Anisotropic Epoxy Networks

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Summary: We present the synthesis, characteristics and curing process of liquid crystalline epoxy monomers containing a central triaromatic mesogenic group. The epoxy monomers were cross-linked with aromatic amines or dicarboxylic acids. In most cases, solid, thermally stable and anisotropic products were obtained. The curing reactions of the monomer were also carried out with selected fillers. The cross-linking process of the composites was monitored by differential scanning calorimetry and dielectric relaxation spectroscopy to compare with analogous liquid crystalline systems not containing filler. Some properties of the cured resin and the composites are described and discussed.

Keywords: anisotropic polymer networks; cross-linking; epoxy; liquid-crystalline polymers; POSS

Introduction

Liquid crystalline properties stabilized by a polymer network have attracted growing interest because of the possibility of combining the mesomorphic and polymeric properties. The simplest way of preparing these materials is by the curing of small-molecule liquid crystalline precursors to which reactive end-groups have been attached. Different types of liquid crystalline polymer networks (LCPNs), their properties and potential applications have been described in recent years in several reviews and books.[1–5] LCPNs have many advantageous properties such as high thermal and mechanical stability, low thermal expansion coefficient, fracture resistance, reduced brittleness and improved resistance to crack propagation, low shrinkage upon curing and high moduli. However, the inherent anisotropy (spontaneous or forced) of the mesogenic molecules is the unique property of these materials.

LCPN are often built up from liquid crystalline epoxy resins (LCE) with rigid aromatic mesogenic groups in the backbone.[6–18] LCEs have many potential applications as high-performance materials, such as matrices in advanced composites and nanocomposites, as new materials for non-linear optics, microelectronics, storage data systems, in automotive and aerospace industry and as mechanical actuators, e.g. artificial muscles, and waveguides.

The properties of LCEs depend on the structure of the epoxy monomers (e.g. the type of mesogenic group and the length of the flexible spacers) and on the structure of the curing agents as well as on the mechanism of the cross-linking reaction. In many studies, formation of LCPNs from mesogenic diepoxides was accomplished by curing with aromatic primary or tertiary diamines.[8,10–16] The products were rigid, highly cross-linked materials with low flexibility. Liquid crystalline elastomers were also obtained from LCEs, usually lightly cross-linked. According to reports,[17,19]

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by curing liquid crystalline epoxy monomers with dicarboxylic aliphatic acids, materials of relatively high flexibility were obtained.

LCEs were also used to prepare composites with selected fillers. Synthesis and properties of materials prepared from LCEs and fillers, such as carbon fibers, nanotubes,[20,21] organoclays[22] and polyaniline nanorods,[23] were described. The last filler also played the role of curing agent. By blending LCEs with fillers, one can reduce the cost of composites, induce preordering of the filler particles and equip the resulting materials with unique physical (optical, electrical) properties.

In this study, we used the liquid crystalline epoxy monomer bis[4-(10,11-epoxyundecanoyloxy) benzoate]-*p*-phenylene (MU22) to prepare anisotropic networks in reaction with selected curing agents. The effects of reactive nanofillers on the curing reaction of this monomer were also studied. As reported in the literature, nanostructured networks can be obtained by co-reacting polyhedral oligomeric silsesquioxane (POSS) epoxides, with a typical epoxy resin (e.g. diglycidylether of bisphenol A) and with Jeffamine D2000.[24] In our study, we used the octaepoxy compound octakis(dimethylsiloxypropylglycidyl ether)silsesquioxane (POSS-OG). The thermal properties of the resulting composites were investigated and the structure of the products cured in the presence and in the absence of POSS-OG was analyzed.

