

## EFFECT OF AGGREGATE MODIFICATION BY ORGANOSILANE COUPLING AGENTS ON THE ADSORPTION BEHAVIOR OF ASPHALT MODELS AND ASPHALT

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### ABSTRACT

The effect of modifying aggregate surfaces by organosilane coupling agents on the adsorption and desorption behavior of asphalt models and asphalt was investigated. The organosilane coupling agents used were hydrocarbon silane of  $C_8$  chain length, thiol silane, and amino silane. These agents were coupled to aggregates composed of limestone and gravel. The adsorption and desorption behaviors of asphalt models and asphalt were determined on treated aggregates and compared to their behaviors on untreated aggregate. The amount of bonding enhancement of the treated versus the untreated aggregate, which is a measure of the comparative resistivity of the asphalt-aggregate interfacial bond to water, caused by treating aggregate with organosilane agents was determined. Highly specific interactions were observed between pairs of asphalt models or asphalts and the organosilane treated aggregate. The highly specific behavior was dependent upon the chemistry of the model or asphalt as well as the chemistry of the silane coupling agent.

### INTRODUCTION

Asphalt-aggregate interfacial interactions are important in the adhesion of asphalt to aggregate. At the interface, the first layer of asphalt must adhere to the aggregate for the adhesive binding action to occur that is required to maintain an asphalt pavement. This adhesive binding must hold through all the stresses that are applied to the asphalt pavement. These stresses include the effect of traffic, changes in daily and seasonal temperature, and the attriting force of water. All of these stresses attack the adhesive forces that hold the asphalt to the aggregate and, hence, the pavement together. These forces include the cohesive forces within the asphalt cement and within the aggregate in addition to the adhesive forces between asphalt and aggregate.

Organosilanes have been used to pretreat aggregate to promote water resistivity between the asphalt and the silane treated aggregate. Divito et al. (1982) compared the efficacy of one organosilane agent and two commercial amine antistripping agents for increasing the water resistivity of three aggregates from different sources. Silane treatment of aggregates showed increased water resistivity at the adhesive bond compared to aggregate treatment with two amine antistripping agents. Graf (1986) showed that diaminosilane produced increased hydrophobic bonding between crushed glass and asphalts. Hence, from this background, the present study for evaluating the potential of organosilane compounds for enhanced, durable bonding was undertaken.

The research presented is focused upon modifying aggregate in order to enhance adhesion between asphalt and aggregate. Aggregates were modified by using organosilane coupling agents with different chemical functional groups, hydrocarbon of  $C_8$  chain length, thiol and amino groups. These silane functional groups were chosen as modifiers for aggregates composed of

granite, limestone, and gravel to increase wetting of the aggregate surface, promote adhesion, and resist water. To evaluate the effect of the surface coupled organosilane agent, the adsorption and desorption behaviors of asphalt models and asphalts were measured on the silane-treated aggregate. The adsorption behavior was measured by adsorbing the asphalt models and asphalt from organic solution and developing an isotherm of their behavior. The desorption behavior was determined by adding water at adsorption equilibrium to the asphalt model or asphalt-aggregate system. The amount of bonding enhancement between the asphalt model or asphalt and the silane-treated versus the untreated aggregate provided a measure of the comparative resistivity to water rendered by treating the aggregate with organosilane coupling agents.

## EXPERIMENTAL

**Materials.** The asphalt model compounds used for this study were benzoic acid, 1-naphthol, phenanthridine, and phenylsulfoxide, all of which were obtained from Aldrich with purities of 99+%. The asphalts (AAD-1, AAK-1, and AAM-1) used were obtained from the Strategic Highway Research Program's (SHRP) Material Reference Library (MRL). These asphalts came from different sources and were different viscosity grades.

