Characterization of an Epoxy Resin Modified with Natural Oil-Based Reactive Diluents

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Summary: Modified natural oils - epoxidized soybean and rapeseed oils were tested as reactive diluents for viscosity regulation of Bisphenol A-based low-molecular-weight epoxy resin. Satisfactory viscosity reducing ability of epoxidized oils as well as non-Newtonian rheological behaviour of the resin diluted with modified oils were demonstrated. Co-crosslinking of mixed oil-resin compositions using isophorone diamine was studied showing essential decreasing of the reaction heat and slight increasing of the peak maximum temperature. Mechanical properties, thermal stability, water absorption and chemical resistance of the epoxy resin modified with natural oils were also investigated.

Keywords: epoxy resin; mechanical and thermal properties; rapeseed oil; viscosity

Introduction

As nontoxic, biodegradable and renewable raw materials, modified vegetable oils are widely used for the modification (e.g. as plasticizers or stabilizers) and preparation of different polymers (mostly polyesters and polyurethanes).[1] However, there are only a few data about using natural oils for the modification and synthesis of epoxy resins.[2–5] Possibility of using of epoxidized natural oils as reactive diluents for epoxy resins was studied and the results are presented in this work.

Materials

Epoxidized soybean oil (ESO) (Boryszew S.A., Poland, epoxy value: 0.369 eq./100 g, iode value: 2.92 mol/100 g, containing about 25 g/100 g of monounsaturated fatty acids and 60 g/100 g of polyunsaturated fatty acids) and epoxidized rapeseed oil (ERO) (Kruszwica S.A., Poland, epoxy value: 0.280 eq./100 g, iode value: 25.70 mol/100 g, containing about 66 g/100 g of monounsaturated fatty acids and 27 g/100 g of polyunsaturated fatty acids) were applied as modified natural oils. Low-molecular-weight epoxy resin Rütapox 0162 (Bakelite AG, Germany; epoxy value: 0.582 eq./100 g) contained almost pure diglycidyl ether of Bisphenol A was selected for this research. Pure epoxy resin and mixing resin-oil compositions were crosslinked by commonly used hardener isophorone diamine (Aradur 46, Huntsman, Germany, H^+ active equivalent: 95 g/eq., amine value: 320 mg KOH/g).

Results and Discussion

Viscosity reducing ability of epoxidized soybean oil and rapeseed oil was tested in the compositions with Bisphenol A based low-molecular-weight epoxy resin Rütapox 0162. It was found that the oils tested exhibit strong viscosity reducing ability comparable to commercial grade reactive diluents (e.g. monoepoxides as 2-ethylhexylglycidyl ether, EGE) (Fig. 1).

Although it is necessary to use a few times more oils than the monoepoxide diluent EGE (Table 1), it is still possible to

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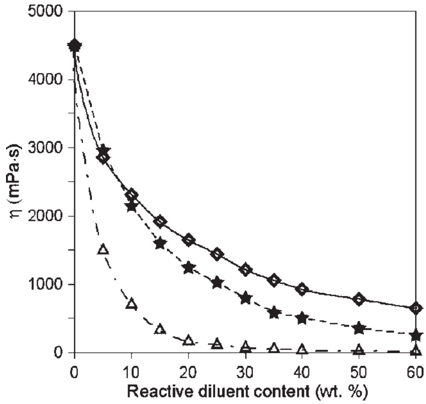

Figure 1.
Fluxing of Rütapox 0162 using: (◇) ESO, (★) ERO and (△) EGE.

Table 1.
Percentage of the reactive diluents in the compositions of Rütapox 0162 necessary to obtain the assumed viscosity.

