

Assessment of modified lignin cationic emulsifier for bitumen emulsions used in road paving



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ABSTRACT

The utilization of Kraft lignin as cationic emulsifier in the preparation of bitumen emulsions has been assessed in this work. Thus, Kraft lignin was previously modified in alkaline medium in presence of tetraethylene pentamine (TEPA) and formaldehyde, according to the Mannich reaction. Solubility in water phase as a function of pH demonstrated the amphoteric nature of the reaction product, which enables its potential application in cationic bitumen emulsions. Bitumen emulsions stabilized by modified Kraft lignin (MKL) were further studied. Different B/W ratios, which mainly affected the high-shear-rate-limiting viscosities, yielded more similar mean droplet diameters than different pHs, whose effect on viscosity was mainly at low shear rates. Moreover, viscous flow and linear viscoelasticity tests revealed enhanced rheological performance of the MKL bitumen residue if compared to the parent base bitumen. Finally, half warm mix asphalt (HWMA) specimens containing reclaimed asphalt pavement (RAP) were studied, and the results compared with those corresponding to virgin aggregate. In both cases, the preparation of HWMA with a selected 60/40 MKL bitumen emulsion at 80 °C by gyratory compaction was successful. Compared to the virgin aggregate, the specimen derived from 100% RAP showed much higher mechanical resistance due to a partial blending of fresh binder with RAP aged binder.

1. Introduction

Over the last decades, sustainable development policy is being strongly encouraged in many sectors, including transport infrastructure. In pavements construction, the massive consumption of fossil fuels and highly toxic pollutants emission associated to the use of the standard practice of hot mix asphalt (HMA) technology are two critical environmental concerns [1,2]. As an alternative, reduced-temperature paving technologies using bituminous emulsions may represent up to 7 times lower emission in kg eq. CO₂/ton product and up to 7.5 times lower energy consumption in MJ/ton product, as compared to HMA [3]. These great reductions come from the decrease in binder viscosity which allows for milder workability during manufacture. Hence, even at ambient conditions, mixing and compaction in the reduced temperature method is expected to perform better than in the standard method, as bitumen viscosity at 135 °C is 6 times higher than its corresponding 70/30 (B/W) bitumen emulsion under ambient conditions [4].

Bitumen emulsions are composed of two immiscible phases, that is, 1–50 μm bituminous droplets dispersed into water medium in the

presence of an emulsifier. The emulsifier is an amphiphilic substance with a hydrophilic head and a lipophilic coil. It resides at the interface between the bitumen droplet and the water phase, acting as a stabilizer which reduces the interfacial tension between both phases and facilitates the emulsification process. In terms of the surface charge of the hydrophilic end, cationic emulsifiers are used, by far, in a larger scale than anionic or non-ionic emulsifiers in the bitumen emulsion industry [5]. This is due to its ability to adhere to electronegative siliceous solid aggregates, the most common mineral type on Earth [6,7]. In this regard, functional groups containing nitrogen, i.e. amine, amidoamine and imidazoline, are widely used in the hydrophilic end of cationic emulsifiers [5] due to its known ability as adhesion promoters [8].

Interestingly, lignin, a by-product of pulping industry, has presented a potential use as a building unit for cationic emulsifiers [9,10]. Depending on the sources, from hardwood or softwood, and importantly the previous treatment used, i.e. sulfate (Kraft) process, sulfite process, etc., a wide variety of lignin is available. Together with cellulose, lignin represents the most abundantly available biopolymer on Earth. However, only a small amount of it is being utilized to manufacture commercial products, and the rest is mainly burnt for energy [10,11]. To

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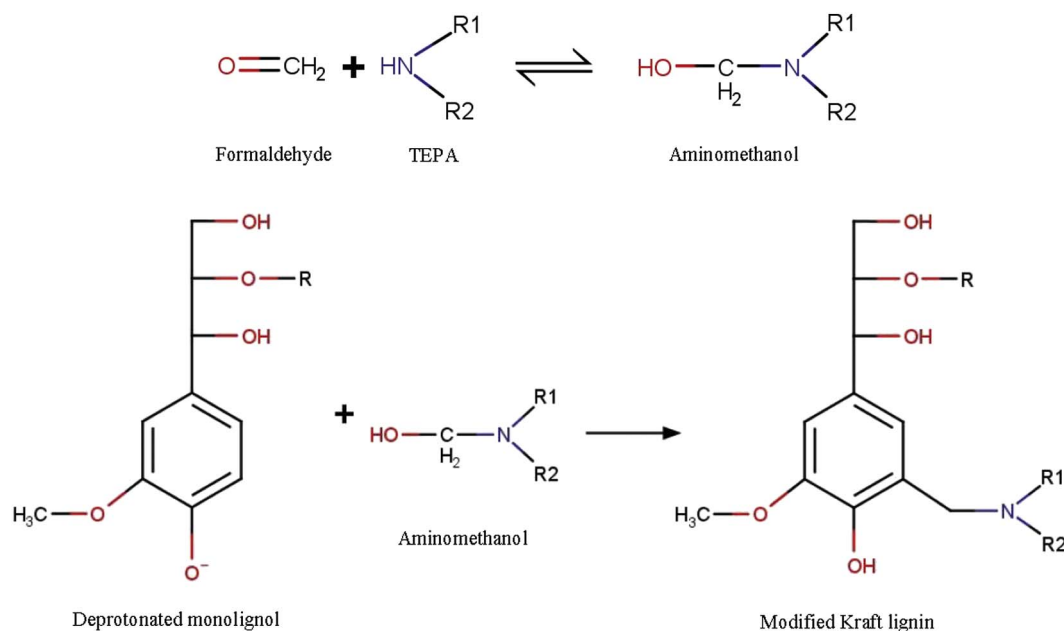


