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Application of Modified Natural Oils as Reactive Diluents for Epoxy Resins

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Summary: Bisphenol A based low-molecular-weight epoxy resin was modified with epoxidized soybean oil, which exhibit viscosity reducing ability comparable to commercial grade active diluents. The studied compositions showed a non-Newtonian rheological behavior, typical for Bingham liquids. 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 were used to calculate the flow-activation energy (E_a) using the Arhenius equation. Studies of co-crosslinking of mixed oil-resin compositions using isophorone diamine showed essential decrease of the reaction heat and peak maximum temperature. Mechanical properties, thermal stability, water absorption and chemical resistance of the epoxy resin modified with natural oil, were also investigated. Compositions of epoxy resin Ruetapox 0162, modified with the oil diluent, 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. Compositions with the high contents (up to 60 weight %) of the oil were flexible materials with fast elastic recovery.

Keywords: epoxy resins; mechanical and thermal properties; natural oil; viscosity

Introduction

Modified vegetable oils are widely used as new renewable raw materials for the preparation and modification (e.g. as plasticizers or stabilizers) of different polymers.[1] There are only a few papers about using natural oils for the synthesis[2,3] and modification[4–8] of epoxy resins or curing agents[9] for them. Unfortunately, epoxy resins are rigid and rather brittle materials. They are characterized by high tensile, bending and compression strengths, high modulus of elasticity, but with low elongation at break and low impact strength. Moreover, the high viscosity of epoxy resins is also a problem, since it makes processing difficult. Non-reactive and reactive diluents are used for reducing and controlling viscosity of these resins. Diluents can also play the role of internal plasticizers due to their structure. The goal of this work was using of modified natural oil in the both meanings, as reactive diluent and as internal plasticizer.

Materials

Low-molecular-weight epoxy resin Ruetapox 0162 (Bakelite AG, Germany; epoxy value: 0.582 eq./100 g) selected for this research contained almost pure diglycidyl ether of Bisphenol A. 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) was applied as modified natural oil. Isophorone diamine

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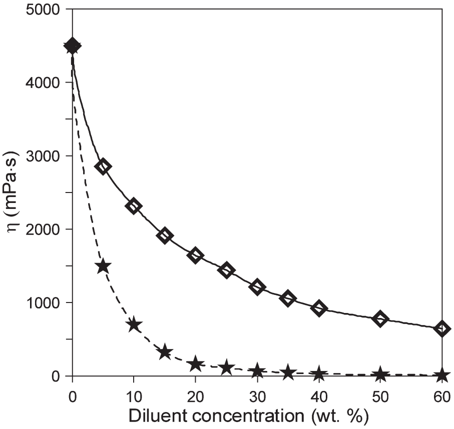

Figure 1.
Fluxing of Ruetapox 0162 using: (★) 2-ethylhexyl-glycidyl ether and (◇) epoxidized soybean oil.

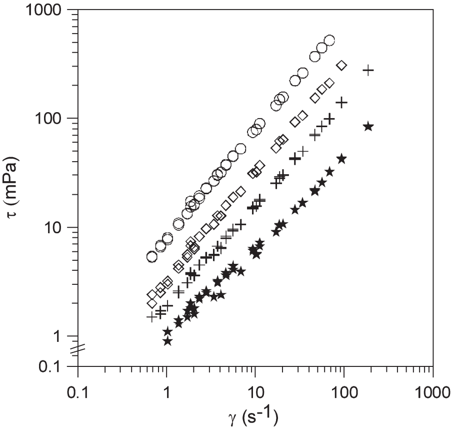

Figure 2.
Flow curves of the compositions of Ruetapox 0162 with epoxidized soybean oil – viscosity 700 mPa · s (temperature: (○) 25 °C, (◇) 35 °C, (+) 45 °C and (★) 65 °C).

(Aradur 46, Huntsman, Germany, H^+ active equivalent: 95 g/eq., amine value: 320 mg KOH/g), commonly used hardener for coating and construction epoxy materials, was chosen as crosslinking agent for mixing resin-oil compositions.

Results and Discussion

Viscosity reducing ability of the epoxidized oil was tested. It was found that the soybean oil exhibits strong viscosity reducing ability comparable to other commercial reactive diluents – such as 2-ethylhexyl-glycidyl ether (EGE) (Fig. 1).

It is necessary to use 5 times more oil than the monoepoxide (Table 1), but it is still possible to reduce epoxy resin viscosity to value below 1000 mPa · s.

