RHEOLOGICAL EVALUATION OF THE SHORT-TERM AGING OF BITUMEN-RUBBER BINDERS MODIFIED WITH SHALE-OIL RESIDUE AND POLYPHOSPHORIC ACID

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ABSTRACT

This research aims at evaluating the effect of the short-term aging on the rheological properties of bitumen-rubber binders modified with shale-oil residue and polyphosphoric acid. The complex modulus and phase angle values were monitored under different temperatures and loading frequencies. The main conclusions are (1) the short-term aging increases G and decreases δ for a wide frequency spectrum; (2) the short-term aging makes the bitumen-rubber binders less thermically susceptible, markedly the bitumen(72)-rubber(18)-oil(10), the bitumen(71%)-rubber(18)-oil(10)-PPA(1)-1 and the bitumen(85.5%)-rubber(9)-oil(5)-PPA(0.5)-2; (3) the different aging indices ranked the bitumen(72)-rubber(18)-oil(10) and the bitumen(71%)-rubber(18)-oil(10)-PPA(1)-1 as the most sensitive to the short-term aging and the bitumen(82)-rubber(18) and the bitumen(81)-rubber(18)-PPA(1) as the less sensitive to aging, although the pure bitumen is less sensitive than all the bitumen-rubber binders evaluated; (4) the short-term aging increases stiffness of about 44% when the traffic speed goes from high to low: the aged bitumen-rubber binders are stiffer for low traffic speed than for high traffic speed and the result is a material more resistant to rutting but not to fatigue in the strain-controlled mode; (5) all the bitumen-rubber binders suffered an increase of mass loss in comparison with the pure bitumen; and (6) taking a limit of 0.5% for the mass loss, only the bitumen(82)-rubber(18) and the bitumen(81)-rubber(18)-PPA(1) are acceptable and for a limit of 1.0%, all the mixtures are acceptable. The combination of crumb rubber, shale-oil residue and polyphosphoric acid is a good alternative to produce bitumen-rubbers of enhanced quality, but users should pay attention to local specifications on mass loss.*

Keywords: bitumen-rubber binders, shale-oil residue, polyphosphoric acid, master-curves, short-term aging

1. INTRODUCTION

The science of bitumen has been developed, since the beginning of the 20th century, based on the incorporation of different modifiers as elastomeric and plastomeric polymers, acids, recycled materials as crumb rubber and other discarded polymeric-based products, mineral fillers, natural asphalts and oils. The main objective of incorporating modifiers into bitumen is to generate more versatile and durable products in order to resist to the environmental effects and the excessive traffic loading. Although polyphosphoric acid is not a new modifier for bitumen, it started to be used combined with polymers in order to reduce the concentration of them in polymer-modified bitumen.

Because of their technical shortcomings, the formulation of bitumen-rubber binders usually requires the addition of some additives. These additives invariably change expressively the rheological response of the modified bitumen-rubber binders, as previously researched by Faxina and Salomon (2010) and Faxina and Fabbri (2010). Such additives deserve to be carefully studied as they can have some positive effects on the workability of the bitumen-rubber binders. Studying the effect of the short-term aging is also essential in order to evaluate how the workability of the bitumen-rubber binders changes during the construction phase. The objective of this work is to evaluate how the short-term aging changes the rheological behavior of bitumen-rubber binders modified with shale-oil residue and polyphosphoric acid. Complex modulus (G^*) and phase angle (δ) of the virgin and short-term aged samples are monitored and used to obtain aging indices to which the mass loss values are added.

The bitumen modification with polyphosphoric acid is also not a new practice (Baumgardner et al., 2005). Since the 1970's, bitumens have been modified with polyphosphoric acid in order to increase the viscosity without reducing substantially the penetration and to obtain bitumens of higher rutting resistance without reducing the resistance to thermal cracking. According to Thomas and Turner (2008), the use of acids to modify bitumen started in the final of the 1930's, when they were used as catalysts in the blowing process. At that time, the use of the polyphosphoric acid as a catalyst was also investigated.

More recently, the polyphosphoric acid has been used to widen the job-temperature range of the bitumens or their performance grade. The addition of polyphosphoric acid (Baumgardner et al., 2005) is supposed to enhance the rheological properties of the bitumens at the high temperatures, without affecting the performance grade of the material at low temperatures. Orange et al. (2004) pointed out that tests with asphalts using granite as mineral aggregate showed that the polyphosphoric acid is responsible for increasing the resistance to water. It is also mentioned that the polyphosphoric acid can enhance the aging resistance of bitumens (Filippis et al., 1995).

The effect of PPA was described by Orange et al. (2004) as a dispersant of the asphaltene phase, leading to an increase of the interaction surface of the asphaltenes with the maltenic phase of the bitumen. The increase of the asphaltene surface (Martin and Baumgardner, 2006) is supposed to contribute to the interaction with the dispersed crumb rubber, generating a synergic effect on the macroscopic properties of the modified bitumen. It was observed that bitumens of both naftenic nature and aromatic nature interact differently with crumb rubber (Martin and Baumgardner, 2006). These authors suggest that the best results obtained with the naftenic bitumens are related to the interaction between asphaltenes and rubber particles, forming a net (Martin and Baumgardner, 2006). Polyphosphoric acid intensifies the contribution of crumb rubber to enhance the rheological properties of the modified bitumen probably by means of a reorganization of the bitumen macrostructure.

2. MATERIAL, TEST PROTOCOL AND EQUIPMENT

To produce the modified bitumen-rubber binders, the following materials were used: (1) a base bitumen of 50/70 penetration and aromatic nature, supplied by Reduc-Petrobras, graded as a PG 64S-22; (2) a mash #30 crumb rubber supplied by Ecija Comércio Exportação e Importação de Produtos Ltda, obtained by trituration of the treads of light vehicles; (3) a shale-oil residue type AR-5, according to ASTM D 4552-04, obtained from the vacuum residue of shale oil, supplied by SIX-Petrobras; and (4) a polyphosphoric acid commercially named as Innovalt E-200, supplied by Innophos Inc. The mixtures were prepared using a high-shear mixer Silverson model L4R. Table 1 shows the proportions used to prepare the modified bitumen-rubber binders as well as the process conditions and the PG grade at high temperatures according to the Superpave specification.

