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Effect of Preparation Conditions on Crosslinking Behavior of Linseed Oil-Based Thermosetting Polymer

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Abstract

Bio-based materials have received more attention to replace materials from petroleum resources because of sustainability reasons. Plant oil is one of the most interesting raw materials to produce thermosetting polymers. A crosslinking reaction between epoxidized linseed oil and vegetable oil-based crosslinkers is investigated in the present study. Two types of crosslinker including fatty acid dimer and fatty acid trimer were reacted with epoxidized linseed oil. A rotational rheometer equipped with cone-and-plate geometry was used to monitor the progress of three-dimensional network formation. A curing phenomenon was illustrated by the increment in storage modulus of the reaction mixture. The trifunctional crosslinker was more effective than the functional crosslinker for an uncatalyzed system at the reaction temperature of 120ºC. When the crosslinking temperature of the trimer-crosslinker system increased from 120ºC to 140ºC, the induction time for curing decreased around three times. The reaction between epoxidized oil and trimer acid was obviously accelerated by using 4-methyl amino pyridine as a catalyst. Increasing the catalyst content induced a monotonically reduction in the induction time of the curing process. The induction time of the reaction between epoxidized linseed oil and trimer acid with 2% catalyst at reaction temperature of 120ºC was only 18 minutes, which was significantly shorter than that of an uncatalyzed system around seven times.

Keywords: Thermosetting polymer, Epoxidized linseed oil, Fatty acid trimer

1. Introduction

Thermosetting polymer is one class of important polymeric material. A three-dimensional network structure provides some better properties compared with thermoplastic polymers such as solvent resistivity, dimensional stability, and mechanical strength. Epoxy thermoset is commonly used in various fields such as electronic, coating, adhesive, composites and other fields due to its excellent thermal stability, mechanical properties, electrical insulation and chemical resistance (Zhao, An, & Wang, 2021). Nowadays, epoxy resin is a major share of thermosetting polymers business (Qi et al., 2018). Commercial epoxy resin is presently made from diglycidyl ether of bisphenol A (DGEBA) and epichlorohydrin (ECH), which were the petroleum-based materials (Tao et al., 2020). These raw materials of epoxy resin are suspected to have a negative impact on living organisms and ecosystems (Qi et al., 2018). The rapid decrease of nonrenewable resources has motivated the researchers and manufacturers to investigate bio-based and renewable feedstock as the alternative raw materials (Khandelwal, Sahoo, Kumar, & Manik, 2018).

There are several potential bio-based feedstocks such as cellulose, lignin, starch, natural oils and chitin. Bio-based oils can derive from plants and animals as vegetable oils and animal fats. Plant-based oils have gained interest as raw materials due to their low cost, environmental friendliness, availability, non-hazardous, renewability, and possible biodegradability. Triglyceride is a base chemical in plant oils. Natural plant oils typically contain some unsaturated carbon-carbon bonds in their fatty-acid part of triglyceride molecules. This unsaturated site enables direct polymerization and modification. There are various chemical modifications that are performed at unsaturated fatty acids, including acylation, ozonolysis, hydroformylation, dimerization, epoxidation and hydroxylation (Musik, Bartkowiak, & Milchert, 2022).

Among many vegetable oils, linseed oil (LO) is one of the most natural oils that exhibits a high degree of unsaturation. The composition of fatty acid in LO is 53% of linolenic acid, 16% of linoleic acid, and 22% of oleic acid (Janković, Govedarica, & Sinadinović-Fišer, 2020). It has approximately 6.6 carbon-carbon double bonds per molecule of triglyceride (Singh, Sethi, & Manik, 2022). Epoxidation process is potentially useful for increasing the reactivity of LO by the formation of epoxide rings. Epoxidized linseed oil (ELO) is possibly produced by epoxidation reaction between LO and peracid (Samper, Petrucci, Sánchez-Nacher, Balart, & Kenny, 2015). A high reactivity of epoxide groups in ELO can be easily reacted with other chemicals. ELO can be used as raw materials to prepare diluents, fillers, lubricants, coatings, and stabilizers in PVC, PLA and other polymers (Balart, Fombuena, Fenollar, Boronat, & Sánchez-Nacher, 2016; Thuy & Duc, 2020). Chemical reaction between ELO and crosslinking agent results in thermosetting polymer. Chemicals containing amine, anhydride or carboxylic acid functional groups can be possibly used as crosslinkers for ELO. Yahua Chen and co-workers (Chen, Xi, & Zhao, 2016) studied the preparation of thermoset from epoxidized soybean oil and crosslinking agent using 2-ethyl-4-methylimidazole as a catalyst. The bio-based maleopimaric acid crosslinker and two petroleum-based crosslinkers, including hexahydro-4-methylphthalic anhydride (MHHPA) and trimellitic anhydride (TMA), were compared. The thermosets formulated from bio-based crosslinker showed greater in elongation at break and ultimate tensile strength than thermoset derived from petroleum-based crosslinkers. Dimer and trimer of fatty acid is one of the interesting bio-based crosslinking compounds for epoxidized vegetable oil. They can be produced from condensation reactions of unsaturated fatty acids such as oleic acid (C18:1) and linoleic acid (C18:2) (dos Santos Martini, Braga, & Samios, 2009). Besides the types of thermosetting precursors, the crosslinking conditions such as time and temperature of curing, amount and type of catalyst have to be concerned. Different curing parameters undoubtedly result in thermosetting materials with different properties. The total production time of thermosets depends significantly on preparation conditions.

