

*Journal of Microscopy*, Vol. 204, Pt 3, December 2001, pp. 252–257.

Received 7 March 2001; accepted 18 May 2001

# Studies of the microstructure of polymer-modified bitumen emulsions using confocal laser scanning microscopy

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**Key words.** Bitumen, confocal laser scanning microscopy, emulsion, latex, polymer.

## Summary

Polymer-modified bitumen emulsions present a safer and more environmentally friendly binder for enhancing the properties of roads. Cationic bitumen emulsion binders containing polymer latex were investigated using confocal laser scanning microscopy. The latex was incorporated into the bitumen emulsion by using four different addition methods and all emulsions were processed with a conventional colloid mill. The emulsion binder films were studied after evaporation of the emulsion aqueous phase. We show how the microstructure and distribution of the polymer varies within the bitumen binder depending on latex addition method, and that the microstructure of the binder remains intact when exposed to elevated temperature. It was found that a distinctly fine dispersion of polymer results when the polymer is blended into the bitumen before the emulsifying process (a monophasic emulsion). In contrast, bi-phase emulsion binders produced by either post-adding the latex to the bitumen emulsion, or by adding the latex into the emulsifier solution phase before processing, or by comilling the latex with the bitumen, water and emulsifier all resulted in a network formation of bitumen particles surrounded by a continuous polymer film. The use of emulsified binders appears to result in a more evenly distributed polymer network compared to the use of hot polymer-modified binders, and they therefore have greater potential for consistent binder cohesion strength, stone retention and therefore improved pavement performance.

## Introduction

Roads produced with bitumen binders are subjected to many harsh environmental conditions such as traffic

loading, ingress of water, chemical attack and widely fluctuating temperatures. Conventional bitumen often cannot provide the desired resistance to these conditions so modification of the bitumen properties becomes necessary.

Bitumen modified with polymer is a common means of providing resistance to pavement deformation (Whiteoak, 1990). The common pavement technique used in New Zealand is hot spray chip sealing, which requires the bitumen to be applied at a temperature of typically 180 °C and adding solvents such as kerosene, both of which lower the bitumen viscosity to allow easier application. Both of these aspects have significant safety and environmental drawbacks (Whiteoak, 1990). However, emulsifying the bitumen with water eliminates both problems and allows greater product flexibility, because various emulsion-based products such as slurry surfacing and microsurfacing, in addition to spray chip sealing, can be used.

Various polymers such as styrene butadiene rubber (SBR) latex, styrene butadiene styrene (SBS), polychloroprene latex, natural rubber latex and ethylene vinyl acetate (EVA) can be used in the preparation of polymer-modified bitumen emulsions (Whiteoak, 1990; PIARC, 1999). However, latex polymers such as SBR, polychloroprene and natural rubber, because of their liquid form, have a major advantage in an emulsion formulation. The physical form of the latex allows them to be added into a bitumen emulsion manufactured with a colloid mill by either: (1) pre-blending latex into the bitumen before emulsification; (2) comilling (milling the latex, bitumen and emulsifier solution in separate streams simultaneously); (3) adding latex into the emulsifier solution; or (4) post-adding latex to the prepared bitumen emulsion. This gives latex polymers far more processing and performance flexibility. Solid polymers such as SBS and EVA must be dispersed into the bitumen before emulsifying and this method has processing limitations (Rabiot & Jariel, 1993; PIARC, 1999). Bitumen consists of two basic chemical components – high molecular weight asphaltenes

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and lower molecular weight maltenes. The addition of high molecular weight polymers to hot bitumen results in a swelling of the polymer, which in the case of SBS polymer can be up to nine times its initial volume due to the absorption of maltenes (Whiteoak, 1990).

Microscopy techniques have often been used to characterize the microstructure interactions between bitumen and polymers for modified binders and for asphalt concrete (Piazza *et al.*, 1980; Loeber *et al.*, 1996; Rozeveld *et al.*, 1997; Michon *et al.*, 1998). However, there have been few publications on the microstructure and curing aspects of polymer-modified bitumen emulsion binders for cold mix applications. Normally, physical testing methods are employed to characterize the degree of modification of the binder. However, visual observations can help to improve the understanding of the interaction between the emulsified bitumen and polymer after water evaporation and the means by which this interaction may result in improved aggregate retention properties and pavement deformation resistance.

