Rheological Quantification of Bitumen Aging: Definition of a New Sensitive Parameter

Joana Peralta[1], Loic Hilliou[2]*, Hugo M.R.D. Silva[1], Ana V. Machado[2], Jorge C. Pais[1], Joel R.M. Oliveira[1]

[1] C-TAC – Territory, Environment and Construction Centre, Department of Civil Engineering, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

[2] Institute for Polymers and Composites/I3N, University of Minho, Campus de Azurém 4800-058 Guimarães, Portugal

* Corresponding author: loic@dep.uminho.pt
Fax: x351.253.510.336

Received: 11.6.2010, Final version: 16.9.2010

Abstract:
Bitumen is undoubtedly the most important material in the construction and rehabilitation of flexible road pavements. By increasing the temperature, bitumen changes from brittle solid, to viscoelastic solid and finally to Newtonian fluid. The rheological characteristics of bitumen also vary greatly due to aging, which is a phenomenon initiated in the phases of production and application of bituminous (asphalt) mixtures and continued during the life of road pavements. The aim of this work is to study several rheological parameters in order to evaluate if they are able to quantify the aging of various types of bitumens. Four bitumens from the same distillation column in the refinery, but with different penetration grades, were aged by using the RTFOT method, which simulates the aging of the bitumen during the asphalt mixture production and pavement construction. The original (base) and aged bitumens were characterized with conventional tests used in the paving industry, and the results were compared with the rheological characteristics obtained with small amplitude oscillatory shear tests. Aging was assessed at high temperatures (110 to 180°C) through the activation energy computed from the temperature dependence of the Newtonian viscosity. However, the comparison of the characteristic relaxation times extracted from master curves measured at medium/low temperatures (between 25 to 80°C), proved to be the most sensitive indicator of bitumen aging.

Zusammenfassung:
Asphalt ist unzweifelhaft das wichtigste Material bei der Konstruktion und Ausbesserung von flexiblen Straßenbelag. Durch Temperaturerhöhung geht Asphalt von einem spröden Festkörper, zu einem viskoelastischen Festkörper und schließlich zu einer Newtonschen Flüssigkeit über. Darüber hinaus verändern sich die rheologischen Eigenschaften von Aphalt durch Alterung. Dieses Phänomen wird während der Herstellung und Anwendung der Asphaltmischungen initiiert und setzt sich danach fort. Das Ziel dieser Arbeit ist, verschiedene rheologische Parameter zu untersuchen und ihre Eignung zur Charakterisierung des Alterungsverhalten von Asphalt zu evaluieren. Vier Asphaltmischungen aus derselben Destillationskolonne einer Raffinerie mit unterschiedlichen Eindringwerten wurden mit Hilfe der RTFOT-Methode gealtert. Diese Methode simuliert die Alterung von Aphalt während der Herstellung der Asphaltmischungen und des Straßenbelags. Der Ausgangs- und der gealterte Asphalt wurden mit den üblichen industriellen Versuchen getestet und ihre Resultate mit den Ergebnissen von linear-viskoelastischen Scheroszillationen verglichen. Das Alterungsverhalten wurde bei hohen Temperaturen (110°C bis 180°C) durch die Aktivierungsenergie ermittelt, die aus der Temperaturabhängigkeit der Newtonschen Viskosität bestimmt wurde. Es zeigte sich jedoch, dass der Vergleich der charakteristischen Relaxationszeiten, die aus den gemessenen Masterkurven bei niedrigen und mittleren Temperaturen (zwischen 25°C und 80°C) erhalten wurden, der beste Indikator für die Alterung von Asphalt ist.

Résumé:
Le bitume est sans aucun doute le matériau le plus important pour la réhabilitation et la construction de revêtements routiers flexibles. En chauffant, le bitume passe d'un comportement de solide cassant, à celui d'un solide de viscoélastique et finalement à celui d'un fluide Newtonien. Les caractéristiques rhéologiques du bitume varient grandement avec le vieillissement, qui est un phénomène initié dans les phases de production et d'application des mélanges bitumineux (asphalte), et qui continue durant la vie du revêtement routier. Le but de ce travail est d'étudier les paramètres rhéologiques du bitume qui sont les plus sensibles au vieillissement. Quatre bitumes provenant de la même colonne de distillation mais possédant des grades différents, ont été vieillis au moyen de la méthode RTFOT qui simule le vieillissement du bitume lors de la production du mélange d'asphalte et lors de la construction du revêtement. Les bitumes originaux (base) et âgés ont été caractérisés à l'aide de tests conventionnels utilisés dans l'industrie, et les résultats ont été comparés avec les caractéristiques rhéolo-

© Appl. Rheol. 20 (2010) 63293 DOI: 10.3933/ApplRheol-20-63293

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org

indexes listed in Table 5 both suggest that the index proposed here performs better in quantifying bitumen aging. What will be the reason for this?

