# Novel application of time-resolved rheometry to study physical aging: a case study on bituminous binders

Olli-Ville Laukkanen<sup>1,2</sup>, H. Henning Winter<sup>1</sup>, and Jukka Seppälä<sup>2</sup>

<sup>1</sup>Department of Polymer Science and Engineering and Department of Chemical Engineering, University of Massachusetts Amherst, USA

<sup>2</sup>Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Finland

## ABSTRACT

Physical aging refers to the structural relaxation of glassy materials towards their metastable equilibrium state, inducing changes in almost all physical properties. In this paper, we demonstrate how timeresolved rheometry can be used to analyze the time evolution of viscoelastic properties during physical aging. In the experimental section. the effects of temperature, crystallinity and polymer modification on the physical aging of bitumen are investigated, and the application of the time-aging time superposition principle is demonstrated.

## INTRODUCTION

Glasses are inherently out-of-equilibrium systems evolving slowly toward their equilibrium state in a process called physical aging.<sup>1</sup> Physical aging is driven by the attempt to achieve equilibrium density through configurational rearrangements on a molecular scale,<sup>2</sup> and it is accompanied by changes in almost all physical properties both at macrostructural (bulk) and microstructural (molecular) scale.<sup>134</sup>

Among various other characterization techniques (dilatometry, differential scanning calorimetry, different spectroscopic and scattering techniques, etc.), physical aging can be conveniently studied by rheology. In the widely used Struik's protocol<sup>15</sup>, the time evolution of viscoelastic properties during physical aging is monitored by performing a series of creep and recovery tests at increasing aging times. The measured creep data is then often analyzed by means of the time-aging time superposition principle.<sup>6</sup>

In this paper, we describe a novel methodology for analyzing the effect of physical aging on the viscoelastic behavior of glassy materials. Our approach is based on time-resolved rheometry (TRR), a technique that is generally used for the rheological characterization of transient (time-evolving) materials.<sup>7</sup> The TRR technique provides various advantages over the traditional Struik's protocol:

- More comprehensive description of viscoelastic properties at different time scales
- The measurement data is typically more accurate (less noisy)
- The consistency of the measurement data can be checked by means of the Kramers-Kronig relation<sup>8</sup>:

$$\frac{G'(\omega)}{\omega^2} = \frac{2}{\pi} \int_0^\infty \frac{G''(x)}{\omega^2 - x^2} dx \tag{1}$$

• The evolution of rheological properties during physical aging can be monitored continuously

### O.-V. Laukkanen et al.

In the following section, we briefly review the fundamentals of time-resolved rheometry as relevant for the present study.

### DEFINITIONS IN TIME-RESOLVED RHEOMETRY

The term "mutation" is used as a general expression for the changes that affect the molecular mobility, and hence the relaxation patterns of the investigated material.<sup>9</sup> The mutation time  $\tau_{mu}$  is defined as the characteristic time for the rate of change in the material:<sup>7</sup>

$$\tau_{mu} = \left[\frac{1}{g} \left|\frac{\partial g}{\partial t}\right|\right]^{-1}.$$
(2)

The change is not measured directly but indirectly through the property of interest g, which has to be specified for each type of experiment.  $\tau_{mu}$  is defined as the time which is required for a (1/e)-change of property g at the instantaneous rate of change  $\partial g/\partial t$ . Furthermore, the mutation number  $N_{mu}$  is defined as the ratio between the experimental time  $\Delta t$  and the mutation time  $\tau_{mu}$ :<sup>10</sup>

$$N_{mu} = \frac{\Delta t}{\tau_{mu}}.$$
(3)

The mutation number estimates the relative change of a property g during the measurement of a single data point.

It is usually desirable to investigate transient samples specifically by dynamic oscillatory experiments since the experimental time is shorter than in comparable steady experiments and different relaxation modes can be studied almost other.9 independently of each The experimental time  $\Delta t$  in this type of measurement is defined by the time required by the rheometer to take a data point at a specified angular frequency  $\omega$ :

$$\Delta t = \frac{2\pi}{\omega}.\tag{4}$$

Following Eq. (2), mutation times referring to the storage modulus (g = G') and loss modulus (g = G'') can be written as:

$$\tau'_{mu} = \left[\frac{1}{G'} \left|\frac{\partial G'}{\partial t}\right|\right]^{-1},\tag{5a}$$

$$\tau_{mu}^{\prime\prime} = \left[\frac{1}{G^{\prime\prime}} \left|\frac{\partial G^{\prime\prime}}{\partial t}\right|\right]^{-1},\tag{5b}$$

and, consequently, the corresponding mutation numbers are defined as:

$$N'_{mu} = \frac{2\pi}{\omega G'} \left| \frac{\partial G'}{\partial t} \right|,\tag{6a}$$

$$N_{mu}^{\prime\prime} = \frac{2\pi}{\omega G^{\prime\prime}} \left| \frac{\partial G^{\prime\prime}}{\partial t} \right|.$$
 (6b)

