

Binder performance and testing

The effect of sample preparation on the morphology of polymer-modified bitumen by fluorescence and optical microscopy and it's relation to storage stability.

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Abstract

Fluorescence microscopy is commonly used to determine the dispersion of polymer in a polymer-modified bitumen (PmB), with sample preparation having a significant effect on the quality of the observed dispersion. This paper explores the effect of various sample preparation techniques (including EN 13632) on the observed dispersion of a number of common polymers in different bitumens. The relationship between polymer dispersion and storage stability is also explored using EN 13399 and other methods.

1. INTRODUCTION

Polymer modification has significant scope to increase the performance of bitumen and therefore asphalt in a number of areas. Typical examples of the improvements in performance obtained by polymer-modification include increase in ring & ball softening point, reduction in needle penetration, increase in viscosity, improvements in low-temperature properties, modification of rheological character and improvements in cohesion. These performance improvements have been extensively documented in a number of learned publications [1-5] over many years.

Despite the differing chemical nature of thermoplastic and elastomeric polymers [6-8], it is widely accepted that a fundamental requirement for the successful polymer modification of bitumen is the consistent dispersion of the polymer within the bitumen [1-3]. Only when the dispersion of the polymer is consistent will the benefits be fully observed [9-16]. The chemical nature of the bitumen, for example the ratio of maltene to asphaltene fraction, can also have a significant impact on both the dispersion of the polymer and the stability of the polymer-modified bitumen [1-3, 10, 13].

The standard method for evaluation of the dispersion of polymer in bitumen is documented in BS EN 13632 [17]. This method involves placing a sample of molten bitumen into a thermostatically controlled container and allowing it to cool at a controlled rate before transferring to a freezer at -20°C (or lower) and fracturing the surface, before observation of the polymer dispersion using a fluorescence microscope. However, a number of other methods have been proposed as alternatives [14, 19-22], many of which resulted in different morphologies for the polymer-modified binder.

The storage stability of polymer-modified bitumens is documented in BS EN 13399 [23], which involves placing a sample of the binder into a sealed tube, conditioning this at elevated temperature (typically 180°C) for a period of time (typically 72h) and measuring the difference in physical properties of the upper and lower sections.

Earlier work [18,19] has indicated that it may be possible to estimate the tendency for a polymer-modified binder to separate using non-standard fluorescence microscopic techniques. This paper details the effect of sample preparation on the observed morphology and its relation to storage stability of polymer-modified bitumens.

2. MATERIALS AND SAMPLE PREPARATION

Three sources of bitumen were used in the evaluation:

Bitumen AAA: propane de-asphalted, North Sea

Bitumen BBB: visbroken residue, Urals

Bitumen CCC South American

All bitumen sources complied with the specification for 100/150 as stated in BS EN 12591. Four different polymers were used in the evaluation: medium molecular weight, linear SBS containing 31% styrene; high molecular weight, radial SBS containing 30% styrene, low molecular weight, high-vinyl SBS containing 30% styrene with a vinyl content of 30% and ethylene vinyl acetate polymer containing 20% vinyl acetate with a melt flow index (MFI) of 20. Each polymer-modified bitumen contained 4% of polymer. Samples of polymer-modified bitumen were prepared by heating the bitumen to 175°C and adding the polymer while stirring at 300rpm. After completion of the polymer addition, the binder was stirred for a further 15min before transferring to a high-shear, rotor-stator mixer for a further 30min at 5000rpm. The temperature of the binder during this second stage was controlled to 175±10°C.

Samples were prepared for fluorescence microscopy using five different methods. Method 1, the “spotting” technique, involved taking a sample of the molten binder (175±10°C) using a heated glass rod and placing a small drop onto the surface of a microscope slide before protecting it with a glass cover slip. Method 2, the “spot/anneal” technique is identical to method 1, except that the prepared slide was allowed to cool for 5 min after spotting and subsequently annealed by placing it onto a hotplate at 180°C. While on the hotplate, the binder was allowed to flow until it completely covered the underside of the coverslip, then removed to cool to ambient temperature. The typical time for this annealing process was 1min. Method 3, “hot casting” is again similar to the spotting technique except that the host slide was heated to 180°C before application of a drop of molten binder (175±10°C) using a heated glass rod. A coverslip was applied and the binder allowed to flow completely over its underside before removing from the hotplate and allowing to cool to ambient temperature. Method 4, “fracture surface” involved the preparation of a 50 x 6.4 x 12.7mm rectangular slab of binder by filling a shortened bending beam rheometer mould with the molten (175±10°C) binder. The filled mould was allowed to cool to ambient temperature for 20 min before trimming the excess binder using a heated spatula. The trimmed mould was placed in a freezer at -18°C for 10min to allow demoulding before placing the slab placed into a thermostatically controlled chiller bath at -24°C for 30min. The slab was then removed from the bath, placed onto a silicone sheet and fractured by placing a sharp, flat blade onto the 6.4mm surface and applying rapid pressure. The fractured surfaces were stored in a freezer at -18°C before mounting onto a glass slide. Coverslips were not applied to the fractured surfaces. The final preparation method was BS EN 13632[17].

Samples produced using methods 2 and 3 were also suitable for examination using transmission white light microscopy.

Qualitative fluorescence and white light transmission micrographs were obtained at 100-500x magnification using an Olympus BX41 microscope equipped with a high-intensity mercury arc lamp and Leica DFC295 digital camera.

The storage stability of each binder was assessed using BS EN 13399[23] using a temperature of 180°C and a conditioning period of 72h.

3. RESULTS AND DISCUSSION

The physical properties of the 12 polymer-modified binders produced are given in Table 1. Overall, the properties were as expected for the modifiers used. The highest softening points for all modifiers were observed with bitumen BBB, while SBS-R gave the highest softening points generally.

Table 1
Physical Properties of Polymer-modified Binders

CODE	Base Bitumen Properties				PmB Properties				
	Pen/dmm	SPt/°C	Viscosity / cPs		Pen/dmm	SPt/°C	Viscosity / cPs		Storage Stability
			135°C	150°C			135°C	150°C	Δ Spt
AAA-SBS-L	110	43.4	249	130	91	51.1	664	382	0.4
AAA-SBS-R					85	69.0	570	352	>45
AAA-SBS-V					90	52.1	680	360	0.7
AAA-EVA					82	59.6	488	262	0.4
BBB-SBS-L	116	43.5	192	139	66	78.6	754	362	0.5
BBB-SBS-R					69	85.2	1258	548	8.8
BBB-SBS-V					65	74.1	690	342	0.3
BBB-EVA					54	64.4	522	268	0.1
CCC-SBS-L	131	43.1	318	163	75	61.2	866	432	35.5
CCC-SBS-R					76	85.1	920	560	>60
CCC-SBS-V					74	72.6	822	416	3.0
CCC-EVA					85	57.1	614	320	0.1

Key: AAA – Propane deasphalted bitumen base
 BBB – Visbroken residue base
 CCC – South American bitumen base
 SBS-L - linear SBS-modified
 SBS-R - radial SBS-modified
 SBS-V - high vinyl content SBS-modified
 EVA - EVA-modified

The penetration values of the modified binders were as expected and reflected both the nature of the modifier and bitumen. Viscosities were highest with SBS-R except in the case of AAA-SBS-R which was lower than that of the linear and vinyl equivalents. However, it was noted that there was evidence of separation of the polymer in the viscometer tube. The results obtained for AAA-SBS-R were therefore erroneously low.

