

EFFECT OF USING DISPERSANTS DURING THE MIXING OF AGGREGATES WITH POLYMER-MODIFIED ASPHALTS

: A CASE STUDY FOR NOVOPHALT

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ABSTRACT

The present work explores the use of dispersants in lowering the viscosity of asphalt mastics. The study includes the use of three different types of dispersants during the mixing of fine aggregates with one specific type of polymer-modified asphalt, namely, Novophalt that has been selected for a case study. The effect of the dispersants on the selection of the mixing temperature is elucidated. A distinction is made between a lubricant and a dispersant by observing the rheological behavior of the aggregate-asphalt systems under different conditions. It is also shown that stearic acid which acts more like a lubricant has the potential to lower compaction temperatures during the paving of roads.

INTRODUCTION

The mixing of aggregates and asphalt is carried out in an asphalt hot-mix facility¹⁻³ at a predetermined mixing temperature for a certain length of time. The mixing time is carefully controlled so that it is long enough to give a uniform coating of asphalt to all aggregates but short enough to prevent any asphalt film hardening due to exposure to air and heat. This is done based on set procedures laid down by AASHTO T 195 (ASTM D 2489). Besides the mixing time, there are other factors related to the mixing equipment (such as the speed of the rotating unit, its configuration, etc.) that govern the mixing efficiency. One another important factor that controls proper mixing is the mixing temperature.

The correct temperature for aggregate-asphalt mixing is determined by the requirements for achieving dry aggregates, for good particle coating with asphalt, and for proper laying and compaction of the mixture. For unmodified asphalts, the Superpave mix design procedure specifies the mixing temperature based on the binder viscosity of 170 ± 20 cSt measured on a capillary tube viscometer, which is equivalent to viscosity of 140-183 cP if measured using the Brookfield rotational viscometer.

In the case of polymer-modified asphalts, a viscosity level of 140-183 cP is achievable only at high temperatures. At these high temperatures, there is likelihood of binder degradation. If lower temperatures are used, then it is quite likely that the polymer-modified asphalts would show a viscosity that is not constant but dependent on shear rate and that would complicate matters. If mixing is carried out at such temperatures where the viscosity is shear-dependent, then uniform mixing cannot be assured. This is because, during the entire mixing process, the binder sees a range of shear rates due to the variation in the coating thickness of the aggregates as the mixing progresses with time, and it is not easy to decide which shear rate value is to be used as truly representative of the situation.

Bearing the above points in mind, a procedure was set up for determination of the mixing temperature of polymer-modified asphalts under the following constraints⁴.

- 1) The temperature should be high enough to ensure that
 - (a) the binder viscosity is as shear-rate independent as possible,
 - (b) the binder has good fluidity to provide uniform aggregate coating during mixing (for unmodified asphalts, a viscosity range of 150-190 cSt or, equivalently, 140-183 cP is considered to be adequate),
 - (c) the final mix discharge does not cool to below 85°C during laying and compaction.
- 2) The temperature should be low enough to ensure that
 - (a) polymer in the modified binder does not degrade,
 - (b) accelerated hardening of the asphalt in the modified binder does not take place due to exposure to heat and air.
- 3) The temperature should be appropriate to ensure good quality of mixing.

It was found⁴ that the choice of correct mixing temperature is best determined by optimization of the dispersion of the aggregates in the binder. The best dispersion was adjudged by locating the temperature at which the minimum in the relative viscosity (i.e., the ratio of the viscosity of the mastic to that of the binder) occurred. For the two polymer-modified asphalts (Novophalt and Styrelf) used in the study⁴, it was found that a mixing temperature between 163°C and 180°C would be a good recommendation, with a bias toward the higher temperature to maintain as low a viscosity as possible.

It is known⁵ that the use of filler surface modifying agents (i.e., lubricants, dispersants, coupling agents) alters the rheological behavior of most composite systems. Use of such additives opens the possibility of reducing the viscosity level of the aggregate-binder systems and also might bring in the opportunity to use lower mixing temperatures to get the same mix quality. At the same time, a decrease in viscosity of systems due to the addition of dispersants also opens the possibility of recommending lower compaction temperatures.

The purpose of the present work is to determine the effect of some selected dispersants on the mixing of

aggregates with a polymer-modified asphalt. An attempt is made to understand how the alteration in rheological behavior can be used in either varying the mixing temperature or the compaction temperature for added benefits. Further, by determining the rheological properties at the high PG grade temperature, a comparison between the effects of the various dispersants is also made. A distinction is made between a dispersant and a lubricant by observing the rheological behavior of the systems under different conditions.

EXPERIMENTAL DETAILS

Binder

The polymer-modified asphalt chosen as a case-study binder for the present work was Novophalt. This binder was used in the Accelerated Loading Facility (ALF) experiment⁶ at the Turner-Fairbank Highway Research Center (TFHRC) of the Federal Highway Administration (FHWA).

Novophalt is manufactured by Advanced Asphalt Technologies (AAT), Sterling, VA. The base asphalt used for the ALF Novophalt is AC-10. The asphalt is mixed with a certain amount (probably about 6.5%) of low density polyethylene to result in a binder with a performance grade PG of 76-22. The mixing is done in a two-stage high shearing operation. The material is run through a high shear mixer at about 145⁰C and then fed back into the mixer and run again to get a better dispersion. The final mixed material is not stabilized and tends to separate if correct handling procedures are not followed.

Dispersants

The dispersants used in the binder were chosen from three broad categories: titanates, silanes and fatty acids. These additives are known to alter the rheological characteristics of composite systems⁵. Within each category, one representative dispersant at its optimum concentration was selected based on past knowledge and experience⁵. Isopropyl triisostearoyl titanate (KR TTS)⁷, phenyltrimethoxy silane (Z6124)⁸ and stearic acid were chosen as the three dispersants.

Design

The experimental design involved rheological characterization of the binder (with and without dispersant) and filled with 30 volume per cent of diabase to assess the mixing behavior of aggregate with binder. The experimental plan is along the lines followed by Dow et al^{9,10} and discussed in details by Shenoy⁵.