Oil exhibits autofluorescence when irradiated with UV or blue light but for bitumen there is little light emission as the oil phase is mixed with an asphaltene and resin phase, which do not exhibit any fluorescence. However, the polymer has very strong fluorescence emissions. It is therefore possible to analyse the influence and compatibility of polymer in bitumen by the strength and distribution of the light emission (Loeber *et al.*, 1996; Rozeveld *et al.*, 1997). Fluorescence microscopy has often been used to analyse the polymer distribution in bitumen samples (Whiteoak, 1990; Loeber *et al.*, 1996; Lu *et al.*, 1999). The method uses mercury or xenon arc lamps to provide the light source. Although acceptable images are obtained, there are often problems experienced due to out of focus data. This situation is eliminated with the confocal laser scanning microscopy (CLSM) technique because a laser is used to optically section the sample (Rost, 1992; PIARC, 1999). The CLSM technique has been used by several researchers to assess the polymer distribution, network formation and compatibility for polymer-modified bitumen (Lee *et al.*, 1997; Rozeveld *et al.*, 1997; PIARC, 1999) but there is very little information for emulsion binder residue.

This investigation examined the structural network and distributions of the polymer within dried emulsion samples prepared with different latex addition methods. We also explain how these structures improve the binder properties. We examine the way in which the polymer helps bitumen to resist applied stress and we examine the structure of the modified binder after curing at elevated temperature. These investigations help to explain the performance improvement that polymer modification has on emulsion-based road products. This paper compares the effects of the polymer addition mode on the microstructure and polymer distribution within the polymer-modified bitumen emulsion residue.

## Materials and methods

The bitumen used in this study was 180/200-penetration bitumen refined from Middle Eastern crude. A latex elastomer polymer was used to modify the bitumen at a concentration of 3% solids by weight of bitumen.

Four emulsions consisting of bitumen, water, polymer and emulsifier were prepared using a Charlotte G-3 colloid mill (Chemicolloid Laboratories, New York) operating under atmospheric pressure. The polymer was added by four different methods: (1) pre-blending the polymer into the bitumen at 180 °C for 1 h before emulsifying; (2) comilling the latex polymer through the mill with the bitumen and emulsifier solution phases; (3) adding the latex polymer into the emulsifier and water solution; (4) post-adding the latex polymer to the prepared emulsion. A quaternary ammonium slow set cationic emulsifier was used to stabilize the bitumen droplets. The solids content of the emulsions was 62%.

The emulsion residue was obtained by placing a drop of emulsion on a concave microscope slide and drying at ambient temperature for 3 h and then at 60 °C for 4 h in a forced air oven to fully evaporate the water phase. The 60 °C temperature is similar to the maximum pavement temperature expected in the peak of summer and this was chosen to simulate the drying effects for the road surfacing. For comparison, a drop of the polymer-modified bitumen from the pre-blend method before emulsifying was observed. A sample of emulsion using latex addition method (3) was oven dried at 110 °C for 2 h to assess the change in structure with elevated temperature.

A Leica DM-RBE confocal microscope with a TCS 40 laser-scanning head was used to examine the polymer-modified emulsion residues. Images were recorded in fluorescent mode for the binder images using an argon-krypton laser with a wavelength of 488 nm (blue light). A long pass filter LP515 allowed the fluorescent light to reach the detector. A single line scan method was used to view the binder samples. All images were recorded in a 512 × 512 TIFF format.

## Results and discussion

The binder structures produced by adding the polymer latex in the four methods are shown in Fig. 1. The CLSM images taken in fluorescence mode show the bitumen with a polymer network structure formed after evaporation of the water phase. The samples were dried under conditions that would closely match that which occurs on application of the binder to a pavement surface. The resulting microstructures observed should then represent the actual structure of the binder as it would appear on the road.

Three of the addition methods lead to similar microstructures as shown in Figs 1(A–C) where the dark bitumen

droplets are surrounded by a bright polymer phase. The bitumen particles vary from about 2 to 17  $\mu\text{m}$  in diameter. The addition of the latex either to the emulsifier phase Fig. 1(B), or by comilling into the emulsion Fig. 1(C), appears to provide a slightly more even distribution of polymer in the binder than the post-addition of latex. The proposed formation of the structures in Fig. 1(A–C) is shown schematically in Fig. 2. The droplets of bitumen created by shear forces within the colloid mill are surrounded by latex particles and prevented from coalescing by the water–emulsifier phase. Evaporation of the aqueous phase destabilizes the emulsion and the latex particles coalesce to form a continuous polymer film surrounding the bitumen droplets. Takamura & Heckmann (1999) also indicate that this mechanism occurs. The high molecular weight of the polymer helps to reduce the flow of the bitumen at higher temperatures. The asphaltenes provide the strength and stiffness to bitumen and the polymer network surrounding the asphaltenes adds strength and also elasticity, thereby improving the overall binder properties.

