Using thermal analysis methods to better understand asphalt rheology

J.P. Planche[a,*], P.M. Claudy[b], J.M. Létoffé[c], D. Martin[a]

[a] Centre de Recherche Elf Solaize, BP 22, 69360 Solaize, France
[b] CNRS, LMOPS, BP 24, 69390 Vernaison, France
[c] Institut National des Sciences Appliquées de Lyon, Bat. 401, 20 Avenue A. Einstein, 69621 Villeurbanne, France

Abstract

The Strategic Highway Research Program allowed to define some parameters that characterize the rheological properties of asphalt cement(s) (ACs). Those parameters implied that ACs follow the time and temperature superposition principle. However, highly asphaltic or waxy ACs deviate from this rule since their structure changes as a function of time and temperature. Some of these transitions clearly appear on differential scanning calorimetry curves.

This paper shows some analogies between thermo-analytical and rheological properties of ACs. In particular, it emphasizes the roles of crystallized fraction(s) (CFs) and of the glass-transition temperature (T_g) on the whole temperature range of end use. Thus, at low temperatures, CF seems greatly responsible for the physical hardening (PH) occurring with time. PH magnitude also depends on the position of T_g relative to the given conditioning temperature. At higher temperatures, CF also plays a role on the rheological behavior since their dissolution–precipitation mainly occurs at temperatures between $0°$ and $80°C$. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Asphalt cement; Crystallizable fraction; Glass transition; Differential scanning calorimetry; Physical hardening

1. Introduction

Asphalt cement(s) (ACs) are highly complex mixtures whose structure and properties are highly temperature dependent. Earlier [1], differential scanning calorimetry (DSC) was used to directly identify the fractions responsible for the thermal effects, T_g and the crystallizable fraction(s) (CFs). CF crystallization–dissolution was then related to AC physical properties [2]. During the Strategic Highway Research Program (SHRP), Anderson et al. [3–5] reported the physical hardening of ACs at low temperatures. They also showed it was related to a gradual density change occurring over time. Meanwhile, Claudy et al. [6,7] used DSC and thermo-microscopy to relate changes in

AC structure to the time-dependent changes of their rheological properties. This paper reviews the main thermal effect contributions to the physical properties of ACs.

2. Experimental

This study was mainly conducted at the Elf Research Center of Solaize and INSA Lyon (France), and involved over 70 ACs of different origins – straight run vacuum residues from various crude oils and with different penetration grades.

DSC measurements were carried out between -100 and $+100°C$ at a heating rate of $5°C/min$, using a computer controlled Mettler TA 2000 B calorimeter, according to the experimental conditions described earlier [1].

*Corresponding author.

AC rheological properties were characterized by dynamic mechanical analysis (DMA) using a dynamic shear rheometer Rheometrics RDA 700, at various frequencies and temperatures. Additionally, the low-temperature creep properties of ACs were evaluated with the bending beam rheometer from Cannon, according to the conditions developed by SHRP [4].

3. Results

3.1. Structural analysis of ACs

DSC shows several thermal effects according to the crude source (see Fig. 1).

– At very low temperatures ($-50°$ to $-10°C$): the increase in heat capacity can be attributed to the glass transition of the matrix – T_g is taken at midpoint.
– Above T_g a small exothermic effect occurrs, most likely on account of the crystallization of species which do not crystallize during cooling.
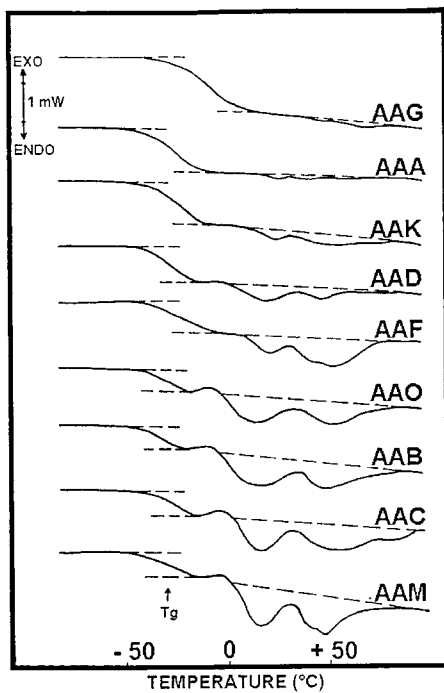

Fig. 1. DSC curves of various asphalt cements from different crude sources [7].

– Between $0°$ and $+100°C$: a broad endothermic effect corresponds to the dissolution of crystallized fractions (CF) in the hydrocarbon matrix. Its magnitude is quantified by integrating the surface area of the endothermic peaks and taking 200 J/g as the dissolution enthalpy [1].

3.2. Correlation with the physical properties

3.2.1. Glass transition T_g

The glass transition is a transition accompanied by a sudden decrease in the shear modulus and an increase in the specific heat and expansion coefficient. Its effect on the Fraass brittle point (FP), used in Europe to estimate the temperature below which the binder is brittle, was presented earlier [2] and shows that FP and T_g were linked together. In this study, the mechanical T_g of eight ACs was measured by DMA. The correlation between this T_g DMA, the temperature at which the loss modulus peaks at low frequency (5 rad/s) and T_g DSC (see Fig. 2) validates T_g DSC relevance to estimate AC low-temperature performance.