Table 1: Component proportions and process conditions

Simple name	Proportion (in mass, %)				Process conditions			PG
	Bitumen	Rubber	Oil	PPA	Temperature (ºC)	Time (min)	Speed (rpm)	
Bitumen-rubber	82	18	0	0	180	90	4,000	76-xx
Bitumen-rubber-PPA	81	18	0	1	180	90, ppa at 60	4,000	82-xx
Bitumen-rubber-oil	72	18	10	0	180	90	4,000	70-xx
Bitumen-rubber-oil-ppa-1	71	18	10	1	180	90, ppa at 60	4,000	76-xx
Bitumen-rubber-oil-ppa-2	85.5	9	5	0.5	180	90, ppa at 60	4,000	64-xx

A TA Instruments rheometer model AR-2000ex was used to monitor the G* and δ values of the virgin and short-term aged samples. The short-term aging was run according to the ASTM D 2872-04. The protocol used to generate the master-curves was: (1) run a stress sweep at 52, 64, 76 and 88°C, at 10 rad/s, using the 25 mm diameter parallel plates and the 1.0 mm gap, in order to estimate the stress level to test the samples in the linear-viscoelastic range at each temperature; (2) run a stress sweep at 40, 28, 16 and 4°C, at 10 rad/s, using the 8 mm diameter parallel plates and the 2.0 mm gap; (3) run a frequency sweep from 0.1 to 100 rad/s at 52, 64, 76 and 88°C, at the stress levels from step 1; (4) run a frequency sweep from 0.1 to 100 rad/s, at 40, 28, 16 and 4°C, at the stress levels from step 2; and (5) generate the master-curve at 25°C.

3. RESULTS AND ANALISIS

Figures from 1 to 5 show that the short-term aging increases the G* values for the whole frequency spectrum. The aging effect is more expressive at lower frequencies and decreases gradually as the frequency increases. At higher frequencies, the aging effect is inexistent for the bitumen-rubber and the bitumen-rubber-PPA, but it increases slightly the stiffness of the asphalt-rubber-oil, the asphalt-rubber-oil-PPA-1 and the asphalt-rubber-oil-PPA-2. The oil is a common element for the last three mixtures and it is responsible for damaging the rheological behavior of these samples at this frequency range. The volatilization is the predominant phenomenon during the mixing process and the shale-oil residue, because of its light nature, is more prone to volatize. When this occurs, the loss mass increases and the bitumen stiffens.