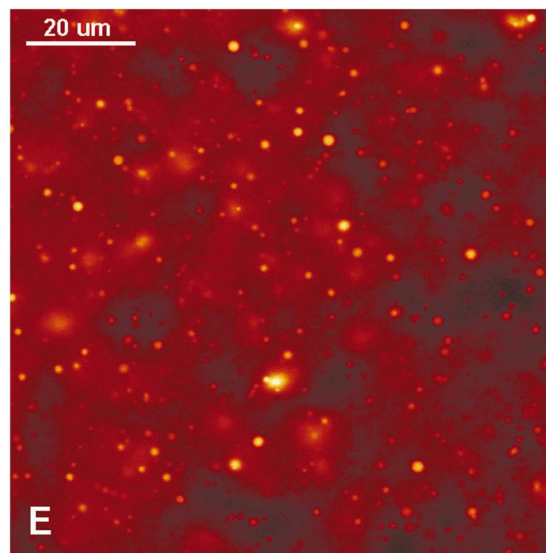
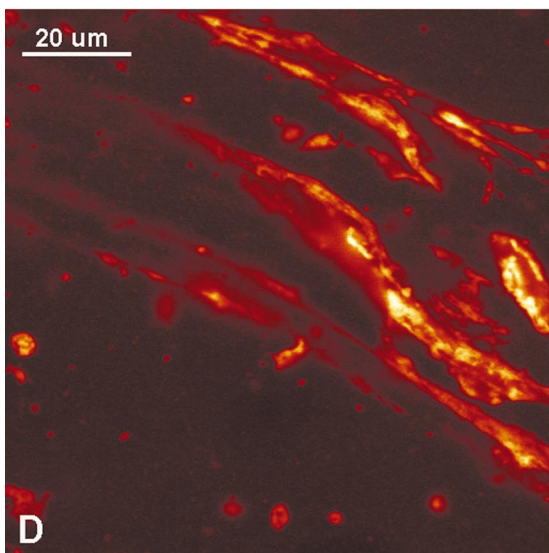
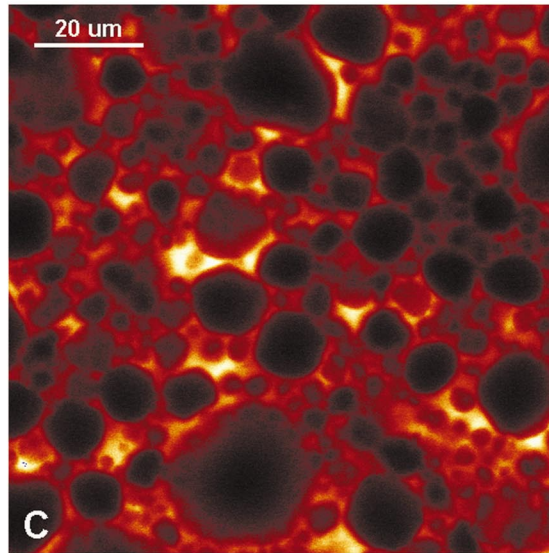
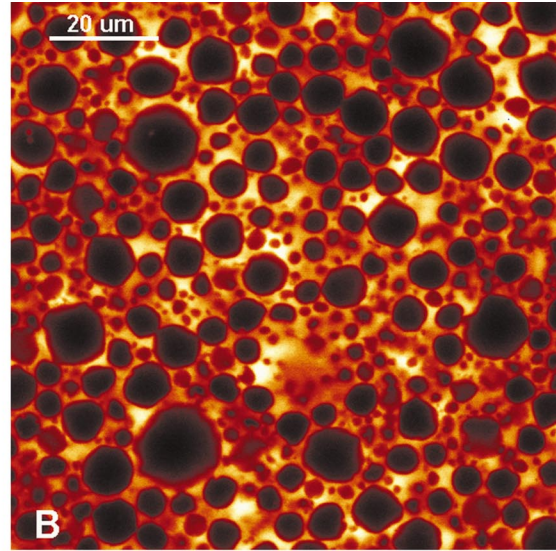
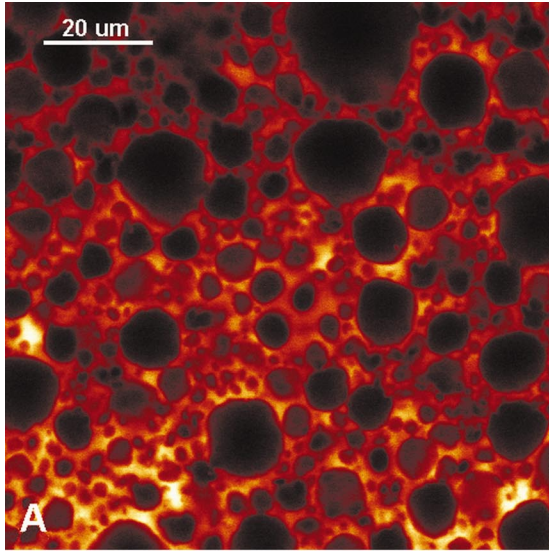
In the polymer-modified bitumen before emulsification the polymer is spread in variable droplet sizes and also contains areas of swollen polymer that has coalesced into large groups (Fig. 1(D)). This effect is consistent with that observed by Bouldin *et al.* (1990) and Whiteoak (1990) for incompatible polymer-modified bitumen. With the same binder after emulsification the resulting microstructure is quite different (Fig. 1(E)). The binder contains discrete smaller particles of polymer, areas of swollen polymer/maltenes phase, and dark areas of asphaltene aggregation. This finer structure indicates an improvement in the bitumen–polymer compatibility.

