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Recycling development and shaping of a thermo-reversible epoxy resin with partial contents of Diels-Alder bonds

I. Lorero [a,*], B. Rico [a], M. Campo [a,**], S.G. Prolongo [a,b,***]

[a] Materials Science and Engineering Area, Rey Juan Carlos University, C/Tulipán s/n, Móstoles, 28933, Madrid, Spain
[b] Instituto de Tecnologías para la Sostenibilidad, Rey Juan Carlos University, C/Tulipán s/n, Móstoles, 28933, Madrid, Spain

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ABSTRACT

Thermo-mechanical recycling and reshaping of dynamic covalent networks is a promising field under development that could help to increase thermoset sustainability. Herein, the reprocessing of a partially reversible epoxy resin with a 0.6 Diels-Alder crosslink ratio, which has a relatively high T_g and a simplified manufacturing route, is studied to determine the optimal conditions for its thermomechanical recycling through milling and hot-pressing, and reshaping. Thus, in this work, we have studied the influence of compaction time, pressure, and temperature on recycled bulk properties. Meanwhile, different heating temperatures and times are also tested to evaluate the cured resin shaping to fix a new geometry and to observe its shape-recovering capability. Their characterization reveals that the recycling method generates dense thermosetting polymers with similar cross-linking structure and behavior, comparable to the virgin resin, inducing light post-curing that increases their glass transition temperature (T_g). The most efficient thermo-mechanical recycling conditions consist of the application of isothermal compaction at 130 °C and 150 bar for 30 min, which leads to resin bulks with comparable properties to the neat resin even after 3 cycles of milling and hot-pressing. On the other hand, the synthesized resin has shown excellent shaping due to the structural relaxation induced by the initiation of retro Diels-Alder reaction, adopting new geometries easily when the samples are heated above their T_g (91 °C) and preserving them after cooling to ambient temperature. Moreover, the samples also show high shape-recovering after heating again up to T_g. This reshaping and recovery have been maintained for several cycles without observing an irreversible lack of shape fixing or shape recovery.

1. Introduction

Thermosets use has been growing in numerous industries due to their good specific mechanical properties and durability. However, their diffusion has led to an environmental problem associated with the end of the life cycle of these pieces, since the molecular structure of thermosets avoids the possibility of recycling. Today, methods such as incineration, pyrolysis, or landfill are used to dispose of thermosets and composite wastes, even though these kinds of practices are a squander of resources and imply pollutant effects. In these last years, a new approach based on dynamic bonds has been developed for thermoset formulations, achieving reversible structures that allow self-healing to extend their life of service, and recycling after the end of use through thermal stimuli [1–3]. The introduction of dynamic bonds into the thermoset structure, named Covalently Adaptable Network (CAN), allows its reorganization through bond exchanging (associative CAN) or disarrangement (dissociative CAN), which makes these resins pass from a stiff state to a loose one assimilable to a thermoplastic nature. Thus, the development of an ideal thermo-reversible thermoset would entail repeated recombination of the network that allows the filling of cracks and discontinuities, healing of damages, and restoration of the original properties after completing the molecular exchanges. Among the different treatments to recycle dynamic resins, it can be remarked the milling of these materials and the subsequent thermo-mechanical treatment of its powder through hot-pressing, the reshaping to change the initial geometries into new useable forms, and the activation of shape-recovering mechanisms to create multi-shape materials.

Milling up to get fine powder for the hot-pressing treatment of CANs

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* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: isaac.lorero@urjc.es (I. Lorero), monica.campo@urjc.es (M. Campo), silvia.gonzalez@urjc.es (S.G. Prolongo).

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has been studied by some authors [4–9]. For example, Ozawa et al. pulverized different networks based on bismaleimide and diamines with disulfide bonds to generate hot-pressed bulks which retain a fraction of the original mechanical properties despite the partially irreversible network [4]. Similar procedures were used for thermo-reversible polyurethanes by introducing Diels-Alder (D-A) crosslinks [5,6] observing in these polymers a full recovery of tensile strength but a partial recovery of the elongation capacity. Within the field of epoxy resins, Memon et al. [7] developed a bio-based vanillin/imine vitrimer that could be reprocessed through hot-pressing up to 3 times retaining 70 % of the original tensile strength. Otherwise, the use of molecules with disulfide bonds also shows a considerable regeneration capability [8,9]. In this sense, there exist developments that retain up to 87 % of their original resistance after 3 cycles of milling and hot-press reprocessing [8]. Otherwise, the introduction of chemical groups that generate switchable crosslinking through D-A reactions is a promising mechanism to achieve reversibility and recycling for epoxy resins [10–19]. Diels-Alder reaction is a cycloaddition between a conjugated diene and a dienophile, in which 4 π-electrons of the conjugated diene and 2 π-electrons of the dienophile react and generate σ-bonds, which are energetically more stable. As a result, an unsaturated ring is formed. More specifically, the use of furan and maleimide groups through furfurylamine (FA) and bismaleimide (BMI) was pointed out by previous studies as an efficient pathway to give reversibility to the thermosetting structures through D-A reactions. The C═C bonds of the maleimide groups (BMI) are electron-insufficient, acting as dienophiles with relatively high reactivity [10]. Meanwhile, FA is a widely used reagent that provides both furan groups, that act as dienes to create a reversible union among both molecules and amine groups to connect the D-A chains to epoxide monomers to complete the thermoset network. By applying this chemical basis, several Diels-Alder resins have been developed and analyzed, standing out for their ability to flow at high temperatures and turn into moldable and recyclable [11–17]. However, this kind of resin usually has notable weaknesses, either due to the need for complex synthesis or due to the lack of mechanical properties. The addition of high contents of D-A crosslinks into the thermoset network incorporates an inherent brittleness [12,18]. To solve this problem, a synthesis that combines reversible D-A crosslinks with conventional covalent non-reversible bonds, ie. epoxy-amine, has been tested. For example, Puyadena et al. [19] developed a partially reversible epoxy network through the reaction of epoxy monomer with FA, BMI, and 4,4′-Methylenedianiline (DDM), which demonstrates an adequate capability to be reprocessed, even improving barely the thermo-mechanical properties with successive hot-pressing cycles. Besides, in previous work [18], the synthesis of D-A epoxy resins, formed by Bisphenol A diglycidyl ether (DGEBA), *m*-xylylene diamine (MXDA), FA, and BMI, were analyzed. As the main conclusion for the applicability of this research, we observed that the addition of FA and BMI up to achieve 60 % thermo-reversible crosslinking bonds (0.6 D-A ratio) generates an epoxy resin with an adequate compromise among recyclability and mechanical performance.

As mentioned before, shaping and shape memory are interesting capabilities of CANs due to the structural relaxation after heating above the activation of molecular exchanges and even more beyond glass transition. Some of these polymers exhibit both high stiffness, and relatively large deformation under heating combined with high shape fixation and high shape recovery [5,20–22], having potential applications in fields such as aerospace, automotive industry [23], and soft-robotics engineering [24]. In this regard, the development of a partially crosslinked resin through the dissociative exchange, D-A, and permanent, diamine-epoxy, bonds can generate a rigid network that can be switched into a two-phase structure (rigid permanent and loosed) after triggering the retro D-A reaction. The combination of rigid and flexible segments in the crosslinking network was pointed out as potentially beneficial for the creation of shape memory polymers [5]. In this regard, the use of D-A linkages constitutes stiff-to-loose switchable segments that allow shapable and shape memory thermosets [5,20–23,25,26].

Following these trends, the present study evaluates the thermo-mechanical recyclability and shaping of a partially reversible D-A thermoset. Thus, according to previous work, an epoxy monomer crosslinked with a 0.6 ratio of dissociative exchange D-A bonds and a 0.4 ratio of permanent covalent epoxy-amine bonds is manufactured using DGEBA, FA, BMI, and MXDA [18]. Thermo-mechanical recycling has been carried out first by milling the obtained resin bulks towards fine powder and then hot compaction of the powder to create new solid bulks. The influence of time, pressure, and temperature on recycled resin properties is analyzed to reach an optimal recycling method. The shaping tests also verify the resin's capacity to adopt and fix a new geometry and recover the original shape by heating up to glass transition temperature (T_g) over multiple cycles.

2. Materials and methods

2.1. Materials

The reagents used for the resin manufacturing were the following: Bisphenol A diglycidyl ether (DGEBA), *m*-xylylene diamine (MXDA), furfurylamine (FA), and 1,1′-(Methylenedi-4,1-phenylene) bismaleimide (BMI). All components were purchased from Merck (Darmstadt, Germany) and used as received.

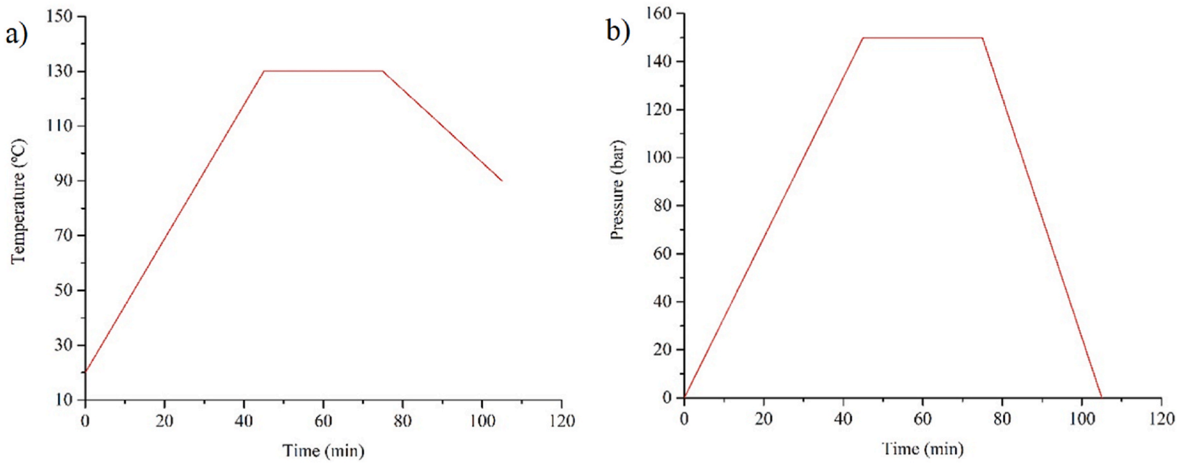

Fig. 1. Scheme of the hot-pressing procedure. Example of compaction maintaining isothermal and isobaric conditions at 130 °C (a) and 150 bar (b) for 30 min.