Experimental Part

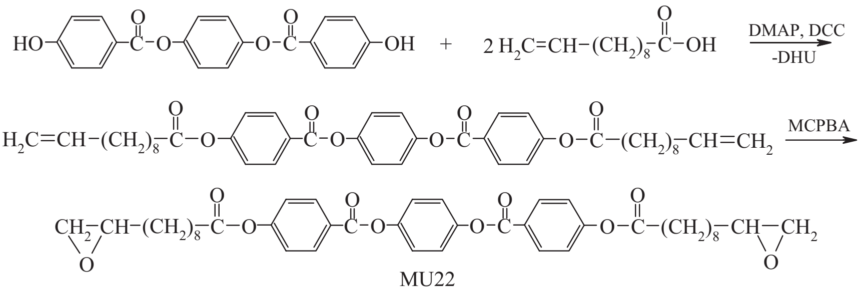
Synthesis

The starting materials were commercial products (Sigma-Aldrich, Fluka, Merck) and were used without further purification. The synthetic scheme leading to epoxy monomer MU22 is presented in Figure 1. The synthetic procedure was described in detail elsewhere.[18] The structure of the epoxy monomer was confirmed by IR and NMR spectroscopy. The epoxy number (moles of epoxy groups per 100 g) of MU22 was 0.277 (calculated: 0.280). The POSS-OG, used as reactive nanofiller, was synthesized according to the method reported in the literature.[25] At room temperature, POSS-OG is a colorless, viscous liquid with epoxy number of 0.392 (calculated 0.414).

Preparation of Samples for Curing

The epoxy monomer MU22 was cured in a polyaddition reaction with 4,4'-diaminodiphenylmethane (DDM) or suberic acid (SA) and with 4-(N,N-dimethylamino)pyridine (DMAP) in ionic polymerization. The compositions in epoxy monomer MU22, curing agent and reactive fillers POSS-OG were also prepared. The chemical structures of the curing agents and POSS-OG are shown in Figure 2.

The amounts of the components in all compositions and the code names of the blends are listed in Table 1. The homogeneous samples of the mixtures were prepared by dissolving the reagents in



DMAP - 4-(N,N-dimethylamino)pyridine
DCC - N,N'-dicyclohexlcarbodiimide
DHU - N,N'-dicyclohexylurea
MCPBA - *m*-chloroperoxybenzoic acid

Figure 1.
Synthetic route to the liquid crystalline epoxy monomer MU22.

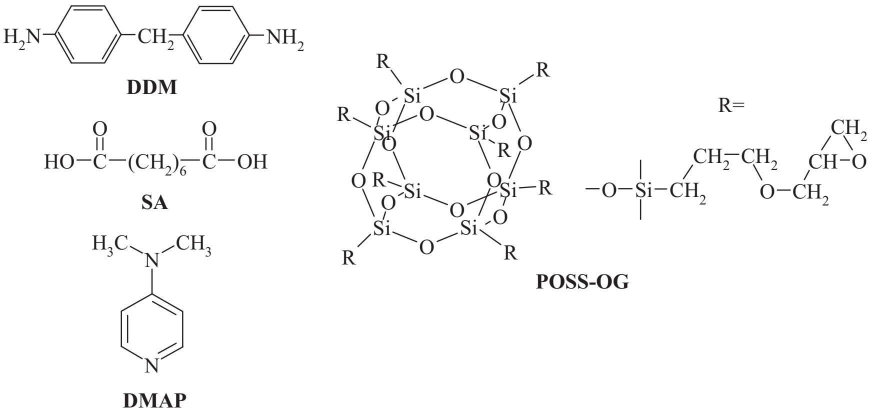


Figure 2.
Chemical structures of the curing agents and the nanofiller POSS-OG.

dichloromethane or acetone. Subsequently, the solvent was evaporated in vacuum at room temperature and the mixture for curing was stored at 5-10 °C before use. The samples containing only POSS-OG and curing agents (DDM and SA in stoichiometric proportions, DMAP in the amount of 1% w/w) were prepared in the same way.

Measurements

IR spectra were recorded on a Paragon 1000 FTIR spectrometer. ^{1}H-NMR spectra were obtained using a Bruker Avance^{II} 500 spectrometer with $CDCl_3$ or d_6-dimethyl sulphoxide as solvent. The textures of the mesophase and cured samples were observed with a Nicon ECLIPSE polarizing optical microscope (POM) equipped with a temperature-controllable hot stage Linkam THMS600 (magnification of 80× crossed polarizers). Differential scanning calorimetry (DSC) measurements were performed using a Mettler-Toledo DSC822^e instrument under a nitrogen atmosphere. Wide-angle X-ray scattering (WAXS) experiments were carried out with a rotating anode (Rigaku 18 kW) X-ray beam with pinhole collimation, a two-dimensional detector (Siemens) 1024 × 1024, and a double graphite monochromator for Cu K_α radiation ($\lambda = 0.154$ nm). The beam diameter was about 0.5 mm, and the sample-detector distance was 80 mm. WAXS analysis was made for the MU22 monomer in different temperature in order to obtain detailed information about the type of the mesogenic phase.