This study aims to develop plant oil-based thermosetting polymers from curing reaction between ELO and plant oil-based crosslinker, including dimer and trimer of fatty acid in this study. We focus on the influence of crosslinker type and crosslinking temperature on curing behavior of this all-plant-oil based epoxy resin. The effect of catalyst content on the induction time of three-dimensional network formation is also explored.

2. Materials and Methods

2.1 Materials

Linseed oil (Virgin grade, Tropicalife) was used as a base oil. Epoxidation reaction of oil was performed using hydrogen peroxide solution 30% w/w (AR, QRëC), formic acid (98.5% w/w, QRëC) and sulfuric acid (98% w/w, QRëC) as reagents. Toluene (99.5%, QRëC) was used as a solvent. Dimer acid (Pripol 1012, CRODA) and trimer acid (Pripol 1040, CRODA) were used as the difunctional and trifunctional crosslinking agents, respectively. The catalyst for crosslinking reaction was 4-dimethylamino pyridine (AR, Sigma-Aldrich).

2.2 Synthesis of epoxidized linseed oil

First, Linseed oil (300 g) was mixed and stirred with toluene (150 g) in a three-neck round-bottom flask equipped with a condenser. Then, Formic acid (35.4 g) was added at room temperature followed by adding sulfuric acid (1.5 ml) dropwise under stirring. The mixture temperature was raised to 60ºC. Hydrogen peroxide (251.1 g) was then added slowly to the solution by equivalent dropping funnel. The mixture was stirred and the temperature was maintained for 6 hours. After cooling down to room temperature, the mixture was separated into aqueous and oil phase. The oil phase was neutralized by washing with distillated water. The trapping water and excess solvent were removed by evaporation process with rotary evaporator. The epoxidized linseed oil was then characterized by FTIR spectroscopy and ^{1}H-NMR.

2.3 Characterization of linseed oil and epoxidized linseed oil

FTIR spectra of linseed oil and epoxidized linseed oil were recorded by FTIR spectrometer (Vertex70, BRUKER) in TR mode within the range from 4000 cm^{-1} to 500 cm^{-1} at a 4 cm^{-1} resolution.

^{1}H-NMR spectra were obtained from ^{1}H-NMR spectrometer (Advance III 300 MHz, BRUKER) using deuterated chloroform ($CDCl_3$) as a solvent. The epoxide content (%) was calculated by using this below equation (Saithai, Jonjanekieat, Chinpa, & Tanrattanakul, 2007; Xia, Budge, & Lumsden, 2015).

$$\%Epoxide = \frac{I_{2.8-3.0}}{I_{2.8-3.0}+I_{5.3-5.6}} \times 100 \qquad (1)$$

where $I_{2.8\text{-}3.0}$ and $I_{5.3\text{-}5.6}$ are integral areas from the ^{1}H-NMR spectrum at 2.8-3.0 ppm and 5.3-5.6 ppm respectively.

