

EFFECTS OF CARBOXYLIC ACIDS ON THE RHEOLOGICAL PROPERTIES OF CRUMB RUBBER MODIFIED ASPHALT

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ABSTRACT

The Federal mandate of 1991-1995 on the use of scrap tires in Federal roadway construction sparked a major interest in gaining a fundamental understanding of the behavior of rubber in asphalt. This study is a systematic elucidation of what chemistry controls the final crumb rubber modified asphalt (CRMA) product quality. We discovered that the type and total acid content in the asphalt are the most influential chemical factors that determine the changes in the important roadway properties of shear modulus (G^*) and loss angle (δ) of CRMA. Low acid (<0.005 mL) asphalts were modified with three types of carboxylic acid and each made into CRMA using typical field mixing conditions of 1 hour at 175°C. Rheological measurements were then made at various storage times up to 192 hours following storage at both 156 and 200°C. We found the changes in CRMA rheological properties correspond to the acid type spiked into the asphalt.

INTRODUCTION

In December 1991 the Intermodal Surface Transportation Efficiency Act (ISTEA) mandated the use of large amounts of rubber from scrap tires in Federally funded roadway construction. In 1995 this mandate was removed but in the time between 1991 and 1995 the mandate sparked much interest in gaining a better understanding of the use of rubber tire material in roadways. Some successful use of tire rubber had been demonstrated for up to twenty years before the mandate in the states of Arizona, California, and Florida. These three states had experimented with the use of finely ground rubber (crumb rubber) mixed with asphalt to make asphalt concrete. Upon examination of their successful uses of this crumb rubber modifier (CRM) to make crumb rubber modified asphalt (CRMA), it became obvious that each state gained a good understanding of the material properties of the CRMA and further employed good engineering design and construction practices in using CRMA to build roads. To a lesser degree, it became obvious that CRMA used in Florida was substantially different from that used in California. This suggested that there were unrecognized differences in materials used by the two states. An attempt was made to trace the sources of CRM and asphalt crude oil sources used by each state. What became apparent quickly was that both Florida and California used consistent supplies of asphalt in their respective states, but that the asphalt crude sources used in the two states were very different from each other. The California DOT reported the asphalt binder behaved somewhat like a mineral filled asphalt. On the other hand, the Florida DOT reported building with a homogeneous material which suggested that the CRM had dissolved, or digested into the asphalt. The experiences with CRMA related above strongly suggested to us that some unique set of CRMA properties can be expected and can be related back to the crude oil source used to produce each asphalt.

To control the rheological properties of crumb rubber-asphalt mixtures, an understanding of the chemistry involved in the CR-asphalt interaction is necessary. We began our study with a systematic analysis of the variables involved in this interaction, i.e., asphalt type, CR type, mixing time and temperature, and particle size and concentration

BACKGROUND

In previous experiments we found CRMs do not swell significantly in whole asphalt at temperatures of 200°C and times up to 1000 hours, but we found a portion of the crumb rubber (CR) appears to dissolve which leads to changes in the rheology of the CRMA. The rheological changes are different among various asphalts and greater than the effect imparted by Teflon of the same particle size. These changes in rheological properties led to an investigation into what component(s) of the asphalt is (are) interacting with the CR. In order to determine the component(s) involved, asphalts from different crude sources were used in mix experiments. The CRMAs were prepared using standard blending procedures (blended for one hour at 175°C) then tested and stored at 200°C. The CRMAs were checked visually and microscopically each day for changes in the CR. Several of the asphalts had no apparent effect on the CR, however one asphalt had a dramatic effect on CR appearance. After five days at 200°C this mixture had the appearance of a neat asphalt (i.e., very smooth and shiny). We repeated the experiment with this particular asphalt, Strategic Highway Research Program (SHRP) asphalt ABD-1, with the same results. This asphalt has a lime treated counterpart (SHRP AAG-1) which had been tested earlier with no apparent interaction with the CR. Lime is added to this asphalt