Reactive diluent	Diluent concentration, wt. %		
	1500 mPa · s	700 mPa · s	500 mPa · s
EGE	5.0	10.0	12,0
ESO	22.9	54.2	–
ERO	16.7	32.5	39,9

reduce epoxy resin viscosity to value below 1000 mPa · s, indispensable for many applications. ERO exhibited stronger viscosity reducing ability than ESO. Viscosity: 1500 mPa · s (dynamic viscosity required for casting resins) and 700 mPa · s (typical viscosity of laminate impregnants) of mixed compositions were selected for further studies. All of the compositions studied showed a non-Newtonian rheological behaviour, typical for Bingham liquids (Fig. 2).

The values of the flow index (n) and the consistency index (k) for the compositions tested in the temperature range 25–65 °C were calculated from the Ostwald-de Waele rheological model and are listed in Table 2 (complete rheological characteristic of ESO compositions was presented in earlier papers[6–8]).

Next, the values of the consistency index were used to calculate the flow-activation energy (E_a) for mixed oil-resin compositions with different concentration of ESO and ERO, using the Arhenius equation (Tab. 2). Decreasing of the flow-activation energy with increasing ESO and ERO concentration can be explained as the lubricant effect of the tested oils in the compositions with the epoxy resin.[2] The values and variation of the flow index and the consistency index proved that the compositions studied are pseudoplastic liquids.

The mixed resin-oil compositions can be co-crosslinked with the resins into homogenous materials using typical hardeners

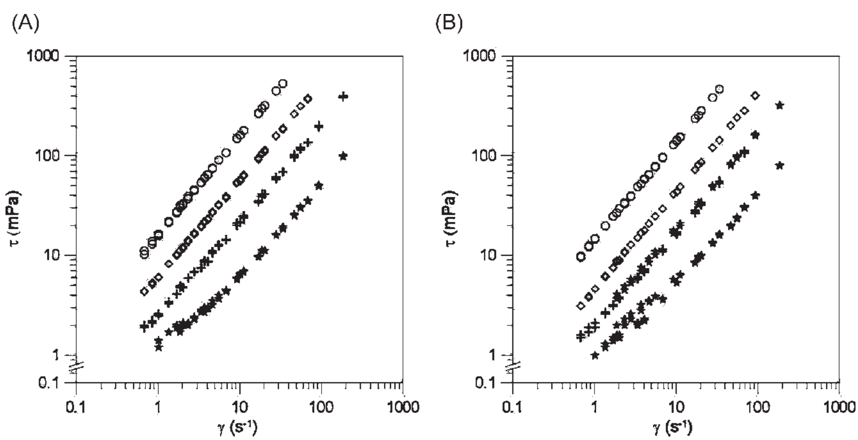

Figure 2.
Flow curves of the composition of Rütapox 0162 with (**A**) epoxidized soybean oil and (**B**) epoxidized rapeseed oil used as the reactive diluents, viscosity 1500 mPa · s: temperature: (○) 25 °C, (◇) 35 °C, (+) 45 °C and (★) 65 °C.

Table 2.
Variation of the flow index (*n*), the consistency index (*k*) and the flow-activation energy (E_a) with temperature (T) and viscosity of ERO compositions.

Composition viscosity	T, °C	*n*	*k*	E_a, kJ/mol
1500 mPa · s	25	0.984	1.447	56.89
	35	0.983	0.455	
	45	0.956	0.199	
	65	0.820	0.091	
700 mPa · s	25	0.890	0.924	52.95
	35	1.014	0.241	
	45	0.980	0.126	
	65	0.866	0.066	
500 mPa · s	25	0.967	0.514	39.35
	35	0.995	0.216	
	45	0.901	0.141	
	65	0.797	0.073	

used for epoxy resins. DSC study of crosslinking of ESO and ERO compositions using isophorone diamine showed significant decrease of the reaction heat and increase of the peak maximum temperature (Table 3). It can increase the time of processing of epoxy compositions and can eliminate internal stresses which cause fracture of final products.

It was found that modification of epoxy resin with epoxidized natural oils resulted in reduction of tensile strength, however essential increase of relative elongation at break was observed for ESO compositions (Fig. 3) and RERO 2500 composition (Table 4).