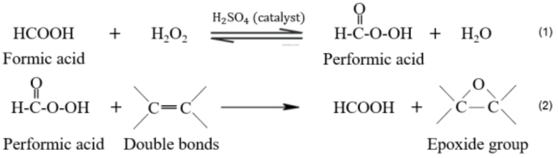
2.4 Investigation of crosslinking behavior by rheological analysis

The curing reaction between epoxidized linseed oil and crosslinking agents was investigated by using rotational rheometer (ARES-G2, TA instrument) equipped with cone-and-plate geometry. The rheological analysis was operated in oscillation time sweep mode at the fixed 5% strain and angular frequency of 1.0 rad/s. The progress of crosslinking reaction was monitored by tracking the increase in storage modulus with time. The epoxidized linseed oil was initially premixed with crosslinker at room temperature. The molar ratio between crosslinking agent and content of epoxide functional group of modified oil was fixed at 1/2. Two types of crosslinking agents, including dimer and trimer of fatty acid, were studied. The influence of crosslinker type on curing behavior was tested at temperature of 120ºC in an uncatalyzed system. The more efficient crosslinker in uncatalyzed system was then chosen to further examine the effect of crosslinking temperature, which was ranged from 120ºC to 140ºC. The network formation between epoxidized linseed oil and optimal crosslinker at optimal temperature was finally explored by varying the catalyst content from 0.0 to 2.0 weighted percent.

3. Results and Discussion

3.1 Characterization of epoxidized linseed oil

The epoxidized plant-based oil was obtained from an epoxidation reaction between linseed oil and performic acid. Hydrogen peroxide was firstly reacted with formic acid to produce peracid using sulfuric acid as a catalyst. The performic acid was subsequently reacted with double bonds of linseed oil to achieve epoxidized linseed oil. Scheme 1 proposes the epoxidation reaction.



Scheme 1. Epoxidation reaction of performic acid with double bond of linseed oil.

The synthesized epoxidized linseed oil was investigated by FTIR spectroscopy. Figure 1 shows FTIR spectra of linseed oil and epoxidized linseed oil. FTIR spectrum of linseed oil displayed the characteristic peak of double bonds in unsaturated fatty acids structure at wavenumber 731 cm^{-1}, 1653 cm^{-1} and 3009 cm^{-1} related to *cis*-CH=CH stretching, C=C stretching and =CH stretching, respectively. The new peak at wavenumber 823 cm^{-1} corresponded to C-O-C vibration of oxirane ring was emerged in FTIR spectrum of epoxidized oil (Figure 1(b)) (López Téllez, Vigueras-Santiago, & Hernández-López, 2009; Nieto, Santiago, & López, 2021). Moreover, the reduction in the intensities of double-bonds characteristic peaks were fairly detected.

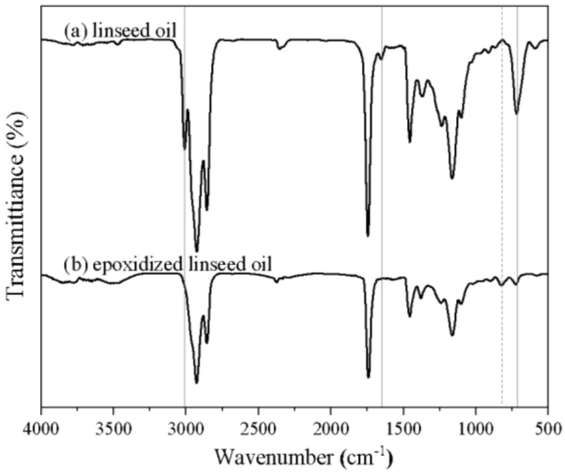
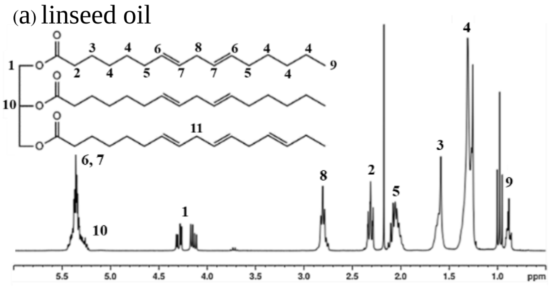


Figure 1. FT-IR spectra of (a) linseed oil and (b) epoxidized linseed oil.

