Dyes and Pigments 123 (2015) 304–316

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Dye conjugation to linseed oil by highly-effective thiol-ene coupling and subsequent esterification reactions

Toshiki Hayashi [a], Algy Kazlauciunas [b], Paul D. Thornton [b, *]

[a] National Printing Bureau of Japan, Odawara, Kanagawa 256-0816, Japan
[b] School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

ARTICLE INFO

Article history:
Received 17 June 2015
Received in revised form
14 July 2015
Accepted 19 July 2015
Available online 29 July 2015

Keywords:
Renewable resources
Linseed oil
C. I. Disperse Red 1
Thiol-ene chemistry
Dye conjugation
Coloured coatings

ABSTRACT

Linseed oil, a renewable material obtained from the ripened seeds of the flax plant, was conjugated with C. I. Disperse Red 1 to yield a coloured macromolecule in two experimentally-simplistic coupling steps. Firstly, the abundant presence of carbon–carbon double bonds in linseed oil was exploited to introduce carboxylic acid functionality to linseed oil *via* a thiol-ene reaction between linseed oil and 3-mercaptopropionic acid. C. I. Disperse Red 1 was then grafted to the carboxylic acid units now present *via* esterification, offering a coloured product in high yields. On average, 39.2% of the carbon–carbon double bonds in each linseed oil molecule were furnished with a C. I. Disperse Red 1 molecule. The remaining carbon–carbon double bonds may therefore be further exploited for chemical crosslinking, ensuring that the product formed is of potential significance as a coloured, bio-based, surface coating product.

1. Introduction

Plant oils are naturally occurring molecules that offer several advantageous features including renewability, biodegradability and cost-effective production. The positive environmental and economic attributes of plant oils have been utilised to synthesise polymers including polyurethanes [1,2] and polyesters [2,3]. Additionally, plant oils have been exploited in the creation of numerous products including coatings and inks [4–8], liquid resin moulds [9,10], plasticisers [10,11], hardeners [12,13], diluents [14], lubricants [15,16], and emollients [17].

The main component of plant oil is a triglyceride molecule that possesses a structure consisting of three linear fatty acid chains that are conjugated to a glycerine molecule by ester bonds [10]. The fatty acid chains are derived from various fatty acids; plant oils have a distinctive composition depending on the plant from which they are obtained and the growing conditions of the plant [10,18]. We are particularly interested in utilising linseed oil (**1**) (Fig. 1) for the development of coloured, bio-derived coatings. Linseed oil is a drying oil, in which each triglyceride molecule contains 6.6 carbon–carbon double (C=C) bonds on average [10]. This plays a vital role in enabling the oil to dry *via* auto-oxidation [19,20]. Linseed oil contains fatty acid chains derived from linolenic acid (18:3, 56.6%), oleic acid (18:1, 19.1%), linoleic acid (18:2, 15.3%), palmitic acid (16:0, 5.5%), and stearic acid (18:0, 3.5%) [10], where the figures in the brackets signify the number of carbon atoms in each fatty acid chain versus the number of C=C bonds, and the content ratio of each fatty acid chain present in linseed oil, respectively. The abundant linolenic acid content of oil promotes its relatively fast drying (or hardening) and suitability to be exploited as a coating product.

The chemical modification of plant oil [10,21–24] may be conducted on several sites present within the chemical structure of the oil including C=C bonds, allylic carbons, ester bonds, and the α-carbon of the ester bonds [10]. Although a limited number of plant oils possess additional functionality, for example the hydroxyl groups that are present in castor oil [25], the introduction of reactive groups to plant oils is imperative to enhance the reactivity of plant oils, and enables the subsequent introduction of functional groups to the oil [10]. Selecting the appropriate type and number of reactive groups, incorporated within the oil enables its properties, including the glass transition temperature and mechanical characteristics, to be altered to match the desired levels [26,27].

There are a number of examples that detail the use of the C=C sites in plant oils for chemical modification. For instance,

---

* Corresponding author. Tel.: +44 (0)113 343 2935; fax: +44 (0)113 343 6565.
E-mail address: paul.d.thornton@leeds.ac.uk (P.D. Thornton).

http://dx.doi.org/10.1016/j.dyepig.2015.07.023

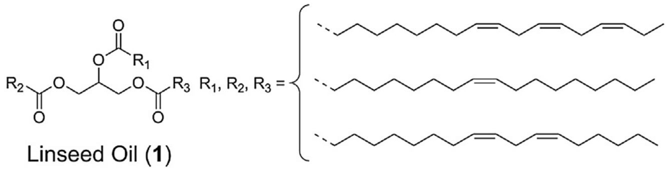

Fig. 1. Chemical structure of linseed oil (**1**). Three main fatty acid chains are shown here.

epoxidised plant oils, particularly epoxidised linseed oil (ELO) [14,26,28] and epoxidised soy bean oil (ESO) [10,14], have received considerable attention as bio-based thermosetting resins with the potential to act as alternative materials to petroleum-based products. Various plant oil-based thrermosets were created by reacting ELO or ESO with cyclic anhydride hardeners such as maleic anhydride or phthalic anhydride [3,28]. ELO and ESO can also be converted into acrylated epoxidised linseed oil (AELO) [5,28] and acrylated epoxidised soy bean oil (AESO) [10,26], respectively, by heating with acrylic acid. They are subsequently formulated to make thermosets by using a diluent such as styrene. Norbornene rings and cyclopentadiene rings have also been introduced into soy bean oil to make homogeneous thermosets that are commercially available as Diluin® (Cargill Industrial Specialties) and ML189 (Archer Daniels Midland Company), respectively [29]. Further examples of thermosets made by the modification *via* the C=C bond of plant oils include the introduction of hydroxyl [1], carboxyl [13], enone [30], aldehyde [31] and phosphorous-based groups [32].

