EPOXY-THIOL THERMOSETS MODIFIED BY CARBAZOLE DECORATED HYPERBRANCHED POLY(ETHYLENEIMINE) FOR OPTICAL APPLICATIONS

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Abstract

New epoxy-thiol thermosets containing carbazolyl moieties were prepared by adding different proportions of a hyperbranched poly(ethyleneimine) with carbazolyl terminated units to diglycidyl ether of Bisphenol A/trimethylopropane tris(3-mercaptopropionate) stoichiometric formulations. This carbazolyl decorated hyperbranched polymer was synthesized from commercially available hyperbranched poly(ethyleneimine) and N-glycidyl carbazole and was characterized by standard procedures.

The influence of adding different proportions of the modifier to the formulation on the curing process was determined by calorimetry after the selection of the most adequate latent initiator, which was a urethane compound, named PDU-250. Its decomposition at a well-defined temperature liberates the amine that initiates the thiol-epoxy curing process.

The materials obtained with different proportions of modifier were characterized by means of thermomechanical analysis. On increasing the proportion of modifier, the glass transition temperature and the damping characteristics increased, but the thermal stability and the homogeneity were reduced.

The films obtained by curing the different formulations exhibited fluorescence maxima at 370-374 nm. The fluorescence quantum yields were in the range of 17-32% and they decreased with the increase of the amount of the modifier in the materials.

1. Introduction

Organic semiconductors have found a wide range of applications in organic light-emitting diodes (OLEDs) [1, 2], organic solar cells [3, 4, 5], organic transistors [6, 7], etc. Special attention is paid to polymer materials due to their great potential for utilization in flexible and large-area devices using liquid composition-based fabrication processes such as spin-coating and inkjet-printing.

Electroactive and photoactive polymers have been investigated for many years because of their great potential in organic electronics [8, 9].

Carbazole-containing compounds have been widely studied because of their useful properties, such as high hole mobility, strong absorption in the ultraviolet spectral region and high photoluminescence efficiency [10,11,12,13]. Hoegl *et.al.* [14] firstly reported the photoconductivity of poly(*N*-vinylcarbazole) (PVK) and established that PVK sensitized with suitable electron acceptors showed high enough levels of photoconductivity to be useful in practical applications. Nowadays, carbazole-containing polymers, like as poly(N-epoxypropylcarbazole) or poly(N-alkylcarbazole), are widely used in a number of commercial devices and processes, such as photocopiers, holographic security stamps, etc. [15].

Many carbazolyl-derivatives have been described for the application as charge-transporting materials [16,17]. However, they exhibit poor mechanical characteristics, low film-forming properties and sometimes ~~concentrational~~ quenching of fluorescence, due to the spatial overlapping of carbazolyl groups [18, 19, 20, 21, 22]. The other limitation occurs in the fabrication of multilayer organic optoelectronic devices when the spin coating method of deposition of the electroactive layers is used. This is the partial mixing ~~solubility~~ of the bottom layer with the top layer during the coating process ~~of the next layer on top~~, since most of the organic electroactive low-molar-mass materials are soluble in similar organic solvents. One of the methods to avoid such problems could be the immobilization of carbazolyl groups in rigid crosslinked structures, insoluble in organic solvents.

During the last years, a number of crosslinked semiconducting polymers have been reported [23, 24, 25, 26, 27]. The direct polymerization of bifunctional semiconducting monomers with the further formation of a network by the convenient curing process seems to be one of the most ~~the~~ promising methods of the fabrication of the active layers of optoelectronic devices [28, 29, 30].

Epoxy resins are highly versatile materials used to prepare crosslinked networks, because of the broad reactivity of epoxy groups, which can react with nucleophiles and electrophiles in stoichiometric and catalytic amounts leading to thermosets with tailored characteristics [31]. According to their versatility, epoxy resins have a huge number of applications such as surface coatings, adhesives, binding and encapsulation materials [32, 33]. They also found application in OLEDs [22, 34].

Among curing agents, thiols can be used in epoxy thermosets fabrication giving rise to transparent and colourless materials. Therefore, the use of thiols as curing agents is highly advisable to prepare thermosets for optical applications [35]. The thiol-epoxy reaction falls in the group of click reactions because of its special characteristics: it is quick, selective, controlled, and enable to reach high conversions [36]. Moreover, the shrinkage on curing and the stresses produced during this process and subsequent cooling are quite low [37, 38].