Table 1.
The curing compositions containing liquid crystalline epoxy monomer MU22.

Sample	Molar ratio of reactive groups
MU22/DDM	1/1
MU22/POSS-OG/DDM	1/1/2
MU22/SA	1/1
MU22/POSS-OG/SA	1/1/2
MU22/DMAP	1/~0.030*
MU22/POSS-OG/DMAP	1/0.25/~0.035*

*by weight with respect to the whole sample

Dielectric response was recorded using dielectric relaxation spectroscopy (DRS). In particular, a high resolution Alpha impedance analyzer coupled with a nitrogen-gas cryostat and a temperature controller were used; all the experimental set-up was from Novocontrol. The process of curing was studied in isothermal conditions, using sandwich-type metal cells. As a result of the measurements, the real and the imaginary parts of the complex permittivity were obtained in the frequency range from 10^{-1} to 10^6 Hz, which were further converted into the electric modulus M (defined as $M^* = 1/\varepsilon^*$). The frequency of the peak observed in the plot of $M''(f)$ can be directly related to the conductivity of the material.

The dynamic mechanical thermal analysis (DMTA) was performed by means of a

DMA 2980 TA Instruments analyzer. The values of storage modulus (E'), loss modulus (E'') and loss factor ($\tan\ \delta = E''/E'$) were recorded as functions of temperature. The testing mode was the tension film clamp with samples having a cross-section about $6 \times 1\ \mathrm{mm}^2$ and a length of 11 mm. The samples were oscillated at a frequency of 1 Hz with an oscillation amplitude 10 μm. The mechanical spectra were obtained using temperature scan rate of $5\ ^\circ\mathrm{C\,min}^{-1}$ starting from −60 °C and ending just above the glass transition temperature of the samples being analyzed.

Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-5500LV instrument. The samples for examination were cryo-fractured in liquid nitrogen.

Results and Discussion

In our previous work, we described the synthesis and curing reactions of epoxy monomer MU22 with aromatic amines, including DDM and DMAP.[18] As determined by DSC, WAXS and by observation in polarizing microscopy (Figure 3), epoxy monomer MU22 exhibits liquid crystalline behavior in the temperature range of 138-189 °C. The curing reaction of MU22 with DDM or DMAP yielded networks having anisotropic (nematic) properties, stable up to 300 °C.

In this work, SA was also used as the curing agent for monomer MU22. Furthermore, POSS-OG was used as a reactive nanofiller in the curing process involving MU22 and accomplished by DDM, DMAP or SA. The reactivity of POSS-OG with selected curing agents was confirmed using DSC and DRS. The curing behavior of MU22 epoxy precursors mixed with selected curing agents and with or without POSS-OG was monitored by DSC, in the dynamic or isothermal modes. The dynamic thermograms of all compositions (Table 1) recorded at a heating rate of $10\ ^\circ\mathrm{C\,min}^{-1}$ are shown in Figure 4. DSC scans of the compositions show the endothermic peaks which correspond to the melting of curing agents and polymorphic transition $\mathrm{crystal}_1 \rightarrow \mathrm{crystal}_2$ of MU22.

