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Microstructure evaluation of polymer-modified bitumen by image analysis using two-dimensional fast Fourier transform

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Abstract

Aiming to quantitatively evaluate the microstructure of polymer-modified bitumen (PMB) for roads, this paper employs the two-dimensional fast Fourier transform (2D-FFT) to process the microscopic and numerical images of four PMBs. The related derivative parameters, including the characteristic frequency and wavelength, are computed from the 2D-FFT power spectrum. The results show that the absence/presence of a characteristic frequency (range) on the power spectrum can indicate the lack/existence of the corresponding periodical structural pattern(s) in the original PMB image. A lower characteristic frequency usually represents a coarser PMB microstructure while a higher one implies a finer PMB microstructure. The 2D-FFT method is thus valid for differentiating various PMB microstructures. The proposed method is also capable of quantitatively evaluating the effects of temperature and the temporal evolution of PMB microstructure during phase separation. As the separation continues, the decrease of characteristic frequency indicates the coarsening process of a PMB microstructure. Additionally, the numerical reproduction of the observed phase separation is evaluated with the same method. The quantitative comparison with the experimental results reveals that the simulations fairly reproduced the microscopy observation results despite some deviation. The proposed method provides a foundation for the microstructure-based modelling of PMB performance in the future.

Keywords: Microstructure; Polymer-modified bitumen; Fluorescence microscopy; Image analysis; Fourier transform

1. Introduction

Polymer-modified bitumen (PMB) is widely used as a high-grade binder for the construction and maintenance of road surface layers in many countries, due to its enhanced performance comparing with the base bitumen [1-3]. As a composite material in a general sense, PMB has been intensively studied for decades in order to understand its composition-structure-property relationship [4]. Among the previous studies, PMB microstructure (in other word morphology) attracted a lot of attention from researchers all over the world [5-32]. This is because the microstructure is not only related to the PMB stability during storage and transport at high temperatures, but also affects the binder properties and thus finally the road performance at service temperatures.

Various microscopes were employed to investigate the PMB microstructure, including optical and electron microscopes. Microscopic results display the microstructure visually by images. However, the evaluation of the observed PMB microstructure relies on the analysis of the captured images. The homogeneity of a microscopic image from the storage temperature is usually qualitatively related to the PMB storage stability. But some previous studies [18-31] did try to evaluate the PMB microstructure quantitatively with the image analysis method. Most of these studies [18-20, 22-24, 26-28, 30] discussed the percentage (area fraction) of the polymer-rich phase while some others analysed the number, size and shape of the polymer-rich droplets [20, 21, 25, 30].

The percentage of the polymer-rich phase in a PMB is determined by the polymer content and the swelling ratio of the polymer modifier. Although it is an important factor, the percentage by itself does not reflect the specific PMB microstructure. Nevertheless, the analysis of polymer-rich droplets might be feasible for PMBs with a dispersed droplet structure, but it does have the difficulty in evaluating more complex structures, e.g. the widely reported ideal PMB microstructure with two interlocked continuous phases. Furthermore, a few derivative parameters from the average pixel information of processed images [29, 31] were recently reported for quantitatively evaluating PMB microstructure and storage stability. However, the simply averaging of the image pixels may erase and hence lead to missing some of the most important PMB structural information. Thus, new quantitative parameters with higher validity are still needed for the effective evaluation of PMB microstructure. The potential applications of these parameters can be, for example, the comparison between the numerical simulation and experimental results, microstructure-based modelling of PMB performance and more.

With the aim to quantitatively evaluate the PMB microstructure, this paper uses a two-dimensional fast Fourier transform (2D-FFT) algorithm to process the PMB microscopic images and computes the related derivative parameters. After a brief description of the studied materials and employed method, the microstructures of four different PMB binders are analysed with the image analysis results. The effects of temperature are discussed. The entire PMB phase separation process observed at different time points is characterised with the computed derivative parameters. Finally, the numerical reproduction of the observed phase separation is assessed and compared with the experimental results.

