Use of coupling agents to stabilize asphalt–rubber–gravel composite to improve its mechanical properties

Miriam Estevez*
Centro de Fisica Aplicada y Tecnología Avanzada, Universidad Nacional Autonoma de Mexico, A. Postal 1-1010, Querétaro, Qro. 76000, Mexico

A R T I C L E   I N F O
Article history:
Received 17 December 2008
Received in revised form 31 March 2009
Accepted 1 April 2009
Available online 23 May 2009

Keywords:
Asphalt
Coupling agent
Gravel
Rubber particles
Modified asphalt

A B S T R A C T
The mechanical performance of rubber-modified asphalt roads depends, besides the intrinsic properties of the constituents (asphalt, rubber and gravel), on their interfaces. To improve the adhesion between constituents, two different coupling agents were required: one to link asphalt with the rubber particles to stabilize the composite creating an elastic network in the interior of the material to improve its elastic recovery, and other to increase the adhesion between the hydrophobic asphalt and the hydrophilic gravel. A phenolic resin was used to link the rubber particles with the asphalt, while a switterionic molecule (phosphatidyl-choline) was used to change the OH groups on the gravel surface by hydrocarbon chains to make it compatible with the asphalt.

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1. Introduction

New polymeric materials with novel properties can be obtained by mixing two or more immiscible polymers which possess, separately, the required properties for the new material. However to obtain high performance materials it is also required to have a good adhesion between phases [1–4]. From these composites, special attention deserves asphalt-based materials. As known, asphalt is one of the most produced organic polymeric materials in the world; it is an important low-cost thermo-plastic material widely used for construction. Asphalt-based materials are widely used in a variety of important applications like: roads binders, adhesives, sealants, and waterproof coatings among others [5]. As a building material, asphalt is exposed to a wide range of loads and weather conditions. However, this material has poor mechanical properties because it is hard and brittle in cold weather, soft and fluid in hot environment and has a low elastic recovery; the brittle character of the asphalt makes easy to fracture it when is subjected to stresses. For these reasons asphalt is usually reinforced with different types of rubbers to improve its mechanical properties [6–8].

A rubber-containing molecular structure widely used to improve the mechanical properties of asphalt (specifically the elastic recovery) is styrene–butadiene block copolymers (SBR). The strong incompatibility between polybutadiene and polystyrene produces, inside the asphalt, an elastic network that renders in a material with excellent elastic recovery and improved mechanical properties [9–11].

1.1. Asphalt–rubber coupling agent

An important rubber-based material used in vehicle industry is the tire rubber. Tires posses a complicated structure with a complex design and are made of different types of rubbers. The huge increase in the number of vehicles and aircraft means a huge number of tires that, once used, are discarded producing a huge contamination. Dispose properly used tires is a technological challenge because non-pollution combustion processes are expensive. A partial solution to reduce the pollution produced by used tires and to improve the quality of the asphalt carpet in roads and highways is to modify the asphalt with rubber particles; these must be homogeneously dispersed and with good adhesion to asphalt [12–15].

Phenol–aldehyde (PA) resins are a family of thermostet compounds of high molecular weight where the phenol rings are linked each other by CH₂ groups (Fig. 1). These resins have been widely used as a binder in a large number of applications: paper, wood powder, husk rice, vulcanization, etc. When a phenol is reacted with an aldehyde, there are three positions in the phenol group susceptible to chemical attack by the aldehyde molecule producing a three functional molecule which can be used to...
generate a highly crosslinked material. Due to the double bond of the polybutadiene molecule, the PA resin reacts chemically with the allyl hydrogen of the allyl group \((\text{C}_3\text{H}_5)\) producing a highly crosslinked material due to the multifunctional character of the PA molecules. Additionally, it is possible, by adjusting the R group (Fig. 1), to obtain materials with different properties (melting temperatures, reactivities, etc.) to react with the asphalt–rubber compound \([16–18]\). Due to the complex chemical structure of asphalt, no schematic representation is shown for the link of asphalt with rubber particles through the use of PA resin; however, this is carried out similarly as the reaction between PA and the polybutadiene as shown in Fig. 1. The vulcanization reaction produced by the PA is similar in nature to the one carried out using sulfur, however, due to the multifunctional character of PA, this is more effective \([19,20]\). The other possibility for the vulcanization reaction, with lower probability to occur, is carried out through the reaction of the PA with the double bond forming quinone groups.

### 1.2. Asphalt–gravel coupling agent

Gravel has been used in pavements from long ago with two main purposes: because it is a hard material it protects the pavement again shear and compression stresses produced by the vehicles and, because it is a ceramic, it protects pavement again degradation by UV radiation \([21–23]\). This is an important component in the pavement construction, and then it is necessary to assure a good adhesion between gravel and asphalt.

