Effect of Tetradecane as low temperature phase change material on bitumen properties

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ABSTRACT

Temperature is significantly influencing the behaviour of asphalt road surfaces. In case of cooling, asphalt pavements become stiffer eventually reaching a brittle state at which thermal cracking may occurs. Phase change materials (PCM) respond to the environmental changes by actively altering their own properties by absorbing, storing, or releasing heat without changing their own temperature. Nevertheless, the application of phase change materials in thermoplastic materials, such as asphalt, has drawn attention only recently. The current study aims with an innovative approach for buffering and controlling extreme low temperatures in asphalt road surfaces by incorporating PCM as an additive for storing heat energy in a latent form. However, the results showed that the addition of PCM as raw material into the bitumen 10/20, 70/100 and 160/220 drastically decreased the conventional characteristics such as penetration and softening temperature as well as the complex modulus. The results of this study reveal that the direct interaction of PCM with bitumen significantly affects the rheological properties of bitumen without storing heat energy in a latent form. Therefore, the choice of a suitable PCM and its incorporation in bitumen (e.g. microencapsulation, shape stabilization) and possible leakage of protected PCM due to breakage of shell is very important in the context of bitumen modification.

Key words: Phase change materials, Bitumen rheology, Thermal cracking, Heat energy

1. INTRODUCTION

Asphalt pavements may experience thermally induced low temperature cracking in cold regions as well as thermal fatigue cracking in areas which experience large extremes in daily temperatures. These thermal cracking mechanisms of asphalt pavement are generally associated to the thermal stresses created when the asphalt binder slowly transforms from a ductile to a brittle material [1]. At low temperatures, asphalt pavements turn brittle and are not able to relax completely from traffic and temperature induced stresses. Hence they may suffer damage through crack initiation and propagation [2].

The use of phase change materials (PCM) as a latent heat storage system is an effective way of storing thermal energy which takes place when the material changes its phase from solid to liquid, or liquid to solid [3]. During the last years, PCM have been widely used in different materials such as concrete for energy saving purposes in buildings or for temperature-regulating textiles, e.g. in case of fire fighter uniforms [4, 5]. PCM with its remarkable capacity for thermal energy storage and stabilization and adaptability to environmental changes can be applied in pavement construction to adjust the temperature of highway pavements [6]. The optimization of the mixing procedure for incorporating PCM in asphalt will be one of the major challenges in determining the feasibility of the concept. Therefore, the method of incorporating PCM in hot mix asphalt (HMA) is still an open topic for researchers. Ma et al., [7] used shape-stabilized PCM, which is a mixture of the PCM with carrier material, carbon and silica in certain proportions. Zhang et al., [8] prepared shape-stabilized composite PCM for overcoming the leakage of PCM. Composite shape-stabilized PCMs (CPCM) were introduced in asphalt mixtures to protect the direct interaction of PCM with the bitumens. They were developed using Tetradecane, silica, Ethyl Cellulose (EC) and dispersant. Such CPCMs adjusted the temperature of the pavement, increasing its adaptability to environmental changes [9]. Manning et al. [10] investigated the feasibility of integrating HMA with PCM by using light weight aggregates (LWA) and proposed the use of protected shells to encapsulate PCM in asphalt mixtures. Dehdezi et al. [11] explored microencapsulated PCM in concrete and reported the breakage of micro shell during service. Therefore, the leakage of PCM in asphalt mixtures due to the breakage of micro shell during mixing and aging process is more probable and requires the need to investigate the direct interaction of PCM with bitumen and its influence on binder rheology. In this study, conventional parameters such as binder penetration and softening temperature were used to assess the physical effect of PCM with bitumen. Temperature sweep tests with Dynamic Shear Rheometer (DSR) were conducted for analysing the rheological behaviour and Differential Scanning Calorimetry (DSC) was used to assess the thermal properties after adding PCM to the selected set of bitumen grades.