**Preparation of Organosilane Aggregate.** Three aggregates, obtained from the SHRP MRL, were used for this study: RC-limestone, RJ-gravel, and RL-gravel. The aggregates, sized to -40+80 mesh, were contacted with 100 ml of 1%, by volume, silane solution for three minutes, filtered, and dried in a vacuum oven at 70°C for 48 hours. The solvent used for the hydrocarbon silane solution was 95%/5% ethanol/water while the thiol silane was prepared using water adjusted to a pH of 4.5. The amino silane was prepared as a water stable solution by the manufacturer, HULS.

**Adsorption and Desorption Experiments.** The adsorption of the asphalt models onto the aggregate was performed by adding varying amounts of aggregate, ranging from 1 to 10 g, into 20 ml of cyclohexane solutions containing 100 mg/l of asphalt model. The samples were agitated for one hour using an orbital shaker and then allowed to settle overnight. Agitation was repeated the next day, followed by one hour of settling. The solution was filtered through a 0.22  $\mu\text{m}$  filter and was analyzed by UV-visible spectroscopy at the wavelength of maximum absorbance of the model compound (Curtis et al., 1991). The adsorption of the asphalt was performed in the same manner except that asphalt solutions, 100 ppm, were prepared in toluene and analyzed at 450 nm.

The desorption experiments for both the asphalt models and the asphalts were conducted similarly. Water introduced at an equivalent volume to the solvent was added into the system after the adsorption step was completed; the amount desorbed was monitored after 48 hours. Both the organic and aqueous phases were monitored for the desorbed material. Increases in the amount of model component or asphalt present in the solvent after the desorption equilibrium had been established were reported as the amount of material desorbed.

The concentrations of the asphalt model or asphalt present in solution after adsorption and desorption were monitored by UV-visible spectroscopy and the amount of model or asphalt adsorbed or the amount of either desorbed was calculated. Adsorption isotherms were developed for asphalt models in combination with silane treated aggregates and natural aggregates. The resulting data were treated by Langmuir analyses and by averaging experimental results on two points of the isotherm data. The relative rankings of both treatments of data for amounts of material adsorbed onto aggregate surface were nearly identical. Thus, all data for the

investigations reported herein, asphalt models and asphalts combined with silane-treated and untreated aggregates, are reported using the experimental average of data obtained from the adsorption isotherms. Surface amounts of material adsorbed were calculated for each system. Desorption experiments were performed at a selected point on the isotherms; the amount desorbed was compared to that of corresponding asphalt model- or asphalt-aggregate systems comprised of natural aggregate.

## RESULTS AND DISCUSSION

**Adsorption and Desorption of Asphalt Model Compounds on Organosilane Treated Aggregates.** Asphalt model compounds of benzoic acid, 1-naphthol, phenanthridine and phenylsulfoxide were adsorbed from cyclohexane solution onto silane-treated and natural aggregates. The mass of asphalt model adsorbed onto all aggregates was determined by UV-visible spectroscopy at a wavelength of maximum absorbance for the adsorbing asphalt model (Curtis et al., 1991). The amount of each specific asphalt model adsorbed onto the silane-treated aggregates was compared to the amount adsorbed on the natural aggregate and has been reported in Table I. Positive signs indicate adsorbed masses increased with organosilane treatment while negative signs indicate adsorption of the asphalt model occurred to a greater extent on the natural aggregate, and thus, indicating organosilane treatment did not increase bonding between asphalt model and aggregate. Water was added to the adsorption system at equilibrium to determine the extent of debonding of asphalt model. The mass of asphalt model adsorbed was determined at adsorption equilibrium, and after desorption equilibrium was attained. The difference in amount of asphalt model adsorbed prior to water addition and after desorption equilibrium is reported as hydrophobic bonding enhancement in Table II. Positive signs on Table II indicate enhanced hydrophobic bonding as a consequence of organosilane treatment while negative signs indicate decreased hydrophobic bonding with organosilane treatment.

