Influence of Processing Conditions on the Rheological Behavior of Crumb Tire Rubber-Modified Bitumen

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ABSTRACT: Traditional or technological studies about crumb tire rubber-modified bitumens (CTRMBs) do not provide detailed rheological information. In that way, this article describes the influence of processing conditions on the linear viscoelastic and viscous behaviors of CTRMBs. The results of the study reveal an exponential increase in dissolved/dispersed rubber with processing temperature and, therefore, lower solid content that affect the rheological behavior in different ways. No influence of the processing device was observed, probably due to the fact that processing temperature (180°C) was not high enough to break up the crosslinked network of the rubber. The presence of rubber particles avoids the negative hardening effects observed for unmodified bitumens, resulting in a more flexible binder at low temperature. At high in-service temperature, better rutting resistance would also be expected for CTRMBs. Flow results at 135°C indicates that modified bitumens can satisfy the AASHTO MP1 requirements if high-enough shear rates are reached. All the CTRMBs studied present segregation, due to rubber settling during storage at high temperature, although an increase in processing temperature seems to enhance its stability. The results obtained seem to indicate that the optimum CTRMB processing temperature is 210°C. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1683–1691, 2007

Key words: modified bitumen; binder; asphalt; rheology; crumb rubber; stability

INTRODUCTION

Bitumen, from crude oil distillation process, is a complex mixture of organic compounds that can be classified, according to their polarity, into two main groups: maltenes and asphaltenes. Asphaltenes are high-molecular-weight species that are insoluble in *n*-heptane, whereas maltenes have lower molecular weight and are soluble in this solvent.[1,2]The widespread use of bitumen relies on its remarkable waterproofing and binding properties that makes it adequate for road pavement and roofing applications.[3]

Ideal performance demands that the binder must be able to withstand low temperatures and the resulting thermal stresses that develop pavement shrinks, resist repeated loading and unloading without exhibiting fatigue failure (cracking), withstand loading to prevent permanent deformation (wheel path rutting), and be capable of being placed, compacted, transported, and stored at safe temperatures.[4–7]

However, increased traffic factors such as heavier loads, higher traffic volume, and high tire pressure have tightened pavements specifications, and consequently, new materials with improved mechanical properties have been developed. The addition of virgin polymers to bitumen is nowadays a good way to obtain modified bitumens with improved properties. In that sense, a large number of papers focused on the use of these polymeric modifiers, like thermoplastic elastomers, polyethylene, block copolymers, etc., have been published.[5,6,8,9] However, the high cost of these materials related to bitumen increases the price of the resulting binder and limits the maximum amount of polymer, making the recycled polymers an interesting alternative from both economical and environmental perspectives.[10] In this sense, powdered rubber, from discarded tires, is one of the most interesting alternatives, since the European legislation prohibited all landfill of scrap tires by 2006.[11] Thus, an extensive study on the use of ground tire rubber in asphalt binders has been performed, pointing out the improved mechanical properties of the binder and the resulting asphalt mixes.[12–16] These improved benefits include increased fatigue life or fatigue resistance, reduced reflective cracking and low temperature cracking, improved tensile strength, ductility, toughness, adhesion, resilience, tenacity, durability, skid resistance, and finally resistance to rutting.[14–16] However, the existing literature regarding crumb tire rubber modifiers in bituminous binders has been focused on using either conventional binder testing procedures or the Superpave protocol.[12–16] It is

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believed that Superpave binder specifications cannot be extended to all modified binders, since certain simplifications used in the current specification cannot estimate their contribution to pavement performance under different traffic and pavement structure conditions.[17] In this sense, a more detailed study of the rheological properties of crumb tire rubber-modified bitumens (CTRMBs) is necessary to understand the binder microstructure and performance in a wide range of frequencies and temperatures.

As has been previously reported, the rheological properties of CTRMBs are largely influenced by different factors such as rubber concentration, particle size, rubber-grinding method bitumen composition, processing conditions, etc.[18–24] As a consequence, the main objective of this article was to study the influence that several processing devices and curing temperatures exert on the rheological and morphological characteristics of the resulting CTRMB. Additionally, the high temperature storage stability of CTRMBs was also evaluated.

EXPERIMENTAL

A 60/70 penetration grade bitumen, donated by Construcciones Morales SA (Spain), was used as a base material for all the experimental mixes. As a modifying agent, a powdered waste rubber, donated by Alfredo Mesalles SA (Spain), derived from discarded tires without metallic and textile contaminants was utilized. This crumb rubber was obtained by grinding tires at ambient temperature and subsequent size classification by screening, having a mean particle size of 0.35 mm. Some compositional characteristics of the crumb rubber used are shown in Table I.

CTRMBs were prepared by mixing crumb rubber (9 wt %) with base bitumen, at different selected temperatures (between 90 and 250°C), for 1.5 h. Two different homogenizers were used: a lab-scale mixing device and a pilot plant rotor–stator device. The pilot plant device incorporates a rotor–stator mixer SD41 SUPER-DISPAX from IKA (Germany) and operates at 8200 rpm and a processing temperature of 180°C. The lab-scale blends were mixed in a low-shear batch mixer using a stirring motor (RW20) from IKA (Germany) and different stirrers: a four-blade impeller, at a rotational speed of 1200 rpm; and an anchor stirrer and a helical stirrer at a rotational speed of 100 rpm. After processing, all the samples were immediately stored at -5°C, to avoid phase separation.

