Fig. 3. Grading size distribution curve of aggregates used.

TABLE II: GRANULOMETRIC PERCENTAGE DISTRIBUTION OF THE STONE AGGREGATES

| Sieve mesh opening | Mass passing (%) | | | | |
|---|---|---|---|---|---|
| (mm) | Coarse aggregate (%) | Medium aggregate (%) | Fine aggregate (%) | Granulometric distribution[a] (10/46/44)[b] | Band C (DNIT 031/2006 – ES) (%) |
| 19.000 | 100.000 | 100.000 | 100.000 | 100.000 | 100 |
| 12.500 | 22.814 | 99.915 | 100.000 | 92.242 | 80 - 100 |
| 9.500 | 3.403 | 83.541 | 100.000 | 82.769 | 70 - 90 |
| 4.750 | 0.609 | 6.330 | 99.970 | 46.959 | 44 - 72 |
| 2.360 | 0.595 | 1.401 | 73.670 | 33.119 | - |
| 2.000 | 0.569 | 1.362 | 67.270 | 30.282 | 22 - 50 |
| 1.180 | 0.182 | 1.267 | 51.320 | 23.182 | - |
| 0.600 | 0.539 | 1.198 | 34.740 | 15.890 | - |
| 0.420 | 0.528 | 1.164 | 28.510 | 13.133 | 8 - 26 |
| 0.300 | 0.517 | 1.136 | 24.050 | 11.156 | - |
| 0.180 | 0.506 | 1.047 | 16.020 | 7.581 | 4 - 16 |
| 0.075 | 0.328 | 0.668 | 7.820 | 3.781 | 2 - 10 |

[a] Basis of definition of the percentage range of size limit of passing stone aggregates.
[b] Percentage composition of coarse, medium and fine stone aggregate, respectively.

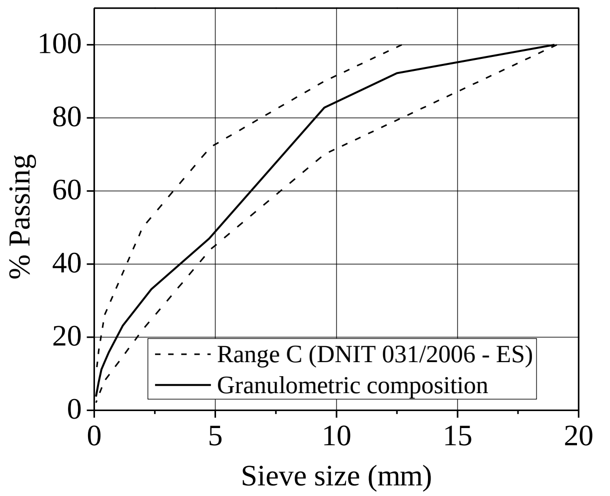



Fig. 4. Percentage of the size distribution of the stone aggregate HMA used.

It is observed that the curves in Fig. 3 meet the category of asphalt coating type HMA because they present characteristics of continuous graduation for fine and uniform aggregates for intermediate and coarse aggregates. Whereas Fig. 4 shows that the granulometry distribution of the aggregate mixture meets the design limits, the C range of the DNIT.

*1) Resistance to surface wear of stone aggregate*

The surface wear resistance of aggregates when subjected to friction was evaluated by means of Los Angeles abrasion test, following the ASTM C131 standard, in sample of 5000 g of coarse aggregate in range B, and sample 5000 g of medium aggregate, passed through a 9.5 mm sieve and retained on a 4.8 mm sieve.

*2) Adherence of asphalt binder to stone aggregates*

The adhesion of PA 50/70 and modified asphalt binders PA-M1-10 and PA-M2-10 to stone aggregates were evaluated using 500 g of coarse, previously selected, washed, and dried asphalt binders. Heated at a temperature of 100°C for 1 hour and mixed with 17.5 g of asphalt binder at a temperature of 120 °C. After cooling for 24 hours at room temperature, the aggregate/binder mixture was placed in a beaker with distilled water and kept at a temperature of 40 °C for 72 hours in an oven with forced air convection. Then, the sample was removed from the water, photographed, and evaluated for adhesion, following the DNER - ME 78/94 standard.

*3) Machining temperature (TU) and compaction (TC)*

Defined the physicochemical characteristics of the asphalt binder PA 50/70 and its modified PA-M1-10 and PA-M2-10, from the respective graphs of apparent viscosity versus temperatures (135 °C, 150 °C, and 170 °C) respectively, the machining temperature ranges (TU) and compaction temperature (TC) was indirectly determined, following the ASTM D4402 standard.

*4) Binder project content by the Marshall method*

Assigning as an initial value of void volume in the asphalt mixture 4%, a value normally used by road pavement engineering professionals in Brazil to calculate the design binder content, 6 (six) bodies cylindrical specimens (CP's), with dimensions 101.5±0.5 mm in diameter and 63.5±1.3 mm in height, are processed in triplicates, with binder contents of 4.0, 4.5, 5.0, 5.5, 6.0 and 6.5% m/m, in TU and TC predefined ranges, from the apparent viscosity graphs of the binders under study as a function of temperature (135 °C, 150 °C and 170°C), applying 75 blows on each face, with a steel socket of 4,540 g, in free fall of 45.72 cm.

