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Sustainable and recyclable thermosets with performances for high technology sectors. An environmental friendly alternative to toxic derivatives

Roxana Dinu[1], Ugo Lafont[2], Olivier Damiano[3] and Alice Mija[1]*

[1]Institut de Chimie de Nice, Université Côte d'Azur, Nice, France, [2]European Space Agency, European Space Research and Technology Centre, Noordwijk, Netherlands, [3]Thales Alenia Space, Cannes, France

This study focuses on the development of environmentally friendly and chemically recyclable thermosets using or a renewable based monomer, the triglycidyl ether of phloroglucinol (TGPh), or a commercial non-toxic tris(4-hydroxyphenyl) methane triglycidyl ether (THPMTGE) monomer. The recyclable polyester thermosets were prepared by crosslinking the two monomers with hexahydro-4-methylphthalic anhydride (HMPA) or methyl nadic anhydride The TGPh-based formulations exhibited lower reaction temperatures and narrower reaction intervals. Additionally, these systems showed higher tan δ values (189°C–199°C), higher crosslinking densities (7.6–7.8 mmol cm^{-3}) and compact networks, crucial for high-performance industries. Tensile tests demonstrated the remarkable mechanical properties of the thermosets, including high Young modulus (1.3–1.4 GPa), tensile stress (55–69 MPa), and an elongation at break around 3%–8%. Moreover, the thermosets exhibited complete dissolution at a temperature of 170°C, with depolymerization times of approximately 2.5 h for TGPh-based resins and 4.5 h for THPMTGE-based formulations. In conclusion, this study shows that sustainable and eco-friendly thermosets with excellent physico-chemical and thermo-mechanical properties, low hydrophilicity, and rapid dissolution capacity can be developed. These thermosets offer a viable alternative to non-recyclable and toxic resins in high-end industrial applications.

1 Introduction

Plastic materials represent one of the most versatile and challenging human innovation, covering multitude of characteristics and therefore facilitating myriad of applications (Geyer et al., 2017). In 2020, the global plastic production was estimated at around 367 million tons (Mt), Europe generating about 55 Mt of the total worldwide production. Although plastics were initially viewed as harmless products, nowadays their massive production and disposal in the environment made them one of the main polluting wastes negatively affecting the ecosystem (Okunola A et al., 2019).

Epoxy-based materials are representing 75% of industrial and domestic needs in thermosetting resins, due to a wide range of valuable properties such as strong chemical and corrosion resistance, low shrinkage on curing, high mechanical properties, high temperature

stability, outstanding adhesion to a variety of substrates, *etc.*, (Sukanto et al., 2021). Usually, epoxy resins are used in various application areas such as structural adhesives, surface coatings, electrical engineering, electronic encapsulation, construction, and high performance applications like construction, automotive, aerospace and space or naval industries (Capricho et al., 2020). Although epoxy materials are extremely needed in all these industries, the chemical compounds used in their production are not the most environmentally friendly. For example, about 90% of epoxy materials are based on diglycidyl ether of bisphenol A (DGEBA), a petro-based molecule derived from bisphenol A (BPA). BPA has been classified as carcinogen, mutagen and reprotoxic (CMR), being prohibited in many countries (Moreman et al., 2017). Due to the unpredictable fluctuations of the oil price and production, the non-renewable nature of fossil derivatives, as well as the growing concerns regarding environmental protection, academic and industrial research have turned their attention to the development of materials based on natural and renewable compounds that are environmentally-safe (Wang et al., 2020; Derradji et al., 2021; Zhang et al., 2022; Briou et al., 2023).

The main objective of this study is the development of epoxy resins starting from natural and renewable resources, for high-tech industries as targeted fields of application. These biobased resins will be compared with homologous resins in which a commercial non-toxic petro-based compound is used as epoxy monomer. The biobased resins were designed starting from phloroglucinol (1,3,5-trihydroxybenzene) which can be naturally extracted from marine brown algae (Ecklonia Cava), from bark of fruit, or can be chemically synthesized by benzene (Chowdhury et al., 2011). The phloroglucinol is mostly used in medical field, but it can be a sustainable alternative to fossil compounds in applications such as thermosetting materials (Genua et al., 2020; Guzmán et al., 2020; Santiago et al., 2020). So a phloroglucinol tris-epoxy based monomer (TGPh) was laboratory synthesized and compared with tris(4-hydroxyphenyl)methane triglycidyl ether (THPMTGE), a tris-aromatic tris-epoxide monomer, which is a commercial and non-toxic product, used in cosmetics, paints, coatings, inks for printing or writing, *etc.*

To develop the resins, we considered the industrial manufacturing requirements of an easy and cost-competitive production protocol. The two epoxy monomers were crosslinked with hexahydro-4-methylphthalic anhydride (HMPA) or methyl nadic anhydride (MNA). Physico-chemical and thermo-mechanical properties of the developed thermosets were investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), Shore hardness tests, tensile tests, water absorption and gel content. The recyclability, but also the biobased carbon content (BCC) and biobased organic carbon (BOC) of the designed thermosets were also investigated to accurately frame the potential application of these resins for high tech industries.

2 Experimental section

2.1 Materials

The triglycidyl ether of phloroglucinol (TGPh, DP = 0.229, M_w = 348.92 g/mol) was laboratory synthetized. The tris(4-hydroxyphenyl)

methane triglycidyl ether (THPMTGE), the hexahydro-4-methylphthalic anhydride (HMPA; 96%), the methyl nadic anhydride (MNA; ≥95%) and the 2-ethyl-4-methylimidazole (2E4M) were purchased from Sigma Aldrich (France) and used as received.

2.2 Thermoset resins synthesis

Thermosets were obtained by mixing the epoxy monomer with the hardener, in the presence of initiator. The formulations were crosslinked by applying a thermal treatment established by DSC studies: 3 h at 120°C and 1 h at 160°C, followed by a post-curing (1 h at 180°C) program.

2.3 Experimental techniques

2.3.1 Differential scanning calorimetry (DSC)

The thermal behaviors were conducted on a DSC 3 Mettler Toledo apparatus. The fresh mixtures of uncured formulations were analyzed in dynamic conditions, from 25°C to 250°C at 10°C min⁻¹. To determine the glass transition (T_g) of the thermosets was employed a cycle of two heating/cooling between 0 and 280°C at a rate of 10°C min⁻¹. The T_g values were recorded as the inflection point of the DSC curves in the second heating scan.

2.3.2 Material density

The density of rectangular samples (50 × 8 × 4 mm³) was analyzed by calculating the ratio of mass to volume. To avoid potential errors, an average of five samples was considered as the final value for each system.

