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THE IMPACT OF AGEING ON THE BITUMEN STIFFNESS MODULUS USING THE CAM MODEL

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Abstract. This article presents the results of the viscoelastic properties of the polymer-modified bitumen produced in Warm Mix Asphalt technology. A Fischer-Tropsch synthetic wax and a liquid surface-active agent (fatty amine) were used as bitumen viscosity-reducing modifiers. All tested parameters were determined after short-term and long-term ageing. The complex modulus G^* and phase angle δ were measured with a cone-plate rheometer. All dynamic tests were performed at 60 °C within the frequency range from 0.005 Hz to 10 Hz. On the basis of the rheological index R determined using the Christensen–Anderson–Marasteanu (CAM) model, it was found that the fatty amine additive slowed down the age-hardening process in the bitumen. In contrast, the synthetic wax increased the stiffness of the bitumen at all levels tested, regardless of the type of ageing simulation process.

Keywords: Christensen–Anderson–Marasteanu (CAM) model, long-term ageing, short-term ageing, viscoelasticity, warm mix asphalt technology.

Introduction

Ageing of bituminous binders involves changes in physical and mechanical properties of the bitumen (Judycki & Jaskuła, 2002). The ageing process starts in the mixing phase, continues through the phases of storage, transport, and placement, and further through the service life of a pavement (Cholewińska, Mazurek, & Iwański, 2014). During the service life, an increase in the asphalt binder stiffness causes bitumen physical hardening (Judycki, 2014).

Due to environmental issues and increased environmental awareness creating the need to reduce the impact of production temperatures (140 °C–180 °C), recent years have seen the development of Warm Mix Asphalt (WMA) technologies (Iwański & Mazurek, 2015). Owing to this, the temperature of both production and placement is reduced by about 20 °C–30 °C relative to conventional Hot Mix Asphalt (HMA) mixtures (Iwański & Mazurek, 2013). One of the ways to obtain this effect is to use modifiers acting as binder viscosity reducing agents and allowing aggregate grains to be coated with binders of temperatures lower than those of a conventional hot binder (Iwański & Mazurek, 2011). These modifiers include a Fischer-Tropsch synthetic wax or liquid service-active agents.

Rheological models are used throughout the world to explain and understand the rheological behaviour of bitumen (Anderson & Marasteanu, 2010). Rheological parameters (complex modulus G^* and phase angle δ), measured at any temperature and frequency, are described by rheological models to an accuracy acceptable for most purposes (Yusoff & Izzi, 2012). This paper applies the Christensen–Anderson–Marasteanu (CAM) model to describe the behaviour of bitumen and predict the ageing process.

1. Christensen–Anderson–Marasteanu (CAM) model

The CAM model (Marasteanu & Anderson, 1996) is a modified version of the Christensen Anderson (CA) model, which provides a better fit of the model to the G^* results within very low and very high frequencies (Kim, 2009). The CAM model is an attempt to improve the stiffness description of non-modified and modified bitumens. It is represented by the following Eq. (1) (Li, Zofka, Marasteanu, & Clyne, 2006):

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$$\left|G^*\right| = G_g \left[1+\left(\frac{f_c}{f}\right)^{v}\right]^{-\frac{w}{v}}, \quad (1)$$

where G^*– complex shear modulus; G_g – glassy modulus; f_c – the frequency at the cross point, Hz; f – measurement frequency; w, v – experimental curve fitting parameters of the CAM model.

The rheological index R was calculated from Eq. (2):

$$R = \frac{\log 2}{v}. \quad (2)$$

The graphical definition (made by this article authors) of the CAM model is shown in Figure 1.

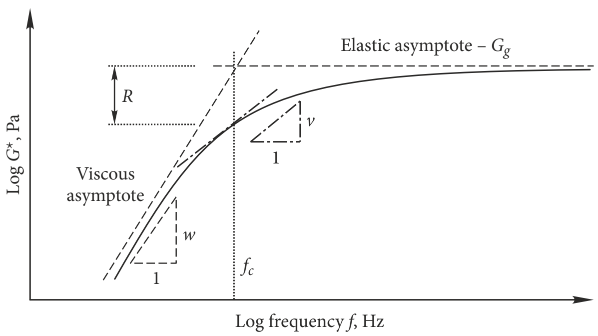

Figure 1. Graphical definition of the CAM model (author: Grzegorz Mazurek)