Various mixes of aggregate - binder were prepared using the following procedure. Measured quantity (97.98 gms) of binder was heated to a specified temperature for 80 minutes. At the same time, measured quantity (102.52 gms) of diabase (to make 30 volume percent mastic) was also heated to the same specified temperature for 80 minutes. The binder was removed from the oven, measured quantity of the selected dispersant was added and stirred for 1 minute at 600 rpm with a mechanical stirrer. Then diabase powder was added to it and it was further stirred for 2 minutes at 600 rpm. The mixture was then poured directly into the Brookfield viscometer for viscosity

measurements at a selected temperature of 135°C. All viscosity measurements on the Brookfield viscometer were carried out under steady shear. At each shear rate, data points were collected under steady shear condition by allowing reasonable lapse of time between each value. The same procedure was followed exactly for generating a control blank sample without aggregates. 100 gms of binder were heated to the specified temperature for 80 minutes, dispersant added, stirred for (1+2=) 3 minutes and then poured for Brookfield viscosity measurement at 135°C.

For each binder-dispersant system, three different samples were prepared using the procedures described in the above two paragraphs. In each case, only the temperature of mixing was different, namely, 150°C, 180°C and 200°C. The Brookfield viscosity data, however, was taken on all three samples at one single temperature of 135°C.

Each sample was also characterized on the Dynamic Shear Rheometer at one single temperature of 76°C, which corresponds to the high temperature of the PG value of 76-22.

Equipment Used

The Brookfield Viscometer was used for obtaining viscosity versus shear rate data. Various spindles (SC4-21, SC4-27 and SC4-34) were used for generating the data covering a reasonably wide shear rate range. A soak time of 20 minutes was prescribed for all samples. At each shear rate, a sufficient elapse of time was allowed to ensure that the data was at steady shear.

The Rheometrics Dynamic Shear Rheometer (DSR) was used for generating the dynamic data at the temperature of interest with a set of parallel plates of 25 mm diameter following the procedure given in the AASHTO provisional specifications¹¹. The samples for the test were prefabricated using a silicone rubber mold. The data were generated using a frequency sweep covering a range from 0.1 radians/s to 100 radians/s with 33 data points, using appropriate strains to maintain the generated data within the linear viscoelastic range of response.

RESULTS AND DISCUSSION

No Dispersant

Figure 1 (a) shows the variation of viscosity with shear rate at one selected temperature of 135°C when three samples of Novophalt without a dispersant were mixed with the same quantity of diabase but at different mixing temperatures. Since all the three samples in Figure 1 (a) have the same quantity of diabase in the same binder Novophalt, and the viscosity measurements are taken at the same temperature of 135°C, the curves in Figure 1 (a) should have been identical. There should have been one single curve in Figure 1 (a); however, that is not the case and this indicates that the dispersion level is not the same in each of the samples in Figure 1 (a).

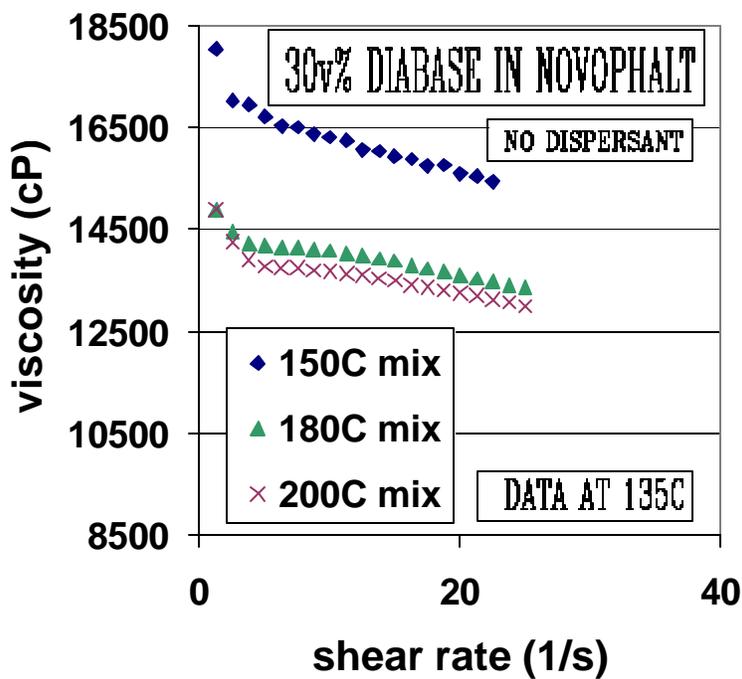
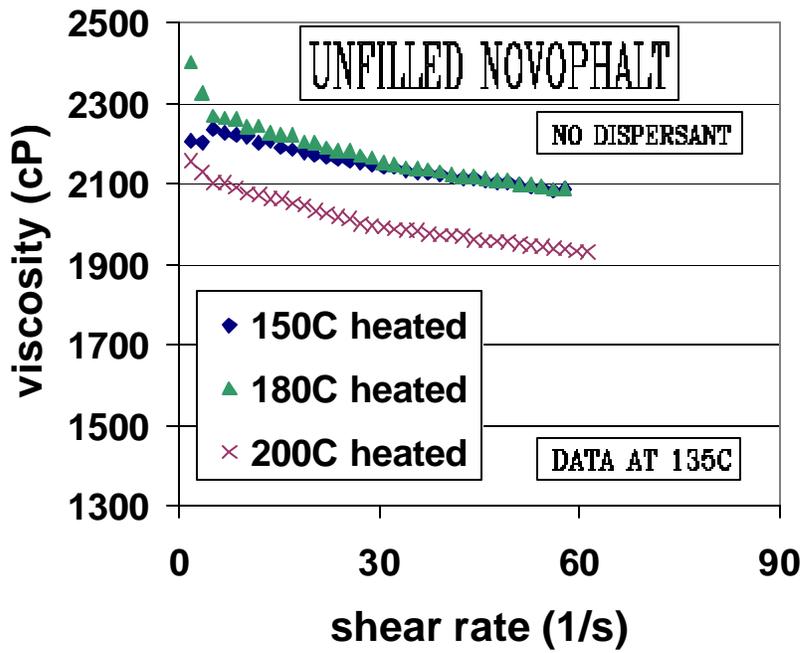


Figure 1 (a) :
 Variation of steady shear viscosity with shear rate at 135°C for Novophalt with no dispersant and mixed with 30 volume percent diabase at three different temperatures of 150°C, 180°C and 200°C.

