Azo Dye Functionalized Monomer Derived from Linseed Oil

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We report here the synthesis of an azo dye bearing monomer by grafting 4-hydroxy-4'-nitroazobenzene onto the epoxidized linseed oil (ELO) backbone thus leading to coloured epoxidised compounds. The reaction product was further crosslinked with ELO under acidic conditions ($BF_3 \cdot Et_2O$), obtaining a coloured crosslinked material, which was characterised by FTIR spectroscopy and thermo gravimetric analyses. Prior to the azo dye functionalization, the starting material (ELO) has been characterized by spectroscopic (^{1}H-NMR and FTIR) methods in order to chemometrically determine the chemical composition and the epoxide amount per gram of ELO. The chemometric approach is exhaustively presented.

Keywords: epoxidised linseed oil, azo dye grafted copolymer, epoxidation degree, ^{1}H-NMR, FTIR

A present priority of the chemical industry is to find viable alternatives to exhaustible raw materials, considerable attention being focused on renewable resources such as vegetable oils [1].

By epoxidation of unsaturated vegetable oils a large variety of compounds with different fields of applications can be obtained [2-4]. Because of the remarkable reactivity of the oxirane rings, epoxidised vegetable oils represent valuable synthons for various compounds (polyols, polyamines), as well as for polymeric materials [5, 6]. Among vegetable oils, highly unsaturated oils such as linseed oil (LO) are the most interesting for different applications *via* their epoxidised derivatives [2].

Epoxidised vegetable oils are usually characterized by oxirane oxygen content, epoxide equivalent, epoxide index and iodine value (to express the unreacted double bonds amount) [7]. This approach is laborious and not convenient if many samples have to be analysed. On the other hand, ^{1}H-NMR was intensively used to monitor the epoxidation reaction of oils and fatty acid methyl esters [8, 9], for the structure elucidation of the epoxidation products [3] or the epoxide yield determination [9]. For the composition determination the GC method is a good choice, but only on the relatively volatile and thermally stable esters. If the epoxidised triglycerides are transesterified in order to be gas-chromatographically analysed, the method becomes time-consuming and less accurate [10] and precautions must be taken to preserve the highly reactive oxirane rings [11].

Materials containing azobenzene moieties have been intensively investigated in recent years because of their unique photo-responsive properties induced by the *cis-trans* isomerization of the azobenzene units [12, 13]. Azobenzene chromophores have important characteristics, such as intense color, high thermal stability (up to 350° C) and the possibility of photochemically or thermally induced *cis-trans* isomerization of the azo group – not to mention other advantages such as easy preparation, increased solubility or hyperpolarizability – which make them very attractive for top applications in the field of dyes, liquid crystals, non-linear optics and erasable data storing [14].

In many applications azobenzene chromophores are not covalently bound to the polymer backbone, but added as low-molecular weight dopants to a polymer matrix [15, 16]. In the recent years, covalently bound azo chromophores have attracted considerable interest because of their improved properties [17, 14]. Epoxy composites with diverse chemical structure that contain azo groups could exhibit optical anisotropy when excited with polarized laser light in the blue region [18]. Surprisingly, although very simple as chemical structure and synthesis technique from easily available raw materials, 4-hydroxi-4'-nitro-azobenzene has not been used as chromophore for polymer applications.

We report here the synthesis and characterization of a monomer from epoxidized linseed oil (ELO), covalently grafted with 4-hydroxy 4'-nitro-azobenzene through oxyrane ring opening reaction. As an example for its potential uses, we have performed the co-polymerization of the obtained azo grafted monomer (azo-ELO) with ELO, thus obtaining an azo chromophore grafted polymeric material for potential non-linear optical applications. Prior to functionalization, the starting material (ELO) has been characterized by spectroscopic (^{1}H-NMR and FT-IR) methods in order to chemometrically determine the chemical composition and the epoxide amount *per* gram of ELO. The chemometric approach is exhaustively presented.

Experimental part

Materials and equipment

ELO was obtained from Chemont S.A., Mouscron, Belgium.

^{1}H-NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer, operating at 9.4 Tesla, corresponding to the resonance frequency of 400.13 MHz for the ^{1}H nucleus, equipped with a direct detection four nuclei probe head and field gradients on z axis. The NMR samples were prepared by dissolving 0.5 mL oil in 0.5 mL $CDCl_3$ and analyzed in 5 mm NMR tubes (Wilmad 507). The chemical shifts are reported in ppm, using TMS as internal standard. Typical parameters for ^{1}H-NMR spectra were: 30° pulse, 4s acquisition time, 6.4 kHz spectral window, 8 scans, 52 K data points. The FID was not processed prior to Fourier transformation.

