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INVESTIGATING THE AGEING PROCESS OF POLYMER MODIFIED BITUMEN USING A MODIFIED THIN-FILM OVEN TEST IN THE ASPECT OF RECYCLING PURPOSE

BADANIE PROCESU STARZENIA ASFALTU MODYFIKOWANEGO POLIMERAMI PRZY ZASTOSOWANIU ZMODYFIKOWANEJ METODY CIENKIEJ WARSTWY W ASPEKCIE RECYKLINGU

STRESZCZENIE. Asfalt modyfikowany polimerami (PMB) to szeroko stosowany materiał do budowy dróg. Powszechnie asfalt modyfikowany polimerami wytwarzany jest poprzez mieszanie bitumu z różnymi rodzajami kopolimerów styrenowo-butadienowo-styrenowych (SBS) oraz, w razie potrzeby, z innym dodatkiem, takim jak środek sieciujący, w celu poprawy wydajności materiału. Proces starzenia asfaltów modyfikowanych polimerami jest bardziej złożony niż niemodyfikowanego asfaltu ze względu na interakcje molekularne między asfaltem a polimerem. Wcześniejsze badania sugerują, że modyfikator polimeru dominuje w degradacji chemicznej asfaltów modyfikowanych polimerami podczas starzenia krótkoterminowego, podczas gdy starzenie długoterminowe jest zdominowane przez utlenianie bitumu. W rezultacie destrukt asfaltowy zawierający asfalt modyfikowany polimerami jako spoiwo nadal zawiera polimer w swoim składzie chemicznym, co podkreśla potrzebę kompleksowego zrozumienia procesu starzenia asfaltów modyfikowanych polimerami. W obecnej praktyce destrukt asfaltowy jest podgrzewany przed zmieszaniem z materiałami pierwotnymi, aby umożliwić reaktywację jego starzejącego się spoiwa. W niniejszym badaniu zaproponowano metodę cienkiej warstwy (TFOT) jako metodę symulacji starzenia, ze zmianami czasu i temperatury w celu symulacji starzenia podczas procesu mieszania destruktu asfaltowego. Zjawisko utleniania bitumu przeważnie dominuje w procesie starzenia. Z analizy wskaźników ilościowych wynika, że w warunkach krótkiego czasu trwania i niższej temperatury degradacja polimeru pomaga w krótkim czasie ograniczyć proces starzenia. Co więcej, badanie DSR wykazało, że starzenie spowodowało wzrost złożonego modułu asfaltu modyfikowanego polimerami przy jednoczesnym zmniejszeniu kąta fazowego, co wskazuje na utwardzenie i przesunięcie w kierunku bardziej elastycznego zachowania. Najbardziej widoczny efekt starzenia można zaobserwować w niższej temperaturze testowej dla kąta fazowego i wyższej temperaturze testowej dla modułu zespolonego. Ogólnie rzecz biorąc, temperatura warunków starzenia odgrywa bardziej znaczącą rolę w dyktowaniu wpływu starzenia na asfalt modyfikowany polimerami niż czas jego trwania.

SŁOWA KLUCZOWE: asfalt modyfikowany polimerami, recykling, destrukt asfaltowy, starzenie, FTIR.

ABSTRACT. Polymer Modified Bitumen (PMB) is a widely used material for road construction. Commonly, PMBs are produced by mixing bitumen with various types of Styrene-Butadiene–Styrene (SBS) copolymers and, if necessary, with another additive such as a cross-linking agent to improve the material's performance. The ageing process of PMBs is more complex than unmodified bitumen due to molecular interactions between the bitumen and the polymer. Previous studies suggest that the polymer modifier dominates the chemical degradation of PMBs during short-term ageing, while long-term ageing is dominated by bitumen oxidation. As a result, RAP containing PMB as its binder still contains polymer in its chemical composition, emphasizing the need for a comprehensive understanding of the ageing process of PMBs. In current practice, RAP is heated before being mixed with virgin materials to allow reactivation of its aged binder. This study proposes a modified Thin-Film Oven Test (TFOT) as an ageing simulation method, with variations in time and temperature to simulate ageing during the RAP mixing process. The bitumen oxidation phenomenon mostly dominates the ageing process. From quantitative indices analysis, under short duration and lower temperature conditions, the polymer degradation helps to resist ageing shortly. Moreover, the DSR test shows that ageing caused the PMB to increase in complex modulus while decreasing in phase angle, indicating hardening and shifting toward more elastic behaviour. The most prominent effect of ageing can be observed at lower test temperature for phase angle and higher test temperature for complex modulus. Generally, the ageing conditions' temperature has a more significant role in dictating the ageing effect on PMB than the duration.