2.3.3 Dynamic mechanical analysis (DMA)

Thermo-mechanical behavior of the samples was investigated using a Mettler Toledo DMA 1 apparatus equipped with a three-point bending clamp. Mechanical properties were determined under heating from −50°C to 280°C at a heating rate of 3°C min⁻¹ with a 1.0 Hz oscillating stress and 20 μm amplitude.

2.3.4 Hardness tests

The materials' stiffness was studied using a Zwick Roell 3116 hardness tester equipped with a Shore D hardness device, using a loading force of 50 N. The stiffness values were measured in accordance with ISO 7619-1, ASTM D2240 and ISO 868 standards. Each system was evaluated five times, the hardness value being determined as their average.

2.3.5 Tensile testing

Mechanical properties of the developed thermosets were investigated based on ASTM D638-08 standard using an Instron 34SC-5 device equipped with a 5 kN load cell. Measurements were performed on dog-bone V-type specimens using a crosshead speed of 5 mm min⁻¹. Ten measurements for each system were realized and averaged for better accuracy of the results.

2.3.6 Thermogravimetric analysis (TGA)

Thermal stability of the thermosets was conducted under oxidative or inert atmosphere on a Mettler Toledo TGA
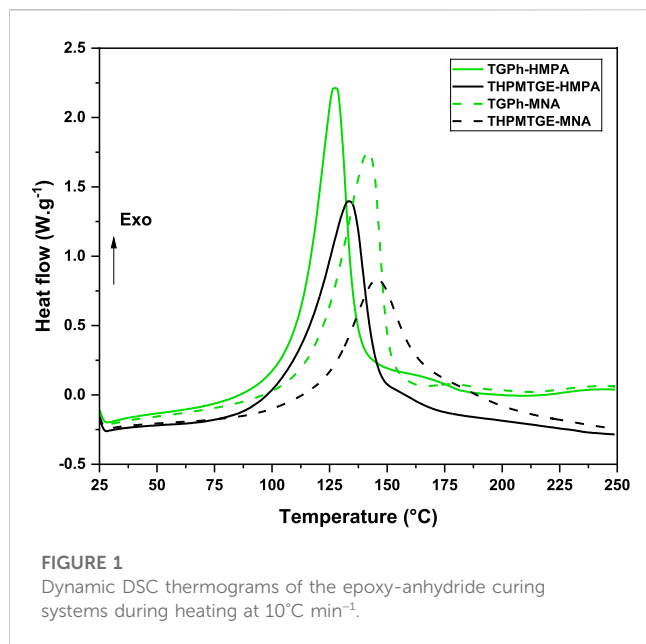
FIGURE 1
Dynamic DSC thermograms of the epoxy-anhydride curing systems during heating at 10°C min^{-1}.

TABLE 1 DSC parameters of epoxy-anhydride curing reactions.

Sample	T_{peak} [°C]	T_{onset} - T_{end} [°C]	ΔH [J.g^{-1}]
TGPh-HMPA	127	58–201	292
THPMTGE-HMPA	134	61–233	289
TGPh-MNA	141	58–212	258
THPMTGE-MNA	146	65–236	247

2.3.10 Scanning electron microscopy (SEM)

The tensile fracture morphology of the thermoset resins was investigated by SEM. The analyzed samples were first coated with platinum and then studied in a Tescan Vega 3 XMU SEM device using an acceleration voltage of 5 kV.
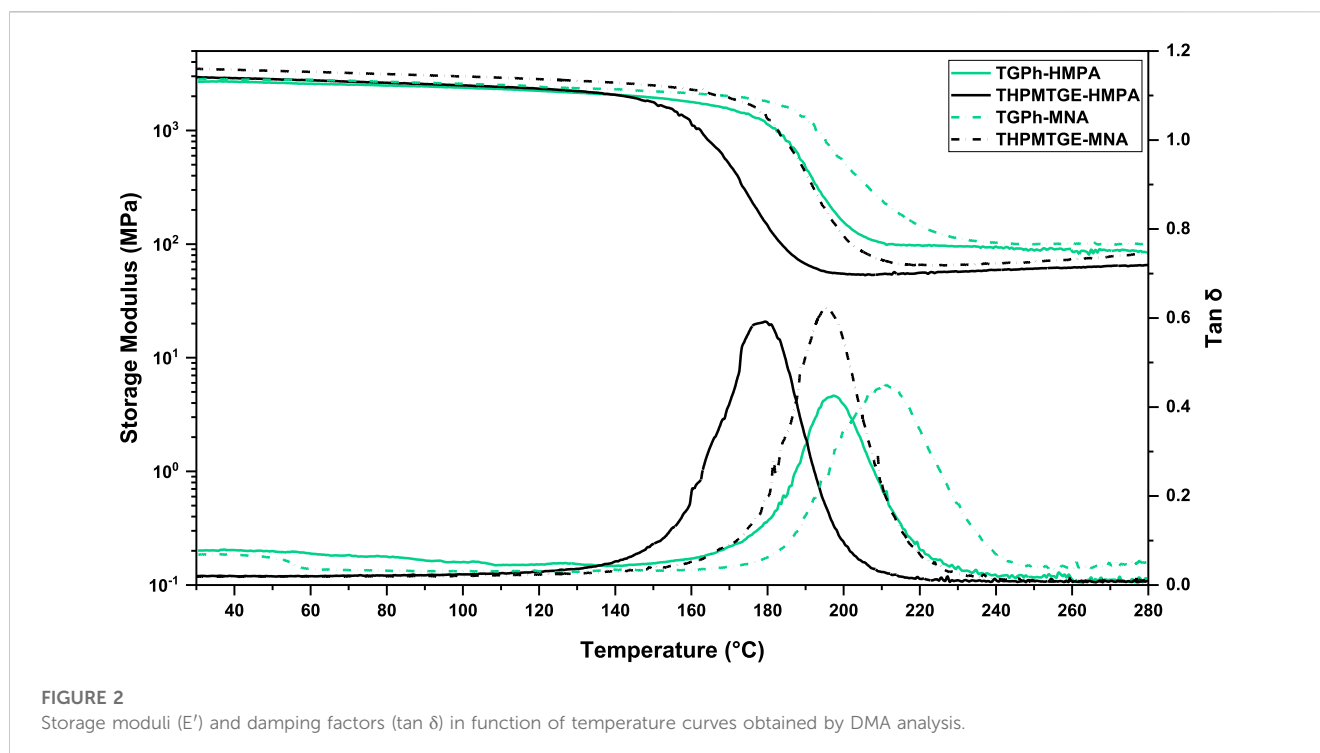
3 Results and discussions

3.1 Curing behavior of the epoxy/anhydride systems

The evolution of the heat flows during the dynamic heating of the four crosslinking formulations are displayed in Figure 1, while the reaction enthalpy (ΔH), the temperature interval of the reaction (T_{onset}-T_{end}), but also the maximum reaction peak temperature (T_{peak}) are given in Table 1.