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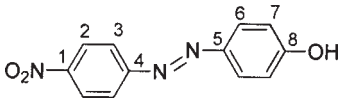
FTIR spectra were recorded on a Bruker Vector 33 instrument, equipped with a Pike Miracle ATR device (ZnSe crystal), without solvent, acquiring 32 scans for background and 64 scans for sample acquisition, 2 cm^{-1} optical resolution. Spectra were recorded in the 590-5400 cm^{-1} range, collecting 2495 points with a DLATGS detector.

UV-VIS spectra of 10^{-4} M solutions (in CH_2Cl_2) were recorded on a Thermo Scientific Evolution 220 spectrophotometer (Thermo Insight software).

Thermo gravimetric analysis (TGA and DTG) was done on a TA Instrument Q 500. The sample of 10 mg was heated from 20 to 700°C at 10 °C/min scanning rate under a constant nitrogen flow of 100 mL/min.

Epoxide equivalent (EE) was determined in duplicate by HCl addition on the epoxy group and titration of the acid excess with NaOH 0.1 M solution.

4-hydroxy-4'-nitroazobenzene was synthesized by azo coupling reaction of the diazonium salt of 4-nitroaniline and phenol. 6.9 g (50 mmole) 4-nitroaniline, 86 mL distilled water and 13.38 g (11.4 mL) HCl 36 % are mixed with a magnetic stirrer; after cooling at 5 °C, 11.5 g of $NaNO_2$ 30% solution (50 mmoli) are added drop wise. The reaction mixture is then maintained at the same temperature and continuous stirring for 1 h in order to complete the diazonium salt formation. The excess of HONO is decomposed with sulphamic acid; activated charcoal is added and the solution is filtered. Separately, 4.85 g (51.5 mmole) phenol are dissolved in 38.43 g sodium acetate solution 20% and 150 mL distilled water, the solution is then cooled at 8°C and the solution of the diazonium salt of 4-nitroaniline previousely prepared is then added dropwise. The reaction mixture is stirred for 1 h at 8°C, then the temperature is raised to room temperature and maintained for 12 h with continuous stirring. The reaction product is vacuum filtred and dried at 60°C. The crude product is recrystallized from acetonitrile.



[1]H-NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.37 (d, 2H, J = 8.8 Hz, H^2); 7.98 (d, 2H, J = 8.8 Hz, H^3); 7.94 (d, 2H, J = 9.2 Hz, H^6); 6.90 (d, 2H, J = 9.2 Hz, H^7); 5.4 (s, 1H, -O*H*);

FTIR (ATR, cm^{-1}): 3423 (ν_{O-H}); 1330 ($\nu_{N=N}$); 1500 (ν_{NO_2}).

UV-VIS (10^{-4} M sol. in CH_2Cl_2): λ_{max} = 376.74 nm.

Grafting of 4-hydroxy-4'-nitroazobenzene on ELO. A mixture of 1.0 g (1.0 mmole) ELO, 0.025 g (2.0 mmole) 4-hydroxy-4'-nitroazobenzene, 0.12 g (2.0 mmole) KOH and 20 mL acetone was placed in a round bottom flask equipped with reflux condenser, Ar inlet and magnetic stirrer. The reaction mixture was kept under reflux (56°C) for 4 h on an oil bath. The reaction mixture was then allowed to cool to room temperature and acetone was removed on a rotary evaporator. The residue was dissolved in 30 mL distilled water and extracted three times with 20 mL ethyl ether portions. The combined extracts were washed two times with distilled water and then dried on anhydrous $MgSO_4$. After filtration and solvent evaporation, an orange amorphous product was obtained (yield 83%).