TABLE I
Compositional Characteristics of the Fresh Crumb Rubber Used Non-processed

Material	wt %
Total rubber hydrocarbon (natural and synthetic rubber)	50
Carbon black	32
THF extractable	11
Ash	4

Blank samples, i.e., bitumen processed without crumb rubber, were also obtained from both lab and pilot plant devices at 180 and 250°C (Bitumen-180, Bitumen-250).

Asphaltene content of unmodified bitumens was analyzed by the procedure outlined in ASTM D 3279-97. The remaining solid rubber after processing was determined by a filter test described in a previous paper.[25]

Linear viscoelastic and viscous flow measurements were performed using a CS-rheometer, RheoStress RS150, from HAAKE GBR (Germany). Frequency sweep (0.01–100 rad/s) tests were carried out at constant temperature (between -10 and 75°C), within the linear viscoelastic range, using a serrated plate-and-plate geometry (10 and 20 mm diameter, 1–3 mm gap). Viscous flow measurements were performed at 50 and 135°C with a serrated plate-and-plate geometry (30 and 35 mm diameter, 1–3 mm gap).

Previously, different studies concerning wall effects (influence of the ratio between plate-and-plate gap and particle size) were performed. Thus, different gaps with parallel plates (1–3 mm) and mixing rheometry geometries (vane and helical ribbon) were used. At temperatures below the settling point of the particles, viscous flow tests conducted with wide plate-and-plate gaps showed viscosity values similar to those obtained with vane geometries, where wall effects are not significant.

The morphology of the resulting CTRMBs was studied by optical microscopy. A LTS-350 Heating-Freezing Stage, manufactured by Linkam Scientific Instruments (UK), coupled to a standard Olympus BX51 microscope, from Olympus Optical (Japan), was used. Samples were placed on the hot stage of the device at 75°C.

Storage stability was evaluated by a test procedure developed in our laboratory, storing vertically samples in cooper tubes, at 180°C, for 12 h. More detailed information on this method can be found elsewhere.[19] The storage stability was followed by carrying out frequency sweep tests in the linear viscoelasticity range, at 50°C, on samples taken at different heights (0, 10, 20, and 30 cm) of the testing tube.

RESULTS AND DISCUSSION

Although bitumen rheological thermosimplicity is quite controversial,[26–28] empirical master curves of the linear viscoelasticity functions, as a function of frequency, may be obtained when the values of tan δ versus complex modulus for bitumen, at different temperatures, match on a unique curve,[20] giving a clear insight on its behavior in a wider range of time

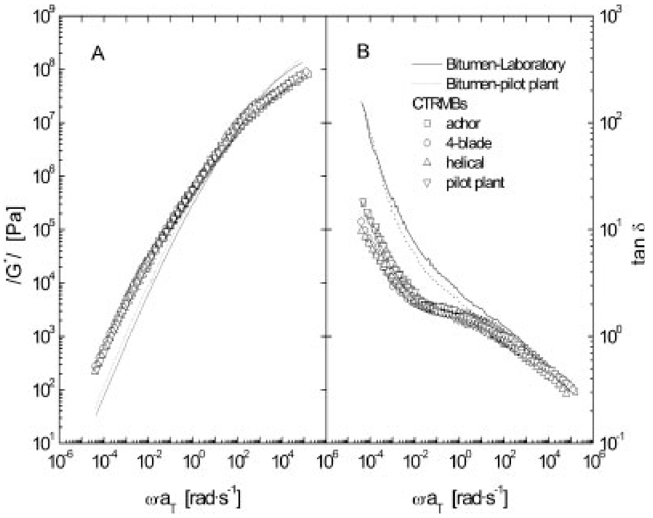

Figure 1 Master curves of the complex shear modulus (A) and loss tangent (B) for unmodified bitumen and CTRMBs processed in different devices at 180°C (reference temperature: 25°C).

and temperature. Thus, as can be seen in Figures 1 and 3, the frequency dependence of the linear viscoelastic functions of the different neat and modified bitumen studied, obtained at different temperatures (between −10 and 75°C), can be empirically superposed onto master curves, at a reference temperature of 25°C, using an empirical shift-factor a_T.