In the present work, we studied the preparation of thermosets by the condensation of diglycidylether of bisphenol A (DGEBA) and trimethylolpropane tris(3-mercaptopropionate) (TTMP)

for immobilization of a hyperbranched polymer decorated with pendant carbazolyl moieties. The hyperbranched polymer was synthesized from commercial poly(ethylenimine) (PEI) and N-(2,3-epoxypropyl)carbazole. This polymer was used as modifier in the preparation of thermosets with different concentration of carbazolyl moieties. The curing process was investigated by differential scanning calorimetry. Thermomechanical, thermogravimetric and photoluminiscent properties of the resulting materials were evaluated.

2. Experimental

2.1. Materials

Trimethylopropane tris(3-mercaptopropionate) (TTMP) was purchased from Sigma-Aldrich and used without further purification. 9-(2,3-Epoxypropyl)carbazole (EPK) was purchased from Reakhim and was twice recrystallized from isopropanol before use, m.p. 109-111ºC. Diglycidylether of bisphenol A (DGEBA, GY240, Huntsman, epoxy equivalent 182 g/eq) was dried at 50°C under vacuum for 12 h. Poly(ethyleneimine) (PEI) Lupasol® FG with molar mass of 800 g/mol was obtained from BASF and dried at 50ºC under vacuum for 12 h. According to the data sheet, the relationship (NH_2/NH/N) was (1/0.82/0.53). The amine precursors, used as latent catalysts, were Technicure® LC-80 (is an encapsulated imidazole) and Technicure® PDU-250 (N,N-dimethyl phenyl urea); both from AC Catalysts. Organic solvents were purchased from Scharlab and were purified by standard procedures.

2.2. Modification of hyperbranched poly(ethyleneimine) with 9-(2,3-epoxypropyl)carbazole

0.5 g (0.62 mmol) of poly(ethyleneimine) (PEI) and 1.95 g (8.75 mmol) of 9-(2,3-epoxypropyl)carbazole (EPK) were dissolved in 50 mL of ethanol and refluxed for 48 hours. When the carbazole derivative disappeared (TLC, eluent - acetone:hexane, 1:2), the reaction was stopped and the solvent was eliminated. The solid product was dissolved in chloroform and then was precipitated into ethanol. The procedure was repeated twice. The solid product (PEI-Cbz) was dried in the vacuum oven overnight.

^{1}H NMR (400MHz, CDCl$_3$), δ, ppm: 7.83-8.11 (broad peak, 4,5-H_{Ar}-Cbz), 6.99-7.47 (broad multiplet, 1,2,3,6,7,8-H_{Ar}-Cbz), 3.62-4.19 (broad peak, -CH$_2$CHCH$_2$- of EPK) and 1.49-2.49 (broad peak from PEI core).

^{13}C NMR (75.4MHz, CDCl3), δ, ppm: 140.9, 125.7, 122.8, 120.3, 119.0, 109.3, 68.5, 67.5, 52.5, 47.2 and 46.3.

ATR-FTIR, cm^{-1}: 3327 (w), 3053 (w), 2936 (w), 2825 (w), 1590 (m), 1482 (s), 1448 (s), 1323 (s), 1214 (m), 1154 (m), 1122(m), 741 (s), 719 (s) and 615 (w).

The amount of carbazole in the obtained polymer was estimated to be 59.6 wt% by ^{1}H-NMR spectroscopy.

T_g determined by DSC: 88ºC

Thermal stability determined by TGA in N_2 atmosphere: $T_{5\%}$= 334ºC; T_{max}=368ºC.

2.3. Preparation of curing mixtures

The formulations were prepared by adding the selected amount of PEI-Cbz polymer (content of carbazole moieties in the range of 5-30 wt%) into a stoichiometric mixture of DGEBA and trimethylopropane tris(3-mercaptopropionate) (TTMP) (3 mol of DGEBA by 2 mol of TTMP). Then, 0.5 phr of LC-80 (parts of catalyst for hundred parts of epoxy resin) or 2 phr of PDU-250 were added. Table 1 shows the compositions of all the formulations studied.

Table 1. Notations and compositions of the formulations in weight percentages

Sample	*Weight % PEI-Cbz*	*Weight % DGEBA*	*Weight % TTMP*
5% Cbz	8.5	52.9	38.6
10% Cbz	17.0	48.0	35.0
15% Cbz	24.6	43.6	31.8
20% Cbz	33.7	38.3	28.0
25% Cbz	38.9	35.3	25.8
30% Cbz	47.4	30.4	22.2

2.4. Characterization

^{1}H NMR spectra were recorded with a "Bruker Avance III" (400 MHz (^{1}H), 100 MHz (^{13}C)) spectrometer using deuterated chloroform solutions. All the data are given as chemical shifts in δ (ppm), taking $(CH_3)_4Si$ as the internal standard.

