

Fatty Acid Derivatives in Radiation Curable Coatings

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Introduction

Vegetable oil derivatives have a long history in coating technology as binder resins in air drying systems¹. The traditional resin is either the vegetable oil itself, e.g. linseed oil, or an alkyd modified resin with polyunsaturated fatty acids. These resins dry via an auto-oxidation process where the unsaturated fatty acid is oxidized by atmospheric oxygen to form a crosslinked polymer. The reactions involved are mainly of free radical nature and often accelerated by a metal salt, cleaving the formed peroxides. The reaction scheme is very complex and varies depending on the structure of the fatty acids involved and the reaction conditions².

The use of traditional vegetable oil based coatings has continuously declined during the last decades, although the coatings in many cases exhibit very good properties. Replacement of vegetable oil by synthetic binder resins is caused by some drawbacks associated with vegetable oils. Being a triglyceride (figure 1), natural oils normally contain an average content of several different fatty acids depending on the crop source. Not all of these fatty acids are wanted for the coating performance and they may cause problems such as yellowing and cracking.

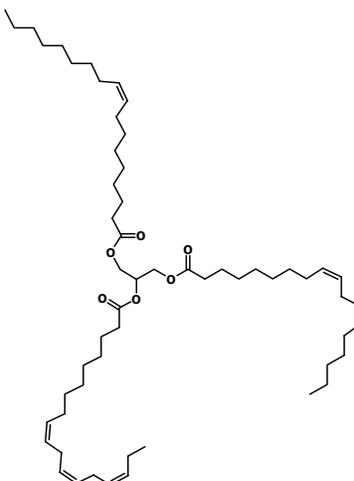


Figure 1. Schematic structure of linseed oil.

The fatty acid content (often referred to as the fatty acid pattern) not only varies between different crops but also depend on the growth conditions, harvest conditions, and purification process. These variations bring in an uncertainty concerning the reproducibility of the raw material composition and also introduces a higher cost associated with the purification process. Present in the oil, are also a number of saturated fatty acids which cannot participate in free radical crosslinking reactions. These components can later migrate out of the cured coating and show up as a waxy film on the coating surface.

The traditional drying mechanism via a free radical auto-oxidation route is furthermore rather slow, making it less attractive for rapid industrial coating processes. The oxidation is

also associated with emission of volatile low molecular weight degradation products that might be irritant.

On the other hand, vegetable oils have some advantages compared to synthetic alternatives, e.g. the coatings can be cured at ambient conditions on large structures and they exhibit properties which makes them suitable for protection of wood substrate. In addition, vegetable oils are derived from a renewable resource, which is the main reason why they presently receive an increased attention. A great deal of work has thus been presented concerning new ways to reduce the drawbacks of traditional vegetable oil coatings and introduce novel systems^{3,4}. Modern crop development has introduced new crops that contain optimized fatty acid patterns for air-drying coatings⁵. It also allows other functional groups to be introduced into the fatty acid why new crosslinking chemistries can be employed.

The two most common functional groups, besides the alkenes, in unsaturated fatty acids are epoxy^{6, 7, 8, 9} and hydroxyl³. Both these groups exist in naturally occurring oils such as vernonia and castor oil. The hydroxy functional fatty acid has been used as a precursor for further functionalization, e.g. acrylation, or as comonomer in isocyanate resins. Epoxy groups can either be naturally occurring or obtained by epoxidation of unsaturated oils such as soybean or linseed oil when the number of epoxy functionality will depend on the amount of initial unsaturation in the oil and the success of the epoxidation process. After epoxidation however, there is still a number of unreactive, saturated fatty acids present in the oil. Consequently, reproducible properties is hard to obtain and it is difficult to evaluate the relation between the initial composition and the final properties of the crosslinked coating. Will the saturated fatty acids in the oil act as a softener? Can it crystallize? To what extent does it affect the mechanical properties? It is furthermore not clear how different epoxy groups contribute to the final thermoset properties depending on the functionality. How do two epoxy groups derived from the unsaturations on linoleic acid (two unconjugated double bonds in the alkyl chain) compare to two epoxy groups from two oleic acid chains (one double bond on each alkyl chain)? This dispersity in composition makes it difficult to predict the exact properties of these systems.