2. Materials and method

2.1. Materials

Four different PMB binders are studied in this paper, i.e. PMB1, PMB2, PMB3 and PMB4. They all contain the same 5% linear styrene-butadiene-styrene (SBS) copolymer as the modifier by weight of the blend. The SBS copolymer has a weight average molecular weight of 189000 g/mol. But the four base bitumen binders in the PMBs are from different sources despite the same penetration grade 70/100. The PMBs were prepared in laboratory by mixing the modifier and base bitumen binders at 180 °C with stirring at about 500 rpm for 3 hours. The conventional PMB properties, including penetration, softening point, penetration index and 180 °C storage stability, were tested and listed in Table 1.

Table 1. Polymer-modified bitumen properties

Property	Method	PMB1	PMB2	PMB3	PMB4
Penetration, 25 °C (0.1 mm)	EN 1426	57	52	56	52
Softening point, Ring & Ball (°C)	EN 1427	76.0	85.0	77.8	65.0
Penetration index	EN 12591	4.1	5.1	4.3	2.1
180 °C storage stability, softening point difference (°C)	EN 13399	25.5	0.0	-1.0	32.0

2.2. Method

2.2.1. Microscopy observation and numerical simulation

Both experimental and numerical PMB microstructure images are analysed and discussed in this study. The experimental images of the four PMB binders were captured by a fluorescence microscope at room temperature. The thin film method [15] was used for the microscope slide preparation by spreading a drop sample with a cover slip and fast cooling of the sample from a higher temperature. Due to the small amount and thin film of PMB for each slide, it is believed that the observations of thin film samples can represent the original PMB morphology at higher temperatures. In addition to the ordinary observation of PMB slides prepared from 180 °C, isothermal annealing conditioning was conducted for different time (0 s, 300 s, 600 s, 1800 s and 3600 s) to capture the phase separation process in the unstable PMBs. To minimise the orientation effects because of sample flowing during the spreading and conditioning, the observation was focusing on the centre areas of the slides. For more details on the experimental procedure, please refer to [17]. Although [17] focused on exploring the driving forces for the phase separation in PMB, this paper presents a new approach to PMB microstructure evaluation. To investigate the sensitivity of the new approach on evaluating the effects of temperature, the microscopy observation results of samples from 160 °C and 120 °C [33, 34] are studied in this paper. They were the observation results of the same four PMBs after 1 hour of isothermal annealing conditioning at the specified temperatures following the same experimental procedure.

Furthermore, numerical images from simulations are also analysed in this study. A previous paper by the authors [35] presented the used phase-field model for the phase separation in PMB and numerically reproduced the microscopy observation results of the same PMBs as in this paper during the entire phase separation process. However, the assessment of numerical reproduction on the basis of the experimental results remained an issue in spite of the visual similarity, i.e. how to compare a numerical simulation with respect to the experimental results. In this study, the experimental and numerical PMB microstructure images are processed and analysed with the same method. The computed derivative parameters of the experimental and numerical images are compared and discussed for numerical reproduction assessment.

2.2.2. Image analysis using 2D fast Fourier transform

Image analysis is the extraction of physical information from an image. In terms of microstructure characterisation, the 2D-FFT processing of microscopic images has been a widely-used method for reciprocal space image analysis of metal and polymer systems [36-42], although its use was hardly ever reported for PMBs. With this method, a microstructure is usually characterised by its 2D-FFT power spectrum. A 2D-FFT power spectrum in the reciprocal space (k space), which is computationally obtained from an original microscopic image, corresponds to an image experimentally obtained by small angle scattering (light, neutron or X-ray) [36, 42]. Thus, it has the unique strength in characterising the internal structure and obtaining the direct structural information of disordered systems.

For example, Figure 1a presents the schematic diagrams (256×256 pixels) of three different PMB microstructures: homogeneous, fine and coarse structures. A high grey value represents a polymer-rich phase. It is easy to visually distinguish the homogeneous structure from the binary ones. However, assuming the same phase percentages and no droplet, the fine and coarse structures can hardly be quantitatively differentiated with the previous reported methods. But the 2D-FFT method is capable of distinguishing them in the frequency domain. If drawing a line in the schematic diagrams (e.g. the yellow line in Figure 1a) and extracting the pixel grey level along the line, the differences between the microstructures can then be characterised by the frequency of the grey level signals, as shown in Figure 1b (zero, high and low frequencies respectively).