The storage stability of the polymer-modified binders were broadly as expected with SBS-R being the least stable in the three base bitumens. However, it was interesting that SBS-R was more stable in bitumen BBB (visbroken) than in bitumen AAA, indicating that the former bitumen has a greater affinity for this polymer. SBS-V was the most stable of the SBS polymers across the range of bitumens and was generally stable. EVA proved to be stable in all bitumens as expected.

Fluorescence and white light micrographs are given in figures 1-12. Some general observations can be made, which are applicable to all of the samples. Firstly, both BS EN13632 and the fracture surface technique produce samples which are difficult to observe due to the random nature of the fracture and difficulty in ensuring a perfectly flat surface. Secondly, samples containing EVA were more difficult to analyse using the spot, spot-anneal and hot casting techniques due to relatively indistinct phase boundaries between the polymer and bitumen. Thirdly, the observed morphology for each binder is significantly different depending on the preparation method. Samples prepared

according to BS EN 13632 tended to show coarse dispersions, with discrete polymer domains dispersed within a continuous bitumen phase. Both the type of polymer and the base bitumen influences the dispersion obtained using BS EN13632. This is particularly apparent with samples prepared using bitumen CCC (fig. 9-12)

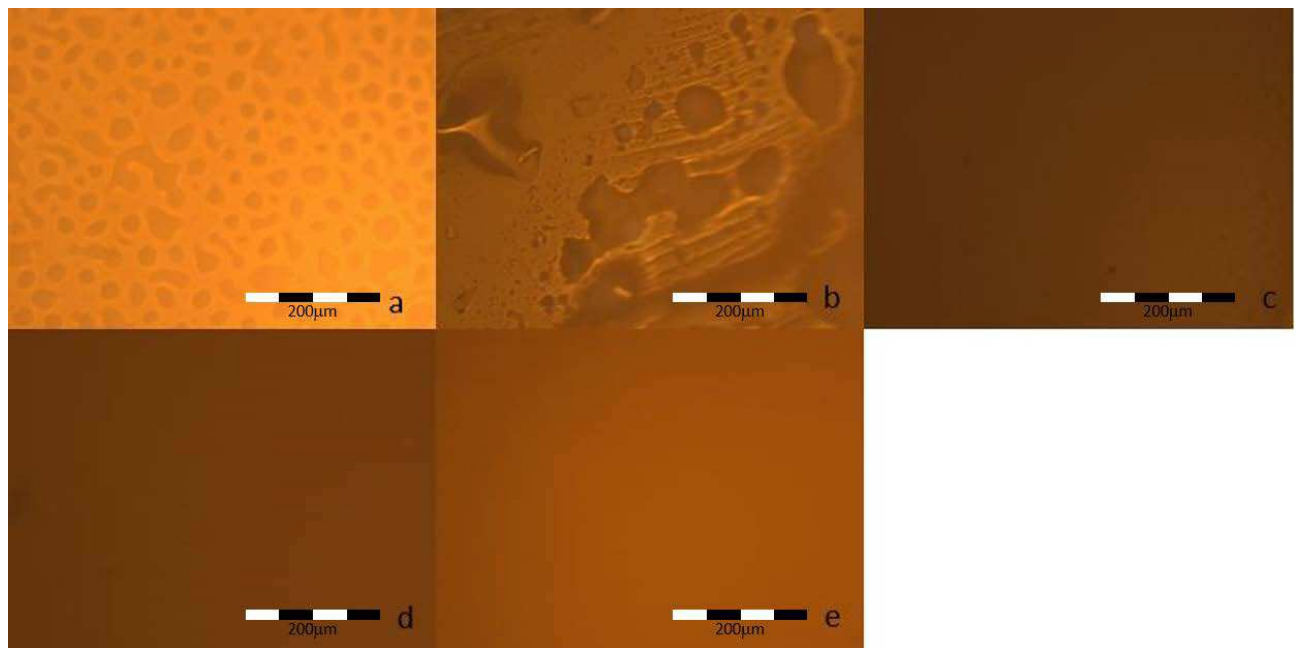


Figure 1 Micrographs of bitumen AAA modified with EVA. Key: a-EN 13632, b-fracture surface, c-spot, d-spot annealed, e-hot

Sample AAA-EVA (fig. 1) shows a coarse, globular dispersion when prepared using BS EN 13632 (a) with the corresponding fracture surface (b) showing random globular or angular polymer domains within the bitumen matrix. It is clear that the slower rate of cooling achieved in BS EN 13632 allows for a greater degree of separation of the polymer. Each of the samples prepared by direct application of the binder onto the microscope slide (c-e) resulted in consistent, fine polymer domains which were rather indistinct. Neither the annealing process (d) hot casting (e) resulted in any significant change in the polymer dispersion. AAA-EVA was stable according to BS EN 13399.