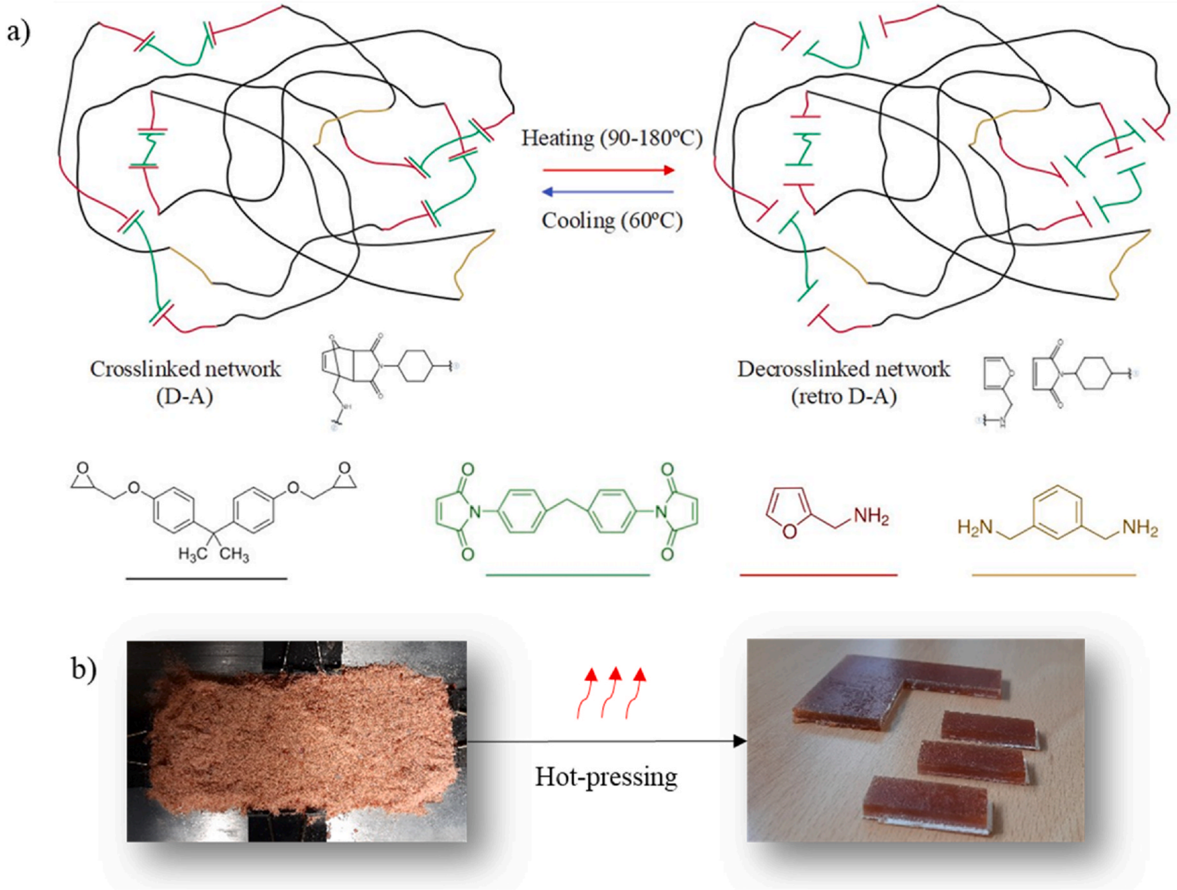

Fig. 2. Scheme of D-A crosslink engagement and disengagement (a), and thermo-mechanical recycling of the 0.6 D-A ratio resin (b).

2.2. Manufacturing

The initial resins were made according to a developed method in previous work [18]. Specifically, the composition used in this work corresponds to a 0.6 D-A ratio (60 % of reversible crosslink and 40 % of irreversible crosslink). The adjustment of reagent masses was done according to the following equations:

$$m_{FA} = \frac{m_{DGEBA} \bullet Neq_{DGEBA}}{Mw_{DGEBA}} \bullet \frac{Mw_{FA}}{Neq_{FA}} \bullet DA_{ratio} \tag{1}$$

$$m_{BMI} = \frac{m_{FA}}{Mw_{FA}} \bullet Mw_{BMI} \bullet \frac{1}{2} \tag{2}$$

$$m_{MXDA} = \frac{m_{DGEBA} \bullet Neq_{DGEBA}}{Mw_{DGEBA}} \bullet \frac{Mw_{MXDA}}{Neq_{MXDA}} \bullet (1 - DA_{ratio}) \tag{3}$$

Being m_{DGEBA} and m_{FA} the mass of DGEBA, and FA; Neq_{DGEBA}, Neq_{FA}, Neq_{MXDA} the molar equivalents of DGEBA, FA, and MDXA; Mw_{DGEBA}, Mw_{FA}, Mw_{BMI}, Mw_{MXDA} the molar mass of DGEBA, FA, BMI, and MXDA; and DA ratio the molar percentage of Diels-Alder chains.

First, the reagents DGEBA and BMI were mixed and heated up to 80 °C to further mechanical stirring and degassing for 15 min. After, the reagents FA and MXDA were added, and the mixture was molded to obtain the polymers. The curing cycle was set in two steps: first at a temperature of 100 °C for 6 h, to generate covalent bonding, and a second stage of 60 °C for 12 h, to generate the Diels-Alder crosslinking.

After curing, the samples were crushed to a fine powder in a 300 W power small miller with titanium-coated stainless-steel blades and then put in a mold for their compaction with a hot-pressing machine Labecon 300 to generate new solid bulks. Different parameters of hot pressing were tested to analyze its influence on the behavior of the recycled resins and to determine the optimum process. In this aspect, the pressure, temperature, and time have been evaluated from 50 to 150 bar, at 110 and 150 °C, and from 10 min to 40 min, respectively in isothermal and isobaric treatments. After hot pressing, the samples were placed in an oven and maintained at 60 °C for 12 h to regenerate the Diels-Alder crosslinking. Fig. 1 shows an example of the procedure. Each treatment consists of a first ramp of 45 min of pressurization and warming, followed by an isothermal and isobaric step to generate the solid bulk, which finishes with a third step of cooling below T_g and pressure release during 30 min.

2.3. Characterization

Attenuated total reflectance-Fourier Transform Infrared spectroscopy (ATR-FTIR) was used to analyze the chemical structure of the resins. To this purpose, scans from 600 to 4000 cm^{-1} were done using a Spectrum 100 from PerkinElmer (Waltham, MA, USA).

Differential Scanning Calorimetry (DSC) tests were carried out with a DSC25 device from TA Instruments (New Castle, DE, USA) by setting a ramp from 30 to 240 °C with a 10 °C/min heating rate.

Thermogravimetric analyses (TGA) were performed on a TGA/DSC 1 from Mettler Toledo (Columbus, OH, USA). The characterized samples were heated from 40 to 650 °C in a N_2 atmosphere, using a heating rate of 10 °C/min.

Thermomechanical properties were measured by dynamical thermomechanical analysis (DTMA) with a Q800 from TA Instruments. Tests were made in single cantilever mode with an amplitude of 1 % regarding sample thickness and a frequency of 1 Hz. Thermomechanical data were collected in a temperature range from 30 °C to 150 °C with a heating rate of 2 °C/min.

Flexure tests were carried out at ambient temperature on a universal

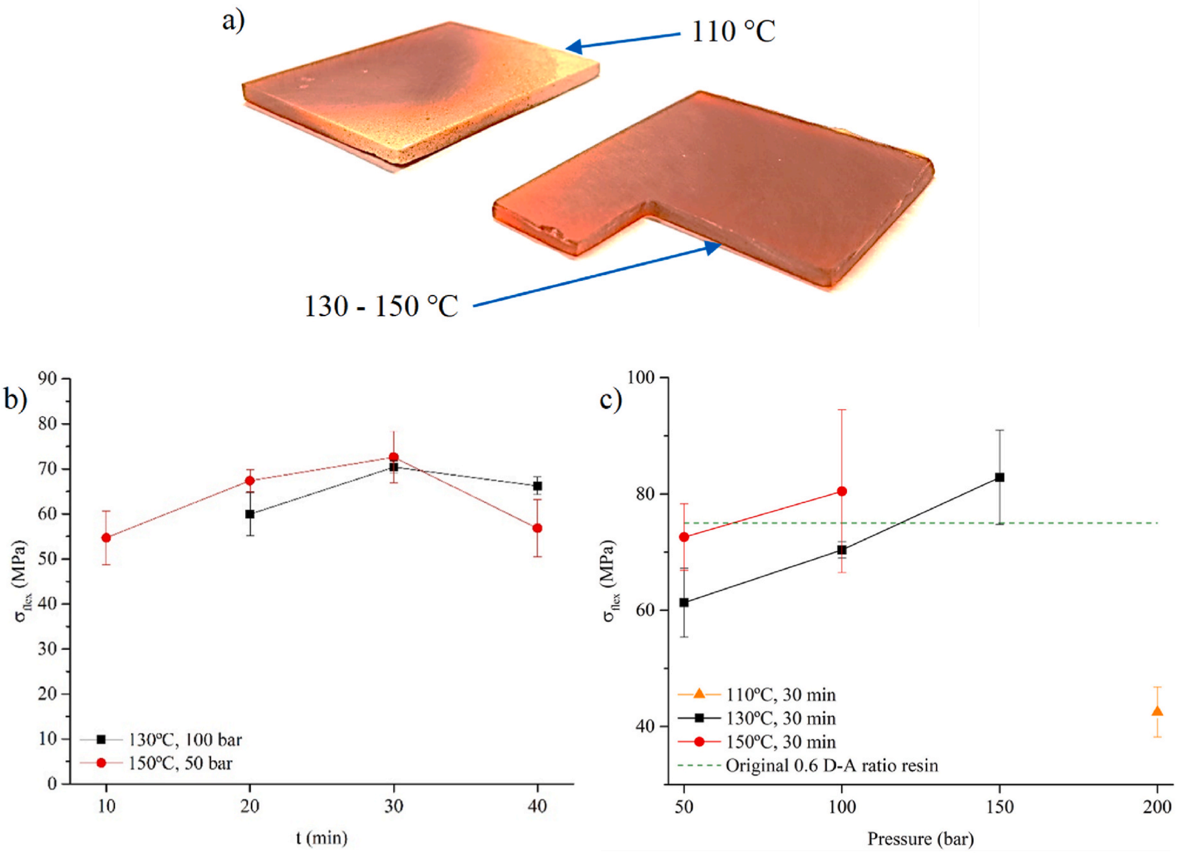

Fig. 3. Photographs of recycled resins at different hot-pressing temperatures (a), and Flexure strength of the recycled resins as a function of temperature, pressure, and time of the hot-pressing process (b, c).