From Figure 1 it can be observed a similar curing profile for both epoxy monomers with the selected anhydrides. The crosslinking reaction of the epoxy/anhydride systems appears as quite narrow (excepting THPMTGE/MNA system) and well-defined exothermic peak. The TGPh-based formulations display a lower onset temperature of reactions at around 58°C, compared with the homologous formulations with THPMTGE which are ranged between 61–65°C. At the same time, the biobased monomer formulations have a smaller interval of temperature curing than the commercial one, the exothermic event returning at a quasi-linear response at about 201–212°C vs. 233–236°C for the THPMTGE-based systems. Another parameter giving information on the compounds reactivity is the T_{peak} value of the reaction exothermic peak, lower the T_{peak} value, higher is the formulation reactivity (Liu et al., 2009; Ma et al., 2014). From Table 1 we can notice that the TGPh monoaromatic epoxy monomer generates systems with higher reactivity than the formulations developed with the tris-aromatic epoxide. Also, depending on the anhydride used as hardener, the systems crosslinked with HMPA are more reactive than those with MNA. The reaction enthalpy (ΔH) of the studied systems was determined by integrating the areas under the exothermic event, the obtained values being reported in Table 1. We can notice again similar values of enthalpy for both epoxies cured with the same anhydride.

Based on these thermodynamic results, the TGPh epoxy monomer has a slightly higher reactivity compared with THPMTGE-based systems, while the formulations with HMPA exhibit also higher reactivities than those with MNA.

2 instrument. Samples of 10–13 mg were placed into 70 μL alumina pans and analyzed by heating from 25°C to 1,000°C, at a heating rate of 10°C min^{-1}. The degradation temperature was considered the temperature at which the sample lost 5% of their mass ($T_{5\%}$).

2.3.7 Water absorption (WA%)

The water absorption behavior was investigated based on the ASTM D570 standard test. The conditioned specimens (50°C, 24 h) (W_0) were immersed in distilled water at room temperature. Every 24 h, the samples were extracted from water, wiped with filter paper, and weighed again (W_d). The percentage of water absorbed by the thermosets was calculated using the equation (ASTM D570-982018, 2018):

$$WA, \% = \frac{W_d - W_0}{W_0} \times 100 \qquad (1)$$

2.3.8 Gel content (GC%)

The gel content was determined according to ASTM D2765-16. The *GC* percentage was calculated (ASTM-D2765-16, 2016):

$$GC, \% = \frac{W_f}{W_0} \times 100 \qquad (2)$$

where W_0 - initial mass, and W_f - mass of the dried samples after toluene immersion.

2.3.9 Chemical decomposition

The developed thermosets were chemically recycled by immersion of samples in a 0.30 mol/L solution of 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD) in ethylene glycol (EG). The polymer content was ~5 wt% of the total mass of the solution. These so prepared immersions were maintained in oven at 170°C and normal pressure until the thermosets were completely dissolved.

FIGURE 2
Storage moduli (E′) and damping factors (tan δ) in function of temperature curves obtained by DMA analysis.

TABLE 2 Thermomechanical parameters of TGPh- and THPMTGE-thermosets.

Thermoset	Density [g/cm³]	Shore D	E' at 25°C [GPa]	tan δ [°C]	$T_{g\text{-DSC}}$ [°C]	ν [mmol·cm⁻³]	M_c [g/mol]
TGPh-HMPA	1.16	87	2.9	189	178	7.62	152
THPMTGE-HMPA	1.17	90	3	179	167	4.74	248
TGPh-MNA	1.22	88	3.1	199	184	7.98	144
THPMTGE-MNA	1.13	85	3.5	196	181	6.38	220

3.2 DMA properties of the thermoset resins

The thermomechanical properties of the designed thermosets investigated by DMA are displayed in Figure 2, and the related parameters are given in Table 2. For both TGPh- and THPMTGE-based thermosets, the storage modulus (E′) curves show the classical pattern for thermosets behavior during heating, with the three regions. Depending on the monomer nature, the value of E' at room temperature is slightly higher for the systems based on the tris-aromatic epoxy (3–3.5 GPa) compared to those of mono-aromatic TGPh (2.9–3.1 GPa). Then, the systems crosslinked with MNA are stiffer at 25°C than the ones with HMPA anhydride. The storage modulus in the rubbery region is directly proportional with the crosslink density (ν) which was calculated according to rubber-elasticity theory: (Flory, 1953):

$$\nu = \frac{E'}{3RT} \qquad (3)$$

where E' - rubbery modulus, R - gas constant, and T - absolute temperature (at ~ tan δ + 90°C). The average mass of segments

between crosslinks (M_c) was calculates according with Tobolsky equation (Tobolsky, 1960)
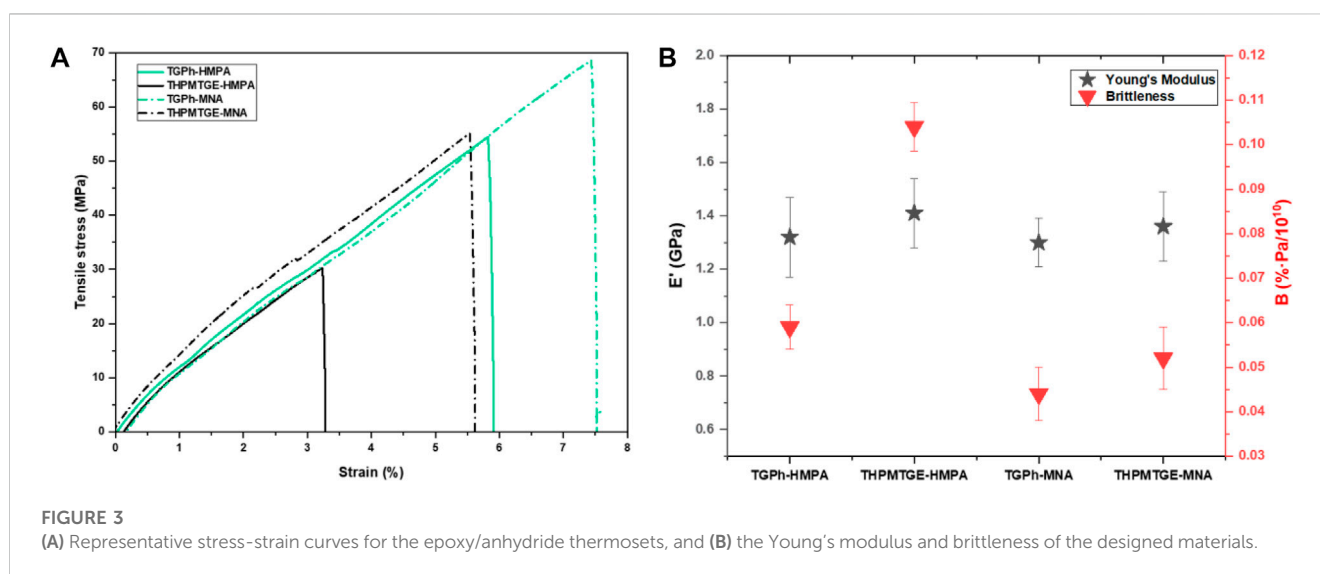
$$M_c = \frac{3\rho RT}{E'} \qquad (4)$$