Fig. 1. Molecular structure prediction during Mannich reaction for the preparation of MKL, represented as monolignol, formaldehyde and amine functional group reaction. Adapted from [13].

obtain a cationic emulsifier product based on the Mannich reaction, a compound containing an amine functional group is attached to lignin, with formaldehyde as a second reagent [9,12,13]. In alkaline medium, the reaction occurs between a lignin carbon with high electron density and an intermediate substance (aminomethanol) which was initially formed from the reaction of formaldehyde and the amine [9], shown in Fig. 1.

This type of modification permits the use of various types of lignin, among them, lignin extracted by a Kraft process, which is a highly adopted technology in pulping industry [13]. Hence, selection of Kraft lignin as raw material is of high interest, that also presents a potential use as properties modifier [14]. Similarly, options are also available for the amine group selection, though it is limited to primary ($-\text{NH}_2$) or secondary ($-\text{NH}$) amine. In this study, tetraethylene pentamine (TEPA), where in Fig. 1 $\text{R}_1 = \text{C}_{2n}\text{H}_{1+5n}\text{N}_n$ and $\text{R}_2 = \text{C}_{2(4-n)}\text{H}_{1+5(4-n)}\text{N}_{4-n}$, for $0 \leq n \leq 2$, with three secondary and two primary amine, was chosen as reagent. High expectation was put on its emulsifying ability and further adhesive properties of its binder, given the high number of amine groups involved in the molecule.

For that purpose, this work assesses the potential use of TEPA modified Kraft lignin (MKL) as cationic emulsifier of bitumen emulsions. In that sense, the methodology was established as follows: a) influence of pH on the solubility in aqueous medium of the cationic emulsifier; b) investigation on the influence of pH, B/W ratio and processing on the MKL bitumen emulsions droplet size distribution and their flow behavior at 30 °C; c) evaluation of the MKL bitumen emulsions breaking rate and further study on the relation between the rheological properties and microstructure of their residues; and d) feasibility of developing half warm mix asphalt (HWMA) containing reclaimed asphalt pavement (RAP) with the use of MKL cationic bitumen emulsions.

2. Experimental

2.1. Materials

Alkali or Kraft lignin (KL) CAS no.: 8068-05-1, brown powder (insoluble in acidic aqueous solution) with MW of 10,000 g/mol, was used as a precursor to obtain MKL. This lignin presented ash content of 3.14 wt% and elemental composition (wt%) as follows: C: 61.15, H:

6.72, N: 2.18, O: 26.92, S: 2.54. In this case, if all the sulfur is assumed to be found as sulfonate groups, the $-\text{SO}_3^-$ content would be of 6.35 wt %. Amination, through the Mannich reaction, was followed by reacting KL with tetraethylene pentamine (TEPA) and formaldehyde (supplied as 37 vol% aqueous solution). All reagents were purchased from Sigma Aldrich, Spain. The bitumen used to manufacture the emulsions was kindly supplied by Repsol S.A. (Spain). Values of penetration of 190 dmm and Ring-and-Ball softening temperature of 39 °C were measured according to European Standards EN 1426:2007 and EN 1427:2007, respectively. Finally, in order to assess the potential use of the emulsions in HWMA, two types of aggregates were selected: a) RAP, provided by Repsol S.A. Spain, was extracted from a road in Madrid; and b) a siliceous aggregate, used as reference, from Arido Velilla S.A. Spain.

2.2. Emulsions and samples preparation

In the preparation of the emulsifier, previously optimized quantities of 1 g KL and 1.4 g TEPA were initially solubilized in 50 mL of alkaline (pH of 13) aqueous solution, at 60 °C, under stirring at 1000 rpm. Then, a quantity of formaldehyde equivalent to TEPA in moles was added to conduct the Mannich reaction for at least 4 h. To prepare the emulsion aqueous phase, the concentrated MKL was diluted up to the final desired concentration with deionized water and the pH was then adjusted using HCl in 37 vol% aqueous solution.

The preparation of the bitumen emulsions was performed according to the following three different methods: A) batch mixing of bitumen at 140 °C with water at 60 °C in a homogenizer IKA UT T50 with a toothed rotor-stator G45 M dispersing element at 10,000 rpm for 4 min; B) one pass in-line mixing for 3 s, of both phases, in a colloid mill type C45-2939 (bitumen and water phases at same temperatures as before) at 6000 rpm; and C) similar as in (A) performed in a shorter processing time of 2 min. Aiming to investigate the influence of pH, B/W ratio and processing procedure on the emulsion properties, the nine emulsion cases presented in Table 1 were developed. Thus, pH was varied between 1 and 7, and the B/W ratio from 50/50 to 70/30. A constant concentration of the surfactant MKL of 0.75 wt% (with respect to overall emulsion) was always used.

Residual binders were obtained by the evaporation method outlined in UNE-EN 13074-1:2011. This method minimizes the damage provoked to the binder with a view to its further characterization.

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