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DAMPING PROPERTIES OF SOME EPOXY RESIN - LIQUID CRYSTALLINE DYESTUFF COMPOSITES

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In this paper were studied epoxy systems made of diglycidylether of bisphenol A (DGEBA) containing a liquid crystalline dye (LC). When the LC content in the composite materials was increased an enhancement of thermal stability and a lowering of mass loss in thermo-gravimetric analysis was observed. Moreover, the storage modulus decreased stepwise when LC content was increased.

Keywords: thermo-mechanical, dye, epoxy, liquid crystal, toughening

1. Introduction

Bisphenol A epoxy resins are the most used thermosetting polymers due to their good mechanical, chemical, thermal properties and excellent adhesion to a variety of surfaces that make them suitable for many different applications. Because of their highly cross-linked structure, epoxy resins suffer from excessive brittleness [1,2]. Thus, this drawback restricts them from finding applications in the areas where high impact strength properties are required. Therefore, many studies have been conducted to improve the damage tolerance and toughness/stiffness balance while maintaining other properties.

A commonly approach used to improve the strength is the tailoring of epoxy backbones with hard-soft segments based on aromatic and aliphatic sequences or curing of epoxy resins with tailored hardeners to obtain polymers which posses low cross-linking density and high flexibility [3-5]. Another approach consists of adding impact modifiers to epoxy resins prior to curing. Epoxy flexibilizers and epoxy toughening agents are usually used for obtaining systems with enhanced impact strength and other mechanical properties.

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Combination between the rigid mesogenic groups and flexible chains is proper to be used to improve the toughness of the epoxy-modified systems containing liquid crystalline compounds.

This study is focused on epoxy systems with high flexibility and good thermal properties using a nematic liquid crystalline dyestuff as filler. An azomethine-azoic dye was mixed in different ratios with bisphenol A epoxy resin prior to curing with 4,4'-diaminodiphenylmethane (DADM) [6,7]. Azomethine group which is a rigid structure, frequently used as a mesogenic unit and flexible aromatic ether linkage, made from the dyestuff molecule a good candidate as a modifier for improving flexibility of the epoxy thermosets [8-10]. The curing behavior of bisphenol A epoxy resin changed dramatically due to the introduction of the dyestuff and a study of the effect on the hardening is essential for designing, analyzing and optimizing this type of epoxy composites [11].

2. Experimental

The nematic liquid crystal 4-[(4-methoxybenzylidene)amino]azobenzene (LC) was synthesized and purified in our laboratory (m.p.140-144°C), as was previously described [12]. Cross-linked epoxy resins were prepared by mixing diglycidyl ether of Bisphenol A (DGEBA) with LC until a homogenously composition was obtained, followed by the addition of the stoichiometric amount of 4,4’-diaminodiphenylmethane (DADM). Thermal curing was performed at 120^0C for 7 hours and the cured casts were cut into suitable dimensions required for testings.

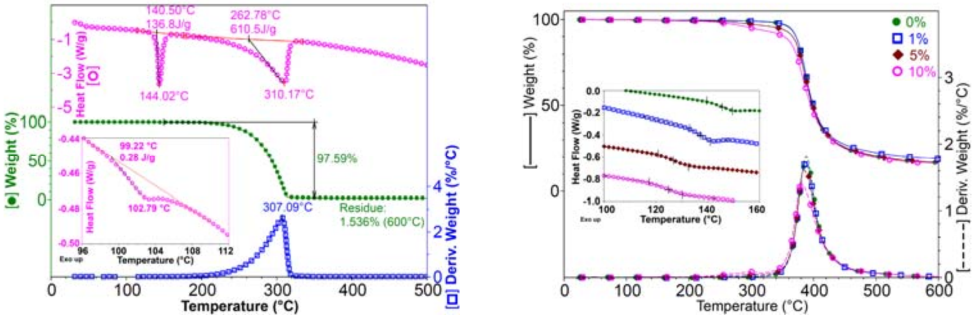
Dynamic-mechanical properties, modulus and glass transition temperatures were determined with a DMA Q800 apparatus (TA Instruments) in temperature scan mode (three replicates for each composite), using dual cantilever clamp, the most common for materials which can be formed into rectangular bars (sample geometry 60×12.7×4 mm), with a heating rate of 3°C/min at a fixed frequency level of 1 Hz (oscillating amplitude: 20 μm, temperature range: 30-200°C) and step-wise isothermal frequency scans at 5 frequencies (0.1, 1, 10, 50, 100 Hz) with a furnace temperature increment of 5 degrees Celsius.