**Adsorption of Asphalt Models.** Adsorption behaviors were observed to be specific for the different combinations of silane coupling agent, the asphalt model compound, and the aggregate examined. Three organosilane agents, hydrocarbon, thiol, and amino, were used to treat the surface of three selected aggregates, one limestone and two gravels, that are commonly used in road pavements. The adsorption behavior of organic compounds, containing functional groups that are representative of those in asphalt, on silane-treated aggregates was compared to the adsorption behavior of the same organic compound on natural aggregate. This comparison has been reported in Table I as percent change in adsorption amount for each asphalt model/treated aggregate combination.

Few silane-treated aggregate/asphalt model combinations showed increased adsorption of asphalt models in comparison to adsorption amounts produced on the natural aggregate. Adsorption masses of benzoic acid and phenanthridine on hydrocarbon-treated RC-limestone increased to 20-34% with approximate error of  $\pm 10\%$ . Thiol-treated RC-limestone exhibited an increase in adsorption amount of benzoic acid,  $25\% \pm 13\%$ , compared to its adsorption on the natural aggregate. Additionally, increased adsorption,  $32\% \pm 23\%$ , of phenanthridine was observed for thiol-treated RC-limestone. Adsorption amounts for all other combinations of asphalt models and all silane-treated aggregates showed no change or decreased adsorption amounts compared to adsorption on the natural aggregate.

Most thiol treatments of RC-limestone and RJ-gravel resulted in greater decreases in adsorption amounts of phenylsulfoxide, 1-naphthol, and phenanthridine, by nearly a factor of 2,

than those observed for these same models on thiol-treated RL-gravel. Amino-treated RJ-gravel and RL-gravel yielded large decreases, greater than 50%, in adsorbed amounts of all models, except for benzoic acid. Phenylsulfoxide presented little or no change in adsorption mass with hydrocarbon-treated RC-limestone, hydrocarbon-treated RL-gravel, and thiol-treated RL-gravel. Additionally, benzoic acid showed little or no change in adsorption mass for hydrocarbon-treated RL-gravel, thiol-treated RJ-gravel, and amino-treated RC-limestone.

For most of the systems, the propagated error associated with increases or decreases in adsorption mass of asphalt models for treated aggregates was dominated by the aggregate rather than the asphalt model or the silane treatment. This suggests that the chemical composition of the aggregate is the dominant factor for adhesion and subsequent durability for asphalt road pavements. Propagated error associated with organosilane treated RC-limestone adsorption masses of asphalt models were roughly 10%. Propagated error for treated RL-gravel ranged from 10-30%, and for RJ-gravel ranged from 20-48%.

**Desorption and Bonding Enhancements.** The desorption amounts of asphalt models from the silane-treated aggregates were system specific with the type of silane coupling agent and aggregate being influential in the desorption behavior. Silane treatments of nearly all aggregates resulted in enhanced hydrophobic bonding, i.e., less desorption of the asphalt models with the silane-treated aggregate than with the natural aggregates. Most of the treated aggregates retained more of the adsorbed model compounds in the presence of water, thus, indicating more durable bonding with less sensitivity to water. Hence, desorption percents were observed to be less with silane-treated aggregates than those observed for the natural aggregates.

A few combinations of asphalt models and silane-treated aggregates showed that silane treatments yielded no advantage in hydrophobic bonding. All silane treatments of RC-limestone in combination with 1-naphthol exhibited no change in hydrophobic bonding as compared to natural aggregates. Lack of change in hydrophobic bonding was also observed for all organosilane treatments of RJ-gravel in combination with phenylsulfoxide. Thiol-treated RC-limestone combined with phenylsulfoxide and thiol-treated RL-gravel combined with phenanthridine or benzoic acid indicated little or no change in percent desorptions with silane treatment as compared to those obtained for the same systems in combination with natural aggregates. Amino treatment of RC-limestone aggregate was especially deleterious for hydrophobic bonding of 1-naphthol which suggested that pairing asphalts with high phenolic content with amino-treated RC-limestone should be avoided.

