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A Comparison of the Syntheses of High Molar Mass Epoxy Resins on the Basis of two Groups of Modified Vegetable Oils

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Summary: Application of epoxidized and hydroxylated natural oils as a new group of environmentally friendly and renewable raw materials for the synthesis of high molar mass epoxy resins is described. Selected vegetable oils were first oxidized and next reacted with mono and diethylene glycols. Obtained epoxidized soybean, rapeseed, linseed and sunflower oils were used together with Bisphenol A in the fusion process. Analogously, hydroxylated soybean and rapeseed oils were reacted with commercial grade Bisphenol A-based low molar mass epoxy resin. The fusion process was carried out in the presence of selected catalysts (*i.e.*, lithium chloride, 2-methylimidazole, triphenylphosphine and triethanolamine) giving high molar mass epoxies. The relationship between type of modified oil used in the synthesis and reaction conditions and properties of synthesized resins (*e.g.*, value and distribution of average molar mass, contents of epoxy groups and colour) is discussed.

Keywords: epoxy resins; fusion process; renewable resources

Introduction

Importance of high molar mass epoxy and epoxy ester resins, used mainly as industrial powder can and coil coatings, molding powders and adhesives,[1,2] implicates search for new raw materials and methods for their synthesis.[3–5] High molar mass epoxies are synthesized either by the reaction of bisphenols with stoichiometric amount or small excess of epichlorohydrin, or more often, in the fusion process using different bisphenols and low or medium molar mass epoxy resins.[6,7] Simultaneously, the application of natural oils as nontoxic, renewable and biodegradable raw materials and additives for different polymers[8,9] still grows. Various possibilities of using modified natural oils in the technology of epoxy resins have also been reported.[10–15] Therefore, the application of epoxidized vegetable oils in place of low/medium molar mass resins, as well as hydroxylated oils in place of bisphenols in the fusion reaction with Bisphenol A (BPA) or BPA-based epoxy resin is proposed. The epoxy value, colour, number/weight-average molar mass and polydispersity of the resins obtained were studied in relation to the reaction conditions and are discussed in this work.

Materials

Epoxidized soybean oil (Boryszew S.A., Poland), rapeseed oil (Kruszwica S.A., Poland), linseed oil (Institute of Natural Fibres in Poznań, Poland) and sunflower oil (Fatty-Processing Plant in Warsaw, Poland) were used as the commercial grade products as received. Selected oils were epoxidized and next hydroxylated according to the procedure described earlier,[16,17] giving products characterized in Table 1.

Bisphenol A (GE Cartagenie, Spain; purity 99.93%, melting temperature 156.8 °C,

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Table 1.
Characteristics of modified oils used for the synthesis of high molar mass epoxy resins.

Modified oil	Epoxy value (mol/100 g)	Hydroxyl value (mgKOH/g)	Water content (wt. %)	Viscosity (mPa · s)
Epoxidized soybean oil (ESO)	0.363	–	0.0198	400.0
ESO/monoethylene glycol (S-MEG)	0.010	299.9	0.6832	4450.4
ESO/diethylene glycol (S-DEG)	0.048	203.3	0.5137	5612.9
Epoxidized rapeseed oil (ERO)	0.280	–	0.0112	102.0
ERO/monoethylene glycol (R-MEG)	0.033	203.4	0.4811	6849.0
ERO/diethylene glycol (R-DEG)	0.011	259.0	0.2453	1631.0
Epoxidized linseed oil (ELO)	0.280	–	0.0085	407.2
Epoxidized sunflower oil (ESnO)	0.370	–	0.0129	156.4

colour 5 in Hazen colour scale, *o-p* isomer contents 0.0109%, phenol contents 0.0066% and water contents 0.14%) was used. Commercial grade epoxy resin Ruetapox 0162 (Bakelite AG, Germany; epoxy value 0.582 mol/100g, viscosity 4833 mPa · s, colour <2 in Gardner colour scale) was chosen for this research. Lithium chloride, 2-methylimidazole, triethanolamine and triphenylphosphine (Merck, Germany, pure for the synthesis) were used as catalysts without any additional purification.