2. MATERIALS AND METHODS

Three different penetration grade bitumens, 10/20, 70/100 and 160/220, were used. Bitumen samples were provided by commercial suppliers; therefore, details related to binder formulation are unknown. Normal Tetradecane (n-C_{14}) with melting point near 6°C makes it suitable for “low temperature” energy storage applications. Therefore, to study the impact of low temperature in bitumen, Tetradecane was selected as low temperature PCM due to its melting and crystallization temperature range from 5 to 6°C with purity of 99% (Sigma-Aldrich®, Switzerland).

The blending of Tetradecane with concentration of 1%, 5% and 10% by mass of bitumen was performed using a speed mixer (SpeedMixer™, DAC 150.1 FVZ) at 2000 rpm during 2 minutes. The temperature at the time of blending was 140°C, 130°C and 120°C, for bitumens 10/20, 70/100 and 160/220, respectively. Penetrations and softening points of bitumen unmodified and modified with PCM (Tetradecane) were determined according to European standard EN 1426 and EN 1427, respectively. Dynamic shear properties were measured with a Physica MCR 301 DSR (Anton Paar® GmbH., Austria) in a parallel plate configuration on 2 mm thick specimens with 8 mm in diameter. The upper and bottom plate faces were roughened to ensure good adhesion between plate and binder at low temperature [1]. Peltier Systems H-PTD200 and P-PTD200 (Anton Paar® GmbH., Austria) were used for cooling. A temperature ramp from 20 °C to -10 °C within 90 min (corresponds to a cooling rate of -0.44 °C/min) was used while applying oscillatory shear strain with constant strain amplitude (0.1%) and frequency (1 Hz) in order to avoid damaging the sample. The thermal analysis of PCM modified and unmodified bitumen was determined with DSC. Heat flow versus temperature was measured for the second heating cycle at a heating rate of 10°C/min.

3. RESULTS AND DISCUSSION

The results of bitumen penetration test are illustrated in Fig. 1(A). No significant effects on penetration grade of bitumen 10/20 are observed after adding 1% Tetradecane. However, the penetration grade alters when modifying bitumen with 5% and 10% PCM. It was noticed that bitumen becomes relatively soft when Tetradecane is added directly in concentrations of 1%, 5% and 10%. The soft bitumen 160/220 could not be modified with 10% PCM which resulted in bitumen flowing at room temperature; even after adding of 5% Tetradecane, the penetration results exceeded the maximum limits of the Penetrometer reading range. Similar behaviour was noticed for bitumen 70/100 when modified with 10% Tetradecane.

The softening point results shown in Fig. 1(B) indicate that the addition of Tetradecane causes a decrease in softening temperature irrespective of the bitumen type. The decrease in softening point is higher for higher concentration of Tetradecane, i.e. 10% by mass of the bitumen. After adding 5% and 10% Tetradecane, the softening point for the bitumen 70/100 and 160/220 is almost near room temperature.

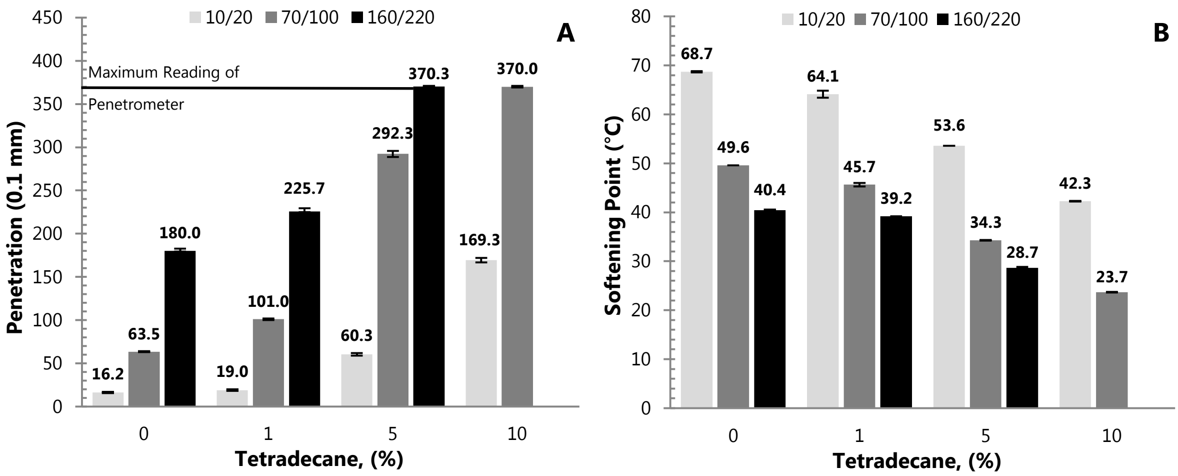

Figure 1: Effect of PCM modification on penetration (A) and softening point (B) of the different bitumens

