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Phase-Destabilization Mechanism of Polymer-Modified Bitumens in Quiescent Annealing

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ABSTRACT

Beights in the indicating and insulating materials is modified with polymers to improve its performance in service conditions. Almost all polymers are incompatible with bitumen, and at high temperatures due to relatively very low viscosity of the bitumen phase, are separated from it. These lead to a considerable limitation in the use and handling of polymer-modified bitumens. An understanding of the mechanisms of phase separation of these incompatible mixtures help to improve methods of transportation and handling of polymer-modified bitumens. According to direct observations of the behavior of polyethylene particles in medium of molten bitumen confirm the indirect conclusion already made by others, (coalescence based phase separation) and reject any possibility of occurring Ostwald ripening. This conclusion can also generalized to viscoelastic incompatible polymer blends. Prog. Color Colorants Coat. 2(2009), 53-59. © Institute for Color Science and Technology.

1. Introduction

The polymer-modified bitumens (PMBs) are amongst very important construction materials which play critical roles in insulating materials, asphalt binders and protective coatings. The value of PMBs remains in the compatibility and morphology of these very complicated systems. An understanding of the phase separation mechanism in these systems is of the prime importance. Stability and storage of mixtures of bitumen and polymers are detrimental factors in melting, storage, transferring, transportation and handling of PMBs. Bitumen is normally (or mainly) a complex mixture of many different chemicals which form into a temperature sensitive colloidal structure [1-4].

About three quarters of bitumen production by volume is used in road constructions. Roads are of the most important matters of consideration in transportation. Transportation, as a whole, is important to the global and local economies. In the past asphaltic pavements were constructed using the non-modified bitumen which had

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been prepared from dual distillation of crude oil at atmospheric pressure followed by under vacuum distillation. This type of bitumen is of its intrinsic shortcomings. Therefore, many efforts have been devoted to develop high-performance bitumens, especially those concering (PMBs) [1]. Different polymers can be used in modification of bitumins. Some polymers are specially tailored for bitumen modification, e.g. styrene-butadienestyrene tri-block or styrene-ethylne-butylene-styrene copolymers (SBS and SEBS) and ethylene-vinyl acetate copolymer (EVA). However, some commodity polymers, such as: polyethylene, may be also used in bitumen modification [1, 2].

From the commercial point of view, due to the low cost production technology and availability of the monomers, polyethylene could be the best choice in bitumen modification. Meanwhile, all types of polymer-modified bitumens should be stored at high temperatures prior to being mixed with aggregates in a hot-mix asphalt production plant. At the high temperatures, *i.e.* 163°C, the polymer (the dispersed phase in bitumen matrix) is in liquid state and of a lower density but higher viscosity as compared with those of molten bitumen.

In a polymer-bitumen emulsion system at high temperatures polymer particles are very fine and there exist also some large polymer particles. The very small micron-sized molten polymer particles, e.g. polyethylene, are very soft and ready to coalesce soon after meeting each other followed by rupture of the bitumen film separating them. These tiny particles are able to move upon Brownian motion mechanism. In real practice, inside a storage tank, the situation for PMB is a little different from what happens under microscope. In a three-dimensional space, once the particles coalesce, the volume of the resulting droplet become larger than the individual precursors. This causes an increase in the buoyancy force acting on the resulting droplet. As a result, the formed droplet moves upward faster and captures other slow upward moving particles in its way to the surface of the emulsion. Finally, the mechanism of phase separation in PMB systems is defined as coalescence followed by creaming [2]. The final result is a large difference between the concentration of polymer on the top and in the bottom of the emulsion system. This breakdown of the emulsion leads to an extensive deterioration of performance of the polymer-modified bitumen.

In the literature there are too many studies which have been carried out on the polymer blends [5-27] and

emulsions [28-30]. Some researchers have claimed the mechanism of Ostwald ripening to be responsible for the breakdown of polymer blends [7, 31] and emulsions [28-30]. In this mechanism, the diffusion of individual polymer chains in the matrix is necessary for leaving small high-energy particles and reaching joining to large low-energy particles. However, it is more or less impossible for Ostwald ripening mechanism to be considered for high viscosities and elastic polymer blends, whereas, it may be suitable to explain the mechanism in low viscosity media. In some other works, the coalescence have been found to be as a mechanism responsible for phase coarsening in the phase separation or coarsening under quiescent conditions [21-27]. Meanwhile, due to the viscoelastic properties of the polymer blends resulting from the existence of differences in dynamics of the components, a new mechanism called "viscoelastic phase separation" might be introduced [32].

The concept of phase separation mechanisms in polymer blends was successfully used in preparation of polymeric membranes [33-34]. In the light of these technically important aspects of phase separation some reviews were observed [31-32]. Others tried to model the phase behavior of different systems [31, 35-38] and some researches were devoted to the kinetics of phase separation [39-40].

Bitumen is available in both oil-in-oil (polymer modified bitumens) [1-2, 41-46] and oil-in-water (bitumen emulsions) [47-48] forms. Therefore, finding out the mechanism of phase stabilization and phase separation is of prime importance for product developers and consumers.