Increase of epoxidized oils concentration leads to decrease of flexural and compression strengths of cured compositions (Table 4, Figs. 4 and 5). No essential change in compressive strain was observed, although deflection of ERO compositions increased significantly. Substantial reduction of hardness was observed (Fig. 6); however, this reduction was followed by increase of impact strength (even by 90% for ERO composition with starting viscosity 2500 mPa · s, Tab. 4).

Modification with epoxidized oils reduced crosslink density of the epoxy

Table 3.
DSC data of the curing process of the mixed resin-oil compositions.

Composition viscosity, mPa · s	ΔH_c, J/g	T_{onset}, °C	$T_{max.}$, °C	T_{end}, °C
4 500	456.7	24.9	98.1	204.7
2 500	451.3	30.4	99.3	216.0
1 000	387.7	22.1	106.3	185.6
700	376.0	26.9	106.6	203.3
500	310.0	24.4	107.6	182.2

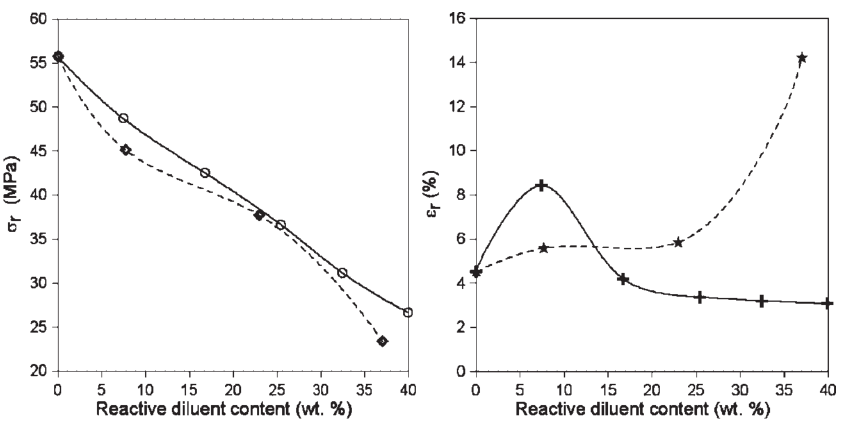

Figure 3.
Effect of epoxidized oils content on tensile strength (◇ - ESO, (○ - ERO) and relative elongation at break (★ - ESO, + - ERO) of studied compositions.

Table 4.
Selected mechanical properties of the cured mixed resin-oil compositions.

Composition	Rütapox 0162	RERO 2500	RERO 1500	RERO 1000	RERO 700	RERO 500
ERO concentration, %	0	7.45	16.73	25.42	32.47	39.91
Tensile strength, MPa	55.7	48.7	42.5	36.6	31.1	26.7
Tensile modulus, MPa	2549.0	2095.3	1846.9	1426.9	1360.5	1281.4
Relative elongation at break, %	4.5	8.4	4.2	3.4	3.2	3.1
Flexural strength, MPa	81.5	70.2	60.5	49.1	43.4	36.7
Flexural modulus, MPa	2207.9	2023.3	1747.0	1495.0	1300.3	1087.0
Compression strength, MPa	70.6	40.3	38.9	36.4	35.0	28.8
Ball indentation hardness, MPa	122.9	94.8	75.6	71.2	65.1	60.8
Impact strength (Charpy), kJ/m^2	9.4	17.9	16.6	13.1	13.0	11.4