[1]H-NMR($CDCl_3$, 400 MHz), δ (ppm) : 0.90 (t, 3H, CH_2-CH_2-C*H*$_3$); 1.07 (t, 3H, -CH=CH-CH_2-C*H*$_3$)**;** 1.25-1.33 (m, -C*H*$_2$-); 1.70 (m, -HC(O)CH-C*H*$_2$-CH(O)CH-); 2.9 (m, -*H*C(O)CH-CH_2-CH(O)C*H*-); 3.2 (m, -HC(O)C*H*-CH_2-C*H*(O)CH-); 2.17 (t, 2H, -CO-C*H*$_2$-); 4.20 (m, 4H, -C*H*$_2$OCO-); 5.22 (t, 1H, -C*H*OCO-); 6.98 (d, *J* = 8.8 Hz, 2H, H_{ar}); 7.93 (d, *J* = 8.8 Hz, 2H, H_{ar}); 7.98 (d, *J*=8.99 Hz, 2H, H_{ar}); 8.37 (d, *J*=8.99 Hz, 2H, H_{ar}).

FTIR (ATR, film, cm^{-1}): 3459, broad band (ν_{OH}); 2925, 2855 ($\nu_{C-H\ asym,\ sym}$); 1463, 1387 ($\delta_{CH\ from\ CH2\ and\ CH3}$); 1738 ($\nu_{C=O}$); 1342 ($\nu_{N\equiv N-\ asym}$); 1279 ($\nu_{N\equiv N-\ sym}$); 1241, 1161 and 1106 ($\nu_{C-O}$),; 1137 ($\nu_{Ar-O-CH2-\ sym}$); 822 ($\nu_{C-O-C\ from\ epoxy\ ring}$); 724 ($\rho_{CH2}$).

UV-VIS (10^{-4} M sol. in CH_2Cl_2):λ_{max} = 368.30 nm.

Crosslinking of azo dye grafted epoxidised linseed oil with ELO 0.4 g (0.4 mmole) ELO, 0.42 g (0.4 mmole) epoxidised linseed oil grafted with 4-hydroxy-4'-azobenzene (azo-ELO) and 40μL BF_3-Et_2O are stirred in a capsule. The reaction occured instantaneously and an orange solid mass was obtained. The reaction product is insoluble in usual solvents (diethyl ether, petroleum ether, methylene chloride, acetone, dioxane, chloroform, dimethylsulphoxide).

FTIR (ATR, film, cm^{-1}): 3544 broad band (ν_{OH}); 2920, 2854 ($\nu_{-CH2-,-CH3\ asym,\ sym}$); 1703 ($\nu_{C=O}$); 1344 ($\nu_{N=N-\ asym}$); 1283 ($\nu_{N=N-\ sym}$); 1048 ($\nu_{C-O-C\ asym}$); 725 ($\rho_{CH2}$).

Results and discussions

Prior to functionalization, a detailed characterization (both structurally and compositionally) of the starting ELO was performed by means of ^{1}H-NMR and FT-IR spectroscopy.

Composition of ELO

ELO was characterised by its ^{1}H-NMR (fig. 1) and FTIR (fig. 2) spectra. Chemical shifts and peak assignments are presented in table 1.

^{1}H-NMR data (fig. 1) show that the raw material LO was totally epoxidised, since the integral of the weak signal at 5.6 ppm (corresponding to the unsaturated protons in LO) is insignificant.

In view to obtain the chemometric equations for the composition determination, the following notation is adopted:

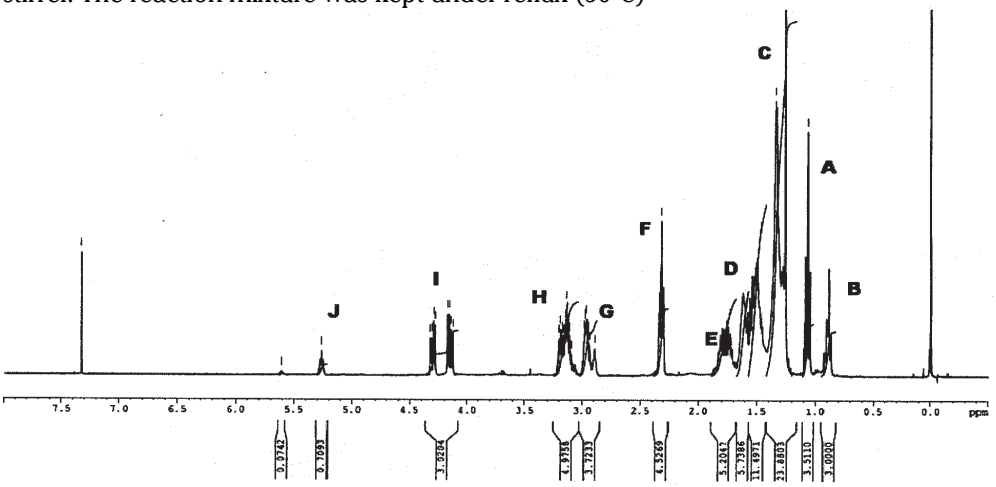


Fig. 1. ^{1}H-NMR spectrum of ELO.