Assessing dispersion by looking solely at the filled system data does not give the complete picture. It is important to see how the unfilled binder changes rheologically during the mixing operation. Figure 1 (b) shows the viscosity versus shear rate curves for unfilled Novophalt without a dispersant at the identical fixed temperature of 135°C, but each has seen the identical thermal and shear history as the filled binders when mixed at 150°C, 180°C and 200°C.

Figure 1 (b) : Variation of steady shear viscosity with shear rate at 135°C for unfilled Novophalt with no dispersant and heat treated at three different temperatures of 150°C, 180°C and 200°C.



In Figure 1 (b), the viscosity of the unfilled Novophalt should have been progressively increasing when heat treated at higher and higher temperatures due to binder aging. However, this is not seen to be the case. In fact, the viscosity of the unfilled Novophalt heat treated at 200°C is lower than those heat treated at 150°C and 180°C. This is because there is a competing mechanism involved. Whereas on one hand, the asphalt in the Novophalt causes an increase in viscosity due to aging, the polymer in the Novophalt, on the other hand, causes a decrease in the viscosity due to thermal and mechanical degradation. These competing factors become more obvious at the higher temperatures. When the effects of asphalt aging and polymer degradation are comparable, the viscosities of the material heat treated at two different temperatures can be nearly identical as is the case at 150°C and 180°C in Figure 1 (b).

When discussing filled system data, the above discussed factors must be taken into consideration. Simply by observing the filled system data as shown in Figure 1 (a) does not give the entire information. Actually, it is the relative viscosity data that should be analyzed so that the effect of the matrix in the filled system is eliminated. This then gives a better representation of the dispersion level of the aggregates in the mix. Figure 1 (c) shows the relative viscosity obtained by taking the ratio of the viscosity of the filled binder to the unfilled binder at a shear rate of 20 sec⁻¹ and 135°C. For Novophalt without a dispersant, it can be seen from Figure 1 (c) that the relative viscosity goes through a minimum at around 180°C. Thus, in order to maintain good quality of mixing, it would be important to keep the mixing temperature to a level around 180°C when dealing with Novophalt without a dispersant.

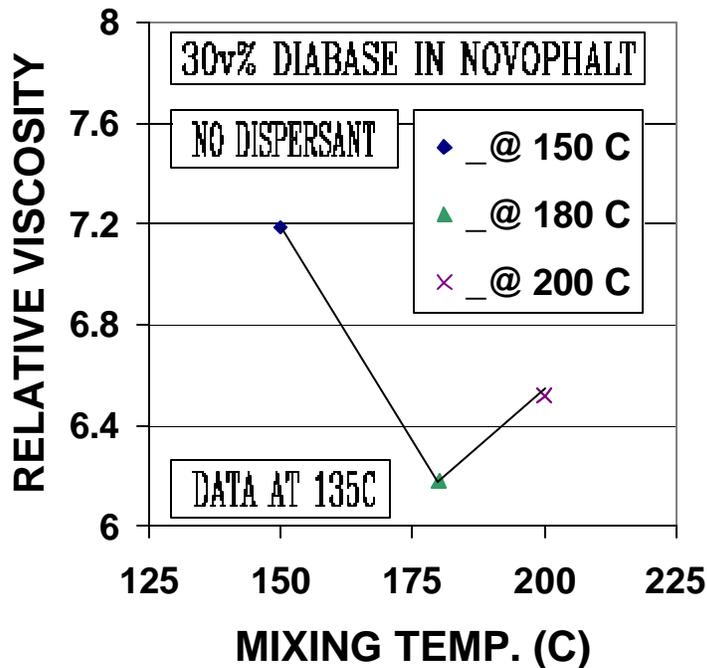


Figure 1 (c): Variation of the ratio of viscosity (with and without filler at a shear rate of 20 sec^{-1} and 135°C) versus mixing temperature for Novophalt with no dispersant that is mixed with 30 volume percent diabase at three different temperatures of 150°C , 180°C and 200°C .

Titanate KRTTS

Figure 2 (a) shows the variation of viscosity with shear rate at one selected temperature of 135°C when three samples of Novophalt with titanate KRTTS were mixed with the same quantity of diabase but at different mixing temperatures. The dispersion level is not the same in each of the samples in Figure 2 (a) as three different curves were obtained for the three mixing temperatures. The three curves obtained are also not the same as those in Figure 1(a). The presence of titanate KRTTS has effectively changed the viscosity levels of each of the samples. The major drop in viscosity due to the addition of the titanate KRTTS is seen to occur at the mixing temperature of 150°C . At the other two temperatures, the viscosity reductions are not so drastic.

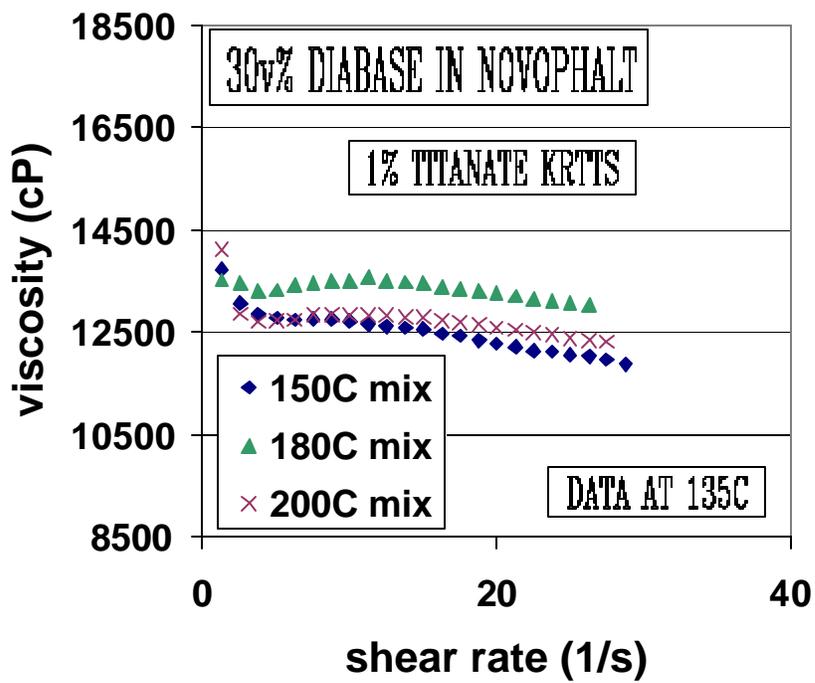


Figure 2 (a) :
 Variation of steady shear viscosity with shear rate at 135°C for Novophalt with titanate KR TTS and mixed with 30 volume percent diabase at three different temperatures of 150°C, 180°C and 200°C.