The sample can be considered quasistable when the mutation number for both G'and G'' is sufficiently small, typically  $N_{mu} < 0.1$ .<sup>11</sup> It is also worth noting that usually G'changes more rapidly than G'' in transient materials, and therefore  $N'_{mu} > N''_{mu}$ .<sup>7,9</sup>

## EXPERIMENTAL

#### **Materials**

Physical aging of bitumen is known to have a major impact on the low-temperature cracking of asphalt pavements.<sup>12,13</sup> Hence, in the experimental part of this study, we investigate physical aging in various bituminous binders. To study the effect of crystallinity, physical aging in semicrystalline and non-crystalline bitumen samples is compared. In addition, in order to assess the effect of polymer modification on physical aging, bitumen modified with different amounts (0-10 wt%) of styrenebutadiene-styrene (SBS) triblock copolymer is investigated. Further details of the investigated bituminous binders can be found elsewhere 14,15

#### Rheological characterization

Small-diameter parallel plate rheometry<sup>16</sup> was used to measure the rheological properties of the bituminous binders near and below the glass transition temperature  $(T_g)$ . A stress-controlled Malvern Kinexus Pro rheometer was equipped with 4-mm diameter parallel plate geometry, and a Peltier plate and active hood were used to control the temperature of the test specimen within  $\pm 0.1$ K. To avoid moisture uptake and ice formation in the test specimen, the Peltier hood was purged with dry nitrogen gas. Time-resolved data were obtained by cyclic frequency sweep (CFS) experiments<sup>7</sup>. The frequency range from 62.8 to 0.628 rad/s was repeatedly scanned while keeping the temperature constant. The strain amplitude was kept low ( $\gamma_0 = 0.01 - 0.03$  % depending on the measurement temperature) in order to ensure linear viscoelastic material response and to ensure that physical aging is not influenced by mechanical rejuvenation. Moreover, the normal force control of the rheometer was enabled to avoid the build-up of thermal stresses in the test specimen upon cooling. For each CFS experiment, a new test specimen was prepared above  $T_g$  and then quenched to the measurement temperature at a cooling rate of approximately 10 K/min. All measurement data were corrected for torsional instrument compliance as described by Schröter et al.<sup>17</sup> and Laukkanen<sup>16</sup>.

## **RESULTS AND DISCUSSION**

Fig. 1 shows CFS data for a semicrystalline bitumen sample (melting enthalpy  $\Delta H_m = 7.1 \text{ J/g}$ ) measured at the nominal glass transition temperature of -23.9 °C. Physical aging is observed to result in a significant increase in stiffness and elasticity. Similarly to many polymer glasses<sup>18-22</sup>, the storage modulus increases linearly with the logarithm of aging time at the early stages of physical aging. After about  $10^5$  s ( $\approx 28$  h), the viscoelastic response becomes independent of the aging time as the sample reaches a metastable equilibrium glassy state (i.e. physical aging ceases).



Figure 1. Evolution of frequency-dependent (a) dynamic moduli and (b) loss tangent in semi-crystalline bitumen during physical aging at  $T_g = -23.9$  °C.

Mutation numbers corresponding to the CFS data of Fig. 1 were calculated, and it was observed that  $N'_{mu} >> N''_{mu}$  at all aging times. Sample mutation is fastest duirng the early stages of physical aging, but still  $N'_{mu} < 0.0023$  even at the lowest oscillation frequency of 0.628 rad/s. We thus conclude that the sample can be considered quasistable during the experimental time, hence confirming the validity of the measured CFS data.