FTIR spectra were recorded using a Perkin Elmer Spectrum GX II FT-IR System, equipped with attenuated total reflection (ATR) technique.

UV spectra were recorded with Aventes AvaSpec-2048XL spectrometer. Thin films were prepared directly on the quartz glass using drop casting technique. The solutions of the formulations (10 mg/cm^3) in chloroform were poured on the glass. After evaporation of the solvent the curing was performed.

Fluorescence spectra and fluorescence decay curves were recorded by Edinburgh Instruments FLS980 spectrometer with TMS300 monochromators and a red cooled detector (Hamamatsu R928P). Fluorescence quantum yields were measured using integrated sphere of a 120 mm inside diameter spherical cavity calibrated with two standards: quinine sulfate in 0.1 M H_2SO_4 and rhodamine 6G in ethanol. Clean quartz glass was used for the reference. Each fluorescence quantum yield measurement

was repeated 5 times and the error range was estimated. Fluorescence decay curves of the samples were recorded using a time-correlated single photon counting technique utilizing the nF920 Nanosecond Flashlamp as an excitation source.

Differential scanning calorimetry (DSC) analyses were carried out on a Mettler DSC−821e or on a Mettler DSC-822e calorimeter. Samples (5-10 mg) were cured in aluminium pans in a nitrogen atmosphere (100 mL/min). The calorimeter was calibrated using indium standard (heat flow calibration) and an indium−lead−zinc standard (temperature calibration).

In the dynamic curing process, the degree of conversion by DSC (α_{DSC}) was calculated as follows:

$$\alpha = \frac{\Delta h_T}{\Delta h_{dyn}}$$

where Δh_T is the heat released up to a temperature T, obtained by integration of the calorimetric signal up to this temperature, and Δh_{dyn} is the total reaction heat associated with the complete conversion of all reactive groups.

The thermal stability of the cured samples was determined by thermogravimetric analysis (TGA), using a Mettler TGA/SDTA 851e thermobalance. All the experiments were performed under inert atmosphere (N_2 at 100 mL/min). Pieces of the cured samples with an approximate mass of 8 mg underwent thermal degradation between 30 and 900°C at a heating rate of 10°C/min.
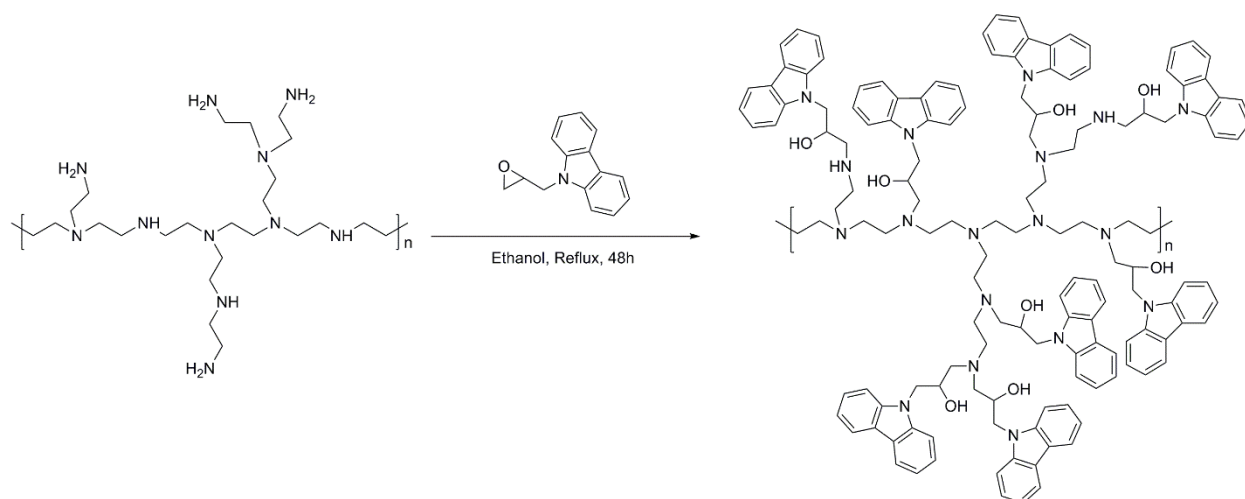
Dynamic mechanical thermal analyses (DMTA) were carried out with a TA Instruments DMA Q800 analyzer. The samples for analysis were prepared by isothermal curing in a mould ($10 \times 7.6 \times 1.2$ mm^3) at 120°C for 60 min and post-curing at 150°C for 60 min. The samples were carefully polished to ensure constant dimensions. The analyses were carried using 3-point bending clamp with support of span of 15 mm. The viscoelastic properties of the cured material were determined using 2°C/min heating rate from 30 to 120-180°C. The frequency was of 1 Hz and the oscillation amplitude of 10 μm.