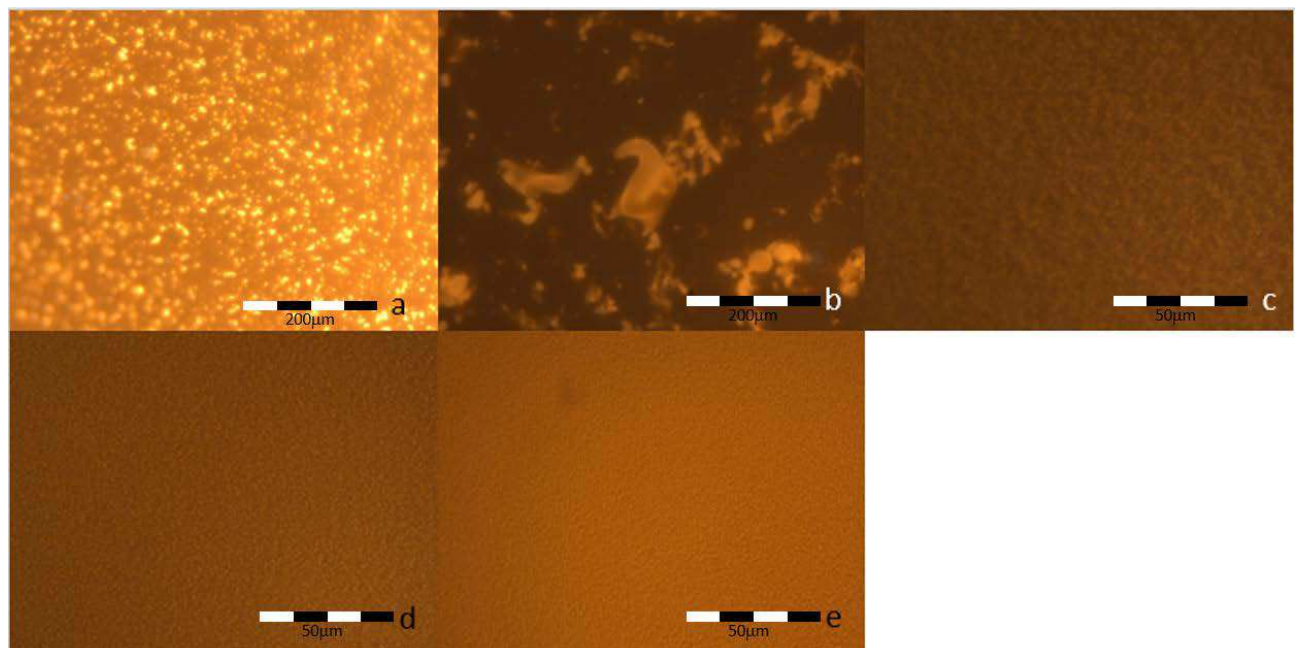


Figure 2 Micrographs of bitumen AAA modified with SBS-L. Key: a-EN 13632, b-fracture surface, c-spot, d-spot annealed, e-hot

Sample AAA-SBS-L (fig. 2) behaved in a similar fashion to AAA-EVA in that BS EN 13632 and the fracture surface revealed significant separation of the polymer. However, in this case the dispersion observed using BS EN 13632 (a) was, in this case significantly finer than that with the fracture surface which indicated gross phase separation (b). Minor

differences were observed between the direct application methods (c-e) but these were rather subtle with the spot annealed and hot cast samples being practically identical. AAA-SBS-L was stable according to BS EN 13399.

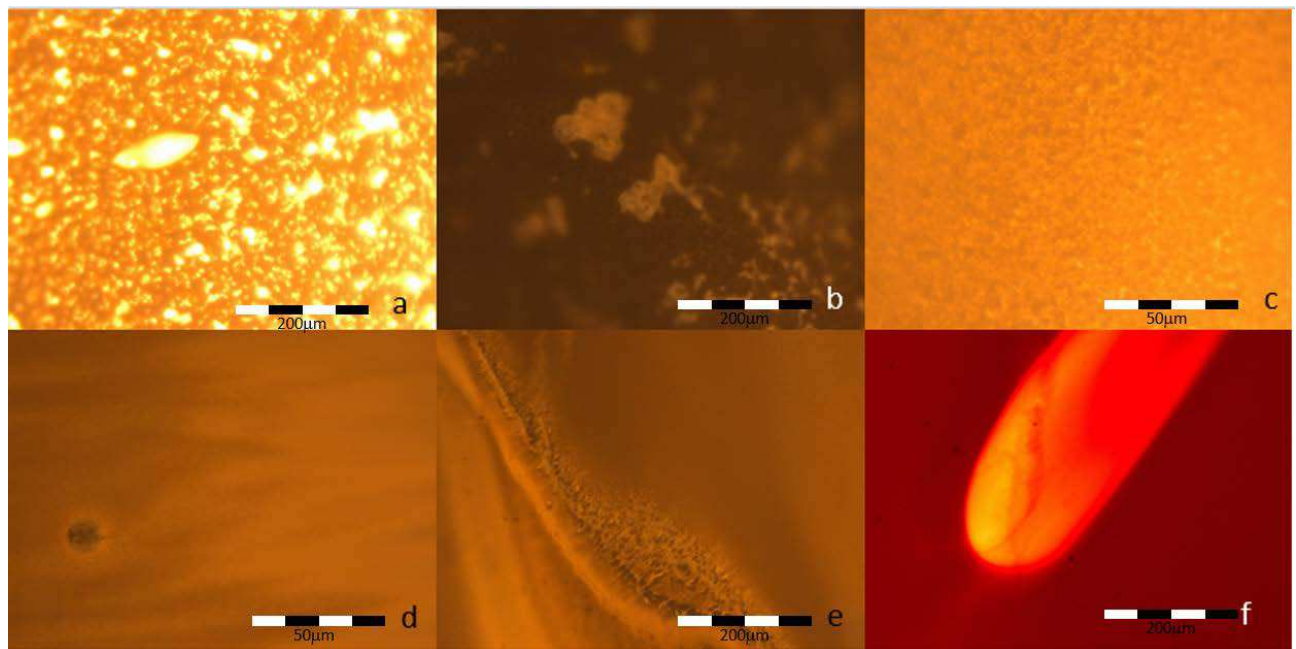


Figure 3 Micrographs of bitumen AAA modified with SBS-R. Key: a-EN 13632, b-fracture surface, c-spot, d-spot annealed, e-hot, f-hot (white light transmission)