testing machine Zwick Z100 (Ulm, Germany), in three-point bending mode using a 500 N load cell with a crosshead speed of 1.5 mm min^{-1}, by ASTM D790. The fracture surfaces were sputtered with a thin layer of gold and observed via Scanning Electron Microscopy (SEM) using a Hitachi S3400 N (Tokyo, Japan) to investigate their morphology and quality.

Vickers microhardness was measured by applying 980.7 mN loads with a Shimadzu HMV-2T indentation tester (Kyoto, Japan).

Using an S6E stereo microscope from Leica Microsystems (Wetzlar, Germany), powder particles from bulk milling were observed at low magnifications.

To complete the mechanical analysis and determine if the thermo-mechanical recycling methods introduce any porosity in resins, the densities of the original and recycled samples were measured using the Archimedes method according to ASTM B962-08.

The shape fixity and recovery ratios were determined by a U-type test [27]. These tests were performed with rectangular specimens (2 × 5 × 60 mm^3), according to the following steps: (1) Samples were heated using a convective oven up to 91 °C, corresponding with the T_g; at 120 °C, which is the point of maximum softening of this polymer according to previous DMTA characterization; and 150 °C, which corresponds with the disengagement temperature of the *-exo* D-A isomer, which is a more stable form of the D-A adduct that demands higher amounts of energy to be detached [18]. The samples were bent into U-shape molds with a 180° curvature, referred to as "stored angle" (Θ_S) with a radius of 19 mm. Then, the U- shaped specimens were cooled at room temperature and removed from the mold. The bending angle, fixed after 2 h at room temperature, was recorded as a "fixed angle" (Θ_F). After that, the U-shaped specimens were put into an oven and heated up to T_g from 2 to 60 min, being placed horizontally to avoid gravity effects. A remarkable shape recovery was observed during these thermal treatments, and the angle of the final specimens was measured as the "recovered angle" (Θ_R). Shape fixity ratio (S_F) and shape recovery ratio (S_R) were calculated through Equations (4) and (5):

$$S_F = \left(1 - \frac{\theta_S - \theta_F}{\theta_S}\right) \bullet 100 \tag{4}$$

$$S_R = \left(1 - \frac{\theta_F - \theta_R}{\theta_F}\right) \bullet 100 \tag{5}$$

3. Results and discussion

3.1. Optimization of hot-pressing parameters

Hot-pressing conditions, such as pressure, time, and temperature, govern the powder sintering process. Pressure is needed to deform powder particles and to increase the real contact surface, allowing molecular interactions while the temperature activates the exchange retro Diels-Alder reaction. The adequate parameters selection allows molecular disengagement and diffusion, and proper recycling of the resin as represented in Fig. 2. In any case, CANs diffusion and joining are complex and multi-variate processes that also depend on polymer properties and the geometries of grains and surfaces that are put in contact [28,29]. An incomplete process, whether caused by any of the three mentioned parameters, leads to chain diffusion lacks in the interfaces and then to heterogeneous porous materials, with corresponding depauperate mechanical properties. In this study, the flexural strength of the materials was taken as the reference property to set the optimum parameters of hot-pressing and different conditions were tested to analyze the effect of different parameters. In that way, it was observed that reducing the temperature below 130 °C does not allow

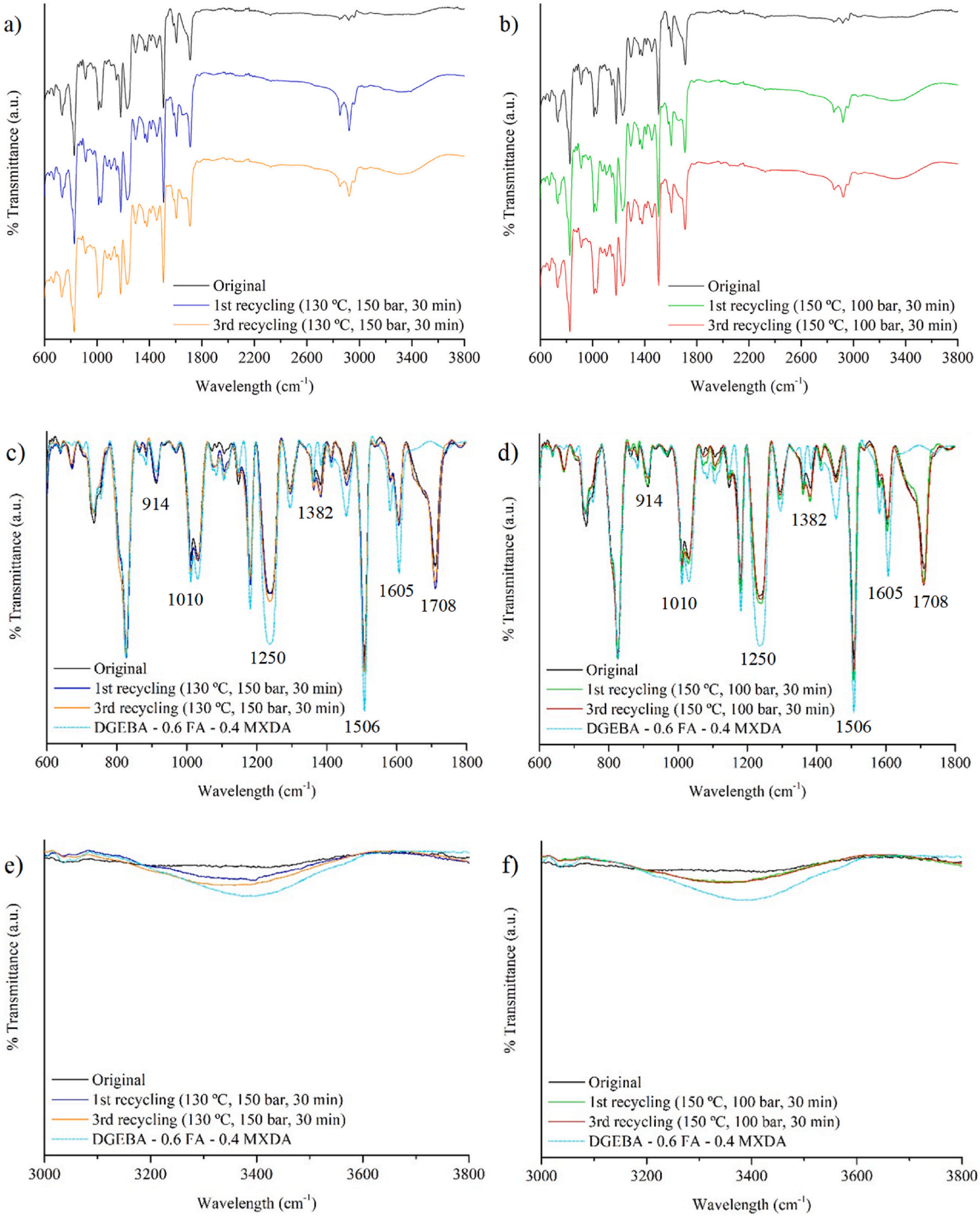

Fig. 4. FTIR spectra of the 0.6 D-A system as cured and recycled with optimized hot-pressing processes: 1 and 3 cycles at 130 °C, 150 bar for 30 min (a), and 1 and 3 cycles at 150 °C, 100 bar for 30 min. Specific FTIR comparisons from 600 to 1800 cm^{-1} (c, d), and from 3000 to 3600 cm^{-1} (e, f) including a DGEBA resin crosslinked with a 0.6 FA molar ratio without adding BMI.

optimum thermo-mechanical recycling (Fig. 3a). Despite the retro Diels-Alder reaction starts at 90 °C approximately, the temperature range of disengagement reaches above 150 °C. In this regard, it should be taken into account that D-A bonds present two different isomers: the kinetic product, known as the *-endo* isomer, which has a quicker formation and disengages at lower temperatures (from 90 to 120 °C), and the *-exo* isomer, whose formation requires higher amounts of energy in exchange of more thermodynamic stability, remaining bound until 150 °C approximately [30]. Fig. 3b and c shows the values of flexural strength of the recycled resins depending on hot-pressing conditions. As mentioned, temperature plays a principal role, and the attempts made at 150 °C present acceptable recovering at only 50 bars of pressure. To obtain similar results at 130 °C, the pressure must be raised to force the powder particles and increase the contact area to compensate for the incomplete Diels-Alder decrosslinking. If the process is tried at lower temperatures (e.g., 110 °C), the solids are not properly rebuilt, showing