3. Results and discussions

3.1. Preparation of PEI-Cbz

In the present work, we have modified commercially available poly(ethyleneimine) (Lupasol® FG) with molecular weight of 800 g/mol with 9-(2,3-epoxypropyl)carbazole using ethanol as the solvent as shown in Scheme 1, taking advantage of the epoxy-amine click reaction. PEI is advantageous in reference to other commercially available hyperbranched structures for modification purposes, because of the presence of reactive amino groups in its structure, which react quite easily with glycidyl moieties. Other commercially available Boltorn and Hybrane hyperbranched polymers have hydroxyl end groups, which are more difficult to modify. Another advantage of PEI is that the low molecular weight of its structural unit allow introducing a high proportion of modifying units (Cbz) per gram. Additionally,

hyperbranched polymers are less viscous than analogous linear polymers, hinder crystallization to occur and present a higher proportion of reactive chain ends.

Scheme 1. Modification procedure of PEI to obtain PEI-Cbz.

Taking into account the degree of polymerization of PEI, the proportion of NH_2/NH/N and the equivalent number of amino groups by gram of PEI, the average number of active groups per molecule was calculated and resulted to be 7.9 primary, 6.4 secondary, and 4.2 tertiary amino groups. Only NH_2 and NH can react with EPK, being the primary amines able to react twice with epoxides while secondary amines could react only once. Therefore, by average, a PEI molecule could incorporate a maximum of 22.2 carbazole moieties in the structure of the modified PEI.

The reaction between epoxides and amines follows an S_N2 nucleophilic substitution mechanism, which can be somehow affected by steric hindrance [39]. Primary amines are more nucleophilic than secondary amines and therefore, it is foreseeable that all primary amino groups in PEI will be converted into secondary amines in the reaction with EPK. By ^{1}H NMR spectroscopy it was determined that the reaction of secondary amino groups with EPK was not complete (globally only 14 eq of EPK reacted) and subsequently only *ca*. 6 secondary amino groups, in average, per molecule were converted into the tertiary amines. This fact can be explained by the existence of steric hindrances, produced by the size of carbazolyl groups attached to the hyperbranched structure or to the inner position of the NH reactive groups. Another effect limiting the degree of substitution can be the early precipitation of the modified polymer due to π−π interactions among carbazole units, which insolubilize the modified polymer from the reactive medium, when a certain degree of substitution is reached. In previous studies in the modification of PEI with allyl glycidyl ether, the complete modification was achieved which seems to support that the responsible of the lower degree of modification reached in the present work is the carbazole moiety [40].

The degree of modification of the polymer was estimated by NMR spectroscopy. In the ^{1}H NMR spectrum a broad peak at 3.62-4.19 ppm appeared, attributable to the protons of the aliphatic moiety of the reacted EPK, while the signals of aromatic protons appear between 7 and 8 ppm. The signals of PEI at 1.49-2.49 ppm appear very broad in the NMR spectrum of the modified polymer because of the higher molecular weight of the polymer that makes difficult the movement of the core with the subsequent reduction of the relaxation time. The determination of the degree of modification was done from the integration of the signals corresponding to the aromatic protons of carbazole and the protons of the PEI nucleus as reported in a previous paper [41]. The carbazole decorated poly(ethyleneimine) has a Tg of 88ºC and is thermally stable in the range of temperature below 300ºC.

3.2. Study of the curing process

The thiol-epoxy reaction has been reported by several authors [42, 43, 44]. Thiol groups require a base to increase their nucleophilicity by forming thiolates capable to attack epoxides, but amines usually lead to very reactive systems with a too short pot-life. Recently, the use of latent amine precursors has been reported [45] which allows to trigger the curing process by heat at high temperature. In that study, two latent precursors were tested: LC-80 (which is an encapsulated imidazole) and PDU-250 (which is a urethane). It could be proved that a higher proportion of PDU-250 than LC-80 (2 and 0.5 phr, respectively) were required as curing initiators [45].