Syntheses of high molar mass epoxy resins were carried by the fusion process in the presence of the catalysts, at the temperature range depending on the catalyst type (130–160 °C), under nitrogen to minimize oxidative degradation. Weight ratio of Bisphenol A to epoxidized oil and hydroxylated oil to Ruetapox 0162 epoxy resin was calculated from rearranged equation,[2,17] assuming the epoxy value of the synthesized resin of 0.100 mol/100 g (Table 2):

$$x \cdot n_{EO} - 2 \cdot n_{BPA} = y \cdot n_{ERf}$$

where:

x – number of epoxy groups in epoxidized oil,
y – final number of epoxy groups in epoxy resin,
n_{EO} – number of moles of epoxidized oil,
n_{BPA} –number of moles of BPA,
n_{ERf} –number of moles of high molar mass epoxy resin.

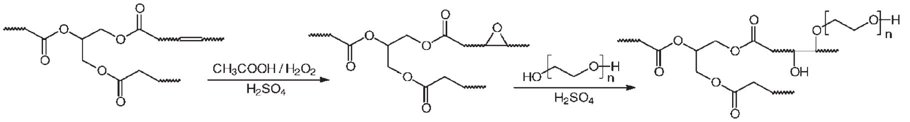
The amount of catalysts was 0.0002 mol per mol BPA and 0.0001 mol per mol hydroxyl groups in the hydroxylated oil, in all syntheses.

Results and Discussion

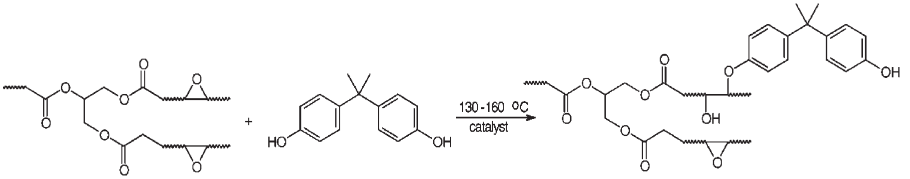
There are two possibilities of replacement of petrochemical raw materials with modified vegetable oils in the synthesis of high molar mass epoxy resins via the fusion process. Suitable derivatives of natural oils can be prepared in the simple reactions of epoxidation and subsequent hydroxylation (Scheme 1), using different glycols.

Table 2.
Amounts of reagents for the fusion processes.

Modified oil	BPA/Oil ratio (g/100g oil)	Oil/Ruetapox 0162 ratio (g/100 g resin)
Epoxidized soybean oil (ESO)	25.56	–
ESO/monoethylene glycol (S-MEG)	–	76.27
ESO/diethylene glycol (S-DEG)	–	104.68
Epoxidized rapeseed oil (ERO)	18.44	–
ERO/monoethylene glycol (R-MEG)	–	104.64
ERO/diethylene glycol (R-DEG)	–	86.17
Epoxidized linseed oil (ELO)	18.44	–
Epoxidized sunflower oil (ESnO)	27.66	–



Scheme 1.
Modification of natural oils used (n = 1 for hydroxylation using monoethylene glycol and n = 2 for hydroxylation using diethylene glycol).



Scheme 2.
Reaction of epoxidized natural oils with Bisphenol A.

Using of epoxidized oils in place of low/middle molar mass epoxy resins (Scheme 2) was checked as the first method of the synthesis.

After dissolving of BPA in the epoxidized oil at 110 °C, the temperature was raised to the value necessary for the catalyst activity, (*i.e.,* to 130 °C for TEA, 150 °C for 2-MI and TPP, and, 160 °C for LiCl and for the synthesis without catalyst). These catalysts are commonly used as catalysts for the synthesis of high molar mass epoxy resins by the fusion process. Although, 2-MI is used as a curing agent for high molar mass epoxy resins, its small amount ensured that final products were obtained uncured.

All syntheses were monitored by determination of the epoxy value and weight-average molar mass. Decrease of content of epoxy groups, followed by increase of weight-average molar mass was observed in all reactions (Figure 1), even those carried out without catalyst (Table 3).