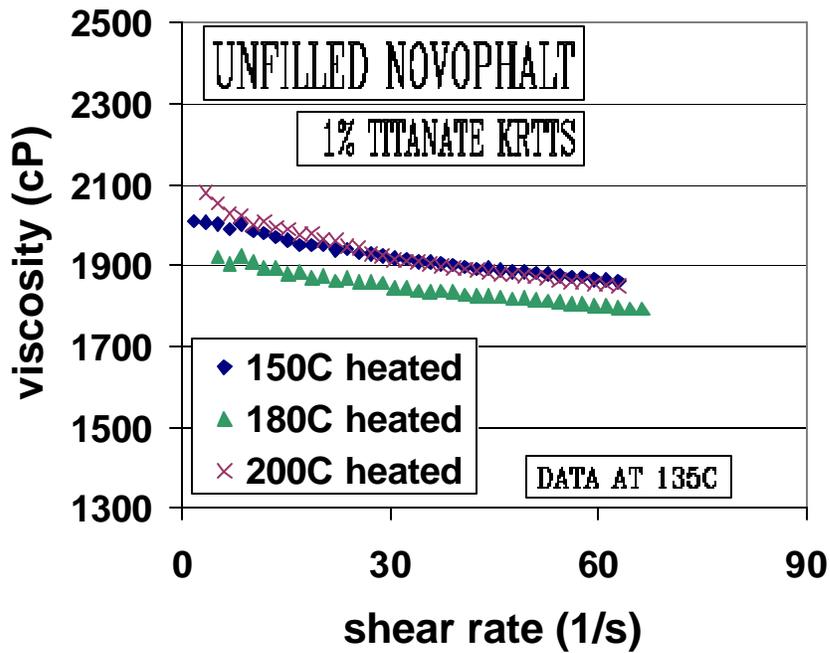


Figure 2 (b) :
 Variation of steady shear viscosity with shear rate at 135°C for unfilled Novophalt with titanate KR TTS and heat treated at three different temperatures of 150°C, 180°C and 200°C.

In the case of unfilled Novophalt with titanate KRTTS, it is seen from Figure 2 (b) that addition of the dispersant results in viscosity reduction. The effect of the dispersant is the least at the temperature of 200°C as can be seen by comparing Figures 1 (b) and 2 (b).

In Figure 2 (c), it can be seen that the relative viscosity goes through a maximum at around 180°C. This is in direct contrast to the behavior observed without the addition of a dispersant as shown in Figure 1 (c). The minimum relative viscosity value of 6.19 that occurred at a mixing temperature of 180°C in Figure 1 (c) is approximately equal to the relative viscosity value of 6.29 that is attained at a temperature of 150°C in the presence of titanate KRTTS. This implies that by addition of the dispersant KRTTS, it should be possible to lower the mixing temperature from 180°C to 150°C and yet achieve the same level of dispersion. Adjudging the level of dispersion through the relative viscosity values between a system with a dispersant and one without a dispersant may not always be appropriate. This is because the dispersant often reacts with the surface of the particles and this leads to a higher resistance to deformation. Thus, while lower agglomeration leads to lower viscosity, a reaction with the particles of the system gives rise to higher viscosity. The net effect may be a greater relative viscosity and yet be a better dispersed system. Hence, it becomes necessary to support the relative viscosity information with other rheological data before a more definitive conclusion is drawn, as done in a later section.

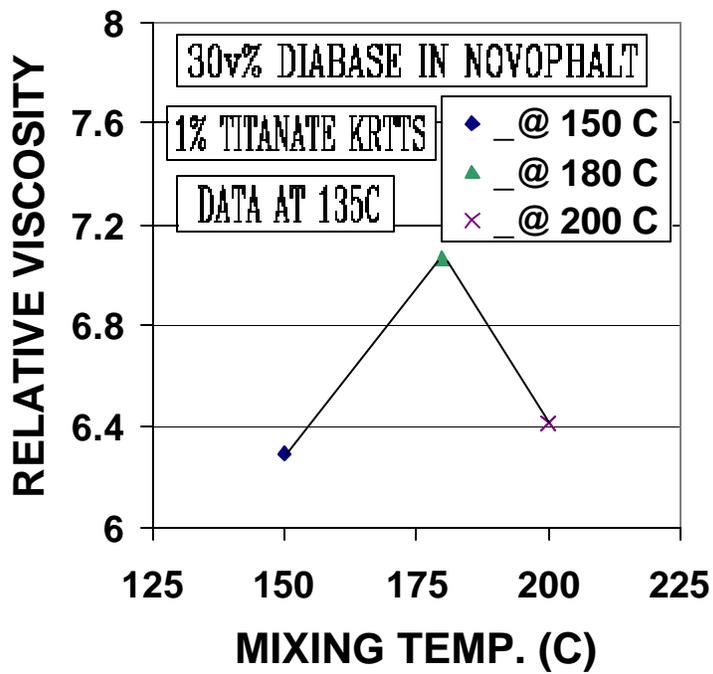


Figure 2 (c): Variation of the ratio of viscosity (with and without filler at a shear rate of 20 sec^{-1} and 135°C) versus mixing temperature for Novophalt with titanate KR TTS that is mixed with 30 volume percent diabase at three different temperatures of 150°C , 180°C and 200°C .

