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Automotive brake pads made with a bioresin matrix

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ABSTRACT

By using biosourced raw materials such as condensed tannins and furfuryl alcohol a biosourced thermoset resin was developed and used and tested for a new application: as a resin matrix of automotive brake pads. The manufacturing procedure developed is particularly easy. Automotive brake pads based on this green resin were characterized and showed excellent braking properties and wear resistance when used under real car, full scale test conditions. Their mechanical resistance was found to be comparable to that of commercial automotive brake pads bonded with synthetic phenolic resins. They tolerated well the severe stresses induced by a strong braking like an emergency braking: 50 km/h (31 mph) until complete standstill and showed braking distances comparable or shorter than commercial brake pads.

1. Introduction

During the last decades a continuous increase of oil prices has occurred. As a result, considerable research has been done to develop new biobased materials. Replacing petrochemicals by biosourced chemicals is possible in many different industrial sectors. Natural and renewable materials coming from agriculture or forestry such as furfuryl alcohol and condensed polyflavonoid tannins have been used to develop new biobased materials: biobased adhesive resins (Pizzi, 1983, 1989, 1994; Zhou et al., 2013), insulation foams and floral foams (Tondi et al., 2008, 2009a,b; Basso et al., 2014a,b; Lacoste et al., 2013; Lagel et al., 2014a,b), high tech paper laminates (Abdullah et al., 2013, 2014), biobased composites (Sauget et al., 2014), and finally polyurethanes (Pizzi, 1979a,b; Basso et al., 2014a,b) even without using isocyanates (Thebault et al., 2014, 2015). More recently new thermoset plastics based on a natural tannin-furanic thermoset resin were developed (Li et al., 2013; Lagel et al., 2014a,b, 2015). These resins are based on the coreaction of furfuryl alcohol and tannins. They were developed to replace industrial oil-derived resins, like synthetic phenolic resins, which are used in different applications, like, for instance, in brake pads manufacture.

This work is a part of an approach of reduction and elimination of hazardous components for humans and the environment. Indeed after the ban of asbestos (since the 1st of January 1997 in France), which was used in brake pads preparation, the aim in few year is to replace formaldehyde by other component and also to use more and more biosourced chemicals and materials.

Development of biobased resins for brake pads has been thought before, and this based on a number of different materials. The use of biobased resins such as castor oil was already envisaged for brake lining in a USA patent in 1932 (Rosner, 1932). Lignin based polymers were also proposed for this application (Lora and Glasser, 2002). The most actively researched materials, at present, for biobased brake pad matrices are cardanol (Voirin et al., 2014), and biobased polyamides (Feldmann and Bledzki, 2014), towards both of which it appears that considerable industrial research has been oriented.

In this article, firstly the possibility of preparing brake pads made with biobased resin based on tannins was studied for the first time. This application is rather demanding due to the stresses induced on the pad by the car braking system (Antanaitis, 2016). Secondly, the formulation of the tannin resin was further modified from the ones developed earlier by Li et al. (2013) and Lagel et al. (2014a,b, 2015) to obtain with ease a good performance and while improving greatly its ease of application. Both these improvements are essential and determining to be able to implement the new mate-

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rial in industrial production. Wear resistance (thickness and weight losses), emergency braking efficiency and Brinell hardness tests were investigated.

2. Material and methods

2.1. Materials

Quebracho (*Schinopsis lorentzii* and *balansae*) wood tannin extract (Fintan QSTW) powder was supplied by SilvaTeam (San Michele Mondovi', Italy). It must be pointed out that this tannin extract after water extraction from the wood, undertook a second extraction in ethanol to eliminate the majority of carbohydrates present. This type was used as while slightly more expensive it gives resins of much better performance.

Furfuryl alcohol (98%), polyethylene glycol 400 (PEG 400), ethylene glycol, *para*-toluene sulfonic acid (pTSA, with a purity of 97.5%) were purchased from Acros Organics, (Geel, Belgium).

Glycerol phosphate acidic ester was synthetized following Hoxie's example 1 (Hoxie, 1968).

Tung oil was purchased from Oleobois (Vendargues, France).

Xiameter OFX-0193 Fluid (DC 193), a silicone polyeter copolymer, was purchased from Dow Corning, (Midland, United States).

Graphite was provided by Condat (Chasse-sur-Rhône, France).

Liquid neoprene glue was purchased from Würth, (Künzelsau, Germany).

For this work, two different sizes of abrasive particles were used. There were purchased from Centre des Abrasifs, (Valenciennes, France). Abrasive particles are aluminium trioxide (Al_2O_3): Alu 36 (grain size of 0.4 mm) and Alu 60 (grain size of 0.25 mm).

