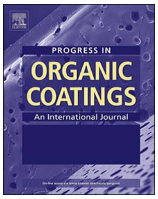
Progress in Organic Coatings 111 (2017) 354–360

Contents lists available at ScienceDirect

Progress in Organic Coatings

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



Preparation and characterization of polymeric dispersants based on vegetable oils for printing ink application

Nadia A. Yossif[a], Nadia G. Kandile[a], Mohamed A. Abdelaziz[b,*], Nabel A. Negm[c]

[a] Chemistry Department, Faculty of Women, Ain Shams University, Cairo, Egypt
[b] R & D Department, Degla Chemicals, Cairo, Egypt
[c] Petrochemicals Department, Egyptian Petroleum Research Institute, Cairo, Egypt

ARTICLE INFO

Keywords:
Vegetable oils
Printing inks
Polymeric dispersants
Pigment
Castor oil

ABSTRACT

In this work, a novel vegetable oil-based polymers were prepared by epoxidation of soybean oil (SBO) and castor oil (CO) followed by ring opening reaction of epoxidized oil with polyether amine and poly propylene glycol. The prepared polymers were characterized by FTIR and GPC. The properties of vegetable oils and epoxidized vegetable oil (EVO) were studied. The prepared polymers were employed as novel polymeric dispersants for pigment dispersion in solvent based printing ink application. The mechanical and optical properties of prepared ink were studied. The net technical properties of the new ink formulations are relatively comparable to the prepared printing ink from standard polymeric dispersant. The polymeric dispersant 2 (PD2) and polymeric dispersant 4 (PD4) gave the best optical and mechanical properties among the prepared polymers.

1. Introduction

The manufacture of printing ink is a technologically advanced, highly specialized and complex process [1]. Preparation of stable, homogeneous and fine dispersion of pigment is not facile because it's prone to aggregate. The dispersion of pigment is strongly affect the optical properties such as color strength, transparency, gloss and mechanical properties such as adhesion of printed ink film [2–4]. Stabilization of pigment dispersion is usually results from adsorption of dispersing agent molecules from solution onto the particle surface of the pigment creating repulsive forces between the particle in suspension either through electrostatic repulsion or from steric prevention of coagulation. The degree of dispersion of a particle suspension may be defined as the extent to which the individual powder particles become separated from one another in the liquid medium [4–6]. Polymeric pigment dispersants are copolymers with pigment affinic "anchoring groups" and soluble polymeric chains [7,8]. The polymeric dispersants are used to obtain homogeneous dispersion of the pigment in the liquid phase that leads to weak viscosity and allows high pigment loading and high tinting strength [9–11]. Coating and ink additives are used in small quantities; however their impact on coating performance and application can be dramatic. Their judicious use often spells the difference between meeting ultimate performance requirements or failure. There are over two dozen additive types employed in coatings and inks with global sales in 2009 of just over USD 5 billion. The main leading types of these additives are dispersants, foam control agents, rheology modifiers, slip & rub materials, and wetting agents. Global consumption of these five additives in 2009 was 781,000 tons worth USD 3.47 billion. Overall, a 5.5% annual rate of growth is forecast for additives through 2010 [12]. Nowadays there are three groups of polydispersing agents produced by BASF: polyurethane of high-molecular-weight (Efka®4000 Series), and low molecular weight (Efka®5000 and Efka®6000 Series) and polyacrylate polymer dispersants (Dispex®, Pigment disperser and Ultradispers® range). Polyurethanes are the best dispersants for viscosity depression in the mill base. This gives higher pigment loadings, more economical mill base formulations with fewer volatile organic compounds (VOCs). Polyacrylates polydispersants have much wider compatibility in non-polar as well as highly polar systems. They generally have a higher molecular weight, which ensures effective inter-particle separation. Health-related issues, stringent environmental protection policies, search for cost-effective and alternative materials and the quest for renewability, sustainability and high-performance materials for technical applications have led to intense research in the production of renewable polymers from plant seed oils and shift in focus from the petrochemical based polymers [13,14]. Vegetable oils are a part of large family of chemical compounds known as fats or lipids which made up predominantly of triesters of glycerol and fatty acids (Fig. 1) which can be processed into high value oleochemicals for various industries [15,16].