Silane Z6124

Figure 3 (a) shows the viscosity versus shear rate behavior at one selected temperature of 135°C when three samples of Novophalt with silane Z6124 were mixed with the same quantity of diabase but at different mixing temperatures. The three different curves in Figure 3 (a) imply that the dispersion level is not the same at the three mixing temperatures. The three curves obtained are different from those obtained in Figures 1 (a) and 2 (a). In fact, silane Z6124 performs better in reducing the viscosity levels in comparison to titanate KRTTS. Though the curve for 180°C mix is the lowest of the three in Figure 3 (a), the major drop in viscosity due to the addition of the silane Z6124 is seen to occur at the mixing temperature of 150°C.

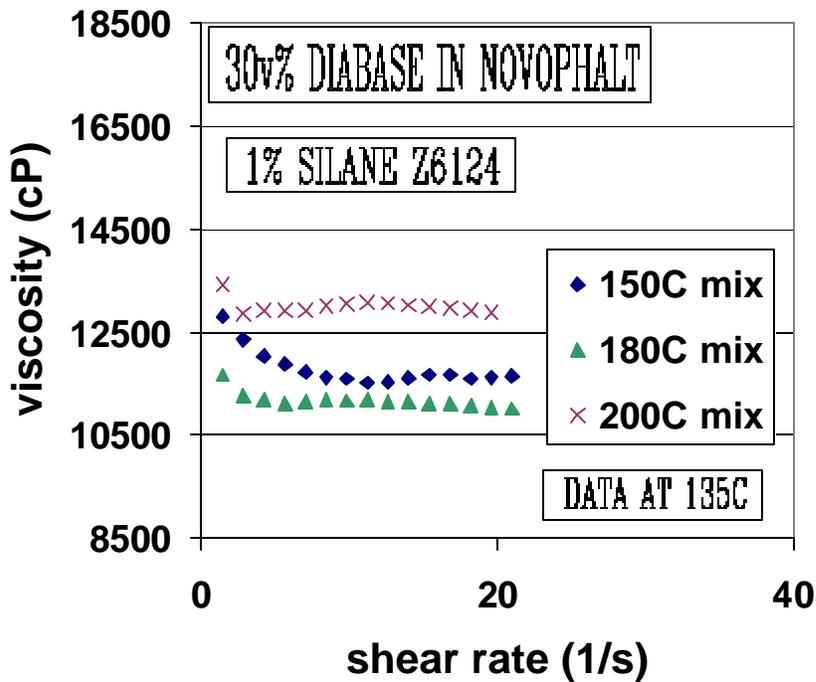


Figure 3 (a) :
Variation of steady shear viscosity with shear rate at 135°C for Novophalt with silane Z6124 and mixed with 30 volume percent diabase at three different temperatures of 150°C, 180°C and 200°C.

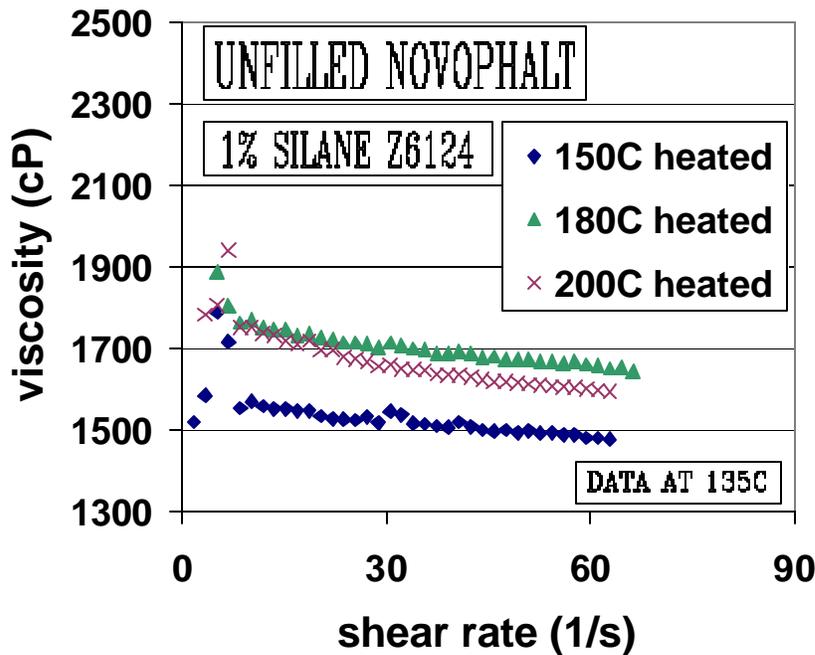


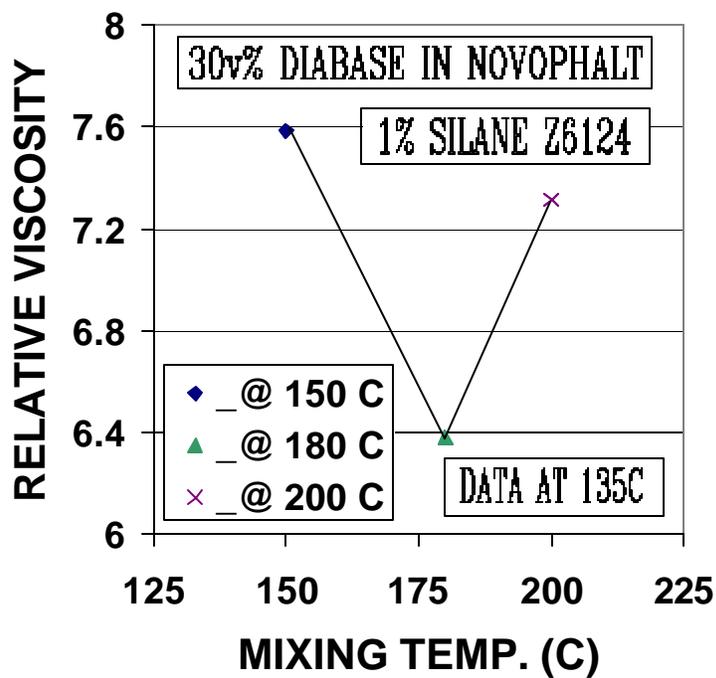
Figure 3 (b) :
Variation of steady shear viscosity with shear rate at 135°C for unfilled Novophalt with silane Z6124 and heat treated at three different temperatures of 150°C, 180°C and 200°C.