The characteristics of a viscoelastic liquid material change with the frequency at which a load is applied. Under a load applied at high frequencies it behaves as a solid, while at low frequencies it may behave as a liquid. A simple example of this viscoelastic behaviour is the Maxwell model [23]. When the penetration test is performed in a bitumen sample, a load (100 g) is applied during a pre-defined period of time (5 s). Consequently, the sample is submitted to a load applied at an equivalent frequency of 0.2 Hz which will capture the material's mechanical intrinsic property at this frequency, provided that linear mechanical excitation, namely small load, is respected. Alternatively, the applied load may result in a non linear mechanical response which will turn any experimental comparison between bitumens a more complex task than simply computing an index from a mechanical response. Regarding the ring and ball test, the deformation of the sample also occurs under stress controlled conditions (the weight of the sphere), and this is obviously performed in the non linear regime since a total strain of 25 mm / 4.4 mm (disk thickness) occurs during the test. In addition, both tests involve a combination of shear and elongational deformations, which contrast with the simple shear field of rotational rheometry (SAOS), thus justifying the higher errors of these empirical tests.

On the other hand, the use of the relaxation times to quantify the aging phenomenon is fully justified and coherent, since this parameter is clearly related to the changes in the colloidal structure of bitumen and stability of asphaltenes, which depends directly on bitumen aging [15]. Lu and Isacsson [11] used traditional, rheological and chemical indexes to quantify bitumen aging and obtained different values, although the bitumen hardening mirrored in the increase in mechanical properties was the result of the chemical changes induced by aging. Hence, the aging susceptibility of bitumen may be ranked differently when different evaluation methods are used. The same range of values were approximately obtained when comparing the values of the ratios of the different parameters studied in this work, for a wide range of temperatures, with a previous rheological study on bitumen aging [11]. The aging index, proposed in that study (based in other rheological and empirical parameters [11]), was usually lower than 2. Thus, the present results indicate that the aging index based on the relaxation times observed in the master curves (after and before aging) is the most sensitive parameter to quantify bitumen aging, since the computed values exceed the ratio of 5 (Table 1).

Finally, the parameters that should be used to quantify aging must be based on the mechanical dependence rather than on the thermal dependence of any viscoelastic function, since the objective of the aging study is to determine the behaviour of the bituminous mixtures in the pavement. Actually, bituminous mixtures applied in road pavements are subjected to significantly larger ranges of applied loads and frequencies than to temperature variations, and generally viscoelastic parameters have low sensitivity to thermal variations.

4 CONCLUSIONS

Any study of bitumen composition and behaviour is a very complex task, since bitumen varies significantly according to its origin and processing of the crude oil. Therefore, the results presented above may not be applicable to all paving grade bitumens. As such, the present study should be applied to a wider set of bitumens (especially materials for which TTS is not valid) as to definitely claim about the usefulness of the proposed aging index. The chemical analysis of bitumens used here before and after aging is also under way, in order to seek for correlations between the proposed aging index and the asphaltene content or, to a larger extent, between the aging index and variations in the content of saturates, aromatics, resins and asphaltenes. Such analysis will help rationalizing the efficiency of the aging index. The main conclusions drawn from this study are the following:

- For the bitumen studied in the temperature ranges tested, it was found that the Arrhenius equation is the one that best describes the thermal dependence of rheological functions, both at service temperatures, using shift factors, a_T, and at production and application temperatures, using the zero shear viscosity, η_o.
- The changes in the temperature dependence of the rheology of bitumen after aging, measured by comparing the activation energy, E_a, values of

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org

the studied bitumens (determined by analysis of η_o), before and after aging, were significant. However, these changes were quantitatively very similar for all tested bitumen (both aged and base). As such, using the thermal dependence of any viscoelastic function will not be an efficient method to quantify the aging.