Figure 1. 2D-FFT analysis of schematic PMB microstructures: **(a)** Schematic diagrams of different PMB microstructures; **(b)** Extracted grey level signals along the line; **(c)** 2D-FFT power spectrum results of the schematic PMB microstructures.

In order to transform the entire 2D schematic diagrams into the frequency domain, a 2D-FFT algorithm is employed in this paper. The principle of this algorithm is described as follow. Let a function $f(r_1, r_2)$ represent the grey level signal of an original image, where (r_1, r_2) is the positional coordinate in the real 2D space. The power spectrum $P(k_1, k_2)$ of the image in the frequency domain [36, 42] is expressed by

$$P(k_1, k_2) = |F(k_1, k_2)|^2, \quad (1)$$

where $F(k_1, k_2)$ is the Fourier transform (FT) of $f(r_1, r_2)$. (k_1, k_2) is the spatial frequency coordinate in the reciprocal space. If $f(r_1, r_2)$ is a continuous function, the FT of $f(r_1, r_2)$ in the continuous form is written as

$$F(k_1, k_2) = \iint f(r_1, r_2) e^{-2\pi j(k_1 r_1 + k_2 r_2)} dr_1 dr_2. \quad (2)$$

However, an image with pixels is in fact a discrete 2D signal. The discrete Fourier transform (DFT) of a square image with $N \times N$ pixels ($N=256$ in this paper) [43] is given by

$$F(k_1, k_2) = \frac{1}{N} \sum_{r_1=0}^{N-1} \sum_{r_2=0}^{N-1} f(r_1, r_2) e^{-j \frac{2\pi}{N} (k_1 r_1 + k_2 r_2)}. \quad (3)$$

For the purpose of rapid DFT computation, many FFT algorithms have been developed. A FFT produces exactly the same result as the DFT. In this study, the power spectrum results of PMB microstructure images are obtained with the image analysis program ImageJ [44] by a 2D-FFT algorithm. With this method, the entire 2D images are transformed into the spatial frequency domain (SI: m^{-1}), with the spatial frequency k defined as

$$k = \sqrt{k_1^2 + k_2^2}. \quad (4)$$

For example, Figure 1c shows the power spectrum results of the three schematic PMB microstructures in Figure 1a. In Figure 1c, the spatial frequency coordinate origin locates at the centre of the power spectrum, indicating the zero frequency of the 2D grey level signal. The area near the centre represents the low frequencies while the area away from the centre means high frequencies. The light intensity distribution of the power spectrum characterises the corresponding PMB microstructure (low frequency for coarse microstructure and high frequency for fine microstructure). It is worth noting here that the scale of a 2D-FFT power spectrum depends on the resolution (pixel density) of the original image. By analysing the power spectrum and computing the related derivative parameters, a PMB microstructure can be quantitatively evaluated and differentiated from others. Real PMB microscopic images are analysed and discussed with this method in the following section of this paper.

3. Results and discussion

3.1. Evaluation of PMB morphology

Figure 2 presents the microscopic images of the four PMB samples from 180 °C. They are representative and agree well with the storage stability test results in Table 1. The observation used two light sources, i.e. ultraviolet (UV) and white light. The fluorescence images by UV reflection have confirmed that the images by white light transmission, as shown in Figure 2, display the phase microstructures of the PMBs. It can be seen in the microscopic images that PMB1 and PMB4 separated into two phases while PMB2 and PMB3 remained homogeneous under this magnification. PMB1 and PMB4 showed different structural patterns in the images. In PMB1, the lighter SBS-rich

phase formed a continuous microstructure. But the PMB4 image displayed very small SBS-rich droplets and short threads in the darker bitumen-rich matrix. These are qualitative descriptions of the images based on visual assessment.