After cooling the CAP's at room temperature (25ºC) on a laboratory bench for 72h, the masses of the dry ($M_s$) and submerged ($M_{sub}$) specimens were measured to calculate the respective volumes ($V$), apparent densities ($d_M$)), theoretical maximum densities ($DMT$), void volumes ($V_v$), bitumen/void ratios (RBV) through equations (5) to (11). Then, graphs of $V_v$ and RBV as a function of the binder contents used were constructed and the design binder content was defined as the arithmetic mean between two central points of these graphs. The volume of CP:

$$V = M_s - M_{sub} \tag{5}$$

Apparent densities:

$$d_M = \frac{M_S}{V} \tag{6}$$

Theoretical maximum densities:

$$DMT = \frac{100}{\frac{\%ag}{d_{ag}} + \frac{\%ai}{d_{ai}} + \frac{\%am}{d_m} + \frac{\%lig}{d_{lig}}} \tag{7}$$

Void volume:

$$Vv = \frac{DMT - d_M}{DMT} \tag{8}$$

Void with binder:

$$\frac{d_M x\ \%lig}{M_{lig}} \tag{9}$$

Void by aggregate stone:

$$VAM = V_v + VCB \tag{10}$$

Bitumen/void ratios:

$$RBV = \frac{VCB}{VAM} \tag{11}$$

where $M_S$ = Weight of dry specimen; $M_{Sub}$ = Weight of the submerged specimen; *ag* = Coarse aggregate; *ai* = Medium aggregate; *am* = Fine aggregate; $M_{lig}$ = Weight of the asphalt binder.

After determining the design binder contents, new CP's were processed in triplicate for each sample under study, cooled on a bench at room temperature (25°C), and evaluated for the behavior of indirect tensile strength test (ITS).

### D. *Indirect Tensile Strength Test (ITS)*

The ITS tests were carried out at a temperature of 25°C, using 3 (three) CP's for each sample, using a Marshall mechanical press, brand Solotest, applying progressive compression force at a speed of 0.8±0.1 mm/s until its rupture, following the procedure established by the ASTM D6931 standard.

## III. Results and Discussion

### A. *Apparent Viscosity and Flow Activation Energy*

Table III shows the apparent viscosity values for the binder PA 50/70 and the modified PA M1-10 and PA M2-10, at 135 °C, 150 °C and 170 °C. A reduction in the apparent viscosity is observed, compared to the binder PA 50/70, in the modified binder PA M1-10, caused by the higher concentration of oily sludge in the modifier M1, and an increase in the apparent viscosity in the modified binder PA M2-10, caused by the higher concentration of rubber from useless tires in the M2 modifier, due to its interaction with aromatic compounds present in the binder, which swells it and hinders its fluidity, as shown in previous studies [28]-[34].

The flow activation energy, in this study, for the modified PA-M1-10 and PA-M2-10, calculated by the Arrhenius equation (2), was 54 kJ/mol and 63 kJ/mol, respectively, 18% and 5% lower than the flow activation energy of PA 50/70 (66 kJ/mol), conferred by the presence of oily sludge, which allows a reduction in energy cost during the processing of the respective HMA's, with lower emission of volatile compounds, as they tend to be processed at temperatures lower than with the binder PA 50/70. This behavior is contrary to binders modified with rubber and polymers, published in the literature [8], [35].

### B. *Penetration*

Penetration is the parameter used in the specification of quality and suitability of asphalt binder for the production of HMA. With the determination of the penetration value, the hardness of the asphalt binder is specified for a better definition of its use. Table III shows the penetration, softening point and density values of the PA 50/70 binder and the modified binders PA-M1-10 and PA-M2-10. It is observed that the presence of a higher concentration of oily sludge reduced penetration resistance, which can be attributed to the fraction of different heavy organic compounds present in the M1 modifier. However, the apparent viscosity value is within the binder classification range 50-70 (0.1 mm, 5 s, 100 g, 25 °C) as per ASTM D5, whereas the addition of M2 modifier increased the apparent viscosity, which gave the binder PA-M2-10 the classification 40-50 (0.1 mm, 5 s, 100g, 25 °C) according to the ASTM D946-09A standard. However, the penetration value for the modified binder PA-M2-10 is compatible with apparent viscosity values found in the literature for binders modified with rubber and polymers [24], [31], [36]-[41].