To investigate the curing evolution of stoichiometric DGEBA-TTPM formulations with 8.5 wt% of PEI-Cbz (sample 5% Cbz, with 5 wt% of carbazole units), we tested both latent amine precursors by DSC, to know the range of temperatures where the curing takes place. Since PEI-Cbz has amino groups in its structure, we also studied the curing evolution without any catalyst. **Figure 1** shows the DSC curing exotherms. The reaction without catalyst starts at *ca.* 150ºC and finishes at high temperature, which can overlap with some degradation or homopolymerization processes. This result suggests that the addition of a base is required since the basicity of the amines from PEI-Cbz is not sufficient. In the figure, the effect of the addition of 0.5 phr of LC-80 and 2 phr of PDU-250 in the curing evolution can be appreciated. In the formulation catalyzed by LC-80 the curing begins at 60ºC, whereas the formulation with PDU-250 reacts at higher temperatures (the reaction starts at *ca*. 115ºC) and this process is very fast. The exotherm of curing catalyzed by PDU-250 is narrow, what corresponds to a latent behaviour. This result is different from the previously reported, since LC-80 gave the narrower exotherm [45]. This observation can be explained by the premature opening of the capsule of LC-80 by the attack of thiolate anions or by the changes in the polarity of the medium, which allows the catalyst to be released before the triggering temperature. The broad shape of the curve in case of LC-80 and the beginning of the exotherm at lower temperature in the DSC thermogram can cause an undesired premature curing, which could start even at room temperature. Due to the desired higher stability of the

formulation during storage at room temperature and the quick curing process, PDU-250 was selected as the catalyst for further studies.
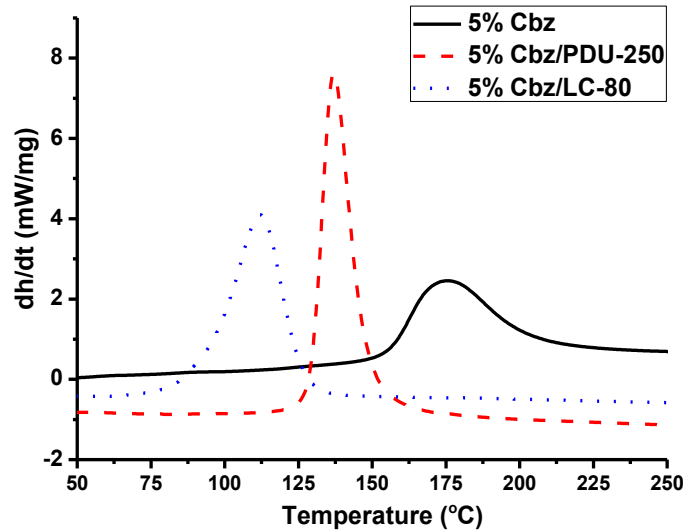

Figure 1. Calorimetric curves recorded at 20ºC/min of the mixtures 5% Cbz without catalyst (5% Cbz), with 0.5 phr of LC-80 (5% Cbz/LC-80) or with 2 phr of PDU-250 (5% Cbz/PDU-250)

In **Table 2** the calorimetric data of the curing process of the formulations with the different content of carbazolyl moieties are collected. The reaction enthalpy is mainly due to the opening of strained epoxy groups and in all cases, the value of the enthalpy per epoxy equivalent is approximately 95-120 kJ/Eq$_{epoxy}$. This observation indicates a complete curing if we take into account that, for the curing of epoxy-amine formulations, the reaction heat is of *ca.*100-110 kJ/eq [46]. However, the enthalpy per gram decreases as the amount of PEI-Cbz increases since the proportion of DGEBA in the formulation becomes lower.

Table 2. Calorimetric data of curing of DGEBA/PEI-Cbz/Thiol/PDU250 mixtures with different content of carbazole moieties (5-30%$_{wt}$).

Sample	*ΔH (J/g)*[(a)]	*ΔH (kJ/Eq$_{epoxy}$)*[(b)]	*T$_{max}$*[(c)]*(ºC)*
5% Cbz	296	104	123.5
10% Cbz	287	110	123.4
15% Cbz	283	120	121.5
20% Cbz	240	116	120.7
25% Cbz	183	95	119.4
30% Cbz	170	103	121.6

a) *Reaction enthalpy per gram of mixture*
b) *Reaction enthalpy per epoxy equivalent*
c) *Temperature of the maximum of the curing exotherm.*