To quantitatively evaluate the observed PMB microstructures, a previously reported parameter, i.e. the area fraction of the polymer-rich phase, can be computed on the basis of the images. But this parameter is valid only for the two-phase PMBs (PMB1 and PMB4), as there is no polymer-rich phase presented in the homogeneous PMBs (PMB2 and PMB3). Another previously reported approach, namely the statistical analysis of polymer-rich droplets, might be feasible for PMB4 but has its difficulty in evaluating the complex-structured PMB1. However, the 2D-FFT method, as a general approach with higher validity, is capable of finding the periodicity (if any) in the images of all PMBs. This is not affected by the specific PMB phase microstructure and its complexity. Meanwhile, the computed area fraction of polymer-rich phase in the two-phase PMBs can be a supplement to the 2D-FFT analysis.

Figure 2. Microscopic images of the four PMB binders from 180 °C: the lighter SBS-rich phase and the darker bitumen-rich phase.

For image analysis, the original colour images in Figure 2 are converted to greyscale digital images of 256×256 pixels with ImageJ. Since this study does not evaluate the equilibrium concentrations but focuses on the PMB microstructure, the greyscale images of the two-phase PMBs (PMB1 and PMB4) are further processed to obtain their binary images with highlighted microstructures. This can assist in enhancing the image signal in some cases (e.g. PMB4 in Figure 2 with low contrast). All the processed images are shown in Figure 3a, where a high grey value represents a polymer-rich phase. Based on these images, the area fraction of the polymer-rich phase in PMB1 and PMB4 can be computed. The results indicate that the polymer-rich phase occupies 65.95% of the area in the PMB1 image while the number is 17.57% for PMB4. This difference is attributed to their different swelling ratio values of the modifier despite the same polymer content in all the PMBs.

Figure 3. Image processing and 2D-FFT analysis of the four PMB binders from 180 °C: **(a)** Processed images; **(b)** 2D-FFT power spectrum results.

Furthermore, the processed images are transformed into the reciprocal space by ImageJ and the 2D-FFT power spectrum results are obtained, as presented in Figure 3b for the samples from 180 °C. To characterise the PMB microstructure, the light intensity of power spectrum is normalized in all directions along the incircle radius of the square image. This is a valid method to characterise isotropic and lightly anisotropic microstructures, which is the case of the studied images and the preferred case for PMB. The radial distribution of normalized light intensity is plotted in Figure 4. An isotropic microstructure with unique frequency typically presents a peak on the plot, i.e. the characteristic frequency peak indicating a bright ring on the power spectrum (e.g. the fine and coarse structures in Figure 1). However, it can be seen in Figure 4 that, for PMB2 and PMB3, the normalized light intensity displays an approximately exponential decay pattern with the spatial frequency. In this case, the absence of a characteristic frequency peak means the lack of periodicity in the original PMB microscopic images. In other words, there is no periodical structural pattern presented in PMB2 or PMB3, which agrees well with the visual assessment of the microscopic images. Nevertheless, it is noticed in Figure 4 that the normalized light intensity of PMB3 shows a very slight increase at the final-stage high spatial frequencies. This might be an indication of the existence of extremely fine microstructure in PMB3, although it needs to be further confirmed with microscopic images of higher resolution or higher magnification.

Figure 4. Radial distribution of normalized light intensity of the 2D-FFT power spectrum results for the four PMB binders from 180 °C.

As for PMB1, Figure 4 shows a plateau at the low spatial frequencies less than 20 mm^{-1} followed by the decay at higher spatial frequencies. There is not a sharp peak, i.e. absolutely dominant frequency, in the power spectrum of PMB1. This reveals the lack of absolutely significant periodicity in the microscopic image of PMB1. However, instead of a sharp characteristic frequency, PMB1 displays a broad frequency range (the plateau) for it. This corresponds to the diffuse pattern on the power spectrum (Figure 3b). Thus, the observed PMB1 microstructure is actually a combination of some periodical patterns with the spatial frequency up to 20 mm^{-1} .