The different binder structure obtained by adding the polymer to the bitumen before emulsification is due to the polymer being dispersed throughout the bitumen. This method of addition produces a monophasic emulsion – a single phase of polymer-modified bitumen droplets, whereas the other methods of latex addition produce bi-phase emulsions, which are a combination of two phases – bitumen droplets and polymer latex droplets. The interaction between the bitumen and polymer latex does not take place until the emulsion breaks, as seen in the binder images in Figs 1(A)–(C) and Fig. 2. Comparing the modified emulsion binders to the modified bitumen in Fig. 1(D), it can be seen that emulsifying leads to a dried binder film that is more

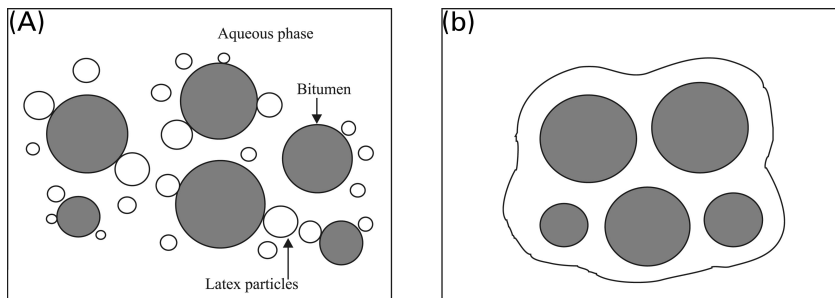
homogeneous and has a better polymer distribution. This should lead to improved binder properties, particularly the ability of the binder to develop consistent cohesion strength and a likelihood of better stone retention. This has definite advantages for spray chip sealing surfaces where stone retention is particularly important.

The CLSM fluorescence mode image in Fig. 3 shows a dried film of polymer-modified bitumen emulsion after a lateral shear stress has been applied. The polymer becomes elongated from the round forms seen in Fig. 1, as it resists the deformation. The elastic properties of the polymer provide resistance to applied stress. These images provide a demonstration of the proposed dynamic interaction between bitumen and polymer suggested by Loeber *et al.* (1996), who proposed that if there is no shear stress the structure consists of a dispersion of round bitumen droplets in a polymer matrix. However, when increased stress is applied the round forms change to a wavy lens form and then to the elongated forms (Fig. 3). The deformation resistance properties imparted by the addition of polymer are important for any type of road surfacing. Chip retention, as already mentioned, is particularly important and the elastic properties of the polymer assist in retaining the chip in the pavement surface. It is often the case that unmodified bitumen possesses insufficient elasticity and strength to resist the stresses that traffic places on the pavement. To complement the microstructure results, the cohesion strengths of the bitumens and the softening points were measured. They were found to be 12  $\text{kg cm}^{-1}$  for the unmodified bitumen compared with 17  $\text{kg cm}^{-1}$  for the polymer-modified binders. This means that the aggregates in a chip seal made with polymer-modified bitumen can better resist displacement due to shear stresses. The softening point of the unmodified bitumen was 39 °C compared to 50–51 °C for the polymer-modified emulsion binders. This improvement in the softening point helps prevent the chips embedding too far into the binder and causing a reduction in skid resistance. The addition of polymer enhances the elasticity and strength of the bitumen. The polymer also provides rutting resistance and reduced lateral displacement to other emulsion based pavements such as slurry surfacing and microsurfacing. Evidence of this has been demonstrated in physical pavement tests in several studies (Asphalt Institute, 1994; PIARC, 1999; Takamura & Heckmann, 1999) and a mechanism for this improvement is shown visually in our study.