Nevertheless, it was found that epoxidized natural oils used in this research exhibited different reactivity towards Bisphenol A (Table 3). Thus, epoxidized rapeseed oil showed the highest reactivity

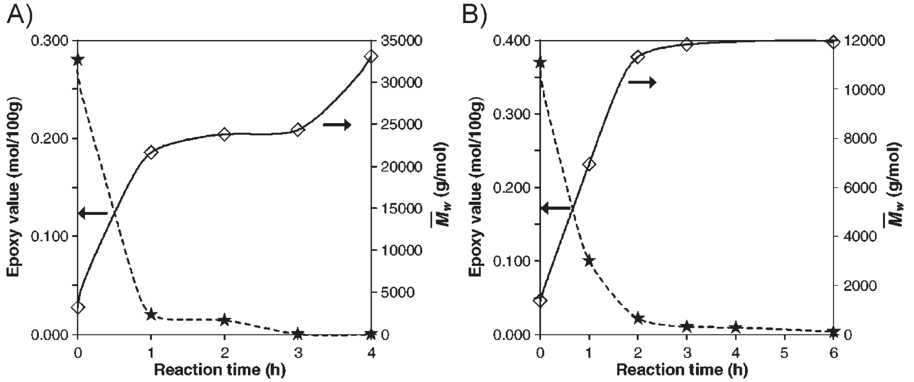


Figure 1.
Variation of (★) epoxy value and (◇) weight-average molar mass during the reaction of (**A**) ELO/BPA carried out in the presence of LiCl and (**B**) ESnO/BPA in the presence of TPP.

Table 3.
Reaction time and properties of the products of studied syntheses.

Catalyst	–	LiCl	TEA	TPP	2-MI
Epoxidized rapeseed oil					
Epoxy value (mol/100 g)	0.005	0	0	0	0
Reaction time (h)	0.5	13$^{a)}$	10$^{a)}$	12$^{a)}$	10$^{a)}$
Epoxidized linseed oil					
Epoxy value (mol/100 g)	0.060	0	0.056	0.101	0.075
Reaction time (h)	0.5	4	3$^{b)}$	1	0.5
Epoxidized soybean oil					
Epoxy value (mol/100 g)	0.281	0.090	0.287	0.270	0.197
Reaction time (h)	13	11	14	10	16
Epoxidized sunflower oil					
Epoxy value (mol/100 g)	0.001	0	0.050	0.003	0.090
Reaction time (h)	3$^{c)}$	20$^{c)}$	10$^{d)}$	6$^{c)}$	5$^{c)}$

$^{a)}$after 1h the product's epoxy value was too low to be determined.
$^{b)}$epoxy value 0.109 mol/100g was obtained after 2 h.
$^{c)}$epoxy value $<$0.100 mol/100g was obtained after 1 h.
$^{d)}$epoxy value 0.092 mol/100g was obtained after 5 h.

and the reaction had to be carried out very carefully to prevent gelation. ELO exhibited very similar reactivity, while the use of catalysts enabled obtaining products with higher molar mass. Selected catalysts are responsible for minimization of gelation as a result of chain branching, for promoting the reaction between phenolic hydroxyl groups and epoxy groups, and, for limiting the side reactions of epoxy-epoxy and epoxy-secondary hydroxyl groups. Products with a comparable epoxy value and molar mass could be synthesized in the ESnO reaction carried out in the presence of TEA and without using of any catalyst (Table 3 and 4). Nevertheless, using of TEA enabled preparation of the resins definitely lighter in colour. Moreover, the processes in the presence of LiCl, TEA and 2-MI could be carried out for a longer time, which led to products with higher molar mass. Different results of the catalyst

Table 4.
Molar mass data (from GPC analysis) and colour of the resins synthesized.

Catalyst	–	LiCl	TEA	TPP	2-MI
Epoxidized rapeseed oil					
$\overline{M}_n$ (g/mol)	3284	2279	2765	2300	2750
$\overline{M}_w$ (g/mol)	25490	8289	10880	8574	9639
P_d	5.29	3.63	3.82	3.73	3.51
Colour (Gardner scale)	14	17	14	16	17
Epoxidized sunflower oil					
$\overline{M}_n$ (g/mol)	2631	2525	1647	3274	2892
$\overline{M}_w$ (g/mol)	9126	11450	9826	11920	10020
P_d	3.74	4.54	3.71	3.46	3.74
Colour (Gardner scale)	12	16	5	15	14
Epoxidized soybean oil					
$\overline{M}_n$(g/mol)	1545	2638	1436	1489	1833
$\overline{M}_w$ (g/mol)	2777	14600	2263	2431	5513
P_d	1.80	5.53	1.58	1.63	3.01
Colour (Gardner scale)	8	12	10	4	15
Epoxidized linseed oil					
$\overline{M}_n$ (g/mol)	2464	3237	3389	2287	2514
$\overline{M}_w$ (g/mol)	8996	33100	23370	8779	11080
P_d	3.65	10.23	6.90	3.84	4.41
Colour (Gardner scale)	6	17	9	6	7