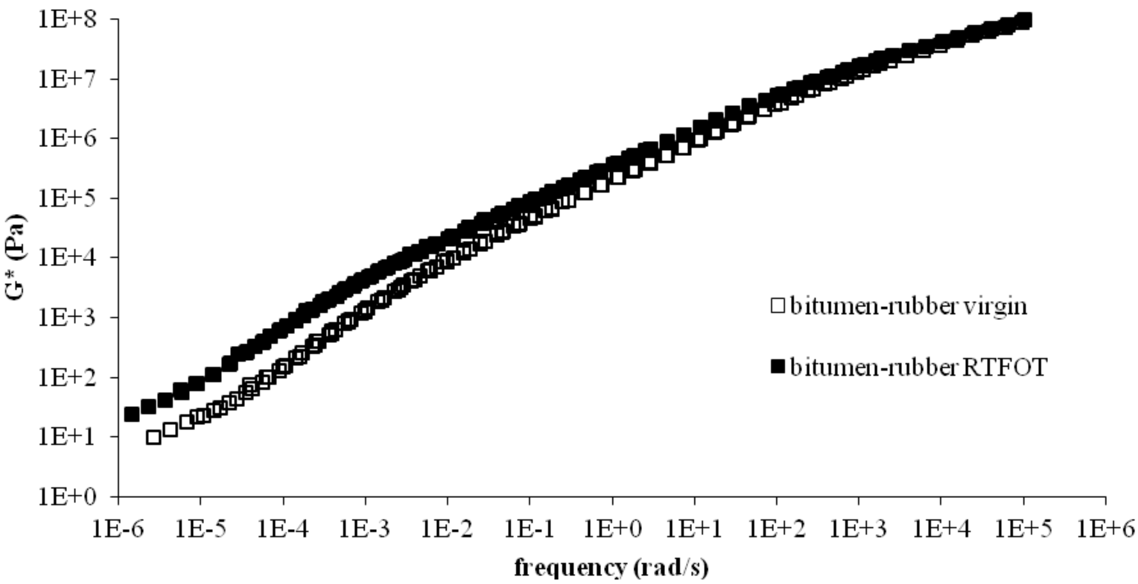

Figure 1: G* master-curves of the bitumen-rubber

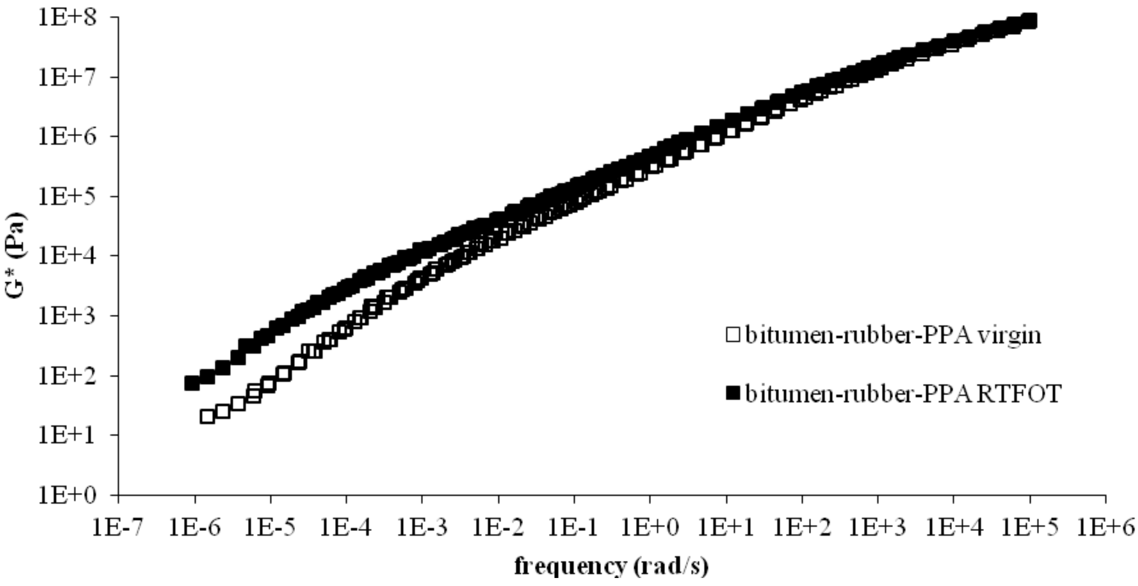

Figure 2: G* master-curves of the bitumen-rubber-PPA

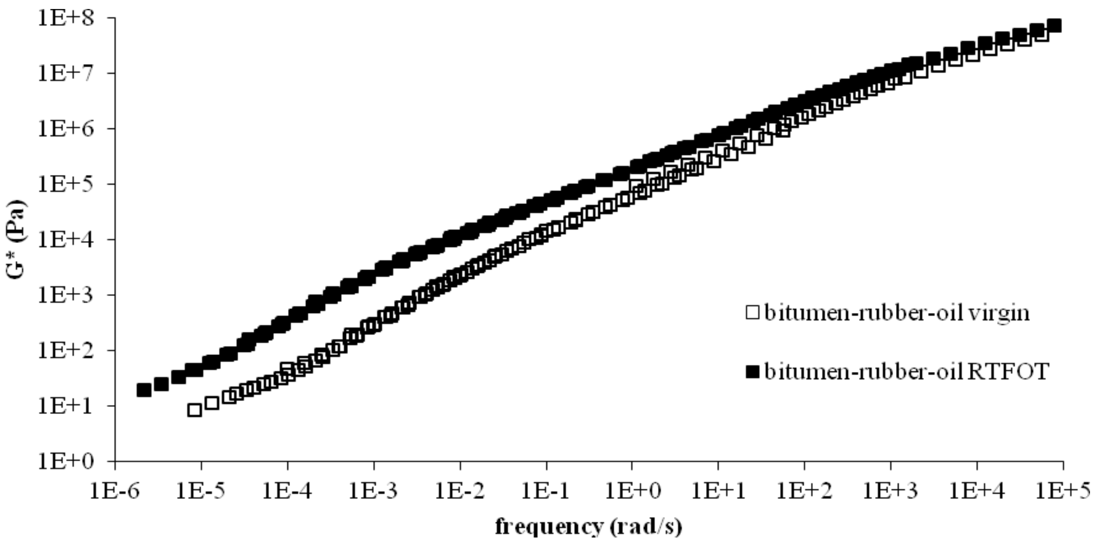

Figure 3: G* master-curves of the bitumen-rubber-oil

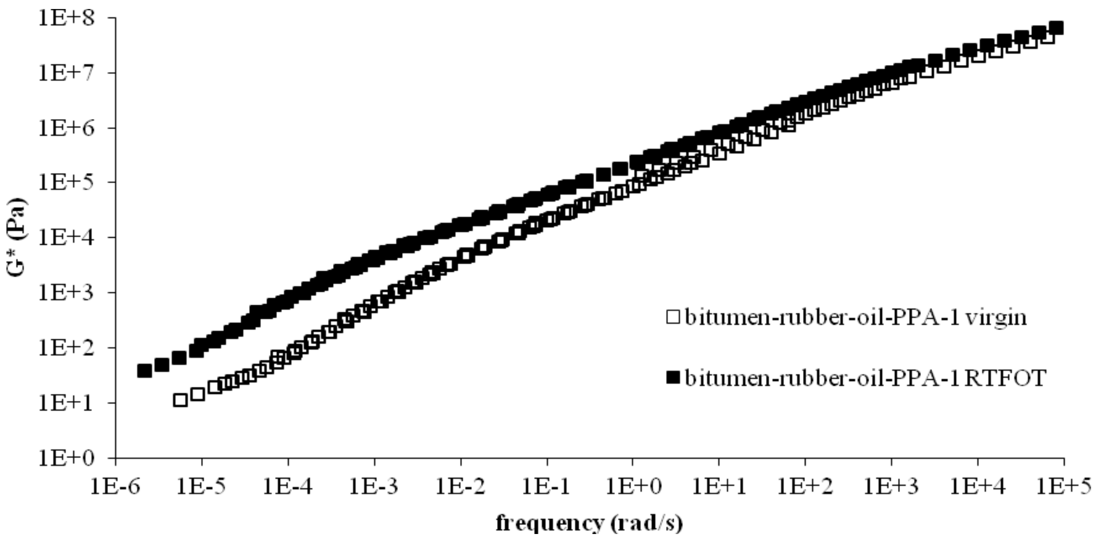

Figure 4: G* master-curves of the bitumen-rubber-oil-PPA-1

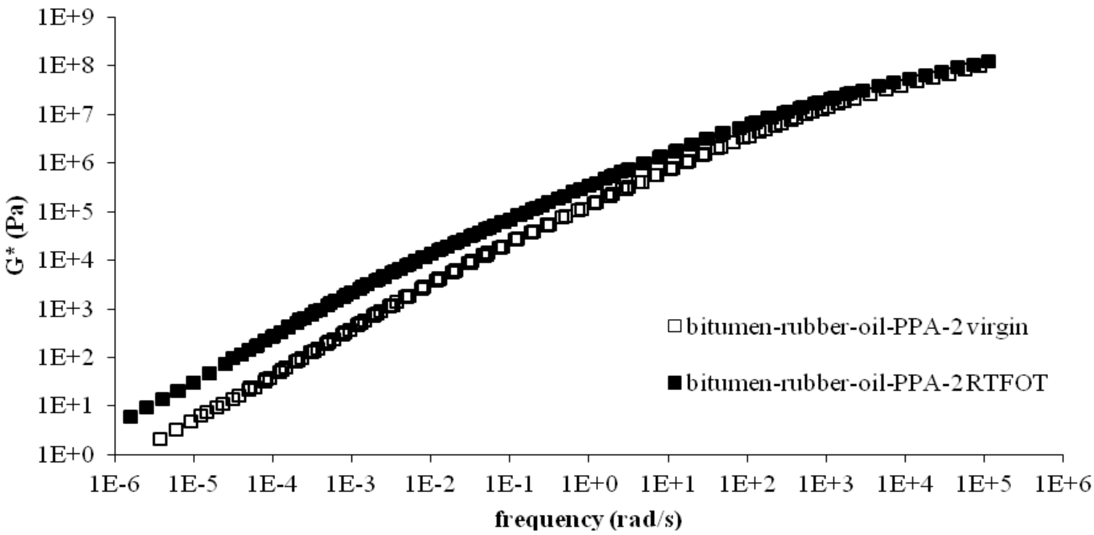

Figure 5: G* master-curves of the bitumen-rubber-oil-PPA-2

The short-term aging increased the bitumen stiffness, especially at high temperatures, improving the rutting resistance of the asphalt. However, such a stiffness increase can reduce the fatigue resistance in the strain-controlled mode, as in this case lower G* values are desired. When fatigue cracking occurs in the stress-controlled mode, higher G* values are indicated and, in this case, the stiffness increase due to the short-term aging is advantageous. When there is a stiffness increase at low temperatures, the thermal-cracking resistance is reduced, but such a “loss” is relative. It is necessary to keep in mind that the interactive effect of crumb rubber and shale-oil residue reduces substantially the stiffness in comparison with the stiffness of the base bitumen. In this case, the stiffness increase due to the short-term aging is counterbalanced, at least partially, with the elasticity increase caused by the crumb rubber. In general, the effect of aging on bitumen-rubber binders is not as harmful as on other bitumens (pure or modified).