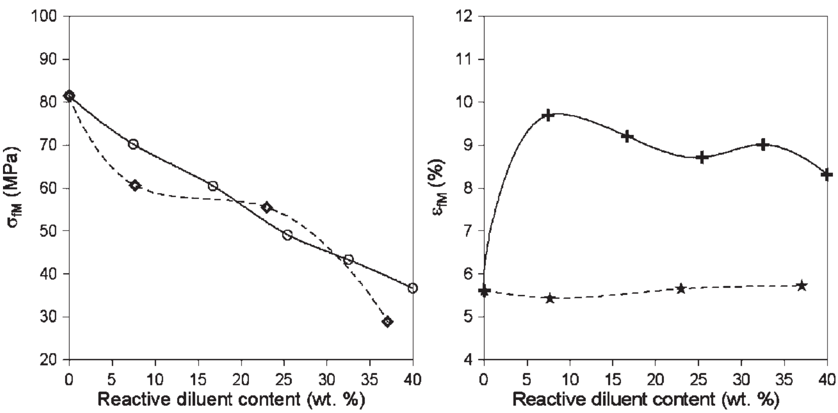

Figure 4.
Dependence of flexural strength (◇ - ESO, ○ - ERO) and deflection (★ - ESO, + - ERO) on concentration of epoxidized natural oils in the compositions with resin Rütapox 0162.

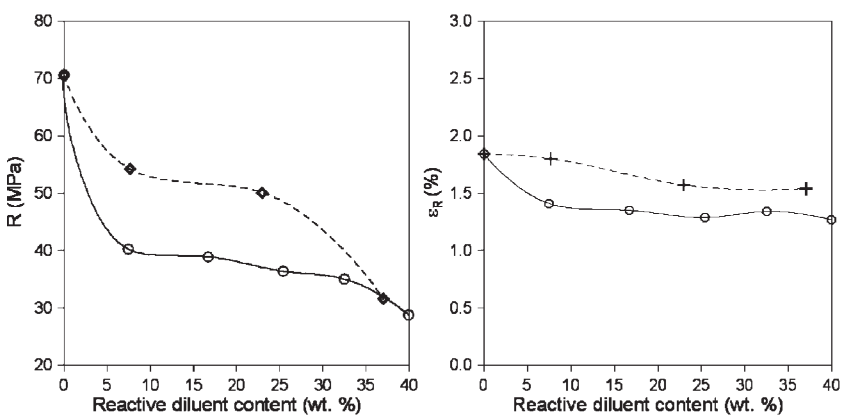

Figure 5.
Effect of epoxidized oils content on compression strength (◇ - ESO, ○ - ERO) and compressive strain (★ - ESO, + - ERO) of the compositions with Rütapox 0162.

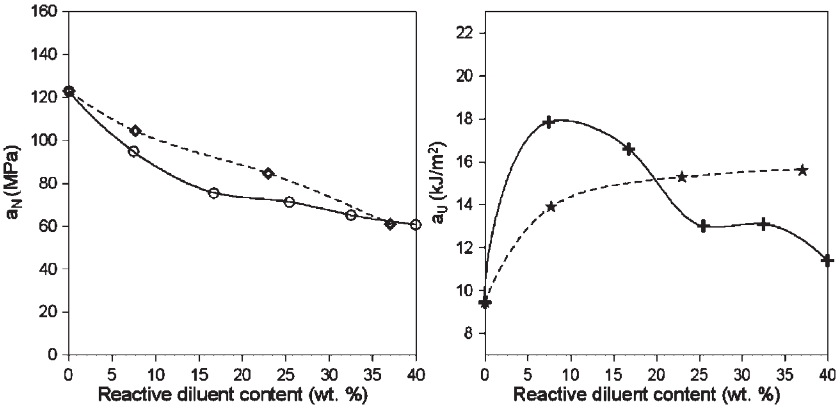

Figure 6.
Dependence of hardness (◇ - ESO, ○ - ERO) and impact strength (★ - ESO, + - ERO) on epoxidized oils concentration.

resin, which resulted only in slight decrease of thermal stability of the compositions (Table 5). Decrease of both initial decomposition temperatures with increase of ERO concentration as well as decrease of char residue were observed.