KEYWORDS: polymer modified bitumen, recycling, RAP, ageing, FTIR.

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1. INTRODUCTION

Bitumen has been consistently studied to understand how it works in connection with the load-bearing capacity and how it affects road construction's quality as a whole. Modification on bitumen is designed to change its rheological, viscoelastic, and ageing properties. Properties include penetration, elasticity, adhesive or cohesive strength [1, 2]. In road construction, this modification can be done by chemical agents, most notably polymers, by mixing then with bitumen. The choice of polymer is because entropy change per unit volume in the mixture will be extremely small. Thus, homogeneity in the mixture can be easier to achieve [3]. Thermoplastic polymers mixed with bitumen are usually in two categories: elastomers and plastomers. Elastomers usually have more elasticity against the pavement at low temperatures, and after the stresses are relieved, the previously caused strains also disappear due to elastic recovery. Plastomers cause the hardening and stiffening to be increased against permanent deformations, and only under a small load do they undergo reversible (elastic) deformations. Usually, they also do not affect or worsen the low-temperature properties [4, 5, 6, 7]. The most popular agents, but not limited to, are Styrene-Butadiene-Styrene (SBS), Polyethylene (PE), and Crumb Rubber. Adding polymer improves bitumen's low-temperature flexibility, permanent deformation, and rutting resistance, thus improving the durability and longevity of pavement construction [8, 9, 10].

The exposure of bitumen to heat, oxygen and sunlight as a result of the production process and during its service life causes the bitumen to age. The combination of those factors is closely associated with the oxidative reaction between bitumen and oxygen and the volatilization of light fraction, increasing the content of polar oxygen-containing molecules and bitumen molecular weight. This process leads to the deterioration of the mechanical and rheological properties of the PMB, resulting in cracking and other types of pavement distress. The degree of ageing depends on the unique exposure conditions, such as the region's climate, UV radiation intensity, and duration of the exposure. The ageing process of PMBs is more complex than unmodified bitumen due to molecular interactions between the bitumen and the polymer. Previous studies suggest that the polymer modifier dominates the chemical degradation of PMBs during short-term ageing, while long-term ageing is dominated by bitumen oxidation. As a result, RAP containing PMB as its binder still contains polymer in its chemical composition, emphasizing the need for a comprehensive understanding of the ageing process of PMBs.

In current practice, RAP is heated before being mixed with virgin materials to allow reactivation of its aged binder during production. In the laboratory, the short-term changes in properties of bitumen as a result of pavement production are simulated by using the Rolling Thin Film Oven (RTFOT) test (ASTM D 2872) and the Thin Film Oven Test (TFOT). However, the RTFOT method is considered unsuitable when applied to PMB bitumen [11]. The test temperature specified in the manual does not correlate to the actual ageing condition, as reported by researchers. Many tests were carried out at higher temperatures to match the field condition. The suitable temperature condition for RTFOT remained unclear [12]. The sample residual taken from the test is very small, thus minimizing its efficiency. Due to its higher viscosity nature, PMB samples may not flow adequately to ensure a uniform film formation when tested [13]. Furthermore, RTFOT shows a lower and weak correlation on an ageing degree compared to the mixed plant samples [14].