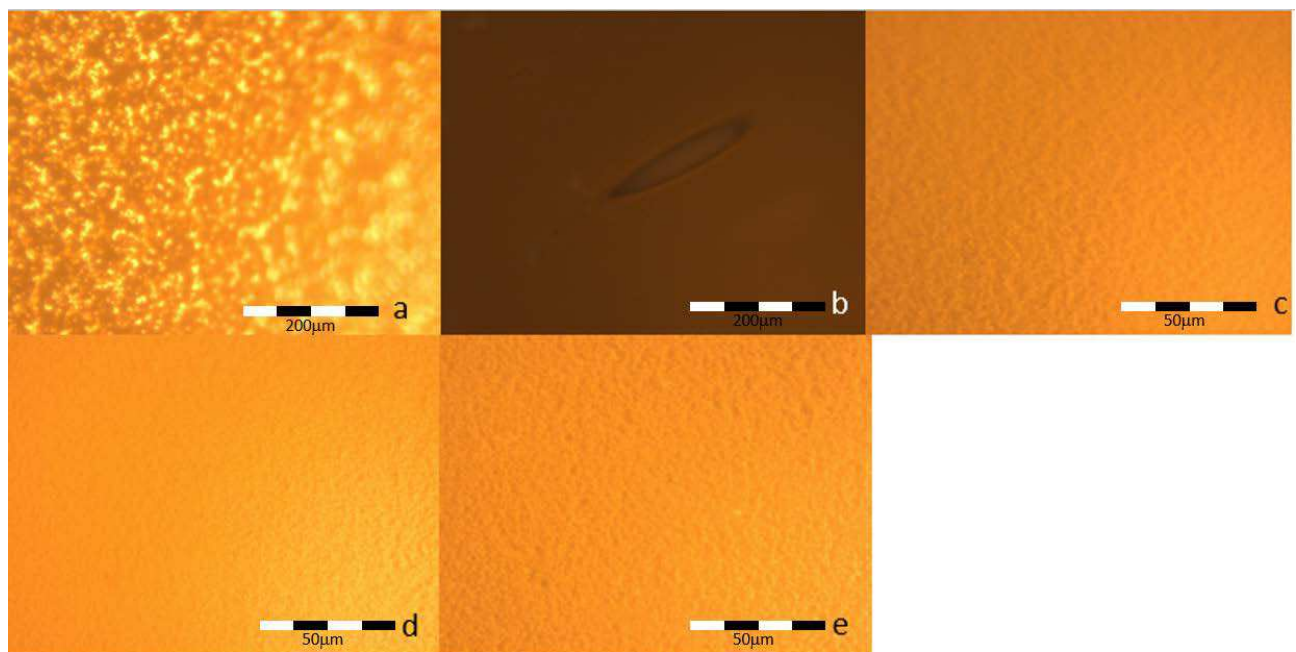


Figure 4 Micrographs of bitumen AAA modified with SBS-V. Key: a-EN 13632, b-fracture surface, c-spot, d-spot annealed, e-hot.

Sample AAA-SBS-R (fig. 3) followed a similar pattern to SBS-L for BS EN 13632 and the fracture surface technique (a-b). However, significant differences in dispersion were observed when using the direct application techniques (c-f). The spot sample (c) shows a fine consistent dispersion which becomes concentrated into polymer- and bitumen-rich domains during the annealing process (d). The hot cast sample (e) shows significant inhomogeneity with concentration of polymer domains across the slide (e). Further dramatic evidence of this can be observed in the white-light transmission micrograph (f), which shows a large isolated polymer domain in a bitumen matrix. AAA-SBS-R was unstable according to BS EN 13632.

AAA-SBS-V (fig. 4) behaved in an almost identical fashion to AAA-SBS-L and was stable. The dispersion of the vinyl polymer was generally finer than that with linear SBS in bitumen AAA.

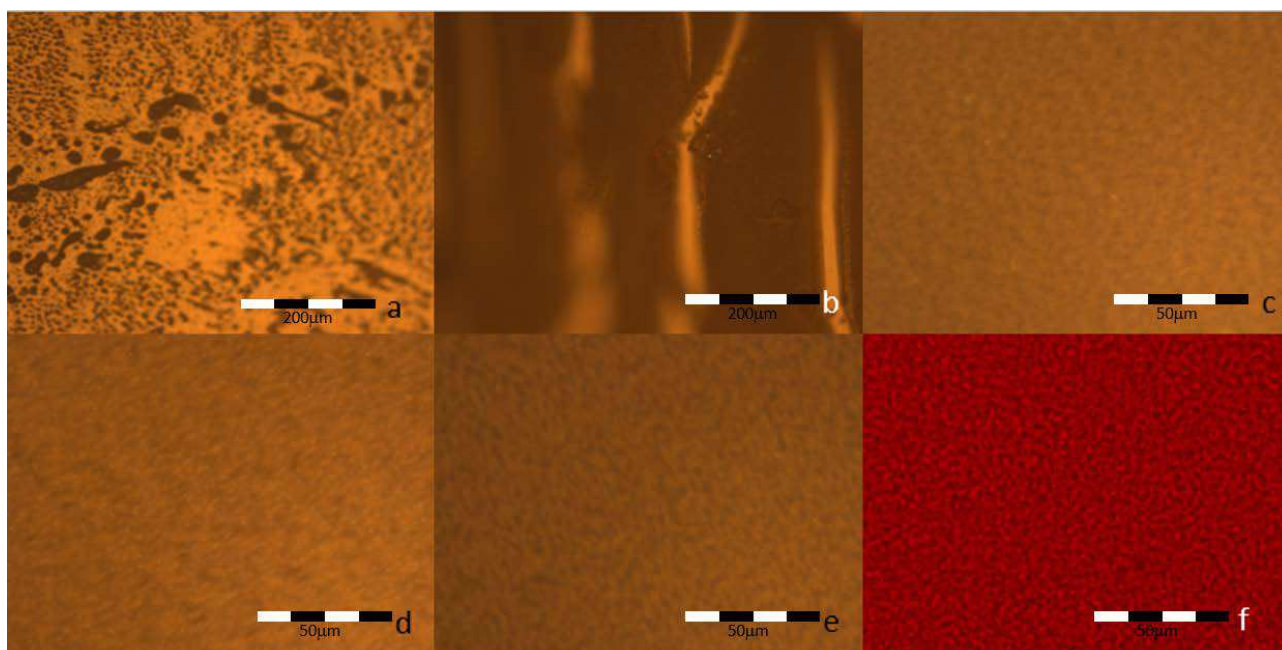


Figure 5 Micrographs of bitumen BBB modified with EVA. Key: a-EN 13632, b-fracture surface, c-spot, d-spot annealed, e-hot, f-hot (white light transmission)

The degree of separation of polymer in sample BBB-EVA (fig. 5) was more dramatic than with bitumen AAA, particularly when using BS EN 13632 and fracture surface (a-b). Greater contrast was observed between the two phases, indicating a greater degree of phase separation. As with bitumen AAA, the direct-applied samples (c-e) showed fine, indistinct phases which were difficult to observe. The consistency of dispersion was significantly easier to observe using white-light transmission with the hot cast sample (f). BBB-EVA was found to be stable according to BS EN 13399.