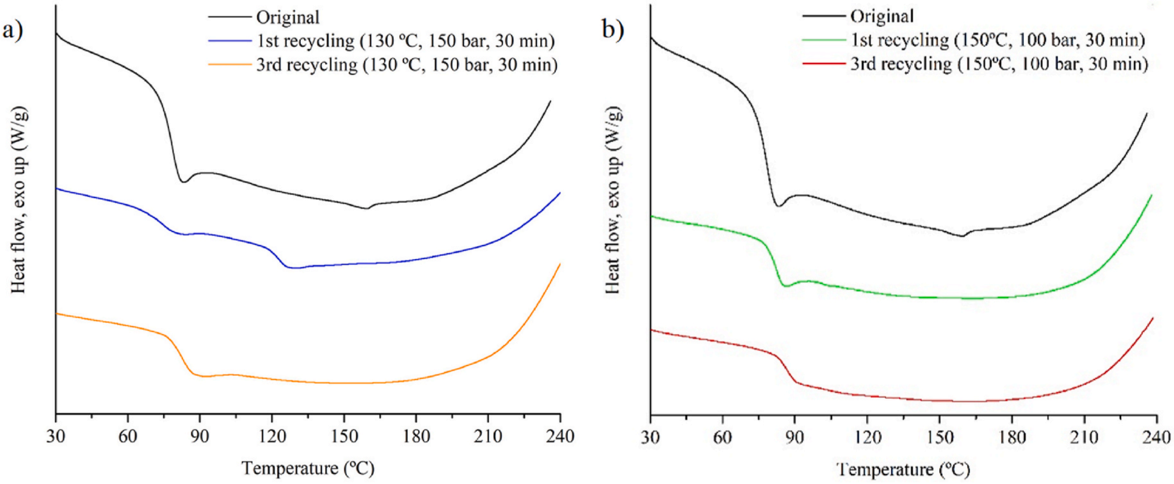

Fig. 5. Comparison of DSC scans of the 0.6 D-A ratio resin as cured with the recycled resins by optimized hot-pressing processes: 1 and 3 cycles at 130 °C, 150 bar for 30 min (a), and 1 and 3 cycles at 150 °C, 100 bar for 30 min.

heterogeneities and poor mechanical properties, even if higher pressures (200 bar) are applied. On the other hand, the increase of the temperature above 150 °C is discarded to avoid possible irreversible reactions involving maleimide groups [13,19]. To fulfill the process, it is necessary to maintain the hot-pressing operation the sufficient time to allow a full joining among powder surfaces. This can be observed clearly in Fig. 3b. The increase of the isothermal and isobaric hot-pressing step time up to 30 min allows to reach maximum of flexural strength for the reprocessed resins that are close to the average value of the original resin (75 MPa). The increase from 30 to 40 min does not generate further increases in mechanical properties. According to the hypotheses about vitrimer welding, it would be reasonable to see a similar evolution. The increase in hot-pressing times during the first minutes has a strong influence on joining strength. Meanwhile, after a certain amount of time, which depends on several factors as the crosslinking density or segment length and stretching, the strength values would tend to approach the values of the original resin, and then the temporal evolution starts to behave asymptotically [28,29,31]. Moreover, it can be seen in Fig. 3b that the increase from 30 to 40 min causes a drop in the strength of the hot-pressed resin at 150 °C. TGA tests in air atmosphere were realized to determine if degradation phenomena occur in the resin due to heat application. In this regard, the resin has good thermal strength and non-severe degradation is observed below 325 °C ($T_{d,5\ \%}$). Results are shown in Figs. S1a and S1b. Fig. S1b shows a TGA scan carried out at a constant temperature of 150 °C. The loss of mass is scarce, near 0.2 % after 2 h. In the absence of degradation, the decay of flexural strength in the resin with longer hot-pressing times could be associated with the obtention of excessively stiff polymer networks due to hot-pressing post-curing [32,33]. Then, for the specific case of the resin of this work, it seems obvious that 30 min is the optimum working time for the isothermal and isobaric steps. Once the parameter of time is fixed, the combination of temperature and pressure is evaluated as shown in Fig. 3c to recover the same values of flexural strength of the non-treated resin. In the case of making the compaction at 150 °C, this target is reached by applying a pressure of 100 bar, meanwhile, the pressure should be increased up to 150 bar if the process is made at 130 °C. As a result of the research, there are two different optimal operating conditions for thermo-mechanical recycling: 150°C-100 bar for 30 min; and 130°C-150 bar for 30 min, which are analyzed in depth to also determine their influence on other properties and their repeatability.

3.2. *Characterization of recycled resins*

3.2.1. *Analysis of the thermo-reversible structure*

As shown in Fig. 4, FTIR analysis of the resins points out that the recycling methods maintain the basic chemical structure and do not provoke side reactions. In this regard, the spectra do not reveal new peaks or significant changes after milling and hot-pressing. The absence of bands at 689 and 755 cm^{-1}, still after recycling, indicates that maleimide ring deformation attributed to the Diels-Alder reaction is kept [14]. Furthermore, the structure in other characteristic bands of FA and BMI, like those from 1010 to 1250 cm^{-1} related to C–O bonds of furan groups, 1382 cm^{-1} (C–N, maleimide), 1506 cm^{-1} (C=C bonds), and 1708 cm^{-1} (C=O, succinimide ring) [34], remain similar compared to the original resin. However, there can be observed slight changes in the intensity of some of these peaks after applying the hot-pressing, as shown in Fig. 4c and d. The intensity of C=C bands at 1506 cm^{-1} increases a little bit after recycling in both routes at 130 and 150 °C, which could be caused by a slight decrease in the Diels-Alder reaction efficiency. After hot-pressing cycles, the resins are placed at 60 °C for 12 h to regenerate the D-A crosslinking, but the variation of this band indicates that a certain amount of the C=C bonds of furan and maleimide groups remain unreacted and do not generate reversible crosslink. To contrast these results and make a more comprehensive explanation, Fig. 4c and d compare the resins of the present work with a reference DGEBA resin used in previous work [18], crosslinked with the same molar ratios of FA (0.6) and MXDA (0.4), but without adding BMI to avoid D-A chains: the absence of BMI and D-A adducts results in a greater presence of carbon double bonds in furan groups that generate stronger characteristic C=C signals at 1506 and 1605 cm^{-1} wavelengths. In this regard, the decreasing of the intensity of these peaks caused by the D-A reaction among FA and BMI, and also the increase after the bonding disengagement through retro D-A reaction was previously analyzed [18]. Therefore, the achievement of restored polymer networks, but with a slight loss of Diels-Alder crosslinks, seems plausible. One possible reason behind the decay of the Diels-Alder network reconstruction could be the resin stiffening caused by hot-pressing post-curing, as discussed below. Besides, these changes in peak intensities can be also observed in those bands corresponding to furan C–O, and maleimide C–N and C=O bonds, which are related to the formation of hydrogen bonds with the hydroxyl groups formed during the curing reaction [12]. The increases in the intensity of these peaks, and the appearance of the broad –OH band from 3000 to 3600 cm^{-1} after the recycling treatment point to a partial loss of the hydrogen bond network formed during the curing cycle of the original resin, as observed

Table 1
DSC and TGA results of the original resin and the recycled resins after 3 cycles.

	Original	3rd recycling (130 °C, 150 bar)	3rd recycling (150 °C, 100 bar)
$T_{g,\ DSC}$ (°C)	77.6	81.3	86.6
$T_{d,1\ \%}$ (°C)	269.8	250.0	272.0
$T_{d,5\ \%}$ (°C)	332.1	325.9	327.5
$T_{d,50\ \%}$ (°C)	398.1	392.3	395.1
T_{max} (°C)	365.1	362.2	361.6
Char yield (%)	24.2	20.9	22.1

in Fig. 4e and f.

Beyond the effects on the thermo-reversible structures, it should be noted that the spectra reveal slight decreases in 914 cm^{-1} peaks after the recycling processes. This band is associated with the residual free oxirane rings [35], which indicates that the hot-pressing process induces a post-curing effect. In this regard, it should be noted that the curing of the virgin resins is done at 100 °C without applying pressure; meanwhile, the hot-pressing recycling is done from 30 to 50 °C warmer under notable pressure. Thus, the remaining free epoxide groups from the initial curing react with non-reacted secondary amines, increasing the crosslinking degree of the recycled resins, an aspect that was also observed by DSC and DMTA scans made in the present work.

DSC scans (Fig. 5 and Table 1) reveal a clear post-curing effect caused by hot-pressing, since it is observed as the T_g of the recycled resins rises from 78 to 81 °C in those treated at 130 °C, and from 78 to 87 °C in those recycled at 150 °C. Besides, the effect on the endothermic curves from 90 to 180 °C corresponding to retro D-A reaction [14,30] is also observable: in any of both process temperatures, the original endothermic peak, around 150–160 °C, fades. After doing 3 recycling cycles, the samples no longer show this obvious endothermic peak and present a broad curve. These changes might point to a certain chemical fatigue of the thermo-reversible structure according to previous studies [14]. In this regard, some authors pointed out that furan and maleimides can undergo different reactions apart from conventional D-A reactions. For example, the formation of double D-A adducts through the bonding of two furan groups and a maleimide could happen under certain conditions at retro D-A reaction temperatures, that is, at hot-pressing conditions [36]. These double D-A adducts show higher thermal stability, and also exothermic signals in DSC scans that can overlap with retro D-A reaction and camouflage the observation of the overall process, as happens in recycled resins at 150 °C from the first cycle. This process might be reversed if the material is heated at higher temperatures, releasing furan and maleimide groups. On the other hand, the irreversible formation of aromatic rings by dehydration is also possible and analyzed in the bibliography [37,38]. Nonetheless, the slopes in the DSC scans above 200 °C, associated with the initiation of the homopolymerization of BMI [39], remain constant, so the triggering of irreversible processes such as aromatization in high quantities can be discarded. Thus, considering the overall variations of FTIR and DSC tests, the formation of double D-A adducts and the stiffening of the resin networks induced by recycling post-curing seem the most plausible factors behind the hindering of full Diels-Alder structure restoration [11].