In Figure 4, PMB4 presents a three-stage curve for its normalized light intensity: a drop in the very beginning, a plateau at the low spatial frequencies less than 40 mm^{-1} and then the slight decay at higher spatial frequencies. Comparing with PMB2 and PMB3, PMB4 has a broad frequency range (the plateau) indicating the existence of a binary microstructure. However, the plateau of PMB4 extends until a higher spatial frequency (40 mm^{-1}) than that of PMB1. This discloses that PMB4 has a finer microstructure than PMB1 with even weaker periodicity. In brief, the 2D-FFT power spectrum shows the periodicity of a PMB phase pattern by the characteristic frequency range while the area fraction of polymer-rich phase denotes the percentages of each phase (if more than one) in the formed pattern. Together, they can thus quantitatively evaluate and differentiate the PMB microstructures.

3.2. Effect of temperature

In the previous section, the microstructures of different PMB binders at 180°C have been analysed and compared. As a continuation, the effect of temperature on PMB microstructure is discussed in this section. Microscopic images of the four PMB binders after 1 hour of isothermal annealing at 160°C and 120°C , as shown in Figure 5a and Figure 6a respectively, are processed and investigated by ImageJ. These original PMB images were by UV reflection and have a different magnification with the previous section. In Figure 5a and Figure 6a, the lighter phase is SBS-rich and the darker phase is bitumen-rich. It can be seen that the PMBs display different microstructures at 160°C despite their similar morphological appearance of binary structure at 120°C . In Figure 5a, both PMB1 and PMB4 present dispersed SBS-rich droplets and/or threads in the bitumen-rich matrix. PMB2 shows a very fine pattern in the image while PMB3 is homogeneous at 160°C .

In order to digitally analyse these microscopic images, the original colour images are processed with the same procedure as described in the previous section. The processed images are respectively presented in Figure 5b and Figure 6b. With these processed images, the area fraction of polymer-rich phase in the two-phase PMBs is computed. The results, as shown in Figure 7, indicate that the polymer-rich phase occupies different fractions of area in images of different PMBs. At a decreased temperature, the area fraction of polymer-rich phase becomes less in both PMB1 and PMB2. This means the polymer swells less at a lower temperature, which is a reasonable trend for PMB [45]. PMB3 goes through a transition from the thermodynamically stable state at 160°C to the unstable state at 120°C . Its polymer-rich phase occupies 16.42% of the area in the image at 120°C . However, PMB4 presents a reverse trend in Figure 7, i.e. increased swelling ratio at a lower temperature. This is an unexpected trend for PMB. It was probably an observation error due to the extremely uneven distribution of the polymer-rich clusters in PMB4 at 120°C . The computed value of area fraction of polymer-rich phase in PMB4 at 180°C (17.57% as mentioned in the previous section) corroborates this probable error from another point of view.

Figure 5. 2D-FFT analysis of the four PMB binders after 1 hour of isothermal annealing at 160 °C: **(a)** Microscopic images; **(b)** Processed images; **(c)** 2D-FFT power spectrum results.

Figure 6. 2D-FFT analysis of the four PMB binders after 1 hour of isothermal annealing at 120 °C: **(a)** Microscopic images; **(b)** Processed images; **(c)** 2D-FFT power spectrum results.

Figure 7. Area fraction of polymer-rich phase in the four PMB binders after 1 hour of isothermal annealing at different temperatures.

Figure 8. Radial distribution of normalized light intensity of the 2D-FFT power spectrum results for the four PMB binders after 1 hour of isothermal annealing at different temperatures: **(a)** PMB1; **(b)** PMB2; **(c)** PMB3; **(d)** PMB4.

Moreover, the processed images are transformed into the spatial frequency domain and the 2D-FFT power spectrum results are presented in Figure 5c and Figure 6c for the two different temperatures respectively. The power spectrum is discussed here by analysing the radial distribution of normalized light intensity, as plotted in Figure 8. It can be seen that PMB1 and PMB4 always display the ‘plateau-decay’ mode for their distribution curves at 160 °C and 120 °C. For both PMBs, however, the plateau moves towards lower frequencies as the temperature drops. This reveals that the PMBs have coarser microstructures at the decreased temperature, which agrees well with the visual assessment of the microscopic images.