From the point of view of frequency susceptibility, or thermal susceptibility as its equivalent, the stepper the curve the higher the change of G* with frequency and the higher the frequency susceptibility. The bitumen-rubber binders are by nature less thermally susceptible because of the higher thermal stability of the crumb rubber particles. Figures from 1 to 5 reveal that the bitumen-rubber binders are less thermal susceptible after the short-term aging. The highest declivity reductions occur for the bitumen-rubber-oil and the bitumen-rubber-oil-PPA-1, which contain high proportions of shale-oil residue, and the bitumen-rubber-oil-PPA-2, which contains lower proportions of the modifiers and consequently a higher bitumen proportion. The lower the proportions of crumb rubber and PPA, the higher the bitumen proportion in the mixture, leading the modified bitumen to present a thermal susceptibility comparable to the pure bitumen.

As illustrated by Figures from 6 to 10, the short-term aging reduces the phase-angle values for almost the whole frequency spectrum. The aging effect is more expressive at frequencies from low to intermediate, correspondent to intermediate to high temperatures. The reduction of the phase-angle values is favorable to the resistances to rutting, fatigue and thermal cracking. Particularly for fatigue in the strain-controlled mode, the reduction of the phase-angle values minimizes the negative effect of aging on G*, contributing to a certain extent to reduce the tendency to crack. As revealed by the poor fitting obtained for the phase-angle master-curves, the samples seem not to meet perfectly the time-temperature superposition principle (TTS), except for the bitumen-rubber-oil-PPA-2. High proportions of crumb rubber apparently cause deviations from the TTS, as also observed for other bitumen modified with high proportions of polymers and PPA.

