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Rheological characteristics of synthetic road binders

Gordon D. Airey *, Musarrat H. Mohammed [1], Caroline Fichter [2]

Nottingham Transportation Engineering Centre, University of Nottingham, Nottingham, NG7 2RD, UK

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Abstract

Most adhesives and binders, including binders for asphalt mixture production, are presently produced from petrochemicals through the refining of crude oil. The fact that crude oil reserves are a finite resource means that in the future it may become necessary to produce these materials from alternative and probably renewable sources. Suitable resources of this kind may include polysaccharides, plant oils and proteins. This paper deals with the synthesis of polymer binders from monomers that could in future be derived from renewable resources. These binders consist of polyethyl acrylate (PEA) of different molecular weight, polymethyl acrylate (PMA) and polybutyl acrylate (PBA), which were synthesised from ethyl acrylate, methyl acrylate and butyl acrylate, respectively, by atom transfer radical polymerization (ATRP). The fundamental rheological properties of these binders were determined by means of a dynamic shear rheometer (DSR) using a combination of temperature and frequency sweeps. The results indicate that PEA has rheological properties similar to that of 100/150 penetration grade bitumen, PMA similar rheological properties to that of 10/20 penetration grade bitumen, while PBA, due to its highly viscous nature and low complex modulus, cannot be used on its own as an asphalt binder. The synthetic binders were also combined with conventional penetration grade bitumen to produce a range of bitumen–synthetic polymer binder blends. These blends were batched by mass in the ratio of 1:1 or 3:1 and subjected to the same DSR rheological testing as the synthetic binders. The blends consisting of a softer bitumen (70/100 pen or 100/150 pen) with a hard synthetic binder (PMA) tended to be more compatible and therefore stable and produced rheological properties that combined the properties of the two components. The synthetic binders and particularly the extended bitumen samples (blends) produced rheological properties that showed similar characteristics to elastomeric SBS PMBs, although their precise viscoelastic properties were not identical.

Keywords: Bitumen; Synthetic polymers; Rheological properties; Viscosity

1. Introduction

Most adhesives and binders, including bituminous binders that are used for road building, are derived mainly from fossil fuels. However, with petroleum reserves becoming depleted and the subsequent need to reduce fossil fuel usage, there is a drive to develop adhesives and binders from alternative sources, especially from renewable sources. Adhesives based on soy protein, starch, cellulose and other polysaccharides have been used over the years for a wide range of adherents such as wood, paper, plastic, metal, leather and glass [1]. Renewable natural resources including sugars, triglyceride oils and proteins have been tested as alternative sources for producing adhesives and binders [1–7]. Large quantities of renewable sources such as triglyceride oils, proteins, starch and other carbohydrates are available from various botanical sources, photosynthetic micro-organisms and algae and there are good technical and economic prospects in utilizing them from these sources. A range of different vegetable oils have been developed in recent years with the knowledge of their physical and chemical properties obtained through the application of scientific research and development [7,8].

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* Corresponding author. Tel.: +44 115 9513913; fax: +44 115 9513909.
E-mail addresses: gordon.airey@nottingham.ac.uk (G.D. Airey), musarrat.mohammed@nottingham.ac.uk (M.H. Mohammed), caroline.fichter@nottingham.ac.uk (C. Fichter).

[1] Tel.: +44 115 98466077; fax: +44 115 9513909.

[2] Tel.: +44 115 9513905; fax: +44 115 9513909.

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This paper presents an initial study of the synthesis of polymer binders from monomers that could in future be produced from triglyceride oils and carbohydrates. The objective of the project is to investigate if these polymers show rheological properties similar to bitumen and if they can replace bituminous materials. Synthetic binders can be used in three ways to ease the demand for fossil fuel based bituminous binders. Firstly, they can be used as a direct alternative binder to traditionally used bitumen (100% replacement). Secondly, these synthetic binders can be used as bitumen modifiers (usually in the order of <10% bitumen replacement) and, thirdly, they can be used as bitumen extenders (part bitumen replacement with percentages between 25% and 75%).