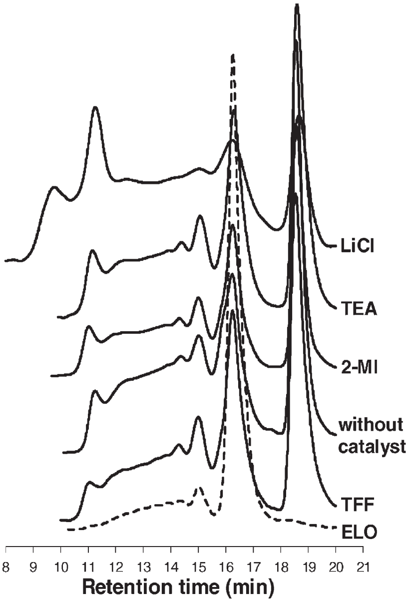
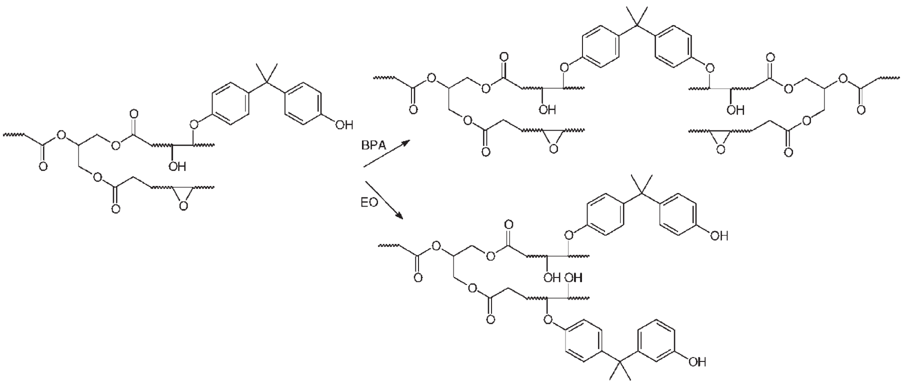


Figure 2.
GPC chromatograms of the products of the reaction ELO/BPA in the presence of different catalysts.

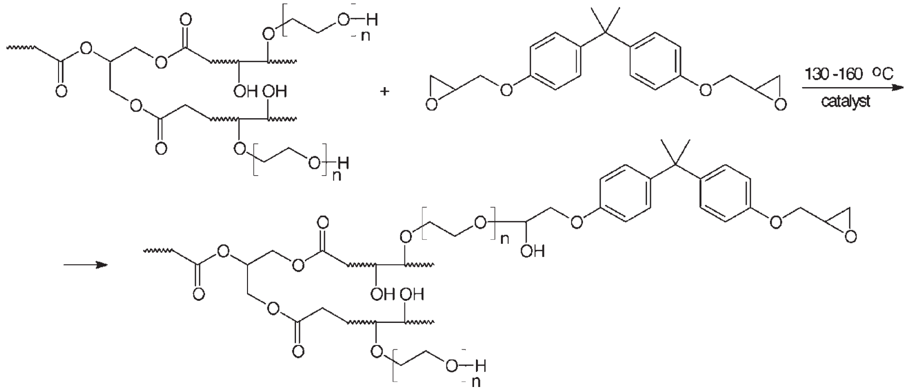
activity could be observed also in the case of other oils (*e.g.,* in reactions of ELO – Figure 2, Tables 3 and 4). However, it is impossible to define exact relations between the type of catalyst and the product properties, *e.g.,* it is impossible to indicate the catalyst responsible for colour or polydispersity of the final products.