Not only for short-term ageing, the standardized PAV long-term ageing (AASHTO R 28-06) is also criticized for its application on PMB by researchers. Especially for SBS modified binders, the test temperature may melt the polystyrene block [15]. Many researchers agreed on procedure modification by extending the time for its ageing simulation. Moreover, studies by Tian and Xu [13, 16] used Thin-Film Oven Test (TFOT) as their selected short-term ageing procedure. Therefore, this study proposes a modified TFOT as an ageing simulation method, with extended variations in durations and temperatures to simulate ageing during the RAP mixing process. The aim is to observe the effect of time and temperature on the PMB ageing process.

2. EXPERIMENT

2.1. MATERIAL

The material used in this study is unaged PMB 25/55-60 with a penetration value of 41 × 0.1 mm and a softening point of 66.5°C. That type of binder is commonly available in the Polish market to ensure a higher chance that the same type of PMB will be found on RAP. Usually used in binder courses, therefore the UV effect can be neglected. Specifically for this research purpose, due to its high viscosity nature, it is used as an example to see how PMB aged as stiffer bitumen is expected to be found in RAP. Moreover, stiffer bitumen has lower susceptibility to ageing [17, 18].

2.2. AGEING CONDITIONING METHOD

The PMB samples were collected in a stainless steel pan with an inner diameter of 140 mm. Each consisting of 50±0.5 g of bitumen sample makes the film sample thickness about 3.2 mm. Bitumen samples were subjected to a modified TFOT method with time and temperature variations. The time ranges from 1h–5h, and temperatures range from 120°C–200°C, thus creating a total of 25 sample types. All samples are coded according to their time and temperature combination, e.g. 2h_140°C for samples that undergo 2 hours of heating at 140°C. Samples after the ageing process were then extracted into a can container.

2.3. TESTING METHOD

2.3.1. FTIR spectrum measurement

The change in chemical composition after the ageing condition is observed using Fourier-Transform Infrared (FTIR) Spectroscopy at room temperature. The spectra were recorded from 4000 cm^{-1} to 600 cm^{-1} at a resolution of 4 cm^{-1}. For each sample, four small pallets of bitumen sample were extracted from the can container and then placed on a small piece of paper. It was followed by taking 20 data trials with 24 scans for each data to enhance the signal to noise ratio of the measurement. The process undergoes three rounds of repetitions to ensure the consistency of the result. The files were then analyzed and modified using the OPUS 8.5 software. The whole set of one sample results is modified to get the average combined spectrums, then correction on the spectrum baseline is applied, and quantitative ageing indices analysis is to be calculated by computing the area below each observed wavenumber peak.

Main changes in the bitumen spectrum are observed on specific wavenumber peaks referring to its chemical bond [7, 19, 20]. Table 1 summarizes the wavenumber peaks to be observed. To quantify the changes in its chemical components, several ageing indices are introduced based on the following formula:

- Aliphatic Index $A_{1350\text{-}1510} / \Sigma_A$
- Aromatic Index $A_{1535\text{-}1625} / \Sigma_A$
- Carbonyl Index $A_{1678\text{-}1725} / \Sigma_A$
- Sulphoxide Index $A_{1010\text{-}1043} / \Sigma_A$
- Σ_A is the sum of every area for each chemical bond index.

Table 1. Wavenumber peaks in reference to ageing

Chemical group	Bond	Approximate wavenumber peak	Ageing indication
Aliphatic	CH_2, CH_3	1460, 1375 cm^{-1}	Small decrease
Aromatic	C=C	1600 cm^{-1}	Small increase
Carbonyl	C=O	1690 cm^{-1}	Increase
Sulphoxide	S=O	1030 cm^{-1}	Increase

For polymer modified bitumen, especially those modified with SBS, an extra index is to be used, namely the Butadiene/Styrene Index ($I_{B/S}$), calculated as $A_{966cm^{-1}}/A_{699\ cm^{-1}}$. It is taken from the fact that polybutadiene molecular is more active than polystyrene. Polybutadiene deteriorates faster during ageing, while polystyrene hardly degrades during the bitumen's lifetime. Therefore, smaller $I_{B/S}$ can mean a higher degree of SBS polymer degradation [7, 21].