to neutralize its high carboxylic acid content. It then seemed logical that carboxylic acid had something to do with the dissolution of the CR. The experiment was repeated with another high acid asphalt, SHRP AAK-2, with the same results (i.e., the CR dissolved). We then removed the acid fraction from the ABD-1, using ion exchange chromatography, and added it to a low acid asphalt, SHRP AAM-1. Asphalt AAM-1 had also been used in the earlier experiment with no dissolution. Crumb rubber was mixed with both samples and stored for several days at 200°C. After several days the acid free ABD-1-CR mixture showed no signs of interaction, crumb particles were still visible in the mixture. However the acid modified AAM-1-CR mixture had the appearance of a neat asphalt. We now had enough evidence of the involvement of carboxylic acid as the active component or a marker of the active component to begin a series of controlled acid doping experiments.

EXPERIMENTAL

The experimental procedure involves the doping of two low acid asphalts, AAB-1 and AAM-1 with various carboxylic acids (9-anthracene carboxylic acid, stearic acid and cholic acid) at 0.01, 0.02 and 0.03 weight percent. The acid was mixed with asphalt by mechanical stirring at 175°C. The acid-doped asphalts were then mixed using a low shear mixer for one hour at 175°C with U.S. Standard #40 mesh (420µm) CRM and U.S. Standard #40 mesh natural tire rubber (NR). Rheological measurements were taken immediately after mixing. Suitable control samples were prepared and rheological measurements were taken for comparison to the CRMA. The remainder of the CRMAs and control samples were then split. Half of the samples were stored at 156°C for up to 192 hours and the other half at 200°C for up to 192 hours. This experiment is still in progress, but the work to date is presented here. All samples were analyzed using an Rheometrics RDA II rheometer, operated in strain control mode.

RESULTS

Figures 1 through 10 show the results of the acid doping experiments for asphalt AAB-1. The time sequence for all of the data points in the figures, except for figures 3 and 4, are not shown; the data are plotted versus the loss angle or G' . Figures 1 and 5 show the shear modulus and the loss angle data taken at 60° and 25°C for samples stored at 156°C. Figures 2 and 6 show the storage and loss moduli data taken at 60° and 25°C for samples stored at 156°C. Figures 3 and 4 show the storage and loss moduli for CR4-9-anthracene carboxylic acid doped AAB-1 and CR4-AAB-1, and CR4-stearic acid doped AAB-1 and CR4-AAB-1 stored at 156°C and measured at 60°C, respectively. In these figures the storage times of the data points are noted. Figures 7 and 9 show the shear modulus and the loss angle data taken at 60° and 25°C for samples stored at 200°C. Figures 8 and 10 show the storage and loss moduli data taken at 60° and 25°C for samples stored at 200°C.

DISCUSSION

Asphalts are viscoelastic fluids and are evaluated using dynamic mechanical analyzers (DMA). When analyzing asphalts the DMA is run in an oscillatory mode which supplies a periodic deformation at a given frequency, ω . The DMA can calculate several material constants including the magnitude of complex shear modulus, loss angle, storage modulus, and loss modulus. The complex shear modulus, $G^*(\omega)$, is a complex function of frequency, as shown in equation (1),

$$G^*(\omega) = \frac{\sigma_0}{\epsilon_0} e^{i\delta} = G' + iG'' \quad (1)$$

where δ is the loss angle at a given frequency, σ_0 is the stress amplitude at a given frequency, and ϵ_0 is the strain amplitude at a given frequency. The loss or phase angle, δ , is a function of the internal friction of the material. For a viscous material the loss angle would be 90° and for an elastic material the loss angle would be 0°. The magnitude of $G^*(\omega)$ is found using equation (2).

$$|G^*(\omega)| = G^* = \sqrt{G'^2 + G''^2} \quad (2)$$

The storage modulus, G' , is the real part of the complex shear modulus and is associated with the storage and loss of energy during the periodic deformation (recoverable deformation). The loss modulus, G'' , represents the imaginary part of the complex shear modulus and is associated with the dissipation of energy and its transformation into heat (permanent deformation). G' and G'' can be found using equations (3) and (4).