In Figure 8, PMB2 presents the ‘decay-plateau-decay’ mode for its distribution curve at 160 °C. This is the indication of its very fine and heterogeneous binary microstructure at that temperature. But at 120 °C, PMB2 shows a broad peak for its characteristic frequency at around 2 mm⁻¹. This discloses that there is a significant periodicity in the microscopic image of PMB2 in Figure 6a. As for PMB3, although its distribution curve always decays and reveals that there is no periodical structural pattern in its microscopic image at 160 °C, a peak is nevertheless presented for its characteristic frequency at 120 °C. The peak is also located at around 2 mm⁻¹, very close to that of PMB2. It can thus be deduced that the structural patterns of PMB2 and PMB3 should be visually similar at 120 °C. The microscopic images in Figure 6a have indeed confirmed this deduction. Based on the above discussion, it is indicated that the 2D-FFT analysis of PMB images is capable of quantitatively evaluating and differentiating PMB microstructures at different temperatures.

3.3. Characterisation of PMB phase separation

After the comparison of different PMB binders and different temperatures in the previous sections, the temporal evolution of PMB microstructure during the phase separation process is characterised and investigated with the 2D-FFT method in this section. The two-phase PMBs at 180 °C, i.e. PMB1 and PMB4, are studied and their microscopic images observed after the isothermal annealing conditioning for different time are presented in Figure 9a and Figure 10a respectively. These images by white light transmission, with the lighter SBS-rich phase and the darker bitumen-rich phase, essentially show the PMB microstructure evolution during the entire phase separation process. Figure 9a displays the development and breakdown of the polymer-rich network in PMB1 while Figure 10a presents the coarsening process of the polymer-rich droplets in PMB4.

Figure 9. 2D-FFT analysis of PMB1 during the phase separation process at 180 °C: **(a)** Microscopic images; **(b)** Processed images; **(c)** 2D-FFT power spectrum results.

Figure 10. 2D-FFT analysis of PMB4 during the phase separation process at 180 °C: **(a)** Microscopic images; **(b)** Processed images; **(c)** 2D-FFT power spectrum results.

For quantitatively characterising the PMB phase separation process, the same procedure as described in the previous sections is followed. The processed images are respectively presented in Figure 9b and Figure 10b. In order to obtain the 2D-FFT power spectrum of the PMBs, the processed images are further transformed into the reciprocal space by ImageJ. The results are presented in Figure 9c and Figure 10c for the two different PMBs respectively. The radial distribution of the normalized light intensity in power spectrum, as plotted in Figure 11, is analysed and discussed with respect to the characterisation of PMB phase separation.

Figure 11. Radial distribution of normalized light intensity of the 2D-FFT power spectrum results for PMB1 and PMB4 during the phase separation process at 180 °C: **(a)** PMB1; **(b)** PMB4.

At the initial point (0 s), Figure 11a indicates that PMB1 displays an approximately exponential decay pattern followed by a very slight increase at the final stage. This means that there is initially no periodical structural pattern in the PMB1 image in spite of the possible existence of extremely fine microstructure. As for PMB4, Figure 11b shows the ‘decay-plateau-decay’ mode for its initial distribution curve, revealing its very fine and heterogeneous binary microstructure at the beginning. After the initial point, however, both PMB1 and PMB4 do present peaks on the distribution curves, although mostly broad, for their characteristic frequencies at the different time points. It can be

seen that, for both PMB1 and PMB4, the peaks show an overall trend towards lower frequencies as time passes. This discloses the coarsening process of the PMB microstructures during phase separation. After these peaks are located, the characteristic wavelength ξ [46] of the observed PMB microstructures can then be calculated, as defined by

$$\xi = \frac{2\pi}{k_m}, \quad (5)$$

where k_m is the characteristic spatial frequency corresponding to the peaks. It is worth noting that the determination of peak locations in this paper is based on the local maximums. The calculation results of ξ at different time points are plotted in Figure 12 for both PMBs, where the characteristic wavelength quantitatively characterises the PMB microstructures and its temporal variation describes the microstructure growth during the entire phase separation process. Since Figure 12 presents overall an upward trend of the characteristic wavelength with time (as indicated by the shadow area), the quantitative relationship of PMB microstructure growth, as well as the area fraction of polymer-rich phase, will be discussed and compared with numerical simulation results in the next section of this paper.