This is technically an important subject to confirm and visualize the mechanism and dynamics of polymer phase separation. This paper aims to envision the polymer phase separation in two dimensions, in order to ratify the mechanism proposed for the phase separation of the PMBs in the literature. This type of observation and experimentally sample preparation is specific to this investigation and has not yet been reported.

2. Experimental

2.1. Materials

Bitumen 150/200 penetration grade (Ultramar, Quebec, Canada) was used in this study. Some of its physical properties are reported in Table 1. The polyethylene was synthesized in the laboratory using Ziegler-Natta catalyst. It was recovered from the reaction vessel as white fine grain powder. The detail of the polymer synthesis was reported elsewhere [49]. According to the rheological data this polyethylene could be considered as an ultra-high molecular weight polyethylene [49]. Its density typically was expected to remain between 0.95 to 1 g/cm³.

2.2. Methods

For preparation of the samples some grains of polyethylene powder were spread on the optical microscope lame then the molten bitumen was poured on this particle arrangement. Thereafter, an optical microscope lamella was put on it (Figure 1). Then the assembly was inserted into the hot zone of a laboratorymade hot-stage, which was equipped with a temperature controller to ensure a uniform temperature throughout the sample. The heating chamber was so designed that light from the source of microscope could pass through the sample and reach the camera (Figure 2). By adjusting temperature at 163°C, the evolution of the morphology was monitored by taking the photographs at given times and 100X magnification.



Figure 1: Arrangement of polyethylene particles in bitumen medium between lame and lamella.





Figure 2: Schematic representation of the hot-stage and optical microscope.

3. Results and discussion

Figure 3 shows the initial stage of the prepared arrangement of the PE particles in the bitumen medium (at t=0). We observe a total number of 9 particles in this picture, and may number them from 1 to 9 beginning with the lowest one in the left and ending with the highest in the right. Therefore, the largest particle is numbered as 8 and the particle located in the left-hand side of it is going to be numbered as 7. According to the scale, the particle number 8 has a diameter larger than 250 microns. In comparison with Figure 4, the size of particles changed due to polymer melting and formation of a thin film. Therefore, the microscope can easily focus on the edge of the particles. As seen in this figure the particles, especially the large ones (*i.e.* number 8), are not round.

After two hours appearances of the polyethylene particles changes to round and flat shapes (Figure 4). In the frame of this figure, we observe only 7 particles, but as we will see in the next figures all particles co-exist up to the end of the experiment (except No. 7). As it is observed, the relative positions of the particles are changed. We may consider particle No. 8 (the largest one) to be more or less non-displaceable,. where the particles No. 3 and 4 move very close to the particle No. 8.

In Figure 5, particle No. 3 distances from particle No. 8, whereas particle No. 7 tends closely to particle No. 8. It appears that the partition between these two particles is solely a thin film of bitumen with about 5 micron thickness. It is obviouse that due to the attractive forces acting between the particles, the large particle (No. 8) changes its shape, in order to be able to exert the highest attractive force possible on particle No. 7 and favors the configuration in which separating bitumen film breaks up and capture the small particle (No. 7).

Because of high thermal energy available to the particles at 165°C, the low viscosity of bitumen medium at this temperature and at high surface energy of the polyethylene in molten state, after a period of time, i.e. less than five minutes, the molten film of the bitumen is ruptured and particle No. 7 diminished (Figure 6), while particle No. 8 deforms and loses its roundness. Meanwhile, all other particles co-exist and are stable in size and shape. After 5 hours and 35 minutes annealing at 165°C, all particles co-exist together, become round and no changes in their sizes is observed (Figure 7).



Figure 3: Relative position of polyethylene particles in molten bitumen medium at annealing time t=0 at 165°C.



Figure 4: Relative position of polyethylene particles in molten bitumen medium at annealing time t=2 hours at 165°C.



Figure 5: Relative position of polyethylene particles in molten bitumen medium at annealing time t=3h50 at 165°C.



Figure 6: Relative position of polyethylene particles in molten bitumen medium at annealing time t=3h55 at 165°C.

All of these observations indicate that the mechanism of phase separation in polymer-modified bitumen must take place by the coalescence process, and the mechanism of Ostwlad ripening has no contribution in the systems. These observations endorse the indirect conclusions made by Hesp [3]

Another important point which can be inferred from these observations is that in viscoelastic systems, such as polymer blends the possibility of occurring Ostwald ripening is also zero. This finding contradicts other researches, such as [7] and agrees some others, such as [22-25].

4. Conclusions

A direct observation of morphological evolution for polymer-modified bitumen was provided. It was directly



Figure 7: Relative position of polyethylene particles in molten bitumen medium at annealing time t=5h30 at 165°C.

observed that the polyethylene particles do not tend to rip in bitumen medium and it was shown that these particles prefer to join together and form larger particles due to interfacial and inter-particle attractive forces. The only obstacle in the process was the existence of partitions made from molten bitumen. Whenever, particles had enough energy to come close together and overcome the thin remained bitumen film which was separating particles, the coalescence of polyethylene particles occured and lead to polymer phase separation. No indication of Ostwald ripening was shown in this system due to the fact that small and large particles coexisted simoltaneously. This was also concluded that mechanism of Ostwald ripening could play any essential role in highly viscoelastic immiscible polymer blends.

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