Gravel is obtained from igneous rocks by a grinding process to a desired particle size. This mineral has several phases and stoichiometry. It is typic to use basalt or granite with a Si:Al molar ratio of 3:1 and 4:1, respectively. These rock minerals are stable under the condition in which they were formed, i.e. at the temperature of molten lava; however they are unstable under the condition in which they were formed, i.e. at the temperature of molten lava; however, due to the chemical and physical conditions at the earth’s surface. These materials are slowly transformed by weathering (exposure to water, oxygen and \(\text{CO}_2\)) changing the initial unstable chemical structure in a more stable one where some the chemical groups are hydrolyzed to form the groups =Si–OH and =Al–OH. The complicated and varied structures of these rock minerals are due to different organizations of the basic silicon–oxygen tetrahedral and the aluminum–oxygen tetrahedral and octahedral structures \([24]\).

Once the asphalt has been compacted, a uniform layer of gravel with specific granulometry is added; this is inlayed to the asphalt by pressure producing only a physical adhesion between phases. The adhesion between the asphalt and the gravel is difficult because the gravel is a hydrophilic inorganic material, while the asphalt is a hydrophobic organic compound. Then it is required to change the hydrophilic character of the gravel surface into a hydrophobic one; this can be done by changing the OH groups on gravel by hydrocarbon chains. To do this the coupling agent must have in its structure a polar part with either ionic or switwitterionic groups to react with the OH groups of the gravel, and a hydrocarbon chain to provide the hydrophobic character to react appropriately with the asphalt. In this case the selected molecule was a switwitterionic compound with two fatty acids of long chain to provide the hydrophobic character, while the polar part consists of a strong dipole moment to react with the OH groups of the gravel. The phosphatidyl-choline (PC) is an inexpensive commercial available material of vegetal origin which posses these characteristics \([25,26]\). The strong dipole moment of this molecule results from a positive charge from the nitrogen and the negative charge from the free oxygen linked to the phosphorous and with a distance between charges of around 7 Å. This large distance between charges increases the probability of link with the groups =Si–O or =Si–OH\(^{+}\) (and the corresponding Al groups) present in the gravel surface.

The aim in this work is to use two different coupling agents to improve the mechanical properties of asphalt carpets: PA to link the rubber particles with the asphalt to produce an elastic network into the asphalt to improve its elastic recovery and mechanical properties; the other coupling agent (PC) to link the gravel with the rubber-modified asphalt to stabilize the composites.

### 2. Experimental

#### 2.1. Samples preparation

The raw materials were characterized before the fabrication of the composites. The asphalt was a non-oxidized commercial asphalt AC-20 (Asphalt 6, PEMEX, México). The rubber particles were obtained by a non-cryogenic grinding process with an average particle size of 356 microns. The asphalt was molten at \((180 \pm 10) ^\circ\text{C}\) and the rubber powder was added slowly and with mild agitation. Once the rubber particles were uniformly distributed into the asphalt, the PA powder was slowly added to obtain a homogeneous; then temperature was reduced.

Several samples were prepared with different compositions (Table 1). These samples were named as: Asphalt:PA:Rubber:PC.Gravel. For example the sample A3:15:3:15:7F was prepared using asphalt 30% wt, crosslinking agent 0.15%, rubber particles 3%, coupling agent 0.15%, functionalized (F) gravel 70% wt.
The samples were prepared by mixing 30 g of molten asphalt with the corresponding concentration of rubber particles under mild agitation to avoid that high shear stresses could degrade the rubber. The blend was considered complete when, under visual inspection, the rubber particles were completely dispersed and no phase separation was observed. After this, PA and other additives were added at the same temperature and stirring conditions.

Separately, PC was dissolved in a mixture of toluene:acetone 2:1; water was added slowly stirring at high shear rate (6000 rpm) for 2 h to obtain an emulsion. This was kept in rest for one day and then applied by spraying to the gravel until it was completely wetted. 70 g of modified gravel was placed in an aluminum foil and covered with the molten rubber-modified asphalt containing the additives. The samples were cooled to room temperature and tested following the norms: ASTM D-882, ASTM D-3967, D-2042 and D-4402.

### 2.2. Mechanical test

Two different mechanical tests were performed on the rubber-modified asphalt according the appropriated norms. The norm ASTM D-882 determines the adhesion of the asphalt with the gravel surface by measuring the lost weight when a gravel stone, previously covered with asphalt, was immersed in a sealed glass bottle full with water and stirred. The gravel stone remained in water for 24 h; after this, the sample was stirred at 6000 rpm during two periods of 15 min, with 5 min of rest in between. The gravel stone was removed from the water, dried carefully and weighted to determine the lost weight by the action of the water and stirring.