Figure 12. Characteristic wavelength of the observed PMB microstructures during phase separation.

3.4. Assessment of numerical reproduction

As mentioned before, a phase-field model for PMB phase separation has been proposed by the authors [35]. The microscopy observation results discussed in the previous section were numerically reproduced by simulating the same condition as the experimental procedure. The simulation results are shown in Figure 13a and Figure 14a for PMB1 and PMB4 respectively, where a warm colour represents a polymer-rich phase. The visual similarity is very high between these simulation results and the microscopic images in Figure 9a and Figure 10a. With the 2D-FFT method, the numerical reproduction is quantitatively assessed and compared with the experimental results in this section.

Figure 13. 2D-FFT analysis of numerical simulation of the PMB1 phase separation at 180 °C: **(a)** Simulation results; **(b)** Processed images; **(c)** 2D-FFT power spectrum results.

Figure 14. 2D-FFT analysis of numerical simulation of the PMB4 phase separation at 180 °C: **(a)** Simulation results; **(b)** Processed images; **(c)** 2D-FFT power spectrum results.

Following the same procedure described previously, the original colour images are processed, as presented in Figure 13b and Figure 14b respectively for the two PMBs. With these processed images, the area fraction of polymer-rich phase in the simulated PMBs is computed. The results are shown in Figure 15 together with the microscopy observation results computed from Figure 9b and Figure 10b. It is indicated that the numerical simulations reproduced the area percentages of the observed PMB microstructures quite well, although PMB1 deviated a bit more than PMB4. The area fraction of polymer-rich phase in PMB4 kept almost constant at all the investigated

time points. However, PMB1 presented a peak value at 300 s for both the microscopy observation and numerical simulation. This peak value reveals that PMB1 was still at the early stage of separation and the equilibrium had not been reached by 300 s. But PMB4, without a peak value, had experienced through the early stage and reached the equilibrium by 300 s. Thus, PMB4 had displayed the coarsening (self-similar growth) process since 300 s at the late stage of separation while PMB1 had done since 600 s. This information is important for the quantitative analysis of PMB microstructure growth, as different laws may apply for the different stages of phase separation [28].

Figure 15. Area fraction of polymer-rich phase for the microscopy observation and numerical simulation of PMB1 and PMB4 phase separation at 180 °C.

Figure 16. Radial distribution of normalized light intensity of the 2D-FFT power spectrum results for numerical simulation of the PMB1 and PMB4 phase separation at 180 °C: (a) PMB1; (b) PMB4.

In order to obtain the 2D-FFT power spectrum of the simulated PMBs, the processed images are further transformed into the spatial frequency domain by ImageJ. The results are presented in Figure 13c and Figure 14c for the two simulated PMBs respectively. The radial distribution of the normalized light intensity in power spectrum is plotted in Figure 16. At 0 s, the distribution curves (without peaks) represent the randomly-located initial values of the simulations. From 300 s, however, both PMB1 and PMB4 present typical peaks on the distribution curves for their characteristic frequencies at the different time points. These peaks also show an overall trend towards lower frequencies as time passes, indicating the coarsening process of the simulated PMB microstructures during phase separation. After these peaks are located, the characteristic wavelength of the simulated PMB microstructures is calculated. The results are plotted in Figure 17 together with the microscopy observation results computed from Figure 11.