3.2.2. Crystallized fractions

Crystallized fraction(s) (CFs) begin to form around $80°C$ and then gradually precipitate as the asphalt is cooled. Therefore, one can assume these structural changes should have a significant impact on the physical properties over this temperature range.

Earlier studies [2] reported the effect of CF on the classical empirical testing of ACs. In particular, they demonstrated that the discrepancies in the Heukelom test data chart are closely related to CF. The horizontal shift DT, temperature difference between the ring-and-ball softening point and the temperature at which AC viscosity is 13 000 Po, was correlated to CF with 60% confidence for 64 ACs.
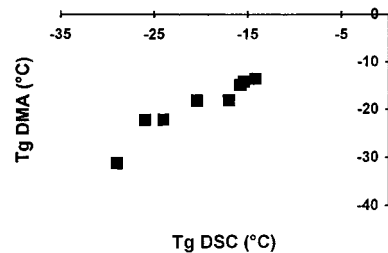

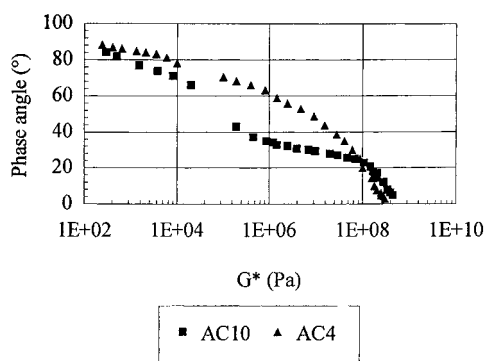Fig. 2. Relationship between T_g measured by DMA and that measured by DSC.

Fig. 3. Rheological behavior of two asphalt cements with different crystallizable fraction contents, as visualized by their Black spaces.

An important effect of CF on AC rheology is presented in the following.

The rheological behavior of AC 4 and AC 10 (respectively, 4 and 11% CF) was studied under dynamic mechanical analysis, at a cooling rate of 0.5°C/min and at a low frequency of 0.22 rad/s. Fig. 3 compares them in a Black space diagram where the dynamic modulus is plotted as a function of the phase angle:

– Near the glassy state: the limiting stiffness modulus of AC 10, more crystalline, is higher than the corresponding limiting stiffness of AC 4.
– Well above the glassy state: the overall rheological behavior of these 2 ACs is quite different; the less waxy one shows a fairly smooth curve, whereas the more crystalline one exhibits a very clear inflection point at 55–60° phase angle and a plateau at a complex modulus of ca. 10^5 Pa. typical of a state transition. This could be attributed to the dissolution or precipitation of the CF. ACs with high CF have higher limiting stiffness moduli and a unique behavior, unlike conventional viscoelastic fluids.

When the experiment is run at a higher frequency (22 rad/s), the plateau effect is less pronounced. This frequency factor confirms that Van der Waals bonds of paraffinic aliphatics are involved since, under high frequency, weak interactions readily loosen.

The rheological behavior of ACs below 60°C is definitely influenced by the presence of crystallizable fractions. AC can no longer be considered as a simple fluid but rather as a high complex material, not always

following the time and temperature superposition principle.

3.3. Physical hardening at low temperatures

3.3.1. Influence of the crystallizable fractions

Claudy et al. [7] reported that CF and T_g increase when the conditioning time increases or the temperature decreases. They also showed that the formation of phases at low temperatures contributes to the isothermal hardening described by Anderson [3–5,8] – change in creep parameters (stiffness modulus (S) and slope (m) vs. the loading time, related to the AC relaxation rate) measured with the bending beam rheometer.

In the SHRP binder evaluation, the amount of physical hardening is measured by the 'physical hardening factor' (PHF). This factor considers both, m and S evolutions according to the following expression:

$$\text{PHF} = (S_{24\,h}/S_{1\,h})^{(m_{1\,h}/m_{24\,h})} \tag{1}$$

Fig. 4 confirms there is indeed a clear relationship between PHF measured at −18°C for 11 ACs and the corresponding CFs.

3.3.2. Kinetics of physical hardening

Fig. 5 shows the evolution of S and m as functions of time at −18°C, for A80 and B80 with, respectively, 3.8 and 0.1% CF. Both these parameters remain fairly stable for the non-waxy B80, whereas for A80, S increases significantly with time, while m decreases.

Warming up A80 for 2 h at 25°C, after 1 day at −18°C, brings both the parameters back to their initial stage. Thus, physical hardening (PH) is completely thermally reversible.

