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## Masonry units bound with waste vegetable oil – Chemical analysis and evaluation of engineering properties

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### H I G H L I G H T S

- Provides further confirmation of the positive use of recycled binders in construction materials.
- Improves the understanding of the mechanism of the vegetable oil based binder.
- Generates further clarification of the chemical changes that occur during the curing process.
- Examines the significance of the chemical changes on some of the physical properties.
- Apparently the stiffness of the oil is not down to cross-linking and increased molecular weight.

### A R T I C L E I N F O

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### A B S T R A C T

Masonry units with attractive environmental credentials can be produced from waste aggregate materials and vegetable oils. Heat curing at low temperatures induces chemical changes in the binder which stiffen the block and afford them a compressive strength which can be compared to existing blocks and bricks. This method allows use of 100% waste materials, which far exceeds the level of replacement possible in traditional concrete and clay matrices. To better understand the chemistry of the vegetable oil binder at different stages of the curing process a range of experiments have been performed including infrared spectroscopy, liquid chromatography and mass spectrometry. Results show production of chain-shortened and oxygenated derivatives and the nature of reactions based on curing time and physical environment of the binder. Compressive strength and mass loss are dependent on curing time and the altered molecular architecture of the oil, but other physical properties are independent of the chemistry and reliant on physical concerns such as aggregate selection.

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### 1. Introduction

The promotion and development of green construction materials has been increasing in recent years, in line with efforts by governments and industry to attempt to reduce energy consumption and carbon emissions. Attempts to improve the environmental credentials of ubiquitous construction materials such as concrete blocks and clay bricks tend to involve the incorporation of wastes or recycled materials either as part of the binder matrix or aggregate portion. A substantial field of research concerning supplementary cementitious materials exists to examine the pozzolanic

properties of incinerator wastes and industrial by-products [1,2]. Such efforts make valuable use of chemically active or inert wastes, thus diverting them from landfill. However, the upper limit of material that can be included without significant detriment to performance tends to be low.

An alternative approach to green construction is the revival of traditional building techniques and vernacular architecture; the use of locally available, sustainable materials typically applied to low-rise construction. Examples include adobe, rammed earth, timber, straw bales and unfired clay bricks [3]. Some of the materials have low strengths, but many have very attractive thermal and acoustic insulation alongside their low embodied CO<sub>2</sub> values.

This study enhances previous work utilising waste aggregate containing building products which used bitumen as a binder [4].

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Manufacture of these units required a step in which the bitumen and aggregates were pre-heated to facilitate mixing. Subsequent modifications employed the addition of waste vegetable oils to the bitumen and aggregate mixture, removing the requirement for the pre-heating step. The results presented in this paper were then the next logical step, with the vegetable oils themselves trialled as the sole binder. The waste vegetable oil binder and waste aggregates can be mixed, compacted and heat cured at low temperatures to form a masonry unit with a compressive strength of 8–10 MPa [5]. The change in strength upon curing was indicative of chemical changes in the oil and therefore a driver for the current investigation. Many assumptions can be and were drawn about the nature of the reactions occurring in the oil during the curing process based on the complex process of free radical oxidation that occurs at the carbon–carbon double bonds in the fatty acid chains present in triacylglycerols (TAGs). Background information is provided by the wealth of literature in food science publishing [6–10] and papers concerning oil-based paints [11,12]. There was, however, a requirement for specific chemical investigation of these units due to the unique physical environment in which the oil is heated and the nature of the aggregates used. The groundwork for durability studies and the stability of the binding matrix will require an understanding of this chemistry, even if full characterisation of the vast range of species is an unrealistic or unnecessary goal.