**Adsorption and Desorption of Asphalt on Organosilane Treated Aggregates.** The SHRP MRL asphalts AAD-1, AAK-1, and AAM-1 were adsorbed from toluene solution onto silane treated and natural aggregates, RC-limestone, RJ-gravel, and RL-gravel. Changes in the amount of asphalt adsorbed on treated aggregates were monitored at 450 nm and compared to asphalt adsorbed onto natural aggregates as reported in Table I. At adsorption equilibrium, water was added to the system to determine the sensitivity of the adhesive bond to water. Any debonding of adsorbed asphalt from the silane-treated aggregates was compared to that observed for natural aggregates and reported as percent bonding enhancement. The bonding enhancement for the silane-treated aggregate for retaining adsorbed asphalt in the presence of water is given as a comparison of the percent desorbed from the silane-treated aggregate to the percent desorbed from the natural aggregate as reported in Table II. Whenever the percent desorbed was greater for the natural aggregate than for the silane-treated aggregate, bonding enhancement occurred as indicated by the positive sign in Table II.

**Adsorption of Asphalt on Organosilane Treated Aggregates.** Hydrocarbon treatment of RC-limestone, RJ-gravel, and RL-gravel resulted in increased adsorption mass for only one combination, hydrocarbon-treated RJ-gravel/AAK-1 asphalt,  $50\% \pm 20\%$ . All other combinations of hydrocarbon-treated RC-limestone and hydrocarbon-treated RJ-gravel presented virtually no change in adsorption mass of AAD-1 and AAM-1 asphalts as compared to those observed for the natural aggregates. Decreases in adsorption masses were observed for hydrocarbon-treated RL-gravel in combination with AAD-1 and AAM-1 asphalts.

Thiol-treated RC-limestone yielded little or no increase in adsorption mass for the three asphalts tested. Significant decreases,  $60\% \pm 12-18\%$ , in adsorption mass of AAM-1 asphalt on thiol-treated RJ-gravel and thiol-treated RL-gravel were observed. AAD-1 asphalt also showed decreased,  $28-38\% \pm 12\%$ , adsorption mass for these same two thiol-treated aggregates. In contrast, a substantial increase in adsorption mass,  $186\% \pm 43\%$ , was observed for AAK-1 asphalt on thiol-treated RJ-gravel.

Amino treatment of RC-limestone and RL-gravel produced no change in adsorption mass of AAD-1 asphalt. No changes were observed in adsorption mass of AAK-1 asphalt on amino-treated RC-limestone or for AAM-1 asphalt mass on amino-treated RL-gravel in comparison to the adsorption mass obtained on the natural aggregates. Increased,  $58-87\% \pm 41-48\%$ , adsorption masses were noted for AAK-1 asphalt on both amino-treated gravels, while decreased,  $27-68\% \pm 6-44\%$ , respectively, adsorption masses were observed for the amino-treated RC-limestone and RJ-gravel aggregates.

In terms of increased adsorption of asphalt mass obtained on organosilane treated aggregates, as compared to asphalt mass obtained on natural aggregates, the data in Table I clearly show that AAK-1 asphalt adsorption was substantially enhanced by all organosilane treatments of RJ-gravel aggregate. Also, little or no enhancement in adsorption mass of any of the asphalts investigated was observed for any organosilane treatments of RC-limestone when compared to natural aggregates.

**Desorption and Hydrophobic Bonding Enhancements for Asphalts.** The specificity of organosilane treated aggregates for individual asphalts are clearly observed in Table II, which presents the percent hydrophobic bonding enhancement for treated aggregates in combination with selected MRL asphalts. Not all combinations showed an enhancement in hydrophobic bonding. For instance, RC-limestone aggregate treated with hydrocarbon, thiol, or amino silanes presented little or no change in bonding with the presence of water. Amino-treated RC-limestone in combination with AAM-1 asphalt indicated a very slight enhancement, compared to natural aggregate, in hydrophobic bonding,  $5.9\% \pm 4.3\%$ , while hydrocarbon-treated RC-limestone paired with AAK-1 asphalt showed a decrease,  $5.9\% \pm 1.6\%$ , for hydrophobic bonding. All other combinations of organosilane treated RC-limestone and asphalts presented no change in hydrophobic bonding as a result of the pretreatments. Thus, it was concluded that hydrophobic bonding between RC-limestone and these asphalts would not be enhanced with organosilane treatment of the aggregate.