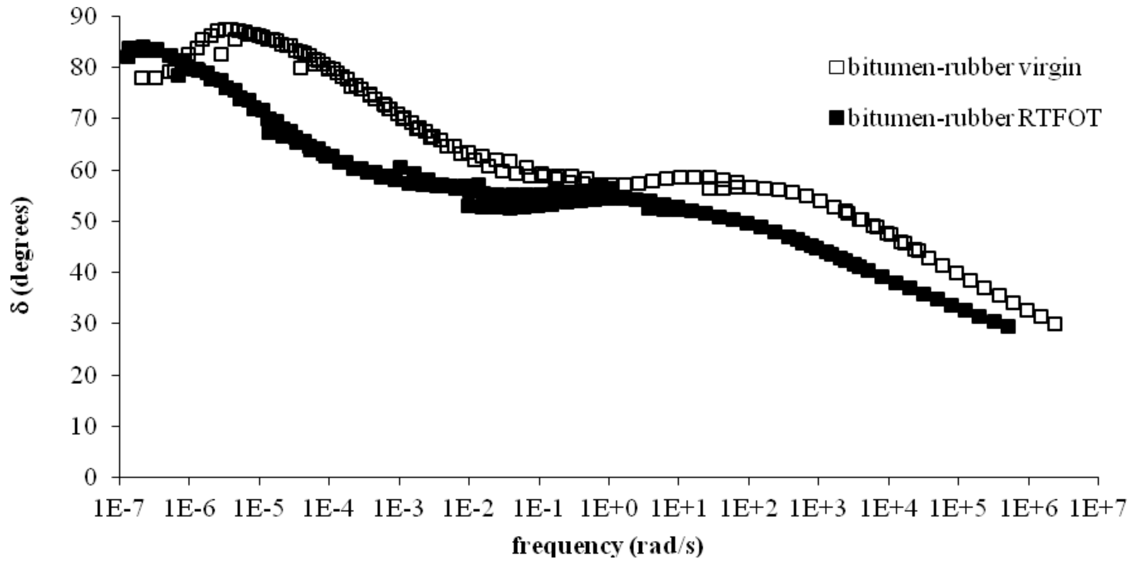

Figure 6: Delta master-curves of the bitumen-rubber

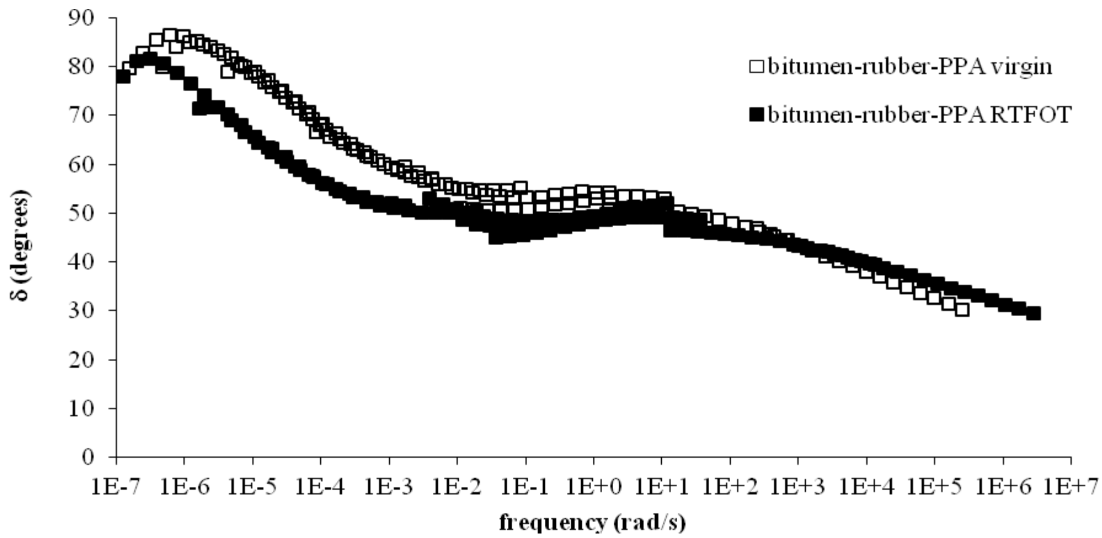

Figure 7: Delta master-curves of the bitumen-rubber-PPA

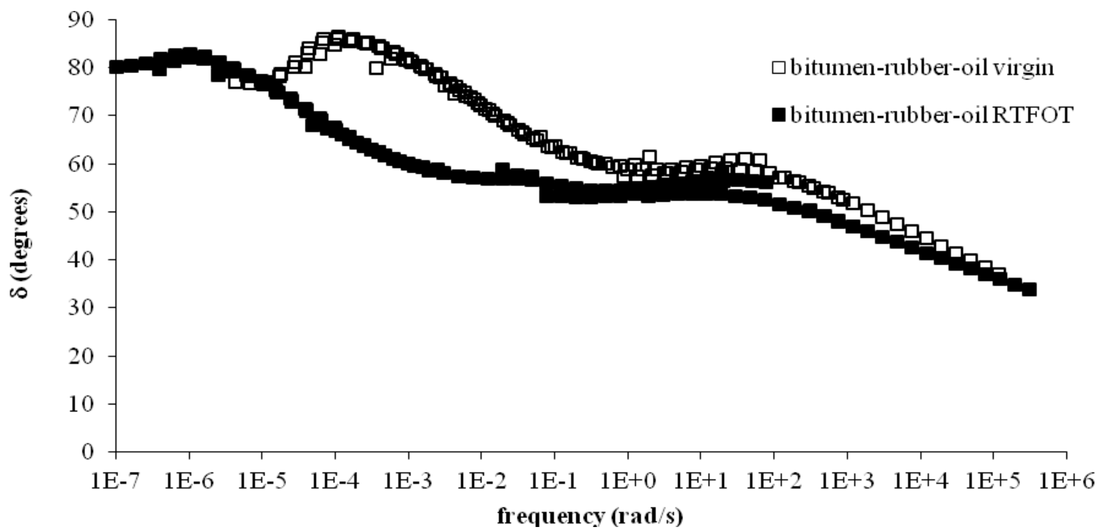

Figure 8: Delta master-curves of the bitumen-rubber-oil

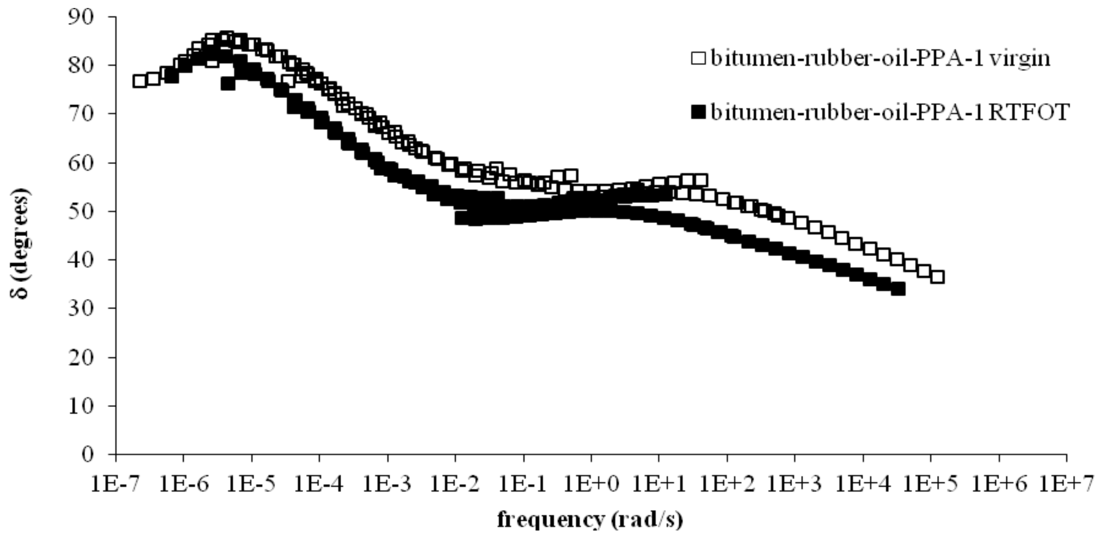

Figure 9: Delta master-curves of the bitumen-rubber-oil-PPA-1

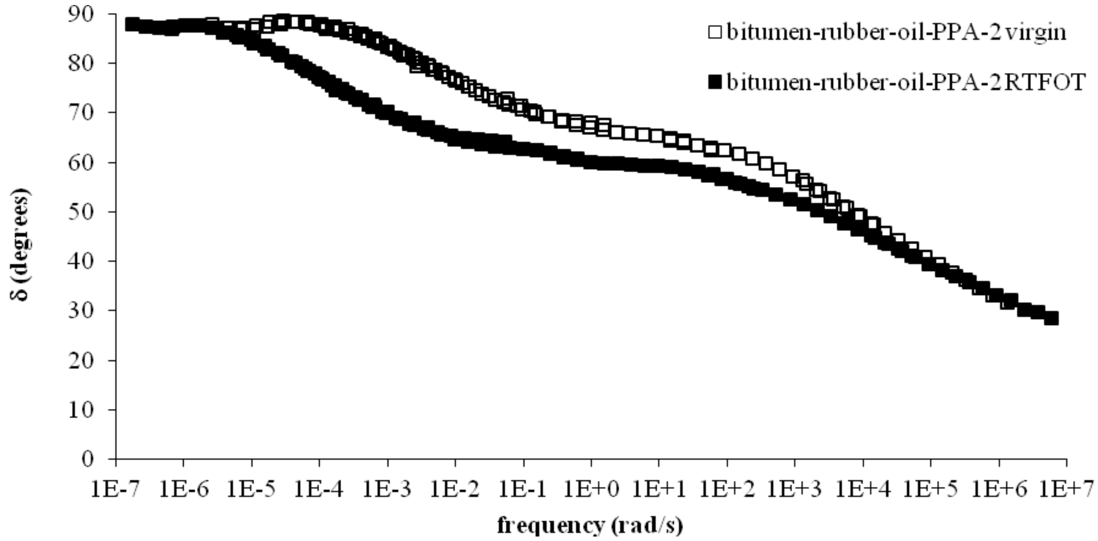

Figure 10: Delta master-curves of the bitumen-rubber-oil-PPA-2

Based on the increase of G* values (Table 2), it is possible to conclude that the bitumen-rubber and the bitumen-rubber-PPA are the less sensitive to the short-term aging, followed by the bitumen-rubber-oil-PPA-2, the bitumen-rubber-oil-PPA-1 and the bitumen-rubber-oil. At low frequencies, around 0.01 rad/s, the bitumen-rubber and the bitumen-rubber-PPA suffer a stiffness increase of about 2 times and the bitumen-rubber-oil-PPA-2, the bitumen-rubber-oil-PPA-1 and the bitumen-rubber-oil have an increase of about 4 times. At higher frequencies, as 10 rad/s, the stiffness increase due to aging is around 2 times: 1.4 times for the bitumen-rubber-PPA, 1.6 for the bitumen-rubber, 1.9 for the bitumen-rubber-oil, 2.1 for the bitumen-rubber-oil-PPA-2 and 2.4 for the bitumen-rubber-oil-PPA-1. Compared with the stiffness increase of the pure bitumen (1.6 times at 0.01 rad/s and 1.3 at 10 rad/s), the stiffness increase shown by all the bitumen-rubber binder is higher. Such results can not discredit the application of the bitumen-rubber binder or even its additivation with extender oil, as it presents additional rheological advantages that compensate the higher aging susceptibility observed for the samples evaluated here.

Table 2: How much G* increased or decreased and how many degrees δ increased or decreased due to the short-term aging, at 25ºC

frequency (rad/s)	Bitumen-rubber		Bitumen-rubber-ppa		Bitumen-rubber-oil		Bitumen-rubber-oil-ppa-1		Bitumen-rubber-oil-ppa-2	
	G*	δ	G*	δ	G*	δ	G*	δ	G*	δ
10^{-6}	-	-2.4	-	-8.3	-	-	-	-0.9	-	-
10^{-5}	3.8	-14.5	6.4	-12.9	5.1	-0.2	7.5	-5.2	5.9	-2.4
10^{-4}	4.5	-17.3	4.6	-11.6	8.8	-18.0	10.3	-7.0	6.7	-10.5