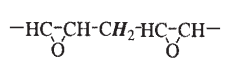
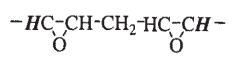
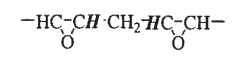
Signal	δ (ppm)	Integral	Proton	Compound
A	1.06	3.5	-CH=CH-CH_2-C***H***$_3$	linolenic acid
B	0.85	3.0	-CH_2-CH_2-CH_2-C***H***$_3$	all fatty acyl chains, except linolenic
C	1.20	23.9	-(C***H***$_2$)$_n$-	all fatty acyl chains
D	1.60	5.7	-C***H***$_2$-CH_2-COOH	all fatty acyl chains
E	1.70	5.2		protons between two epoxy rings
F	2.20	4.5	-C***H***$_2$-COO-	all fatty acyl chains
G	2.90	3.7		„marginal" protons of the epoxy rings
H	3.20	5.0		„internal" protons of the epoxy rings
I	4.20	3.0	-C***H***$_2$-O-CO-R	glycerol (*sn*-1 position)
J	5.30	0.7	-C***H***-O-CO-R	glycerol (*sn*-2 position)

Table 1
CHEMICAL SHIFTS, INTEGRALS AND PEAK ASSIGNMENT OF ELO ^{1}H-NMR SPECTRUM

- *X, Y, Z* and *T* represent the molar ratios of linolenic, linoleic, mono-unsaturated fatty acids (oleic acid), and saturated fatty acids, respectively, in LO;

- I_A, I_B, I_C etc. are integral values of A, B, C etc. signals in the ^{1}H-NMR spectrum.

The triplet B at 0.85 ppm in the ^{1}H-NMR spectrum is generated by the three protons of the terminal methyl groups in all fatty acyl chains, except for those in the linolenyl chains, which give a characteristic triplet at 1.06 ppm (signal A); this one can thus be considered as a *marker* for the identification and quantification of the linolenic fraction in ELO. The balance of protons corresponding to signals A and B allows the quantification of linolenic acid:

$$X = \frac{I_A}{I_A + I_B} = 0.54 \quad (1)$$

For the quantification of linoleic and oleic ratios, the position of the protons with respect to the oxirane rings has to be considered (table 1): the "internal" protons (four in epoxidised linolenic and two in epoxidised linoleic acid) give rise to signal H, while the two "marginal" protons of the oxirane rings in epoxidised linolenic, linoleic, and oleic acids, respectively, generate a type G signal.

Signal E (protons between two oxirane rings) is generated by four protons in the epoxidised linolenyl chain and two protons in the epoxidised linoleyl chain.

The integral *per* proton in the epoxidised linolenyl chain can be calculated by using the *marker* signal A:

$$I_A: \quad \frac{I_A}{3} = 1.17 \quad (2)$$

Thus, the four protons between two oxirane rings in the epoxidised linolenyl chain contribute to the signal E integral with 4 x 1.17 = 4.7. By subtracting this value from I_E, it is possible to calculate the contribution of the two methylene protons between two oxirane rings in the epoxidised linoleyl chain: 5.2 - 4.7 = 0.5. The integral *per* proton in the epoxidised linoleyl chain is thus 0.5 /2 = 0.25.

The ratio of the integrals *per* proton of the epoxidised linolenyl and linoleyl chains is the linolenic/linoleic acid ratio (0.25/1.17 = *Y*/*X*). Thus, the molar ratio of the linoleic acid in ELO is *Y* = 0.12 (12% linoleic acid).

The molar ratio of oleic acid can be determined from the "internal"/"marginal" proton ratio in the epoxy groups, taking into account the specific contribution of each unsaturated fatty acid to signals H and G:

$$\frac{4 \cdot X + 2 \cdot Y}{2 \cdot X + 2 \cdot Y + 2 \cdot Z} = \frac{I_H}{I_G} \quad (3)$$

X and *Y* values being already determined, the molar ratio of oleic acid results from equation (3): $\frac{4 \cdot 0.54 + 2 \cdot 0.12}{2 \cdot 0.54 + 2 \cdot 0.12 + 2 \cdot Z} = \frac{5.0}{3.7}$, thus leading to Z=0.23 (23% oleic acid).