Herein, we present a method to efficiently convey colour to linseed oil through the conjugation of C. I. Disperse Red 1 (DR1) *via* the formation of covalent bonds. This enables the uniform dye distribution into the substrate, preventing dye aggregation. DR1 is a commercially available dye that exhibits second-order nonlinear optical (NLO) effect [33] and photo-responsive properties based on light-induced *trans-cis* isomerisation [34]. The synthesis was accomplished in two straightforward reaction steps. Firstly, thiol-ene click (TEC) reactions are exploited to provide carboxyl (COOH) groups to linseed oil through a reaction with 3-mercaptopropionic acid. This reaction proceeds by following a simple reaction mechanism leading to high product yield, without hindrance by water and oxygen and the production of undesirable side products [35,36]. Esterification was then employed to graft DR1 to the functionalised linseed oil, yielding the desired product in a good, highly reproducible, yield. We have proposed the method of producing a thiol-bearing DR1 *via* chemical modification of DR1, aiming to incorporate the dye into alkene-containing materials by TEC reactions [37]. The method we propose here offers the advantages of simpler reaction procedures and the need for less amount of dye compared to the previous method. It is envisaged that the materials generated are excellent candidates for further employment as precursors to bio-derived coloured coatings.

2. Experimental

2.1. Materials

Linseed oil, C. I. Disperse Red 1 (dye content 95%), 2, 2′-azobis(2-methylpropionitrile) (AIBN), and 4-(dimethylamino)pyridine (DMAP) were purchased from the Sigma–Aldrich Chemical Company. Dichloromethane (DCM), 3-mercaptopropioic acid and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) were supplied by Alfa Aesar. All the materials were used as received.

2.2. Synthesis

2.2.1. Reaction 1: synthesis of modified linseed oil (3)

Linseed oil (**1**) was reacted with 3-mercaptopropioic acid (**2**) in order to furnish **1** with pendant COOH units yielding modified linseed oil (**3**) (Scheme 1 Reaction 1). The COOH group enables **1** to readily react with the hydroxyl (OH) group of DR1 by forming an ester bond in the next reaction step. The average molecular weight of **1** was assumed to be 873.60 g/mol based on reported literature value [10]. In order to prevent oxidation, the equipment was purged with nitrogen prior to the reaction. A mixture of **1** (2.62 g, 3.00 mmol), **2**, and AIBN (325 mg, 1.98 mmol) was added to a round bottom flask and the mixture was heated with stirring at 80 °C under a nitrogen atmosphere for up to 30 h. DCM (50 mL) was then added to the mixture, and the organic layer was washed with sodium chloride aqueous solution (50 mL) four times, then water (50 mL) twice. Following this, the organic layer was dried over anhydrous sodium sulphide. The product underwent heating at 80 °C under reduced pressure for 7 h. A pale yellow clear oil was obtained. The reactions were carried out by varying the amount of **2**, ranging from 0.2 eq. (0.344 mL, 3.95 mmol) to 2.0 eq. (3.45 mL, 39.6 mmol), relative to the amount of C=C bonds (6.6 per molecule) in linseed oil [10]. A blank experiment without **2** was also conducted.

2.2.2. Reaction 2: synthesis of DR1-conjugated linseed oil (5)

The modified linseed oil **3** was then grafted with DR1 (**4**) by esterification [38] to yield DR1-conjugated linseed oil (**5**) (Scheme 1 Reaction 2). 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) was used as a condensation reagent and 4-(dimethylamino) pyridine (DMAP) was used as a catalyst. The average molecular weight of **3** was assumed to be 1282.26 g/mol as calculated from equation (6) (See Supplementary Information for all equations used in this paper). In a round bottom flask maintained under nitrogen, **3** (256 mg, 0.200 mmol), **4** (194 mg, 0.618 mmol), and DMAP (11 mg, 0.090 mmol) were dissolved in DCM (20 mL). A solution of EDC (295 mg, 1.54 mmol) in DCM (10 mL) was added to the flask at room temperature. Stirring at room temperature was then done for varied durations. Following the reaction, washing was performed in the same way as for reaction 1. Following the complete removal of DCM from the organic layer by evaporation, **5** was obtained as a reddish oil. However, unreacted **4** was present as a solid and so the amount of **4** was decreased to the optimal amount (167 mg, 0.532 mmol) (see section 3.2.2), and the same reaction procedure was repeated. The product, **5** was then obtained as a homogeneous reddish oil.

2.3. Characterisation of modified linseed oil (3) and DR1-Conjugated linseed oil (5)

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard, and analysed using MestreNova® Research Lab software. The FT-IR spectra were measured using an ALPHA FT-IR Spectrometer (Bruker Optik GmbH) over a range of 4000–400 cm^{-1}. Mass spectra were measured with a Bruker Maxis Impact mass spectrometer equipped with an electrospray ionisation (ESI) source in positive ion mode over a m/z range of 250–3000.

Thermogravimetric analyses (TGA) were undertaken using a TA Instruments TGA Q50 over the temperature range of +30 °C to +500 °C. The measurements were done at a heating rate of +10 °C/min under a dry nitrogen flow of 40 mL/min for the balance purge flow, and 60 mL/min for the sample purge flow. The onset temperature of the samples was obtained by extrapolating each curve by step transition mode using Universal Analysis 2000