The norms ASTM D-3967, D-2042 and D-4402 establish the consistency of the rubber-modified asphalt by the ring-ball method which consists in determining the time and temperature required to a metal ball with specific weight and geometry passes through an asphalt sample hold by a ring; the sample was kept at that temperature. The performance of the samples in this test was obtained determining the product time and Temperature: \((t \times T)\).

### 3. Results and discussion

A visual inspection of the functionalized gravel showed that their surface was completely covered by the modified asphalt, meaning that the coupling agent avoided the phase segregation. An image of this is shown in Fig. 2. The results of the adhesion gravel–asphalt obtained using the norm ASTM D-882 are reported in Fig. 3. Here it is possible to observe that the best sample was the A3:15:3:15:7F with a lost weight of 0.07 g, followed by the sample A3:0:3:3:7F with 0.17 g, while for pure asphalt the lost weight was 3.00 g; this means that the lost weight was reduced by a factor of 43 respect to pure asphalt. This significant reduction in the lost weight means that the gravel particles were strongly stuck to the asphalt providing a good adhesion and protection to the rubber-modified asphalt carpet. From this figure, it is also possible to see that, as soon as some coupling agent was used, the adhesion properties between the asphalt and the gravel improve significantly.

The results of the consistency of the rubber-modified asphalt, determined according to norms ASTM D-3967, D-2042 and D-4402, are shown in Fig. 4. Here it is reported the \(t \times T\) values for all samples. From this figure it is possible to see that the chemically modified samples perform significantly better (i.e. higher \(t \times T\) values) respect to samples with no additives. As before, the best sample was the A3:15:3:15:7F (680 s°C) followed, far below, by A3:3:3:0:7F.

### Table 1

Chemical compositions of the prepared samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Asphalt (% wt)</th>
<th>Adhesion Agent (%)</th>
<th>Rubber (%)</th>
<th>Crosslinking Agent (%)</th>
<th>Gravel (% wt)</th>
<th>Functionalization of Gravel</th>
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<tr>
<td>A3:0:0:0:7NF</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>70</td>
<td>No</td>
</tr>
<tr>
<td>A3:0:0:0:7F</td>
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<td>0</td>
<td>0</td>
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<tr>
<td>A3:3:3:0:7NF</td>
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<td>0.3</td>
<td>3.0</td>
<td>0</td>
<td>70</td>
<td>No</td>
</tr>
<tr>
<td>A3:3:3:0:7F</td>
<td>30</td>
<td>0.3</td>
<td>3.0</td>
<td>0</td>
<td>70</td>
<td>Yes</td>
</tr>
<tr>
<td>A3:15:3:15:7NF</td>
<td>30</td>
<td>0.15</td>
<td>3.0</td>
<td>0.15</td>
<td>70</td>
<td>No</td>
</tr>
<tr>
<td>A3:15:3:15:7F</td>
<td>30</td>
<td>0.15</td>
<td>3.0</td>
<td>0.15</td>
<td>70</td>
<td>Yes</td>
</tr>
<tr>
<td>A3:0:3:3:7NF</td>
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<td>3.0</td>
<td>0.3</td>
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<td>A3:0:3:3:7F</td>
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<tr>
<td>A3:15:0:15:7F</td>
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<td>0.15</td>
<td>0</td>
<td>0.15</td>
<td>70</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Fig. 2. Image of modified gravel covered with molten rubber-modified asphalt; the gravel surface was completely wetted by the asphalt.

Fig. 3. Plot of lost weight in gravel–asphalt adhesion experiment for all samples.
(510 °C), while for pure asphalt was 300 s °C; this means an increment of more than 100% respect to pure asphalt. These results show that the presence of PA improves the adhesion rubber–asphalt increasing significantly the performance of the composite.

4. Conclusions

The results show that the coupling agents are of fundamental importance to improve significantly the mechanical performance of the asphalt–rubber–gravel system. The crosslinking agent (PA) creates an elastic network into the asphalt linking together the rubber particles and the asphalt, increasing the elastic recovery; this is indicated by the results of the ring-ball method which shows an increment of more than 100%: from 300 s °C for pure asphalt to 680 s °C for the sample A3:15:3:15:7F. The other coupling agent (PC) increases the compatibility and consequently the adhesion between the asphalt and the gravel, reducing the lost weight from 3.00 g for pure asphalt to 0.07 g for A3:15:3:15:7F. Based on these results, the sample with the best performance was A3:15:3:15:7F where the asphalt was added with 3% of rubber particles, the gravel was functionalized with 0.15% of PC and the rubber-modified asphalt crosslinked with 0.15% of PA.

Acknowledgements

The author wants to thank Miss Zorany Hernández for her valuable help in the materials preparation and characterization.