TGA scans (Fig. 6 and Table 1) reveal that neither of the two thermomechanical recycling methods induces significant variations in resin thermal resistance. Regarding the hot-pressing temperature, the resin weight loss observed in TGA curves reaches around 0.2 % at 130 °C, and 0.3 % at 150 °C, which point that these treatments cause a scarce degradation. The behavior of the polymer structure remains, and both

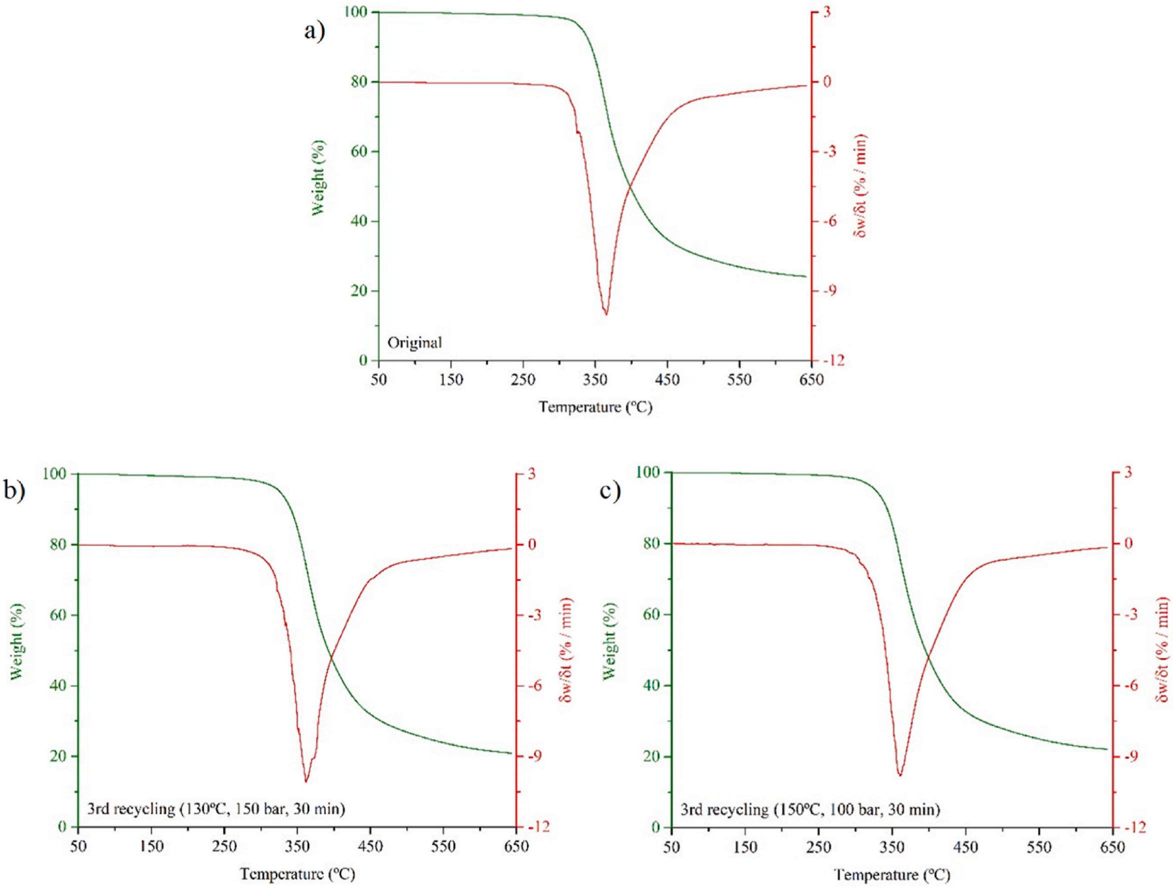

Fig. 6. Thermogravimetric analysis of the original resin (a), and the recycled resins after 3 cycles of milling and hot-pressing at 130 °C and 150 bar for 30 min (b), and at 150 °C and 100 bar for 30 min (c).

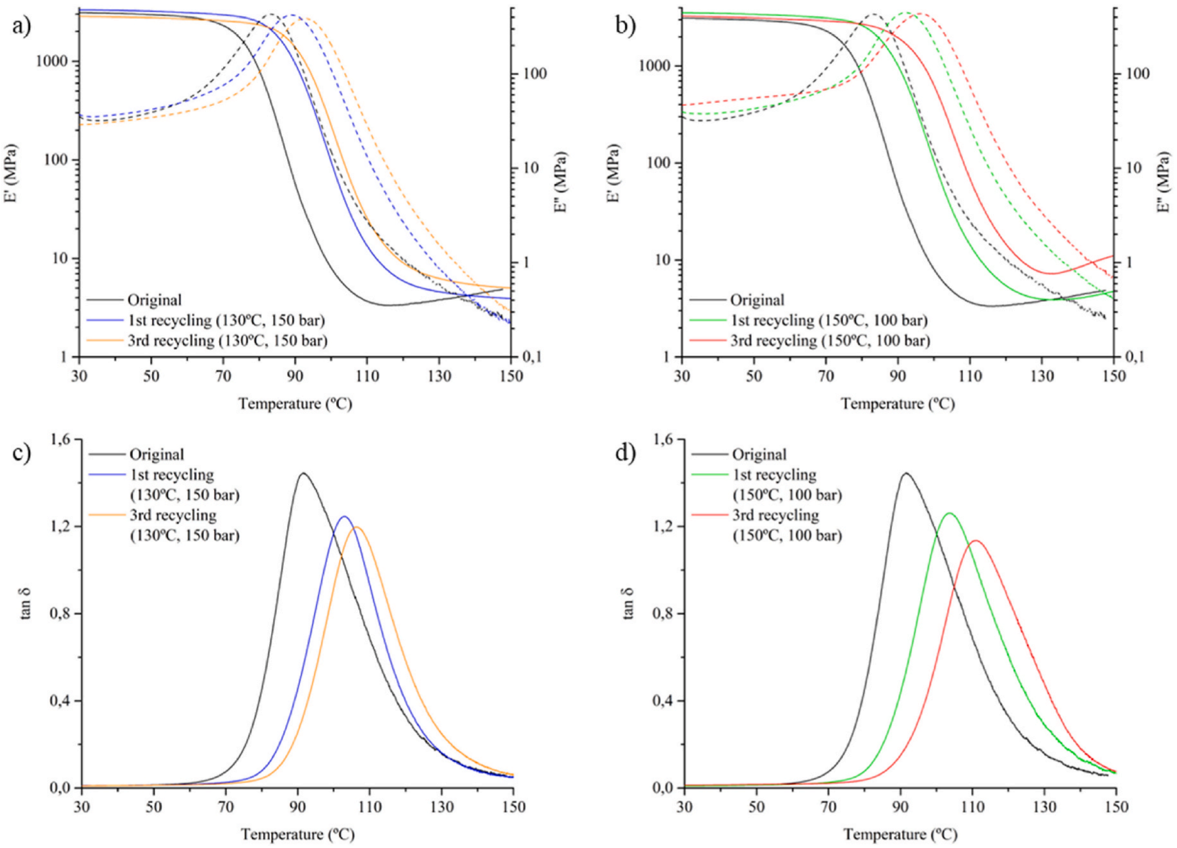

Fig. 7. DMTA analysis of 0.6 D-A ratio resin as cured and recycled by optimized hot-pressing methods: evolution of E' (a,b) and tan δ (c,d) with temperature.

Table 2
DMTA results of original and recycled resins.

	E'$_G$ (MPa)	E'$_{min}$ (MPa)	T$_g$ (E''$_{max}$)	T$_g$ (tan δ $_{max}$)	FWHM
Original	3129 ± 233	3.3 ± 1.3	79.1 ± 1.0	91.1 ± 1.5	23.6 ± 1.8
1st recycling (130 °C)	3325 ± 13	4.2 ± 0.5	88.8 ± 0.2	103.1 ± 0.1	22.9 ± 0.6
3rd recycling (130 °C)	2804 ± 81	4.5 ± 0.5	92.3 ± 0.6	106.4 ± 0.2	24.4 ± 0.8
1st recycling (150 °C)	3532 ± 18	4.5 ± 1.0	89.4 ± 0.6	105.0 ± 0.3	26.0 ± 1.3
3$_{rd}$ recycling (150 °C)	3224 ± 62	5.1 ± 1.9	96.9 ± 0.2	111.4 ± 0.4	28.6 ± 1.0

original and recycled resins show comparable thermal resistances with other D-A epoxy resins before any reprocessing or thermal treatment [15,16,40,41] and other conventional epoxies [15,42]. In this regard, the originally manufactured 0.6 D-A resin reaches a 5 % weight loss after heating up to 332 °C, a behavior that is maintained in the recycled resins after 3 milling and hot-pressing cycles at 130 °C and 150 bar ($T_{d,5\ \%}$ = 326 °C), and 150 °C and 100 bar ($T_{d,5\ \%}$ = 327 °C). Both original and recycled resins start to decompose into gas simultaneously, after exceeding a temperature of 336 °C and reaching 50 % weight loss around 395 °C. The three samples also present similar char yields at 650 °C: 24.2 % for the original resin, 20.9 % for the recycled resin at 130 °C, and 22.1 % for the recycled resin at 150 °C.

3.2.2. Analysis of mechanical and thermo-mechanical properties

DMTA scans (Fig. 7 and Table 2) reveal that the recycling process induces a clear increase in the T_g and storage modulus values of the resins after the first cycle at both 130 and 150 °C. This behavior follows a pattern similar to that observed in previous analyses about thermo-mechanical recycling of vitrimers [43,44] and reversible D-A epoxies [19], principally due to post-curing reaction at high temperature and pressure. Logically, the effect of post-curing is deeper in those samples recycled at higher temperatures (150 °C), in which the maximum of tan delta passes from 91 °C to 105 °C and the storage modulus increases from 3100 to 3500 MPa in first recycling.

