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Modification of Safflower Oil with Triallyl Ether Acrylate Dienophile

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Abstract: Alkyd resins and reactive diluents, which are among the main components of dye and coating industries, have properties such as binding and ease of application. In order to improve the film properties of alkyd resins, a wide variety of modification studies are carried out. In this study, safflower oil was modified with triallyl ether acrylate dienophile (TAEA) with Diels - Alder reactions and the product was called as triallyl ether acrylate safflower oil (TAEASO) reactive diluent. TAEASO has been characterized by Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Spectroscopy (FT-IR) techniques. Then, the different dye formulations were prepared with certain proportions of TAEASO, wetting and drying agents and a soy oil (SO) based alkyd resin. Dye formulations were called as SO, TAEASO10-SO, TAEASO20-SO, TAEASO30-SO, TAEASO40-SO. The viscosity reductions of the dye formulations were determined and then the dye formulations were applied to surface of aluminum plates as a film. The film properties such as drying time, film thickness, pencil hardness, brightness were evaluated after the curing process. The results show that the viscosity reduction is proportional to the ratio of the TAEASO. As a result of the study, the drying time for the reactive diluent with alkyds were 1.5 times faster than alkyd alone.

Keywords: Alkyd, Diels-Alder, safflower, triallyl ether acrylate.

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INTRODUCTION

In recent years, many studies have been carried out to develop an "environmentalist" dye and coating systems (1, 2). In these studies, seed oils are considered as an alternative since they are biodegradable, easily accessible, and renewable. Seed oils are divided into three different categories: drying, half-drying and non-drying according to the number of unsaturated bonds in the fatty acid chain. In the production of binders that are important for the dye and coating industry, seed oils with a high number of unsaturated bonds such as safflower oil, soybean oil, flax oil and tung oil are widely used. The binders produced with these oils form the polymer film easier when applied to the surfaces, thus increasing the drying rate and reducing the drying time. The formation of a polymer film containing a seed oil-based binder is called an auto-oxidative curing.

The auto-oxidation process first begins with the attack of the molecular oxygen to the unsaturated bonds in the fatty acid chain and then is followed by homolytic cleavage of the peroxide to form free radicals. The hydrogen is then separated by isomerization from the methylene group between the C-C bonds (2, 3).

The safflower plant is connected to the family named Compositae (Asteraceae) in Latin and can be planted annually, winter and summer. The oil content of this plant is about 25-27%. This rate has reached up to 46-47% with scientific researches (4). The safflower, which is light in color, has an important place among the oil crops due to its high content of linoleic acid (5). The proportion of linoleic acid and oleic acid in safflower oil is 81% and 10%, respectively. Safflower oil is in the class of drying oils due to its high rate of linoleic acid. Drying oils contain many double bonds in their structures. Linoleic acids are called diene according to the number of double bonds they contain in their structures.

Diels-Alder reactions are a cyclo-addition reactions commonly known in organic chemistry, based on the formation of a ring structure by conjugated diene and dienophile (6-9).

The aims of this study was to develop new materials to replace the need for organic solvents in alkyd-based coatings with more environmentalist reactive diluents and improve the film properties of alkyd resins (10-12). In this study, safflower oil was modified with triallyl ether acrylate dienophile (TAEA) with Diels - Alder reactions and the product was called as triallyl ether acrylate safflower oil (TAEASO) reactive diluent. TAEASO has been characterized by NMR and FT-IR techniques. It was investigated that TAEASO cannot be used as a reactive diluent in alkyd systems. The film properties (viscosity reduction, drying time, gloss and pencil hardness) of alkyd films prepared with TAEASO were investigated.

EXPERIMENTAL

Material and methods

Safflower oil has been obtained from Kayseri in Turkey. Phenothiazine, pentaerythritol triallyl ether (PETAE), acrylic acid (AA), dichloromethane and p-toluene sulfonic acid (p-TSA) have been purchased from Sigma Aldrich.