From Figure 3 (b), it is seen that addition of the

silane Z6124 results in viscosity reduction even in the case of unfilled Novophalt at all temperatures. The maximum reduction in viscosity occurs at the temperature of 150°C as can be seen by comparing Figures 1 (b) and 3 (b).

Figure 3 (c) shows that the relative viscosity goes through a minimum at around 180°C. This is similar to the behavior depicted in Figure 1 (c) for systems with dispersants but different from that shown in Figure 2 (c) for systems with titanate KRTTS. This implies that the mixing temperature selection does not change with the addition of the silane Z6124. The minimum relative viscosity value of 6.38 that occurs at a mixing temperature of 180°C in Figure 3 (c) is slightly higher than the relative viscosity value of 6.19 that is attained at a temperature of 180°C in Figure 1 (c) without a dispersant. This implies that one of the two possibilities is occurring - either (a) the level of dispersion is not truly improved by the presence of the silane Z6124, or (b) the dispersion is improved and the chemical reaction between the silane and the diabase leads to an increase in the resistance to deformation as exemplified by the higher relative viscosity. In any case, the mixing temperature choice cannot be changed. On the other hand, the lower values of the absolute viscosities in Figure 3 (a) generate the possibility of reducing the compaction temperature through the use of silane Z6124.

Figure 3 (c): Variation of the ratio of viscosity (with and without filler at a shear rate of 20 sec^{-1} and 135°C) versus mixing temperature for Novophalt with silane Z6124 that is mixed with 30 volume percent diabase at three different temperatures of 150°C , 180°C and 200°C .



Stearic Acid

Figure 4 (a) shows the variation of viscosity with shear rate at one selected temperature of 135°C when three samples of Novophalt with stearic acid were mixed with the same quantity of diabase but at different mixing temperatures. The presence of stearic acid is seen to drastically change the viscosity levels of each of the samples.

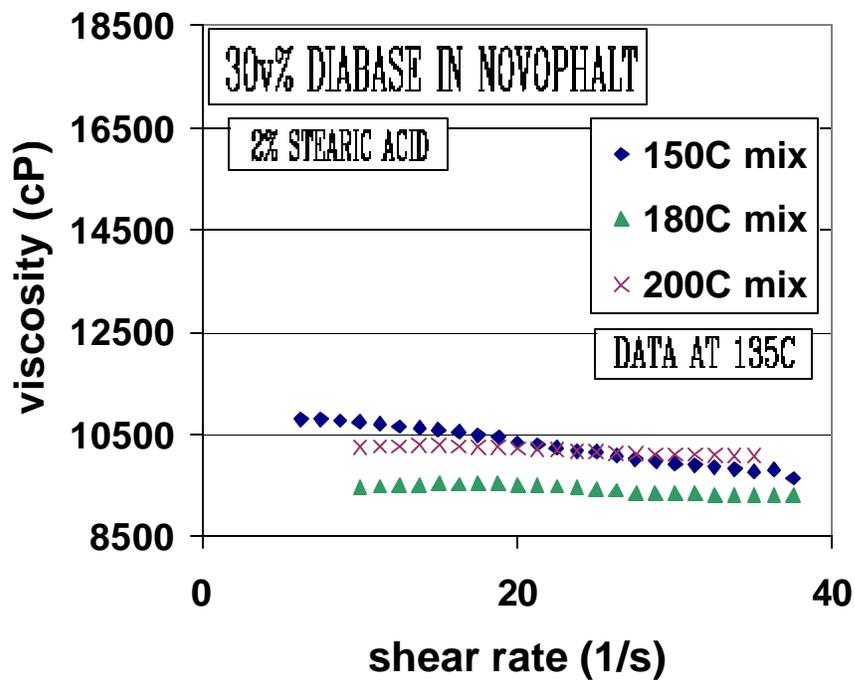


Figure 4 (a): Variation of steady shear viscosity with shear rate at 135°C for Novophalt with stearic acid and mixed with 30 volume percent diabase at three different temperatures of 150°C, 180°C and 200°C.

In the case of unfilled Novophalt with stearic acid, it is seen from Figure 4 (b) that addition of the dispersant results in drastic viscosity reduction.

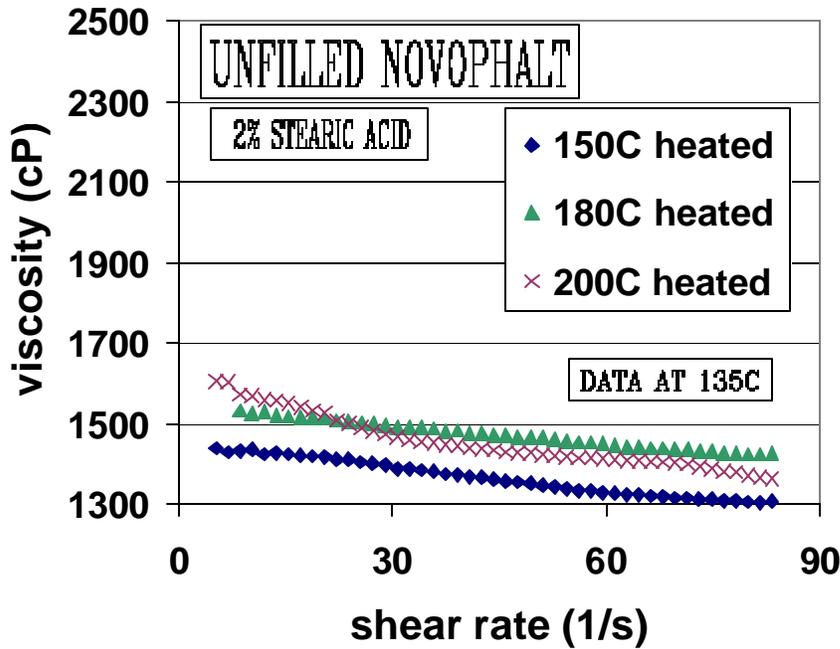
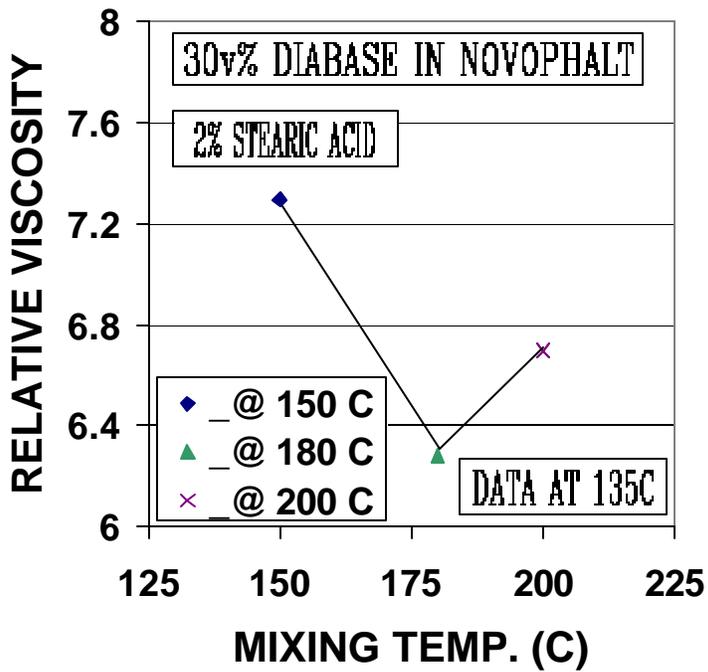