The exothermic effect related to the cross-linking reaction appeared at about 135-140 °C, after the epoxy monomer melted out. The curing reaction resulted in the exothermic peak which interfered with the endothermic transition of melting of both MU22 and the curing agents (especially SA). Hence, the enthalpy of the curing process

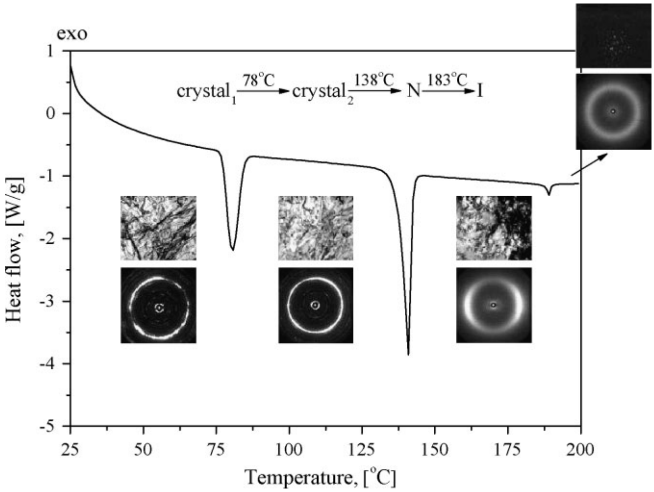


Figure 3.
DSC curve of epoxy monomer MU22 (heating rate $2\ ^\circ\mathrm{C\,min}^{-1}$) with WAXS patterns and POM textures in crystals (Cr), nematic (N) and isotropic (I) phases.

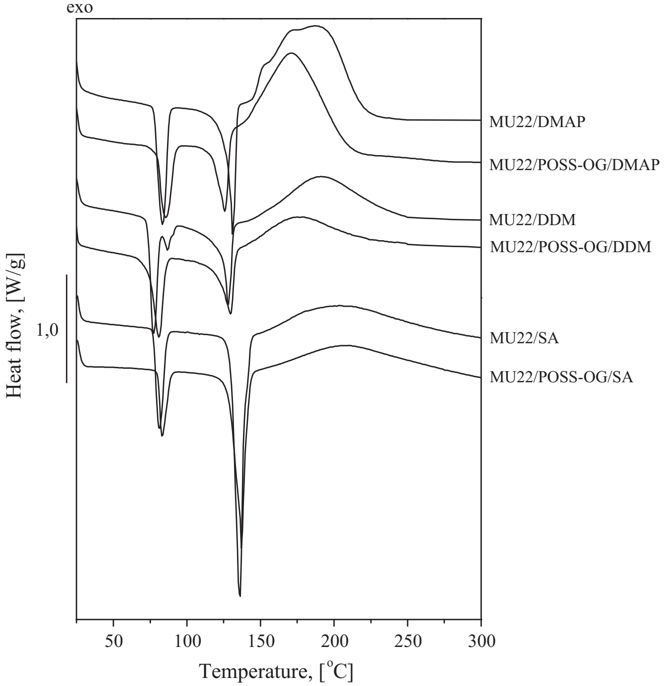


Figure 4.
DSC thermograms of MU22 compositions (heating rate 10 °C min^{-1}).

determined from the DSC thermograms could in fact be lower than the real heat of curing. The compositions with DDM and DMAP showed much steeper initial slope of curing which suggested that the reaction of epoxy compounds with amines proceeded faster than the reaction between epoxy groups with carboxylic acids. It is already known that the activity of epoxy groups in reactions with aromatic amines, either primary ones in polyadditon reactions or tertiary, in ionic polymerization, is higher than the reactivity of epoxies with carboxylic acids.

Furthermore, the addition of the co-reacting compound POSS-OG to the MU22 compositions lowered the heat of curing in comparison to the samples without POSS-OG. The wide temperature range of the exothermic peak for all compositions suggested that post-curing at a higher temperature was necessary. The data from the DSC thermograms for all studied mixtures are summarized in Table 2.

In order to determine the curing and post-curing temperature for each mixture for which a high degree of conversion of reactive functional groups had to be

Table 2.
DSC-determined curing data for compositions of epoxy monomer MU22 with curing agents (DDM, DMAP or SA) and with or without POSS-OG.