The saturated fatty acids molar ratio can then be determined as difference:

$$T = 1 - (X + Y + Z) \quad (4)$$

In conclusion, the composition found for epoxidised fatty acyl moieties is 54% linolenic acid, 12% linoleic acid, 23% monounsaturated fatty acids and 11% saturated fatty acids. This result is in good agreement with literature data [19].

ELO was also characterized by means of its FTIR spectrum. Although we had as starting material an already epoxidized LO (ELO), we consider it is better to compare the FTIR spectrum of ELO with the spectrum of an unepoxidized LO sample. Thus, figure 2 shows the overlapped FTIR spectra of ELO (a) and an LO sample (b).

In figure 2 a weak but distinctive absorption band of the oxirane ring at 822 cm^{-1} (deformation) is visible in the FTIR spectrum of ELO, as well as a shoulder at 1263 cm^{-1} (symmetric stretching of C-O). The typical absorption at 3011 cm^{-1} (C-H stretch) of the C=C double bond in LO spectrum is notably absent in the ELO spectrum, thus supporting the observation based on ^{1}H-NMR spectrum that the LO used was totally epoxidized. Other absorbtion bands in the ELO spectrum – 2926, 2855 ($\nu_{C\text{-}H\ asym,\ sym}$); 1461, 1386 ($\delta_{CH\ from\ CH2\ and\ CH3}$); 1740 ($\nu_{C=O}$); 1243, 1158 and 1097 ($\nu_{C\text{-}O}$); 729 ($\rho_{CH2}$) – are in good agreement with literature data [20].

Average number of epoxy groups per epoxidised triacylglycerol molecule

The average number of epoxy groups *per* triacylglycerol molecule can be calculated by assuming a weighted average of all epoxidised fatty acyl chains in ELO. Since the sample used is totally epoxidised, the linolenyl, linoleyl, and oleyl chains lead to epoxidised moieties bearing three, two and one epoxy groups, respectively (the saturated fatty acyl chains remaining, of course, unreacted).

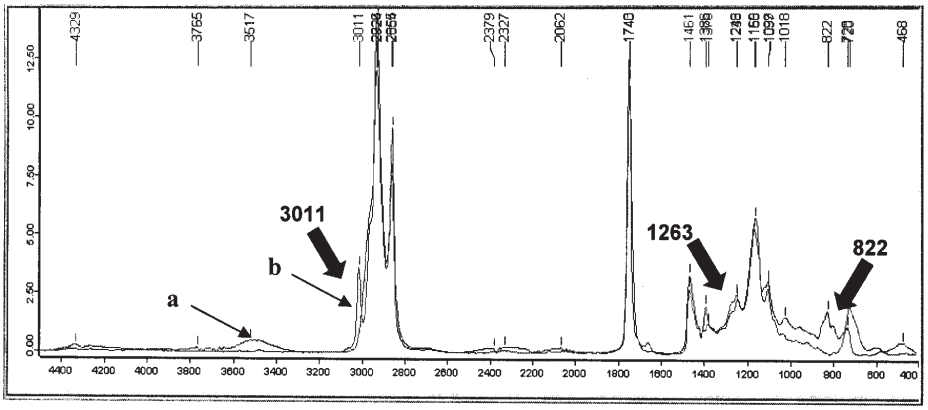


Fig. 2. Overlapped FTIR spectra of ELO (a) and LO (b).

The average number of epoxy groups *per* fatty acid chain (α) is then:

$$\alpha = 3 \cdot X + 2 \cdot Y + 1 \cdot Z = 2.1 \quad (5)$$

and the average number of epoxy groups *per* epoxidised triacylglycerol molecule is 6.3. Further stoichiometric calculations will be based on this value.

Average molecular weight of ELO

The number of methylene (β) groups in the epoxidised acyl chain can be determined based on the the number of methylene groups in each fatty acyl chain and on their weights in the epoxidised triacylglycerol:

$$\beta = 10X + 12Y + 14Z + 15T = 11.7 \quad (6)$$

Note: it was assumed for the saturated fatty acyl chains equal weights for stearyl and palmityl, thus resulting an average saturated chain length of 17 carbon atoms (15 methylene groups).