There are two possibilities of growth of resin molecules in the reaction of epoxidized oils with BPA (Scheme 3).

Typically, the observed decrease of the epoxy value and the increase of the weight-average molar mass of the product were complementary (Figure 1B) that confirms that rather alternate reaction between BPA



Scheme 3.
The possibilities of growth of resin molecules in the reaction with a second molecule of Bisphenol A or another molecule of epoxidized oil (EO).



Scheme 4.
Reaction of hydroxylated natural oils with low molar mass epoxy resin.

and ELO occurred during the fusion process. The data obtained from GPC analysis show that the structure consisting of 3 molecules of EO and 4 or 5 molecules of BPA were dominant. However, the nontypical increase of molar mass at the end of the reaction (Figure 1A) without decrease of the epoxy value proves that the intermolecular reaction between growing molecules occurred, too (Scheme 3).

Using hydroxylated oils instead of bisphenols as reagents in the fusion process with middle or low molar mass epoxy resins is another possibility of use of natural oils for the syntheses studied here (Scheme 4). The reactions of soybean (S-DEG) and rapeseed oils (R-DEG), hydroxylated using mono and diethylene glycols, with Bisphenol A-based low molar mass epoxy resin (Ruetapox 0162) proceeded analogously to the reaction of the epoxidized oils

Table 5.
Parameters of the products of the reactions of hydroxylated oils with Ruetapox 0162 resin in the presence of different catalysts.

Catalyst	Epoxy Value (mol/100g)	$\overline{M}_n$ (g/mol)	$\overline{M}_w$ (g/mol)	P_d	Colour (Gardner scale)
S-MEG					
–	0.071	898	8732	9.72	4
LiCl	0.092	943	9446	10.02	8
TEA	0.219	430	1289	3.00	8
TPP	0.162	660	3905	5.91	4
2-MI	0.141	942	8649	9.18	3
S-DEG					
–	0.080	871	7271	8.35	8
LiCl	0.120	711	4689	6.59	9
TEA	0.199	554	3046	5.50	10
TPP	0.071	1037	10350	9.98	10
2-MI	0.078	829	6056	7.30	10
R-MEG					
–	0.201	499	2196	4.40	4
LiCl	0.243	424	2067	4.88	4
TEA	0.240	532	1718	3.23	5
TPP	0.178	501	2391	4.77	4
2-MI	0.240	517	2324	4.50	5
R-DEG					
–	0.246	413	1592	3.71	4
LiCl	0.280	407	1887	4.69	4
TEA	0.185	837	3271	3,91	6
TPP	0.190	555	2218	3.99	8
2-MI	0.206	474	1654	3.49	5

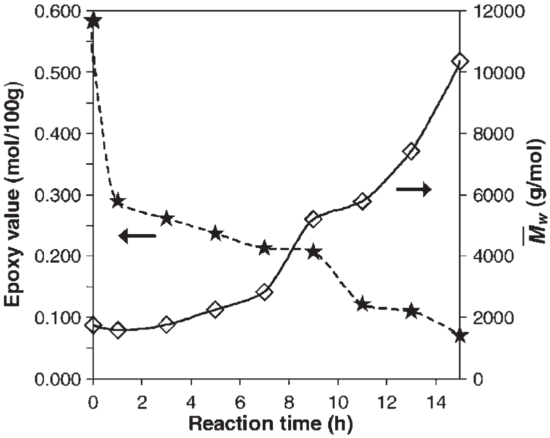


Figure 3.
Variation of (★) epoxy value and (◇) weight-average molar mass during the reaction of oil S-DEG with Ruetapox 0162 resin in the presence of TFF.

described above. High molar mass epoxy resins were obtained in all cases, also without any catalyst (Table 5, Figures 3 and 4).