DSC/TGA analysis of resin samples were carried out in a SDT-Q600 TA Instruments analyzer for simultaneous differential scanning calorimetric (DSC) and thermo-gravimetric (TGA) analysis, using 8-10 mg of sample in alumina pans, helium purge gas (50 ml/min) and a heating rate of 10ºC/min from ambient temperature to 700°C.

3. Results and discussions

From the beginning it is important to notice that a major objective of the study was to obtain highly compatible epoxy composites by using components which contain aromatic groups in their structure.

Thermo-gravimetric analysis on LC compound shows a single step of decomposition which takes place in the range 200-320°C, when almost the entire compound was decomposed. DTG shows a maximum at 307°C which correspond to a large endothermic effect in heat flow of about 610 J/g. The LC compound presents a melting point in the range 140.5-144°C with a thermal effect of about 137 J/g. Before the melting point it was observed the nematic zone where probably crystal-nematic phase transition takes place. Analysis shows that thermal stability of LC compound recommends it as being well suited to use as filler in epoxy composites (Fig.1). In the thermograms of amine cured epoxies a shoulder in weight derivatives was recorded for all samples at about 300°C, corresponding to LC decomposition.



(a) (b)

Fig. 1. Thermal analysis of : (a) LC dyestuff, (b) composites

A comparison between the different cured systems confirms the influence of LC addition to the thermosetting system on the T_g. The modification of epoxy resins with 10% LC downshifts the T_g value with about 20°C thus indicating at least partial miscibility between epoxy/amine systems and LC.

The tan δ glass transition temperature was gradually downshifted to lower temperatures as the LC content was increased in the epoxy composites because LC dyestuff improves flexibility of the cured epoxy systems. Network formation was hindered by the addition of LC compound and is favored only partial motion along axis of the aromatic rings. The decreasing in T_g of the epoxy composites is the result of this behavior. Energy necessary for breaking networks in epoxy matrices is large and thus decomposition takes place in a single step at higher temperatures.

In case of all composites the temperatures at which the maximum of the weight loss occurs are downshifted comparatively with unmodified cured resin. This behavior is due to LC addition and is observable quite well comparing temperatures which correspond to a 5% decomposition degree of the resins (Table 1).

Table 1

Thermal properties of epoxy composites

LC content (%)	TGA					DSC			
	$T_{5\%}$ (°C)	T_{max} (°C)	Weight at T_{max} (%)	Weight loss at T_{max} (%)	Residue at 700°C (%)	Onset (°C)	Tg (°C)	ΔCp (J/(g·°C))	End point (°C)
0	362.63	388.40	66.56	33.44	15.94	139.66	145.62	1.06	149.55
1	361.89	387.72	67.70	32.30	17.97	133.04	137.25	1.25	141.01
5	343.58	384.90	69.23	30.77	16.09	120.93	126.83	1.20	132.62
10	300.83	379.67	70.27	29.73	15.39	117.41	125.00	1.23	130.34

Differences of about 10^0 between DSC and DMA glass transition temperatures are normal. Values are lower than for the Tg determined from the tan δ peak maximum by conventional DMA, at 1 Hz. Tan δ is the ratio between the loss modulus and storage modulus and is a measure of the amount of deformation energy which is dissipated as heat during each oscillation cycle. Two aspects need to be considered before evaluating this result. Firstly, the tan δ maximum will always be observed at higher temperatures than the maximum of loss modulus (E") also used to define a glass to rubber transition (Table 2). Secondly, the glass transition process is a relaxation or time dependent process and its determination depends on measurement frequency and also on heating or cooling rates.