$$G' = G^* \cos \delta \quad (3)$$

$$G'' = G^* \sin \delta \quad (4)$$

It is obvious from the figures that not only are the acids involved in the interaction of asphalt with CRM, but the type of acid is very important in the interaction. Figure 1 shows G^* and δ for AAB-1, acid doped AAB-1, CR4-AAB-1 and CR4-acid doped AAB-1. The samples were stored at 156°C and measurements were taken at 60°C. The data here represent all storage times up to and including the 192 hour. Neat asphalt AAB-1 and acid doped AAB-1 are grouped together in the lower right corner

of the figure. This indicates that the acid doping of AAB-1 has not changed G^* and δ (at 60°C) by any significant amount. The next group of data points are found higher up on the right side of the figure. Each of the data points in this set represents a CR4 mixture, measured immediately after the one hour mix time. A significant increase in G^* due to the addition of the CR4 is observed. The loss angle has gone from -89° to -86° for CR4-AAB-1 (CR4) and to -85° for the CR4-9-anthracene carboxylic acid doped AAB-1 (A), but G^* has increased from 128 Pa to 702 Pa and 1150 Pa, respectively. From Equation (2) it can be seen that this increase in G^* must be accompanied by an increase in G' and/or G'' . Figure 2 shows G' and G'' for these samples. Again the AAB-1 and acid doped AAB-1 are grouped together in the lower left corner. The one hour CR4 mixtures data start in the lower right of the figure and are above the majority of points running from left to right. The CR4-9-anthracene carboxylic acid doped AAB-1 (A) has the largest increase in both G' and G'' , compared to the other CR4 mixtures. The CR4-stearic acid AAB-1 (S) shows the least change in rheological properties, while the CR4-cholic acid AAB-1 (C) is very close to the CR4-AAB-1 (CR4). The data points for the longer storage times run from -82° loss angle to -74° loss angle in figure 1 and from G'' of 300 Pa to -1700 Pa in figure 2. This main stream of data points include the 24 hour to 192 hour storage times. It is important to note that the rheology undergoes the greatest change between the one and 24 hour time period for all CR mixtures. Figure 1 shows that the 24 hour through the 192 hour samples group according to acid type. The CR4-9-anthracene carboxylic acid data is found in the upper left hand side of the figure, the CR4-AAB-1 and CR4-cholic acid AAB-1 are in the next group and finally the CR4-stearic acid AAB-1. Figures 3 and 4 show selected data from figure 2 and the storage times are noted on the data points. In figure 3 we see the data for CR4-9-anthracene carboxylic acid doped AAB-1 and CR4-AAB-1. The CR4-9-anthracene carboxylic acid doped AAB-1 has substantially higher G' 's and G'' 's. The addition of 9-anthracene carboxylic acid to AAB-1 has improved the rheological properties in terms of high (60°C) temperature flow. It is believed that somehow the 9-anthracene carboxylic acid is preventing or favorably controlling the dissolution of the CR. The mechanism involved in this process is not yet understood. Stearic acid, however (figure 4) has the opposite effect. It appears to increase the dissolution of the CR, leading to a degradation of high temperature properties when compared to CR4-AAB-1. Stearic acid is used in rubber production as a processing aid and an accelerant and may accelerate the dissolution of rubber in asphalt. Also, it is important to note that the improvement in properties is time dependent. Each reaches a maximum value of G' and G'' at a different storage time. The CR4-AAB-1 reaches the maximum G' and G'' at 24 hours and then begins to decline. CR4-9-anthracene carboxylic acid doped AAB-1 reaches its maximum at 96 hours, while the CR4-stearic acid doped AAB-1 reaches its maximum values at 24 hours.