TABLE III: Physical Properties of Asphaltic Binder Pa 50/70 and Modified Binders With Mixture of Industrial Waste*

| Physical properties of samples | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Characteristics | | Unit | Values | | | | | Method |
| | | | M1 | M2 | PA 50/70 | PA-M1-10 | PA-M2-10 | |
| Viscosity Brookfield | 135 °C | | - | - | 0.47 ± 0.01 | 0.26 ± 0.00 | 1.11 ± 0.04 | |
| | 150 °C | Pa.s | - | - | 0.22 ± 0.00 | 0.15 ± 0.00 | 0.53 ± 0.00 | ASTM D 4402 |
| | 170 °C | | - | - | 0.10 ± 0.00 | 0.07 ± 0.00 | 0.25 ± 0.01 | |
| Penetration | | °C | - | - | 55 ± 0.57 | 62 ± 1.53 | 40 ± 1.53 | ASTM D5 |
| Softening point | | 0,1 mm | - | - | 48 ± 0.00 | 53 ± 0.25 | 55 ± 0.25 | ASTM D36 |
| Specific gravit | | g/cm$^3$ | 0.99 ± 0.02 | 0.87 ± 0.03 | 1.05 ± 0.02 | 1.05 ± 0.02 | 1.06 ± 0.02 | AASHTO T228 |
| Flow activation energy | | kJmol$^{-1}$ | - | - | 66.00 | 54.00 | 63.00 | Eq. Arrhenius (2) |
| Thermal susceptibility index (ITS) | | - | - | - | -1.5 | +0.1 | -0.5 | Pfeiffer e Van Doormaal |

*: Tire rubber and oily sludge of petroleum.
M1: Mixture 15% tire rubber and 85% of oily sludge.
M2: Mixture 85% tire rubber and 15% of oily sludge.
PA 50/70: Petroleum asphalt with penetration range of 50-70 (0.1 mm).
PA-M1-10: Petroleum asphalt with penetration range of 50-70 (0.1 mm) with 10% of M1 (85% of oily sludge and 15% tire rubber).
PA-M2-10: Petroleum asphalt with penetration range of 50-70 (0.1 mm) with 10% of M2 (15% of oily sludge and 85% tire rubber).

### C. Softening Point

The softening point test estimates the influence of temperature on the softening of the asphalt binder. Used in the classification of conventional and modified binders, this empirical test allowed to determine the temperature range in which changes in the consistency of the binder become visible, indicating its softening.

It is observed in Table III that the modified binders PA-M1-10 and PA-M2-10 presented, respectively, a softening point of 48±0.25ºC. Temperature higher than that of the PA 50/70 binder. The modifiers under study have a softening temperature above the softening temperature of PA 50/70 [5], [6], [22], [23] which certainly increased the softening temperature of the modified binders. However, the results presented are also in agreement with those found in the literature for binders modified with rubber and polymers [3], [4], [6], [24], [28]-[32], [42].

### D. Specific Gravity

The knowledge of the specific mass value of the asphalt binder is used in its dosage in the HMA through the conversion of the specific mass into volume, in the definition of the binder design content. It is observed in Table III that modifiers M1 and M2 present specific mass values close to the specific mass value of PA 50/70. Therefore, the modified ligands PA-M1-10 and PA-M2-10 did not show significant changes in their specific masses compared to PA 50/70. Values are also compatible with those found in the literature for modified ligands [41]-[43].

### E. Adhesiveness of Binder by Stone Aggregates

The adhesion of the asphalt binder to the aggregates is one of the determining parameters in the processing of HMA. The loss of adhesion of the asphalt binder with the aggregate surface (adhesive fracture) as well as the fracture of the film itself (cohesive fracture), whether in the presence of water or not, is the origin of many types of defects in floor coverings, such as fatigue cracking, permanent deformation, and moisture damage [27]. An inefficient adhesion between the binder and the stone constituents promotes early disaggregation and reduces the useful life of the floor covering. In the evaluative test, the adhesiveness is considered good if there is no detachment of the binder film in the aggregate during the test period. Fig. 5 (a, b, c) show photographs resulting from the qualitative evaluation of adhesion assay of the ligand PA-50/70 and of the modified ligands PA-M1-10 and PA-M2-10. It can be observed that the PA-50/70 and modified binders do not show peeling off of the surface of the aggregates, which indicates good adhesion to the stone aggregates.

### F. Los Angeles Abrasion Wear Resistance Test

Los Angeles abrasion test indirectly assesses the toughness to abrasion resistance and hardness of stone aggregates subjected to mechanical degradation by changing their particle size. Table IV shows the results of Los Angeles abrasion and the specific mass of the aggregates, used in the processing of HMA's. The National Department of Infrastructure and Transport (DNIT) of Brazil recommends as acceptable values for wear of aggregates in Los Angeles abrasion test up to 65%. In contrast, the ASTM C131-01 standard presents good values of up to 45%. The values found are lower than those recommended for these standards.

(a) PA 50/70

(b) PA-M1-10 (c) PA-M2-10

Fig. 5. Photograph of post-adhesive test samples: (a) PA-50/70. (b) PA-M1-10 and (c) PA-M2-10.

TABLE IV: PROPERTIES OF AGGREGATES USED ON HMA

| Stone aggregate | Los Angeles (%) | Specific gravit (g/cm$^3$) |
|---|---|---|
| Coarse | 11.75 | 2.65 |
| Medium | 13.61 | 2.60 |
| Fine | - | 2.60 |

### G. Machining Temperature (TU) and Compaction (TC) of HMA

Fig. 6. (a, b, c) graphically show the behavior of viscosity as a function of temperature and the intersection points that define the TU and TC intervals for the sample of PA 50/70 and PA-M1-10 and PA-M2-10, respectively, and Table V shows the TU and TC intervals of the samples under study.