Fourier Transform Infrared Spectroscopy (FTIR) with an Attenuated Total Reflectance (ATR) is a tool that permits the collection of ‘chemical fingerprint’ from a material providing detailed information about its composition and structure. When coupled with a heated stage, it facilitates the analysis of *in situ* measurements of changes that occur during thermal treatment, such as oxidation [13] or gelation [14]. Some products of isomerisation and secondary oxidation not previously noted were highlighted by the time-resolved spectroscopy and spectral processing. Analysis of early stage products via High Performance Liquid Chromatography (HPLC) and offline Electrospray Ionisation Mass Spectrometry (ESI–MS) provided insight into the oxidation mechanisms in the first 4 h of the curing process, as well as some new information about the concentrations and nature of chain-shortened products. Chemical analysis was complemented by selected tests of engineering properties such as compressive strength testing, mass loss during curing, volumetric and gravimetric stability after curing. The work provides an early paradigm and insight into the structure of the system, which is a valuable addition to the canon of green construction. It also supplements and relates to chemical information obtained from studies by Nuclear Magnetic Resonance (NMR) spectroscopy [15], in which consumption of unsaturated hydrocarbons was monitored and signals attributable to secondary oxidation products including aldehydes and epoxides were found.

## 2. Materials and methods

Clean rapeseed oil (KTC, Wednesbury, UK) and the corresponding post-frying waste product were supplied by the University of Leeds catering services. The oil is a standard culinary vegetable oil and the initial approximate fatty acid composition is 62% monounsaturated, 30% polyunsaturated and 8% saturated [16]. The waste rapeseed oil is discarded at discretion based on visual inspection and odour. The waste oil was not processed except for filtering to remove solids and was stored under ambient conditions away from direct sunlight. Thin films of oil cured in the absence of aggregate were prepared by deposition of oil in a petri dish subject to curing in a convection oven at  $160 \pm 5^\circ\text{C}$  and samples were taken at various time intervals, being cut out of the films and stored in Eppendorf tubes at room temperature 24–48 h prior to analysis. This treatment shows how the viscosity of the oil increases and how it changes from a liquid to a gummy, sticky solid.

Block sample preparation was undertaken as described previously [4,5]. In brief, a mixture of waste or model aggregate and oil were mechanically mixed and transferred to  $100 \times 100$  mm steel moulds, compacted at 4 MPa in a hydraulic press, demoulded and cured in a convection oven at  $160 \pm 5^\circ\text{C}$ . Sample details are shown in Table 1. The incinerator bottom ash (IBA) was received from a municipal solid

**Table 1**

Sample properties (aggregate percentages are described in terms of the dry weight total).

Sample type	Coarse aggregate	Fine aggregate	Oil (wt.%)
IBA block	90% IBA < 10 mm	10% IBA < 0.5 mm	12
Glass powder block	None	100% Glass powder < 0.5 mm	30
Thin film	None	None	100

waste incinerator in Rainham, courtesy of Veolia environmental services (UK), and was screened through a 10 mm sieve. A fine filler material was also produced from it by passing through a solid waste grinder with a 0.5 mm aperture sieve screen. Aggregates were oven dried at  $105 \pm 5^\circ\text{C}$  prior to storage. For the HPLC and ESI–MS analysis, block samples were prepared with a soda lime glass powder as a clean model aggregate in lieu of incinerator ashes. Samples for analysis were chiselled from the arrises of the cured blocks.

All infrared spectra were recorded on a Thermo Nicolet Nexus FTIR spectrophotometer using a Graseby Specac Golden Gate temperature controlled single reflection diamond ATR accessory and a liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detector. Spectra of the pre-formed samples were acquired using a resolution of  $4\text{ cm}^{-1}$  and 64 scans using the clean ATR crystal as a background reference. For the *in situ* curing study the number of scans was reduced to 32 to improve temporal resolution. ATR–FTIR requires intimate contact between the sample and the ATR crystal as it collects the spectrum from the few microns at the sample/ATR crystal interface [17]. The pre-formed samples were clamped between the ATR crystal and a sapphire plate using a calibrated torque driver set at 90 cNm to ensure intimate contact. For the *in situ* experiments, the temperature of the ATR accessory was set to  $160^\circ\text{C}$  and 50  $\mu\text{l}$  of waste oil was deposited directly on the ATR crystal surface. For these data both the clean ATR crystal and the sample at  $t = 0$  min were used as background references.