To better highlight how PH can affect the evaluation of AC at low temperatures, the ranking of a wide set of ACs according to their −18°C creep stiffness after 1
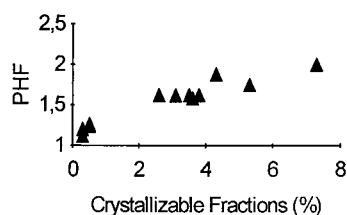

Fig. 4. Influence of the crystallizable fraction content on the physical hardening of asphalt cements.
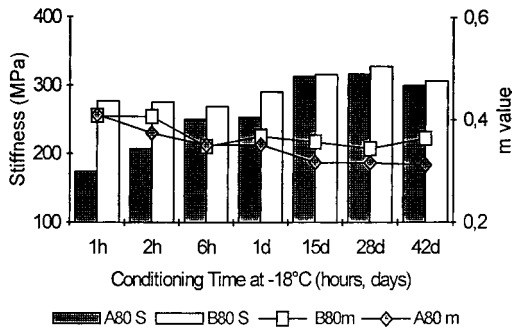
Fig. 5. Physical hardening kinetics at −18°C for AC A80 and B80 with two different crystallizable fraction amounts. Evolution of the creep stiffness and of the creep slope (*m*-value) as a function of time.
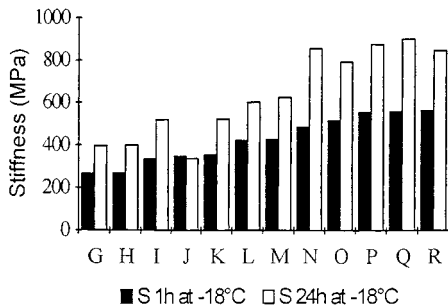

Fig. 6. Influence of the time of conditioning on the asphalt cements ranking, according to their low-temperature stiffness as measured by bending beam rheometer.

and 24 h conditioning at this temperature, is plotted in Fig. 6. Some ACs rank differently before, than after. Thus, AC gradation can be affected by the low-temperature physical hardening. This result is important in terms of specifications.

3.3.3. Influence of the glass-transition temperature

It is now obvious that PH is highly related to the crystallization of some AC fractions. Like any structural change occurring at low temperatures, this crystallization should be affected by the glass transition.

To precisely describe the effect of temperature on PH, three different ACs (C45, D45, E60 with, respectively, 3.6, 0.5, 4.3% CFs) were stored for 24 h at various temperatures. PHF was then plotted against the difference between the conditioning temperature and T_g on Fig. 7. Above T_g, PHF of waxy C45 and E60 increases as the temperature gets closer to T_g. Below
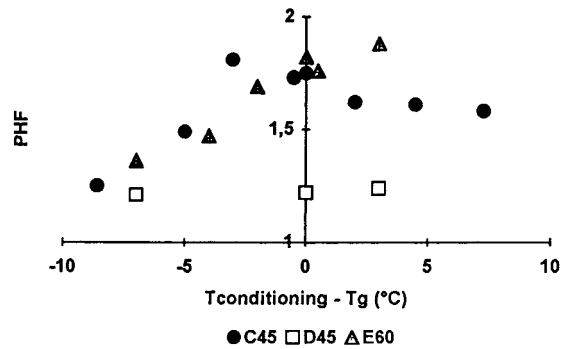

Fig. 7. Effect of the glass transition temperature (T_g) on the physical hardening of asphalt cements.

T_g, PHF decreases to end up close to unity, meaning no PH as in the case for non-waxy D45.

This result confirms that, in a given physical state represented by the difference between the given conditioning temperature and T_g, physical hardening is mostly due to CF.

4. Conclusions

This paper shows some analogies between thermo-analytical and rheological properties of ACs. At low temperatures, crystallized fractions (CF) seem greatly responsible for the physical hardening (PH) occurring with time. The magnitude of PH also depends on the position of T_g relative to the conditioning temperature. At higher temperatures, CF plays a role in the rheological behavior, since it dissolves/precipitates between 0 and 80°C. Although their real effect on the mix itself has not been proven yet, these structural changes are definitely able to interfere in the evaluation of the rheological parameters and should be addressed in the specifications. Finally, AC can no longer be considered as a simple fluid but rather as a highly complex material.

References

[1] P. Claudy, J.M. Létoffé, G.N. King, J.P. Planche, B. Brûlé, Fuel Sci. Tech. Int'l 9(1) (1991) 71.

[2] P. Claudy, J.M. Létoffé, G.N. King, Planche, B. Brûlé Fuel Sci. Tech. Int'l 10(4–6) (1992) 735.

[3] D.A. Anderson, D.W. Christensen, J. AAPT, 61 (1992).

[4] H.U. Bahia, D.A. Anderson, Proceedings of Int'l Symp. on Chem. of Bitumens, Rome, 1, 1991, p. 114.

[5] H.U. Bahia, D.A. Anderson, J. AAPT 62 (1993) 93.

[6] P. Claudy, J.M. Létoffé, G.N. King, J.P. Planche, Proc. of Int'l Symp. on Chem. of Bitumens, Rome, 2, 1991, p. 530.

[7] P. Claudy, J.M. Létoffé, F. Rondelez, L. Germanaud, G.N. King, J.P. Planche, Proc. of ACS, Washington D.C., 1992.

[8] H.U. Bahia, D.A. Anderson, D.W. Christensen, J. AAPT, 61 (1992).