In Figure 17, it can be seen that the simulations fairly reproduced the microscopy observation results despite some deviation. In terms of individual values, the deviation is larger at certain time point than at the others. For example, the result at 3600 s deviates more than the others in Figure 17a while the deviation comes only from the result at 300 s in Figure 17b. As for microstructure growth, the late stage of phase separation can be analysed with the power-law scaling [46-50], i.e.

$$\xi \propto t^\alpha, \quad (6)$$

where t is time and α is the power-law exponent. Power-law fitting is thus carried out with the late-stage data of both PMBs in this study. It should be mentioned here that Figure 15 has indicated that PMB1 was still at the early stage of separation and the equilibrium had not been reached by 300 s. As the consequence, the PMB1 result at 300 s was not included in the power-law fitting. Figure 17 shows that the correlation is good between the characteristic wavelength and time for both the microscopy observation and numerical simulation. However, for both PMB1 and PMB4, the power-law exponent value of the simulation result fitting is lower than that of the microscopy result fitting. The α values are both around 0.3 for the simulations but vary between the experiments. This might be related to the quality of the original microscopy images (e.g. resolution and illumination evenness) as well as the parameter values used in the simulations. Although more experimental data and further development of the model are still needed to verify the specific microstructure growth laws of the studied PMBs, the above results and discussion indicates that the 2D-FFT analysis is a possible approach to the quantitative characterisation of PMB phase separation and assessment of numerical reproduction.

Figure 17. Characteristic wavelength comparison and analysis of the observed and simulated PMB microstructures during the PMB1 and PMB4 phase separation at 180 °C: **(a)** PMB1; **(b)** PMB4.

4. Conclusions

For the purpose of quantitatively evaluating PMB microstructures, this paper uses a 2D-FFT algorithm to process the PMB microscopic and numerical images. The 2D-FFT power spectrum and its radial distribution of normalized light intensity are analysed. The characteristic frequency and wavelength of the observed and simulated microstructures are computed. In addition, the area fraction of polymer-rich phase in the two-phase PMBs is discussed as a supplement to the 2D-FFT analysis.

The investigation on the four PMB binders reveals that the 2D-FFT power spectrum results of different PMB microstructures display different modes of light intensity distribution. The absence/presence of a characteristic frequency (range) indicates the lack/existence of the corresponding periodical structural pattern(s) in the original PMB

image. A lower characteristic frequency usually represents a coarser PMB microstructure while a higher one implies a finer PMB microstructure. The 2D-FFT method is thus valid for differentiating various PMB microstructures. This is not affected by the specific PMB phase microstructure and its complexity. As the phase behaviour of PMB is temperature-dependent, a PMB may hence show different microstructures at different temperatures. The 2D-FFT analysis of PMB images at different temperatures discloses that the proposed method is also capable of quantitatively evaluating the effects of temperature on PMB microstructure.

Furthermore, the temporal evolution of PMB microstructure during phase separation process is characterised in this paper. The late stage of phase separation is quantitatively analysed with the power-law scaling. The results show that the characteristic frequency of a PMB microstructure tends to become lower as the phase separation process continues. Meanwhile, the characteristic wavelength tends to increase. This is the indication of the coarsening process of PMB microstructure during phase separation. Additionally, the numerical reproduction of the observed phase separation is evaluated with the same method and compared with the experimental results. It is shown that the simulations fairly reproduced the microscopy observation results despite some deviation.

The analysis and discussion presented in this paper indicates that the 2D-FFT method is a plausible approach to the quantitative evaluation of PMB microstructure. Its validity is more extensive than the previously reported evaluation methods. Moreover, it provides quantitative parameters (characteristic frequency and wavelength) for comparing different PMB microstructures and hence enables the possibilities of microstructure-based modelling of PMB performance. An example for this can be the microstructure-based rheological study of PMB in the service temperature range, which is of great importance for PMB performance analysis and design. However, this method has its limitations as well. For example, the analysis result may be sensitive to the image processing in some cases. In addition, the result does not give explicit information on the phase composition (i.e. polymer concentration in the phase). Future research is still needed towards a standardization of the image processing and the possibility of quantitatively evaluating the phase composition. For this, a standard processing method to get accurate grey values of the images will be greatly important.

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