Figure 4 (b) : Variation of steady shear viscosity with shear rate at 135°C for unfilled Novophalt with stearic acid and heat treated at three different temperatures of 150°C, 180°C and 200°C.

Figure 4 (c) shows that the

relative viscosity goes through a minimum at around 180°C. The minimum relative viscosity value of 6.28 that occurred at a mixing temperature of 180°C in Figure 4 (c) for Novophalt with stearic acid is close to the value of 6.19 that was obtained for Novophalt without the dispersant as shown in Figure 1 (c). This probably implies that the dispersion level may not be too different in the presence of stearic acid as compared to the system without the dispersant. However, such a conclusion cannot be asserted with authority unless other rheological information is used to support the idea. This is done in the next section. For the moment, at least, it will have to be assumed that the mixing temperature for the system with stearic acid may be taken as the same as the one without a dispersant. But, on the other hand, since the absolute viscosity values are drastically different in Figures 1 (a) and 4 (a), there is a definite advantage in compaction as it leads to the possibility of significantly reducing the compaction temperatures.

Figure 4 (c): Variation of the ratio of viscosity (with and without filler at a shear rate of 20 sec^{-1} and 135°C) versus mixing temperature for Novophalt with stearic acid that is mixed with 30 volume percent diabase at three different temperatures of 150°C , 180°C and 200°C .



Comparison of All Dispersants

Figure 5 (a) shows the effects of the different dispersants for comparison purposes. In all cases, the variation of viscosity with shear rate is shown at one selected temperature of 135°C and the samples of Novophalt with different dispersants are mixed with the same quantity of diabase at same mixing temperatures of 180°C. The titanate KRTTS has the least effect on the viscosity reduction while stearic acid has the greatest effect and silane Z6124 lies in the middle. An identical trend is seen when the unfilled systems are considered as shown in Figure 5 (b).

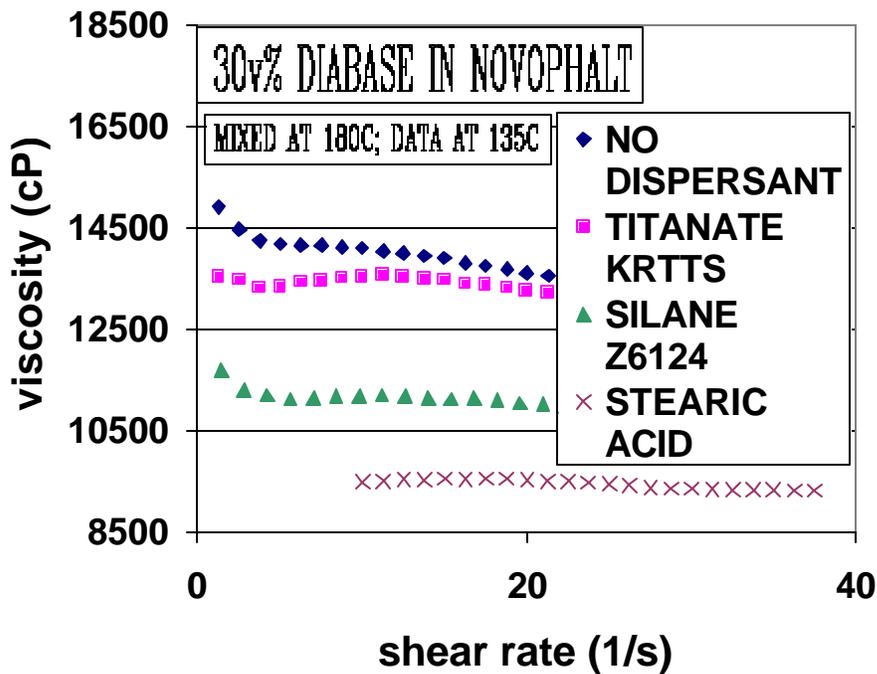


Figure 5 (a) :
Variation of steady shear viscosity with shear rate at 135°C for Novophalt with and without different dispersants, and mixed with 30 volume percent diabase at the temperature of 180°C.