Each parameter in Figure 1 is important to fully characterize the bitumen ageing process at a given test temperature. The parameter f_c, designated as the frequency at the cross point, represents the frequency at which the elastic and viscous portions of the complex modulus G^* are equal and where the viscous asymptote and glassy modulus cross over. Therefore, f_c defines the frequency at which the bitumen passes from the elastic to a viscous state and is interpreted as representing the hardness of the bitumen at a given temperature (Anderson et al., 1994). The parameter w characterizes the rate at which the complex modulus G^* converges with the elastic or viscous asymptote. The parameter v is used to compute the rheological index R. It is closely related to the relaxation spectrum and represents the distance between the asymptotes crossover point and the shear modulus result in the CAM model at frequency f_c (Figure 1). Thus, in the bitumen more susceptible to ageing, with a low asphaltene content, the shear modulus will be lower, the relaxation spectrum will be greater and the rate of the relaxation-induced decrease in the values of stiffness modulus will be less rapid (Marasteanu & Anderson, 1999).

2. Materials and test methods

The test material was polymer modified bitumen PMB 45/80-65 with Fischer-Tropsch synthetic wax (Król, Kowalski, Radziszewski, & Sarnowski, 2015) at three contents, 1.5%, 2.5% and 3.5%, and liquid surfactant (fatty amine – FA) at two contents, 0.3 and 0.6%, added to lower the viscosity level (Cholewińska, Iwański, & Mazurek, 2017).

All parameters were determined before and after long-term ageing in the Pressure Ageing Vessel (PAV) test. Prior to PAV, the samples were subjected to Rolling Thin Film Oven Test (RTFOT) (Słowik & Bilski, 2017). Owing to the addition of the low viscosity modifiers, the temperature of the bituminous mixture production was reduced and the samples were conditioned at 135 °C (instead of conventional 163 °C – by *PN-EN 12607-1: Bitumen and bituminous binders. Determination of the resistance to hardening under influence of heat and air. RTFOT method*).

A 25mm diameter cone/plane testing geometry was used to determine the complex modulus G^* and phase angle δ on all test samples. The tests were performed according to *PN-EN 14770: Bitumen and bituminous binders. Determination of complex shear modulus and phase angle. Dynamic Shear Rheometer (DSR).*

3. Approximation of CAM model parameters

Principal viscoelastic parameters obtained from rheological measurements of the PMB 45/80-65 were the complex modulus G^* and phase angle δ at 60 °C over the frequency range 0.005 to 10 Hz. These parameters are widely applied to analytical methods and pavement design procedures (Kleizienė, Vaitkus, & Čygas, 2016). Parameters of the CAM model were estimated via the non-linear least squares method. Optimisation performed to find the best fit between the experimental and model data was aided by the simultaneous use of Hooke-Jeeves and Quasi-Newton solvers (Chapra & Canale, 2010). As a result, a set of CAM model parameters was obtained (Table 1). The level of the glassy modulus G_g was established to be $1 \cdot 10^6$ Pa (Marasteanu & Anderson, 1996). Coefficients of determination R^2 were more than 99% and confirmed accurate fitting of the CAM model curve to the experimental results at 60 °C.

The model fitting parameters were used to estimate the rheological index R. This parameter is a very useful tool due to its sensitivity to changes in bitumen stiffness in terms of loading time/frequency. Even minor variations in the bitumen stiffness induced by ageing and chemical changes cause a detectable change in rheological index values. Figure 2 shows the graphical interpretation of parameters f_c and w and the calculated rheological index R.

The results for the G^* as a function of frequency for the bitumen with a fatty amine, obtained from the CAM model, are summarized in Figure 3.

Analysis of the ageing effect on the modified bitumen with FA in Figure 2 indicates that the ageing process caused changes of the f_c parameter. The values of parameter fc show that the time after which the modified bitumen demonstrates viscous behaviour becomes shorter with increasing content of fatty amines. This parameter needs to be analysed in conjunction with the w parameter