TABLE V: RANGE OF MARCHING TEMPERATURE (TU) AND COMPACTION TEMPERATURE (TC) DEFINED ON FIGURE 6 TO BINDERS: PA 50/70, PA-M1-10 E PA-M2-10

| Sample | Machining temperature - TU (ºC) | Compaction temperature – TC (ºC) |
|---|---|---|
| PA 50/70 | 154-159 | 143-147 |
| PA-M1-10 | 143-149 | 131-136 |
| PA-M2-10 | 178-185 | 165-170 |

### H. Binder Project Content by Marshall Standard

The binder project content has the function of defining the adequate amount of binder to prevent the premature deterioration of the asphalt concrete for pavement coating due to the insufficient or excess amount of binder that respectively favors the appearance of disaggregation of the stone aggregates and wheel tracks. Fig. 7 (a, b, c) graphically show the behavior of the binder content curves as a function of the values of Vv and RBV for samples PA 50/70, PA-M1-10 and PA-M2-10, respectively.

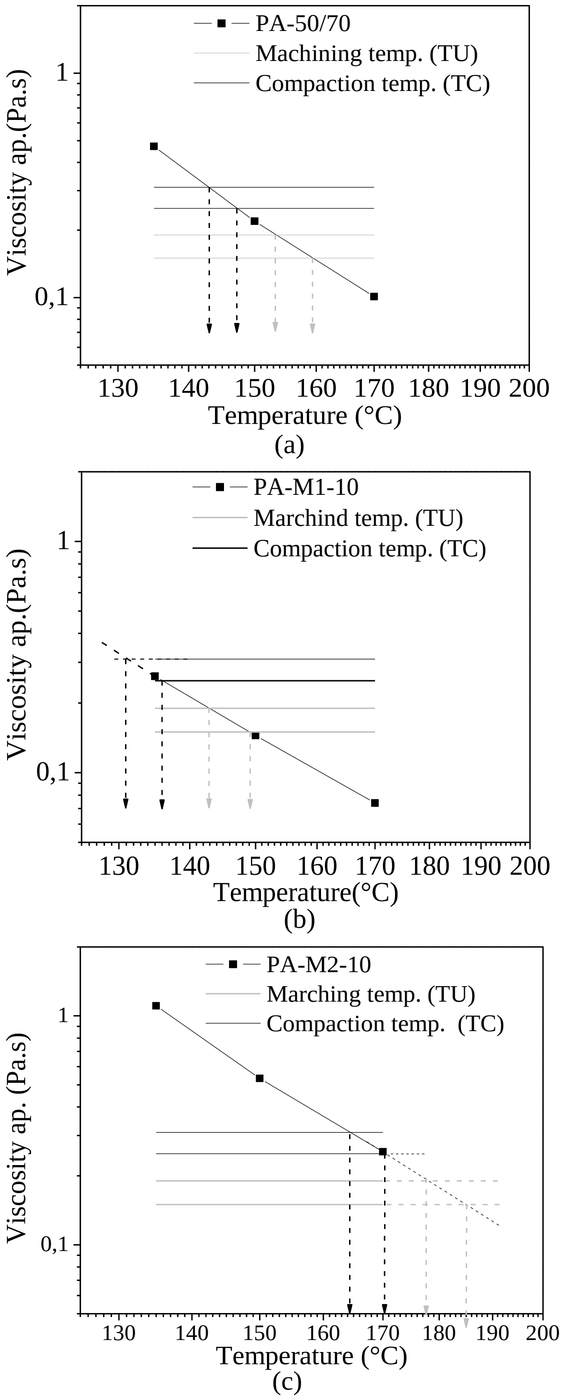



Fig. 6: Determination of marching temperature (TU) and compaction temperature (TC): (a) PA 50/70, (b) PA-M1-10, (c) PA-M2-10.

From the Vv ratio of RBV of the CP's, following the procedures recommended by the ASTM D1559 standard, the design binder content of 5.9% was determined for the binder PA-50/70, 6.3% for the modified binder PA-M1- 10 and 6.4% for the modified binder PA-M2-10. The more significant amount of binder project content found for modified binders concerning PA 50/70 can be attributed to the lower value of the respective apparent viscosities (Table III), which leads to the use of a greater volume of binder to occupy the proportion of voids in asphalt concrete

## *I. Indirect tensile strength test (ITS)*

Fig. 8 shows the results of the ITS assays. It is observed that the mean values obtained for the PA 50/70; PA-M1-10 and PA-M2-10 are equivalent, there is no significant change and above the minimum limit of 0.65 MPa, established ASTM D6931 for coating the road pavement bearing layer, which induces greater resilience to processed HMA.