10^{-3}	3.4	-10.7	2.9	-7.8	7.0	-21.6	6.6	-7.5	5.5	-13.2
10^{-2}	2.4	-8.9	2.1	-4.3	4.6	-15.0	4.2	-6.0	3.9	-11.9
10^{-1}	1.8	-5.1	1.8	-5.3	3.3	-9.4	2.9	-6.2	3.0	-8.0
10^{0}	1.8	-1.6	1.6	-4.6	2.2	-4.9	2.6	-2.5	2.6	-7.8
10^{1}	1.6	-5.8	1.4	-1.2	1.9	-5.0	2.4	-4.5	2.1	-5.9
10^{2}	1.4	-7.2	1.3	-2.4	1.6	-3.9	1.7	-6.9	1.7	-5.7
10^{3}	1.2	-9.5	1.2	0.0	1.4	-4.7	1.6	-7.2	1.4	-4.8
10^{4}	1.1	-8.8	1.1	1.8	1.3	-3.2	1.4	-6.1	1.3	-2.7
10^{5}	-	-6.6	-	3.1	-	-1.1	-	-	-	-1.0
10^{6}	-	-	-	-	-	-	-	-	-	0.5

In terms of phase angle (Table 2), the poor fitting of the phase-angle master-curves does not give a clear vision of the aging effect on the mixtures. The only aspect that it is possible to observe is the elasticity increase expressed by the reduction of the phase-angle values, that is more expressive in the region of low frequencies and less expressive in the region of intermediate frequencies. Such an increase caused by the short-term aging affects positively the resistances to rutting, to fatigue and to thermal cracking, as these resistances are always improved when the materials become more elastic.

The increment of G* varies with the test temperature and also suffers the influence of frequency, as can be observed from Table 3. At the rutting temperature, the average values, at 0.1 and 10 rad/s, are, respectively: 5.1 and 3.2 for the bitumen-rubber-oil-PPA-1, 4.3 and 2.4 for the bitumen-rubber-PPA, 3.7 and 2.9 for the bitumen-rubber-oil-PPA-2, 3.1 and 2.5 for the bitumen-rubber-oil and 3.0 and 2.2 for the bitumen-rubber. According to this ranking, the bitumen-rubber-oil-PPA-1 is the most sensitive to aging and the bitumen-rubber the less sensitive. The stiffness increase of the pure bitumen (1.7 and 1.6 times at the two frequencies) is inferior to the values obtained for the bitumen-rubber binders. The increase of the loading frequency minimizes the stiffness increase caused by the short-term aging. In practice, the stiffness increase suffered by the mixtures is higher at low traffic speed: it ranges from 3 to 5 times at 0.1 rad/s and from 2 to 3 times at 10 rad/s, corresponding to an average increase of around 46%.