The fatty acids of vegetable oils may be saturated and unsaturated

---

* Corresponding author.
E-mail address: zezo_maaan1@yahoo.com (M.A. Abdelaziz).

http://dx.doi.org/10.1016/j.porgcoat.2017.06.005
Received 5 January 2017; Received in revised form 3 June 2017; Accepted 3 June 2017

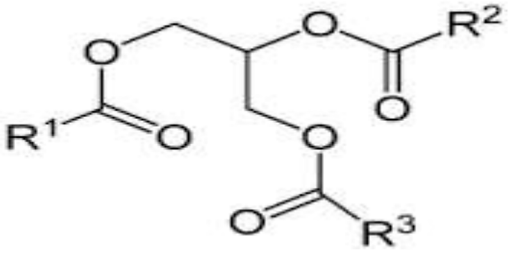


Fig. 1. Triglyceride chain containing three fatty acids by a glycerol center.

fatty acids. Castor oil, cottonseed oil, linseed oil, jatropha oil, rapeseed oil and soybean oil are examples on vegetable oils [16,17]. The unsaturation present (double bond) in vegetable oils can be chemically modified to form epoxidized vegetable oils [17–19]. Epoxidation of double bond has been studied in many papers [20–24]. Epoxidation is generally performed using organic peracids formed in situ via the attack of H_2O_2 on a carboxylic acid in aqueous solution [22]. Due to the high reactivity of the oxirane ring, epoxides can also be used for the synthesis of chemicals like olefinic, carbonyl compounds, alcohols, alkanolamines, glycols and polymers like polyurethanes, epoxy resin, polyesters [23–25].

Since vegetable oils are ecofriendly, sustainable and renewable; both castor oil and soybean oil were the target of this work. Castor oil is obtained from the seeds of the castor oil plant Ricinus. It consists of about 90% ricinoleic acid (12-hydroxy-*cis*-9-octodecenoicacid) which makes it a very useful for industrial purpose like cosmetics, paints, adhesives, plastics, rubbers, and pharmaceuticals [26–28]. Similarly, the major fatty acid in its chemical structure is linoleic acid. Thus these oils were greatly utilized in versatile industrial fields including: coatings, printing inks, adhesives, lubricants and plastics [29–36]. Figs. 2 and 3 represent the structures of castor oil and soybean oil, respectively.

Among the various reactions of oxiranes aminolysis is a classical route to β-amino alcohols formation, an important class of compounds with pharmaceutical and biological properties [37]. Many compounds were prepared by the aminolysis of epoxides with amines under basic or acidic catalysts in organic solvents [38–40]. The chemical structure of Jeffamine is represented in Fig. 4. In the present study, we report the synthesis of ecofriendly polymeric dispersant for pigmented ink application by epoxidation of Soybean oil, Castor oil followed by ring opening using polyether amine and poly propylene glycol.

2. Experimental

2.1. Materials

Chemicals were obtained as follows: polyether amine Jeffamine M-2005 (MW = 2000 g/mol) (Huntsman-Belgium), polypropylene glycol (Invista Specialty Chemicals), castor oil (CO) and commercial cooking-grade soybean oil (SBO) (a local market), ethyl acetate and methanol (Petrochem-KSA), hydrogen peroxide 50% (Piochem), zinc chloride, magnesium sulfate and *p*-toluene sulfonic acid (Oxford), formic acid, acetic acid, sodium chloride, sodium carbonate (ADWIC-Egypt).

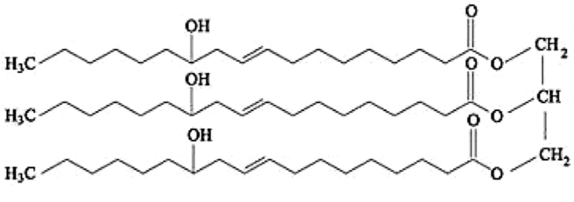


Fig. 2. Major triglyceride of castor oil.