The use of acrylated and epoxidized oils as oligomers or reactive diluents in radiation curable systems might introduce lower cost, lower volatility and lower toxicity. Especially, the photoinduced cationic polymerization of both natural and synthetic epoxidized triglycerides holds promise for industrial use in UV curable coatings, inks and adhesives.¹⁰

It has been shown that free radically initiated thiol – ene coupling can be used to attach unsaturated fatty acids to thiol functional surfaces¹¹. Thiol-ene polymerization have obtained a renewed attention during the last years due to several advantages compared to other free radical polymerizations. The thiol-ene polymerization is not very sensitive to oxygen inhibition, it proceeds by a step-wise reaction mechanism with a late gel point, and the reaction rate is very high^{12, 13, 14, 15}. All together, this makes the thiol-ene reaction very suitable for radiation curable systems.

Another research area, which has attracted a significant interest during the last decade, is how to tailor the properties of thermoset resins by varying the molecular architecture of the resin rather than the chemical functionality. One specific way to do this is to introduce highly branched structures in the resins i.e. dendritic polymers¹⁶. Dendritic polymers, comprising of dendrimers and hyperbranched polymers, are based on monomers that have a potential branching point in every repeating unit. Dendrimers are

fully branched, monodisperse structures while hyperbranched polymers polydisperse and contain linear segments in the structure i.e. a degree of branching less than 1. Hyperbranched polymers are the prime candidates for applications in larger volumes since they are significantly more easily to produce to a lesser cost compared to dendrimers. Dendrimers on the other hand are more well-defined in the structure which is an advantage in high tech applications such as matrixes for drug delivery and optical components.

Hyperbranched polymers exhibit several improved properties compared to their linear analogues when considering them for thermoset coating resins^{17, 18}. The melt viscosity is normally lower for hyperbranched polymers compared to linear structures of the same molecular weight. Hyperbranched polymers have numerous end-groups that greatly affect the properties of the polymers. Modification of the end-groups can be performed either to introduce crosslinkable groups or non-reactive groups that affect properties such as wetting and compatibility.¹⁹ One of the major synthetic difficulties when using hyperbranched polymers for resins is also connected to the large amount of end-groups. The high functionality of the hyperbranched polymers put large demands on reaction employed to modify the end-groups with reactive moieties such as acrylate groups. Even small amounts of side reaction may lead to a significant increase in molecular weight or even gelation of the system.

The present paper describes the use of monomers from vegetable oils sources for radiation curable systems. Cationic polymerization of epoxyfunctional fatty acid derivatives both as low molecular weight monomers and as parts of larger resin structures have been evaluated. A hydroxyfunctional hyperbranched polyether has been evaluated as base for the resin. The effect of resin structure and functionality on the curing performance and end-properties are described. The use of fatty acid derivatives in radiation curable systems will also be discussed from a more general point of view.

Experimental

Materials

The crude vegetable oil (from *Euphorbia lagascae*, containing vernolic acid) was received from Lantmännen (Stockholm, Sweden). Methyl vernoleate was synthesized and purified from the vegetable oil according to procedures previously reported (ref JS#1). Trimethylol propane (TMP) was obtained from Perstorp AB (Perstorp, Sweden). The hydroxyfunctional hyperbranched poly-TMPO was synthesized according to procedures described by Magnusson et al. (ref Helen). All other chemicals used were purchased from either Sigma-Aldrich (Stockholm, Sweden) or Lancaster (Lancashire, United Kingdom) and used as received.

Equipment

All films were polymerized using a Fusion Conveyor MC6R equipped with Fusion electrodeless bulbs standard type BF9. DSC analysis was performed on a Mettler Toledo DSC 820. A Fisherscope H100 microhardness measuring device was used to measure the hardness of the polymerized films. The viscosity of the mixtures was measured using a Brookfield rheometer model DV III. ¹H NMR spectra were obtained on a Bruker Aspect 400 MHz NMR using CDCl₃ as solvent. Size exclusion chromatography (SEC) was performed using a TDA Model 301 equipped with one or two GMHHR-M columns with TSK-gel (Tosoh Biosep), a VE 5200 GPC Autosampler, a VE 1121 GPC Solvent pump and a VE 5710 GPC Degasser, all manufactured by Viscotek Corp. Tetrahydrofuran was used as

the mobile phase. The apparatus was calibrated with linear polystyrene standards, and the molecular weights of the synthesized resins were determined using universal calibration. IR-spectra were recorded on a Perkin Elmer Spectrum 2000 FTIR equipped with a single reflection ATR accessory (golden gate) from Grasseby Specac.