where ρ is the calculated density.

We can observe that the mono-aromatic TGPh epoxide leads to the development of a more compact polymeric network, with a lower mobility of the chains, compared with THPMTGE. The ν of TGPh-thermosets is ranged between 7.6 and 8 mmol cm⁻³, while those with THPMTGE vary between 4.7 and 6.4 mmol cm⁻³. This behavior can be seen also from the M_c values that are lower for TGPh-thermosets, ~144–152 g mol⁻¹, than the commercial one (220–248 g mol⁻¹). Then, among the two anhydrides the highest stiffness was obtained by the system copolymerized with MNA.

The α relaxations (glass transitions) of the designed thermosets were recorded by DMA at the maximum temperature of the damping factor (tan δ), and by DSC ($T_{g\text{-DSC}}$) as the inflection points in the DSC thermograms at the second heating scans (Table 2). Both epoxy monomers led to the development of

TABLE 3 Tensile properties of developed epoxy/anhydride thermosets.

Sample	Young's modulus [GPa]	Tensile stress [MPa]	Elongation at break [%]	Specific modulus (E/ρ) [10^6 m²/s²]	Specific strength (σ/ρ) [kN·m/kg]	Specific length (σ/ρ·g) [km]	B [%·Pa/10^{10}]	Energy at break [J]
TGPh-HMPA	1.32 ± 0.15	55 ± 8.3	5.8 ± 0.58	1.14	47.4	4.83	0.059	0.7 ± 0.26
THPMTGE-HMPA	1.41 ± 0.13	30 ± 6.8	3.2 ± 0.35	1.21	25.6	2.61	0.104	0.2 ± 0.15
TGPh-MNA	1.30 ± 0.09	69 ± 10.2	7.4 ± 0.79	1.07	56.6	5.76	0.044	1.03 ± 0.39
THPMTGE-MNA	1.36 ± 0.13	55 ± 11.8	5.5 ± 0.62	1.20	48.7	4.96	0.052	0.43 ± 0.27

FIGURE 3
(A) Representative stress-strain curves for the epoxy/anhydride thermosets, and **(B)** the Young's modulus and brittleness of the designed materials.

thermoset resins with very high glass transitions, superior to 180°C. TGPh-based thermosets have higher tan δ values, with lower amplitude of the peaks compared to those developed with THPMTGE (Figure 2). The presence of a mono-aromatic ring in the composition of TGPh led to the development of more confined networks with shorter segment chains between crosslinks, generating stiff materials with higher mechanical properties compared to those of tris-aromatic based epoxy thermosets. Also, the anhydride chemical structure is influencing the final properties of the designed thermosets. The less stiff thermoset is the THPMTGE-HMPA one, with a tan δ ~ 179°C, whereas the stiffer is the TGPh-MNA thermoset: tan δ ~ 199°C.

3.3 Tensile tests of the thermoset systems

The Young modulus, tensile stress, and elongation at break of the designed thermoset materials were measured in tensile mode at room temperature and the obtained values are tabulated in Table 3. The stress-strain curves are displayed in Figure 3A.
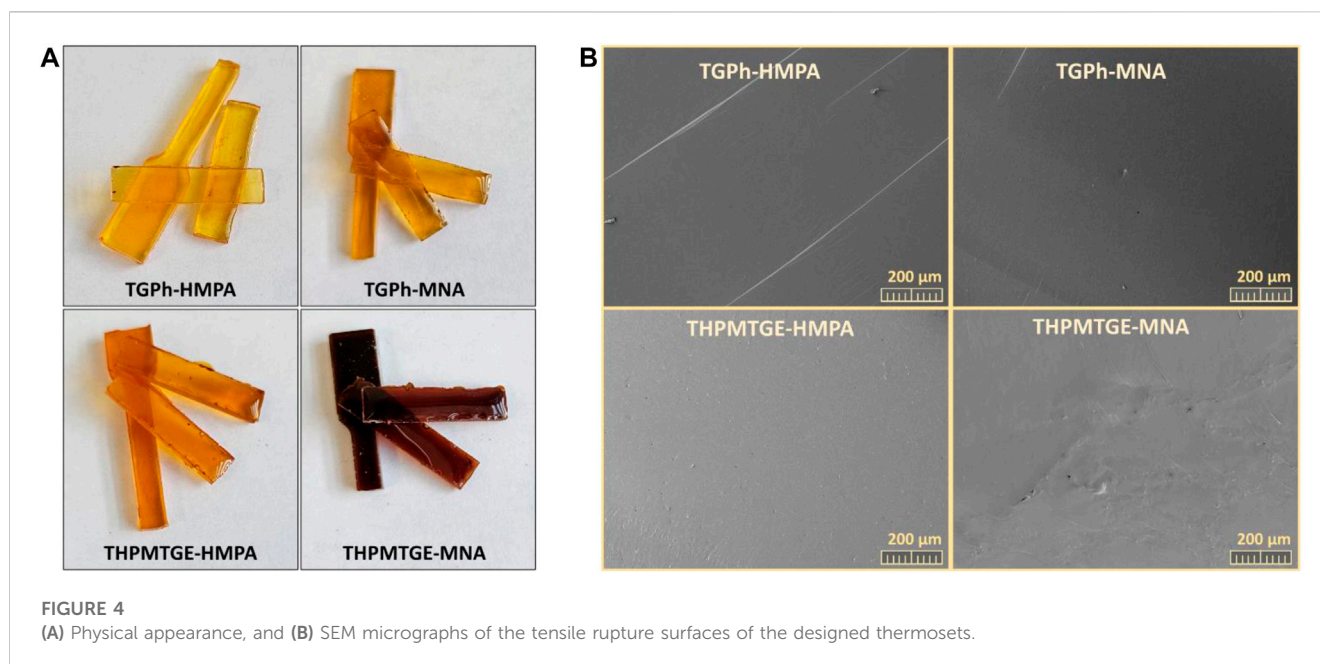
The tensile properties of the TGPh-based thermosets are different to those of materials obtained with THPMTGE monomer. As can be seen from the stress-strain curves (Figure 3A), the TGPh-based materials present a more ductile character (higher strain and area below the curve) compared to the THPMTGE-based system with the same anhydride, which tend to be more rigid and brittle. The tensile stress of the TGPh-based thermosets ranges between 55 and 70 MPa with an elongation at break of about 6–8%, while the tris-aromatic-based materials present lower values, the stress being ~30–55 MPa, and respectively 3–6% elongation at break. The hardener nature also influences the tensile properties of the systems; the MNA-based resins revealing both higher stress and strain values. These low values of the elongation at break can be attributed to the high crosslinking density of the systems (Table 2) which limits the mobility in the polymeric network.