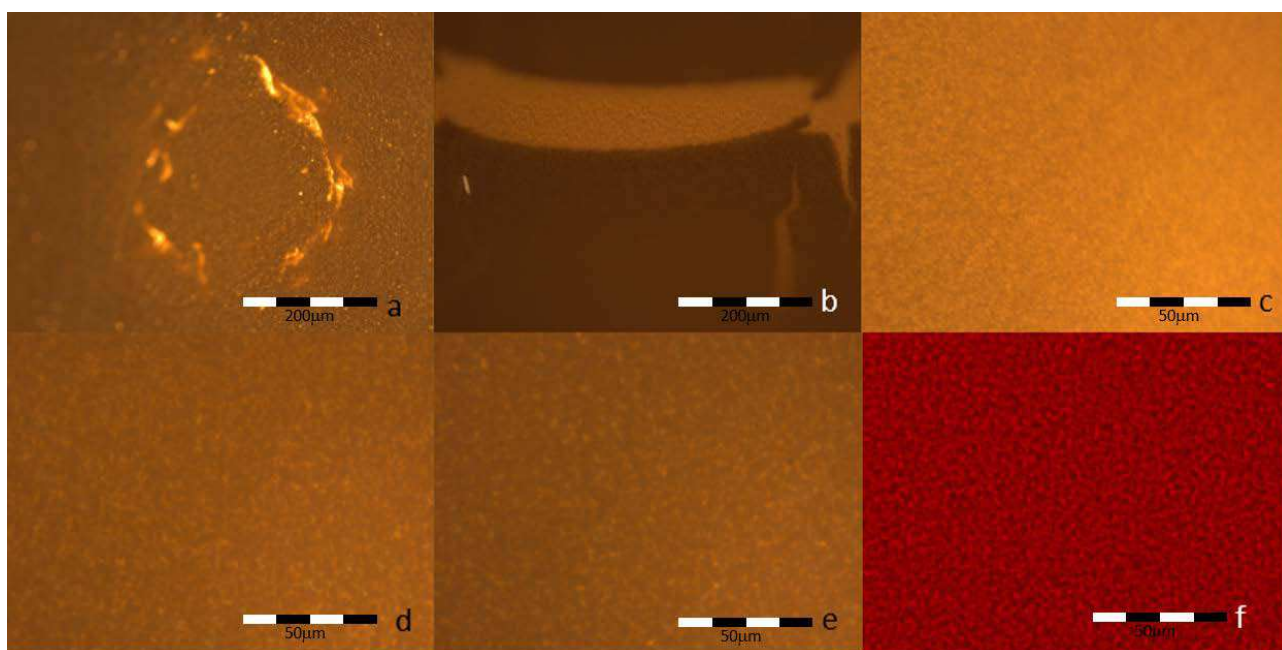


Figure 6 Micrographs of bitumen BBB modified with SBS-L. Key: a-EN 13632, b-fracture surface, c-spot, d-spot annealed, e-hot, f-hot (white light transmission)

BBB-SBS-L (fig. 6) behaved in a similar fashion to AAA-SBS-L although there was greater evidence of gross, macroscopic phase separation in the fracture surface sample (b). The direct samples (c-e) exhibited some subtle differences, particularly in the annealed and hot samples, in which the polymer domains become more coarse and distinct. BBB-SBS-L was found to be stable according to BS EN 13399.

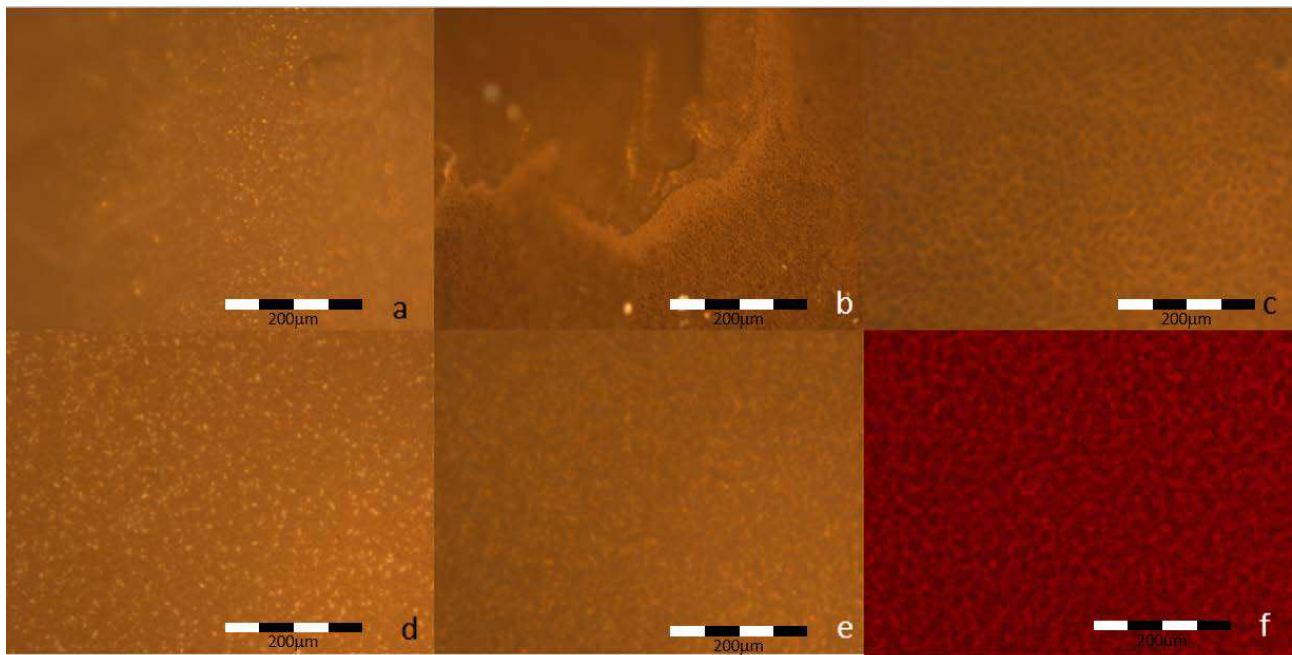


Figure 7 Micrographs of bitumen BBB modified with SBS-R. Key: a-EN 13632, b-fracture surface, c-spot, d-spot annealed, e-hot, f-hot (white light transmission)

The behaviour of BBB-SBS-R (fig. 7) was similar to that of BBB-SBS-L, although the degree of separation observed in the spot annealed and hot samples was much greater. While the spot sample (c) showed a fine network domain, the annealed (d) and hot (e) samples showed distinct, discrete polymer domains indicating that the application of heat had caused the polymer to separate. White light transmission (f) did not, in this case, reveal any significant separation. BBB-SBS-R was unstable according to BS EN 13399.