2.3.2. Rheological test on DSR

Rheological changes in this study were observed using a Dynamic Shear Rheometer (DSR). The strain level is taken to maintain its linear position on the LVE region for the 25mm and 8mm diameter plates. Test temperatures range from 30–70°C for a 25 mm diameter plate and 0–30°C for an 8 mm plate with 10°C intervals and angular frequency range of 0.1, 1.0, and 10 Hz.

3. RESULT AND DISCUSSION

3.1. CHEMICAL CHANGES ANALYSIS

The spectra of PMB 25/55-60 under unaged and several selected aged conditions are presented in Fig. 1. It can be seen that the increase in temperature and time for ageing conditioning resulted in a higher peak for its carbonyl band (1690 cm^{-1}) since this peak is commonly used to characterize ageing in bitumen.

The ageing indices were calculated for each chemical group to study the influence of time and temperature on the bitumen sample, as was mentioned in Table 1, with the additional $I_{B/S}$ index. The calculated values from aged samples are normalized to the unaged PMB 25/55-60 binder for the same ageing indices to evaluate the chemical changes. When the value is equal to 1, the sample is unaged. Figure 2 presents the ageing indices of the carbonyl (a), sulphoxide (b), aliphatic (c), aromatic (d), and $I_{B/S}$ (e) bands. Error bars on the graph are

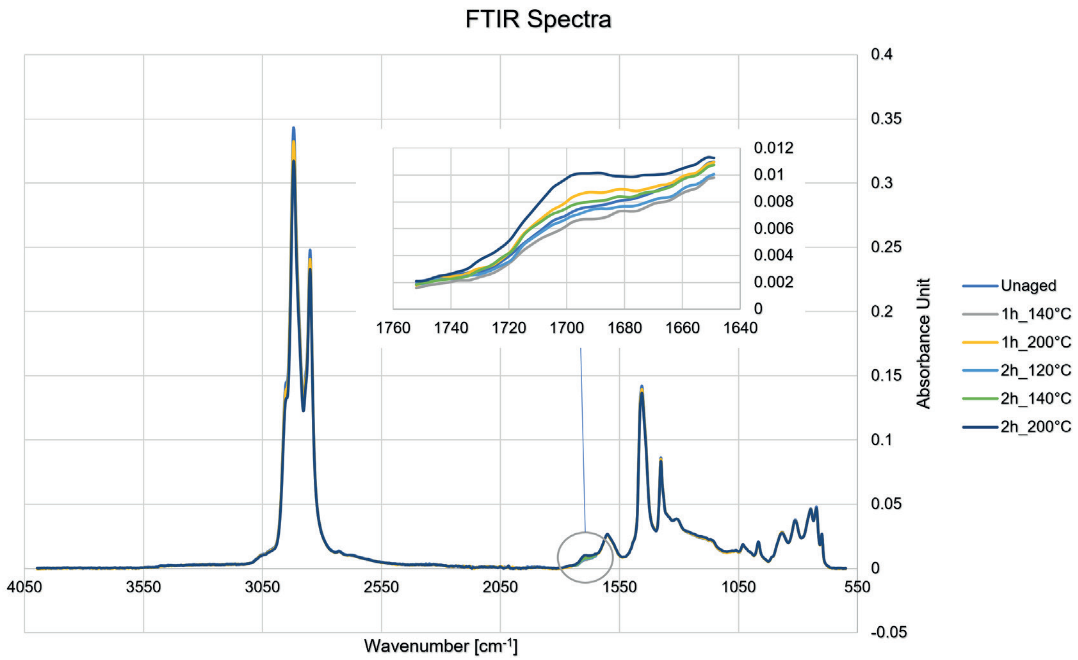

Fig. 1. FTIR spectra of selected samples

not shown due to their diminutive value. For instance, the carbonyl band calculation has 0.02 in standard deviation, hence, it will obstruct the clarity of the figure.