The influence of directly adding Tetradecane into bitumen was clearly noticed after the analysis of the temperature sweep tests. As shown in Fig. 2, the addition of 10% Tetradecane reduces the complex modulus (G*) by up to approximately 90% compared to unmodified bitumen. However, the reduction in G* is limited to about 20% after adding 1% Tetradecane. The reduction in complex modulus of bitumen due to PCM modification is higher in bitumen 10/20 and the impact is even more significant for the high amount of PCM compared to unmodified bitumen 10/20. The testing of bitumen 160/220 with 5% modification was difficult due to its low viscosity. Therefore, the DSR temperature sweep measurements of bitumen 160/220 with only 1% are reported. The reduction in bitumen complex shear modulus might be due to the addition of the small molecules of Tetradecane that subsequently reduces the intermolecular bond strength, as a result tends to move apart the molecules in the bitumen after modification. Since, the internal forces between large molecules with high molecular weight in bitumen mainly govern the deformation behavior of bitumen. Therefore, the addition of Tetradecane resulted in diluting bitumen with significant reduction in complex modulus [12]. Since Tetradecane is a straight chain of hydrocarbons (n-alkanes) and acts as n-paraffin (C_nH_{2n+2}), one of the possibilities of the lower complex modulus of bitumen after modification might be due to the presence of n-alkanes in Tetradecane that precipitate the asphaltene content of bitumen [13]. Consequently, the higher amount of Tetradecane caused an increase in precipitation of asphaltene content and as a result the stiffness of bitumen reduced.