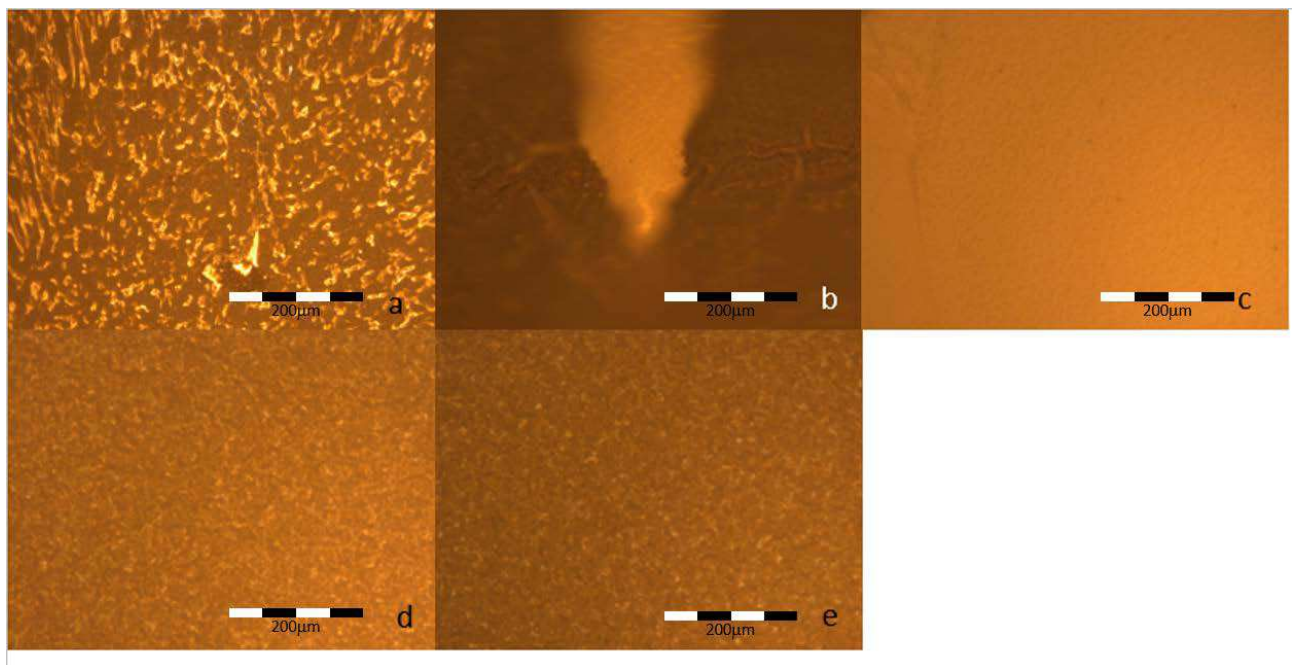


Figure 8 Micrographs of bitumen BBB modified with SBS-V. Key: a-EN 13632, b-fracture surface, c-spot, d-spot annealed, e-hot

Figure 8 shows the micrographs of BBB-SBS-V, which was stable according to BS EN 13399. Unusually, the polymer domains were significantly coarser in both BS EN 13632 and the fracture surface (a-b) than with SBS-L or SBS-R. The direct applied samples (c-e) showed evidence of minor changes, moving to a slightly coarser dispersion.

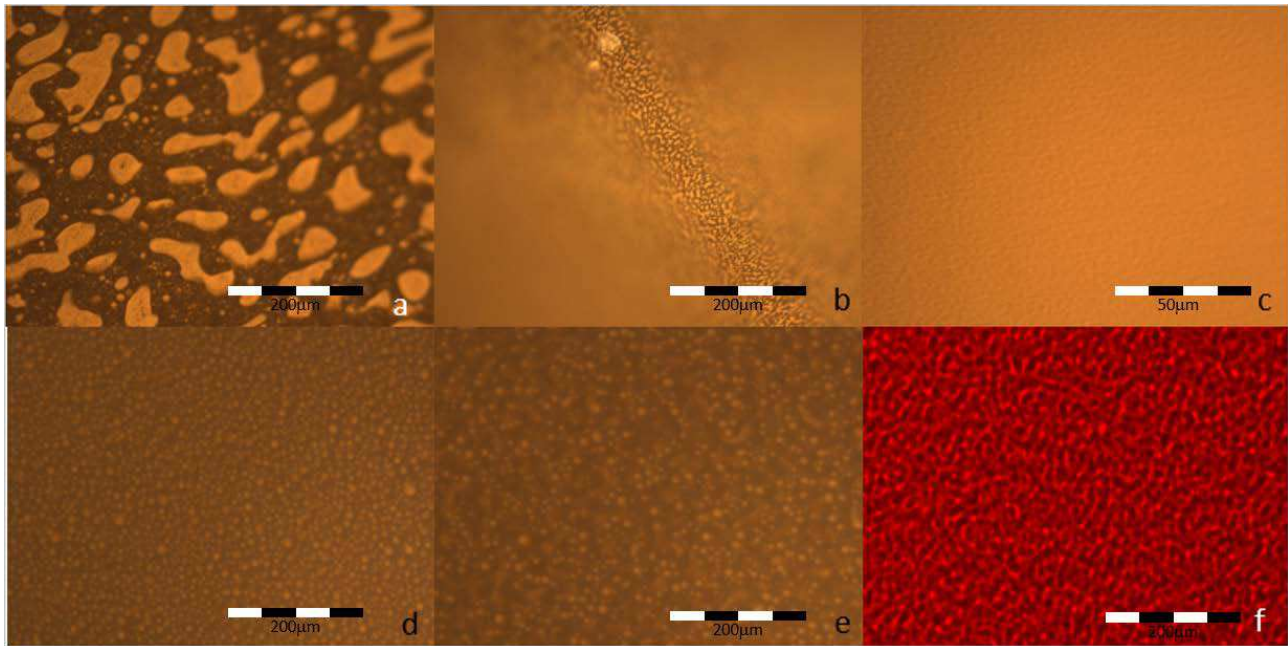


Figure 9 Micrographs of bitumen CCC modified with EVA. Key: *a-EN 13632, b-fracture surface, c-spot, d-spot annealed, e-hot, f-hot (white light transmission)*

Samples prepared using bitumen CCC (fig 9-12) exhibited the greatest degree of separation. CCC-EVA prepared using BS EN 13632 exhibited gross phase separation (a), resulting in large, globular polymer domains within a bitumen matrix. The fracture surface sample (b) showed a finer, more consistent dispersion than with BS EN 13632 again indicating that the slower rate of cooling in the latter method leads to greater phase separation. The direct samples also showed a greater degree of separation with the application of heat (d-f), but binder CCC-EVA was, however, stable according to BS EN 13399.