2.2. Preparation of polymeric dispersants

2.2.1. Epoxidation of vegetable oil

Vegetable oils (50 g) and acetic acid (11.4 mL, in case of castor oil) or formic acid (15 mL, in case of soybean oil) were mixed in a round bottom flask and stirred at 550 rpm under controlled temperature through using a water bath at a temperature of 50 ± 2 °C. To start the epoxidation, hydrogen peroxide 50% solution (26.4 mL) was added drop wisely into the reaction mixture during the first 2 h of the reaction. The molar ratio of the double bonds in the reacted oils (obtained from iodine value of the oil) to hydrogen peroxide ($C{=}C{:}H_2O_2$) was 1:1.7. After the charging of H_2O_2 was completed, the reaction continued under mixing and controlling the temperature at 50 °C for a further 5 h then the mixture was cooled to room temperature [41–43]. To purify the epoxidized oil, it was poured into a 500 mL separating funnel and the oil layer was washed successively with 5% sodium carbonate solution (50 mL) and 5% sodium chloride solution (50 mL), respectively. Ethyl acetate (50 mL) was added to enhance the separation of the oily product from the water phase. The water and solvent were then distilled off under a rotary vacuum evaporator; the oil phase was further dried above anhydrous magnesium sulfate and then filtered, (Scheme 1).

A series of polymeric dispersants were prepared based on two different types of epoxidized vegetable oils (Epoxidized soybean oil, Epoxidized Castor oil) by conventional epoxidation method followed by ring opening using polyether amine and poly propylene glycol.

2.2.2. Preparation of polymeric dispersant 1 (PD1)

PD1 was prepared by ring opening of epoxidized soybean oil in which epoxidized oil (20 g) was mixed with methanol (1.9 mL) in presence of *p*-toluene sulfonic acid as a catalyst and ethyl acetate (100 mL) as a solvent at 50°C for partially ring opening of epoxidized oil. The partially ring opened epoxidized oil was cool down, Jeffamine M-2005 (40 g) was added and the temperature was raised to 75 – 80°C in presence of $ZnCl_2$ as a catalyst. The reaction mixture was left for 4 h then cooled to room temperature [44]. The prepared polymer was purified by filtration of solid catalyst. The excess ethyl acetate was distilled by vacuum distillation to obtain product of approximately 100% solid content.

2.2.3. Preparation of polymeric dispersant 2 (PD2)

PD2 was prepared using epoxidized soybean oil (10 g) following the previous method for preparation of PD1, but using jeffamine M-2005 (20 g) for ring opening of the epoxidized oil [23].

2.2.4. Preparation of polymeric dispersant 3 (PD3)

PD3 was prepared by ring opening of epoxidized soybean oil (10 g) using polypropylene glycol (20 g), where epoxidized soybean oil and polypropylene glycol were mixed in 250 mL round bottom flask in the presence of *p*-toluene sulfonic acid as a catalyst at a temperature of 110°C for 8 h; ethyl acetate (100 mL) was added to the reaction mixture as a solvent [49]. The prepared polymer was filtered and washed by water to remove the catalyst. The excess water and ethyl acetate was distilled by vacuum distillation to obtain product of approximately100% solid content.

2.2.5. Preparation of polymeric dispersant 4 (PD4)

PD4 was prepared by ring opening of epoxidized castor oil (ECO) where ECO (10 g) was mixed with Jeffamine M-2005 (20 g) in 250 mL round bottom flask in the presence of $ZnCl_2$ as a catalyst at 60–70°C for 4 h. Ethyl acetate (100 mL) was added to the reaction mixture as a solvent [23]. The prepared polymer was purified by filtration of solid catalyst, and the excess ethyl acetate was distilled using vacuum distillation to obtain a product of approximately 100% solid content.