However, the carrying out of successive recycling cycles results in a decrease in the storage modulus of the resins as shown in Fig. 7a and b, despite the values of T_g still growing moderately (Fig. 7c and d). In the absence of side reactions such as BMI homopolymerization, D-A adducts aromatization, or significant thermoset degradation, as demonstrated in the previous characterization, there are two probable reasons behind this divergence: an impoverishment of the Diels-Alder network reconstruction, as observed in DSC scans, or a lack of the effectiveness of milling and hot compaction after the first recycling cycle caused by the increase of the resin crosslinking degree. On one hand, the effect of D-A crosslinking degree on the thermomechanical properties of this resin was previously evaluated [18], observing similar drops of the storage module at 30 °C after disengaging the Diels-Alder bonds compared to those observed in Fig. 7 for the 3 times recycled samples. On the other hand, the particle size distribution obtained from recycled bulk milling is more heterogeneous and presents a considerable amount of coarse particles compared to virgin bulk milling (Fig. 8a–c). A heterogeneous size distribution could improve the quality of compaction in some cases by improving the particle packing [28], but if the increase in powder sizes is generalized with the presence of large particles, then the result is the obtention of shorter surface areas and poorer contact and diffusion between polymeric particles [29]. The diminished chain diffusion is a factor that can hinder bulk reconstruction and cause a decrease in the elastic response of the resins. However, the maintenance of other mechanical and physical properties in some cases, as shown below for the

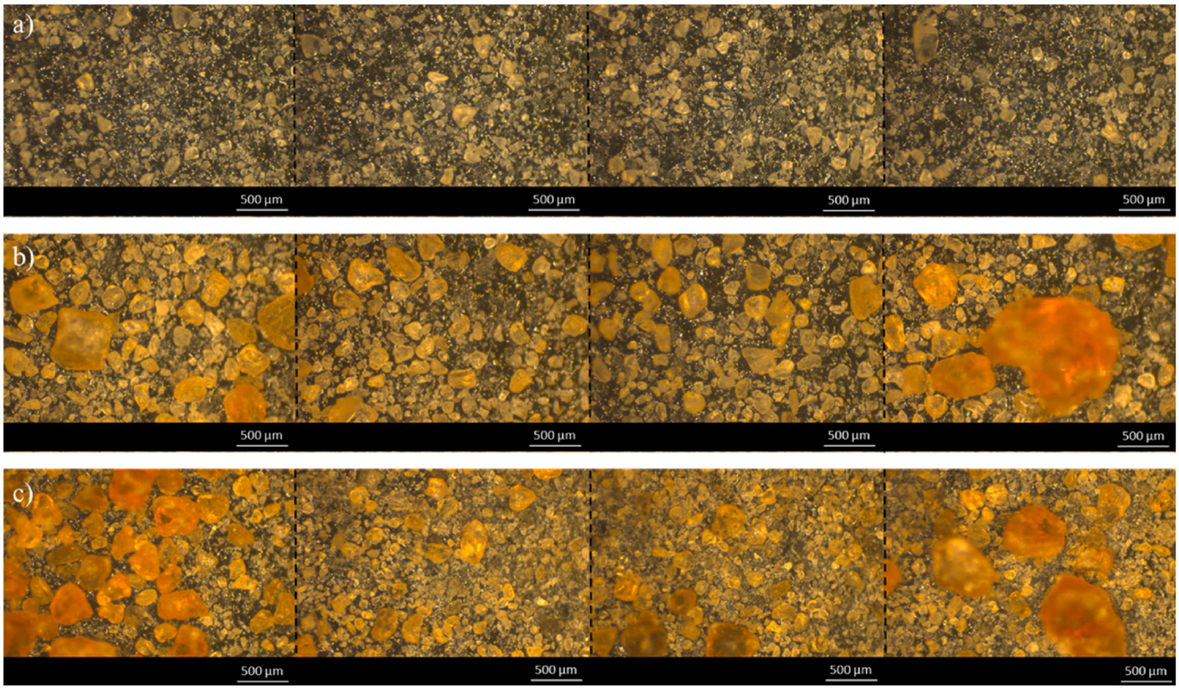

Fig. 8. Optical microscope images of resin powder after first milling (a), before the 3rd recycling at 130 °C and 150 bar (b), and before the 3rd recycling at 150 °C and 100 bar (c).

resin recycled at 130 °C and 150 bar, probably means that this loss of efficiency in bulk reunification is slight and not a preponderant factor to explain the tendencies of the storage modulus at low temperatures, which gives more importance to the state of Diels-Alder crosslinks in this specific property. In this regard, it should be noted that the hot compactions at 150 °C induce changes on tan δ curves, increasing the width of these curves at their half maximums. The widening of these curves usually means an increase in the polymer network heterogeneity. Something that might indicate the existence of a few new crosslinks such as double D-A adducts that could alter the thermo-mechanical behavior of the recycled materials pressed at 150 °C, as mentioned before. The recycled materials still show a clear decrease of the storage modulus at retro Diels-Alder temperatures and only reach low values induced by the network relaxation during bond disengagement (see Fig. S2) [18]. The minimum storage values, as shown in Table 2, are only a bit higher than those observed in the original resin, either by post-curing or minor formation of thermally stable adducts.

Fig. 9a and b shows the evolution of flexural properties of the resin throughout the cycles of recycling made according to the optimized compaction parameters. For the first cycle, both hot-pressing conditions create bulks that not only maintain the original values (corresponding to cycle 0 in Figs. 9a and 75 ± 12 MPa of strength and 2–3 % of break strain), but also achieve slight increases of strength (75–91 MPa for the samples recycled at 130 °C, and 67–95 MPa for the samples recycled at 150 °C). As it was previously confirmed by optic microscopy and DMTA, the adequate powder grain size distribution after the first milling, and the post-curing effect of hot-pressing induce the improvement observed. However, after carrying out 3 recycling cycles, the tendency changes: meanwhile the samples recycled at 130 °C and 150 bar maintain the improvements in flexural strength (83–85 MPa), those recycled at 150 °C and 100 bar undergo a clear drop of mechanical properties (50–65 MPa of strength and 1.8–2 % of break strain). Due to the larger particle size of milled resins after the successive recycling (Fig. 8b and c), the pressure applied during the compaction plays a more relevant role in these cases. Higher pressure is needed to induce a more effective redistribution and a higher plastic deformation of the particles, increasing the contact area, and allowing an effective diffusion and bonding between resin surfaces triggered by retro D-A reaction and thermal softening, which is sufficient from 130 °C. According to the thermal characterization, the differences between the recycled resins at 130 and 150 °C after successive cycles could also be influenced by a possible hindrance on network exchanging if reactions such as double D-A bonds happen during hot-pressing processes.

Microhardness analysis shows similar tendencies (Fig. 9c). The samples recycled at 130 °C and 150 bar maintain similar values (23.4–25.9 HV) regardless of the number of cycles compared to the original resin (23.5–26.5 HV), meanwhile in those recycled at 150 °C and 100 bar, the values after the third cycle descend moderately (22.8–24.8 HV), probably due to an incomplete diffusion and particles joining.

Bulk densities of original and recycled resins were measured to complement the analysis of properties evolution through recycling cycles (Fig. 9d), proving that bulk reconstruction is generally achieved in both processing conditions. Nevertheless, there are slight variations to consider. Those samples recycled at 130 °C and 150 bar can be observed as scarce densification, with a density increase of around 0.2–0.3 %, which is still maintained after 3 cycles. On the other hand, the samples recycled at 150 °C and 100 bar also present a similar increment of density after the first cycle but suffer a faint decrease of density, around 0.2 % less compared to the original resin, after passing through 3 recycling cycles. Despite the measurements point the fact that both recycling methods manage to reconstruct solid bulks, the small changes observed are aligned with the tendencies of the mechanical properties of the samples and point out the importance of increasing the compaction pressure. The scarce decrease of densification leads to a mild apparition of microvoids and defects that may not affect significantly in certain properties such as the stiffness or the storage modulus, but which are critical in other properties more dependent on the appearance of micro discontinuities such as the strength [29]. SEM images of the fractured sections shown in Fig. 10a and b corroborate these observations. The fractography is expected from fragile epoxy thermosets, regardless of whether the samples are original or recycled. However, the fractured samples recycled 3 times at 150 °C and 100 bar present inner defects caused by incomplete powder bonding during hot-pressing (Fig. 10b),