The empirical shift factor always follows an Arrhenius-like dependence with temperature:

$$a_T = \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{1}$$

where T_0 is the reference temperature, 298 K, and E_a is the activation energy. Table II shows the activation energy values estimated from eq. (1). These values are quite similar to those previously reported in the literature for other neat and modified bitumen samples.[29]

Influence of the processing device on the rheology of CTRMBs

Previous results obtained by the authors demonstrated that the addition of 9 wt % crumb tire rubber (mean particle size: 0.35 mm) to a 60/70 penetration grade bitumen (processed at 180°C for 1.5 h) yielded similar rheological characteristics to those obtained by the addition of 3 wt % SBS, a polymer widely used, to the same bitumen.[25] Consequently, these processing conditions were selected to study the influence of the processing device on the rheological characteristics of CTRMBs. Figure 1 shows the evolution of the complex modulus and the loss tangent with frequency, at a reference temperature of 25°C, for modified bitumens processed with different devices. Results from blank samples of unmodified bitumens have been also included in this figure. Negligible differences among the values of both viscoelastic functions for CTRMBs processed in different devices are observed. These results can be explained taking into account that all the samples have the same amount of dissolved/dispersed rubber (Table III). Consequently, similar in-service behavior is expected for the samples studied, independent of the selected processing device.

On the other hand, when modified and unmodified bitumen samples are compared, it is clearly noticed that the addition of rubber leads to an increase in the complex modulus values in the low frequency region and also to a slight decrease in the high frequency zone. Upon the Strategic Highway Research Program (SHRP) reports, this linear viscoelasticity function is related to major distress modes in road pavements, and represents a measure of the total resistance of a material to deformation when exposed to repeated pulses of shear stress and can be directly related to the stiffness of the material.[30,31] Thus, CTRMBs become harder at high temperatures and more flexible at low temperatures, and consequently, improved in-service behavior should be expected.

TABLE II
Activation Energies and Zero-Shear-Rate-Limiting Viscosities, at 25°C, for Non-modified Bitumens and CTRMBs Manufactured at Different Processing Conditions

Sample	Process device	Process temperature (°C)	E_a (kcal/mol)	η_0 (Pa s)
Neat bitumen	–	–	139	1.227×10^5
Bitumen-180	Laboratory 4-blade	180	142	1.765×10^5
Bitumen-250	Laboratory 4-blade	250	150	4.048×10^5
CTRMB	Pilot plant	180	146	1.92×10^6
CTRMB	Laboratory anchor	180	150	1.489×10^6
CTRMB	Laboratory helical	180	148	1.380×10^6
CTRMB	Laboratory 4-blade	180	148	1.750×10^6
CTRMB	Laboratory 4-blade	90	150	3.380×10^5
CTRMB	Laboratory 4-blade	120	149	4.490×10^5
CTRMB	Laboratory 4-blade	210	150	1.175×10^6
CTRMB	Laboratory 4-blade	250	146	1.180×10^6

TABLE III
Solubilized Rubber Percentage in the Modified Bitumen Samples Studied

Sample	Processing device	Processing temp. (°C)	% solubilized
Raw rubber			11
CTRMB	Pilot plant	180	15
CTRMB	Laboratory anchor	180	15
CTRMB	Laboratory helical	180	15
CTRMB	Laboratory 4-blade	180	15
CTRMB	Laboratory 4-blade	90	11
CTRMB	Laboratory 4-blade	120	11
CTRMB	Laboratory 4-blade	210	25
CTRMB	Laboratory 4-blade	250	45

On the other hand, as can be observed in Figure 1(B), a significant reduction in the loss tangent values is observed for CTRMBs, mainly in the low frequency range. This fact indicates an important increase in binder elasticity, which significantly contributes to the improvement of the high temperature properties of the resulting asphalt. Additionally, at intermediate frequencies, a pseudoplateau in tan δ is clearly noticed for modified bitumens, suggesting some microstructural changes as a consequence of rubber addition. Thus, for unmodified bitumens there is a simple transition from the glassy to the terminal region, whereas for CTRMBs an intermediate region appears as a result of the modification. Given that only a small fraction of the added rubber is dissolved or dispersed during processing, this behavior should be mainly attributed to the presence of undissolved rubber after processing. As previously reported, the rubber particle size used in this study (> 5 μm) can be considered large enough to exclude the possibility of any colloid-chemical activity and neglect Brownian motion, so that the observed rheological behavior must be explained in terms of hydrodynamical/mechanical interactions between particles in the bituminous phase.[20,25,32]

The dynamic linear viscoelastic behavior of these systems may be described by a generalized Maxwell model:

$$/G^*/ = \sqrt{\left(G_e + \sum_{i=1}^{N} G_i \frac{(\omega\lambda_i)^2}{1+(\omega\lambda_i)^2}\right)^2 + \left(\sum_{i=1}^{N} G_i \frac{\omega\lambda_i}{1+(\omega\lambda_i)^2}\right)^2} \tag{2}$$

$$\tan\delta = \frac{\Sigma_{i=1}^{N} G_i \frac{\omega\lambda_i}{1+(\omega\lambda_i)^2}}{G_e + \Sigma_{i=1}^{N} G_i \frac{(\omega\lambda_i)^2}{1+(\omega\lambda_i)^2}} \tag{3}$$

where G_e is the elastic modulus. For the sake of clarity, the recalculated viscoelastic functions have not been included in Figure 1.