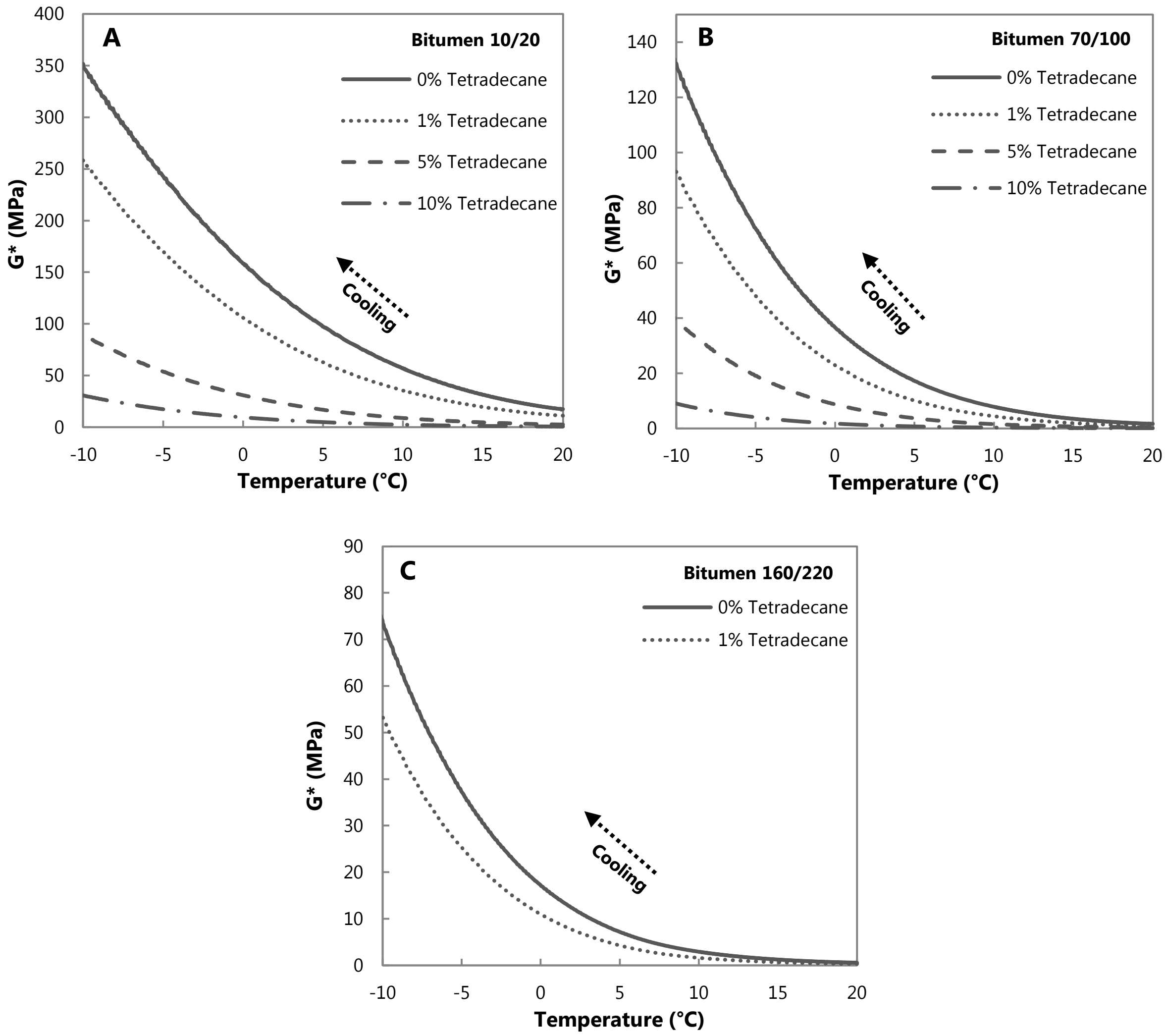

Figure 2: Effect of PCM modification on complex modulus as a function of temperature (Temperature sweep test)

In order to study the effects of PCM on the viscous components of the bitumen, the complex modulus (G*) versus phase angle (δ) were plotted as Black diagrams [14]. These provide an appropriate means of comparing the rheological properties of conventional penetration grade bitumens and modified bitumens. Black curve analysis is particularly convenient because rheological data needed for a mastercurve is directly measured in the DSR, with no mathematical shifts. Black space also captures phase changes in the binder, such as wax crystallization known to cause low temperature physical hardening [15].

As illustrated in Fig. 3, with the change in temperature, the rheological measurements show a combined effect of decrease in complex modulus and increase in phase angle. From Fig. 3 follows that the phase angle increases consistently with the decrease in complex modulus. The modified bitumen loses its elastic properties generally with the increase in temperature. This effect was more prominent in bitumens modified with high concentrations of Tetradecane. Compared to unmodified bitumen, the PCM modified bitumen can be seen as soft material at a relatively low temperature, and a phase separation characteristic appears generally with the increase in temperature. The increase in phase angle at relatively low values of G* indicates that the viscous properties of modified bitumen are more dominant than with the unmodified bitumen. This effect was more pronounced when higher concentrations of Tetradecane were used.