Sample	Maximum temperature [°C]	Total heat of the curing reaction [J g^{-1}] ([kJ mol^{-1} of epoxy groups])
MU22/DDM	190.5	133.7 (54.3)
MU22/POSS-OG/DDM	175.0	86.4 (30.1)
MU22/SA	203.5	119.3 (53.0)
MU22/POSS-OG/SA	210.0	108.2 (41.8)
MU22/DMAP	189.0	240.6 (86.8)
MU22/POSS-OG/DMAP	172.5	192.9 (58.3)

achieved, the DSC analysis was made in isothermal conditions. The temperatures of the isothermal study were selected on the basis of information obtained from the DSC thermograms made during a heating cycle (Figure 4). In the first DSC scan, the curing of a composition was carried out by heating the samples for 60 min at 150, 160, 170, 180, 190, or 200 °C. The heat of the curing process determined from these thermograms increased as the temperature was raised. Then, in the second cycle, the thermal properties of the samples preheated under isothermal conditions were analyzed by DSC in a heating cycle between 25-300 °C. The appearance of endothermic peaks in this cycle, probably due to melting of oligomeric products, indicates only partial conversion of reagents in the first isothermal cycle. On the other hand, the lack of an endothermic peak proves completion of the curing process.

The curing process under isothermal conditions for all compositions was also monitored by dielectric spectroscopy. Examples of the changes related to the ionic conductivity during the cross-linking reaction for the mixture of POSS-OG and suberic acid and the MU22/POSS-OG/SA composition are presented in Figure 5.

As can be seen from the results of the dielectric studies (Figure 5), the curing process is similar for both mixtures. The conductivity gradually decreases in line with the advancing reaction. It can be noticed that both mixtures react fully within about 1.5 hour at 170 °C, although the process is somewhat longer in the case of the MU22/POSS-OG/SA composition.

The optimal curing conditions established by DSC and DRS are as follows:

I). 160 °C/180 min (MU22/DDM, MU22/POSS-OG/DDM, MU22/DMAP and MU22/POSS-OG/DMAP) or 170 °C/180 min (MU22/SA and MU22/POSS-OG/SA),
II). post-curing: 180 °C/120 min (MU22/DDM, MU22/POSS-OG/DDM, MU22/DMAP and MU22/POSS-OG/DMAP) or 200 °C/120 min (MU22/SA and MU22/POSS-OG/SA).

The samples of all compositions were cured in an oven in Teflon matrix at the selected temperatures and times including post-curing. The products after curing in the form of films about 1 mm thick were analyzed by IR spectroscopy, DMTA and SEM. For observations in POM, the samples were prepared under the same conditions between two glass plates with 20-μm spacers.

To investigate the cure reaction, FT-IR spectra were recorded before and after the process. The bands characteristic for epoxy groups at about 915 and 760 cm^{-1} disappeared almost completely from the spectra of all

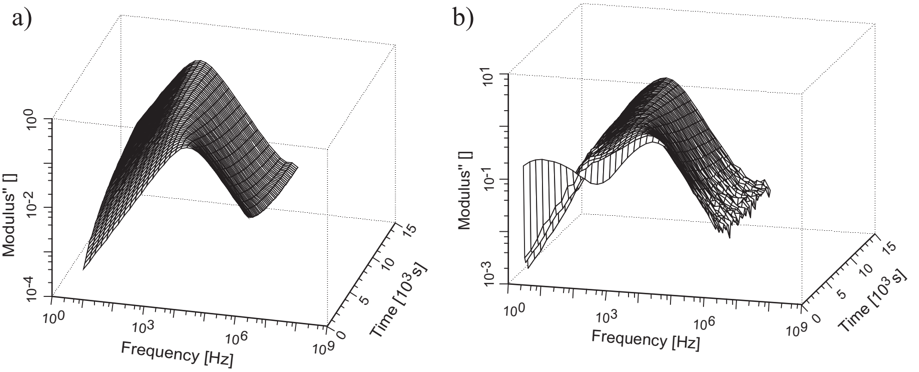


Figure 5.
The dielectric response of the mixtures POSS-OG/SA (a) and MU22/POSS-OG/SA (b) during isothermal curing at 170 °C.