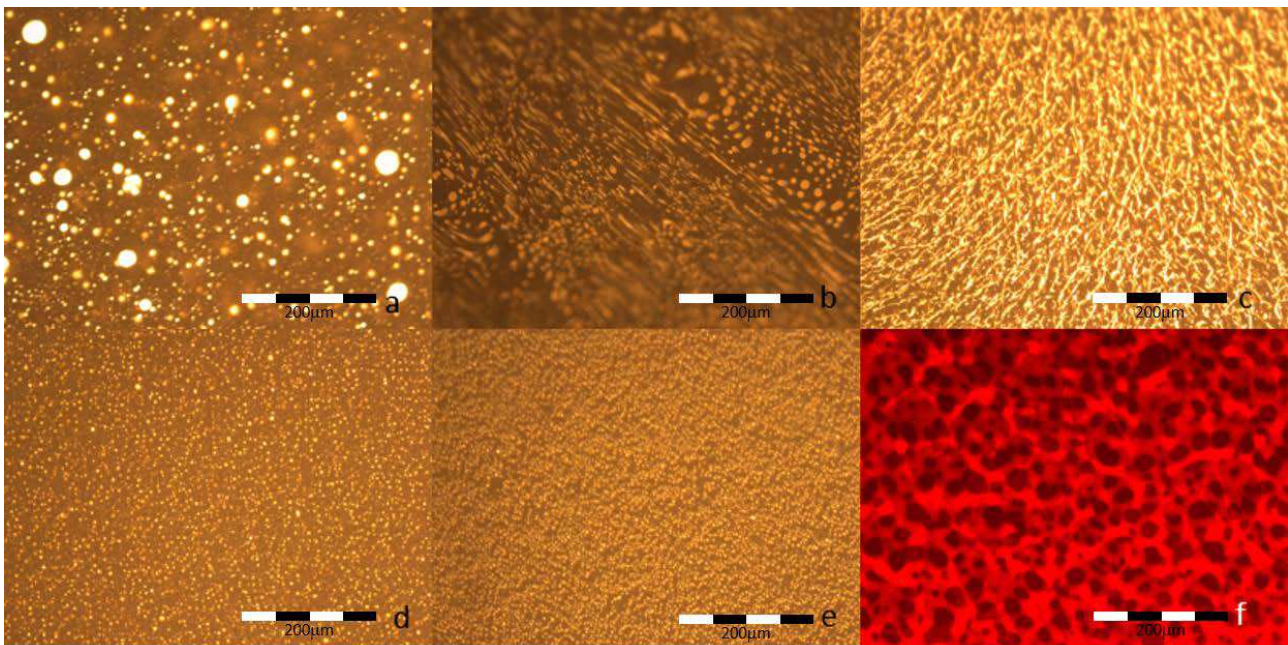


Figure 10 Micrographs of bitumen CCC modified with SBS-L. Key: *a-EN 13632, b-fracture surface, c-spot, d-spot annealed, e-hot, f-hot (white light transmission)*

CCC-SBS-L could be described as “semi-stable” given that the separation according to BS EN 13399 was 8.8°C i.e. it is evident that there was some separation of the polymer, but the binder was not grossly unstable. BS EN 13632 (a) revealed

almost complete separation of the polymer and bitumen phases, with bright, spherical polymer domains being observed. The fracture surface (b) also revealed significant separation with spherical and elongated domains being observed. Significant changes were observed in the direct applied samples (c-f). The spot sample (c) revealed a relatively consistent network, while the annealed (d) and hot cast (e) samples showed distinct, fine, spherical domains. Interestingly, the white-light transmission micrograph (f) revealed a consistent network structure.

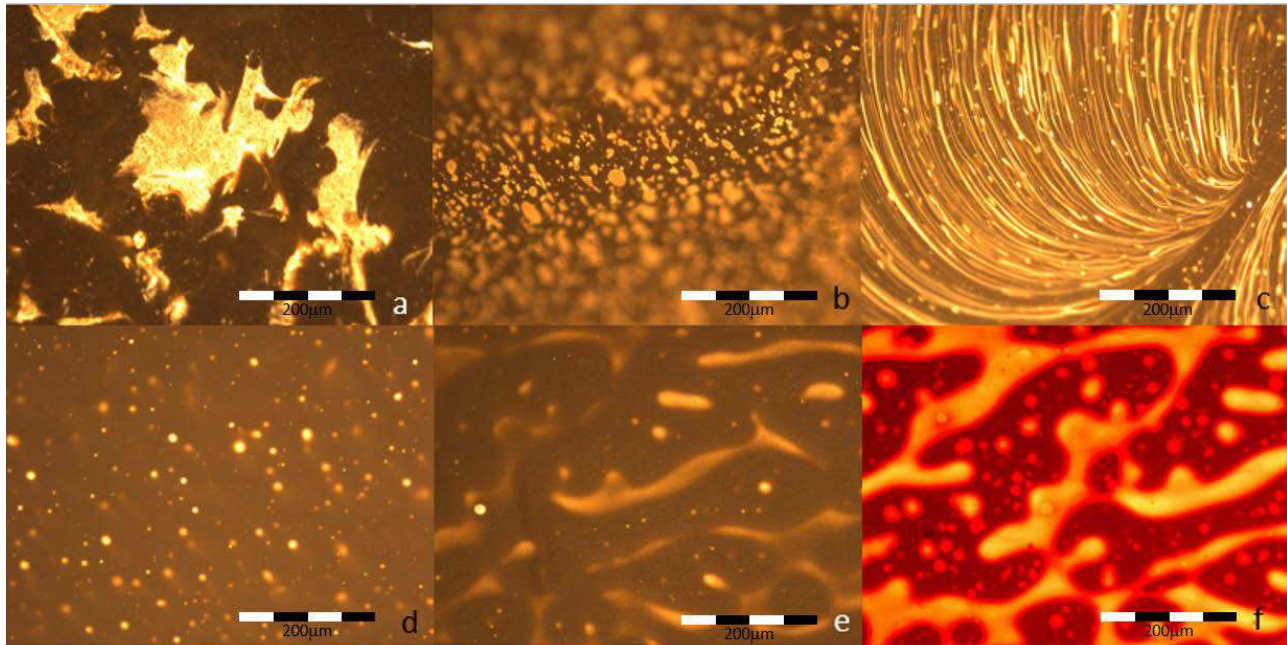


Figure 11 Micrographs of bitumen CCC modified with SBS-R. Key: *a*-EN 13632, *b*-fracture surface, *c*-spot, *d*-spot annealed, *e*-hot, *f*-hot (white light transmission)

CCC-SBS-R exhibited the greatest degree of separation according to BS EN 13399, with $>60^{\circ}\text{C}$ difference in softening point being observed. Gross separation is also evident via the micrographs (fig 11). BS EN 13632 (a) resulted in total separation of the polymer and bitumen phases on a macroscopic scale. The fracture surface (b) revealed a finer, yet still distinct series of spherical and elongated polymer domains. All of the direct applied (c-f) samples exhibited separation. The spot sample (c) showed long “tails” of polymer which became discrete spherical domains on annealing (d) while the hot cast sample (e) showed large, smooth elongated domains. Further evidence of the gross phase separation in CCC-SBS-R can be observed in the white-light transmission micrograph (f) which shows a combination of a large, smooth polymer network and discrete, spherical domains.

