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

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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.

1. Introduction

New polymeric materials with novel properties can be obtained by mixing two or more immiscible polymers which posses, 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 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 thermoset compounds of high molecular weight where the phenol rings are linked each other by CH_2 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

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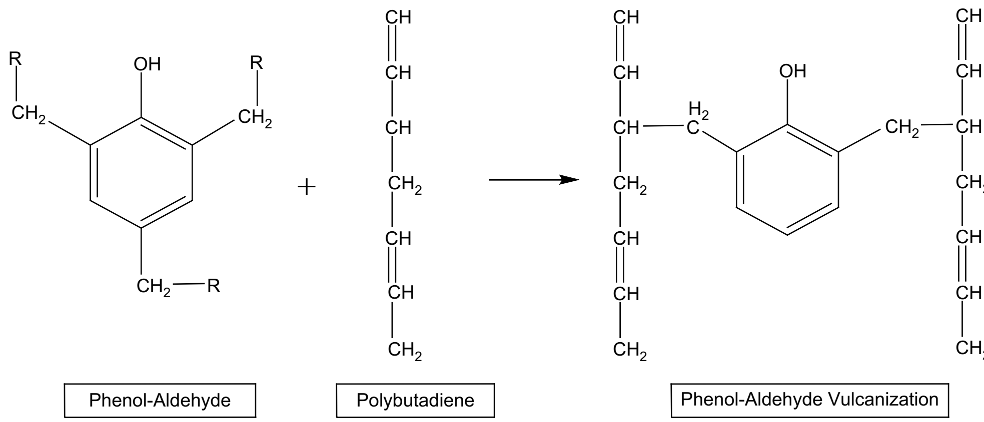

Fig. 1. Chemical reaction between PA resin and polybutadiene.

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 (C_3H_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 is a hard material it protects the pavement again shear and compression stresses produced by the vehicles and, because 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 typical 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 chemical and physical conditions at the earth's surface. These materials are slowly transformed by weathering (exposure to water, oxygen and 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 switterionic 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 switterionic 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–OHH$^+$ (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 composite.

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 $(180 \pm 10)\,^{\circ}C$ 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.

Table 1
Chemical compositions of the prepared samples.

Sample	Asphalt (% wt)	Adhesion Agent (%)	Rubber (%)	Crosslinking Agent (%)	Gravel (% wt)	Functionalization of Gravel
A3:0:0:0:7NF	30	0	0	0	70	No
A3:0:0:0:7F	30	0	0	0	70	Yes
A3:3:3:0:7NF	30	0.3	3.0	0	70	No
A3:3:3:0:7F	30	0.3	3.0	0	70	Yes
A3:15:3:15:7NF	30	0.15	3.0	0.15	70	No
A3:15:3:15:7F	30	0.15	3.0	0.15	70	Yes
A3:0:3:3:7NF	30	0	3.0	0.3	70	No
A3:0:3:3:7F	30	0	3.0	0.3	70	Yes
A3:15:0:15:7NF	30	0.15	0	0.15	70	No
A3:15:0:15:7F	30	0.15	0	0.15	70	Yes

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: ($t \times T$).

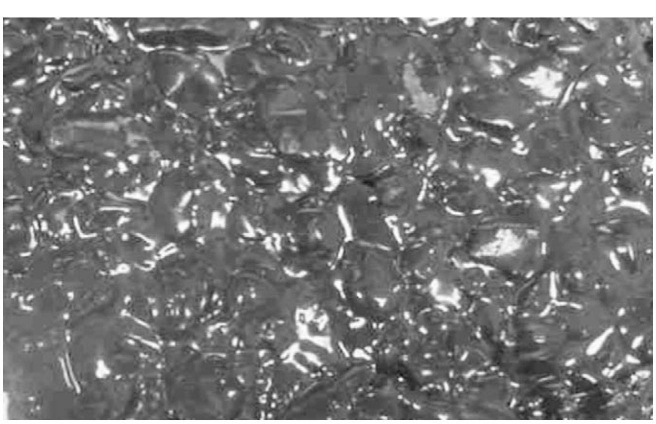

Fig. 2. Image of modified gravel covered with molten rubber-modified asphalt; the gravel surface was completely wetted by the asphalt.