General procedure

Triallyl ether acrylate (TAEA) modified safflower oil has been prepared by two-step reactions. In the first step TAEA was prepared by esterification of PETAE with AA. PETAE (100 g), AA (56.16 g), phenothiazine (1 g), p-toluenesulfonic acid (0.67 g), and dichloromethane (200 mL) were mixed in a three-neck round flask and heated to reflux. The reaction was kept at reflux for 3 h and cooled to room temperature. Dichloromethane was removed in vacuum. Anhydrous diethyl ether (200 mL) was added, and then slowly 5% sodium carbonate solution (200 mL). The organic layer was washed with deionized water (3x200 mL) and dried with anhydrous $MgSO_4$ (50 g). The solvent was removed in vacuum to give triallyl ether acrylate (TAEA) as shown in Figure 1. In a second step, safflower oil (80 g) and obtained TAEA (28 g, 0.09 mol) were added into 250 mL three-necked round flask equipped with stirrer, condenser, and thermocouple. The flask was mixed for 15 min under nitrogen purge, then the temperature was raised to 120 °C and kept for 2 h. The obtained reactive diluent was cooled to room temperature and characterized by ^{1}H-NMR, ^{13}C-NMR and FT-IR.

TAEA modified safflower oil (TAEASO) was formulated with the alkyd resin at four different ratios (10, 20, 30 and 40 wt.-% based on total formulation), 2 % metal drier package (10% cobalt, 80% zirconium, 10% calcium) and 1 % wetting agent. The samples have been applied on flat aluminum plates with a paint applicator in the form of approximately 150 μm thick film and cured at 160 °C and kept for 3 h.

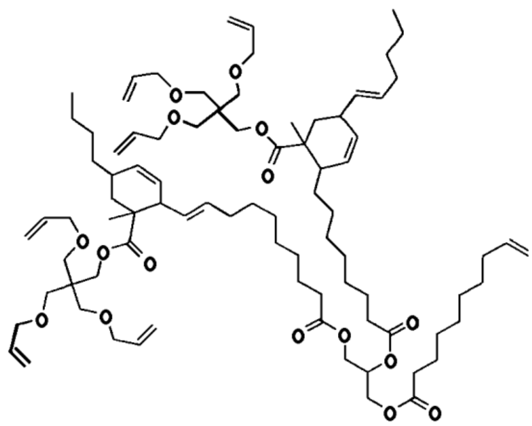

Figure 1: Structures of reactive diluent synthesized via the Diels–Alder reaction: triallyl ether acrylate (TAEA) modified safflower oil.

Characterization

In Diels-Alder reactions, linoleic acid ratio in safflower oil, which acts as diene, has been determined using SGE, BPX70 capillary column (60 m x 0.25 mm x 0.25 μm) with Perkin Elmer Clarus 680 model gas chromatography (GC) device. The method used in GC is TS EN ISO 12966-2. In addition, the characterization of synthesized reactive diluent is in the range of 4000-650 cm^{-1} wavenumber, the resolution is 4 cm^{-1}, and in 4 scans the Bruker AVANCE III 400 MHz device with Perkin Elmer Fourier Transform Infrared Spectroscopy (FT-IR) and ^{1}H, ^{13}C, ^{19}F and ^{31}P probes and Nuclear Magnetic Resonance (NMR) device have been used.

Data for ^{1}H and ^{13}C have been recorded between -2.00 and 10.00 parts per million (ppm) and -10.00 to 150.00 ppm for 500 MHz frequency. The viscosity measurements of the resin samples were made using L4 coded spindle at a speed of 20 rpm with the use of the Fungilab S.A. V.1.2 Alpha Series viscometer at 25 °C. The determination of drying time of films formed as a result of application of resin samples has been made at 20 ± 1 °C in according to DIN standard (DIN 53 150).