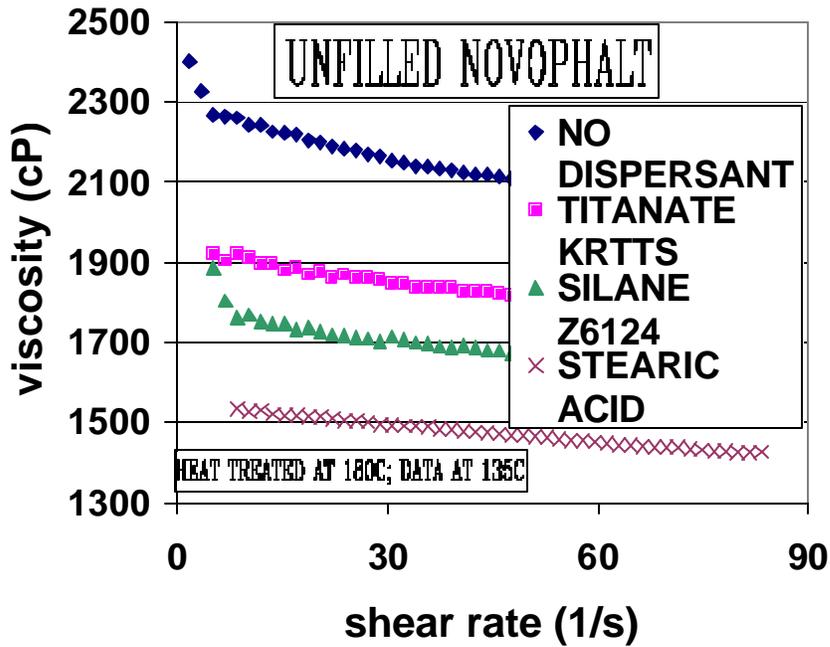


Figure 5 (b) :

Variation of steady shear viscosity with shear rate at 135°C for unfilled Novophalt with and without different dispersants, and heat treated at the temperature of 180°C.

It is important to find out whether addition of the dispersants affects the rheological properties at the PG temperature which

in the case of neat unfilled Novophalt is 76°C as it is slated to be a PG 76-22. The effect of various dispersants on the dynamic complex modulus is shown in Figure 5 (c). It is seen that addition of titanate KRTTS and silane Z6124 both lower the $|G^*|$ values at all frequencies. The presence of stearic acid, however, shows a different trend. At lower end of the frequency range, namely, from 0.1 - 10 radians/sec, it is seen that the curve for the system with stearic acid in Figure 5 (c) does not follow the line shown by the other two dispersants, though at the higher frequency range from 10-100 radians/sec it does.

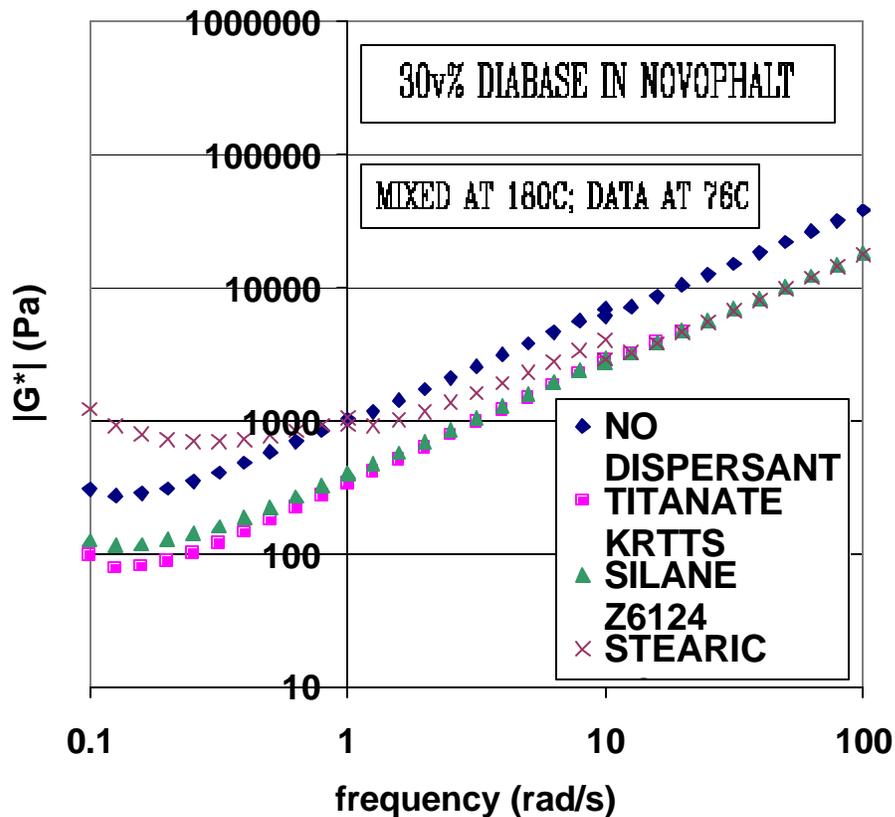


Figure 5 (c) : Variation of dynamic complex modulus with frequency at 76°C for Novophalt with and without different dispersants, and mixed with 30 volume percent diabase at the temperature of 180°C.

The system with stearic acid shows a yield value of the dynamic complex modulus and the variation of $|G^*|$ with frequency is considerably reduced. This implies that when the mastic is cooled from a high temperature of 135°C (temperature of Brookfield viscosity measurement) to the lower temperature of 76°C (temperature of DSR measurement), the diabase particles agglomerate, thus indicating that stearic acid acts more like a lubricant than a dispersant. A true dispersant helps to break up agglomerates and prevents their reformation. The lubricant on the other hand, only facilitates the movement of the particles around each other thereby decreasing the resistance to deformation. The effect of a dispersant as well as a lubricant is to show a reduction in viscosity. But the dispersant retains the lower viscosity behavior under most conditions of deformation, while the lubricant does not. Thus, in the present work, stearic acid is cast as a lubricant based on its rheological behavior while titanate KRTTS and

silane Z6124 are both categorized as dispersants. The advantage of adding titanate KRTTS and silane Z6124 to Novophalt would result in more uniform properties since the aggregates will be better dispersed and there would be less likelihood of finding areas which would have agglomerated regions of aggregates with much higher stiffness accompanied by other areas which are lean in aggregates and low stiffness. The advantage of stearic acid would distinctly be in getting to lower compaction temperatures and probably resulting in pavements which have better resistance to slow traffics due to the yield modulus behavior at lower frequency.

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