In general, the increase of the amount of PEI-Cbz in the mixture slightly lowers the temperature of the maximum of the curing exotherm. The isoconversional analysis was performed to go deeper into the evolution of the curing. **Figure 2** shows the evolution of the conversion against temperature for the curing of the different formulations.
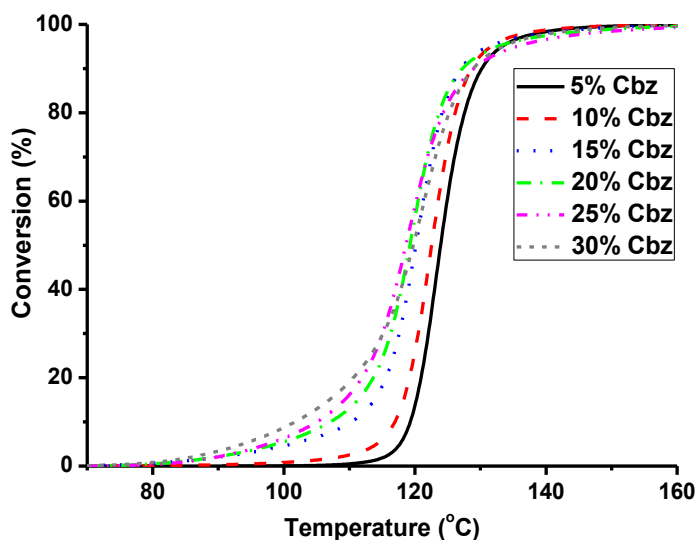

Figure 2. Conversion degrees against curing temperature of the mixtures DGEBA/PEI-Cbz/Thiol/PDU250 with the different weight percentages of carbazole moieties at a heating rate of 10ºC/min.

The increasing amount of PEI-Cbz in the formulation leads to the acceleration in the initial part of the curing process and the result is that conversion curves shift to lower temperatures. The amino groups of PEI-Cbz can apparently act as bases, forming thiolates before the release of the amine from PDU-250 at higher temperatures. Therefore, this initial acceleration can be attributed to the catalytic effect of the amino groups of PEI-Cbz, which decreases the latency of the curing system. This acceleration is not noticeable when the PDU-250 begins to release the amine, which is more active than amino groups in the PEI structure. There are only slight differences in the curing evolution of the samples with the content of carbazole moieties from 15% and above, due to viscosity effects and the lower mobility of the amino groups in the polymeric structure.

3.3. Thermal characterization of the materials.

The thermal stability of the materials prepared was evaluated by thermogravimetry. **Figure 3** shows the differential TGA curves of the thermosets prepared.
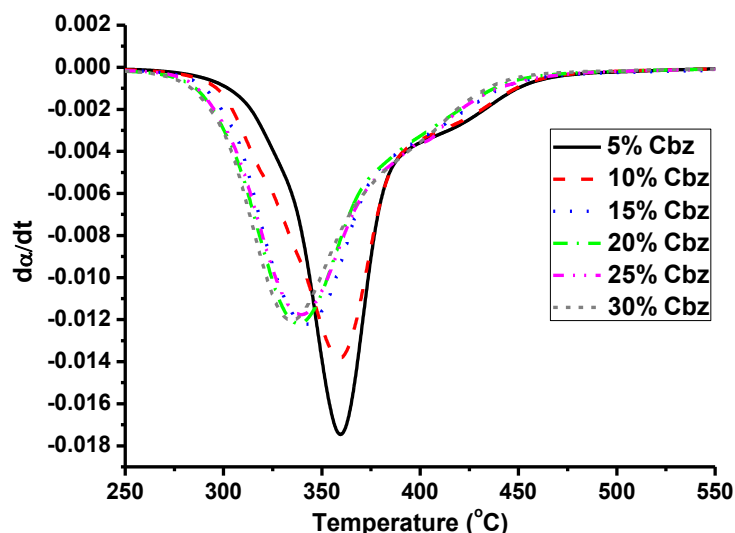

Figure 3. Differential TGA curves recorded at 10ºC/min in N_2 atmosphere of the thermosets with the different percentages of carbazole moieties.

The shape of the differential TGA curves is unimodal with a shoulder at high temperature. On increasing the content of PEI-Cbz modifier in the material the degradation curve shifts to lower temperatures and the curves broaden up to the sample with a 15% of carbazole. The further increase of the content of PEI-Cbz does not cause any considerable effect on the thermal stability of the thermosets. The broadening of the curves indicates more complex degradation mechanism. The characteristic temperatures of the degradation study are collected in **Table 3**. The initial temperature of degradation, which is the most significant value in terms of the thermal stability, decreases with the increase of the content of PEI-Cbz. The comparison of the thermal stability of these materials with that of the neat DGEBA-TTMP thermoset, reveals the reduction of the initial temperature of degradation by 20-30 ºC [45]. This reduction is due to the presence of the PEI structure, which leads to the degradation at lower temperature than epoxy thermosets prepared with tertiary amines as curing agents (from 400 to 330ºC of temperature of initial degradation) [47].