Silane treatment of RJ-gravel aggregate resulted in contrasting behaviors for hydrophobic bonding that were dependent on the asphalt type. Silane treated RJ-gravel combined with AAK-1 asphalt yielded decreased,  $17-40\% \pm 5-7\%$ , hydrophobic bonding compared to natural aggregate and AAK-1 asphalt, while, no change or an increase in hydrophobic bonding was observed for all silane treated RJ-gravel with AAD-1 and AAM-1 asphalts. Thiol-treated RJ-gravel/AAD-1 asphalt showed substantial hydrophobic bonding enhancement of  $38\% \pm 9\%$ . AAM-1 asphalt indicated improved resistance to debonding by water when combined with

hydrocarbon and amino treated RL-aggregate as evidenced by bond enhancements of  $17\% \pm 6\%$  and  $29\% \pm 9\%$ , respectively.

No change in hydrophobic bonding enhancement for AAK-1 asphalt was observed for organosilane treated RL-gravel aggregates in comparison to desorption of AAK-1 asphalt from natural RL-gravel. Hydrocarbon and amino-treated RL-gravel in combination with AAD-1 and AAM-1 asphalts produced slight increases in hydrophobic bonding. Thiol-treated RL-gravel aggregate in combination with these same two asphalts produced decreased bonding enhancements.

### SUMMARY

For the combinations of silane-treated aggregates, asphalt models, and asphalts tested, there was no relationship observed between increased adsorption amounts and increased hydrophobic bonding in comparison to similar investigations involving natural aggregates. Although, increased adsorption mass for some asphalt models and a few asphalts was observed, increased adsorption mass did not translate into increased resistance to water. Differences were observed in the hydrophobic bonding with the type of organosilane treatment employed for specific aggregate/asphalt model or asphalt combinations. The following conclusions point to the specificity of the interactions between all components of the asphalt pavement.

- Silane treatment of RC-limestone provided no advantage for increased hydrophobicity.
- None of the silane agents tested in this work provided any enhancement for hydrophobic bonding of AAK-1 asphalt to the selected aggregates, RC-limestone, RJ-gravel, and RL-gravel.
- Thiol-treated RJ-gravel provided increased water resistivity for bonding of AAD-1 asphalt.
- Hydrocarbon and amino-treated RJ-gravel provided greater water resistivity for AAM-1 asphalt than did identical silane treatments of RL-gravel.
- Hydrocarbon and amino-treated RL-gravel yielded small hydrophobic bonding enhancements for AAD-1 and AAM-1 asphalts.

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Table I. Percent Change<sup>a</sup> in Adsorption Amounts<sup>b</sup> of Asphalt Models and Asphalts on MRL Aggregates Treated With Organosilanes