Thus, taking into account that the epoxidised acyl chain is made of α epoxy groups, β methylene groups, and one methyl group, its formula is $C_{2\alpha+\beta+1}H_{2\alpha+2\beta+3}O_{\alpha}$, which leads to $C_{16.9}H_{30.6}O_{2.1}$. Next, the average molecular formula of ELO can be computed: $C_{6+16.9\cdot3}H_{5+30.6\cdot3}O_{6+2.1\cdot3}$, which means $C_{56.7}H_{96.8}O_{12.3}$, its average molecular weight being $M_{TG} = 974$. The average number of moles of ELO *per* gram is 1.03 mmole/g and the average number of epoxy groups *per* gram of ELO is $n_{epoxy\ groups} = 1.03\ mmole \cdot 6.3 = 6.49$ mmole.

This result is in good agreement with the EE determined by HCl addition on the epoxy group and titration of the acid excess with NaOH solution.

Grafting of an azo dye cromophore onto ELO

By grafting chromophoric groups in less than stoichiometric amounts onto the ELO backbone, a coloured reaction product can be obtained which still has unreacted epoxy groups. These groups can further react to yield coloured crosslinked products. In contrast with azo dye dopped polymeric materials, the chromophore in this case is chemically bonded onto the crosslinked product backbone, which results in a better colour stability of the grafted material.

The azo dye used for grafting was 4-hidroxy-4'-nitroazobenzen, the reaction being carried out under alkaline conditions, in acetone (*scheme 1*):

The azo dye grafted monomer was characterized by ^{1}H-NMR, FTIR and UV-VIS spectra.

For the quantitative study of the grafting reaction, the ^{1}H-NMR signal at 5.22 ppm (given by the proton in the *sn*-1 position) is considered as reference signal. By comparing its integral with the integrals of the signals in the aromatic region, it results that the grafting ratio chromophore/triacylglycerol was 1:1 (one molecule of azo dye *per* one molecule of ELO). In fact, it can be noticed from the spectrum (signals in the spectral region 2.9-3.3 ppm) that the epoxy groups were not quantitatively reacted.

The presence of 4-hidroxy-4'-nitroazobenzen moiety in azo-ELO is also proven by the FTIR spectrum. The azo-ELO spectrum exhibits specific absorption bands for the chromophore, such as 1342 ($\nu_{N=N-asym}$), 1279 ($\nu_{-N=N-sym}$) and 1137 ($\nu_{Ar-O-CH2-sym}$). On the other hand, another evidence is the increase of intensity of the broad band at 3459 (ν_{-OH}), which is due to the free –OH groups occuring from the oxirane ring opening reaction.

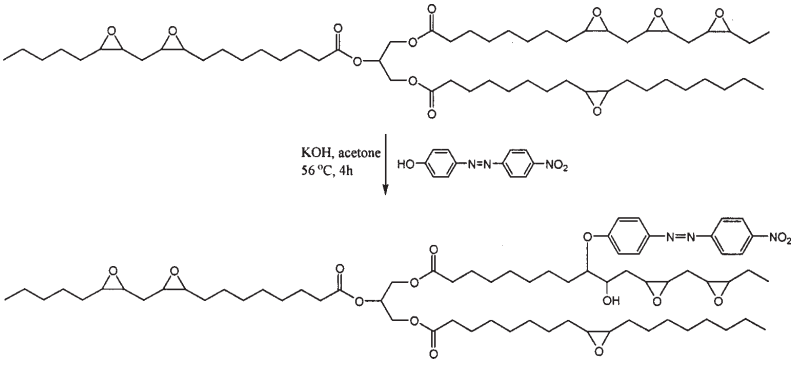
The grafting of the chromophore onto ELO is also proven by the fact that in the UV-VIS spectrum the absorption maxim is slightly shifted from 376.74 nm (in 4-hidroxy-4'-nitroazobenzen) to 368.30 nm in azo-ELO.

Crosslinking of ELO and its azo dye grafted derivative (azo-ELO)

Azo-ELO was co-polymerized under acidic conditions (BF_3-Et_2O) with ELO in 1:1 (g/g ratio) to yield an orange crosslinked product, which was found to be insoluble in usual solvents.

The reaction product was structurally characterized by FTIR spectroscopy, TGA (fig. 3) and DTG (fig. 4) analyses.