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Table 3. Thermogravimetric and thermomechanical data of the thermosets.

Sample	TGA		DMTA		
	$T_{5\%}$ $(^oC)^{(a)}$	T_{max} $(^oC)^{(b)}$	T_g $(^oC)^{(c)}$	$Width_{1/2}^{(d)}$	Peak area
5% Cbz	318	360	58	15	26
10% Cbz	311	359	63	20	35
15% Cbz	304	342	71	29	44
20% Cbz	299	338	75	32	43
25% Cbz	301	340	78	40	51
30% Cbz	297	335	87	39	53

a) Temperature of the initial decomposition on TGA at 10ºC/min calculated for a 5% weight loss.

b) Temperature of maximum decomposition rate based on the TGA data at 10ºC/min.

c) Temperature of glass transition, indicated as maximum of tan δ peak.

d) Width of the peak at the half height.

The viscoelastic properties of the materials prepared were determined by DMTA. **Figure 4** shows the tan δ plots, recorded at 1Hz, of the different thermosets obtained. **Table 3** collects the main parameters determined by this technique. DMTA curves show a unimodal relaxation, typical of homogeneous materials, but as the concentration of carbazole moieties increases the tan δ curves are shifted to higher temperatures and broaden, indicating a lower homogeneity. The temperatures of the maximum of tan δ increase, from 58 to 87ºC on increasing the carbazole content (**Table 3**). In a previous work, a temperature of the maximum of tan δ of 45 ºC was determined for the neat material [45]. Moreover, the width at half height and the area under the tan δ curve increases on increasing the concentration of PEI-Cbz, indicating a lower homogeneity of the network structure but better damping characteristics in a broader temperature range.
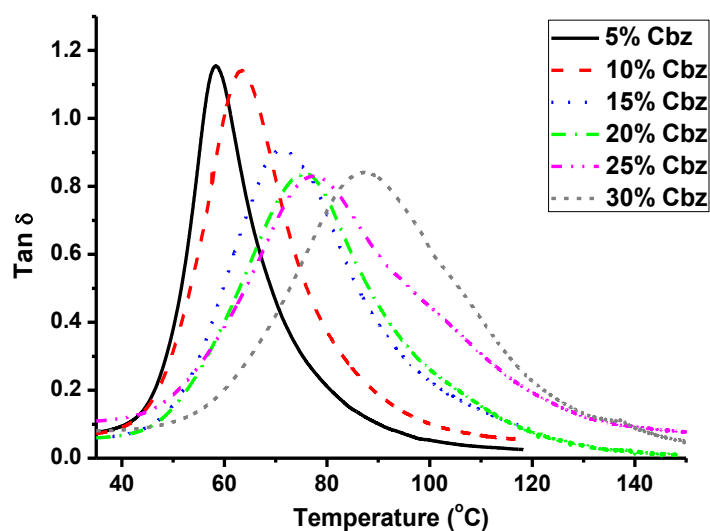
Figure 4. Tan δ versus temperature at 1 Hz for obtained thermosets with the different content of carbazole moieties (5-30%$_{wt}$).

3.4. Optical and photophysical characterization of the materials

The synthesized compounds are crosslinked polymers, hence they are not soluble in any organic solvents. Thus, absorption and photoluminescence spectra were recorded of the thin films of the thermosets. The optical and photophysical data are collected in **Table 4.** The absorption spectra of the synthesized materials cover the near-ultraviolet region (200–400 nm) and the absorption bands typical for N-substituted carbazolyl chromophore due to n→σ*, π→π* and n→π* transitions are observed (**Figure 5**). A characteristic intensive absorption band at 264 nm is due to n→σ* transition, whereas the band at 298 nm can be ascribed to the π→π* and the band at 350 nm to n→π* transition [48].