This model considers a superposition of a series of N independent relaxation processes, each process having a relaxation time λ_i and a relaxation strength G_i. The resulting distribution or spectrum of relaxation times may be used to obtain the zero-shear-limiting viscosity of the material, η_0, as follows:

$$\eta_0 = \sum_{i=1}^{N} G_i \lambda_i \tag{4}$$

The values of η_0 estimated from eq. (4), at 25°C, are presented in Table II. As expected, the zero-shear-rate-limiting viscosity values of the CTRMBs processed at 180°C are quite similar. On the contrary, they are much higher than those corresponding to unmodified bitumen samples.

On the other hand, the shear rate dependence of viscosity, at 50°C, for the aforementioned unmodified bitumen and CTRMBs samples is presented in Figure 2. As can be observed, all the flow curves show an apparent limiting viscosity in the low shear rate range, η_0, followed by a power-law decrease in viscosity. The Carreau model fits these flow curves fairly well.

$$\eta = \frac{\eta_0}{\left(1 + (\lambda_c \dot{\gamma})^2\right)^{(1-n)/2}} \tag{5}$$

where η_0 is the zero-shear-rate limiting viscosity, n is a dimensionless parameter, $n - 1$ being the slope of the shear-thinning region, and λ_c is a characteristic time of the material, defined as $\lambda_c = 1/\dot{\gamma}_c$, where $\dot{\gamma}_c$ is the critical shear rate for the onset of this intermediate region. The values of the Carreau parameters are presented in Table IV.

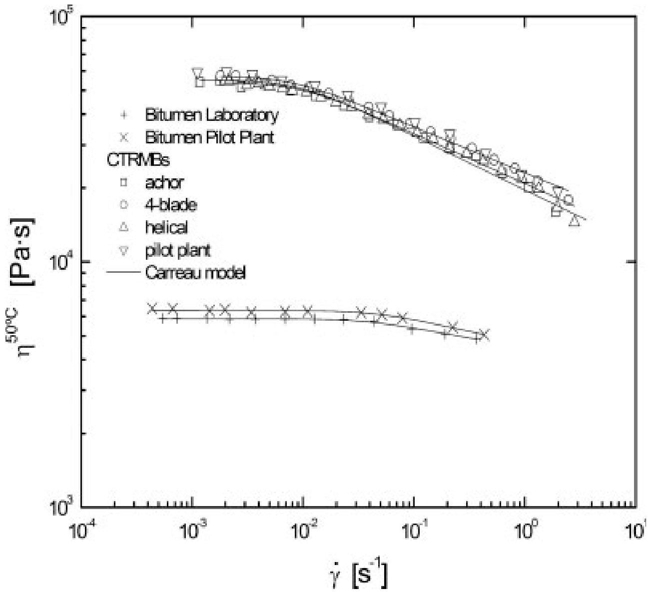

Figure 2 Viscous flow curves, at 50°C, for unmodified bitumen and CTRMBs processed in different devices at 180°C.

TABLE IV
Influence of Processing on Carreau's Model Parameters, at 50°C, for Unmodified Bitumen and CTRMBs

Sample	Processing device	Processing temp. (°C)	η_0 (Pa s)	λ_c (s)	n
Bitumen	Neat	–	4.65×10^3	6.6	0.904
Bitumen	Laboratory 4-blade	180	5.88×10^3	27.4	0.916
Bitumen	Pilot plant	180	6.35×10^3	22.2	0.899
Bitumen	Laboratory 4-blade	250	1.96×10^4	805	0.936
CTRMB	Pilot plant	180	5.88×10^4	91.5	0.788
CTRMB	Laboratory anchor	180	5.51×10^4	109	0.780
CTRMB	Laboratory helical	180	5.38×10^4	105	0.796
CTRMB	Laboratory 4-blade	180	5.65×10^4	112	0.809
CTRMB	Laboratory 4-blade	90	2.75×10^4	116	0.859
CTRMB	Laboratory 4-blade	120	3.05×10^4	114	0.854
CTRMB	Laboratory 4-blade	210	5.33×10^4	99	0.787
CTRMB	Laboratory 4-blade	250	4.97×10^4	102	0.804

At this temperature, 50°C, CTRMBs show, once again, similar viscosity values, as a consequence of comparable rubber digestion levels.

As can also be observed, rubber addition to bitumen has different effects on Carreau's model parameters. Thus, an increase in viscosity is noticed, a fact that may favor an increase in the rutting resistance of the blends.[33,34] On the other hand, a change in the viscous behavior is shown, since rubber addition produces a remarkable decrease in n and, therefore, an increase in the slope of the shear-thinning region. In addition, λ_c clearly increases for CTRMBs and, consequently, the Newtonian region is shifted to lower shear rates when compared with unmodified bitumens.