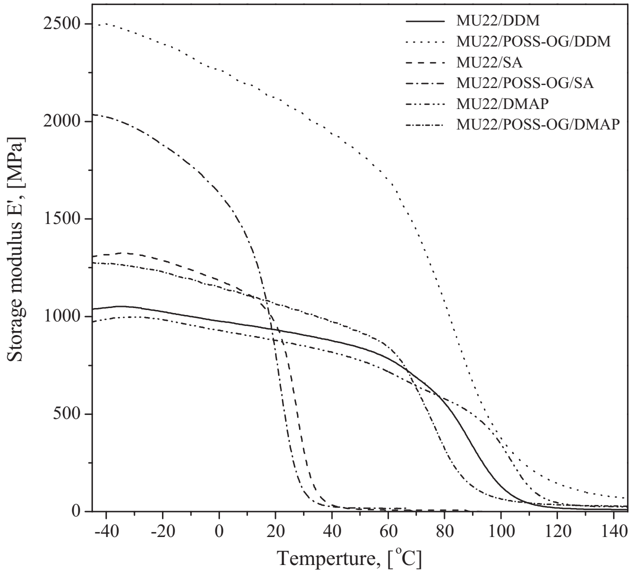


Figure 6.
DMTA thermograms of the cured compositions of epoxy monomer MU22.

samples after curing. This confirms the high degree of conversion of reactive groups in the cross-linking reaction and that the curing process was practically completed.

Thermomechanical properties of compositions cross-linked with or without the co-reactive compound POSS-OG were determined by DMTA. DMTA thermograms of all six networks are presented in Figure 6. Figure 7 shows *tan δ* as a function of temperature. The glass transition temperature, corresponding to the maximum of

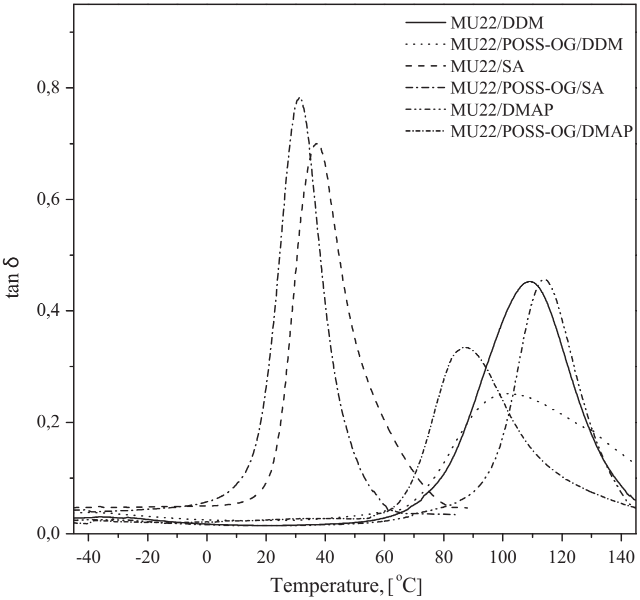


Figure 7.
Temperature dependence of tan δ of cured compositions of epoxy monomer MU22.

Table 3.
Glass transition temperature and storage modulus at −40 °C of the epoxy monomer MU22 cured with DDM, DMAP or SA, with or without POSS-OG.

Sample	T_g [°C]	E' at −40 °C [MPa]
MU22/DDM	110	1045
MU22/POSS-OG/DDM	101	2450
MU22/SA	36	1317
MU22/POSS-OG/SA	31	2023
MU22/DMAP	114	986
MU22/POSS-OG/DMAP	87.5	1271

the *tan δ* peaks and the values of storage modulus in the glassy state were established. These parameters are listed in Table 3.

As expected, the highest glass transition temperature has the composition with the highest mesogen concentration in the network MU22/DMAP, in which an anionic catalyst of polymerization was used as a curing agent. T_g decreases slightly for the composition cured with the primary diamine DDM. The resins cured with SA have the lowest value of T_g. A decrease of T_g for the composition cured with POSS in comparison with the analogous samples without this co-reacting fillers is also observed. It is probably related to the plasticizing effect of flexible aliphatic chains from POSS-OG compounds in cured networks. On the other hand, the samples cured with POSS-OG are stiffer in the glassy state and exhibit higher values of storage moduli than the analogues without this component.