The data pattern in figures 5 and 6 are similar to that in figures 1 and 2, though the AAB-1 and acid doped AAB-1 data points show a slight change rheological properties (figure 6). The effect of the acid type is quite apparent from the data in all of the figures. In figure 1, CR4-stearic acid doped AAB-1 samples show less of a change in G^* and δ than the CR4-AAB-1 samples for all storage times. Figures 7 through 10 show comparable data for samples stored at 200°C with the addition of natural rubber AAB-1 mixtures (NR). In these figures the contrast between the one hour sample (G^* 's -480 Pa to 1150 Pa) and the 24 through 192 hour samples (G^* 's under 400 Pa) is quite dramatic. Also the loss angles in figure 5 are higher than those in figure 1. After 24 hours at 200°C, the increase in G' and G'' due to the addition of CR4 has been negated by the increased dissolution of the CR4. The G'' has decreased from 1150 Pa for CR4-9-anthracene carboxylic acid doped AAB-1 to 189 Pa, and G' from 105 Pa to 19 Pa. Figures 7 and 8 show the data for the samples stored at 200°C and measures at 25°C. The data show that NR-AAB-1 has properties similar to the acid doped AAB-1, and the effect of the rubber is minor after 24 hours. In previous studies it was found that the natural rubber dissolved in all asphalts tested within a few hours of mixing. The data points at a loss angle of $70^\circ+$ are those for the long storage time.

CONCLUSIONS

The addition of carboxylic acids to asphalt AAB-1 produces varying amounts of rheological change in the crumb rubber mix. The interaction is acid type and temperature dependant. The rheological changes occur at a fairly low temperatures in asphalts (typically mixed at 165° to 175° C) in a relatively short time. This is similar to the mixing conditions commonly employed at a CRMA road construction site. At higher temperatures, the interaction proceeds more rapidly. The effect of carboxylic acid type is fairly pronounced. The improvement in high temperature properties for the CR4-9-anthracene carboxylic acid doped AAB-1 is striking, while the CR4 stearic acid doped AAB-1 exhibits a decrease in rheologic properties. The cholic acid added to AAB-1 appears to have almost no effect on the rheology of the CRMA. Each asphalt contains varying types and amounts of naturally occurring carboxylic acids; therefore each crumb rubber mixture will have different properties based on the asphalt composition. The most important aspect for CRMA in roadways may be the fact that the CRMA undergoes a dramatic change in rheologic properties within 24 hours of mixing the CRM and asphalt. It is during this time period that the CRMA is combined with aggregate and the pavement is laid. If the CRMA is graded immediately after mixing, then by the time it is

mixed with aggregate the properties will have changed. It is not until 48, or in some cases 72 hours, after mix that the rheological properties appear to stabilize (figures 1 through 4).

The addition of crumb rubber to asphalt poses many challenges to the paving industry. Only by understanding the chemistry of these systems will we be able to predict the rheological properties of the CRMA.

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Key for figures: Neat→AAB-1, A→9-anthracene carboxylic acid modified AAB-1, S→stearic acid modified AAB-1, C→cholic acid modified AAB-1, CR4→AAB-1 and CR4, A-CR4→9-anthracene carboxylic acid modified AAB-1 and CR4, S-CR4→stearic acid modified AAB-1 and CR4, C-CR4→cholic acid modified AAB-1 and CR4 and NR→AAB-1 and natural rubber.

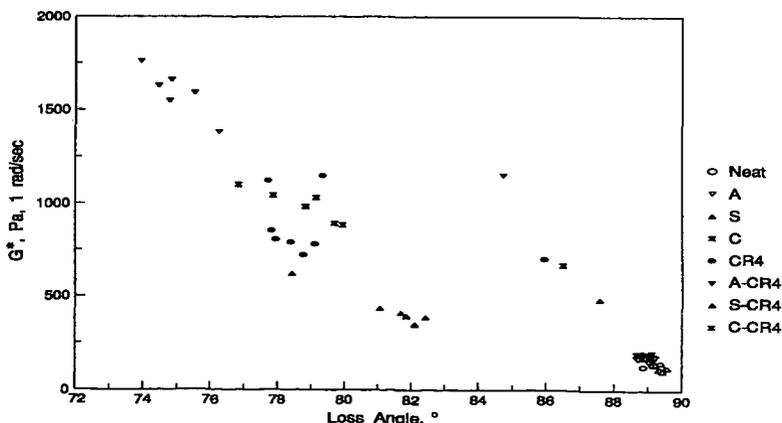


Figure 1. Shear modulus and loss angle of asphalt AAB-1, acid doped AAB-1, and CR mixtures at 60°C and storage temperature of 156°C.