Finally, it is worth pointing out that, although there is no influence of the processing device characteristics on the rheological behavior of CTRMBs, some differences are observed for unmodified bitumens. Thus, samples processed in the pilot plant device display larger viscosity values at 50°C than those processed at lab scale. This is related to an enhanced bitumen oxidation in the pilot plant device that yields an increase in asphaltene content (Table V).[35,36]

Influence of processing temperature on the rheology of CTRMBs

Empirically superposed master curves of unmodified bitumen and CTRMBs samples processed, at different temperatures, in a lab-scale device with a four-blade impeller are portrayed in Figure 3. As can be observed, an increase in processing temperature does not qualitatively change the linear viscoelastic behavior of unmodified bitumen, although the complex shear modulus values increase and the loss tangent is shifted to lower values in the whole experimental frequency window. The increase in $/G^*/$ can be considered as a hardening process as a consequence of processing (primary aging). Bitumen ageing is a very complex process that produces a variation of both chemical composition and colloidal structure.[35,36] The increase of asphaltene content, reported in Table IV, as a consequence of processing would explain these effects.

On the contrary, processing temperature has a more complex influence on the linear viscoelasticity functions of CTRMBs. Thus, an increase in processing temperature from 90 to 120°C yields higher $/G^*/$ values in the low frequency region, while a further increase in temperature up to 250°C results in lower values of this viscoelastic function. On the contrary, in the high frequency region, the sample processed at 250°C shows the highest $/G^*/$ values, while they are minimum for the sample processed at 210°C.

On the other hand, Figure 3(B) demonstrates that tan δ shifts to lower values as CTRMB processing temperature increases, above all at low frequencies, which indicates an increase in binder elasticity. Furthermore, a remarkable enhancement of the pseudoplateau region in tan δ at intermediate frequencies, and a decrease in its values in the low-medium frequency region are observed for CTRMBs processed at temperatures higher than 120°C. This result is somehow surprising and seems to indicate some microstructural changes related to tire digestion in the resulting binder as a consequence of processing.

Figure 4 shows the values of the complex modulus (at −10 and 75°C, and 10 rad/s) as a function of binder processing temperature. As can be noticed, an increase in processing temperature for unmodified bitumen and CTRMBs generally gives rise to higher values of $/G^*/$, at 75°C, although almost constant val-

TABLE V
Asphaltene Content for Unmodified Bitumen as a Function of Processing Conditions

Process temp. (°C)	Processing device	% asphaltenes
Neat bitumen	–	20.2
180	Laboratory 4-blade	21.2
180	Pilot plant	21.9
250	Laboratory anchor	23.8

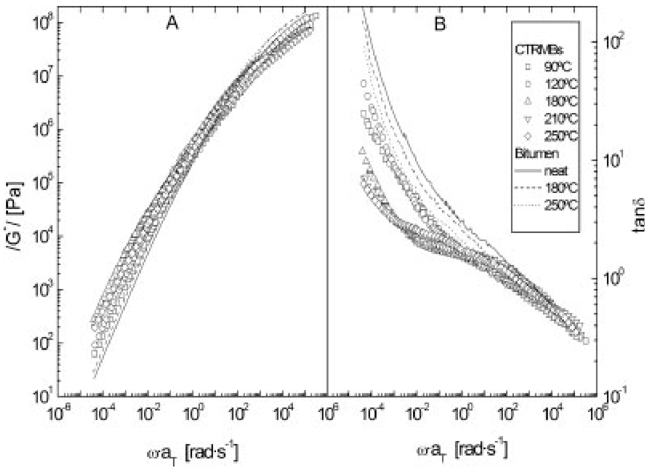

Figure 3 Master curves of the complex shear modulus (A) and loss tangent (B) for unmodified bitumen and CTRMBs processed, at different temperatures, in a lab-scale device with a four-blade impeller (reference temperature: 25°C).

ues are apparent for CTRMBs for processing temperatures higher than 180°C. In this sense, an increase in complex modulus values in the high in-service temperatures range causes enhanced rutting resistance of the resulting pavement.[5,37] In addition, the behavior at low in-service temperatures must also be taken into consideration, since an increase in /G*/ makes the binder less flexible and more fragile, and more susceptible to develop thermal cracking.[6] Thus, at −10°C, a continuous increase in the complex modulus values with processing temperature is observed for unmodified bitumen, whereas the values of this linear viscoelasticity function for CTRMBs pass through a minimum for the sample processed at 210°C. It is worth mentioning that, above 90°C, CTRMBs show lower values of /G*/ at −10°C than unmodified bitumen, and the differences are more pronounced as processing temperature increases. Consequently, high processing temperatures cause negative effects on the performance of unmodified bitumen, while on the contrary, the addition of crumb rubber induces better in-service properties at both low and high temperatures. The results obtained seem to indicate that the optimum CTRMB processing temperature is 210°C.