Generally, based on the calculated indices, we can confirm that the bitumen sample experienced ageing to a certain degree, referring to the signs in Table 1. The carbonyl peak at 1690 cm^{-1} and sulphoxide at 1030 cm^{-1} are commonly used to characterize the oxidation process in a bitumen. It can be observed that the general trend is that the increase in temperature leads to an increase in the formation of carbonyl compounds, while sulphoxide does not seem to have significant changes. The sulphoxide index is an important factor in analyzing the oxidation level. Nivitha et al. reported that modified binders tend to have a similar rate of sulphoxide formation [22]. Even after a prolonged time, the index will experience reduction due to the decomposition of sulphoxide, as investigated by Branthaver et al. [23].

For carbonyl compound, however, it can also be observed that samples undergo 1h, 3h, and 5h at 140°C, with a 5–10% reduction in value, meaning the sample somehow "rejuvenates" itself to resist the oxidation process. To evaluate the reason behind this phenomenon, in the case of polymer modified binder, polymer materials are known to blend in with the base bitumen and create nodules that swell from absorbing the light bitumen fraction, forming an island-like structure as reported in [24, 25, 26]. This light bitumen fraction may "leak" due to the degradation of the polymer molecule and mixed with the aged fraction. Figure 2 (e) also confirms the lower value of $I_{B/S}$ values for 1h, 3h, and 5h samples at 140°C, which means that those samples undergo a higher rate of polymer degradation (around 2–6%) compared to the other sample conditions. That is also why some researchers often found the softening point of PMB after short-term ageing to be decreased, indicating a softer form [18, 27]. As for the 2h and 4h samples in 140°C, the carbonyl index slightly increases from the reference unaged sample. That may happen due to inaccuracy in reproducibility, particularly during the baseline correcting and averaging, causing imprecision in calculating the area of the spectra. Additionally, polymer degradation is lower for a sample that undergoes 4h and 5h in 200°C. That suggests that bitumen oxidation prevails over polymer degradation for higher and longer ageing conditions.

The swelled polymer may hinder the pathway for oxygen diffusion and create less oxygen availability to the bitumen molecule. It is also worth noticing that the better the dispersibility of the asphaltenes content, the higher the formation of the carbonyl compound [28]. However, the modifier molecules disturbed the asphaltenes network, leading to reduced carbonyl formation [22, 29].