The ^{1}H-NMR spectra of LO and ELO are depicted in Figure 2. In LO spectra, chemical shift (δ) at 2.1 ppm (5), 2.8 ppm (8) and 4.1-4.3 ppm (1) related to allyl protons (-C$\mathbf{H_2}$-CH=CH-), hydrogens between two double bonds (-CH=CH-$\mathbf{CH_2}$-CH=CH-) and methylene protons of hydrogens of glycerol (-CH-C$\mathbf{H_2}$-O-) respectively. In ELO spectra, the characteristic epoxy hydrogens signals at δ equaled to 1.5 ppm (5) and around 2.8-3.0 ppm (6') assigned to protons adjacent to oxirane ring (-CH_2-O-CH_2-C$\mathbf{H_2}$-) and hydrogens of epoxide group (-C$\mathbf{H_2}$-O-C$\mathbf{H_2}$-), respectively (Khandelwal et al., 2018; López Téllez et al., 2009). After epoxidation, the intensity of vinyl protons of alkene (-C**H**=C**H**-) at 5.3-5.6 ppm obviously decreased, which confirmed the successful epoxidation process. Based on chemical reaction (2) of Scheme 1, the carbon-carbon double bonds were changed to be epoxide groups during epoxidation reaction. The integral areas of protons at the positions of 2.8-3.0 ppm corresponded to protons of epoxide groups and those of 5.3-5.6 ppm corresponded to protons of alkene groups were effectively used to determine the epoxide content of the synthesized product. The carbon-carbon double bonds of LO were transformed to be epoxide groups around 87.5% (Salih et al., 2015), which was calculated based on equation 1.

(a) linseed oil



(b) epoxidized linseed oil

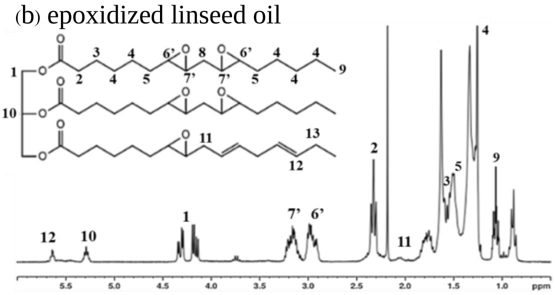


Figure 2. ^{1}H-NMR spectra of (a) linseed oil and (b) epoxidized linseed oil.

3.2 Influence of preparation conditions on crosslinking behavior

The effect of preparation conditions on crosslinking behavior of epoxidized plant-based oil was monitored by rheological analysis by using cone and plate rheometer. Storage modulus versus time was tracked in oscillation time sweep mode.

3.2.1 The effect of crosslinker type

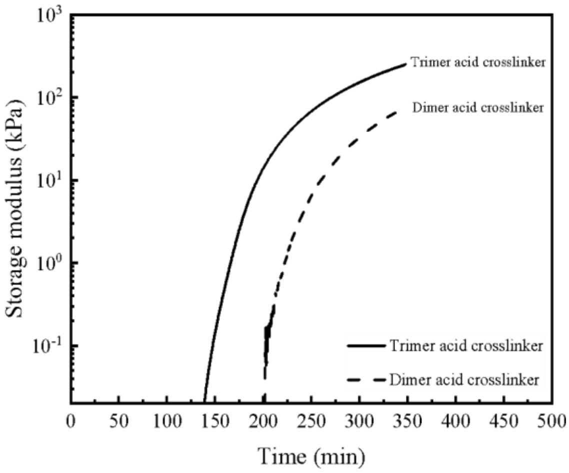


Figure 3. Storage modulus (kPa) vs time (min) of the reaction between epoxidized linseed oil and crosslinker in uncatalyzed system.

The comparison between using trimer acid and dimer acid as a crosslinking agent for ELO was studied by fixing curing temperature at 120ºC in an uncatalyzed system. The results are presented in Figure 3. The shorter induction time and also higher storage modulus were obviously detected for the reaction system using trimer acid as a crosslinking agent. The larger molecular size of trimer acid might retard the diffusion movement. However, it contained trifunctional active sites to react with the epoxide groups of ELO. Therefore, the results implied that the number of functional groups was more influential than the size of the crosslinker. Trimer acid was consequently an appropriate crosslinking agent for ELO.

3.2.2 The effect of crosslinking temperatures

The reaction between ELO and trimer acid at temperature of 120ºC and 140ºC in an uncatalyzed system was examined. The results are displayed in Figure 4. The results indicated that the reactivity of crosslinking reaction between trimer acid and ELO noticeably depended on temperature. The thermal energy could accelerate the diffusion ability of both ELO and trimer acid, which favored the formation of crosslinking networks. The decrease of induction time from 127 min to 44 min was observed when the crosslinking temperatures increased from 120ºC to 140ºC.