Figure 5 shows the viscous flow behavior, at 50°C [Fig. 5(A)] and 135°C [Fig. 5(B)], for unmodified bitumen and CTRMBs manufactured at different processing temperatures. Figure 5(A) demonstrates that an increase in processing temperature always yields higher viscosity values, at 50°C, for unmodified bitumen, above all at 250°C, although they are inferior to those corresponding to CTRMBs processed at any temperature between 90 and 250°C. Similarly, an increase in CTRMB processing temperature up to 180°C gives rise to higher viscosity values at 50°C. However, viscous flow curves are slightly shifted to lower values for CTRMBs processed at higher processing temperatures. The Carreau model fits the experimental flow curves fairly well. As can be seen in

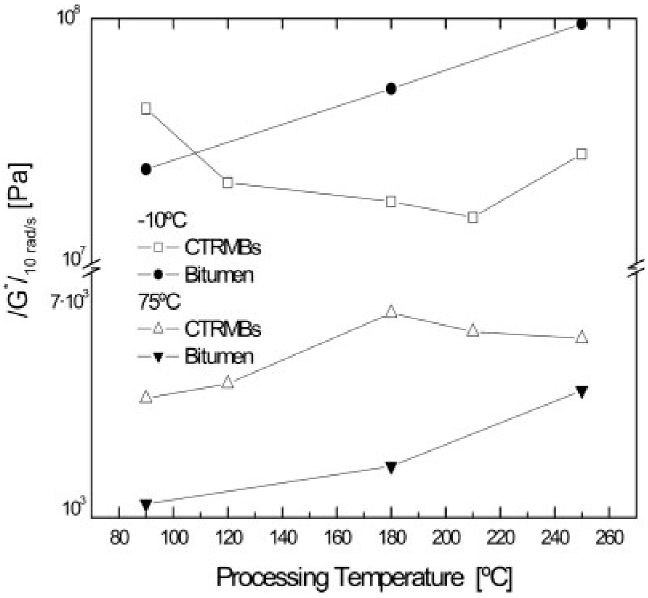

Figure 4 Evolution of the complex shear modulus (at −10 and 75°C, and 10 rad/s) with processing temperature for unmodified bitumen and CTRMBs.

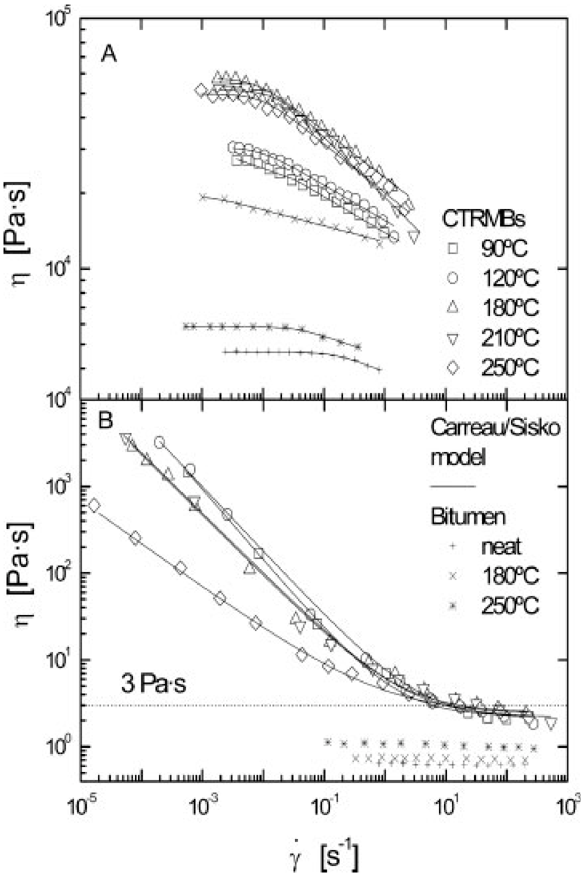

Figure 5 Viscous flow curves, at 50°C (A) and 135°C (B), for CTRMBs processed at different temperatures.

TABLE VI
Influence of Processing on Sisko's Model Parameters, at 135°C, for CTRMBs

Sample	Processing device	Processing temp. (°C)	η_∞ (Pa s)	k_s (Pa s)$^{2-n}$	n
CTRMB	Laboratory 4-blade	90	2.25	3.30	0.184
CTRMB	Laboratory 4-blade	120	2.10	5.69	0.255
CTRMB	Laboratory 4-blade	180	2.49	3.69	0.301
CTRMB	Laboratory 4-blade	210	2.28	4.02	0.305
CTRMB	Laboratory 4-blade	250	2.35	2.12	0.497

Table IV, the characteristic time, λ_c, increases with processing temperature, and consequently, the critical shear rate for the onset of the shear-thinning behavior decreases. The values of the exponent n are close to 1 (Newtonian behavior) and slightly increase with processing temperature. Rather different behavior is observed for CTRMBs. Thus, the values of λ_c remain almost constant, and n slightly decreases.

At 135°C, unmodified bitumen is always Newtonian, whereas CTRMBs shows shear-thinning behavior at low and intermediate shear rates, and a clear tendency to a high-shear-rate limiting viscosity [Fig. 5(B)]. Once again, CTRMBs exhibit higher viscosities than unmodified bitumen, as has been reported by other authors.[19,25,38] In addition, an increase in binder processing temperature gives rise to an increase in unmodified bitumen viscosity at 135°C, being the values well below 3 Pa s (limiting values required by AASHTO MP1). On the contrary, CTRMBs viscosity values are above this limiting viscosity at low shear rates. Only at high shear rates, the viscous flow curves tend to approach this value. The viscous behavior of CTRMBs, at 135°C, can be described by the Sisko model:[39]