RESULTS AND DISCUSSION

The use of reactive diluent obtained by Diels-Alder reaction with TAEA dienophile of safflower oil as an alternative diluent in alkyd resins has been investigated in this study. The double bond ratio is important in terms of efficiency in improving the drying properties of alkyd resin. Therefore, the double bond ratio determined in GC is shown in **Table 1.**

Table 1: Fatty acid compositions of safflower oil.

Sample	Fatty acid	Fatty acid (%)
Safflower oil	Oleic acid (C18:1)	17.99
	Linoleic acid (C18:2)	72.61
	Palmitic acid (C16:0)	6.55
	Stearic acid (C18:0)	2.43
	Arachidic acid (C20:0)	0.32
	Myristic acid (C14:0)	0.09

Fatty acid compositions of drying oils are different from each other. As with the Diels-Alder reaction carried out by Brunner and Tucker between tung oil and styrene, the double bonds in dienes react with dienophiles. Depending on the presence of double bonds, three different (alkyl siloxane, triallyl ether acrylate, and fluorinated alkyl) groups with Tung oil acrylate monomer have been functionalized with Diels-Alder reactions to form the new three reactive diluents (13).

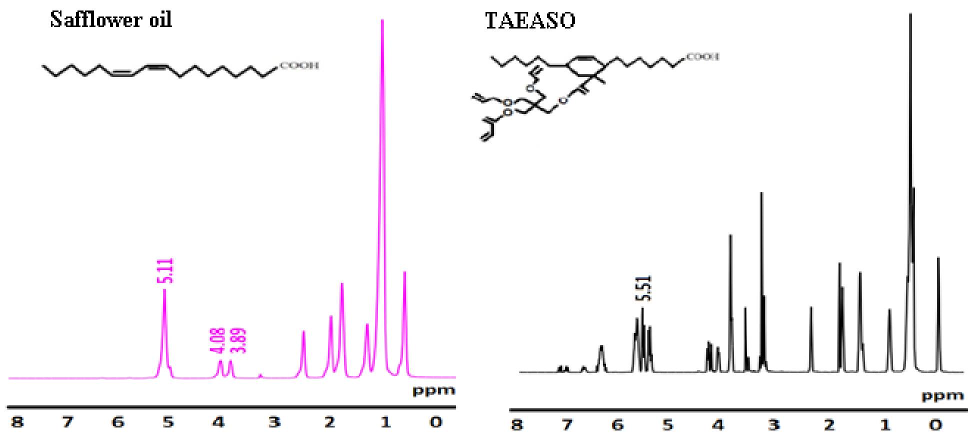

Figure 2: ^{1}H-NMR spectra of safflower oil and TAEASO.

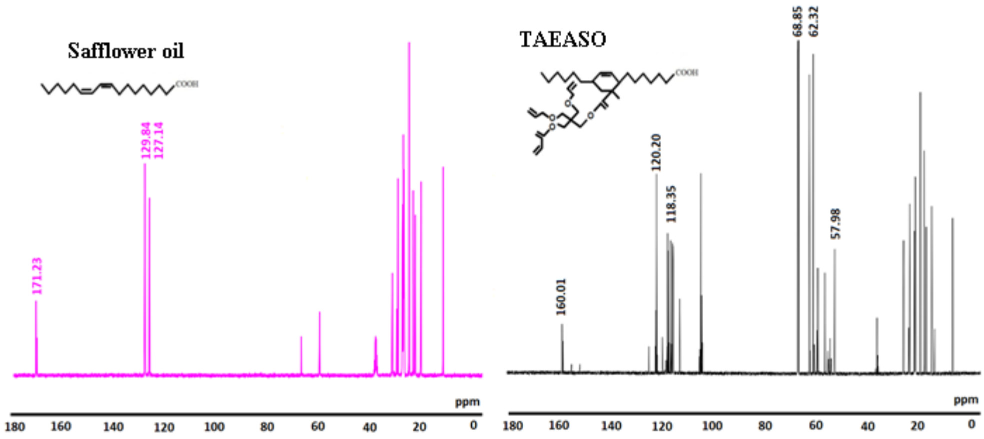

Figure 3: ^{13}C-NMR spectra of safflower oil and TAEASO.