Chromatography was performed on a Dionex (Camberley, UK) system with a P680 quaternary pump and a membrane degasser, ASI-100 sample injector and PDA-100 photodiode array detector set to a primary wavelength of 215 nm and a secondary range of 210–230 nm. A C18 Zorbax ODS analytical column (length = 250 mm, diameter = 46 mm, particle size = 5  $\mu\text{m}$ , pore size = 300 Å) with a guard cartridge of the same type (Agilent) was used. Acetonitrile, propan-2-ol (Fisher, Loughborough, UK) and hexane (Acros, Geel, Belgium) were all HPLC grade. The acetonitrile and propan-2-ol made up the mobile phase and the bulk of the injection mixture and were vacuum filtered prior to use. The injection mixture was 58% acetonitrile, 37% propan-2-ol, 5% hexane (v/v/v), which has been used as a mobile phase composition [18].

Clean and waste oil samples were dissolved in the injection solvent to a concentration of 10 mg/ml. The absolute concentration of cured samples could not be measured, since solubility varies upon curing. However, a decrease in solubility was observed as curing progressed, due to formation of cross-links. These samples were washed and vortexed thoroughly with an amount of the injection solvent proportional to a concentration of 10–15 mg/ml; where the latter value assumes a yield of 100% solubility. All samples were spun at 13,000 rpm for five minutes in a bench-top centrifuge and the supernatant retained. The samples recovered from blocks were spun down twice; once to pellet the bulk of the solid material and the supernatant was spun again to ensure no glass powder fines which could cause damage to the equipment remained.

A gradient of acetonitrile into propan-2-ol was used throughout. The gradient programme was 0–5 min, 0–30% propan-2-ol linear, 5–60 min 30–80% propan-2-ol linear, held for 10 min and returned to 100% acetonitrile and held for 15 min re-equilibration. The flow rate for all analyses was 0.5 ml/min and the column oven temperature was  $25^\circ\text{C}$ . Injection volume was 20  $\mu\text{l}$ . All samples collected were stored in varying proportions of the mobile phase solvent mixture from the HPLC analysis, i.e. directly transferred from fraction tubes to Eppendorf tubes and stored at  $-20^\circ\text{C}$ . Fractions obtained from the oxidised oil samples were diluted 1:1 with 20 mM ammonium acetate but were also diluted with the injection solvent mixture from the HPLC analysis (acetonitrile/propan-2-ol/hexane, 58/37/5) where necessary to obtain a suitable mass spectrum for ion selection for MS/MS.

MS and MS/MS analysis was performed by Z-spray nano-electrospray ionisation mass spectrometry on a quadrupole-IMS-orthogonal time-of-flight mass spectrometer (Synapt HDMS; Waters UK Ltd., Manchester, UK). The mass spectrometer was operated in positive ion TOF–MS mode with a capillary voltage of 1.9 kV, cone voltage of 25 V, nano-electrospray nitrogen gas pressure of 0.1 bar, backing pressure of 2.34 mbar and a trap bias of 4 V. The source and desolvation temperatures were set at  $80^\circ\text{C}$  and  $350^\circ\text{C}$  respectively. During TOF–MS acquisition, nitrogen was used as the collision gas in the Triwave, with a pressure of  $2.4 \times 10^{-3}$  mbar in the trap and transfer regions and  $2.64 \times 10^{-4}$  mbar in the IMS cell. For MS/MS analysis the precursor ion was selected by the quadrupole and dissociation of the precursor was induced in the trap region of the Triwave device by increasing the potential difference between the source and trap ion guides. Data were acquired over the mass range for a minimum of one minute. Mass calibration was performed by a separate injection of sodium iodide at a concentration of  $2\text{ }\mu\text{g}\text{ }\mu\text{L}^{-1}$ .

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