At normal temperature addition of LC to DGEBA/DADM system reveals that stiffness shifted towards higher values compared to unmodified epoxy resin. When the temperature was increased in the proximity of LC nematic transition range, an inversion in the stiffness behavior of the composites was recorded (Fig. 2).

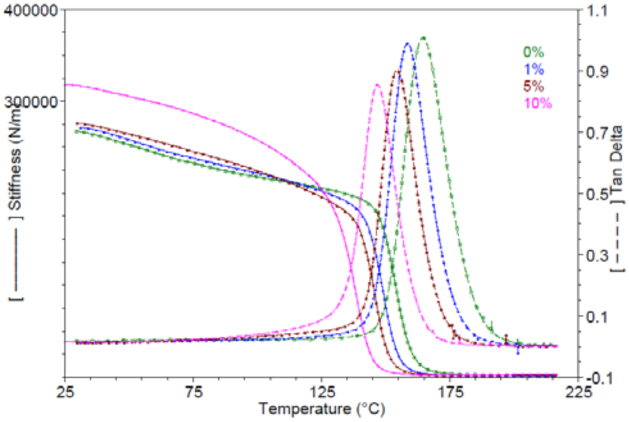


Fig. 2. Stiffness and tan δ vs. temperature of epoxy composites

The storage modulus decreased with increasing temperature indicating that all epoxy composites gradually change from stiff to flexible materials during the heating. When the LC content was increased up to 5% the storage modulus at room temperature was lowered with about 15% from its original value. An explanation can be the ability of the LC compound to alter the rigidity of the networks allowing motions of some backbone segments. However, when the LC content was increased up to 10%, the storage modulus became higher with about 10% than that of unmodified epoxy resin. This indicates that the motion of epoxy matrix chains is restricted, by the rigidity of LC mesogenic units until the transition temperature is attained. Thus, the addition of LC compound was not intended to alter high dynamic modulus and thermal properties of the simple cured resin (Table 2).

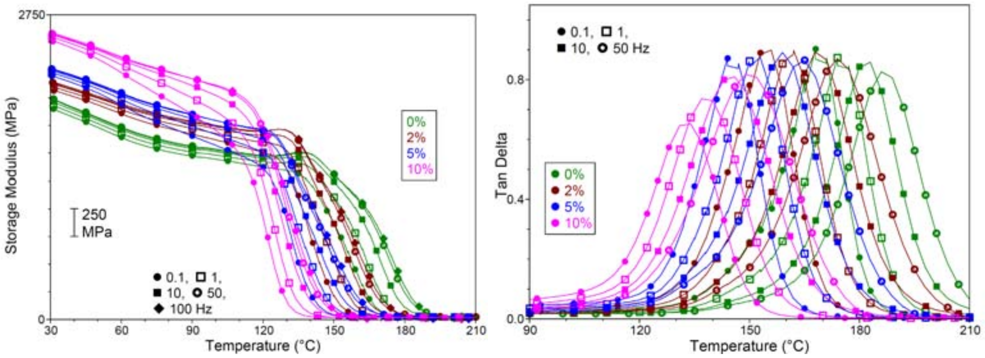
Table 2

Thermo-mechanical properties of epoxy composites

LC content (%)	Cross-linking density (mol/cm^3)	Loss Modulus		Tan δ		Storage Modulus		
		E” peak max. (MPa)	$T_{max.}$ (^{o}C)	peak max.	$T_{max.}$ (^{o}C)	Onset, (^{o}C)	T_g (^{o}C)	E' (Mpa)
0	0.264	259.2	155.11	1.007	164.42	144.77	154.06	599
1	0.257	244.5	150.01	0.9890	158.41	141.65	149.10	584
5	0.228	200.5	146.68	0.9028	154.75	137.01	145.93	517
10	0.290	242.0	138.67	0.8539	146.73	124.90	138.38	658

While the content of LC in epoxy resin become higher, interactions between LC molecules and epoxy backbone become stronger due to aromatic rings which interact by van der Waals forces, while hydroxyl groups generated in the cross-linking process are involved in hydrogen bonds with methoxy groups of LC molecules. But physical interactions are sufficiently weak to allow segmental motions along the axis of the aromatic rings, which are responsible for a slight decrease in the T_g of the cured systems. Loss modulus manifests the same trend confirming the changes in damping characteristics when the LC content was increased in the epoxy matrix.