In the FT-IR spectrum, the increased intensity of the broad absorption band at 3600-3200 cm^{-1} in the azo dye



Scheme 1: Grafting reaction of 4-hidroxy-4'-nitroazobenzen onto ELO

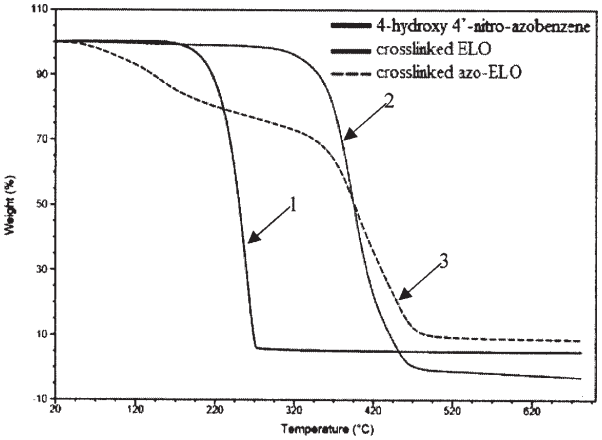


Fig. 3. Overlapped TG curves of 4-hidroxy-4'-nitroazobenzen (1), crosslinked ELO (2) and crosslinked azo-ELO (3)

grafted crosslinked product is due to the existence of free –OH groups in the chromophore neighbourhood. The proof that the crosslinking reaction has occured is the fact that the spectrum lacks the characteristic epoxy bands (both at 822 cm^{-1} and 1263 cm^{-1}). The absorption bands of the chromophore – at 1344 ($\nu_{N=N-asym}$) and 1283 ($\nu_{N=N-sym}$) – are also evident.

In order to analyse the thermo stability of the crosslinked azo-ELO, we considered opportune to compare it with the ungrafted crosslinked ELO and the starting 4-hidroxy-4'-nitroazobenzen (figs. 3 and 4).

As it can be noticed from the thermo gravimetric analysis, the crosslinked ELO has the best thermo stability, the massive weight loss occurring at temperatures higher than 300°C (TGA was performed in N_2 atmosphere). The DTG curves allure shows that grafting of the azo dye moiety on the ELO backbone determines a significant decrease of the final crosslinked product (crosslinked azo-ELO) stability. On the other hand, the covalent grafting of 4-hidroxy-4'-nitroazobenzen on the polymer backbone is beneficial by increasing the dye stability, because in the case of the crosslinked azo-ELO the characteristic peak for the decomposition of the ungrafted dye (at 260.82 °C) is not present. The peak at 151.16°C can be assigned to the water loss from the dehydration of the free –OH groups formed during the oxirane ring opening.

Conclusions

An azo dye grafted monomer was obtained from ELO and 4-hydroxy-4'-nitroazobenzene. The starting material (ELO) and the coloured monomer (azo-ELO) were characterized by FT-IR and ^{1}H-NMR. ^{1}H-NMR technique allowed characterization of ELO in terms of its fatty acid composition, the average number of epoxy groups *per* molecule and molecular weight. Preliminary polymerization tests were performed for the synthesized azo dye grafted monomer. The thermo stability of the obtained crosslinked product was investigated in comparison with the ungrafted crosslinked material and the parent azo dye. The thermo stability is influenced by the decomposition of the azo dye, but we consider direct azo dye grafting on the polymeric backbone as a method to improve the overall thermo stability of the dye.

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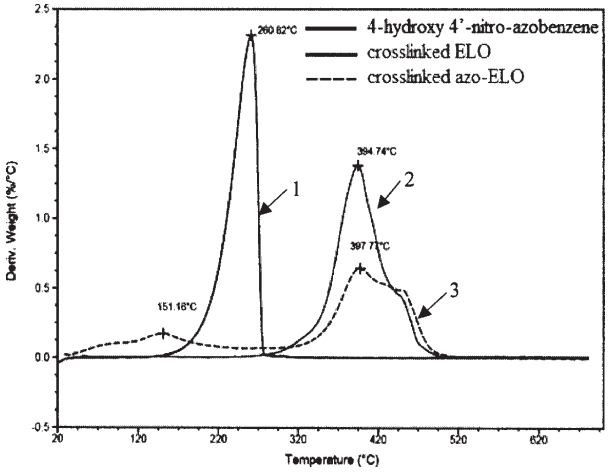

Fig. 4. Overlapped DTG curves of 4-hidroxy-4'-nitroazobenzen (1), crosslinked ELO (2) and crosslinked azo-ELO (3)

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