- The most significant changes in the rheological behaviour due to aging were observed when comparing the relaxation times, τ, obtained from master curves of bitumen before and after aging, at service temperatures.
- The aging index assessed by the relaxation times is also more effective than the indexes obtained through the empirical tests (penetration, ring and ball and apparent viscosity) typically used by the road paving industry to characterize bitumen aging.
- Data taken from the literature and encompassing bitumens from a different origin, also show the same trend, namely that the proposed index for aging is effective in quantifying and discriminating betweens bitumens (see Table1). We note here that the aging index was computed at a single temperature (25°C), without relying on TTS.

REFERENCES

[1] Dongré R, Youtcheff J, Anderson DA: Better roads through rheology, Appl. Rheol.6 (1996) 75 – 82.

[2] Glover IC: Wet and Dry Aging of polymer-asphalt blends: chemistry and performance, PhD Thesis, Louisiana State University and Agricultural and Mechanical College – Department of Chemistry (2007).

[3] Stangl K, Jäger A, Lackner R: The effect of styrene-butadiene-styrene modification on the characteristics and performance of bitumen, Chem. Monthly 138 (2007) 301 307.

[4] Oyekunle, LO: Certain relationships between chemical composition and properties of petroleum asphalts from different origin, Oil & Gas Sci. Technol. – Rev. IFP 61:3 (2006) 433 – 441.

[5] Lesueur D: The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification, Adv. Colloid Interface Sci. 145 (2009) 42 – 82.

[6] Jones DR IV, Kennedy TW: The asphalt model: Results of the SHRP Asphalt Research Program, SHRP A-001, Center for Transportation Research University of Texas (1992).

[7] Vijay R, Deshpande AP, Varughese S: Nonlinear rheological modelling of asphalt using White-Metzner model with structural parameter variation based asphaltene structural build-up and breakage, Appl. Rheol. 18 (2008) 23214.

[8] Christensen Jr DW, Anderson DA: Interpretation of dynamic mechanical test data for paving grade asphalt cements, Proceedings of the Association of Asphalt Paving Technologists 61 (1992) 67 – 99.

[9] Zanzotto L, Stastna J, Vacin OJ: Thermomechanical Properties of Several Modified Asphalts, Appl. Rheol. 10 (2000) 185 – 191.

[10] Martinez-Boza F, Partal P, Navarro FJ, Gallegos C: Rheology and microstructure of asphalt binders, Rheol. Acta 40 (2001) 135 – 141.

[11] Lu X, Isacsson U: Effect of ageing on bitumen chemistry and rheology, Const. Build. Mater. 16 (2002) 15 – 22.

[12] Siddiqui MN: NMR finger printing of chemical changes in asphalt fractions on oxidation, Petrol. Sci. Technol. 27 (2009) 2033 – 2045.

[13] Mouillet V, Farcas F, Besson S: Ageing by UV radiation of an elastomer modified bitumen, Fuel 87 (2008) 2408 – 2419.

[14] Romera R, Santamaría A, Peña JJ, Muñoz ME, Barral M, García E, Jañez V: Rheological aspects of the rejuvenation of aged bitumen, Rheol. Acta 45 (2006) 474 478.

[15] Mastrofini D, Scarsella M: The application of rheology to the evaluation of bitumen ageing, Fuel 79 (2000) 1005 – 1015.

[16] Rahman MM: Characterisation of Dry Process Crumb Rubber Modified Asphalt Mixtures, PhD Thesis, University of Nottingham, School of Civil Engineering (2004).

[17] Branco F, Pereira P, Picado-Santos L: Pavimentos Rodoviários, Edições Almedina, Coimbra (2005).

[18] Polacco G, Vacin OJ, Biondi D, Stastna J, Zanzotto L: Dynamic master curves of polymer modified asphalt from three different geometries, Appl. Rheol. 13 (2003) 118 – 124.

[19] Schröter K, Hutcheson SA, Shi S, Mandanici A, McKenna GB: Dynamic shear modulus of glycerol: Corrections due to instrument compliance, J. Chem. Phys. 125 (2006) 1 – 4.

[20] Anderson AD, Christensen DW, Bahia HU, Dongre R, Sharma MG, Antle CE, Button J: Binder Characterization & Evaluation, Vol. 3, Physical Characterization, SHRP-A-369, National Academy of Science, Washington DC (1994).

[21] Larson RG: The structure and rheology of complex fluids, Oxford University Press, New York (1990).

[22] Williams ML, Landel RF, Ferry JD: The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids, J. Am. Chem. Soc. 77 (1955) 3701 – 3707.

[23] Ferry JD: Viscoelastic properties of polymers, Wiley, New York (1980).

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org