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# Effect of bitumen fluxing using a bio-origin additive

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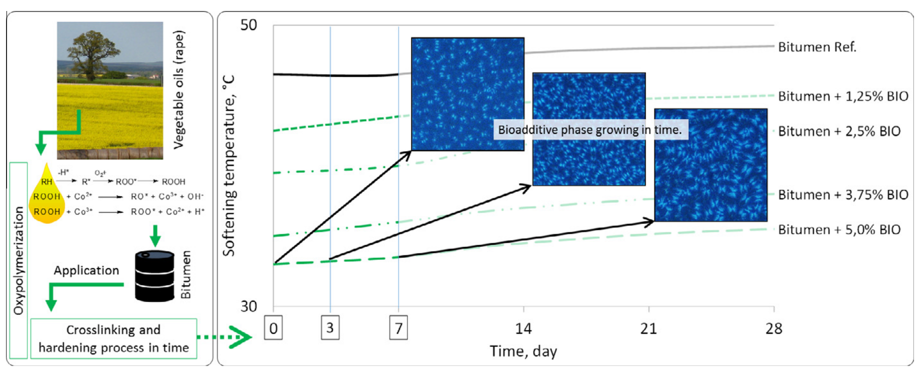
## HIGHLIGHTS

- Small bioadditive amount (1.25%–5.0%) decreases binder consistency.
- Bituminous + bioadditive are subjected to the oxypolymerization reaction.
- Highest consistency increment occurs during first 14 days.
- Bioadditive content (3.75%–5.0%) gives effective binder consistency recovery.
- Bioadditive hardening process is more effective with softer binders.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Currently, the bio-binder or bio-origin polymers can be successfully used for bituminous binder modification. Bio-derived oil is also used as a flux additive for binders or as an additive in reclaimed asphalt pavement technology.

The main goal of the research was to investigate a new method of bituminous binder fluxing with bio-derived additive. In this technology, bioadditive decreases binder viscosity during production processes and then, once asphalt pavement is placed, gradually reconstructs binder viscosity as a result of oxidative polymerization. Based on the Dynamic Shear Rheometer, Ring and Ball tests and fluorescent microscopy, changes in time in biomodified binder were studied. Three binders with various performance grade values with different bioadditive addition were tested. Binders fluxed with bioadditive were conditioned for up to 56 days in order to evaluate oxidative polymerization reaction.

Base on the conducted tests it can be stated that vegetable oils and their methyl ester containing polyunsaturated fatty acids can be used as an ecological flux for bituminous binders. As a result of oxypolymerization reaction, partial consistency recovery is possible for bituminous binder with bioadditives. It was found that effectiveness of oxidative polymerization reaction is mainly dependent on bioadditive content and binder performance grade.



## 1. Introduction

Current policies and public expectations are continuously pushing towards durable, low energy materials obtained from renewable resources. New, innovative materials such as binders, polymers and composites are developed with new bio-materials

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compounds. Such trend, observed also in pavement construction, resulted in materials development in terms of utiliziation of waste/byproduct materials and application of chemical additives improving properties of asphalt pavements [1–4]. Currently most promising technologies are reclaimed asphalt pavement (RAP), warm mix asphalt (WMA) and application of bio-derived materials allowing for reduction of petroleum-based binder content [5]. Abovementioned technologies provides modern system utilizing all types of recent engineering materials in the engineering design.

Bio-derived materials are produced using various raw materials and are combined with bituminous binder in a wide range of proportions: 100% binder replacement, an extender (25–75% replacement) or a modifier/additive (up to 10% replacement) [6–8]. As studied earlier [8–12] such materials, beside other properties, may also change the binder stiffness and those of the asphalt mixture, allowing for the rejuvenating action. Influence on both low and high temperature performance of the asphalt mixture should also be deeply recognized [13,14]. In addition to the rejuvenating benefits, bio-derived materials can be utilized to allow for the higher RAP addition using traditional hot mix asphalt (HMA) configuration or in the WMA technology. Such applications would improve carbon footprint of the produced material and may positively influence the Life Cycle Analysis (LCA) of asphalt pavement.

Vegetable origin binder may change viscosity of the binder allowing for the lower asphalt mixture production temperature [15]. Once vegetable oils and methyl esters of fatty acids, obtained by transesterification of these oils, are used as bitumen fluxes, hardening of the binder is obtained not by the solvent evaporation to the atmosphere (like for the typical cutbacks) but by crosslinking of the unsaturated fatty acids (as a result of its reaction with oxygen). When acting as a flux agent, they replace the use of conventional petro-chemical products which are flammable and leads to the evaporation to the atmosphere of volatile organic compounds (VOCs) [16].