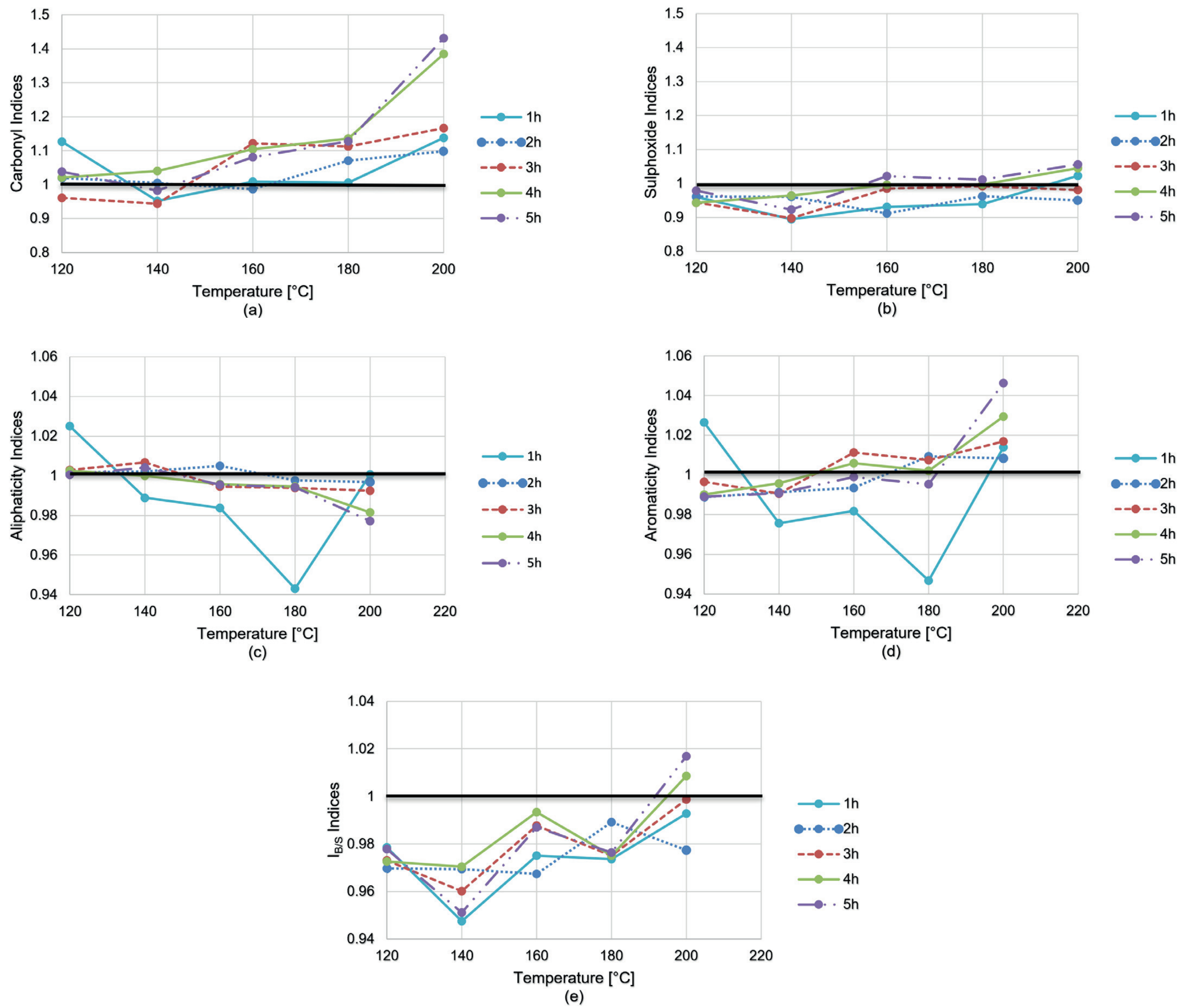

Fig. 2. Ageing Indices (a) Carbonyl; (b) Sulphoxide; (c) Aliphaticity; (d) Aromaticity; and (e) $I_{B/S}$

The Aliphaticity and Aromatic indices are connected with each other. The process of forming an aromatic bond corresponds to the decrease in aliphatic structures at the same time. Aromatization in bitumen due to ageing corresponds to forming aromatic rings to join each other and subsequently increasing its viscosity due to cluster formation. Nevertheless, for the sample that undergoes 1 hour of ageing condition, the aromatization differs from the rest of the sample, possibly due to the short ageing duration. Moreover, the different values seem to be small in magnitude, therefore they can be overlooked.

3.2. RHEOLOGICAL ANALYSIS

Figure 3 shows the complex modulus value G* diagrams and phase angle δ for selected bitumen samples on 0.1, 1.0, and 10 Hz to showcase the effect of different times and temperatures on its rheological properties. In PMB ageing, it is generally understood that polymer degradation makes the sample less stiff and elastic, while bitumen oxidation makes the sample stiffer and more elastic [30].

We acknowledge that polymer degradation and bitumen oxidation happen at the same time. The complex modulus graphs show the ageing in PMB samples, causing the complex modulus G* value to increase, which indicates hardening. The phase angle δ graphs show a decreasing trend in higher test frequency, indicating an increase in the elastic behaviour of the bitumen. It is also worth noticing that the 2h_140°C and 5h_140°C samples exhibit fairly same G* values while comparing 5h_120°C and 5h_200°C or 2h_140°C and 2h_200°C shows a notable difference.

