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Suitability of Chitosan as an emulsifier for cationic bitumen emulsions and its behaviour as an additive to bitumen emulsion

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HIGHLIGHTS

- Chitosan was tested as an emulsifier for cationic bituminous emulsions.
- Chitosan has significantly increased the viscosity of bitumen emulsion.
- Chitosan altered the floating and settling tendency of bitumen emulsion.
- New model was proposed to describe the effect of Chitosan on bitumen emulsion.

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ABSTRACT

Chitosan contains amine and amino groups which have the ability to generate cationic type surfactants when combined with H^+ ions. It has a high potential for use as a cationic emulsifier for negatively charged siliceous aggregates for paving of roads in Sri Lanka. Water soluble Chitosan was tested for suitability as an emulsifier in the production of cationic bituminous emulsions. The amine emulsifier currently in use was fractionally replaced with Chitosan and tested for emulsion properties; emulsion viscosity, storage stability, settlement, sieve test and breaking of emulsion. The viscosity of the emulsion was found to increase significantly from 16 SFS to 50 SFS and from 20 SFS to 72 SFS for Cationic Rapid Setting type (CRS1) emulsion and Cationic Slow Setting type (CSS1) emulsions respectively. For both types of emulsions, an exponential growth in viscosity was found to occur at a critical Chitosan to bitumen ratio of 0.0028. Results of storage stability indicated a tendency for floating, while in the presence of Chitosan, within the first 24 h of preparation. However, a settling tendency developed for both types of emulsion when in longer storage as indicated by a 5 day settlement test. A new model based on the interaction between reactive groups of Chitosan and bitumen emulsion droplets was proposed to describe the effect of Chitosan on bitumen emulsion.

1. Introduction

Bitumen emulsion is used as an alternative to the application of hot molten bitumen in road maintenance and construction work [1]. It develops better interactions with the aggregate at room temperature and releases very low amounts of volatile organic compounds compared to hot molten bitumen [2,3]. The size of droplets in bitumen emulsion is 0.1–20 microns and the bitumen which is the dispersed phase represents 40–75% (w/w) of the emulsion [4]. Water represents 25–60% in the dispersed medium along with 0.1–2.5% of emulsifier and other minor additives.

Bitumen is extracted as the distillation residue of crude oil. There are four main groups of substances in bitumen namely; asphaltene, saturates, aromatics and resins. Asphaltenes are highly polar aromatic complexes which comprise 5–25% of bitumen. Saturates are non-polar aliphatic hydrocarbons mixed with alkyl naphthenes and alkyl aromatics. Aromatics comprise 40–65% of bitumen and are non-polar hydrocarbons with unsaturated rings. Resins are polar structures having small amounts of oxygen, sulphur and nitrogen [5]. Depending on the crude source, the composition of bitumen can vary and hence properties like viscosity can notably vary.

Based on the surface charge of droplets in the dispersed phase, bitumen emulsions are of three types; cationic, anionic and non-ionic emulsions. Cationic type of emulsions are the most commonly used since most aggregates are siliceous in nature and are

