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Epoxidized Vegetable Oils for Bio-based Thermoset Epoxy Resins

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PURPOSE OF THE ABSTRACT
Vegetable Oils (VO) constitute the single, largest, easily available, low cost, non-toxic, non-depletable and biodegradable family yielding materials that are capable of competing with fossil fuel derived petro-based products[1]. Therefore, they find innumerable industrial applications such as plasticizers, biodiesel, lubricants, adhesives, biodegradable packaging materials, printing inks, paints and coatings.

VO are generally composed by triglycerides which are comprised of three fatty acids joined at a glycerol junction. Fatty acid varies from 14 to 22 carbons in length, with 0 to 3 double bonds and may even contain a functional group. The most important fatty acids are shown below (Figure 1).
Considering oils diversity, SPECIFIC POLYMERS wishes to take this advantage to modulate thermo-mechanical properties of thermoset epoxy materials. Doing that, intensive chemical modifications are reduced and green synthetic pathway is preserved. Moreover, SPECIFIC POLYMERS pays a significant attention to the non-edible aspect for the selection of the vegetable oils.
Thus, a large range of VO (castor oil, St John's wort oil, Rose Hip seed oil, ...) with various double bonds content (from 3meq/g to 8meq/g) was selected. Evaluation of the composition of each oil (omega-3, omega-6, omega-9, saturated fatty acids) and the double bond content were performed by NMR 1H to adapt the epoxidation process conditions. Thus, epoxidation was performed by using an eco-friendly triphasic system with hydrogen peroxide, acetic acid and a supported acid catalyst (Figure 2). The use of this procedure enables us to develop a general method for the epoxidation of vegetable oils.

All synthesized epoxidized oils were characterized by NMR 1H titration and SEC-THF/PS standard. These analyses allow to validate the chemical structure and to determine both the epoxy content and eventual side-reactions which may occur depending on the raw vegetable oil quality. Epoxidized vegetable oils were obtained with high yield and high purity. Obtained results highlight epoxy content range from 2.5meq/g to 7meq/g.

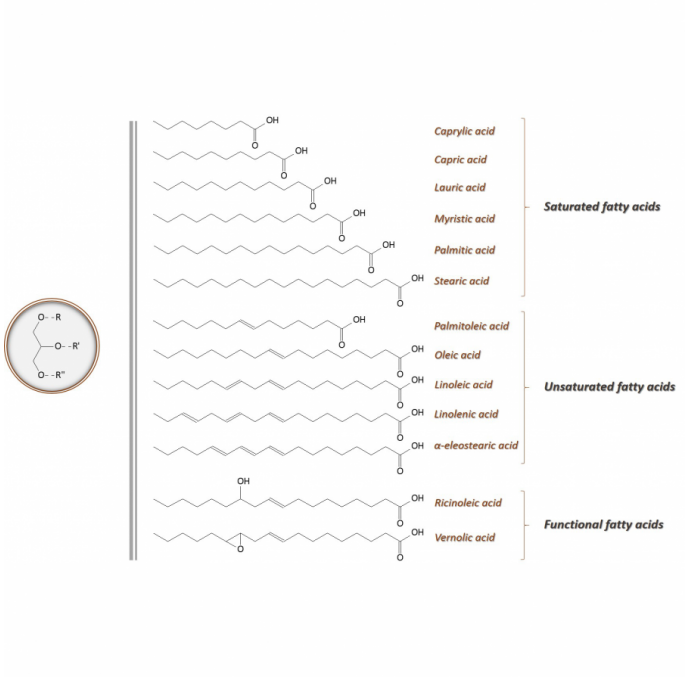
This relatively soft epoxidation procedure avoids side-reactions and provides an epoxy content accessibility from 2.5meq/g to 7meq/g.

Several experiments were set out to assess and compare the thermal and mechanical properties of thermoset materials prepared from epoxidized VO. In that way, various initiators and hardeners were confronted to select the most promising curing system. Curing conditions were selected studying the crosslinking reaction by isothermal

Differential Scanning Calorimetry (DSC) analyses. Thermomechanical properties (Glass Transition Temperature (Tg), Stress relaxation and Degradation temperature) of all prepared materials were measured by Differential Scanning Calorimetry (DSC), Dynamic mechanical analysis (DMA) and Thermogravimetric analysis (TGA) respectively.

TGA measurements showed that the obtained materials are thermally stable up to 250°C, which is comparable to the values commonly obtained with fossil-derived thermosets. DMA analysis revealed that Tg (°C) values vary from 40°C to 70°C depending on the selected oil. Interestingly, the elastic modulus fluctuates from 80 to 400MPa before Tg and from 0.2 to 3MPa after Tg.

FIGURES



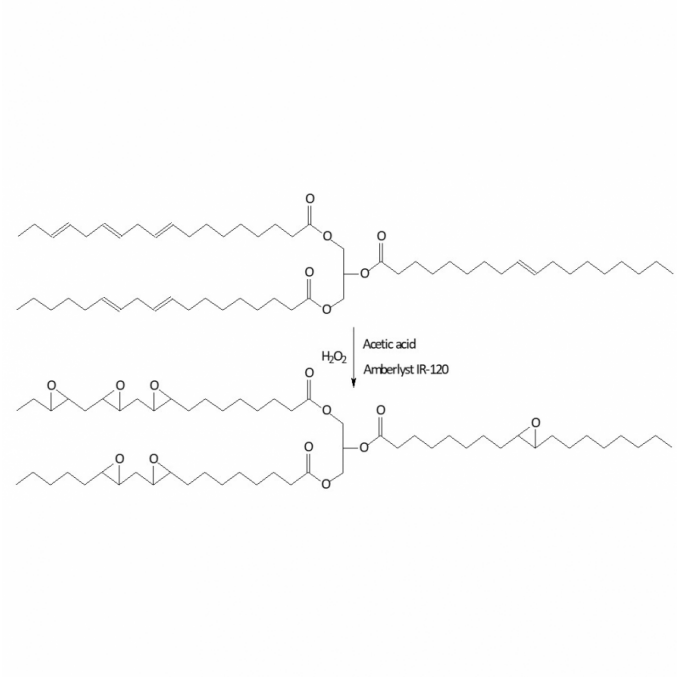


FIGURE 1

Figure 1

Structures of the most important fatty acids

FIGURE 2

Figure 2

Synthesis pathway of epoxidized Vegetable Oils

KEYWORDS

Bio-based Epoxy | Vegetable oils | Thermoset Materials

BIBLIOGRAPHY

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