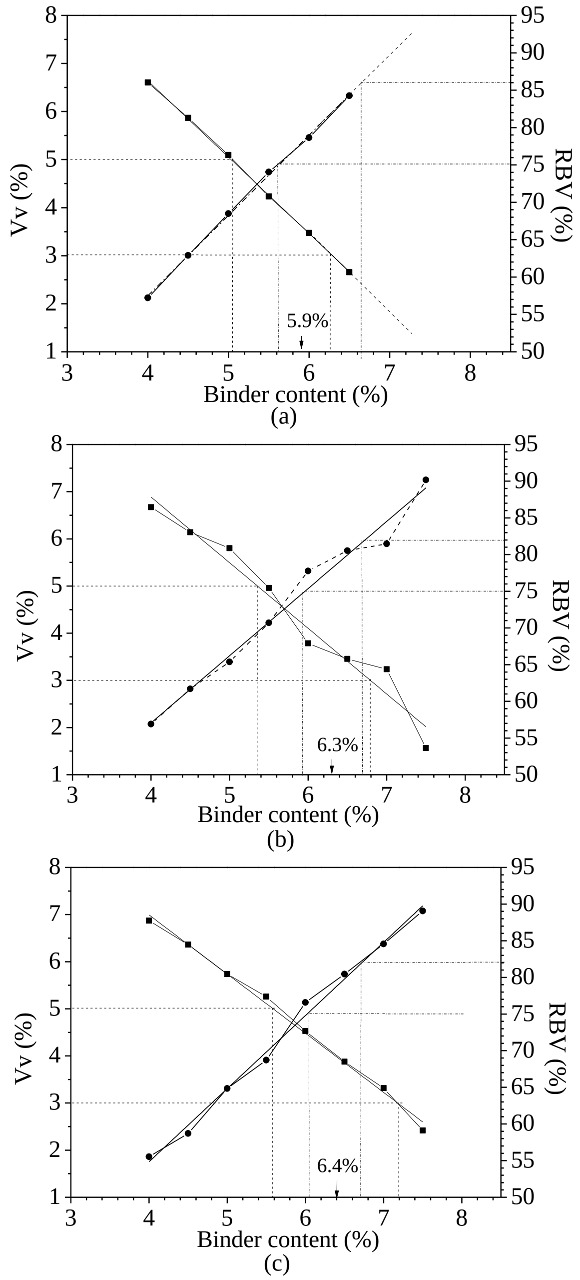



Fig. 7. Vv e RBV by function binder project content: (a) PA 50/70, (b) PA-M1-10, (c) PA-M2-10.

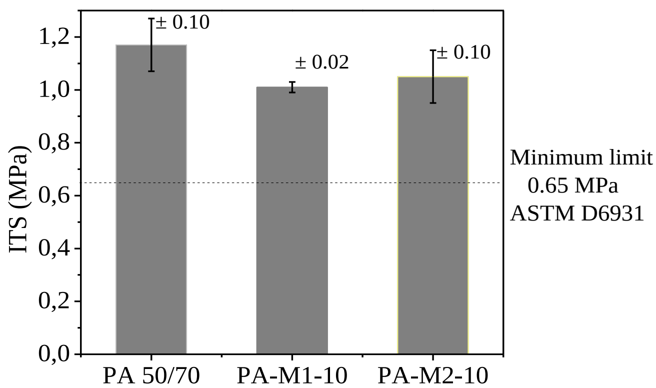



Fig. 8. *Indirect tensile strength test of HMA's with binders*: PA 50/70, PA-M1-10 e PA-M2-10.

## IV. Conclusion

From the results of testing samples in the laboratory, the following conclusions could be made:

1) The modified binder PA-M1-10, with a higher concentration of oily petroleum sludge, maintained the classification by penetration of the binder PA 50/70, whereas the PA-M2-10 changed to the 40-50 classification, according to ASTM D946-09A standard, which agrees with the literature regarding the hardening of the binder in the presence of tire rubber.

2) The activation energy of the modified ones suffered a reduction, with a greater value for the modified PA-M1-10, which can be attributed to the higher concentration of oily petroleum sludge.

3) The empirical properties evaluated: apparent viscosity, penetration, softening point, specific mass, and thermal susceptibility index (IST), measured following normative and conventional procedures, met the specification for asphalt binder in a HMA mixture.

4) The binder project content of modifieds, PA-M1-10 and PA-M2-10 were slightly higher than that of PA 50/70. However, they meet the requirements by DNIT 031/2004-ES standard.

5) Adhesion of modified binders to stone aggregates was compatible with PA 50/70.

6) The mechanical behavior of the indirect tensile strength tests ITS of HMA's with modified binders were compatible with PA 50/70 and met the established ASTM D6931-12 standard.

Hence, it is concluded that the mixtures of solid waste, tire rubber, and oily sludge, at the concentrations studied, have potential use as a modifier of the asphalt binder PA 50/70 to be used in HMA processing.

## Acknowledgment

The authors are grateful to D.Sc. Cheila Gonçalves Mothé from Chemical School of Federal University of Rio de Janeiro - UFRJ (*in memoriam*), for the great scientific discussions and teachings; to Graduate Program in Chemical and Biochemical Process Engineering (EPQB/UFRJ), for the opportunity of carrying out this research; to the coordinating professor and to the technicians of the Geotechnics and Pavement Laboratory (GeoPav./DEC/UFS) for the processing and analysis of the asphalt mixtures, to EMURB-Aracaju/SE-Brazil, for the supply of the mineral aggregates and the PA 50/70 binder and stone aggregates and to Petrobras-SA for the supply of asphalt, oily sludge and the financial support given to the North-Northeast Asphalt Network (contractual institutional term 00500022845.06.04.SAP/R3 No. 4600218997).