Synthesis of TMP-trivernoleate

0.58 g TMP (4.3 mmol), 4.03 g (13.0 mmol) methyl vernoleate and 0.5 ml 0.1 M NaOH in MeOH were added to a 10 ml flask and left stirring at 80°C under argon flow for 24 hours. The product was purified using flash chromatography on silica gel and a 5:95 mixture of EtOAc:hexane with a yield of 56%.

¹H NMR (CDCl₃): δ = 0.9 (m, CH₃), 1.25-1.45 (br, aliphatic CH₂), 1.5 (m, CH₂CH₂CHOCH), 1.6 (t, CH₂CH₂COO), 2.0 (m, CH=CHCH₂CH₂), 2.3 (t, CH₂COO), 2.1 - 2.4 (m, CHOCHCH₂CH=CH), 2.9 (m, CHOCH), 4.0 (s, COOCH₂) and 5.4-5.6 (m, CH=CH).

Synthesis of hyperbranched polyether vernoleate

1.75 g hyperbranched poly-TMPO (15.4 mmol OH), 4.89 g (15.8 mmol) methyl vernoleate was added to a 10 ml flask together with 2 ml 0.1 M NaOH in MeOH and stirred at 90°C for 48 hours under argon flow. The product was dissolved in hexane and purified with flash chromatography on silica gel using hexane and 10:90 EtOAc:hexane with a yield of 60%.

¹H NMR (CDCl₃): δ = 0.9 (m, CH₃), 1.25-1.45 (br, aliphatic CH₂), 1.5 (m, CH₂CH₂CHOCH), 1.6 (t, CH₂CH₂COO), 2.0 (m, CH=CHCH₂CH₂), 2.3 (t, CH₂COO), 2.1 - 2.4 (m, CHOCHCH₂CH=CH), 2.9 (m, CHOCH), 3.2 (br, CH₂OCH₂ in polyether), 3.5 (br, CH₂OH in polyether), 4.0 (s, COOCH₂ in polyether), and 5.4-5.6 (m, CH=CH).

Polymerizations

In addition to the pure hyperbranched polyether vernoleate (poly-TMPO-vernoleate), methyl ester and TMP-trivernoleate, three mixtures with different composition of poly-TMPO-vernoleate and methyl vernoleate were prepared. The amount of methyl ester added was 10, 20 and 30 percent by weight. In all mixtures the amount of photoinitiator, octyloxydiphenyliodonium hexafluoroantimonate was 2 wt-%. All samples are listed in table 1. Films of each mixture were applied on glass plates and irradiated with 300 mJ/cm² as determined by measuring the intensity with a UVICURE[®] Plus from EIT Inc., Sterling, VA, USA. The thickness of the dry films were measured, and found to be between 24 and 29 μm.

Results and discussion

Synthesis

The hydroxyfunctional hyperbranched polyether (poly-TMPO) used as a core molecule for the resin was synthesized by cationic polymerization of trimethylolpropane oxetane (TMPO) as monomer, figure 2. This synthesis is easily performed in bulk using a thermal onium salt as initiator.^{20, 21} Previous studies²⁰ have revealed that the molecular weight of this polyoxetane is limited to a few thousand Daltons due to intramolecular side reactions i.e. the polymerization is self limiting with respect to molecular weight. The polyether is furthermore highly branched due to reaction of the hydroxyl groups of the monomer. The numerous hydroxyl end-groups are also very suitable for further modification. The backbone itself will not be very susceptible to reactions when for example performing esterification of the hydroxyls. The poly-TMPO has previously shown to exhibit a low viscous non-entangled Newtonian behaviour in the molten state.