An increasing in oscillation frequency shifted the tan δ peak to a higher temperature because of the time dependence of the glass-rubber transition. Below this temperature the material react too slow and behaves as a solid, while above this temperature the material relaxes faster than the deformation takes place and behaves as a viscous liquid (Fig. 3).



(a) (b)

Fig. 3. Storage modulus (a) and tan δ (b) as a function of temperature at various frequencies

Frequency dependence confirms the transition as a relaxation. The modulus of the material before and after this transition is relatively constant at approximately 2577-2025 MPa and respectively 20-22 MPa for a 10% LC content, at 100 Hz. The glass transition temperature, defined by the peak of tan δ, is shown to be between 68.5°C and 168.1°C depending on the frequency and the LC content.

Because Dynamic Mechanical Analysis (DMA) is used to investigate relaxation events and T_g is a key parameter, we calculated the activation energy of this process by representing a plot of ln frequency against 1/temperature which is known as an Arrhenius plot (Fig. 4).

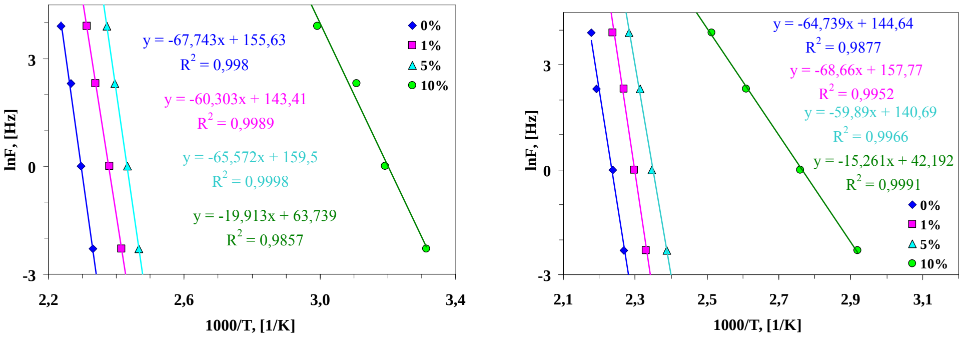
Running a multi-frequency scan and calculating the activation energy of the transition allows us to decide that the transitions were T_g values. The activation energy for a real T_g is roughly 400 kJ/mol (Table 3).

Table 3

Activation energy of epoxy composites

LC content (%)	Activation energy Ea (kJ/mol)	
	Loss modulus peak max.	Tan δ peak max.
0	563	538
1	501	558
5	545	480
10	165	127

The obtained activation energy values show that this parameter is reduced in epoxy-LC composites with respect to simple epoxy resins. The activation energy follows a decreasing trend together with T_g values. It was observed a linear relationship between frequency and the reciprocal of temperature, commonly illustrated by an Arrhenius plot. The slope of each line is equal to negative the activation energy divided by the gas constant.



(a) (b)

Fig. 4. Arrhenius plot of ln Frequencies vs reciprocal of temperature peak max for: (a) E”and (b) tan δ

As the flexibility increases in the epoxy composites comparatively with simple epoxy resin, the crystallinity decreases and as a result the activation energy decreases. This behavior is a characteristic of this type of epoxy-LC composites which have the glass transition temperature near the LC nematic transition.

4. Conclusions

Experiments show that a higher compatibility and homogeneity of the obtained composites was achieved in all analyzed samples because aromatic groups were involved from all the components (epoxy resin, hardener and filler).

Based on the results of the dynamic mechanical analysis, there are large differences in the mobility between the molecular chains of the original epoxy resin and its composites with LC dyestuff.

Analysis shows that the filler act as a toughening agent for the epoxy resins improving their flexibility.

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