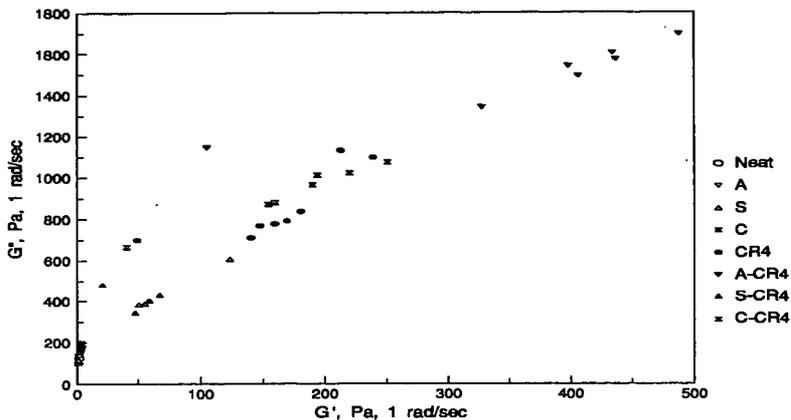


Figure 2. Storage and loss moduli of asphalt AAB-1, acid doped AAB-1 and CR mixtures at 60°C and storage temperature of 156°C.

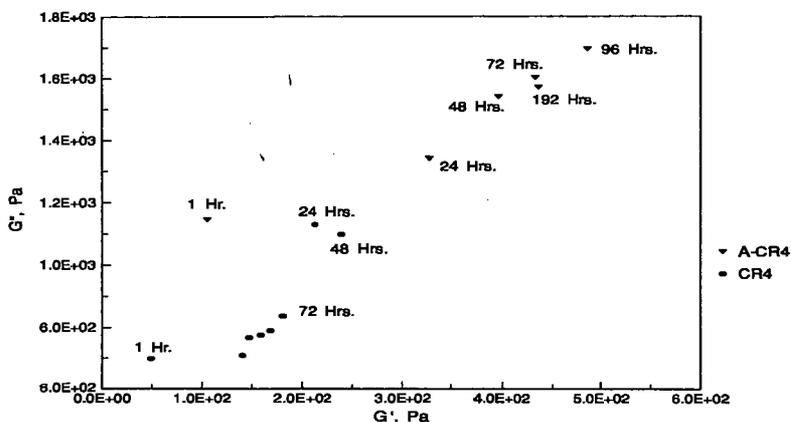


Figure 3. Storage and loss moduli for CR4 9-anthracene carboxylic acid doped AAB-1 and CR4 AAB-1 at 60°C and storage temperature of 156°C.

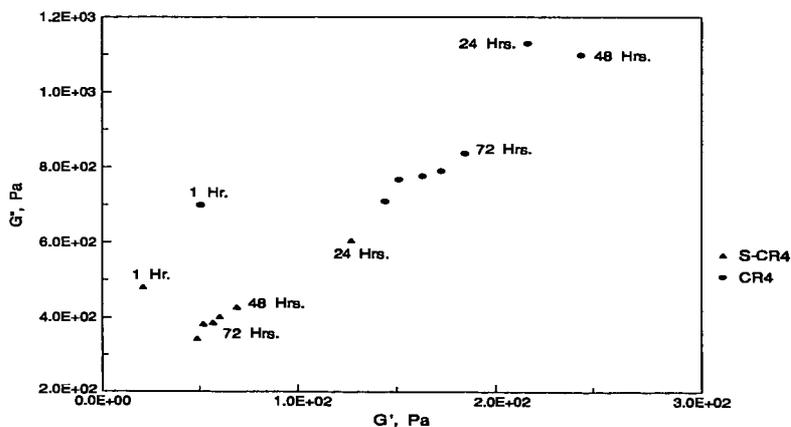


Figure 4. Storage and loss moduli for CR4 stearic acid doped AAB-1 and CR4 AAB-1 at 60°C and storage of 156°C.