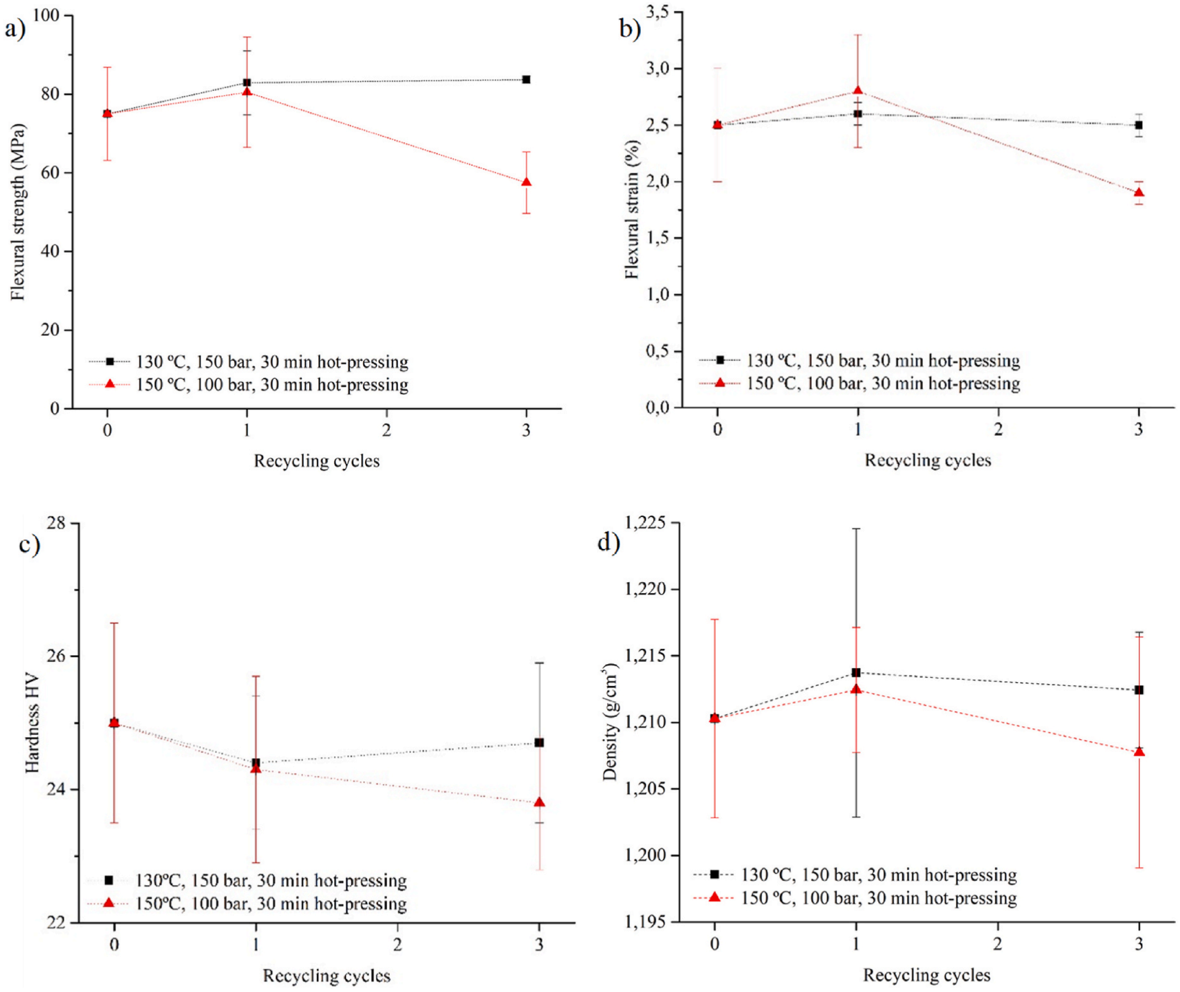

Fig. 9. Comparison of properties of the 0.6 D-A ratio resin as cured and recycled by optimized hot-pressing methods: flexural resistance (a), flexural strain (b), Vickers hardness (c), and bulk densities (d).

meanwhile the other cross-sections, corresponding with the samples recycled one or three times at 130 °C and 150 bar, appear without discontinuities.

In summary, the first compactions at 130 and 150 °C induce a notable post-curing effect on the resin that increases glass transition and stiffness. In the absence of an accurate analysis of the milling process, it seems that recycled bulks are also tougher and require higher energy rates to reduce them to fine powder, which decreases the milling efficiency and generates a significant number of coarse particles that difficult the subsequent recycling. The results after 3 recycling cycles show that increasing compaction pressure is a more effective solution to overcome this problem. The increase from 130 °C to 150 °C would help to disengage *-exo* D-A isomers, according to the theory and DSC results observed in Fig. 5, and favor chain diffusion, but its impact without high compaction pressures is limited. Of course, it would be reasonable to think that the obtention of solid bulks with optimal mechanical properties too after 3 cycles at 150 °C is possible by increasing compaction pressure up to 150 bar, by using more aggressive grinding methods, or by applying an intermediate heat treatment to reverse possible double D-A bonds but, in any case, those processes would have less energy efficiency compared to the compactions made at 130 °C.

3.3. Thermal shaping and shape recovering

In addition to thermo-mechanical recycling methods consisting of milling for its subsequent reunification with specific geometries and volumes for new applications, reshaping represents a more simple, quick, and efficient alternative to change an end-of-use piece to a new useable form if the original volume is enough to fulfill the new requirements. To get new shapes to a thermoset, heat is needed until its structure is relaxed sufficiently, either by reaching the rubbery state or triggering chain exchanges. According to DMTA and DSC results, it was decided to test the shaping at three different temperatures: 91 °C (T_g and starting of retro D-A reaction), 120 °C (temperature of minimum value of E'), and 150 °C (D-A *-exo* isomer dissociation). The selection of these three temperatures is done to analyze the possible effects of the polymer softening and bons disengagement on shaping. In the bibliography, it can be observed that some thermosets can be shaped with new geometries by heating above T_g, applying deformation, and freezing to ambient temperature before releasing the piece [23,45]. In this regard, previous analysis aboard reshaping by heating at T_g +10 in order to place the materials in rubbery plateau and minimize their stiffness [27]. Nevertheless, the addition of dissociative crosslinks on epoxy resins has a deep effect on network stiffness, so lower temperatures (T_g) can be tested. Looking at the DMA curve of the 0.6 D-A ratio epoxy resin used in this work, shown in Fig. S2, it can be observed that the storage modulus shows a clear drop until 120 °C due to bond dissociation [18]. This effect of heating thermomechanical response, and also the increase of heating up to 150 °C to fully disengage the D-A bonds, can benefit the resin shaping and shape recovery. For example, in a recent analysis with partially dissociative nanocomposites doped with carbon nanotubes [46], it was observed that it was necessary to heat the samples from

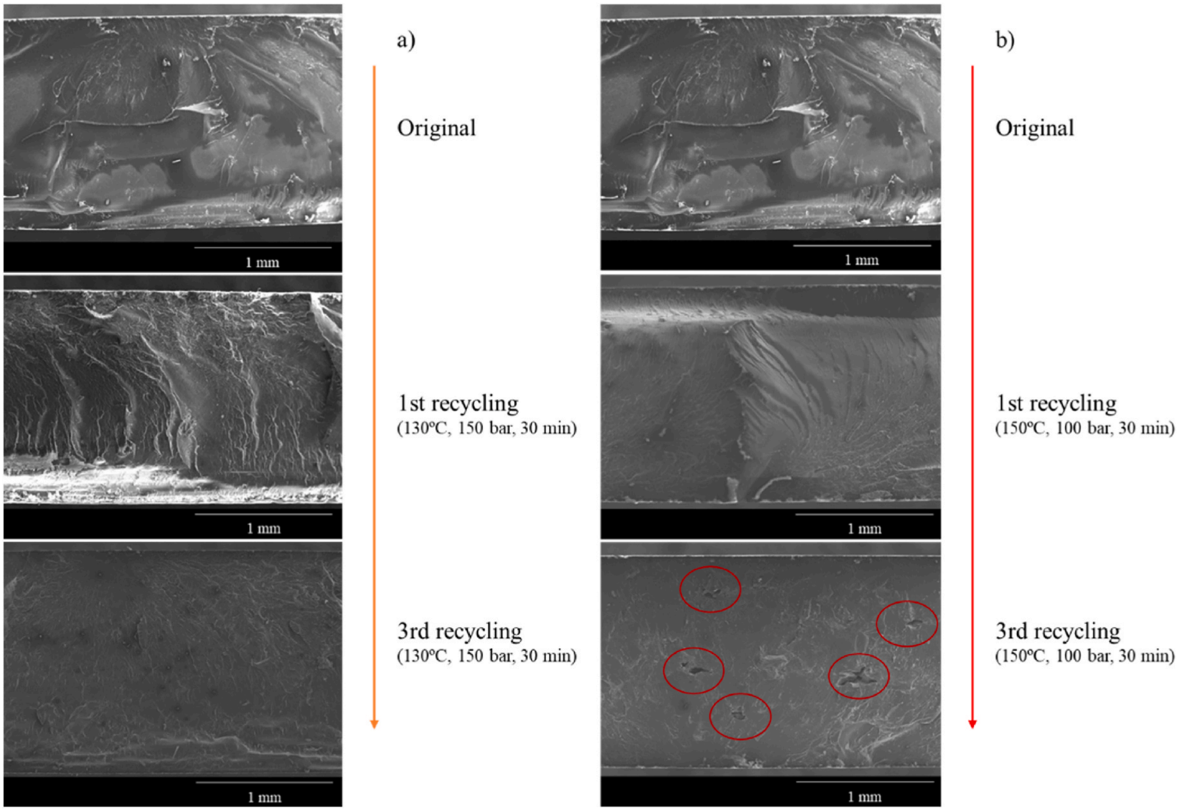

Fig. 10. SEM images of fracture surfaces of 3-point bending flexure test samples: original resin and recycled resins after 1 and 3 cycles at 130 °C and 150 bar for 30 min (a), and after 1 and 3 cycles at 150 °C and 100 bar for 30 min (b).

120 °C to 150 °C to avoid network mobility restrictions caused by nanofillers and to get enough capability to allow the elastic strains without breaking or without observing spring back effects. As shown in Fig. 11a and b, the results after doing the shaping with the 0.6 D-A ratio resin at the three temperatures are identical, and a practically full fixing of the mold shape is achieved. After a first observation of the results, it could be interpreted that shaping and shape memory (Fig. 11c) are mainly governed by glass transition in this resin, allowing adequate shape fixation and stress relaxation. In this regard, Li et al. pointed out that the glass-to-rubbery modulus ratio (E'_g/E'_r) should reach or exceed 100 for good shape memory performances [5]. However, a more detailed study of DMTA results reveals an indirect influence of the D-A structure, while its decrosslinking reaction induces a notable relaxation in the polymer structure (Fig. S2) [18] that enhances resin shaping. For the resin used in this work, the E'_g/E'_r ratio rounds about 150 at 91 °C and reaches values higher than 1000 at 120 °C (Fig. S3 and Table S1). These E'_g/E'_r ratios rise according to the content of dissociative crosslinking, as observed in the previous analysis [18] shown in Fig. S4. The high relaxation given by D-A chains under disengaging differs notably from those obtained in other permanent thermoset networks. To compare, a purely irreversible DGEBA-MXDA presents an E'_g/E'_r ratio of around 27 at T_g and reaches values closer to 120 after heating above $T_g + 10$ (Fig. S3 and Table S1). The higher E'_g/E'_r ratios are not only proper of irreversibly crosslinked resins [27], in so far as other associative CANs as disulfide-epoxy [47] or imine-epoxy [7] vitrimers with constant crosslink degrees present similar tendencies. In conclusion, the differences in thermo-mechanical properties point out that using partial contents of dissociative bonds, as Diels-Alder, could give a more efficient solution for those applications that demand re-shapable thermosets. In this way, the results demonstrate the possibility of combining plenty of reshaping without losing network consistency, as in pure dissociative networks.