CCC-SBS-V, which was stable according EN 13399, showed gross phase separation with samples prepared according to BS EN 13632 and fracture surface (Fig 12 a-b). The direct applied samples (Fig 12 c-f) showed subtle changes in morphology with the application of heat (c-f). The spot sample (c) exhibited a fine, consistent dispersion of small spherical domains, which coarsened slightly on annealing (d). The hot sample (e-f) was generally consistent, with some larger, spherical domains present. White-light transmission (f) revealed a consistent polymer network in the hot sample.

Four polymer-modified binders were unstable according to BS EN 13399, three of which were modified using radial SBS polymer and the other, linear. Each of these binders exhibited changes in morphology in the direct-applied samples with distinct differences between the spot, spot-annealed and hot cast samples. In all cases, the change is from a network domain in the spot samples to discrete domains in the spot-annealed and hot cast samples, indicating that the radial polymer separates from the bitumen both during the annealing process and under the action of heat in the hot samples. It is therefore concluded that the spot-anneal and hot cast sampling techniques can be used to indicate the instability of some polymer-modified bitumens.

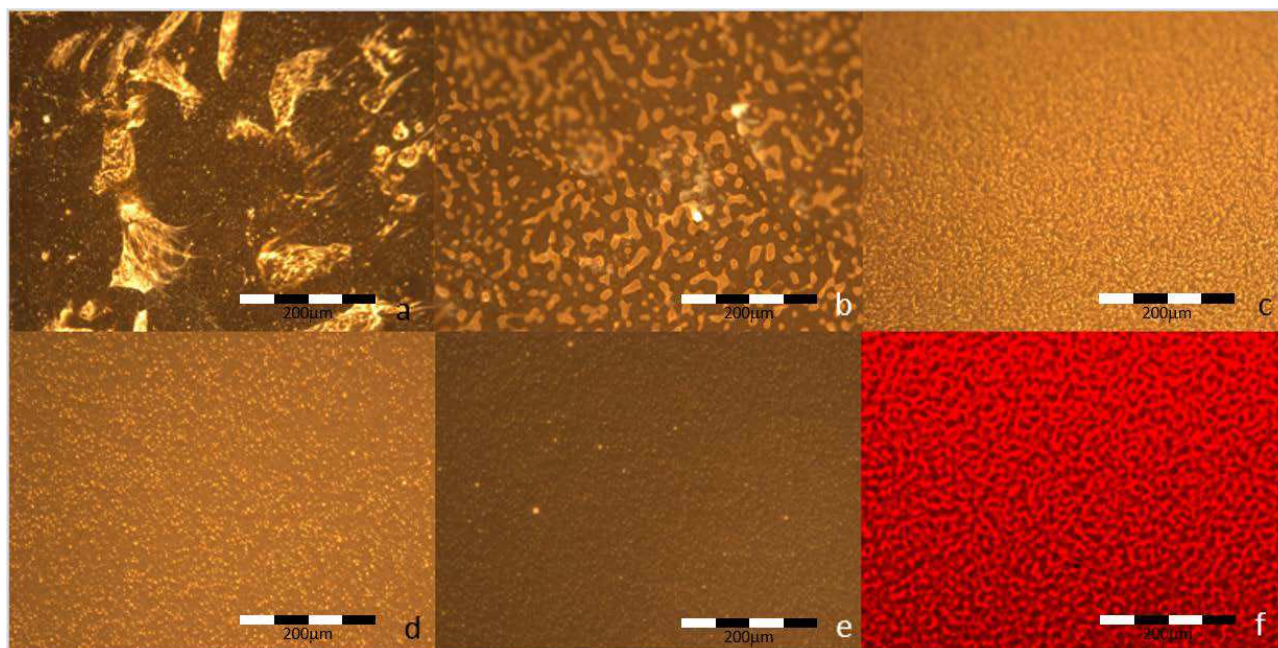


Figure 12 Micrographs of bitumen CCC modified with SBS-V. Key: a-EN 13632, b-fracture surface, c-spot, d-spot annealed, e-hot, f-hot (white light transmission)

Transmission white-light microscopy was found to be complementary to fluorescence microscopy in the deduction of separation. However, for this technique to be useful it is essential that a very thin film of polymer-modified binder is generated to allow sufficient light to pass through the sample.

Both BS EN 13632 and the fracture surface technique tend to result in separation of the polymer from the bitumen and, in the majority of cases, result in dispersions which are coarser than with the other techniques. This study has also demonstrated that the morphologies generated using BS EN 13632 and the fracture surface technique can not be used to indicate instability according to BS EN 13399.

CONCLUSIONS

This study has confirmed that sample preparation has a significant effect on the observed morphology of polymer-modified bitumens. The current standard preparation method, BS EN 13632, tends to result in coarse morphologies indicative of gross phase separation. However, this phase separation does not correlate well with instability as measured using EN 13399. In some cases, binders which exhibit gross separation when prepared according to BS E 13632 were found to be stable under BS EN 13399 while in others the converse was true. In particular, EVA modified binders presented gross phase separation when prepared under BS EN 13632 but were fully stable under BS EN 13399.

It is also concluded that the fracture surface technique does not correlate with BS EN 13399. Almost all of the binders assessed using the fracture surface technique exhibited phase separation, while only four were unstable according to EN 13399.

Both EN 13632 and the fracture surface technique produce irregular surfaces which are difficult to observe under the microscope and therefore their practical use is questionable. A further issue with these preparation techniques is the time taken to produce a suitable sample and the use of sharp blades which impacts on their practicality in a production or quality control environment. Both techniques have preparation times in excess of one hour, followed by fracture at low temperature using a sharp blade.

In contrast to the above, the direct application techniques (spot, spot-annealed and hot-casting) exhibited excellent correlation with storage stability as determined under BS EN 13399 and confirms work previously published [24,25]. Instability is best indicated by a change in morphology between the spot and spot-annealed samples and, in all cases studied, where a significant change occurred, the binder was found to be unstable under BS EN 13399. The hot-casting method, however, is also a good indicator of storage stability as those binders which exhibited gross phase separation when prepared using this technique were also unstable under BS EN 13399.

The rapid indication of instability and phase separation indicated using the direct application techniques has the potential to be a useful technique in rapidly screening polymer-modified bitumens for storage stability in both product development and quality control.

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