The Young modulus values for the materials with mono-aromatic TGPh-based monomer are slightly lower (~1.3 GPa) than those based on the tris-aromatic THPMTGE that have values of about 1.4 GPa. Based on these results, we can appreciate that all the developed thermosets have a stiff character similar with the commercial resins used in high-performance areas such as Master Bond EP21TDCHT-LO: σ = 24.1 MPa & Young modulus = 1.21 GPa; Henkel Loctite® ECCOBOND EO7021: σ = 48 MPa & Young modulus = 1.45 GPa; Milliken® Veloxx LVP: σ = 37.9 MPa & Young modulus = 1.52 GPa, etc.

The energy at break of the thermosets were determined, the obtained values being given in Table 3. This parameter represents

FIGURE 4
(A) Physical appearance, and **(B)** SEM micrographs of the tensile rupture surfaces of the designed thermosets.

the energy absorbed by the systems at the time of failure, or more precisely, the necessary energy that must be invested in a material to be able to break. In this study, the obtained energy at break values confirms the mechanical behavior of the materials presented previously, so that materials with TGPh are more ductile, needing more energy to be broken, while materials with tris-aromatic epoxy require lower energies, describing a slightly more brittle character of the designed materials. This fragile character or not of the materials was also characterized and determined based on the studies reported by Brostow et al. (2006); Brostow. (2011); Brostow and Hagg Lobland (2010) The thermoset brittleness (*B*) was calculated based on the equation:

$$B = 1 / \varepsilon_b E' \tag{5}$$

where ε_b is elongation at break (tensile test) and E' is the storage modulus at room temperature and 1.0 Hz (DMA). It is known that the lower the *B* value, the less brittle and more resistant is the material. The lower values of *B* for the systems based on mono-aromatic monomer (0.044–0.059%·Pa/10^10) depict a greater stability at break for these networks, compared with the networks built with the tris-aromatic THPMTGE monomers (0.052–0.104%·Pa/10^10). Physical appearance and the surface morphology of the fractured samples after the tensile tests are depicted in Figure 4. These SEM images of fractures shows a sharp cutting, an homogeneous and smooth surface, which is correlated to a perfect and straight break during the tensile tests, the samples not being fragmented or torn.

For a more in-depth characterization of the mechanical properties of the materials as well as for fitting them as accurately as possible into a certain field of applicability, important parameters for the industry such as specific modulus, specific strength and specific length were calculated and reported in Table 3. Specific modulus and specific strength are distinct characteristics that characterize the maximum

strength of a material that can hold it at a minimum weight. Regarding the specific modulus, the biobased materials show slightly lower values (1.07–1.14 10^6 m^2/s^2) compared to those of the THPMTGE-based materials, being in opposition to the values of the specific strength which are higher for the TGPh-based thermosets (47–57 kN·m/kg) compared to THPMTGE ones (26–49 kN·m/kg). Specific length of the materials represents the maximum self-supporting length of a material before it breaks. From Table 3 it can be stated that the TGPh-thermosets are more resistant (4.83–5.76 km) than the ones with THPMTGE (2.61–4.96 km).

The superior mechanical properties of the systems based on TGPh and THPMTGE support and confirm the capability of these thermoset resins for replacing the BPA-based systems used in high technology sectors such as construction, automotive and transport, naval, or aerospace and space.

3.4 Thermal stability of TGPh- and THPMTGE-thermosets

The thermal behavior of the thermosets was studied in both oxidative and inert atmospheres. Graphical representation of mass loss as function of temperature is displayed in Figure 5, and the data summarized in Table 4.

The decomposition temperature ($T_{5\%}$) of the tested systems was settled as the temperature at which 5 wt% of their mass is degraded. The TGPh-thermosets exhibit a high $T_{5\%}$, ranged between 290–310°C, very close to the THPMTGE materials (300–320°C) or other commercial ones used in high-end applications like Master Bond EP41S-6: $T_{5\%} = 260$°C, Aremco Aremco-Bond™ 2,330: $T_{5\%} = 300$°C or EPO-TEK® EK 2000: $T_{5\%} = 300$°C. Based on the anhydride nature, systems crosslinked with HMPA have higher thermal stability (with ~20°C) compared to those with MNA. The heat tolerance limit temperature of the polymeric materials, called the
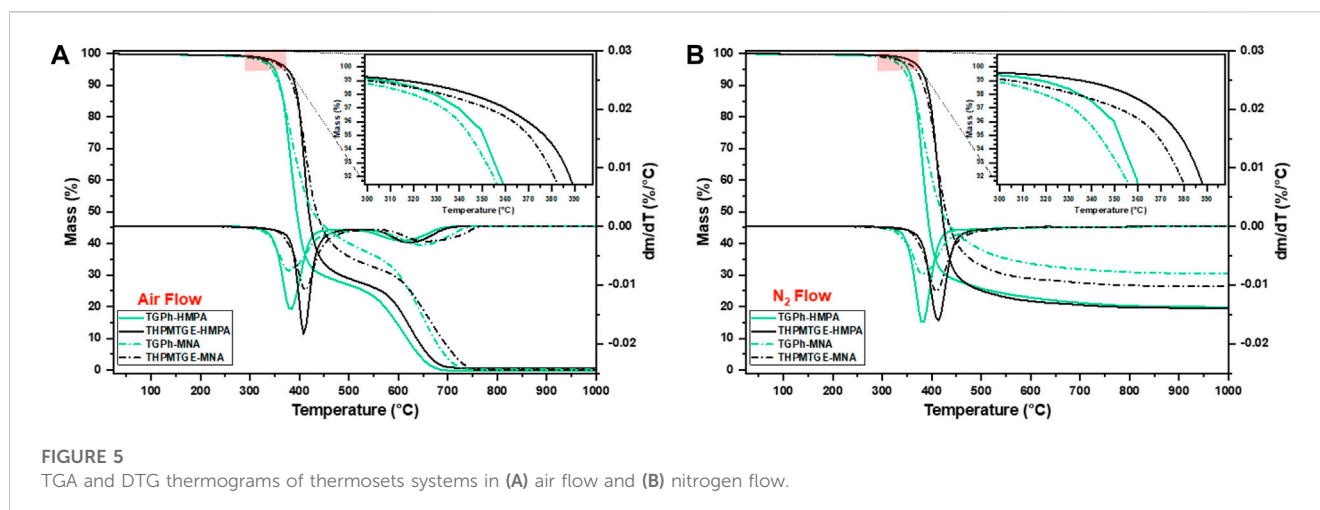
FIGURE 5
TGA and DTG thermograms of thermosets systems in **(A)** air flow and **(B)** nitrogen flow.