### O.-V. Laukkanen et al.

The application of the time-aging time superposition principle to the analysis of CFS data is illustrated in Fig. 2. Fig. 2(a) shows the frequency-dependent viscoelastic response of semi-crystalline bitumen at physical different stages of aging. interpolated from the CFS data of Fig. 1. These frequency sweep curves are then shifted horizontally to obtain the master curves in Fig. 2(b). The excellent overlap of the curves confirms the validity of the timeaging time superposition principle. Furthermore, the validity of the measured

viscoelastic response is verified by fitting the generalized Maxwell model to the measurement data; this confirms that the Kramers-Kronig relation (Eq. (1)) is satisfied.<sup>23</sup>

Time-aging time shift factors  $a_{te}$  are obtained from the master curve construction.<sup>1,6</sup> A linear trend is often observed in the plot of log  $a_{te}$  vs. log  $t_e$ , the slope being defined as the aging shift rate:<sup>1</sup>

$$\mu = \frac{d \log a_{te}}{d \log t_e}.$$
(7)



Fig. 2. Application of the time-aging time superposition principle to the CFS data of Fig. 1. (a) Interpolated frequency sweep response at different stages of physical aging. (b) Master curves obtained by horizontally shifting the frequency sweep data of part (a). The dashed lines represent the fits of the generalized Maxwell model. (c) Aging time shift factors obtained from the construction of master curves in part (b).

As shown in Fig. 2(c),  $\mu$  is roughly 0.60 when the semi-crystalline bitumen is aged at its nominal  $T_g$ . Similarly to Fig. 1, the plateauing of this curve indicates that physical aging ceases after approximately 10<sup>s</sup> s ( $\approx$  28 h).

We performed CFS experiments at various temperatures in the vicinity of the nominal glass transition temperature ( $T_g$ -10  $K \le T \le T_g + 10$  K) and observed that physical aging occurs both above and below the nominal  $T_g$  of the semi-crystalline bitumen. This is in contrast to the general view that physical aging takes place only below  $T_g$ .<sup>1</sup> The observed unusual temperature dependence of physical aging can be attributed to the broad glass transition of bitumen, as it was observed by differential scanning calorimetry (DSC) that the glass transition region of this bitumen sample extends beyond the experimental temperature range of this study ( $T_g$ -10 K  $\leq T \leq T_g$ +10 K). The rate of physical aging is observed to be highest at the nominal  $T_g$  ( $\mu \approx 0.60$ ), while physical aging gradually slows down above and below  $T_g$  ( $\mu \approx 0.40$  both at  $T_g$ -10 K and *T<sub>g</sub>*+10 K).

Our results show that physical aging is much less significant in non-crystalline bitumen ( $\Delta H_m = 0.0 \text{ J/g}$ ), as expected based on previous studies<sup>24-27</sup>. It may be speculated that crystalline fractions hasten the formation of rigid amorphous phase at low temperatures,<sup>28</sup> hence making physical aging more severe in semi-crystalline bitumen.

Finally, we observe that SBS polymer modification has a major impact on the physical aging of bitumen. The time-aging time superposition is found to be valid, but in addition to horizontal shifts, also vertical shifts need to be applied in the construction of master curves when bitumen is modified with large amounts ( $\geq$ 7 wt%) of SBS. Considering our previous observations on the morphology of SBS modified bitumen,<sup>14</sup> we attribute the occurrence of the vertical shifts to the formation of continuous SBS-rich network structure in bitumen.

#### CONCLUSION

We have demonstrated that time-resolved rheometry is a powerful tool for analyzing the evolution of viscoelastic properties during physical aging. The effects of temperature, crystallinity and polymer modification on the physical aging of bitumen have been successfully quantified, demonstrating the sensitivity of this technique. In the future, we expect to see this technique applied to the physical aging characterization of various types of glassforming systems.

## ACKNOWLEDGMENTS

Financial support from the Osk. Huttunen Foundation and Nynas AB is gratefully acknowledged.

## REFERENCES

1. L. C. E. Struik. "Physical aging in amorphous polymers and other materials." Ph.D. thesis, Delft University of Technology, 1977.

2. S. L. Simon. "Aging, physical." in *Encyclopedia of Polymer Science and Technology* (Wiley Online Library, 2001).

3. I. M. Hodge. "Physical aging in polymer glasses." *Science* 267 (1995): 1945–1947.

4. J. M. Hutchinson. "Physical aging of polymers." *Prog. Polym. Sci.* 20 (1995): 703–760.

5. L. C. E. Struik. "Volume relaxation in polymers." *Rheol. Acta* 5 (1966): 303–311.

6. R. D. Bradshaw, and L. C. Brinson. "Physical aging in polymers and polymer composites: an analysis and method for timeaging time superposition." *Polym. Eng. Sci.* 37 (1997): 31–44.