Modifier Aggregate	Asphalt Models					Asphalts		
	Benzoic Acid	Phenylsulfoxide	1-Naphthol	Phenanthridine	AAAD-1	AAK-1	AAAM-1	
Hydrocarbon								
RC-limestone	+20 ± 11*	+10 ± 11*	-23 ± 8	+24 ± 10	+3 ± 47*	0	-5 ± 34*	
RL-gravel	-26 ± 22	-53 ± 32	-42 ± 10	-32 ± 25	-17 ± 30*	+50 ± 20	+4 ± 16*	
RL-gravel	-14 ± 16*	+7 ± 41*	-16 ± 10	+32 ± 23	-13 ± 9	0	-34 ± 19	
Thiol								
RC-limestone	+25 ± 13	-31 ± 8	-43 ± 32	-67 ± 12	-15 ± 32*	-12 ± 39*	-26 ± 28*	
RL-gravel	+8 ± 21*	-71 ± 35	-65 ± 14	-45 ± 19	-28 ± 12	+186 ± 43	-60 ± 12	
RL-gravel	-21 ± 15	+7 ± 30*	-26 ± 8	-18 ± 13	-38 ± 3	-18 ± 20*	-62 ± 18	
Amino								
RC-limestone	+4 ± 10*	-71 ± 9	-63 ± 7	-82 ± 6	+2 ± 45*	-16 ± 41*	-68 ± 44	
RL-gravel	-35 ± 26	-89 ± 38	-69 ± 12	-89 ± 22	+43 ± 30	+87 ± 48	-27 ± 6	
RL-gravel	-46 ± 16	-73 ± 30	-53 ± 7	-63 ± 16	+53 ± 64*	+58 ± 41	+6 ± 35*	

a. Percent Change =  $\left( \frac{\text{Amount Adsorbed on Natural Aggregate} - \text{Amount Adsorbed on Treated Aggregate}}{\text{Amount Adsorbed Natural Aggregate}} \right) \times 100$

b. Adsorption Amounts: + Increased with Treatment  
- Decreased with Treatment

c. Propagated Error, Percent

\* Values were considered insignificant due to large propagated error.

**Table II. Percent Bonding Enhancement<sup>a</sup> for Organosilane Treated Aggregates for Hydrophobic Asphalt-Aggregate Bonding**

Aggregate Model/Asphalt	Percent Enhancement in Hydrophobic Bonding		
	Organosilane Treatments		
	Hydrocarbon	Thiol	Amino
RC-limestone			
Benzoic Acid	+23.2 <sup>b</sup> ±1.5 <sup>d</sup>	+11.1±2.8	+14.3±1.6
Phenylsulfoxide	+48.7±3.2	-1.1±3.2*	+32.8±6.5
1-Naphthol	-2.7±5.6*	-18.0±6.0	-119±6.8
Phenanthridine	+49.8±19.8	+24.2±6.5	+25.8±16.0
RJ-gravel			
Benzoic Acid	+192±3.0	+80.7±2.7	+119±4.7
Phenylsulfoxide	+9.5±10.1*	+15.8±18.6*	-1.4±16.4*
1-Naphthol	+192±15	+12.8±8.6	+93.2±2.8
Phenanthridine	+8.5±2.9	+29.4±2.9	+64.6±11.3
RL-gravel			
Benzoic Acid	+10.4±6.5	+11.7±14.0*	+23.9±1.7
Phenylsulfoxide	+13.9±6.3	-15.2±4.4	+15.8±4.8
1-Naphthol	+39.0±12.0	+10.3±8.4	+65.9±1.4
Phenanthridine	+22.0±13.3	-4.5±16.3*	+13.3±11.2
RC-limestone			
AAD-1	-19.5±20*	-14.4±20*	-8.1±20*
AAK-1	-5.9±1.6	-0.3±1.8*	+0.8±3.0*
AAM-1	+3.6±4.2*	-2.3±4.8*	+5.9±4.3
RJ-gravel			
AAD-1	-5.5±6.5*	+37.7±8.8	+5.3±8.1*
AAK-1	-40.4±4.9	-36.5±6.6	-17.2±6.7
AAM-1	+16.6±6.1	-1.0±4.8*	+28.8±8.6
RL-gravel			
AAD-1	+9.8±8.8	-14.9±8.6	+14.3±9.8
AAK-1	-2.7±14.0*	+2.8±14*	+6.2±14*
AAM-1	+8.0±1.5	-4.1±1.7	+14.5±4.0

a. Percent Bonding Enhancement = (% Desorption on Treated Aggregate - % Desorption on Natural Aggregate).

b. Increased Hydrophobic Bonding.

c. Decreased Hydrophobic Bonding.

d. Propagated Error, Percent.

\* Values were considered insignificant due to large propagated error.