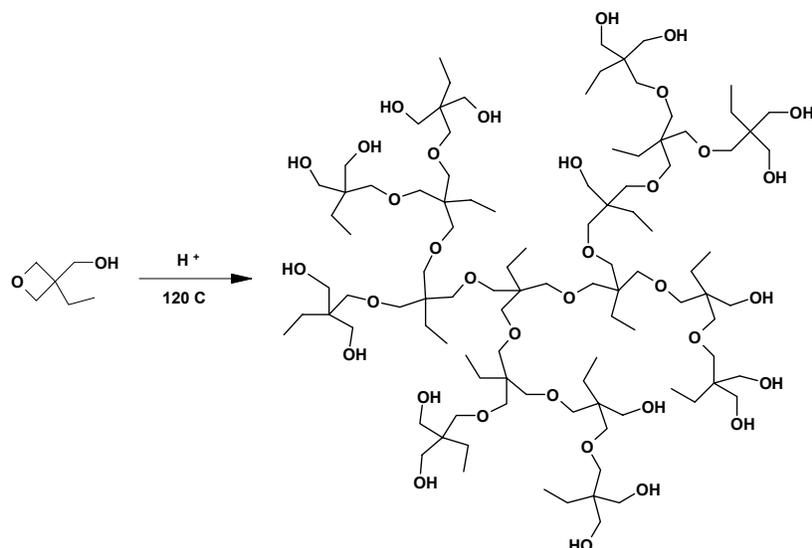


Figure 2. Synthesis of a hydroxyfunctional hyperbranched polyether from TMPO.

The synthesis of the methyl ester, the TMP-trivernoleate and the poly-TMPO-vernoleate were all performed under basic conditions without ring-opening of the epoxy group showing that this is versatile synthetic route for resin synthesis, Figure 3. The structures of the synthesized products were all confirmed with FTIR and H-NMR. Even small amounts of side reactions would also have resulted in a broadening of the molecular weight (or even gelling) when synthesizing the poly-TMPO-vernoleate due to the high functionality of this resin. The M_n and M_w of the poly-TMPO-vernoleate was 5000 and 19000 g/mol respectively.

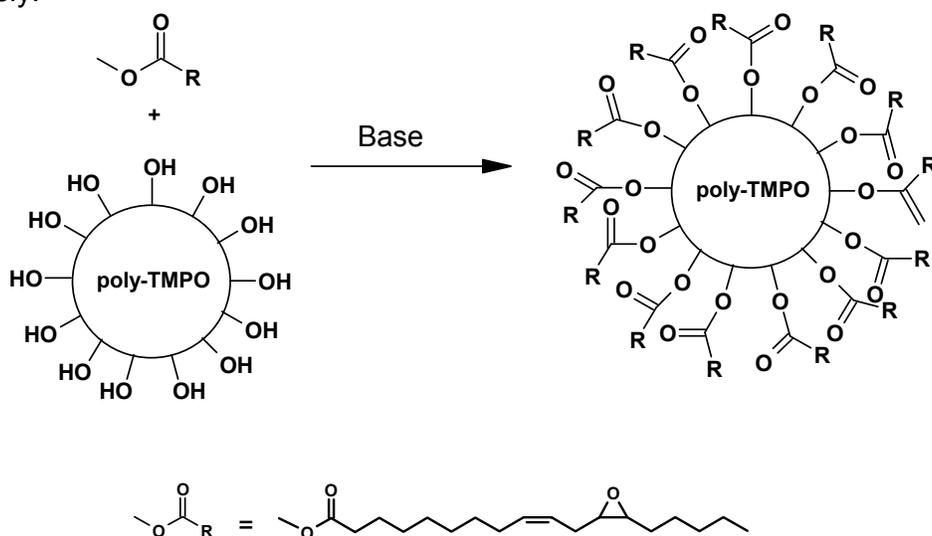


Figure 3. Schematic description of the synthesis of poly-TMPO-vernoleate

The purification of methyl vernoleate with MPLC was furthermore rather simple since this fatty acid differs in polarity compared to the other fatty acids in the vernonia oil. The successful synthesis of is important since it defines the starting point for the final thermoset and its properties.