Table 1. Results of fitting the CAM model at 60 °C

Modifier type	Additive amount, %	Ageing treatment	CAM model parameters			Rheological index R	R^2
			f_c, Hz	v	w		
Reference	0	NEAT	0.020	0.216	3.117	1.391	99.8
Fatty Amine (FA)	0.3	NEAT	0.526	0.241	2.111	1.254	99.9
Fatty Amine (FA)	0.6	NEAT	40.823	0.262	1.211	1.149	99.8
Synthetic Wax (SW)	1.5	NEAT	10.147	0.282	1.141	1.067	99.5
Synthetic Wax (SW)	2.5	NEAT	387.323	5.912	0.691	0.051	99.5
Synthetic Wax (SW)	3.5	NEAT	4792.207	4.326	0.564	0.069	99.8
Reference	0	RTFOT + PAV	0.140	0.164	1.616	1.841	99.3
Fatty Amine (FA)	0.3	RTFOT + PAV	0.150	0.158	1.551	1.905	99.5
Fatty Amine (FA)	0.6	RTFOT + PAV	3404.622	5.082	0.687	0.059	99.1
Synthetic Wax (SW)	1.5	RTFOT + PAV	1604.168	5.316	0.718	0.056	99.9
Synthetic Wax (SW)	2.5	RTFOT + PAV	702.847	6.250	0.698	0.048	99.9
Synthetic Wax (SW)	3.5	RTFOT + PAV	557.710	6.576	0.683	0.046	99.9

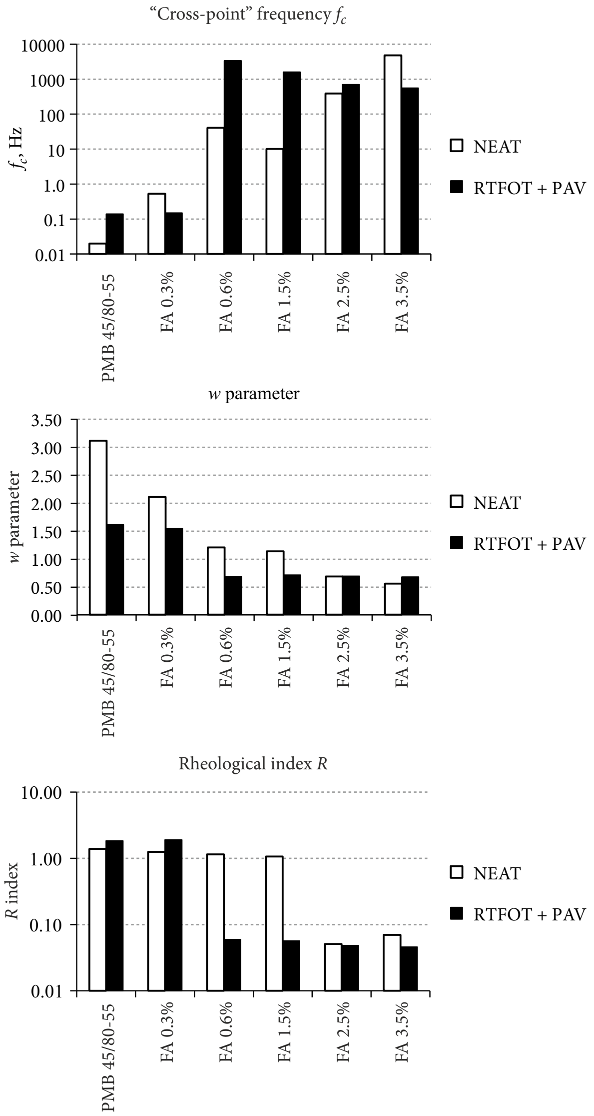

Figure 2. CAM model parameters at 60 °C

to see that compared to the reference bitumen, the modified bitumen becomes plastic very quickly after adding the fatty amine and that the shear modulus G^* results will be quickly convergent with the ideally viscous behaviour of the bitumen, as shown by the w parameter. A combination the CAM model parameters indicates that the use of excessive amount of fatty amines leads to an increase in plastic deformation of bituminous mixtures. This observation is also confirmed by the results in Figure 3, where each time FA is added, the stiffness modulus decreases relative to the reference value. The reduced value of the rheological index R shows that adding FA exacerbates sensitivity of the modified bitumen to the time of loading. After ageing, the parameter f_c increased slightly at a significant decrease of w in the reference bitumen. However, the rheological index R indicates the increased sensitivity of the bitumen