**Fig. 1.** CLSM images of residual modified binder after evaporation of the emulsion water phase and showing the polymer network structures. The dark particles are bitumen and do not fluoresce. Polymer network formed by: (A) post-adding latex polymer to the manufactured emulsion; (B) addition of the latex into the emulsifier solution phase and emulsifying with the bitumen; (C) comilling the latex with the bitumen and emulsifier solution phases; (D) & (E) latex polymer preblended into hot bitumen (D) before emulsification and (E) binder after emulsification. In (A)–(C) the polymer encapsulates the bitumen droplets. In (D) the polymer distribution is coarse and uneven, indicating incompatibility between the polymer and bitumen, whereas in (E) the polymer distribution is much more even but has a different microstructure compared to the latex addition methods in (A)–(C).







**Fig. 2.** (a) Schematic illustration of the modified emulsion showing the latex particles remaining in the aqueous phase surrounding the bitumen droplets. (b) Evaporation or destabilization of the aqueous phase results in the latex particles forming a continuous polymer film around the bitumen droplets.

Compatibility of the polymer with bitumen is important for optimum binder performance and has been the subject of many studies (Piazza *et al.*, 1981; Bouldin *et al.*, 1990; Whiteoak, 1990; Lu *et al.*, 1999). Compatible binders are those that have an even distribution of polymer throughout the bitumen and preferably are of a fine network structure. The binder in Fig. 1(d) is a polymer-modified bitumen used for hot spray sealing and shows incompatibility as the polymer has coalesced into localized agglomerations and this can lead to aggregate stripping problems due to the poor polymer distribution. This is important, as hot spray sealing is the main pavement method utilized in New Zealand and the binder quality largely determines whether it will perform to expectations. The source and composition of New Zealand's bitumen has a defining impact on bitumen–polymer compatibility (West, 1985; Transit, 1993), and the bitumen is normally incompatible. Polymer-modified bitumen requires compatibiliser additives or

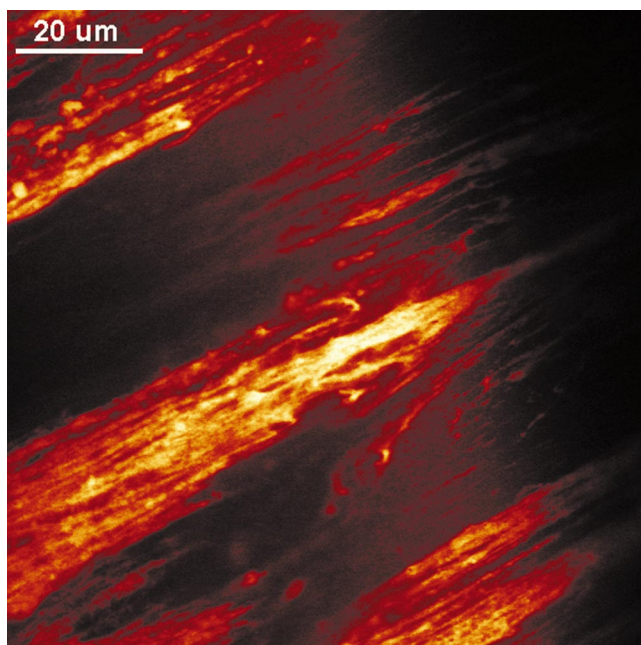
cross-linking agents to reduce these problems. However, as seen in the binder images in Figs 1(A)–(C), the addition of latex to a bitumen emulsion can provide homogeneous polymer distribution in the dried binder without the need for compatibiliser additives. In addition to the safety and environmental benefits of emulsions, there appears to be a significant improvement in the binder polymer distribution and hence in pavement performance.