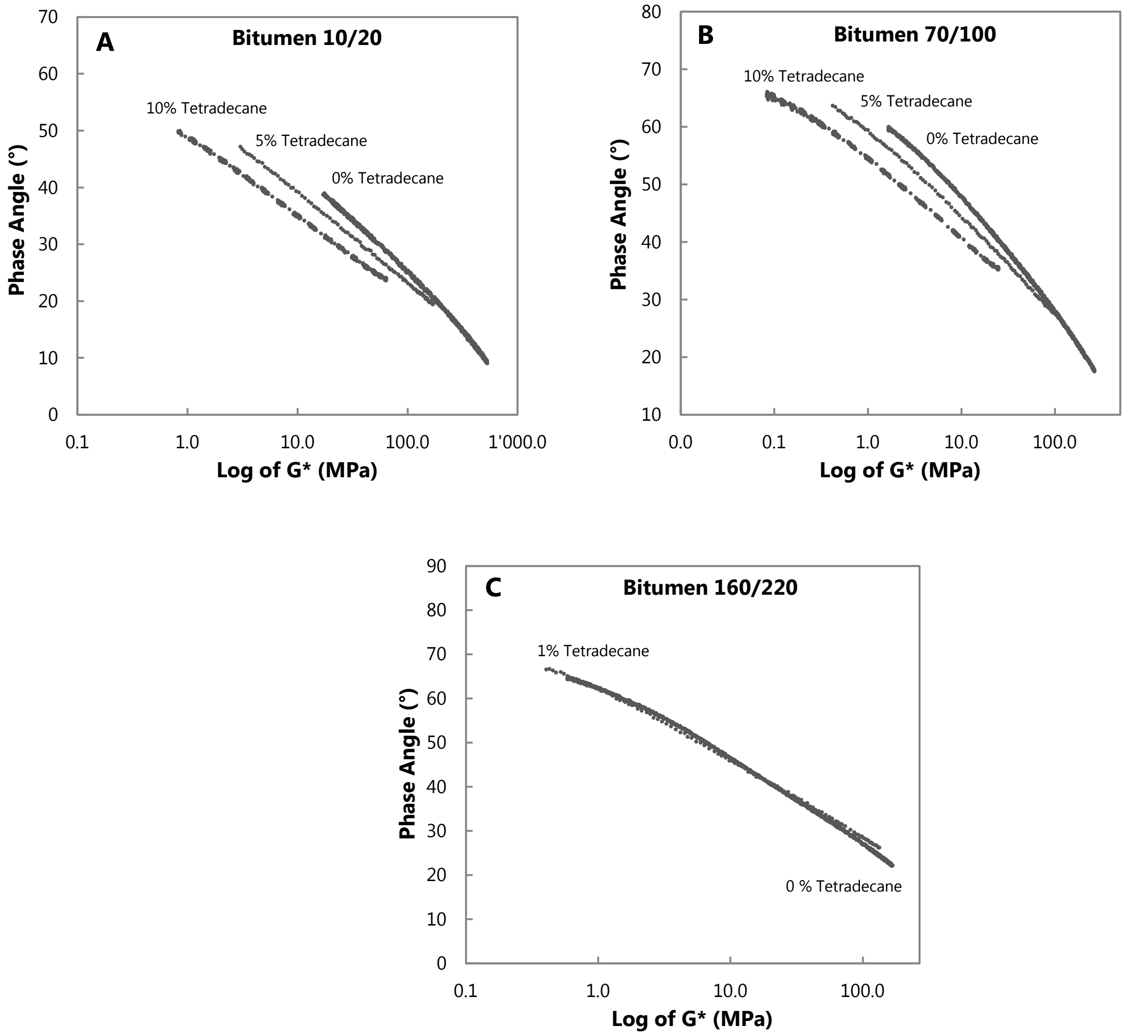

Figure 3: Effect of PCM modification on rheological parameters (Black curves)

The thermal behavior of bitumen 70/100 modified with only 5% PCM was analyzed to monitor the modification effects using calorimetry (Dynamic Scanning Calorimeter DSC). Figure 4 depicts the heat flow versus temperature curves for bitumen 70/100 with unmodified and 5% Tetradecane modification. As seen previously in the results of penetration, softening point and DSR temperature sweep tests, the incorporation of phase change materials resulted in lowering the stiffness of bitumen regardless of their initial properties.