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

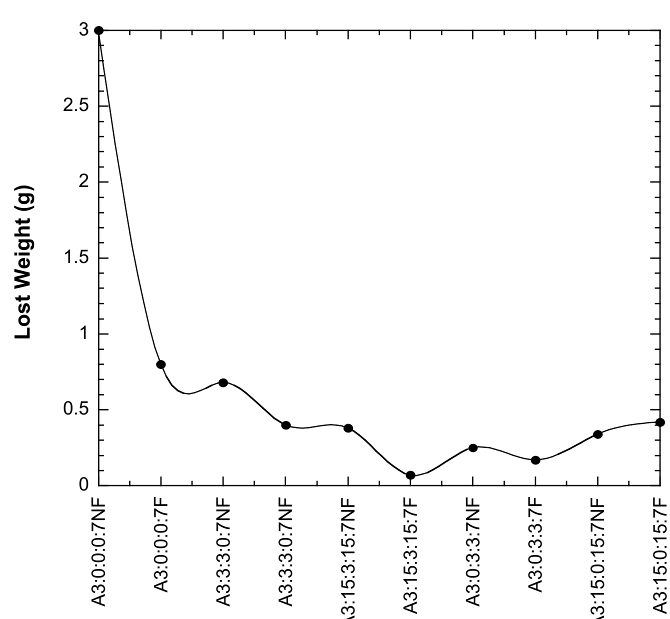

Fig. 3. Plot of lost weight in gravel–asphalt adhesion experiment for all samples.

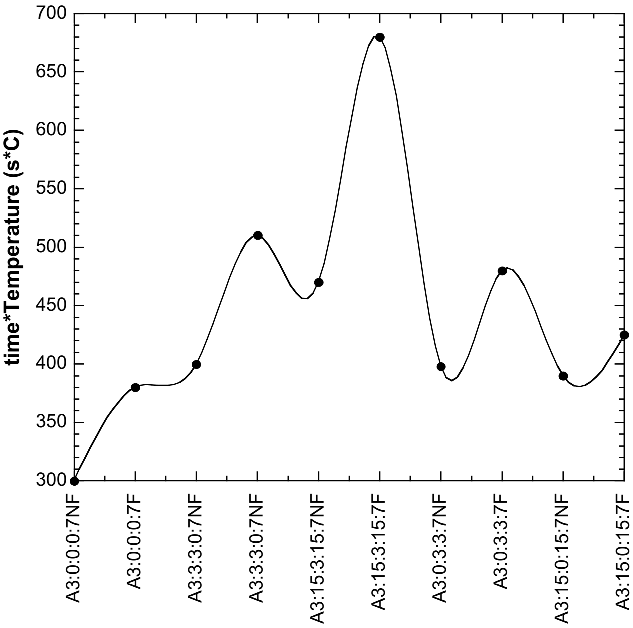

Fig. 4. Plot of the product ($t \times T$) in the ring-ball experiment for all samples.

(510 s °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.