$$\eta = \eta_\infty + k_s \dot{\gamma}^{n-1} \tag{6}$$

where η_∞, is the high-shear-rate limiting viscosity, k_s is the consistency index, and n is the power law or flow index. As can be observed in Table VI, the parameter n increases with processing temperature, while the high-shear-rate limiting viscosity, η_∞, show quite similar values. From an engineering standpoint, this last result is important, since industrial operations such as pumping, handling, and mixing of bitumen occur in the high-shear-rate range previously mentioned. As has been previously remarked, the existing AASHTO MP1 procedure requires a maximum binder viscosity of 3 Pa s, at 135°C. However, this method has been developed for Newtonian bitumen and is not well defined for highly shear-thinning materials like CTRMBs. Consequently, this criterion may be violated if the asphalt can be pumped and mixed at safe temperatures, i.e., at high shear rates.[25]

Relationship between microstructure and rheology of CTRMBs

As has been mentioned earlier, the rheological behavior of CTRMBs is not influenced by the processing device and impeller geometry used for their manufacture. Conversely, other authors have found a clear dependence of binder properties with the mixer speed.[23] In this sense, as can be observed in Table III, the rubber percentage dissolved/dispersed in the bituminous phase is always quite similar (15%) for all the samples processed at 180°C, whereas the percentage of soluble components in raw rubber is around 11%. Consequently, only about 4% rubber is dissolved or dispersed in the bitumen due to partial depolymerization (breaking of the backbone of the main chain) and devulcanization (cleavage of the sulfur crosslink bonds) of the rubber particles.[23,24] Consequently, the influence of the processing device was not significant, because the temperature (180°C) was not high enough to produce rubber depolimerization/devulcanization to a great extent.[24]

On the contrary, the final properties of CTRMBs are largely dependent on processing temperature. As reported in Table III, the rubber solubilized in the bitumen phase remains constant and equal to the initial value for processing temperatures comprised between 90 and 120°C, and consequently, these conditions are not severe enough to break up the chemically crosslinked network. Thus, the observed rheological behavior would be a consequence of the presence of rubber particles swollen by light components of the maltenic fraction.[13,20,40] By increasing processing temperature, the dissolution/dispersion of rubber into the bitumen is clearly enhanced due to faster rates of breaking crosslink bonds. Then, two different effects influence the rheological properties of the resulting product. The first one is related to the bituminous phase, which is modified by an increased amount of soluble components.[25] The second effect is associated with the remaining solid rubber, whose concentration decreases.[20] Additionally, rubber particles are reduced in size as a consequence of the disgregation process, which also affects the rheological properties of CTRMBs.[19]

The resulting morphology is shown in Figure 6. Dispersed non-dissolved rubber particles are clearly observed for CTRMBs processed at 90, 120, and 180°C. No significant differences are noticed, because of the small differences in the amount of dispersed/solubilized rubber. A rather different morphology appears for binder manufactured at higher processing temperatures, since only a continuous dark phase is