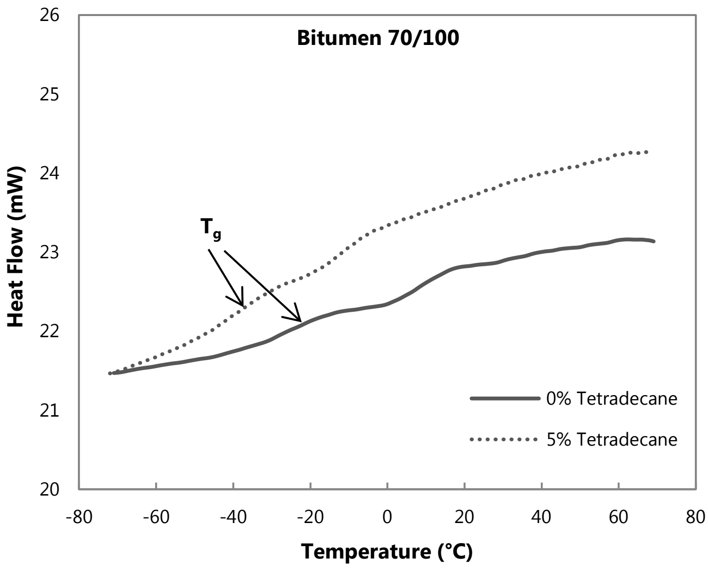

Figure 4: Thermal characterization of modified and unmodified bitumen with 5%. PCM (DSC Curves)

Moreover, an important thermal characteristic of bitumen that must be analysed is the so called glass transition temperature (T_g), where temperature above which bitumen molecules starts gaining mobility. From a macroscopic point of view, this thermal transition is at the boundary of two different asphalt behaviors that is glassy at low temperature ($T<T_g$) and viscoelastic at high temperature ($T>T_g$). The unmodified bitumen 70/100 show a first step in the heat flow curve indicating the overall glass transition at low temperatures between -10 to -35°C. Besides, another transition step can be observed around 2 to -20°C indicating a second, i.e. local, glass transition of still solid components in the bitumen or the melting of the crystallized natural wax. Similar thermal behavior has been reported, e.g. by Soenen et al. [16], where during heating a glass transition temperature is found and followed by the melting of the natural wax existing in the bitumen. By the addition of Tetradecane in bitumen 70/100, the thermal behavior of the modified bitumen is affected. On the one hand, the PCM contained in the modified bitumen does not show any melting peak (Figure 4) around the melting temperature of the Tetradecane (i.e. T_m = 6 °C), which indicates that the Tetradecane did not crystallize during cooling and, consequently, did not store or release heat in latent form (i.e. Tetradecane does not act as PCM in bitumen). On the other hand, the mean impact of the presence of Tetradecane is only the physical modification of bitumen as can be seen clearly in the heat flow curves. Indeed, the previously observed thermal transitions (T_g) in unmodified bitumen are shifted to lower temperatures (Figure 4). The former result is of importance, since a decrease in the glass transition temperature reflects the softening of the bitumen with addition of PCM. This result is in agreement with the rheological measurements demonstrating the dramatic effects of the Tetradecane incorporation on the stiffness of bitumen tested. Beside the change in T_g an increase in heat capacity of modified bitumen was also observed which indicates the increase of the storage of heat.

4. CONCLUSIONS

The physical interaction of PCM (Tetradecane) with different grades of bitumen (160/220, 70/100 and 10/20) was evaluated using the conventional bitumen penetration and softening point test. The effect of modification on bitumen rheology was further analysed by using temperature sweep measurements with the DSR. Moreover, the thermal properties of bitumen 70/100 modified with 5% PCM were assessed by using the differential scanning calorimetry. The direct addition of Tetradecane as raw PCM material into the bitumen extremely decreased the penetration, softening temperature and complex shear modulus. These results indicate that the PCM application method is very important in the context of asphalt mixture modification and any leakage of encapsulated PCM could significantly affect bitumen properties. Furthermore, no melting peaks were observed around the melting temperature of Tetradecane (T_m = 6 °C) when interacting directly with bitumen, which reveals that the Tetradecane did not crystallize upon cooling and therefore does not store or release heat in latent form. In contrast, the mean impact of the presence of Tetradecane was only the physical modification of bitumen. Therefore, the use of suitable microencapsulation to protect Tetradecane as PCM and its importance during mixing procedures must be considered for the purpose of energy storage in bitumen at low temperature. Moreover, using porous material such as PCM carrier (light weight aggregate, fillers) can be an alternative to protect the direct interaction of these materials with bitumen.

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