statistical heat resistance index (T_s), was determined using the equation (Ma et al., 2014; Ma et al. (2017):

$$T_s = 0.49 [T_{5\%} + 0.6 (T_{30\%} - T_{5\%})] \tag{6}$$

where $T_{30\%}$ represents the temperature at which the material loses 30% of its mass. As can be seen (Table 4), the T_s values of the TGPh-thermosets are slightly lower than those obtained for the THPMTGE, but remain similar to the commercial ones, being classified as heat-resistant materials (T_s = 100–200°C). (Heat resistance index and classification of plastic profile products, n. d.) The thermal behavior of thermosets in the oxidative atmosphere shows two main stages of decomposition mechanism (Figure 5A). The first degradation step, ranged between 330–470°C with a maximum at around 380–420°C, represents the main degradation stage of the materials in which the mass loss is ~62–73% and can be attributed to the thermolysis of the polymeric network. In the second decomposition stage, the thermo-oxidative degradation takes place between 550–750°C with a maximum degradation at ~ 630–700°C (Pan et al., 2015).

Regarding the thermal behavior of the thermoset systems in the inert medium (Figure 5B), it is described by a single stage of pyrolysis between 340–450°C. In this case, the thermal decompositions of the TGPh-based systems are slightly lower (69–79%) than those of THPMTGE thermosets (73–81%), so less organic volatiles are produced during decomposition. Then, the crosslinked systems with MNA generate slightly more thermally stable systems compared to those with HMPA.

The carbon residue at 850°C in nitrogen atmosphere (C_{y850}) was determined and used to calculate the Limit Oxygen Index (*LOI*) based on the equation (van Krevelen, 1975; Kumar and T'Ien, 2012):

$$LOI = 17.5 + 0.4 \times C_{y850} \tag{7}$$

From Table 4, we can notice that the C_{y850} values of the TGPh-thermosets are superior to those of THPMTGE ones, and the MNA-based thermosets present higher char yield values compared to those crosslinked with HMPA. It is known that the layer formed of carbon residue can act as a protective barrier against fire, thus giving the material good flame retardant properties (van Krevelen, 1975). The good fireproofing performance of the thermoset materials was

confirmed by the obtained *LOI* values. Materials with *LOI* > 26% are classified as "self-extinguishing" systems (Tobias Weiss et al., 2011). As can be seen in Table 4, all the designed systems, except THPMTGE-HMPA (*LOI* = 25.36%), have values superior to 26%. Then, the TGPh thermosets exhibit higher flame-retardant properties (*LOI* = 26–30%) compared to the non-toxic commercial-based epoxy systems (*LOI* = 25–28%).

3.5 Moisture behavior, gel content, BCC and BOC%

The moisture behavior of the polymers can lead to various reversible or irreversible changes in the materials properties that could affect their performances. The material's water absorption capacity can be influenced by a multitude of factors, both physical (crosslinking protocol, parameters, microcracks, voids) and chemical (presence of polar groups and free hydroxyl) (Nogueira et al., 2001; Bouvet et al., 2016; Pereira and D'Almeida, 2016; Toscano et al., 2016; Capiel et al., 2018).

In the case of the thermosets produced in this study, the water uptake values after 24 h of immersion are very low, being ranged between 0.46–0.52% for TGPh thermosets and 0.32–0.39% for THPMTGE ones (Figure 6A).

It could also be observed that the systems with MNA have a higher hydrophilicity than those with HMPA. The designed bio-resins present a very good hydrostability being comparable with commercial products used for aerospace and electronics areas (Cookson Group STAYCHIP® 3,105 = 1.5%; Henkel Loctite® ABLESTIK 2053S Epoxy = 1%; Hexcel® F161 Epoxy Resin = 2.8%, *etc.*).

The gel content of the designed systems was determined by solvent method. The obtained values were superior to 99.5% for all the systems, proving the proper and complete crosslinking of the thermoset materials.

The biobased carbon content (*BCC*) of the designed systems was determined in accordance to the Pan et al. (2011) using the equation:

$$BCC = \frac{\sum (W_{100\%} \cdot TC_{100\%})}{\sum (W_{100\%} \cdot TC_{100\%}) + \sum (W_{0\%} \cdot TC_{0\%})} \cdot 100 \tag{8}$$

TABLE 4 Thermogravimetric properties of the designed thermosets.