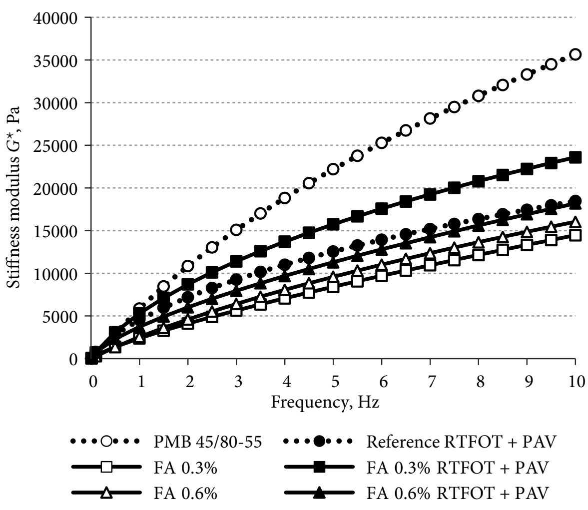

Figure 3. Complex modulus G^* of PMB 45/80-65 bitumen modified with fatty amine versus frequency at 60 °C

to loading time. After ageing, the modified bitumen with fatty amines became a loading time-sensitive material subject to rapid softening and transition to the viscous material. The viscous response is propably a result of the bitumen softening associated with the presence of fatty amines and the degradation of polymer chains (Airey, 2003). The viscous response of the bitumen modified with a high FA content (0.6%) after ageing is interpreted as the anti-ageing action of the fatty amines and, consequently, as a combined effect of polymer chain degradation and FA-induced softening of the base bitumen. The photographs taken using an epifluorescence microscope according to *PN-EN 13632: Bitumen and bituminous binders. Visualisation of polymer dispersion in polymer modified bitumen* supplemented the analysis. A comparison of Figure 4a and Figure 4b highlights a finer character of the modified bitumen containing FA after ageing. This suggests an increase in the uniformity of polymer phase dispersion or the effect resulting from the breaking of Styrene–Butadiene–Styrene (SBS) chains. The change in the polymer phase structure confirms previous inference about the ageing character, based on the CAM model analysis.

The results of rheological properties (CAM model) of the polymer-modified bitumen with Fischer -Tropsch wax show slightly different trends. Shear modulus results versus frequencies obtained from the CAM model are shown in Figure 5.

Higher values of the average G^* distribution as a function of frequency and the lower value of the rheological index R were observed with the addition of the F-T wax compared to the effect of the FA addition. After ageing, the R index in the F-T wax modified bitumen was at a similar level on the logarithmic scale (Figure 2 (w parameter)). Analysis of f_c and w parameters indicates that before ageing, the bitumen stiffens with the increasing content of the wax, with a narrow frequency range for stress relaxation. Moreover, the low w suggests that despite high sensibility to loading time (narrow relaxation spectrum) caused by the low rheological index, the velocity of bitumen transition to the viscous material is extremely low. The ageing process caused minor changes of rheological parameters in the CAM model, which suggests high homogeneity of the modified bitumen-synthetic wax combination. Figure 4c illustrates microscopic observations. The "needles" dispersed in the polymer phase manifest the presence of synthetic wax crystallites. However, the presence of the wax crystallites increases the stiffness modulus of the modified bitumen compared to the reference bitumen. The crystallites dominate the image of the polymer phase, which shows that compared to fatty amines, synthetic wax more extensively inhibits the softening of the polymer-modified bitumen due to polymer chains degradation.

The analysis presented above was supplemented with the global evaluation of both the correlations between rheological parameters of modified bitumen with additions of FA and synthetic wax and the basic bitumen properties, such as penetration, softening point temperature and Fraass temperature, as compiled in Table 2.

No significant correlation was found between the values of parameter w and Fraass temperature (T_{FRAASS}) or between the rheological index R and penetration (p > 0.05). The correlation between the basic and rheological

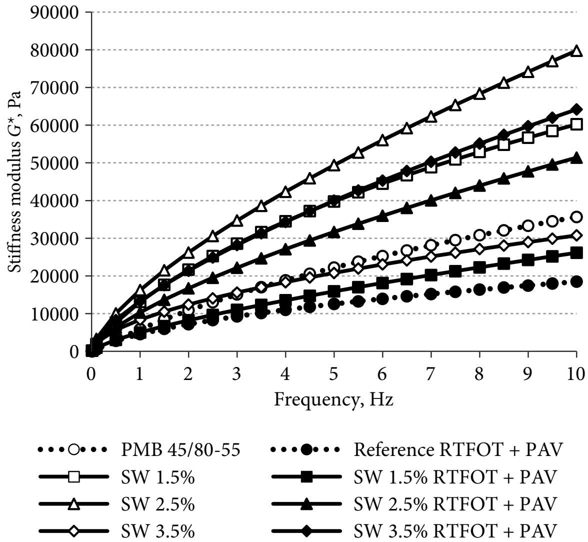

Figure 5. Complex modulus G^* of the PMB 45/80-65 bitumen modified with synthetic wax versus frequency at 60 °C