## References

[1] Gama DA, Rosa Jr JM, Melo TJA, Rodrigues JKG. Rheological studies of asphalt modified with elastomeric polymer. *Constr. Build. Mater*. 2016; 106: 290-295.
Doi: https://doi.org/10.1016/j.conbuildmat.2015.12.142.

[2] Diab A, Enied M, Singh D. Influence of aging on properties of polymer-modified asphalt. *Constr Build Mater*. 2019; 196: 54-65. Doi: https://doi.org/10.1016/j.conbuildmat.2018.11.105.

[3] Ouming X, Feipeng X, Sen H, Amirkhanian SN, Zhenjun W. High temperature rheological properties of crumb rubber modified asphalt binders with various modifiers. *Constr Build Mater*. 2016; 112:49-58. Doi: https://doi.org/10.1016/j.conbuildmat.2016.02.069

[4] Da Graça DCS, Cavalcante EH, Cardoso G.. Avaliação da estabilidade de estocagem de ligante asfáltico modificado com blenda de borra oleosa de petróleo e borracha de pneus. *Scient. Plena*. 2015; 11(11). 113310-1 p. Doi: https://doi.org/10.14808/sci.plena.2015.113310.

[5] Naime R.. Meio ambiente e ecossistemas. *Eco Debate*. ISSN 2446-9394. 2015.
Disponível em: <https://www.ecodebate.com.br/2015/01/08/meio-ambiente-e-ecossistemas-artigo-de-roberto-naime/>.

[6] Zhang F, Hu C. The research for crumb rubber/waste plastic compound modified asphalt. *J. Therm. Anal. Calorim*. 2016; 124: 729-741. Doi: https://doi.org/10.1007/s10973-015-5198-4

[7] Liu H, Chen Z, Wang W, Wang H, Hao P. Investigation of the rheological modification mechanism of crumb rubber modified asphalt (CRMA) containing TOR additive. *Constr. Build. Mater*. 2014; 67: 225-233. Doi: https://doi.org/10.1016/j.conbuildmat.2013.11.031

[8] Da Graça DCS, Cardoso G, Mothé CG. Thermal behavior of asphalt binder with modifying agents from industrial residues. *J. Therm. Anal. Calorim.* 2019; 138: 3619-3633. Doi: https://doi.org/10.1007/s10973-019-08371-w.

[9] Santana RR, Santos R, Cavalcante EH, Cardoso G. Estabilidade e adesividade de ligante asfalto modificado com blenda de borra oleosa de petróleo com borracha de pneu. *Materia*. 2017; 23:1. Doi: https://doi.org/10.1590/S1517-707620170001.0313.

[10] Biswas A, Potnis S. Plastic bituminous roads: a sustainable technology for better handling distresses. *Eur. J. Engin. Tech. Resear*. 2022; 7(1): 63-69. Doi: http://dx.doi.org/10.24018/ejers.2022.7.1.2695.

[11] Wen G, Zhang Y, Zhang Y, Sun K, Fan Y. Rheological characterization of storage-stable SBS-modified asphalts. *Polymer Testing*. 2002; 21: 295-302. Doi: https://doi.org/10.1016/S0142-9418(01)00086-1.

[12] Alatas T, Yilmaz M, Kök BV and Koral A. Comparison of permanent deformation and fatigue resistance of hot mix asphalts prepared with the same performance grade binders. *Constr. Build. Mater*. 2012; 30:66-72. Doi: https://doi.org/10.1016/j.conbuildmat.2011.12.021.

[13] Yang SH, Lee LC. Characterizing the chemical and rheological properties of severely aged reclaimed asphalt pavement materials with high recycling rate. *Constr. Build. Mater*. 2016; 111:139-146. Doi: https://doi.org/10.1016/j.conbuildmat.2016.02.058.

[14] Zhang F, Hu C, Zhang Y. The effect of PPA on performances and structures of high-viscosity modified asphalt. J. Therm. Anal. Calorim. 2018; Doi: https://doi.org/10.1007/s10973-018-7740-7.

[15] Behnood A, Gharehveran MM. Morphology, rheology and physical properties of polymer-modifed asphalt binders. *Eur Pol. Journal*. 2019; 112: 766-791. Doi: https://doi.org/10.1016/j.eurpolymj.2018.10.049

[16] Wang Q, Li S, Wu X, Wang S, Ouyang C. Weather aging resistance of different rubber modified asphalts. *Constr. Build. Mater*. 2016; 106: 443-448. Doi: https://doi.org/10.1016/j.conbuildmat.2015.12.138.

[17] Xiang L, Cheng J, Kang S. Thermal oxidative aging mechanism of crumb rubber/SBS composite modified asphalt. *Constr. Build. Mater*. 2015 75: 169-175. Doi:
https://doi.org/10.1016/j.conbuildmat.2014.08.035.