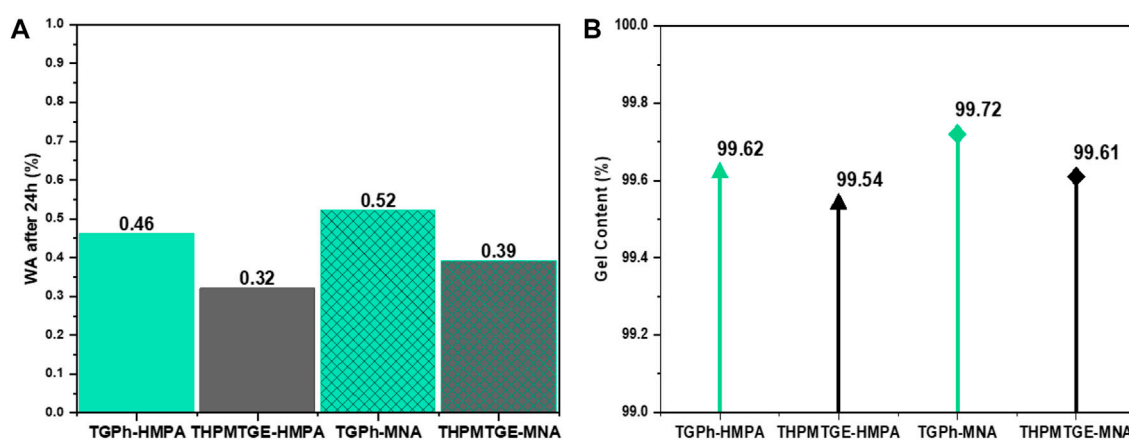| Sample	TGPh-HMPA		THPMTGE-HMPA		TGPh-MNA		THPMTGE-MNA	
	Air	N_2	Air	N_2	Air	N_2	Air	N_2
$T_{5\%}$ [°C]	310	315	320	330	290	300	300	300
$T_{30\%}$ [°C]	380	380	400	408	388	388	410	408
T_{dmax} [°C]	380	380	409	410	379	380	415	409
C_{y850} [%]	0	22.03	0.7	19.65	0.2	30.69	0	26.6
LOI [%]	N/A	26.31	N/A	25.36	N/A	29.78	N/A	28.14
T_s [°C]	172	174	180	185	171	173	179	179

FIGURE 6
Graphical representation of **(A)** absorbed water % after 24h of immersion and **(B)** gel content % by solvent method (in toluene).

where $W_{100\%}$ is the mass of the 100% biobased constituent, $TC_{100\%}$ - total carbon of the 100% biobased component, $W_{0\%}$ - mass of the 0% biobased constituent, and $TC_{0\%}$ - total carbon of the 0% biobased component. In this study, the TGPh epoxy monomer is made from renewable raw materials being 100% biobased, while the THPMTGE, MNA and the initiator (2E4M) are currently totally made by fossil derivatives being 0% biobased. The biobased organic carbon (Norton and Devlin, 2006) (BOC) was also calculated:

$$BOC = \frac{\sum bio - based\ carbon}{\sum bio - based\ carbon + \sum petro - based\ carbon} \cdot 100 \quad (9)$$

The phthalic anhydride (and its derivatives as HMPA) is still produced from petrochemical derivatives, (Hester E. Andrews, 1920), but intensive studies have led to the development and even the implementation (at the laboratory level, kilograms) of new natural and renewable routes to produce it (Mahmoud et al., 2014; Thiyagarajan et al., 2015; Giarola et al., 2016). Therefore, the BCC and BOC of the designed systems were calculated (Table 5) considering both situations for the HMPA hardener: as being petroleum-based (Merck, Sigma Aldrich), and biobased (by new methods).

As can be seen in Table 5, in the first case where the monomer and the hardeners are fossil-based, the BCC and BOC are 0% (THPMTGE-based thermosets), while when the monomer is biobased (TGPh), the BCC values are about 55–58% and BOC = 74–77%. Based on regulation, (NCS-16785, 2016), materials which have biobased carbon content >30% are classified as biobased.

If we consider the HMPA as a biobased hardener, the BCC and BOC are close to 100% in the systems developed with biobased TGPh, obtaining values of 99% BCC and 99.5% BOC.

3.6 Chemical decomposition of thermoset materials

It is known that, generally, the thermosets do not have the recycling characteristics of some thermoplastics (Pascault and Williams, 2010; Parameswaranpillai et al., 2021). In this study, the designed thermosets were subjected to depolymerization by dynamic bond exchange reaction (BER) in 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD)-ethylene glycol (EG) solution. Generally, these types of bonds are stable in normal conditions and become

TABLE 5 BCC and BOC calculated values for the designed thermosets systems.

Sample	BCC [%]		BOC [%]	
	Petro-based hardener	Biobased hardener	Petro-based hardener	Biobased hardener
TGPh-HMPA	58	98.87	77	99.52
THPMTGE-HMPA	0	32.22	0	14.92
TGPh-MNA	55	55	74	74
THPMTGE-MNA	0	0	0	0

SCHEME 1
Transesterification mechanism allowing recyclability, under thermo-catalytical effect.