Moreover, the consequence of reducing the crosslink density of the epoxy resins as well as more hydrophilic nature of the natural oils used resulted also in higher water absorption of the compositions, compared to the base unmodified resin (Table 6).

Additionally, the increased water absorption resulted in lower chemical resistance of the materials studied (Table 6).

Table 5.
Initial decomposition temperatures (IDT) and char residues for compositions with different concentration of ERO and pure resin Rütapox 0162.

Composition	IDT_1, °C	IDT_2, °C	$T_{10\%}$, °C	$T_{20\%}$, °C	$T_{50\%}$, °C	Char residue, %
Rtapox 0162	147.4	302.5	261.3	341.6	369.9	21.4
RERO 2500	149.3	296.1	254.3	343.5	371.1	11.3
RERO 1500	142.1	291.1	246.0	340.5	371.4	9.6
RERO 1000	142.3	296.9	252.3	343.4	373.7	14.9
RERO 700	146.4	298.2	261.5	342.6	369.8	9.6
RERO 500	137.5	288.6	236.5	335.5	372.8	11.4

Table 6.
Water absorption and chemical resistance of the crosslinked compositions with different concentrations of epoxidized rapeseed oil and pure resin Rütapox 0162.

Medium	H_2O	10% HNO_3	75% H_2SO_4	40% NaOH	Ethyl acetate
ERO concentration (wt. %)	Mass change (wt. %) after 14 days				
0	0.744	1.643	1.175	1.217	6.911
7.45	0.967	2.001	−0.281	1.325	10.630
16.73	1.284	2.092	−0.709	1.453	18.080
25.42	1.730	2.336	−2.614	1.203	23.060
32.47	2.270	2.509	−7.438	1.505	31.050
39.91	2.837	3.484	−14.650	1.843	40.060

Conclusions

Epoxidized soybean and rapeseed oils exhibit viscosity reducing ability comparable to commercial grade active diluents for epoxy resins. The studied compositions of Rütapox 0162 resin with ESO/ERO showed a non-Newtonian rheological behavior, typical for Bingham liquids. Co-crosslinking of mixed oil-resin systems with isophorone diamine shows essential decrease of the reaction heat (even by 30%) what significantly facilitated the compositions processing. The incorporation of epoxidized oils into the crosslinked structure of epoxy resin resulted in reduction of mechanical strength and thermal stability; however, compositions modified with the oil diluents, preserved very good mechanical properties of the epoxy resins and demonstrated relatively low water absorption as well as high chemical resistance. The compositions displayed even higher impact strength than pure epoxy resin due to plasticizing effect of the built-in oil. In conclusion, epoxidized natural oils can be applied as an alternative diluents in place of volatile and harmful commercial mono-epoxy reactive diluents.

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[1] S. N. Khot, J. J. Lascala, E. Can, S. S. Morye, G. I. Williams, G. R. Palmese, S. H. Kusefoglu, R. P. Wool, *J. Appl. Polym. Sci.* **2001**, *82*, 703.
[2] F. Mustafa, I. Bicu, C. N. Cascaval, *J. Polym. Eng.* **1997**, *17*, 491.
[3] S. J. Park, F. L. Jin, J. R. Lee, *Macromol. Rapid Commun.* **2004**, *25*, 724.
[4] J. Zhu, K. Chandreshekhara, V. Flanigan, K. Shubhender, *J. Appl. Polym. Sci.* **2004**, *91*, 3513.
[5] A. Shabeer, A. Garg, S. Sundararaman, K. Chandreshekhara, V. Flanigan, S. Kapila, *J. Appl. Polym. Sci.* **2005**, *98*, 1772.
[6] P. Czub, proceeding of the POLYCHAR-14 World Forum on Advanced Materials, Nara 17-22.04.2006, p. 116.
[7] P. Czub, *Macromol. Symp.* in press.
[8] P. Czub, *Polimery* **2006**, *11–12*, in press.