[18] Shen J, Li B, Xie Z. Interaction between crumb rubber modifier (CRM) and asphalt binder in dry process. *Constr. Build. Mater*. 2017; 149: 202-206. Doi: https://doi.org/10.1016/j.conbuildmat.2017.04.191.

[19] Ge D, Yan K, You Z, Xu H. Modification mechanism of asphalt binder with waste tire rubber and recycled polyethylene. *Constr. Build. Mater*. 2016; 126: 66-76.
Doi: https://doi.org/10.1016/j.conbuildmat.2016.09.014.

[20] Sultana S, Bhasin A. Effect of chemical composition on rheology and mechanical properties of asphalt binder. *Constr. Build. Mater.* 2014; 72: 293-300. Doi: https://doi.org/10.1016/j.conbuildmat.2014.09.022.

[21] Guangji H, Jianbing L, Guangming Z. Recent development in the treatment of oily sludge from petroleum industry: A review. *J. Hazar Mater*. 2013; 261:470-490. Doi:
https://doi.org/10.1016/j.jhazmat.2013.07.069.

[22] Jasmine J, Mukherji S. Characterization of oily sludge from a refinery and biodegradability assessment using various hydrocarbon degrading strains and reconstituted consortia. *J Enviro Manage*. 2015; 149(1): 118-125. Doi: https://doi.org/10.1016/j.jenvman.2014.10.007.

[23] Wang R, Zhao Z, Qianqian Y, Xiang Y, Wang Z. Additive adsorption behavior of sludge and its influence on the slurrying ability of coal–sludge–slurry and petroleum coke-sludge-slurry. *App Therm Engin*. 2018; 128: 1555-1564.
Doi: https://doi.org/10.1016/j.applthermaleng.2017.09.133.

[24] Sanaa J, Adewale G, Shadi WH. Recent improvements in oily wastewater treatment: Progress. challenges. and future opportunities. *J. Enviro. Sciences*. 2015 Nov.; 37 (1): 15-30.

Doi: https://doi.org/10.1016/j.jes.2015.04.011.

[25] Silva DC, Lucas CRS, Juviniano HBM, Moura MCPA, Dantas TNC, Dantas Neto AA. Analysis of the use of microemulsion systems to treat petroleum sludge from a water flotation unit. *J. Enviro. Chemi. Engi*. 2019; 7: 102934. Doi: https://doi.org/10.1016/j.jece.2019.102934.

[26] Bernucci LB, Motta LMG, Ceratti JAP, Soares JB. Pavimentação asfáltica: formação básica para engenheiros". Rio de Janeiro. PETROBRAS. ADEBA. 2006.

[27] Shirini B, Imaninasab R. Performance evaluation of rubberized and SBS modified porous asphalt Mixtures. *Constr. Build. Mater*. 2016; 107: 165-171. Doi: https://doi.org/10.1016/j.conbuildmat.2016.01.006.

[28] Zhang F, Hu C, Zhuang W. The research for low-temperature rheological properties and structural characteristics of high-viscosity modified asphalt. J Therm Anal Calorim. 2018; 131:1025-1034.

[29] Rasool RT, Song P, Wang S. Thermal analysis on the interactions among asphalt modified with SBS and different degraded tire rubber. Constr Build Mater. 2018; 182:134-143.

[30] Zhang F, Hu C. Influence of aging on thermal behaviour and characterization of SBR compound-modified asphalt. J Therm Anal Calorim. 2014; 115: 1211-1218. doi: 10.1007/s10973-013-3338-2.

[31] Zhang F, Hu C. The research for thermal behaviour. creep properties and morphology of SBS-modified asphalt. *J Therm Anal Calorim.* 2015; 121: 651-661. Doi: 10.1007/s10973-015-4595-z.

[32] Zhao X, Wang S, Wang Q, Yao H. Rheological and structural evolution of SBS modified asphalts under natural weathering. *Fuel*. 2016; 184: 242-247. Doi: https://doi.org/10.1016/j.fuel.2016.07.018.

[33] Tang P, Mo L, Pan C, Fang H, Javilla B, Riara, M. Investigation of rheological properties of light colored synthetic asphalt binders containing different polymer modifiers. *Constr. Build. Mater.* 2018; 161: 175-185. Doi: https://doi.org/10.1016/j.conbuildmat.2017.11.098.

[34] Kim H, Lee SJ, Amirkhanian SN. Rheology of warm mix asphalt binders with aged binders. *Const. Build. Mate*r. 2011; 25:183-189. Doi: https://doi.org/10.1016/j.conbuildmat.2010.06.040.

[35] Bringel RM, Alencar AEV, Soares JB, Soares SA, Nascimento DR, Costa EF. Thermo-rheological behavior of modified bitumens adding virgin and waste polymers. 2008. https://www.researchgate.net/publication/261063347. Accessed November, 2021.

[36] Lima CS, Tomé LGA, Sant'ana HB, Soares JB, Soares SA. Estudo do comportamento reológico por meio de curvas mestras dos ligantes asfalto-borracha. Instituto Brasileiro de Petróleo. Gás e Biocombustíveis-IBP. 2008; <http://ceasf.petrobras.com.br/portalPublicacao.do?method=view&codigo=1334>.