Figure 2 and **3** show ^{1}H-NMR and ^{13}C-NMR spectra of safflower oil alkyd for comparison with the Diels–Alder adducts.

Figure 2 shows the ^{1}H-NMR spectra of safflower oil and TAEASO. The Diels- Alder reaction between dienophiles and safflower oil take results in the reduction of the resonances of conjugated double bonds at nearly 5.11 ppm. New resonances appear at nearly 5.51 ppm respectively due to the cyclohexene ring created during the Diel-Alder reaction. Most of the peaks are assigned to the structure of Triallyletheracrylate modified safflower oil in **Figure 2.**

Further analysis was performed via ^{13}C-NMR. **Figure 3** shows the ^{13}C NMR spectra of safflower oil and TAEASO. The assigned peak of ^{13}C-NMR of safflower oil is shown in **Figure 3**. The resonance at nearly corresponds to the unsaturated carbon, the resonance at nearly 160.01 ppm is due to the carbonyl groups in safflower oil. Comparing to the assigned ^{13}C-NMR spectra of reactive diluents with safflower oil shown in Figure 4, a new carbonyl group appears at nearly 120.20 ppm corresponding to the attachment of TAEASO to the safflower oil back bone (8).

FT-IR spectra of safflower oil and TAEASO are shown in **Figure 4**. and **Table 2.** FT-IR was used to determine crosslinking bonds situation with triallyl ether acrylate addition (14).

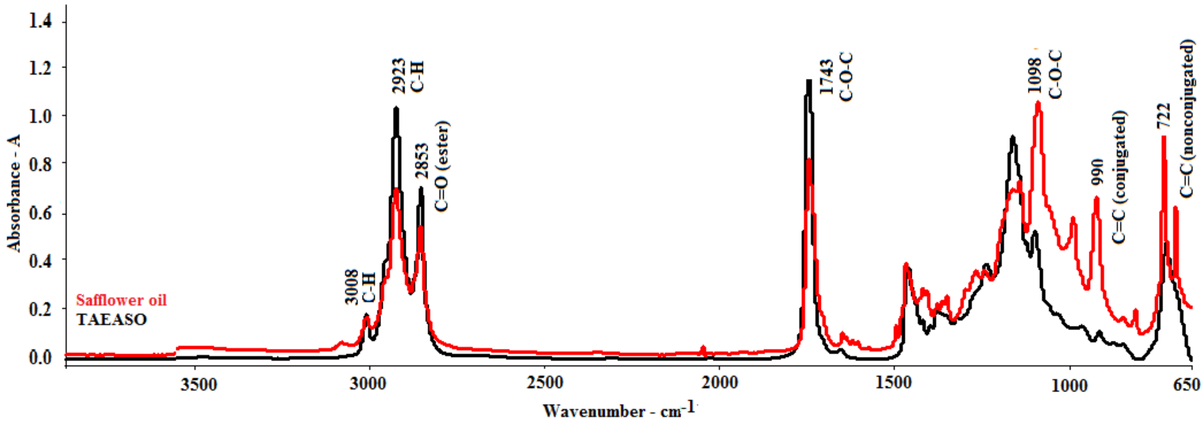

Figure 4: FT-IR spectra of safflower oil and TAEASO.

Table 2: FT-IR spectra of safflower oil and TAEASO.