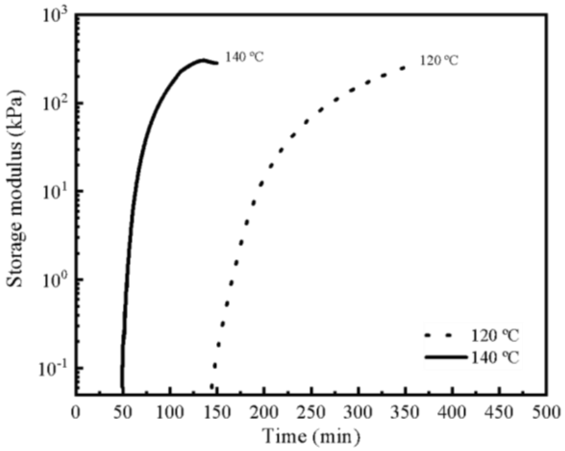
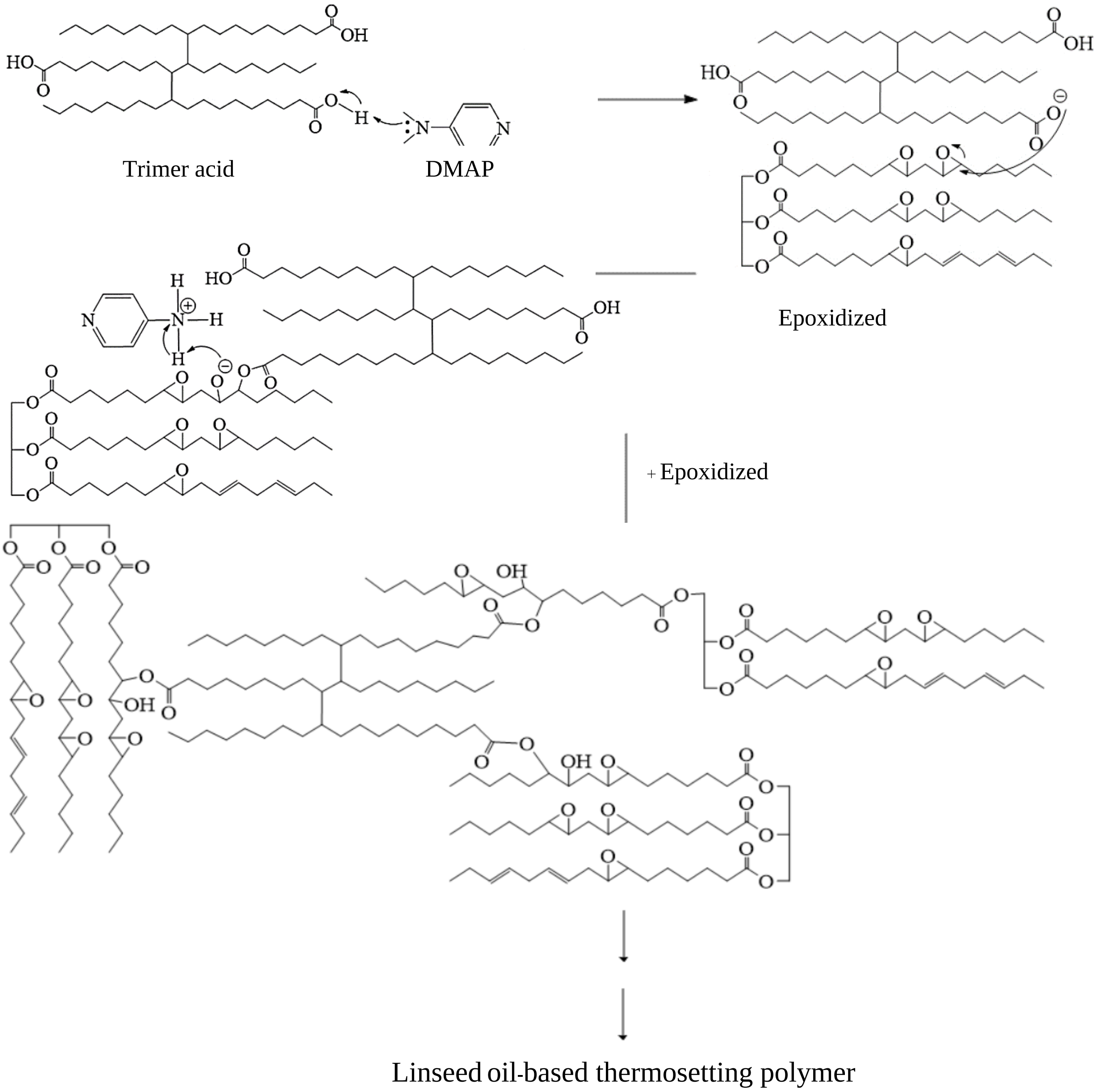


Figure 4. Storage modulus (kPa) vs time (min) of the reaction between epoxidized linseed oil and trimer acid at different temperatures.