The obtained thermosets exhibit fluorescence with the emission maxima in the range of 368-374 nm. The clear vibrational structure, which is characteristic of N-alkyl carbazole derivatives, is not observed. The Stokes shift is relatively small, which means that there is no significant change in the geometry of the photoactive moiety in excited state.
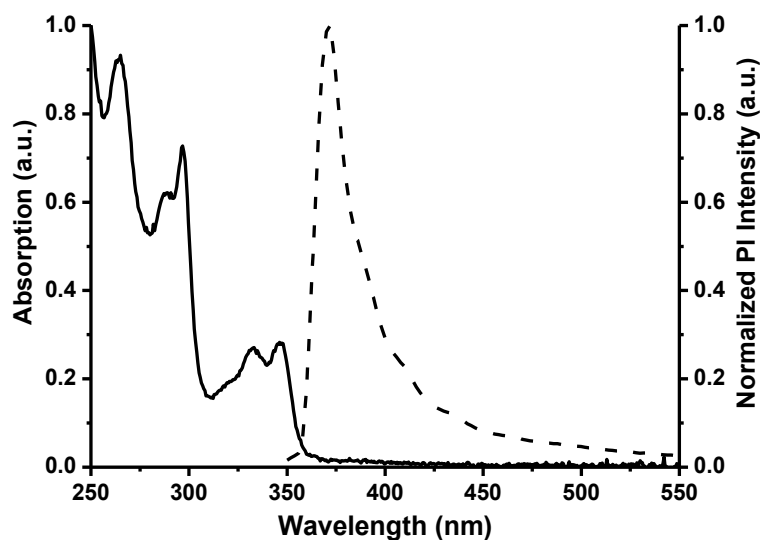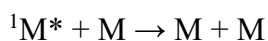
Figure 5. Absorption and fluorescence spectra (dashed line) (λ_{ex}=330nm) of the solid film of the thermoset with 20% of carbazole moieties.

The synthesized polymers exhibit single exponential fluorescence decays with the lifetimes decreasing with the increase in the concentration of chromophore. The neat PEI-Cbz polymer possess the lowest fluorescence lifetime. Therefore, it could be assumed that increasing the concentration increases the probability that energy can migrate from one chromophore to another by non-radiative process. The interaction of an excited molecule $^1M^*$ with a ground state may in some instances lead to electronic quenching of the excited state, which could be visualized by the following scheme [19]:

$$^1M^* + M \rightarrow M + M$$

Fluorescence quantum yields decrease on increasing the concentration of chromophore. It could be assumed that the reason for this is the self-quenching. Very low fluorescence quantum yield of neat PEI-Cbz polymer relative to that of thermosets could be also caused by reabsorption quenching of emmited energy, due to the significant overlap of absorption and emission spectra.

Table 4. Optical and photophysical characteristics of the thermosets.

Sample	λ_{max}^{UV}, nm[a]	λ_{max}^{FL}, nm[b]	Stokes Shift, nm[c]	τ, ns[d]	$\Phi_{FL}\pm2\%$, %[e]
PEI-Cbz	348	368	20	2.35	8.9
5% Cbz	346	370	24	6.97	31.9
10%Cbz	346	370	24	6.66	29.8
15%Cbz	346	372	25	6.28	27.7
20%Cbz	346	372	25	4.67	21.5
25%Cbz	346	372	27	4.25	17.5
30%Cbz	346	374	28	3.74	16.6

(a) Lowest-energy absorption maxima in UV-VIS spectra of thin films;

(b) FL spectra of thin films;

(c) Stokes shift estimated by the equation: Stokes shift= λ_{max}^{FL} - λ_{max}^{UV};

(d) τ – Fluorescence lifetimes determined for thin films.

(e) Φ_{FL} – fluorescence quantum efficiency determined for thin films;

4. Conclusions

A carbazole decorated hyperbranched polymer (PEI-Cbz) was synthesized from hyperbranched poly(ethyleneimine) and 9-(2,3-epoxypropyl)carbazole and then characterized and it was used as a modifier in thiol-epoxy formulations.

The catalyst selected to initiate the thiol-epoxy curing in the presence of PEI-Cbz was N,N-dimethyl phenyl urea (PDU-250) because of the good latency shown in the curing process. The addition of PEI-Cbz to the formulation led to an initial acceleration of the curing process, attributable to the presence of amino groups in the modifier.

The glass transition temperatures of the thermosets increased with the increase of the amount of carbazole modifier in the composition. They were in the range of 58-87°C. The thermal stability of the materials slightly reduced on increasing the amount of the modifier. The homogeneity of the materials was reduced but damping characteristics were enhanced on increasing the amount of PEI-Cbz in the formulation.

The films of the obtained thermosets exhibited fluorescence maxima at 370-374 nm. The fluorescence quantum yields of the solid samples were found to be in the range of 17-32%. They decreased with the increase of the amount of the modifier in the initial mixtures.

5. References

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