7. M. Mours, and H. H. Winter. "Timeresolved rheometry." *Rheol. Acta* 33 (1994): 385–397.

8. H. C. Booij, and G. P. J. M. Thoone. "Generalization of Kramers-Kronig transforms and some approximations of relations between viscoelastic quantities." *Rheol. Acta* 21 (1982): 15–24.

## O.-V. Laukkanen et al.

9. H. H. Winter, M. Mours, M. Baumgaertel, and P. R. Soskey. "Computer-aided methods in rheometry." in *Rheological Measurement* (Springer, 1998): 47–98.

10. H. H. Winter, P. Morganelli, and F. Chambon. "Stoichiometry effects on rheology of model polyurethanes at the gel point." *Macromolecules* 21 (1988): 532–535. 11. H. H. Winter, and M. Mours. "Rheology of polymers near liquid-solid transitions." in *Neutron spin echo spectroscopy viscoelasticity rheology* (Springer, 1997): 165–234.

12. J. L. Freeston, G. Gillespie, M. Paliukaite, and R. Taylor. "Physical Hardening in Asphalt." in *Proceedings of the Sixtieth Annual Conference of the Canadian Technical Asphalt Association (CTAA), Winnipeg, Manitoba* (2015): 53–81.

13. O. P. Togunde, and S. A. M. Hesp. "Physical hardening in asphalt mixtures." *Int. J. Pavement Res. Technol.* 5 (2012): 46–53.

14. O.-V. Laukkanen, H. Soenen, H. H. Winter, and J. Seppälä. "Low-temperature rheological and morphological characterization of SBS modified bitumen." *Constr. Build. Mater.* 179 (2018): 348–359.

15. O.-V. Laukkanen, H. H. Winter, and J. Seppälä. "Characterization of physical aging by time-resolved rheometry: fundamentals and application to bituminous binders." *Rheol. Acta* 57 (2018): 745–756.

16. O.-V. Laukkanen. "Small-diameter parallel plate rheometry: a simple technique for measuring rheological properties of glass-forming liquids in shear." *Rheol. Acta* 56 (2017): 661–671.

17. K. Schröter, S. A. Hutcheson, X. Shi, A. Mandanici, and G. B. McKenna. "Dynamic shear modulus of glycerol: Corrections due to instrument compliance." *J. Chem. Phys.* 125 (2006): 214507.

18. A. J. Kovacs, R. A. Stratton, and J. D. Ferry. "Dynamic Mechanical Properties of Polyvinyl Acetate in Shear in the Glass Transition Temperature Range." *J. Phys.* 

Chem. 67 (1963): 152–161.

19. A. B. Brennan, and F. Feller III. "Physical aging behavior of a poly (arylene etherimide)." *J. Rheol.* 39 (1995): 453–470.

20. R. A. Venditti, and J. K. Gillham. "Isothermal physical aging of poly(methyl methacrylate): Localization of perturbations in thermomechanical properties." *J. Appl. Polym. Sci.* 45 (1992): 501–506.

21. A. V. Cugini, and A. J. Lesser. "Aspects of physical aging, mechanical rejuvenation, and thermal annealing in a new copolyester." *Polym. Eng. Sci.* 55 (2015): 1941–1950.

22. J. Y. Cavaille, S. Etienne, J. Perez, L. Monnerie, and G. P. Johari. "Dynamic shear measurements of physical ageing and the memory effect in a polymer glass." *Polymer*. 27 (1986): 686–692.

23. H. H. Winter. "Analysis of dynamic mechanical data: inversion into a relaxation time spectrum and consistency check." *J. Non-Newton. Fluid Mech.* 68 (1997): 225–239.

24. D. Anderson, and M. Marasteanu. "Physical Hardening of Asphalt Binders Relative to Their Glass Transition Temperatures." *Transp. Res. Rec. J. Transp. Res. Board* 1661 (1999): 27–34.

25. D. A. Anderson *et al.* "Binder characterization and evaluation. Volume 3: Physical characterization." Strategic Highway Research Program, SHRP-A-369 (1994).

26. P. Claudy *et al.* "A new interpretation of time-dependent physical hardening in asphalt based on DSC and optical thermoanalysis." in *ACS Symposium on Chemistry and Characterization of Asphalts, Washington,* 

DC (1992).

27. J. Planche, P. Claudy, J. Létoffé, and D. Martin. "Using thermal analysis methods to better understand asphalt rheology." *Thermochim. Acta* 324 (1998): 223–227.

28. P. Kriz. "Glass Transition and Physical Hardening of Asphalt." Ph.D. thesis, University of Calgary, 2009.