Two values of viscosity of mixed compositions were selected for further studies: 1500 mPa · s (dynamic viscosity required for casting resins) and 700 mPa · s (typical viscosity of laminate impregnants). All of the studied compositions showed a non-Newtonian rheological behaviour, typical for Bingham liquids (Fig. 2).

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

Reactive diluent	Diluent concentration, wt. %	
	700 mPa · s	1500 mPa · s
EGE	10.0	5.0
ESO	54.2	22.9

The data obtained in the temperature range 25–65 °C were used for calculation of the values of the flow index (*n*) and the consistency index (*k*) using the Ostwald-de Waele rheological model (Table 2). Next, the values of the consistency index were used to calculate the flow-activation energy (E_a) using the Arhenius equation (Table 2).

The values of the flow index decrease slowly and the values of the consistency index decrease significantly both with increasing temperature and concentration

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 ESO compositions.

Composition viscosity	T, °C	*n*	*k*	E_a, kJ/mol
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	
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	

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	328.9	42.3	98.2	182.0
2 500	298.6	43.7	98.2	164.8
1 500	252.6	39.5	95.4	154.3
1 000	210.2	43.2	104.5	172.7
700	158.5	40.2	93.3	138.2

of the epoxidized oil. Also, the values of the flow-activation energy decrease with increasing oil concentration, which can be explained as the lubricant effect of oil.[10] The values and variation of the flow index proved that the compositions studied are pseudoplastic liquids.

Epoxidized soybean oil offers very good miscibility with epoxy resins and can be co-crosslinked with the resins into homogenous materials using typical hardeners used for epoxy resins. Crosslinking of mixed oil-resin compositions using isophorone diamine was studied using DSC method and showed essential decrease of the reaction heat (even by 50%) and peak maximum temperature (Table 3). It is very important effect, because it can increase the time of processing of epoxy compositions and can eliminate internal stresses which cause fracture of final products.

Modification of epoxy resin with epoxidized soybean oil resulted in reduction of tensile strength, however significant increase (even by 10 times) of relative elongation at break was observed (Fig. 3).

Increase of epoxidized oil concentration leads to decrease of flexural and compression strengths of cured compositions (Table 4). No essential change in deflection was observed, although compressive strain increased slightly. Substantial reduction of hardness was observed (Fig. 4), but this reduction was followed by increase of impact strength (even by more than 120%).

It was found that the incorporation of epoxidized soybean oil into the crosslinked structure distinctly decreased glass temperature from 69 °C for unmodified epoxy to 14 °C for the composition with starting viscosity of 700 mPa · s (Fig. 5).

Moreover, the loss tangent of the compositions changed in wide range of temperatures and these results showed that epoxy resins modified with soybean oil can be used as efficient vibration dampers (Fig. 6).

Generally, the compositions studied can be classified into two different groups of materials from the point of view of mechanical properties depending on the concentration of built-in modified oil. Compositions with high contents of the epoxidized soybean oil are flexible materials with fast elastic recovery and improved impact strength, while the compositions with lower amount of oil diluent preserve very good mechanical properties of the base epoxy resins.

Addition of epoxidized soybean oil reduced crosslink density of the epoxy resin, which resulted in decrease of thermal stability of the compositions (Table 5). Decrease of initial decomposition tempera-

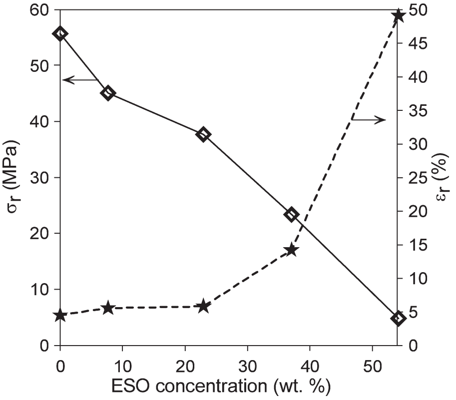

Figure 3.
Effect of epoxidized soybean oil content on (◇) tensile strength and (★) relative elongation at break.

Table 4.