Wavenumber (cm^{-1})	Functional group
3008	C-H
2923	C-H
2853	CH_2
1743	C=O (Ester)
1180	C-O-C
1098	C-O-C
990	C=C (conjugated double bonds)
722	C=C (non-conjugated double bonds)

In **Figure 4**, the band at 990 cm^{-1} was attributed to conjugated double bonds (8). 722 cm^{-1} are attributed to cis-C=CH bending. In the course of the Diels-Alder, conjugated double bonds were greatly reduced which indicated the cycloaddition to the safflower oil (13). The cycloaddition indicates the consumption of double bonds in the fatty acids as a result of autoxidative crosslinking (15).

Properties of dye formulations

In recent years, manufacturers have been trying to reduce the cost of alkyd resins. They make new attempts to improve the film properties of alkyd resins and to enhance their usage in coating applications (16-20). The solution and film properties such as viscosity, drying time, gloss, thickness and pencil hardness of dye formulations containing TAEA in different ratios were investigated and the results obtained are given in **Table 3.**

Viscosity reduction is expected by addition of reactive diluents to alkyd resins. Alkyd resins containing certain proportions of reactive diluents have been compared with neat alkyd. The viscosity of the samples has been investigated as a function of the dienophile amount. The results are shown in Table 3. The viscosity of neat alkyd has been measured approximately 1603 cP. Addition of reactive diluent to alkyd has reduced viscosity as expected. The maximum viscosity reduction rates in alkyd containing, TAEASO10-SO, TAEASO20-SO, TAEASO30-SO and TAEASO40-SO, are 37%, 55% 71% and 75%, respectively. The reason for this difference is the involvement of conjugation and the cycloaddition in Diels-Alder reactions of safflower oil with dienophile.

According to these results, it is considered that reactive diluents obtained can replace organic solvents used as diluents in the alkyd.

Table 3: Viscosity, viscosity reduction, drying time and film properties of alkyd and alkyd/diluent mixtures.

Sample	Viscosity Reduction %	Drying Time, hour	20º Gloss	60º Gloss	Pencil Hardness
SO	-	21	101,3	90,3	2B
TAEASO10-SO	37	13	110,3	101,1	B
TAEASO20-SO	55	14	110,2	100,3	B
TAEASO30-SO	71	15	102,4	91,8	B
TAEASO40-SO	75	15	101,3	90,7	B

As a result of Diels-Alder reactions of safflower oil with reactive diluents, the cross-linking mechanism has been changed. Therefore, it is important to investigate the drying time. Drying time experiments have been carried out in room conditions (25 °C).

The results of drying time are shown in **Table 3** drying is directly related to the reduction of safflower oil added into the alkyd and reduction of viscosity. TAEASO containing alkyd resins have a drying time of more than 24 hours. The drying time of alkyd containing TAEASO is about 1.5 times less than the drying time of the alkyd without the reactive diluent. This is the result of the presence of more reactive groups in TAEASO.

CONCLUSIONS

Diels-Alder reactions have been used for the modification of safflower oil with TAEA dienophile in certain proportions. Dienophile including acrylate molecule, triallyl ether acrylate (TAEA), have been used to determine the ability to cycloaddition of the safflower oil with Diels-alder reactions at chosen temperature and atmospheric pressure. The experimental conditions have been determined by taking into account the physicochemical properties of the acrylate molecule. As a result of the study, it has been determined that the viscosity reduction in alkyd resins with reactive diluent may reach up to 75%. In addition, it has been observed that drying time decreases by addition of reactive diluents into alkyd resins. Additional TAEA dienophile properties such as the gloss appear to not be significantly affected by the diluent content. The neat alkyd films have same thickness as those films that contain the reactive diluents in certain proportions. The pencil hardness of the films improved as predicted for the reactive diluents.

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REFERENCES

1. Muizebelt WJ, Hubert JC, Nielen MWF, Klaasen RP, Zabel KH. Crosslink mechanisms of high-solids alkyd resins in the presence of reactive diluents. Progress in Organic Coatings. 2000 Dec;40(1–4):121–30.