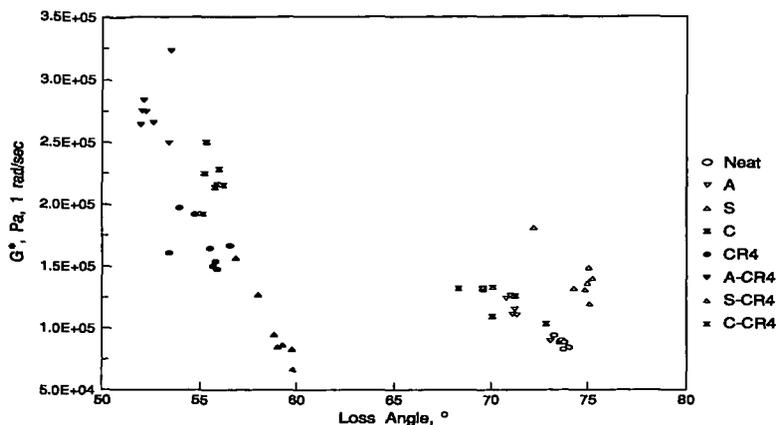


Figure 5. Shear modulus and loss angle of asphalt AAB-1, acid doped AAB-1 and CR mixtures at 25°C and storage temperature of 156°C

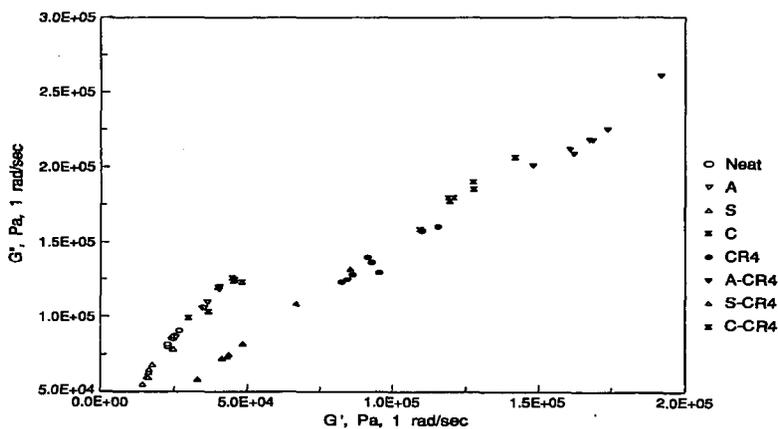


Figure 6. Storage and loss moduli of asphalt AAB-1, acid doped AAB-1 and CR mixtures at 25°C and storage temperature of 156°C.

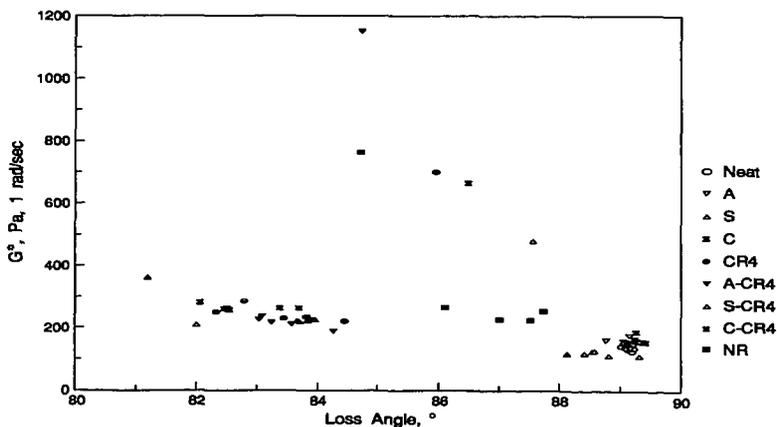


Figure 7. Shear modulus and loss angle of asphalt AAB-1, acid doped AAB-1 and CR mixtures at 60°C and storage temperature of 200°C.