[37] Feitosa JPM, Alencar AEV, Filho NW, de Souza JRR, Castelo Branco VTF, Soares JB, Soares SA, Ricardo NMPS. Evaluation of sun-oxidized carnauba wax as warm mix asphalt additive. *Constr. Build. Mater*. 2016; 115: 294-298.

[38] Khan IM, Kabir S, Alhussain MA, Almansoor FF Asphalt design using recycled plastic and crumb-rubber waste for sustainable pavement construction. *Proc Engineer*. 2016; 145: 1557-1564. Doi: https://doi.org/10.1016/j.proeng.2016.04.196.

[39] Wang. M.; Liu. L. Investigation of microscale aging behavior of asphalt binders using atomic force microscopy. *Constr. Build. Mater. 2017;* 135: 411-419. Doi: https://doi.org/10.1016/j.conbuildmat.2016.12.180.

[40] Singh M, Kumar P, Maurya MR. Strength characteristics of SBS modified asphalt mixes with various aggregates. *Constr. Build. Mater*. 2013;41: 815-823. Doi: https://doi.org/10.1016/j.conbuildmat.2012.12.062.

[41] Khatri S, Tamrakar GBS. Experimental investigation of bituminous concrete mix using rice husk ash as a mineral filler. *Inter. J. Scienc Research*. 2019; 8(10): 1702-1705. Doi: 10.21275/ART20202294.

[42] Nwaobakata C, Agwunwamba JC. Influence of periwinkle Shells ash as filler in hot mix asphalt. *Inter. J. Scienc Research.* 2014; 3(7): 2369-2373. Doi: 10.21275/020141340.

[43] Ibrahim SK. Effect of polystyrene polymer modifier and glass powder filler on the mechanical characteristics of hot mix asphalt. *Inter. J. Scienc Research.* 2018; 7(3): 1881-1886. Doi: 10.21275/ART20179776.

**Denes Carlos Santos da Graça** was born at Pão de Açúcar-AL, Northeast of Brazil, on May 31, 1982. He obtained a Bachelor of Industrial Chemistry (2009) and Master's degree in Chemical Engineering (2013), Federal University of Sergipe (UFS), Doctor Science degree of Chemical Engineering (2019), Federal University of Rio de Janeiro (EQ/UFRJ), both in Brazil. He has experience in laboratory analysis by Fourier transform spectroscopy in the Infrared region, optical microscopy, thermal and rheological analysis of materials, working mainly on the following topics: modified binder with industrial waste, mechanical and rheological behavior of asphalt mixtures for road pavement, and chemical and physical-chemical characterization of materials. E-mail: dagracadcs@yahoo.com.br. ORCID: 0000-0002-1042-139X.

**Michelle Gonçalves Mothé** was born at Rio de Janeiro-RJ/Brazil. She obtained a Bachelor of Chemical Engineering (2007) and Master degree in Science (2009), Federal University of Rio de Janeiro (EQ/UFRJ), Doctor Science degree in Engineering (2012), Federal University of Rio de Janeiro (EQ/UFRJ), with a sandwich internship at the Institut National Polytechnique de Grenoble (GINP)/France in 2010. She worked as a Chemical Engineer at Águas do Brasil S.A / Gestão e Manutenção de Saneamento LTDA in 2008. She has 100 works published in national and international magazines and congresses. She is the author of the translation of the book "Rheology and Rheometry: Practical and Theoretical Foundations. President of the Brazilian Association of Rheology. Master and Doctoral advisor of the Graduate Program at the EPQB/UFRJ School of Chemistry. She works in the area of organic processes in Characterization of Materials by Thermal Analysis and Rheology; Treatment and use of solid waste, Study of heavy oil flow, Characterization of Polymers and Nanomaterials by Thermal Analysis; Study of Modified Asphalt Binders; Synthesis and Characterization of Biofuels; Rheological Study of Polysaccharides in the Food, Development of Cosmetic Materials, She was a temporary professor at the Department of Organic Processes at the Federal University of Rio de Janeiro, and is currently an Adjunct Professor at the School of Chemistry at the Federal University of Rio de Janeiro. ORCID: 0000-0002-22637841.

**Gisélia Cardoso** was born at Riachuelo-SE, Northeast of Brazil, on Juny 8, 1950. She obtained Bachelor Chemical Engineering (1979), Federal University of Sergipe (UFS), Master degree in Chemical Engineering (1994), Campinas State University (UNICAMP), Doctor Science degree of Science and Engineering of Materials (2000), Federal University of São Carlos (UFSCar), both in Brazil. She is a Titular Professor at the Federal University of Sergipe, in the Materials Teaching Subject, assigned to the Department of Chemical Engineering. She is part of the Graduate Programs in Chemical Engineering and Civil Engineering at the same institution. She works in the field of Chemical Process Engineering. Research lines of interest: synthesis and modification of polymers, rheological behavior of materials, asphalt mixtures for pavement coating, and development of an additive to correct the flow profile of heavy oil. ORCID: 0000-0003-2640-3441.