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References

[1] Yan Bing, Zhao Li-min, Liu Jin-liang. Molecular assembly and photophysical properties of covalently bonded rare earth polymeric hybrid materials phenol–RE–MSMA (MS). Journal of Photochemistry and Photobiology A: Chemistry 2008;199(2):50–6.
[2] Grujicic M, Sellappan V, Mears L, Xuan X, Seyr Norbert, Erdmannand Marc, et al. Selection of the spraying technologies for over-coating of metal-stampings with thermo-plastics for use in direct-adhesion polymer metal hybrid load-bearing components. Journal of Materials Processing Technology 2008;198(5):300–12.
[3] Yan Bing, You Jia-Yong. In situ sol–gel composition of luminescent hybrid material incorporated with terbium coordination polymers. Journal of Materials Processing Technology 2005;170(6):363–6.
[4] Rees DWA. Nutting creep in polymer composites. Journal of Materials Processing Technology 2003;143(3):164–70.
[5] Polacco Giovanni, Berlincioni Stefano, Biondi Dario, Stastna Jiri, Zanzotto Ludovit. Asphalt modification with different polyethylene-based polymers. European Polymer Journal 2005;41(6):2831–44.
[6] Huang Yue, Bird Roger, Heidrich Oliver. Development of a life cycle assessment tool for construction and maintenance of asphalt pavements. Journal of Cleaner Production 2008;17(6):283–96.
[7] Fukumori Kenzo, Matsushita Mitsumasa, Okamoto Hirotaka, Sato Nario. Recycling technology of tire rubber. JSAE Review 2002;25(5):325–8.
[8] Brostow W, Lobland HEHagg, Narkis M. Sliding wear, viscoelasticity and brittleness of polymers. Journal Materials Research 2006;21(7):2422–8.
[9] Krauss G. Modification of asphalt block polymer of butadiene and styrene. Rubber Chemistry and Technology 1982;55(6):1389–91.
[10] Vargas MA, Chavez AE, Herrera R, Manero O. Asphalt modified by partially hydrogenated SBS tri-block copolymers. Rubber Chemistry and Technology 2005;78(8):620–43.
[11] Wang YP, Liu DJ, Li YF, Wang YP, Gao JM. Preparation and properties of asphalts modified with SBS/organobentonite blends. Polymers & Polymer Composites 2006;14(6):403–11.
[12] Polacco Giovanni, Muscente Antonio, Biondi Dario, Santini Simona. Effect of composition on the properties of SEBS modified asphalts. European Polymer Journal 2006;42(4):1113–21.
[13] Myhre M, MacKillop DA. Rubber recycling. Rubber Chemistry and Technology 2002;75(5):429–74.
[14] Findik F, Yilmaz R, Koksal T. Investigation of mechanical and physical properties of several industrial rubbers. Materials & Design 2004;25(2):4–8.
[15] Atal Ajay, Levendis Yiannis A. Comparison of the combustion behaviour of pulverized waste tires and coal. Fuel 1995;74(8):111–8.
[16] Vermeulen R, De Hartog J, Swuste P, Krombout H. Trends in exposure to inhalable particulate and dermal contamination in the rubber manufacturing industry. The Annals of Occupational Hygiene 2000;44(4):276–8.
[17] Alajbeg Andja. Products of non-flaming combustion of phenol–formaldehyde resin foam. Journal of Analytical and Applied Pyrolysis 1986;9(5):255–63.
[18] Jahangir Lutful Majid, Samuelson Olof. Chromatography in aqueous solution on styrene–divinylbenzene resins. Journal of Chromatography A 1980;193(3):197–206.
[19] Akiba M, Hashim AS. Vulcanization and crosslinking in elastomers. Progress in Polymer Science 1997;22(4):475–521.
[20] Datta RN, Huntink NM, Datta S, Talma AG. Rubber vulcanizates degradation and stabilization. Rubber Chemistry and Technology 2007;80(2):436–80.
[21] Dawson T, Lingham K, Yenn R, Beveridge J, Moore R, Prentice M. Heathrow terminal 5: building substructures and pavements. Proceedings of the Institution of Civil Engineers - Civil Engineering 2008;161(7):38–44.
[22] Berdahl P, Akbari H, Levinson R, Miller WA. Weathering of roofing materials - an overview. Construction and Building Materials 2008;22(8):423–33.
[23] Palmer Jr WD. Paving with roller compacted concrete. Concrete Construction - World of Concrete 2005;50(6):45–50.
[24] Spiessl SM, MacQuarrie KTB, Mayer KU. Identification of key parameters controlling dissolved oxygen migration and attenuation in fractured crystalline rocks. Journal of Contaminant Hydrology 2008;95(12):141–53.
[25] Simpson Carol. Deformation of granites rocks across the brittle–ductile transition. Journal of Structural Geology 1985;7(3):503–11.
[26] Yaralı O, Yaşar E, Bacak G, Ranjith PG. A study of rock abrasivity and tool wear in coal measures rocks. International Journal of Coal Geology 2008;74(7):53–66.