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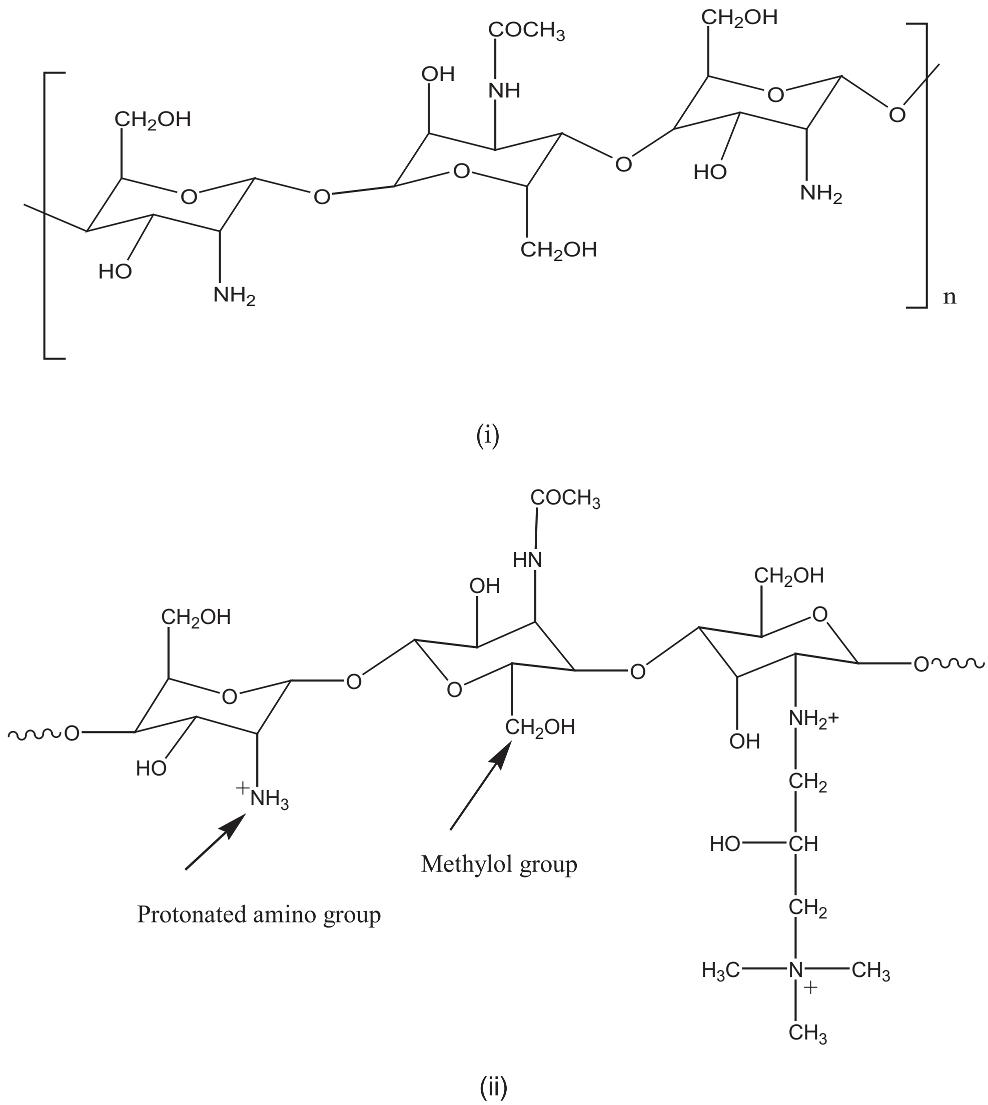

Fig. 1. Structure of (i) Chitosan and (ii) protonated Chitosan.

electronegative [6]. The development of negative charge in siliceous aggregates is mainly due to the deprotonation of silanol groups. The time taken for phase separation and coagulation of bitumen after application is defined as the set time and hence, four types of bitumen emulsions are identified as rapid setting, medium setting, quick setting and slow setting. The most commonly used emulsions in industry are called Cationic Rapid Setting 1 (CRS1) and Cationic Slow Setting 1 (CSS1). CRS 1 emulsions are used in road maintenance work, especially for surface applications such as sand sealing and chip sealing. Such applications require faster set times in order to open the road for traffic. The most important rheological property of CRS1 type emulsions is the viscosity. With lower viscosity, bitumen emulsion can run off while higher viscosity may block the spraying nozzles. CSS1 type emulsions are used in applications such as priming and cold mixing with aggregates having fine fraction which requires a higher setting time. These applications need slower interaction between the aggregate and the emulsion to provide sufficient mixing time before phase separation. Therefore, set time is the most important property for CSS1 type emulsions [6].

Cationic bitumen emulsion is produced using emulsifiers which have the ability of forming cationically charged head groups like fatty amines, fatty amidoamines, fatty imidazolines and fatty quaternary ammonium salts [7–9]. The most common cationic emulsifiers for bituminous emulsions are those consisting of a hydrophobic tail and a lipophilic head group of nitrogenous compounds. The hydrophobic tail may consist of 12–18 carbon atoms and they are commonly produced from a tallow mixture of myristic acid, palmitic acid, stearic acid and oleic acid [10].

Chitosan is a linear polysaccharide having oxo, hydroxyl, ether and amine groups (Fig. 1(i)) as functional groups. Chitosan is manufactured by the deacetylation of Chitin which is extracted from fish waste; exoskeletons of crustaceans such as prawns and crabs. Deacetylation reactions remove the acetyl groups attached to the amino groups of Chitin [11]. Acids such as hydrochloric acid can convert Chitosan to cationic emulsifiers by protonation of the reactive amino groups.

Protonated amine groups in Chitosan (Fig. 1(ii)) provide it with the potential for the formation and stabilization of cationic type oil-in-water emulsions and hence it is used in many different types of oil and water emulsion systems [12–17]. On the other hand, Chitosan is an amphiphilic polyelectrolyte and can therefore combine both electrosteric and viscosifying stabilization mechanisms [18]. Hence, Chitosan could be effectively used in emulsification and stabilization of non-polar substances like paraffin oil without adding any other surfactants. The possible mechanism may be the