Properties of the resins before cure

The viscosity of the different resins and mixtures are listed in Table 1. These results show that the hyperbranched resin has a relatively low viscosity considering the high molecular

weight of the resin. The results further show that the methyl ester strongly reduces the viscosity of the mixtures to viscosity levels suitable for coating applications. The methyl esters are not volatile at ambient conditions why the methyl esters can be considered to be suitable as reactive diluents.

Table 1. Samples compositions and viscosities of resin mixtures.

Resin mixtures (% w/w)				
Sample no.	Poly-TMPO-vernoleate	Methyl vernoleate	TMP-trivernoleate	Viscosity (mPas)
1	~	~	100	150
2	100	~	~	4080
3	90	10	~	1760
4	80	20	~	865
5	70	30	~	460
6	~	100	~	9

The similarity in structure between the methyl ester and the end-groups of the poly-TMPO-vernoleate afforded no problems with miscibility between the components.

Curing performance

All mixtures were polymerized with a dose of 300 mJ/cm². IR-spectra of the films revealed a significant decrease of the epoxy peak at 823 cm⁻¹ i.e. no detectable amount of residual epoxy groups remained after polymerization. H-NMR on the polymer of the pure methyl vernoleate did not show any detectable residual amount of epoxy groups. The molecular weight of the linear poly-methyl vernoleate was determined to a M_w of 6800 g/mol corresponding to a DP of 27. These results show that the secondary epoxy group of vernolic acid polymerizes readily under the set conditions. Previous attempts to polymerize vernolic acid derivatives have failed due to poor miscibility of other onium salts with fatty acid derivatives.

Final film properties

Thermal analysis of the films from that the T_g shifts approximately 10°C per 10% methyl vernoleate added to the poly-TMPO-vernoleate resin, table 2. The T_g's range from 16°C for pure poly-TMPO-vernoleate to -18°C for sample containing 30% methyl ester. The use of pure methyl vernoleate with also ensures that it is not fractions of non-reactive methyl esters that induce the differences. The methyl vernoleate is reacted in the middle of the fatty acid chain creating a two side branches from the main chain. These side branches are proposed to act as soft segments in the formed network. The fatty acids on poly-TMPO-vernoleate have a more restricted mobility since one end of the fatty acid is attached to the poly-TMPO-core molecules leaving only one "free" part of the fatty acid chain after the polymerisation. The effect contribution of the core structure can furthermore be seen when comparing the cured films of poly-TMPO-vernoleate and TMP-trivernoleate. The T_g differs with almost 40°C showing the effect of functionality and core structure on the properties. This also shows that it is possible to vary the properties to a large extent depending on the structure of the core molecule used. A further increase in final T_g could probably be obtained either by a further increase in functionality or by the use of another, more rigid, core structure.

Table 2. Thermal and mechanical properties of the cured films.

Sample no.	Tg of cured films (°C)	Hardness (HU)
1	-21	3.55
2	16	8.11
3	4	4.11
4	-10	3.50
5	-18	3.10

The hardness data exhibit a logical trend with a decrease in hardness with increasing amount of methyl vernoleate. The larger difference between sample 2 and 3 can be attributed to the fact that the measurement on the film from pure poly-TMPO-vernoleate was made close to the glass transition temperature whereas the other measurements were performed well above Tg. Comparing the Tg and hardness data from samples 1, 4, and 5 also indicate that the both differences in network density (functionality of the resin) and the rigidity of the core structure will affect the final properties. Samples 1 and 4 have a similar hardness but different Tg while samples 1 and 5 have similar Tg but different hardness.

Conclusions

The present work describes a versatile route to synthesize a hyperbranched resins with epoxyfunctional fatty acid end-groups. The hyperbranched scaffold that the methyl vernoleate is attached to is a hydroxyfunctional hyperbranched polyether made by cationic polymerisation of trimethylol propane oxetane. The fatty acid modified resin polymerise readily by itself or together with methyl vernoleate as a reactive diluent as determined with H-NMR and FTIR. Methyl vernoleate act as a suitable reactive diluent for the system reducing the viscosity to acceptable levels.

Acknowledgements

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