a) PMB 45/80-65 reference

b) PMB 45/80-65 + 0.6% FA

c) PMB 45/80-65 + 3.5% SW

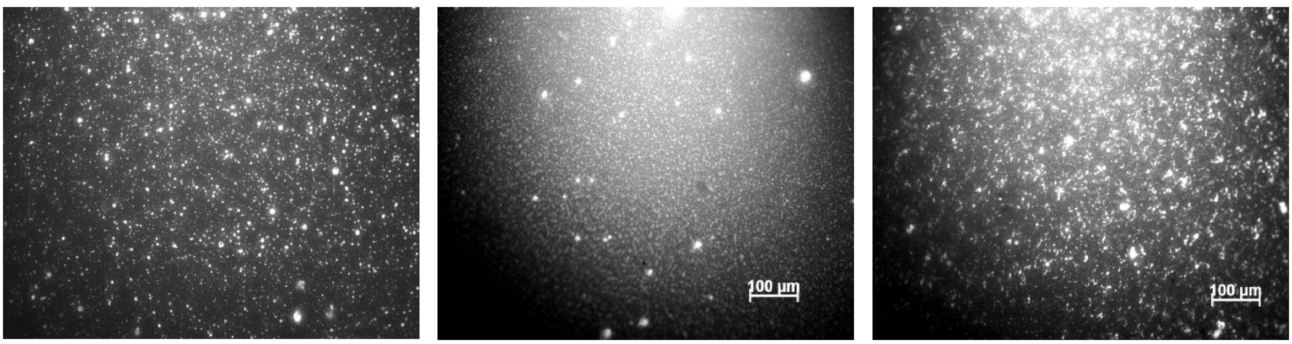

Figure 4. Fluorescence microscopy (zoom × 200) images of bitumen after ageing (RTFOT + PAV)

Table 2. Correlation matrix of basic properties and CAM model parameters

Variable	Correlations table Red-coloured values are significant		
	Penetration, ×0.1 mm	$T_{R\&B}$, °C	T_{FRAASS}, °C
R-index	$r = 0.560$ $p = 0.058$	$r = -0.610$ $p = 0.034$	$r = -0.580$ $p = 0.048$
w	$r = 0.590$ $p = 0.045$	$r = -0.660$ $p = 0.020$	$r = -0.560$ $p = 0.057$
v	$r = -0.620$ $p = 0.033$	$r = 0.620$ $p = 0.032$	$r = 0.620$ $p = 0.032$

parameters of the bitumen was low, with $r < 0.65$. In addition, the corresponding *p*-value is close to the critical level of 0.05. Therefore, the ageing of polymer-modified bitumen with FA or F-T wax has to be explained, in addition to the basic parameters, by advanced rheological assessment techniques accounting for the effect of the loading time.

Conclusions

The following conclusions were formulated based on the tests performed.

1. The Christensen–Anderson–Marasteanu (CAM) model fit values for the polymer-modified bitumen with synthetic wax and fatty amines at 60 °C show a high correlation at the level of more than 99%.
2. Fatty amines reduce the complex stiffness modulus of the reference bitumen before and after ageing.
3. As a result of ageing, the modified bitumen with fatty amines becomes a material sensitive to loading time and consequently shows a viscous response.
4. The use of synthetic wax increases the loading time sensitivity of bitumen (narrow relaxation spectrum) caused by a low level of the theological index; however, the velocity at which the bitumen will reach the viscous character is very low.
5. Synthetic wax is an insignificant factor in the bitumen or polymer homogeneity changes and contributes to an increase in the complex stiffness modulus of the reference bitumen, thus, influencing the deformation reduction in bituminous mixtures produced with the wax.
6. The presence of synthetic wax has a positive effect of inhibiting the decrease in the modified bitumen viscosity due to the degradation of polymer chains.
7. The basic bitumen parameters were found to show weak correlation with the Christensen–Anderson–Marasteanu (CAM) model parameters, what explains very well the changes of the stiffness modulus in the bitumens under analysis. To perform a comprehensive analysis of ageing, more advanced rheology methods have to be used.
8. The synthetic wax additive contributes to reaching higher results of complex modulus G^* than fatty amines additive.
9. The aging process causes an increase in complex modulus G^* results in case of fatty amines modified bitumen. However, in case of wax modified bitumen a decrease in G^* results was observed after RTFOT+PAV conditioning.

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