Table 3: Changes of G*, δ, G*/sinδ and G*.sinδ, due to the short-term aging, at 0.1 and 10 rad/s (0.1/10)

Sample name	temperature (°C)							
	4	16	28	40	52	64	76	88
G* [how much increased or decreased]								
Bitumen-rubber	1.4/1.1	1.8/1.3	2.0/1.6	2.5/1.7	3.3/1.8	3.3/2.1	2.8/2.4	2.4/2.4
Bitumen-rubber-PPA	1.4/1.1	1.7/1.3	1.9/1.5	2.3/1.6	3.1/1.7	4.8/2.1	5.6/2.6	3.6/3.0
Bitumen-rubber-oil	2.3/1.6	2.8/2.2	3.4/2.5	4.3/2.4	4.0/2.1	3.4/2.6	2.7/2.8	2.3/2.7
Bitumen-rubber-oil-PPA-1	2.0/1.6	2.2/1.9	2.6/2.0	3.4/2.0	5.6/2.4	6.5/3.1	5.1/3.7	3.4/3.7
Bitumen-rubber-oil-PPA-2	2.0/1.4	2.7/1.8	3.5/2.3	3.8/2.4	4.7/2.7	3.9/2.9	3.3/3.0	3.0/2.8
δ [how many degrees increased or decreased]								
Bitumen-rubber	-5.5/-2.2	-3.9/-4.6	-7.5/-3.8	-11.4/-3.7	-12.6/-8.5	-4.0/-11.7	-0.2/-9.6	0.4/-6.8
Bitumen-rubber-PPA	-4.7/-2.0	-4.1/-4.2	-6.0/-4.0	-10.9/-4.1	-13.6/-6.5	-15.9/-11.8	-8.4/-16.4	1.8/-14.3
Bitumen-rubber-oil	-6.9/-5.3	-4.1/-7.2	-12.3/-3.5	-17.7/-5.5	-11.9/-9.1	-1.8/-12.3	2.8/-10.3	3.1/-7.5

Bitumen-rubber-oil-PPA-1	-4.5/-3.4	-3.5/-4.5	-10.3/-2.9	-16.4/-5.0	-18.1/-11.0	-9.4/-17.2	-1.5/-16.4	1.3/-11.5
Bitumen-rubber-oil-PPA-2	-8.5/-4.8	-7.0/-8.0	-11.1/-6.9	-10.8/-6.9	-7.5/-9.9	-1.3/-9.6	-0.1/-6.9	-0.1/-4.0
G*/sinδ e G*.sinδ [how much increased or decreased]								
	G*.sinδ				**G*/sinδ**			
Bitumen-rubber	1.3/1.1	1.7/1.2	1.9/1.6	2.3/1.6	3.6/1.9	3.3/2.3	2.8/2.4	2.4/2.4
Bitumen-rubber-PPA	1.2/1.1	1.6/1.2	1.7/1.4	2.0/1.5	3.5/1.9	5.3/2.4	5.8/3.0	3.6/3.3
Bitumen-rubber-oil	2.1/1.5	2.7/2.0	3.0/2.4	3.8/2.2	4.2/2.3	3.4/2.8	2.7/2.9	2.3/2.8
Bitumen-rubber-oil-PPA-1	1.9/1.5	2.1/1.7	2.3/1.9	2.9/1.9	6.3/2.7	6.7/3.6	5.1/4.1	3.4/3.9
Bitumen-rubber-oil-PPA-2	1.8/1.2	2.6/1.6	3.2/2.2	3.7/2.3	4.8/2.9	3.9/3.1	3.3/3.0	3.0/2.8

At the fatigue temperatures (Table 3), the average values, at 0.1 and 10 rad/s, are, respectively: 3.2 and 2.2 for the bitumen-rubber-oil, 3.0 and 2.0 for the bitumen-rubber-oil-PPA-2, 2.6 and 1.8 for the bitumen-rubber-oil-PPA-1, 1.9 and 1.5 for the bitumen-rubber and 1.8 and 1.4 for the bitumen-rubber-PPA. According to such a ranking, the bitumen-rubber-oil is the most sensitive to aging and the bitumen-rubber-PPA is the less sensitive. The stiffness increase of the pure bitumen at these two frequencies is 1.4 and 1.2 times, indicating that the bitumen-rubber binders are more sensitive to aging than the pure bitumen. As observed at the rutting temperatures, the increase of the loading frequency minimizes the hardening caused by aging. In practice, the stiffness increase suffered by the mixtures is higher at low traffic speed: it ranges from 3.2 and 1.8 times at 0.1 rad/s and from 2.2 and 1.4 times at 10 rad/s, corresponding to an average increase of around 42%.

The observed reduction of the phase-angle values (Table 3) from 52 to 88ºC at 0.1 rad/s ranges from 2 to 9 degrees and at 10 rad/s it ranges from 8 to 14 degrees, corresponding to average values of respectively 4.9 and 10.6 degrees. At the temperatures from 40 to 4ºC, the reduction of the phase-angle values varies from 6 to 10 degrees at 0.1 rad/s and from 4 to 7 degrees at 10 rad/s, corresponding to average values of respectively 8.3 and 4.6 degrees. These changes are relatively small, but they are higher at 10 rad/s at the rutting temperatures and at 0.1 rad/s at the fatigue temperatures. For both cases, the reduction of the phase-angle values is advantageous, but it is relatively more favorable to the rutting resistance when the traffic speed is high and to the fatigue resistance when the traffic speed is low. The reduction of the phase-angle values for the pure bitumen between 52 and 88ºC at these two frequencies is 0.4 and 2.0 degrees and between 40 and 4ºC it is 3.4 and 3.2 degrees.

The average values of the parameter G*/sinδ at 0.1 and 10 rad/s (Table 3) are, respectively, 5.4 and 3.6 for the bitumen-rubber-oil-PPA-1, 4.5 and 2.6 for the bitumen-rubber-PPA, 3.7 and 2.9 for the bitumen-rubber-oil-PPA-2, 3.2 and 2.7 for the bitumen-rubber-oil and 3.0 and 2.3 for the bitumen-rubber. The stiffness increase of the pure bitumen (1.7 and 1.6 times at the two frequencies) is inferior to the values obtained for the bitumen-rubber binders. Similarly to the conclusions observed for the G* increase, the bitumen-rubber-oil-PPA-1 is the most sensitive to aging and the bitumen-rubber is the less sensitive. Although both mixtures show the same PG grade (PG 76-xx), the bitumen-rubber modified with shale-oil residue and PPA is more sensitive to aging because of the high oil proportion. The increase of the rutting parameter is higher at low traffic speed: it ranges from 3.0 and 5.4 times at 0.1 rad/s and between 2.3 and 3.6 times at 10 rad/s, corresponding to an average increase of around 41%.