Further analysis was conducted based on Figure 3 on the degree of G* and δ values and their percentage change related to the unaged state. Observation is based on the result for selected test temperatures of 20°C and 60°C to simulate service temperature and extreme near softening value temperature, respectively, on 1 Hz frequency. The calculated changes are presented in Figure 4. The sample undergoes ageing for 2 hours at 140°C and has 4% increase of G* in both test temperatures compared to the unaged sample. For samples with the same ageing duration but at 200°C, 50% of the average increase in

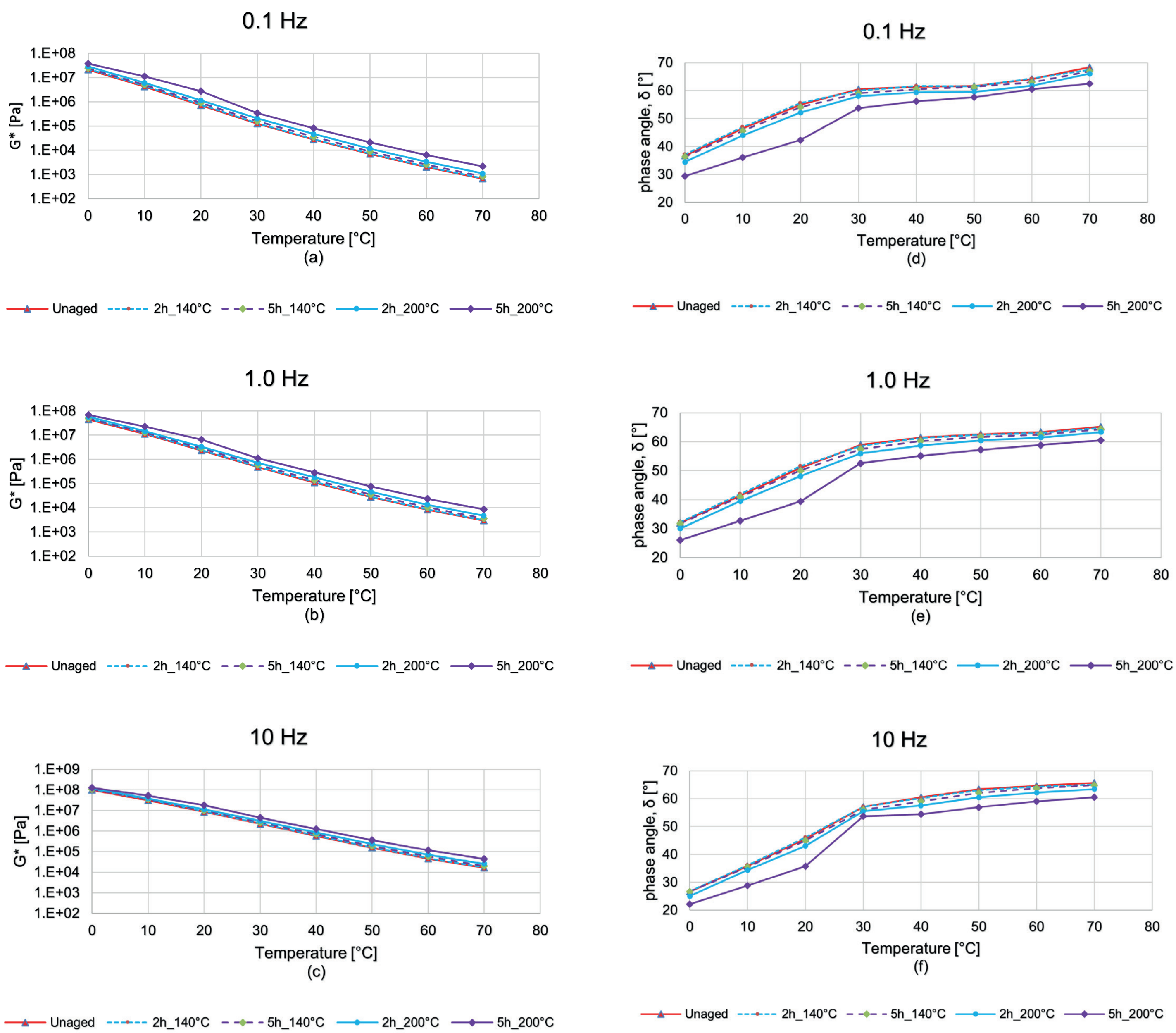

Fig. 3. Complex modulus G* a), b), c) and phase angle δ d), e), f) in 3 different frequencies