FIGURE 7
Physical appearance of the thermosets before and after immersion in TBD/EG solution.
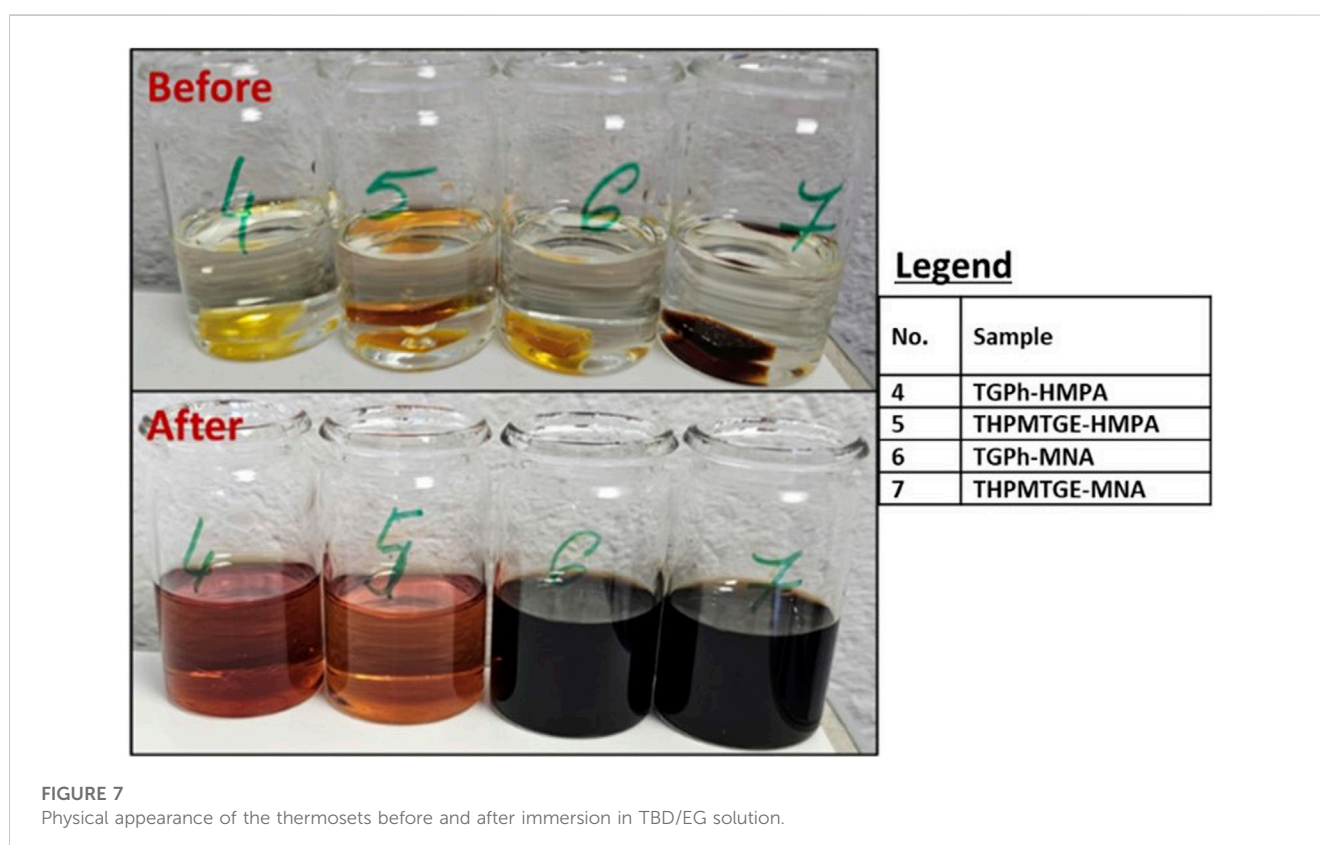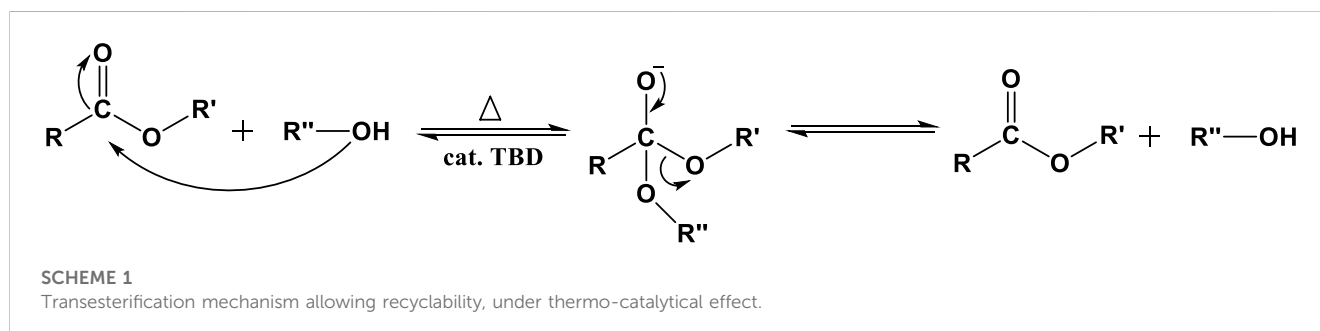
dynamic under the action of different stimuli (Chakma and Konkolewicz, 2019). The TBD/EG solution was used to depolymerize the polyester thermosets through transesterification reactions between ester linkages and hydrohyl groups (Scheme 1). Thus, when thermoset samples are introduced into a TBD/EG solution under temperature influence, reactive hydroxyl groups present in alcohol-catalyzed molecules diffuse into the network and swell the polymer structure; once entered the polymeric network, the −OH groups attack the ester bonds and break the long polymeric

chains into short segments thus leading to the decomposition of the thermoset network (Kuang et al., 2018a; 2018b; Shi et al., 2019; Mu et al., 2022; Wu et al., 2022; Jung et al., 2023).

Figure 7 is represented the physical appearance of the epoxy-based thermosets before and after dissolution test at 170°C. As can be seen, all the thermosets were completely decomposed in the alcoholic solution, only the duration was different.

The dissolution of the biobased thermosets was much faster, being completely depolymerized in about 2.5 h, while the complete dissolution time of the materials based on petro-based epoxy monomer was almost double (4.5 h). This behavior can be explained by the higher content in aromaticity of THPMTGE-based materials, which confers a greater stability as in the case of water absorption that was slightly low for these systems (Shi et al., 2019; Shi et al., 2022).

4 Conclusion

In this study, environmentally friendly and chemically recyclable thermosets were developed starting or from a natural and renewable resource, such as triglycidyl ether of phloroglucinol (TGPh), or from a commercial non-toxic tris(4-hydroxyphenyl) methane triglycidyl ether (THPMTGE). Their physico-chemical and thermo-mechanical properties were investigated and compared. According to DSC investigation it was found that the systems developed with the biobased epoxy monomer have both the maxim temperature of the reaction and the interval of the reaction shifted towards lower temperatures compared to the THPMTGE-based ones, these criteria being critical for industrial manufacturing. Based on DMA results, the biobased TGPh-thermosets have higher tan δ values (189–199°C), higher crosslinking densities (7.6–7.8 mmol cm^{-3}) and lower average molecular mass between crosslinks (144–152 g/mol) compared to the THPMTGE-resins, thus generating compact and stiff networks, crucial properties in the high-performance industry. The remarkable mechanical properties of these thermosets were also supported by the results of tensile tests, where Young's modulus ranged from 1.3 to 1.4 GPa, tensile stress of about 55–69 MPa, and an elongation at break around 3–8%. The brittleness factor was also calculated, thus demonstrating the lower presence of fragile character in the developed resins: for TGPh B = 0.044–0.059%·Pa/10^{10}), and for THPMTGE B = 0.052–0.104%·Pa/10^{10}). Also, the developed thermosets were completely dissolute in TBD/EG solution at temperature of 170°C, the time required for the depolymerization of TGPh-based resins being of about 2.5 h, and for the formulations based on THPMTGE monomer was around 4.5 h.

Concluding, sustainable and eco-friendly thermosets were developed, with excellent physico-chemical and thermomechanical properties, with low hydrophilicity and with a fast dissolution capacity. These thermosets are real competitors for the non-recyclable and toxic resins used in high-end industry.

Data availability statement

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

Author contributions

RD and AM contributed to conception and design of the study, methodology, investigation, and validation; RD: data curation; RD and AM: writing—original draft preparation; RD, UL, OD, and AM: writing—review and editing. All authors contributed to the article and approved the submitted version.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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