The morphology of the cured composites was studied by using scanning electron microscopy and polarizing optical microscopy. The analysis of fracture surface of cured samples in SEM revealed a significant difference in the fracture propagation for compositions with or without POSS-OG filler (Figure 8). The surface of samples cured without POSS-OG is rough which suggests high toughness and fracture resistance. As explained by Carfagna et al.,[26] the cured liquid crystalline resins are composed of anisotropic domains of random orientation. These materials are, therefore, inhomogeneous. This kind of morphology causes high toughness in comparison with conventional epoxy resins. The addition of reactive filler to compositions of liquid crystalline epoxy precursor significantly changed the structure of the cured materials. For the samples cured with POSS-OG, a uniform shell-like fracture surface was observed, typical for brittle materials.

On the other hand, the cross-linked epoxy monomer MU22 with POSS-OG had optical properties similar to those of the resin not containing POSS-OG. Both materials had anisotropic properties and the textures of all compositions were similar to the texture of monomeric MU22 in nematic phase. To illustrate this,

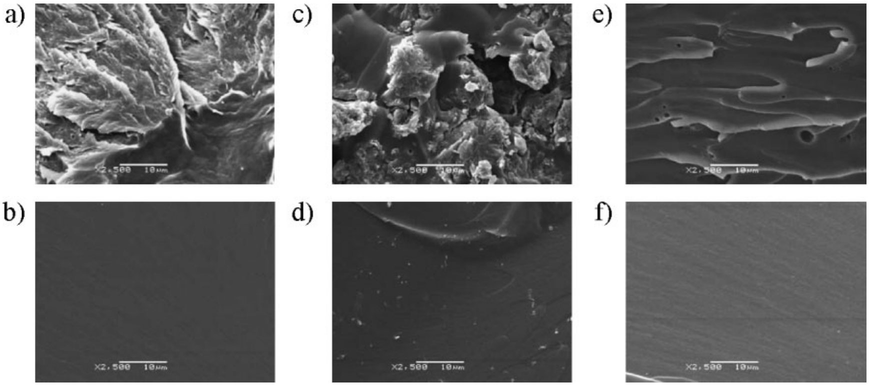


Figure 8.
Scanning electron micrographs of the fracture surface of cured compositions: MU22/DDM (a), MU22/POSS-OG/DDM (b), MU22/SA (c), MU22/POSS-OG/SA (d), MU22/DMAP (e), MU22/POSS-OG/DMAP (f).

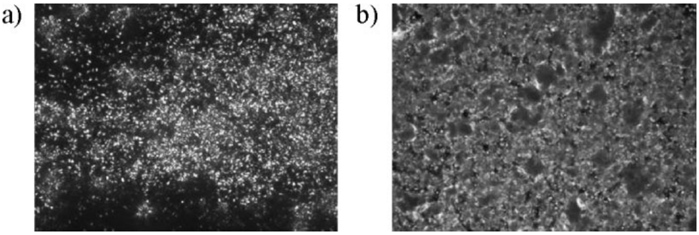


Figure 9.
POM textures of cured compositions: MU22/SA (a) and MU22/POSS-OG/SA (b).

POM images of compositions cured with SA are presented in Figure 9.

Conclusion

The reactive filler octaepoxy polyhedral oligomeric silsesquioxane (POSS-OG), added to the systems comprising liquid crystalline epoxy monomer and selected curing agents, affects mostly the fracture properties of cured compositions. DSC and DRS analyses indicate that the presence of POSS-OG does not change substantially the cross-linking reaction and that the octafunctional POSS-epoxy monomer reacts and co-reacts with liquid crystalline epoxy monomers. The addition of POSS-OG fillers to the liquid crystalline epoxy monomer does not affect the optical anisotropic properties of cured samples. The textures of cured compositions with or without reactive fillers observed in polarizing optical microscopy are both typical for the nematic liquid crystals. The POSS-OG filler changes, however, the thermomechanical properties of cured products and makes the epoxy composites stiffer in the glass region with a shell-like fracture surface, typical for brittle materials of reduced fracture toughness. This co-reactive component also reduces the glass transition temperature of the composites.

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