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

Composition	Ruetapox 0162	RESO 2500	RESO 1500	RESO 1000	RESO 700
ESO concentration, %	0	7.68	22.95	37.02	54.19
Tensile strength, MPa	55.7	45.1	37.7	23.4	4.9
Tensile modulus, MPa	2549.0	1935.9	1370.9	1113.8	198.7
Relative elongation at break, %	4.5	5.6	5.9	14.2	49.1
Flexural strength, MPa	81.5	60.6	55.6	28.9	4.7
Flexural modulus, MPa	2207.0	1769.0	1487.2	875.1	154.1
Compression strength, MPa	70.6	54.2	50.1	31.6	5.7
Ball indentation hardness (* Shopper apparatus), MPa	122.9	104.3	84.7	61.0 (31.2)*	7.8 *
Impact strength (Charpy), kJ/m^2	9.4	13.9	15.3	15.6	21.5

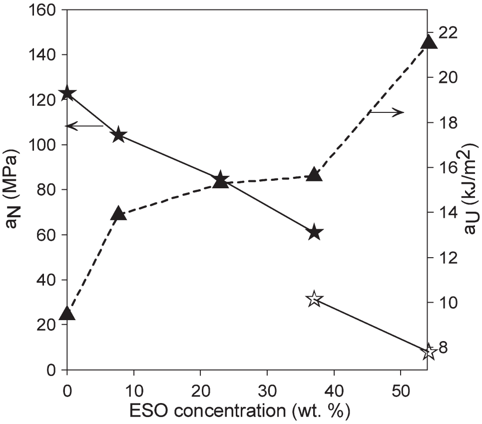

Figure 4.

Dependence of (★) hardness (☆ - Schopper) and (▲) impact strength on ESO concentration.

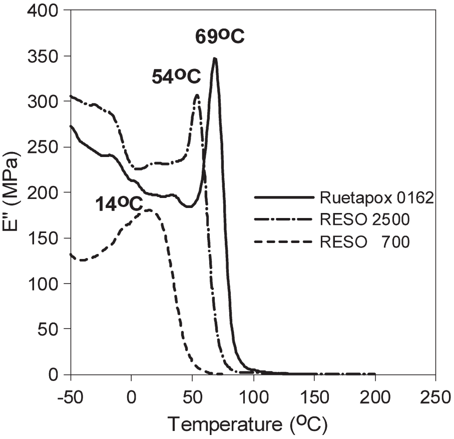

Figure 5.

Loss modulus (E″) of Ruetapox 0162 and its compositions with ESO.

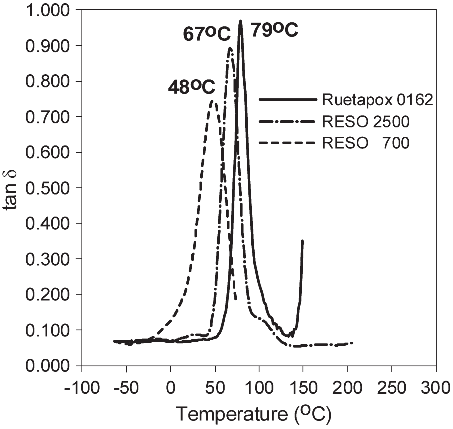

Figure 6.

Loss factor (tan δ) of Ruetapox 0162 and its compositions with ESO.

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

Composition	IDT_1, °C	IDT_2, °C	$T_{10\%}$, °C	$T_{20\%}$, °C	$T_{50\%}$, °C	Char residue, %
Ruetapox 0162	135.1	287.4	303.9	341.5	392.2	38.7
RESO 2500	130.7	269.7	239.4	328.4	368.7	22.3
RESO 1500	121.1	226.2	266.6	322.9	368.2	21.6
RESO 1000	118.1	160.3	240.5	325.4	368.7	9.6
RESO 700	145.1	239.0	275.5	320.1	366.5	11.5

ture with increase of epoxidized soybean oil concentration as well as decrease of char residue were observed. This means that the compositions modified with oil degraded to a higher degree.

The consequence of reducing the cross-link density of the epoxy resins as well as more hydrophilic nature of the oil used resulted also in higher water absorption of the compositions, compared to the base unmodified resin. The increased water absorption resulted in lower chemical resistance of the materials studied.

Conclusions

The epoxidized oil studied shows satisfactory viscosity reducing ability. The epoxy resin modified with that oil shows non-Newtonian rheological behaviour, typical for Bingham liquids. What is very important from the processing point of view, co-crosslinking of mixed oil-resin systems with isophorone diamine shows essential decrease of the reaction heat and peak maximum temperature. On the other hand, where mechanical properties are concerned, the mixed oil-resin compositions can be classified into two different groups of materials depending on the concentration of built-in modified oil: (i) compositions with lower amounts of the oil diluent, which have good mechanical properties characteristic for epoxy resins, relatively low water absorption as well as high chemical resistance, and, (ii) compositions with high contents of the epoxidized soybean oil, which are flexible materials with fast elastic recovery. In conclusion the epoxidized soybean oil can be applied as an alternative diluent in place of volatile and harmful commercial monoepoxy reactive diluents.

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