Gawel et al. [16] presented solutions to optimize the oxidation conditions for rapeseed and linseed oils, as well as the corresponding methyl esters, in order to obtain environmentally-friendly bitumen fluxes.

The other solution based on the replacement of the volatile solvents used in cut-back bitumen was described by Simonen et al. [17]. It consists of linear and branched C10–C20 alkanes. This technology is based on vegetable oils, animal fats and hydrogen. The studies on test road sections suggested that the binding rate for bio-flux was slow, which was confirmed by the low increase in the indirect tensile strength of the mixture.

Critical issue related to application of the bio-derived additive fluxing of the bitumen is the final viscosity of the bitumen and stiffness of the mixture placed in the pavement. While fluxing is desired during mixture production, placement and compaction, it is no longer appreciated once road is open to traffic [18,19]. Pougetand Loup [20] developed solution to assess the linear viscoelastic properties during thermal ageing of semi-coarse asphalt concrete (SCAC) containing bio-binders.

## 2. Objective and scope

This paper discusses a new idea of bitumen fluxing with bio-derived additive. The main objective of the research presented in this paper was to investigate influence of bio-derived additive on binder rheological properties and to assess reversible fluxing action of the bitumen with bioadditive. Such findings can be potentially useful for the application of the bitumen fluxed with bioadditive for surface treatments, HMA recycling or in WMA technology. Bitumen fluxed with bio-derived additive has a large potential for application in RAP technology, since it can, on one hand, improve the technological properties (e.g., improved blending of RAP with virgin materials) and on the other hand can also partially rejuvenate binder in RAP.

This paper is composed of two main parts: the one describing chemical concept of the reversible fluxing process and of the laboratory part. Laboratory experiments were conducted on three bituminous binders with different consistency. In order to assess fluxing effectiveness, bioadditive was added to each binder at four concentration levels. Samples were conditioned to study hardening process as a result of the chemical process – sicativation. Based on the changes in the binder rheological properties, the magnitude of reversible fluxing action was determined.

## 3. Chemical mechanism of vegetable bitumen fluxes hardening

The suitability criterion for vegetable oils and the corresponding methyl esters for obtaining environment-friendly bitumen fluxes is their reactivity to the oxypolymerization reaction, which raises the viscosity of the stock, thus contributing to its hardening and drying. The efficiency of polymerization depends on the number of double bonds and their position in the aliphatic chain of fatty acid. Vegetable oils comprise a variable number of double bonds depending on their composition. The composition of the oils (shown in Table 1) and hence its reactivity to oxypolymerization is genotype-specific and therefore variable and depends on the climatic conditions [21,22].

Drying Oils contain fatty acids with three and two double, such as linolenic or linoleic acids (Fig. 1) [24]. Other most common fatty acids encountered in the composition of vegetable oils are monounsaturated (oleic acid) or saturated acids (stearic and palmitic). The higher the content of polyunsaturated fatty acids in the vegetable oils is increases the reactivity to polymerization process.

Oxypolymerization of the fatty acids present in the vegetable stocks is a multistage process and leads to the crosslinking of their structural units [25]. The primary reactions to be considered are:

- the oxidation and the formation of hydroperoxides,
- the decomposition of hydroperoxides and the subsequent crosslinking.

The initial stage of the oxidation process is a hydrogen abstraction with the alkyl radical formation (Fig. 2). The most susceptible component to oxidation is the methylene carbon adjacent to double bond in the aliphatic chain of fatty acid. Radicals react with the molecular oxygen to peroxy radicals and subsequently hydroperoxides. Addition of the molecular oxygen to the polyunsaturated fatty acid causes conjugation double bond in the aliphatic chain. Hydroperoxides can decompose to alkoxyl radicals leading to the formation of alcohols, ketones or aldehydes and then carboxylic acids.

The termination stage of the polymerization process is crosslinking, as shown in Fig. 2. The formation of higher-molecular compounds occurs by radical addition to conjugated double bonds or radical recombination, with the formation of ether, alkyl and peroxy bridges. However, dialkylperoxides (peroxy bridges) are quite unstable and can decompose to alkoxyl radicals.

**Table 1**
Unsaturation degree and composition of vegetable oils (after [23]).

| Number of double bonds in the aliphatic chain | Fatty acid content, %wt. | | | |
|---|---|---|---|---|
| | Rapeseed oil | Soybean oil | Sunflower oil | Linseed oil |
| 0 | 7 | 20 | 15 | 7 |
| 1 | 63 | 20 | 17 | 18 |
| 2, 3 | 30 | 60 | 68 | 75 |