3.2.3 The effect of catalyst content

The crosslinking mechanism of epoxidized linseed oil with trimer acids using 4-dimethylamino pyridine (DMAP) as catalyst is proposed in Scheme 2. The effect of catalyst contents on curing reaction was studied by fixing crosslinking temperature at 120ºC in trimer acids-crosslinker system. The results are illustrated in Figure 5. DMAP could significantly accelerate the network formation. In the present study, the induction time is defined as the time interval required to detect a significant increase in storage modulus at the early stage of curing. The uncatalyzed systems exhibited the longest induction time of around 129 minutes. Figure 6 depicts the influence of catalyst content on induction time. The induction time decreased with increasing catalyst content. The induction time of the reaction mixture catalyzed by 2.0% DMAP was only 18 minutes, which was shorter than that of the uncatalyzed system around 7 times. However, the efficiency of the catalyst was alleviated in the systems with high catalyst concentration. The relationship between the induction time and catalyst were downward curves with decreasing slope. The rate of crosslinking reaction might be considered from the slope of the curve in Figure 5. The data revealed that the curing rate also increased with increasing catalyst content.



Scheme 2. Crosslinking reaction of epoxidized linseed oil with trimer acid.

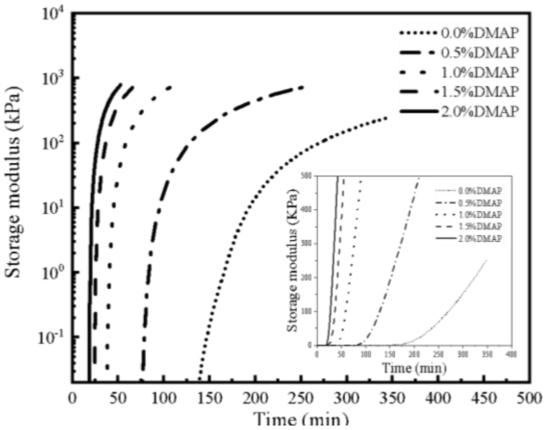


Figure 5. Storage modulus (kPa) vs time (min) of the crosslinking reaction between epoxidized linseed oil and trimer acid with different DMAP contents. [the insert represented the linear curve]

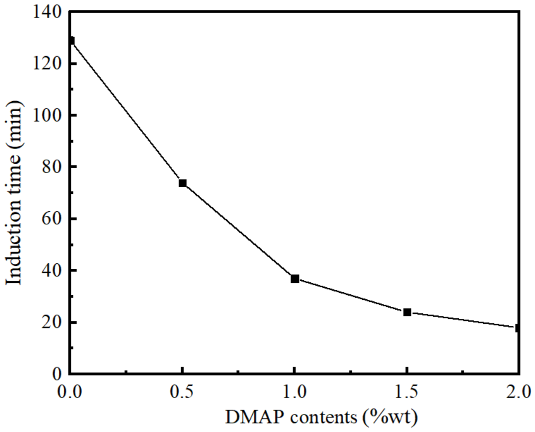


Figure 6. The induction time of the crosslinking reaction between epoxidized linseed oil with trimer acid at different DMAP contents.

4. Conclusions

In this work, the epoxidized linseed oil was synthesized via the in-situ epoxidation reaction and the achievement was confirmed by FTIR spectroscopy and ^{1}H-NMR. The obtained epoxidized linseed oil was subsequently crosslinked by trimer and dimer of fatty acid. Trimer acid crosslinker was more effective than dimer acid for an uncatalyzed system at the reaction temperature of 120ºC because of the higher number of active functional groups. The induction time for curing of an uncatalyzed system decreased around 3 times with increasing the crosslinking temperature from 120ºC to 140ºC. At reaction temperature of 120ºC, the induction time of the 2.0%-DMAP catalyzed system was only 18 minutes whereas that of the uncatalyzed system was 129 minutes. However, the efficiency of catalysts tended to decrease in the systems with high catalyst content.

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