Roving of fiberglass of 270 g/m^2 used came from Sinto, (Aubagne, France). Roving of fiberglass are woven fiberglass.

Mineral wool (N°3 very thin) was purchased from Würth, (Künzelsau, Germany).

Commercial automotive brake pads from Brembo, (Curno, Italy) were used as a control.

2.2. Resin synthesis

The amounts are given for a pair of brake pads.

Firstly, furfuryl alcohol and quebracho tannins were mixed together during 15 s. Secondly PEG 400, tung oil, DC 193 and neoprene were added (Basso et al., 2015). Thus graphite and glycerol phosphate acid were added for the relevant formulations. After each addition the mixing time is 15 s.

Finally a 65% ethylene glycol solution of pTSA was added as a catalyst. The proportions were inspired by previous works (Lagel et al., 2014a,b, 2015) and they are shown in Table 1.

2.3. Automotive brake pads development

By observing commercial automotive brake pads and after some research about this subject, it was found that in the 1960's, automotive and trucks brake pads were composed of fiberglass, mineral fibers, metal fibers, carbon and synthetic fibers to provide semi-metallic with higher performance than asbestos (which is now forbidden) (Blau, 2001). Indeed, brake pads are most of the time composed by:

- Abrasives such as aluminium oxide, iron oxides, quartz, silica etc. . .
- Friction modifiers, such as antimony trisulfide, carbon (graphite), ceramic microspheres etc. . .
- Fillers, such as anti-oxidants, asbestos, barium sulfate, rubber etc. . .

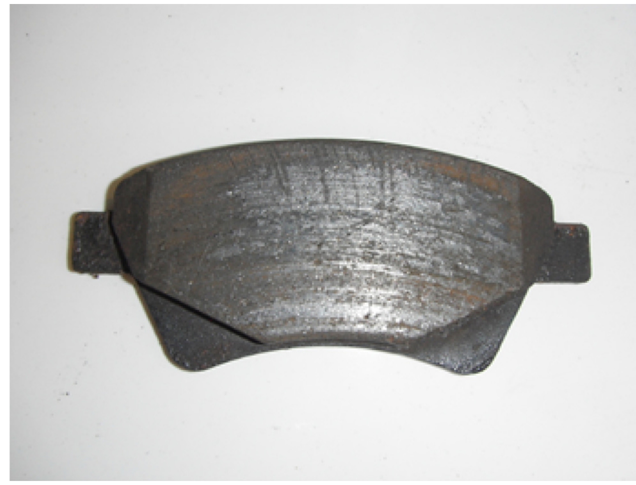

Fig. 1. Commercial brake pad after braking test.

- Reinforcements, such as fibers: mineral wool, fiberglass etc. . .
- Binder Materials, such as phenolic resin which is the most common binder.

After mixing all the components, the dough which will become the friction lining is compacted in mold and cooked at high temperatures (160 and 200 °C). During this phase, the rubber binders are cured. Thus the material is definitively stabilized (Felten, 2013).

In this work some additives, like glycerol phosphate acidic ester which is known to be a flame retardant, were added to the resin.

The amount of abrasive particles was added to the resin and it was well mixing. Samples were done in an aluminium mold whose walls were coated with silicone sheet. Firstly one layer of fiberglass was put in the bottom of the mold, after the half of the abrasive resin was placed. Then, a second layer of fibreglass was placed and above this the second part of abrasive resin. Eventually a third layer of fiberglass was put on the top of that.

This system was put in a hot press during 1 hour at 200 °C (150 °C was also used in order to decrease energy consumption) and with a pressure of 80 kg/cm^2. Then, samples were cooled and were stuck on metallic plates in order to be identical to the commercial brake pads. These being also composed of a pad bonded onto a metallic plate (Fig. 1). So samples can be used like automotive brake pads. Concerning the quantity of abrasive particles, three amounts were tested: 150%, 75% and 50% (Table 1). These percentages are linked to the mass of the resin. For example, for a percentage of 150%: if there are 100 g of resin there will be 150 g of particles. Abrasive particles used are aluminium trioxide (Al_2O_3): Alu 36 (grain size of 0.4 mm) and Alu 60 (grain size of 0.25 mm).

The fibers were incorporated in two different ways. Indeed, for fiberglass they can be placed on each side of the brake pad, or they can be cut in little (no more than 5 mm length) and mixed with the resin. For mineral wool, it can be placed in the middle of the brake pad or they can be cut in little (no more than 5 mm length) and mixed with the resin.

2.4. Automotive brake pads and resin characterization

2.4.1. Determination of the emergency braking efficiency and wear resistance

The emergency braking efficiency of the automotive brake pads developed in this work was determined by testing them with a cycle of ten emergency braking (50 km/h counter until complete standstill of the car). The car was a Renault Scenic I (about 1300 kg).