However, the resins with the particular epoxy value were synthesized only from modified soybean oils. Moreover, all resins obtained from the hydroxylated oils showed a lower degree of polymerization than the products of the reactions of epoxidized oils (Table 5), even if the reactions were carried out for 15h. It was found, that hydroxylated rapeseed oils exhibited lower reactivity than the epoxidized one. Generally, the epoxy resins with lighter colour were obtained from the hydroxylated oils rather than from the epoxidized ones. Analogously, two ways

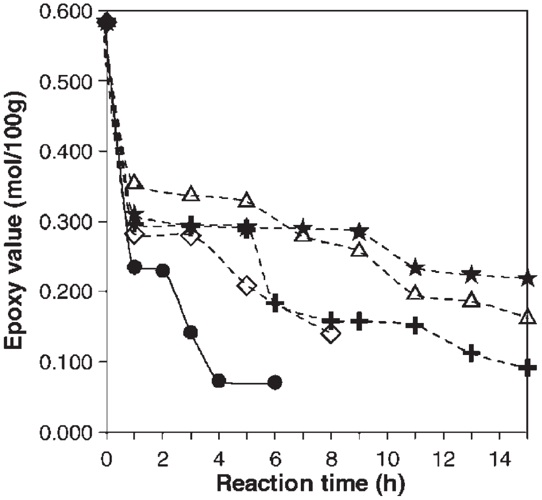
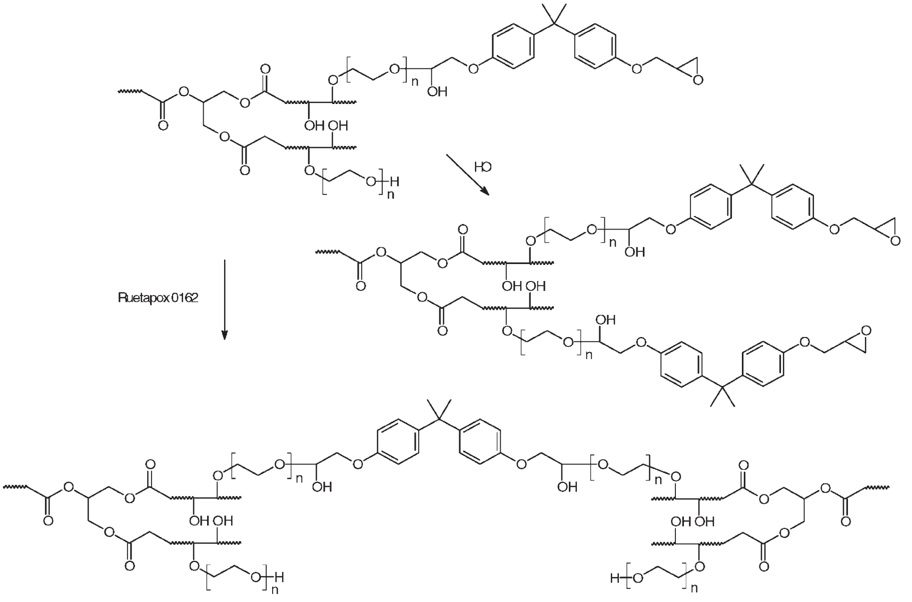


Figure 4.
Variation of epoxy value during the reaction of S-MEG/Ruetapox 0162 carried out: (●) without catalyst, and, in the presence of (✚) LiCl, (◇) 2-MI, (△) TPP and (★) TEA.



Scheme 5.
The subsequent reactions of the growing macromolecules with low molar mass epoxy resin or with hydroxylated oil (HO).

of the molecule growth are possible in the fusion processes with the hydroxylated oils (Scheme 5).

Taking into account the variation of the epoxy value, weight-average molar mass and GPC data, it can be concluded that the reactions between low molar mass epoxy resin and HO are more likely than the intermolecular reactions.

Conclusions

The natural oils are cheap, renewable and environmentally friendly materials. The results obtained in this research show that both groups of modified vegetable oils: the epoxidized and the hydroxylated oils can be applied as raw materials for the synthesis of high molar mass epoxy resins. These oils can partially replace petrochemical raw materials such as bisphenols and Bisphenol A-based epoxy resin typically used in the fusion process. Nevertheless, the resins containing not only elastic chains of triglycerides but also rigid Bisphenol A units are still synthesized using these methods. By choosing the proper type of oil modification and the most effective catalyst it is possible to synthesize epoxy resins characterized by light colour, low epoxy value, different contents of hydroxyl groups and different degrees of polymerization. Moreover, all products of syntheses are viscous liquids, a fact that is very important from the point of view of processing and application, especially for coating materials.

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