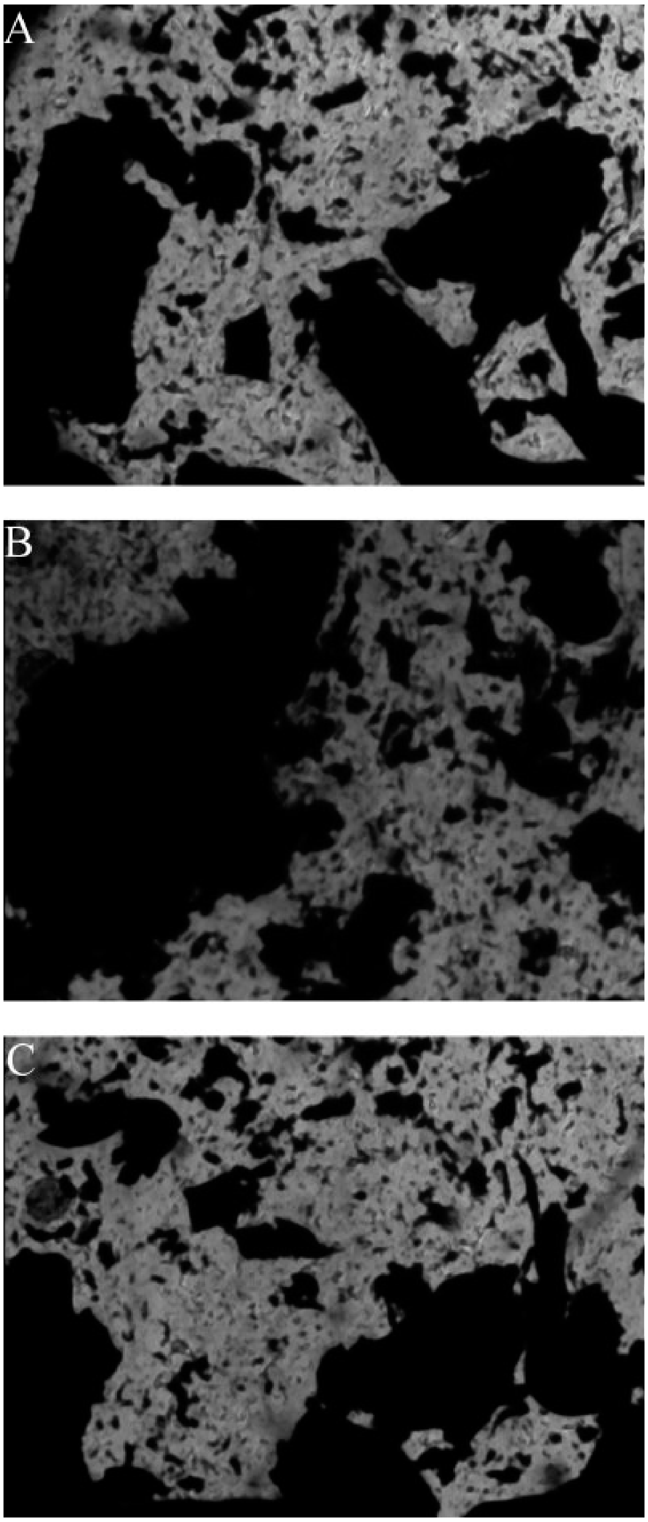

Figure 6 Optical microscopy observations of CTRMBs processed at different temperatures: (A) 90°C; (B) 120°C; (C) 180°C.

seen (data not shown). This fact is probably due to the disgregation of the rubber, which increases the amount of small dispersed particles. Direct observations of a filter paper after filtration tests confirm this fact. Furthermore, these small particles are responsible for a reduction in filtration rate during solid content determination.

The referred morphological changes have opposite effects on the linear viscoelastic behavior of the samples. Thus, rubber solubilization give rise to an increase in elastic and viscous moduli values in the high in-service temperature range,[25] while a reduction in solid content and nonspherical particle size decreases the values of the linear viscoelastic moduli.[19,20] The results obtained seem to indicate that the optimum CTRMB processing temperature is 210°C.

High temperature storage stability of CTRMBs

One of the most important technical problems involving road pavements building is the phase separation or segregation during polymer-modified binder storage at high temperature. It has been found that rubber particle size and concentration are factors that affect the potential for separation of rubber particles in the bitumen during storage.[12,19,20]

In this work, a storage stability index has been defined as the ratio between the value of the elastic modulus, at 0.1 rad/s and 50°C, at the bottom of the settling tube and its corresponding value at 30-cm depth (Fig. 7). A global index of one would indicate that the binder is stable, whereas higher values give clear indications of rubber particle sedimentation. Figure 7 demonstrates that all the samples studied are clearly unstable under the selected storage conditions. However, this figure also shows that an increase in processing temperature from 120 to 210°C yields more stable modified bitumens, whereas a subse-

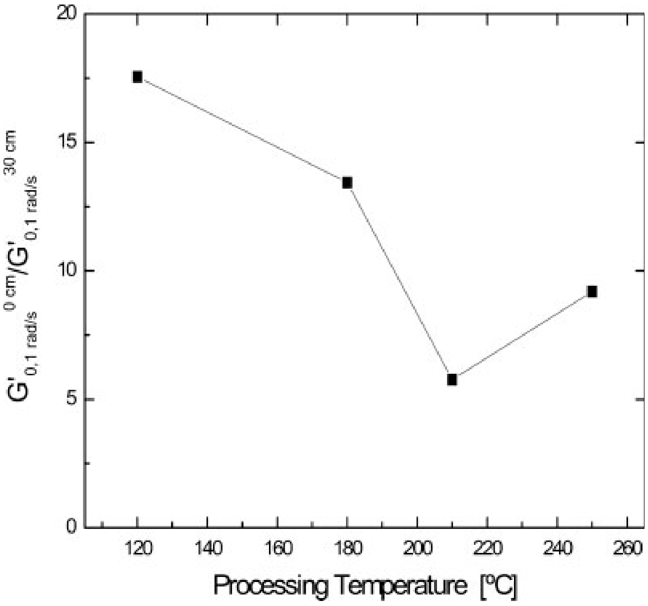

Figure 7 Effect of processing temperature on the storage stability index of the modified binders studied.

quent increase in processing temperature up to 250°C destabilizes the binder.

CONCLUSIONS

The rheological properties of CTRMBs are largely dependent on their manufacturing conditions, specially processing temperature. Thus at low processing temperatures (90 and 120°C), the chemical crosslinked network of the rubber remains practically unaltered, and the corresponding rheological properties are a consequence of the interactions between bitumen and swollen rubber particles. Higher processing temperatures lead to partial depolymerization/devocalization of the network, increasing the amount of components that are incorporated to the bitumen phase and, consequently, reducing both solid concentration and rubber particle size. On the contrary, the processing device and impeller geometry used to manufacture CTRMBs (at 180°C) have an almost negligible influence on the rheology of the modified binders studied. All the CTRMBs studied present segregation, because of rubber settling during storage at high temperature, although an increase in processing temperature seems to enhance its stability. The results obtained seem to indicate that the optimum CTRMB processing temperature is 210°C.

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