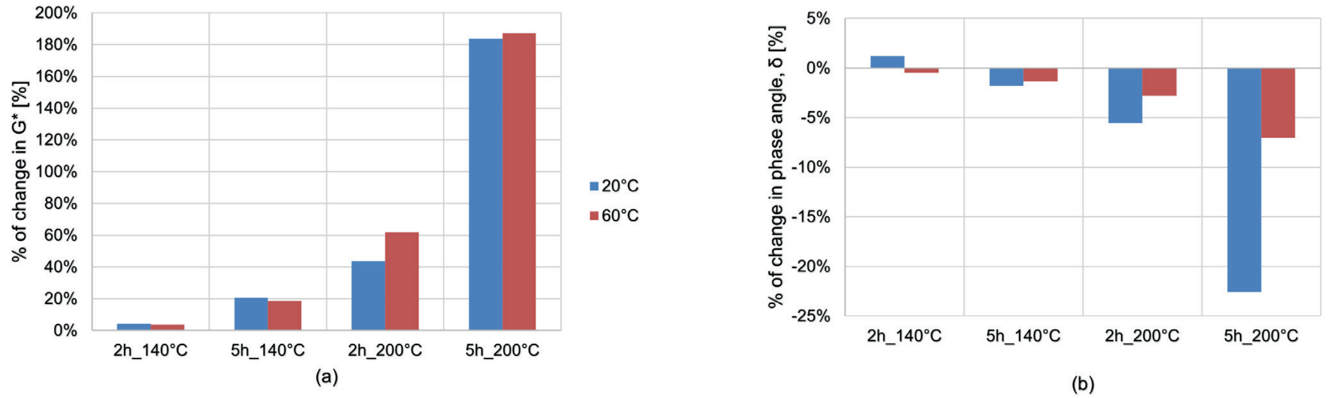

Fig. 4. Percentage changes of (a) G* and (b) δ values of selected samples

both test temperatures was observed. In the most extreme ageing condition of 5 hours at 200°C, a 180% increase in G* value was observed compared to the unaged sample.

The same trend also applied to the change of δ value. The least ageing condition of 2 hours and 140°C does not significantly reduce δ value. At the same time, 5 hours and 200°C give a 7% reduction at 60°C and 22% at 20°C. Therefore, it can be said that conditioning duration for tested PMB does not significantly change the rheological properties of bitumen. One should apply more caution to the temperature effect instead.

4. CONCLUSIONS

The study investigates the ageing effect on PMB that undergoes different durations and temperatures. The evolution of chemical properties in PMB as the effect of ageing was monitored using indices from FTIR spectroscopy results corresponding to the bitumen oxidation and polymer degradation. Moreover, the rheological changes were evaluated based on complex modulus and phase angle. Bitumen oxidation and degradation of polymer occurred simultaneously. The bitumen oxidation is observed using the carbonyl band as the reference peak. As expected, the higher the duration and temperature of ageing conditioning will result in the higher oxidation degree. The bitumen oxidation phenomenon mostly dominates the ageing process. However, polymer degradation prevails at lower temperatures and shorter duration and helps "rejuvenate" the binder.

From rheological analysis, ageing caused the PMB to increase in complex modulus, while the decrease in phase angle indicated hardening and an increase in the elastic manner. Short duration and low temperatures ageing do not cause significant changes. The most prominent effect of ageing can be observed at lower test temperatures for phase angle and higher test temperatures for complex modulus value.

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