2. Teng G, Soucek M, Vick B, Simonsick W, Sen A. Spectroscopic investigation of the blowing process of soyabean oil. Surface Coatings International Part B: Coatings Transactions. 2003 Sep;86(3):221–9.

3. Martyak NM, Alford D, Picker R, Dowling C. Controlled oxidative curing of tung oil. JCT coatingstech. 2005;2(16):36–41.

4. Mallegol J, Gonon L, Commereuc S, Verney V. Thermal (dsc) and chemical (iodometric titration) methods for peroxides measurements in order to monitor drying extent of alkyd resins. Progress in Organic Coatings. 2001;41(1–3):171–6.

5. Metcalfe DS, Elkins DM, Hughes HDM. Crop production: principles and practices. 4th ed. New York: Macmillan; 1980. 774 p.

6. Muizebelt WJ, Donkerbroek JJ, Nielen MWF, Hussem JB, Biemond MEF, Klaasen RP, et al. Oxidative crosslinking of alkyd resins studied with mass spectrometry and NMR using model compounds. J Coatings Tech. 1998 Jan;70(1):83–93.

7. Muizebelt W, Nielen MWF. Oxidative Crosslinking of Unsaturated Fatty Acids Studied with Mass Spectrometry. Journal of Mass Spectrometry. 1996;31(5):545–54.

8. Wutticharoenwong K, Dziczkowski J, Soucek MD. Tung based reactive diluents for alkyd systems: Film properties. Progress in Organic Coatings. 2012 Apr;73(4):283–90.

9. Ni H, Skaja A, Soucek M, Simonsick W, Zhong W. Alkoxysilane-modified polyurea coatings. Polymeric Materials Science and Engineering[Polym Mater Sci Eng]. 1999;81:405–406.

10. Wold CR, Soucek MD. Mixed metal oxide inorganic/organic coatings. J Coatings Tech. 1998 Jul;70(7):43–51.

11. Tuman S, Soucek M. Novel inorganic/organic coatings based on linseed oil and sunflower oil with sol-gel precursors. JCT, Journal of coatings technology. 1996;68(854).

12. Ballard RL, Tuman SJ, Fouquette DJ, Stegmiller W, Soucek MD. Effects of an Acid Catalyst on the Inorganic Domain of Inorganic−Organic Hybrid Materials. Chem Mater. 1999 Mar;11(3):726–35.

13. Wutticharoenwong K, Soucek MD. Synthesis of Tung-Oil-Based Reactive Diluents. Macromol Mater Eng. 2010 Dec 10;295(12):1097–106.

14. Salata R, Pellegrene B, Soucek M. Migration of fluorinated alkyd and fluorinated tung oil additives for partially self-stratifying coatings. Progress in Organic Coatings. 2019 Aug;133:406–17.

15. Salata RR, Pellegrene B, Soucek MD. Synthesis and properties of a high solids triethoxysilane-modified alkyd coatings. Progress in Organic Coatings. 2019 Aug;133:340–9.

16. Park HS, Jeon YJ, Kim SK, Kang DW. Synthesis and Physical Properties of Two-Component Polyurethane Coatings Containing Alkyd and Polyester Polyols. Korea Polym J. 1997;5(4):256–61.

17. Sailer RA, Soucek MD. Oxidizing alkyd ceramers. Progress in Organic Coatings. 1998 Jan;33(1):36–43.

18. Sailer RA, Wegner JR, Hurtt GJ, Janson JE, Soucek MD. Linseed and sunflower oil alkyd ceramers. Progress in Organic Coatings. 1998 Feb;33(2):117–25.

19. Thanamongkollit N, Soucek MD. Synthesis and properties of acrylate functionalized alkyds via a Diels–Alder reaction. Progress in Organic Coatings. 2012 Apr;73(4):382–91.

20. Wang C, Jones F. Stability and film properties of tung oil modified soybean alkyd emulsion. J Appl Polym Sci. 2000;78(9):1698–706.