The bitumen modifier market is already very well developed with the use of petroleum derived polymers to modify the performance of conventional bituminous binders dating back to the early 1970s [9], with these modified binders subsequently having decreased temperature susceptibility, increased cohesion and modified rheological characteristics [10–15]. Globally, approximately 75 percent of modified binders can be classified as elastomeric, 15 percent as plastomeric with the remaining 10 percent being either rubber or miscellaneously modified [16,17]. Elastomers modify bitumen by having a characteristically high elastic response and, therefore, resist permanent deformation by stretching and recovering their initial shape. Plastomers modify bitumen by forming a tough, rigid, three dimensional network to resist deformation. Within the elastomeric group, styrenic block copolymers have shown the greatest potential when blended with bitumen [18]. Other examples of elastomers used in bitumen modification include natural rubber, polybutadiene, polyisoprene, isobutene isoprene copolymer, polychloroprene and styrene butadiene rubber. One of the principal plastomers used in pavement applications is the semi-crystalline copolymer, ethylene vinyl acetate (EVA). EVA polymers have been used in road construction for over 25 years in order to improve both the workability of the asphalt during construction and its deformation resistance in service [19–22].

Due to the dominance of traditional polymer modifiers, such as SBS and EVA, the synthetic polymer binders produced in this study were only considered as bitumen replacements and bitumen extenders. Three types of acrylate based polymer binders were produced using atom transfer radical polymerization (ATRP) and their fundamental rheological (viscoelastic) properties determined by means of dynamic (oscillatory) mechanical analysis using a dynamic shear rheometer (DSR) and presented in the form of temperature and frequency dependent rheological parameters. The synthetic polymer binders were also used with conventional bitumen to produce a range of blends (extended bitumen) and their rheological properties were also quantified using the DSR. Finally the synthetic binders and blends were compared with conventional bitumens and standard polymer modified bitumens (PMBs).

2. Synthesis of binders

Samples of polybutyl acrylate (PBA), polyethyl acrylate (PEA) and polymethyl acrylate (PMA) were synthesised from butyl acrylate, ethyl acrylate and methyl acrylate respectively, by ATRP. The ATRP technique involves the abstraction of a halogen from an alkyl halide, methyl-2-bromopropionate (MBP), by a transition metal compound such as copper bromide (CuBr) and a ligand N,N,N',N',N''-pentamethyl diethylenetriamine (PMDETA) in a redox process. This produces an alkyl radical that undergoes propagation as in conventional free radical polymerization. However, the free radicals are also able to abstract the halogen back from the metal, reproducing the dormant species. These processes are rapid, and the dynamic equilibrium that is established favours the dormant species. The concentration of the active radicals is therefore very low, limiting radical–radical coupling/disproportionation reactions as the principal mode of termination.

Butyl acrylate (BA), ethyl acrylate (EA) and methyl acrylate (MA) (all from Aldrich, 99.9%) were distilled at atmospheric pressure over calcium hydride (CaH_2). MBP (Aldrich, 99.9%) and PMDETA (Aldrich, 99.9%) were used as received. CuBr (Aldrich, 98%) was also directly used as received without any further treatment in order to avoid an oxidation of the Cu(I) compound in the open air. A required amount of CuBr was introduced to a three-necked round bottom flask containing a magnetic stirrer and connected with a three-way stopcock and a condenser. The flask was then sealed with a rubber septum and was cycled five times between vacuum and nitrogen, using a high purity nitrogen gas. The mixture containing required amounts of monomer, initiator and ligand was degassed by nitrogen purging for 30 min before it was injected to the reaction flask using a syringe. The reaction flask was then placed in a preheated oil bath at a desired temperature. After a given time, the reaction was stopped by quenching and the reaction mixture was dissolved in tetrahydrofuran (THF). The reaction conditions are given in Table 1. The dissolved polymer solution was passed through a neutral alumina column to remove copper bromide catalyst. The polymer solution was precipitated into a large amount of methanol and water (1:3) mixture. The precipitated polymer was then dried and was characterized by dynamic mechanical analysis (DMA).

Table 1 shows the condition of polymerisation, percentage yield, molecular weight, reaction temperature and reaction time of the polymerized butyl acrylate, ethyl acrylate and methyl acrylate. At a reaction temperature of 50 °C, only a trace amount of product yield was obtained. Therefore, a higher reaction temperature was chosen as lower reaction temperatures produced less radical species, owing to a poor dissociation of C–X (X refers to an halogen atom such as Br, Cl, etc.) bonds in the initiator and in the propagating chain ends. As a result, a few active species were produced and thus only a few monomers experienced a propagation step. This resulted in low percentage yield