The resistance to higher temperatures of the modified emulsion residue is shown in Fig. 4. This shows a binder sample from the emulsion produced by latex addition method (3), but after drying at 110 °C for 2 h. The polymer has prevented the bitumen from flowing significantly under the higher temperature and the network support microstructure remains. Because the polymer has effectively encapsulated the bitumen, the residue film is displaying the properties of the polymer rather than the bitumen particles. The microphotograph shown in Fig. 4 illustrates how the polymer prevents the bitumen from flowing at higher temperatures and why it is required for roads in hot climatic areas. This modification prevents the bitumen binder adhering to vehicle tyres in very hot summer weather. It also stops the pavement softening under load to limit permanent deformation (rutting).

In bi-phase emulsion manufacture the latex polymer is not exposed to temperatures above 85–90 °C. However, in monophasic emulsions the pre-blended bitumen and polymer is processed at temperatures up to 180 °C to allow adequate dispersion of the polymer in the bitumen. At temperatures approaching 200 °C there is an increased risk of both polymer and bitumen degradation occurring. This can have an adverse effect upon the quality of the polymer-modified bitumen residue and presents a major advantage with bi-phase emulsions.

## Conclusions

Cationic bitumen emulsion binders containing polymer latex were investigated using confocal laser scanning microscopy, which proved to be a useful technique for this application. The emulsion binder films were studied after evaporation of the emulsion aqueous phase. We have shown how the



**Fig. 3.** CLSM image of a polymer-modified bitumen emulsion binder after drying and exposure to lateral shear strain, showing elongation of the polymer to resist deformation.

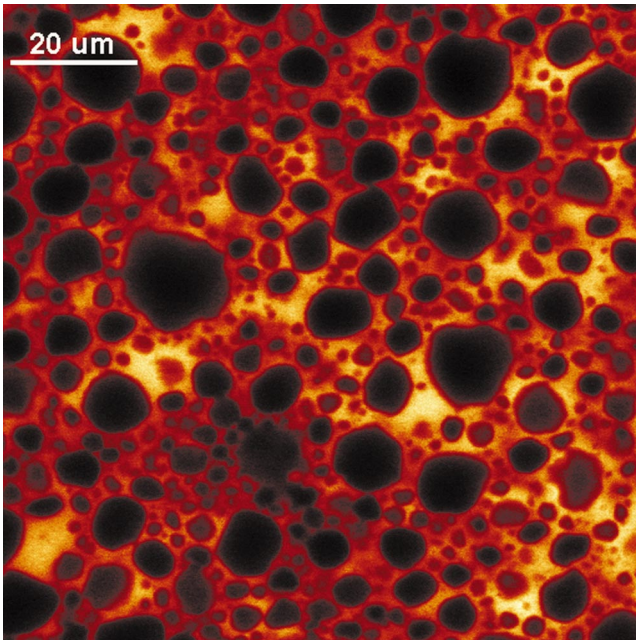


Fig. 4. CLSM image of a polymer-modified bitumen emulsion binding after curing at 110 °C. The polymer network around the bitumen particles remains intact even after elevated temperature exposure.

structure and distribution of the polymer varies within the bitumen binder depending on latex addition method, and that the structure of the binder remains intact when exposed to elevated temperature. We have also shown how the polymer elongates under stress to improve the bitumen binder resistance to deformation. It was found that the polymer dispersion within a monophasic emulsion binder (polymer is blended into the bitumen before the emulsifying process) is distinctly fine throughout the bitumen. However, the bi-phase emulsion binders (produced by either post-adding the latex to the bitumen emulsion, adding the latex into the emulsifier solution phase before processing or comilling the latex with the bitumen, water and emulsifier) resulted in a network formation of bitumen particles surrounded by a continuous polymer film. This difference in polymer dispersion and binder structure requires further investigation to determine if there is a significant effect on binder performance. The results in this study show that emulsified binders appear to have a more homogeneous distribution of polymer compared to hot polymer-modified binders, and therefore have greater potential for consistent binder cohesion strength, stone retention and consequently improved pavement performance.

## Acknowledgements

We thank L. Nickless of Massey University for the use of the CLSM and technical assistance provided.

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2001-05-01

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