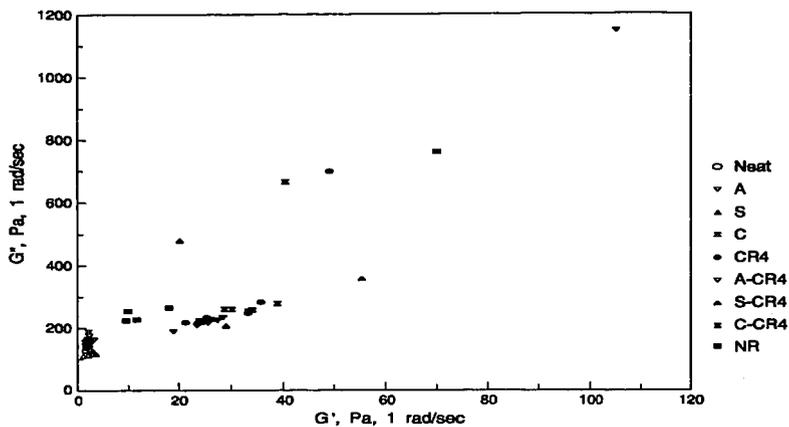


Figure 8. Storage and loss moduli of asphalt AAB-1, acid doped AAB-1 and CR mixtures at 60°C and storage temperature of 200°C.

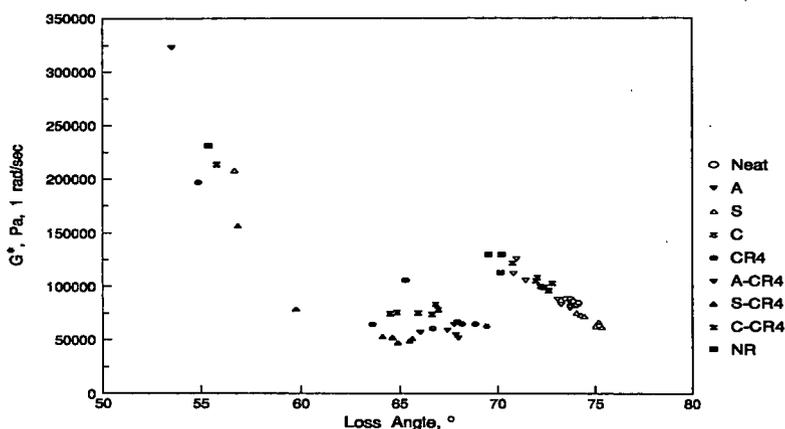


Figure 9. Shear modulus and loss angle of asphalt AAB-1, acid doped AAB-1 and CR mixtures at 25°C and storage temperature of 200°C.

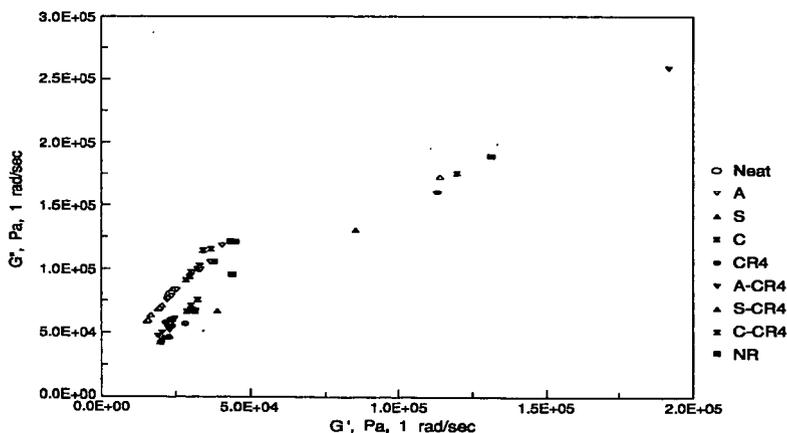


Figure 10. Storage and loss moduli of asphalt AAB-1, acid doped AAB-1 and CR mixtures at 25°C and storage temperature of 200°C.