The fatigue parameter of the Superpave specification must be monitored using long-term aged samples, but it is used here only as an element to evaluate the effect of the short-term aging at the range of temperatures where fatigue cracking occurs. The average values of the fatigue parameter, at 0.1 and 10 rad/s, are respectively: 2.9 and 2.0 for the bitumen-rubber-oil, 2.8 and 1.8 for the bitumen-rubber-oil-PPA-2, 2.3 and 1.7 for the bitumen-rubber-oil-PPA-1, 1.8 and 1.4 for the bitumen-rubber and 1.6 and 1.3 for the bitumen-rubber-PPA. According to such a ranking, the bitumen-rubber-oil is more sensitive to aging and the bitumen-rubber-PPA is the less sensitive. The stiffness increase of the pure bitumen at these two frequencies (1.4 and 1.2 times) is inferior to those observed for the bitumen-rubber binders. Similarly to the conclusions obtained for the range of temperatures where rutting occurs, the increase of the loading frequency minimizes the stiffness increase caused by aging. The hardening suffered by the mixtures is higher at low traffic speed: it ranges between 2.9 and 1.6 at 0.1 rad/s and between 2.0 and 1.3 times at 10 rad/s, corresponding to an average increase of 38%.

Table 4 presents the values for mass loss obtained from the short-term aging procedure. All the mixtures showed an increase of the loss mass because of the additivation, as the mass loss of the pure bitumen was 0.15%. Taking a limit for mass loss of 0.5%, only the bitumen-rubber and the bitumen-rubber-PPA are acceptable. Taking a limit of 1.0%, all the formulations would be acceptable. For a limit of 0.8%, only the bitumen-rubber-oi-PPA-1 would be inadequate, because of its high concentration of shale-oil residue and PPA.

Table 4: Mass loss

Sample name	Replicates	Mass loss (%)
Bitumen-rubber	5	-0.26
Bitumen-rubber-ppa	5	-0.38
Bitumen-rubber-oil	4	-0.78
Bitumen-rubber-oil-PPA-1	5	-0.95
Bitumen-rubber-oil-PPA-2	5	-0.56

4. CONCLUSIONS

The following conclusions deserve to be mentioned:

- the short-term aging increases the G* values and decreases the δ values for a wide frequency spectrum;
- the short-term aging makes the bitumen-rubber binders less thermically susceptible, markedly the bitumen-rubber-oil, the bitumen-rubber-oil-PPA-1 and the bitumen-rubber-oil-PPA-2;
- the different aging indices ranked the bitumen-rubber-oil and the bitumen-rubber-oil-PPA-1 as the most sensitive to the short-term aging and the bitumen-rubber and the bitumen-rubber-PPA as the less sensitive to aging, although the pure bitumen is less sensitive than all the bitumen-rubber binders evaluated;
- the short-term aging increases stiffness of about 44% when the traffic speed goes from high to low: the aged bitumen-rubber binders are stiffer for low traffic speed than for high traffic speed; the result is a material more resistant to rutting but not to fatigue in the strain-controlled mode;
- all the bitumen-rubber binders suffered an increase of mass loss in comparison with the pure bitumen;
- taking a limit of 0.5% for the mass loss, only the bitumen-rubber and the bitumen-rubber-PPA are acceptable and for a limit of 1.0%, all the mixtures are acceptable.

Based on the conclusions obtained here, the combination of crumb rubber, shale-oil residue and polyphosphoric acid is a good alternative to produce bitumen-rubbers of enhanced quality. The shale-oil residue plays an important role as extender oil, reducing the mixing and compacting temperatures and allowing the production of bitumen-rubbers with higher rubber proportions but with acceptable viscosity values. The polyphosphoric acid stiffens the bitumen-rubber at the rutting temperatures with small effects on fatigue and thermal cracking resistances, showing an indirect benefit in terms of the reduction of the viscosity of the bitumen-rubber as it allows the use of lower crumb-rubber contents. Users should pay special attention to the local specifications on mass loss, as the shale-oil residue can increase substantially the mass loss if its proportion is inappropriately chosen.

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REFERENCES

Baumgardner, G., Masson, J-F., Hardee, J., Menapace, A., Williams, A. (2005). Polyphosphoric acid modified asphalt: proposed mechanisms. *Association of Asphalt Paving Technologists*, v.74, p.283-305.

Faxina, A. L., Salomon, D. (2010). *Short-term aging of bitumen-rubber binders compounded with extender oil and polyphosphoric acid*. In: 20th Bitumen Meeting. Rio de Janeiro, Proceedings, Brazilian Institute of Petroleum, Gas ans Biofuels - IBP, Rio de Janeiro, p.113-126. [in portuguese]

Faxina, A. L., Fabbri, G. T. P. (2010). *Rheological behavior of bitumen-rubber binders compounded with shale-oil residue and polyphosphoric acid*. In: 24th Congress of Research and Teaching in Transports. Rio de Janeiro, Proceedings - CD, Brazilian Association of Research and Teaching in Transports - Anpet, Rio de Janeiro. [in portuguese]

Fillipis, P., Giavarini, C., Scarsella, M. (1995). Improving the ageing resistance of straight-run bitumens by addition of phosphorus compounds. *Fuel*., v.74, n.6, p.836-841.

Martin, J. V., Baumgardner, G. (2006). *A new method to produce polymer modified asphalt with crumb rubber and polyphosphoric acid: combining recycling and performance*. In: Asphalt Rubber 2006 Conference – Progress through flexibility, Palm Springs, Proceedings, Braga, p.903-930.

Orange, G., Dupuis, D., Martin, J.V. (2004). *Chemical modification of bitumen throught polyphosphoric acid: properties-microstructure relationship*. In: 3rd Eurasphalt & Eurobitume Congress, Viena, Proceedings, CD, p.733-745.

Thomas, K. P., Turner, T.F. (2008). Polyphosphoric-acid modification of asphalt binders. *International Journal of Road Materials and Pavement Design*, v.9, n.2, p.181-205.