According to the good results in shape fixation, the shape memory capability of the resin was tested by heating the thermoformed samples up to T_g (91 °C). The results shown in Fig. 11c demonstrate an excellent shape recovery: a full return to the initial form is achieved by maintaining the temperature of the samples at 91 °C for 60 min. Other times, from 2 to 20 min, were also tested to observe the overall process. As mentioned in the introduction, thermally triggered shape memory effects in polymers have been widely studied in the bibliography and are typically governed by structural and stress relaxation phenomena [20,21,23]. Considering the test conditions, it is worth noting that the temperature not only leads the resin to a rubbery state but also allows a partial disengagement of the *-endo* D-A isomers [30] that lose the structure further. The combination of rigid and flexible segments by adding reversible bonds into the crosslinked network was previously pointed out as a pathway to increase the shape memory effect [4], due to an enhancement of chain mobility in soft points of the thermoset. Retro D-A reaction has a quick kinetic compared to the slow speed of D-A bond formation, needing only a few minutes for the detachment [48]. Thus, a notable shape recovery during the first minutes of heating would be expected. As observed in Fig. 11c, the main quantity of shape recovering is achieved in the initial 10 min: after 2 min, the S_R value gets 31 %, which rises to 70 % after 5 min and reaches 90 % at 10 min of heating.

Shaping and shape recovering were tested cyclically to check if the resin showed a deterioration in its capacities with successive deformations and recoveries. As shown in Fig. 11d, the sample maintains its results invariant after 3 cycles and presents a slight decrease after the 5th cycle, in which the sample shows a faint curvature and S_R reaches 97.9 %, a value, nonetheless, still remarkable. This decrease is caused by the effect of cyclic heating on the polymer network, which generates a post-curing effect that increases T_g, as seen before in thermo-mechanical recycling. To confirm this hypothesis, the sample was thermoformed for the 6th time and heated up to 110 °C to ensure that T_g was exceeded. As a result, the sample showed a full recovery after 60 min of heating. The small curvature previously observed after the 5th cycle disappeared

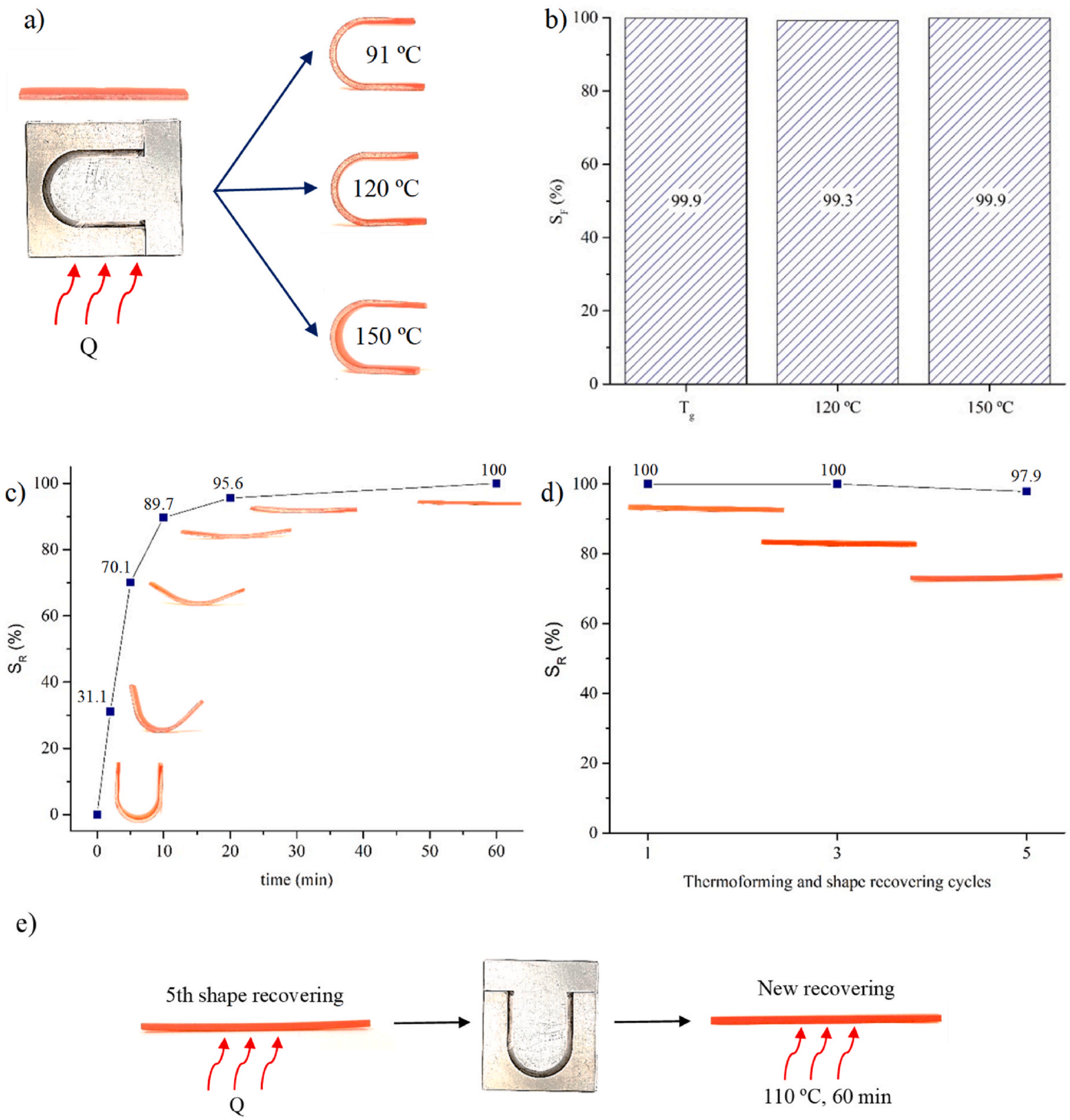

Fig. 11. Scheme of shaping at 91 °C, 120 °C, and 155 °C (a) and shape fixity ratios at these temperatures (b). Shape recovering after heating at 91 °C from 2 to 60 min (c). Shape recovering after several cycles of shaping at 120 °C and recovering at 91 °C for 60 min (d). Illustration of a 6th shape recovering made at a higher temperature (110 °C) to overcome the increased glass transition temperature caused by post-curing (e).

(Fig. 11e). In conclusion, the results show that the manufactured resin can be thermoformed several times and thermally stimulated to recover its previous shape, fully or partially, depending on what is needed.

4. Conclusions

Different pathways of reutilization: milling + hot pressing, and reshaping, for end-of-use pieces of a DGEBA resin crosslinked with 0.6 D-A (BMI and FA) and 0.4 MXDA molar ratios are analyzed. The resin shows adequate crosslinking reversibility that allows the generation of recycled solids conserving the structure and even increasing some mechanical and thermo-mechanical properties under optimized compaction conditions. This reversibility also helps to facilitate the adoption and fixation of new shapes, and grants shape memory through heating for several cycles.

To obtain accurate thermo-mechanical recycling methods, the effect of different parameters of operation on the resin properties was analyzed. According to the results, the following conclusions could be settled.

1. The parameters of hot-pressing should be carefully adjusted according to the properties of the resin. Regarding the 0.6 D-A ratio resin used in this work, Diels-Alder bonds detach above 90 °C. Still, it is needed to apply 130 °C at least to ensure enough network disengagement and structure relaxation. A high pressure, equal to or superior to 100 bar, should be applied to force grain reordering and plastic deformation to ensure interfacial contact. Besides, isobaric and isothermal compaction time should be adjusted to 30 min to allow retro D-A reaction, particle deformation, and interfacial chain diffusion to ensure dense bulk reconstruction.
2. Two different optimal hot-pressing parameter combinations were determined according to the 3-point bending test, results by applying

isostatic and isothermal compactions at 130 °C and 150 bar, and 150 °C and 100 bar for 30 min. Recycled bulk characterization points, that the first cycle of hot compaction achieves dense material without side reactions or degradation, but induces post-curing, increasing T_g and storage modulus, and reconstitution of Diels-Alder crosslinks is interfered. Otherwise, properties such as strength, break strain, hardness, density, and thermal resistance are conserved.

3. Consecutive milling of recycled bulks is less efficient, which generates coarse grains that hinder further recycling. To overcome this question, the compaction pressure plays a determining role in forcing grain deformation and ensuring interfacial diffusion. It is more effective than further temperature increases to stimulate further retro D-A reaction. In this way, the hot-pressing made at 130 °C and 150 bar achieve dense bulks after 3 recycling cycles, meanwhile, the 3 times hot-pressed resins at 150 °C and 100 bar present micro voids and discontinuities that depauperate mechanical properties as strength and break strain.
4. Retro Diels-Alder reaction contributes to relaxing the polymer structure from 90 °C, increasing glass-to-rubbery modulus ratio and resin shaping compared with conventional thermosets or associative CANs. In this way, the DGEBA – 0.6 D-A ratio samples show full shape fixations from 91 °C (T_g) onwards. Shaping is a relatively quick operation that only induces slight post-curing after several cycles. In that way, the samples can be reshaped successively. They can also recover their previous form entirely by shape memory effect through stress relaxation and partial D-A disengagement if heated again until it equals or exceeds T_g.

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CRediT authorship contribution statement

I. Lorero: Investigation, Writing – original draft. **B. Rico:** Investigation. **M. Campo:** Writing – review & editing, Resources, Project administration. **S.G. Prolongo:** Conceptualization, Funding acquisition, Resources, Writing – review & editing.

Declaration of Competing interest

The authors declare no conflict of interest.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

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