"Use of eco-friendly epoxy resins from renewable resources as potential substitutes of petrochemical epoxy resins for ambient cured composites with flax reinforcements"

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Abstract

In the last years, some high renewable content epoxy resins, derived from vegetable oils, have been developed at industrial level and are now commercially available; these can compete with petroleum-based resins as thermoset matrices for composite materials. Nevertheless, due to the relatively high cost in comparison to petroleum-based resins, their use is still restricted to applications with relatively low volume consumption such as model making, tuning components, nautical parts, special effects, outdoor sculptures, etc. in which, the use of composite laminates with carbon, aramid and, mainly, glass fibers is generalized by using hand layup and vacuum assisted resin transfer molding (VARTM) techniques due to low manufacturing costs and easy implementation. In this work, we study the behavior of two high renewable content epoxy resins derived from vegetable oils as potential substitutes of petroleum-based epoxies in composite laminates with flax reinforcements by using the VARTM technique. The curing behavior of the different epoxy resins is compared in terms of the gel point and exothermicity profile by differential scanning calorimetry (DSC). In

addition, overall performance of flax-epoxy composites is compared with standardized mechanical (tensile, flexural and impact) and thermal (Vicat softening temperature, heat deflection temperature, thermo-mechanical analysis) tests. The curing DSC profiles of the two eco-friendly epoxy resins are similar to a conventional epoxy resin. They can be easily handled and processed by conventional VARTM process thus leading to composite laminates with flax with balanced mechanical and thermal properties, similar or even higher to a multipurpose epoxy resin.

1. Introduction.

In the last decade a growing interest in the use of materials from renewable origin has been detected. This is mainly due to an increasing sensitiveness about the environment and growing concern about recycling, biodegradability, upgrading, etc. This is particularly accentuated in the polymer composites industry since great amounts of petroleum-based polymers are used. The use of fibers from renewable resources such as flax, jute, hemp, kenaf, among others, is increasing as they can offer interesting properties thus allowing their use as reinforcements for conventional applications which do not require extremely high mechanical performance and even in some technical applications. [1-6] Research on the use of natural fibers as reinforcements in petroleum-based polymeric matrices has been extensively studied and the use of sisal, flax, jute, kenaf, hemp, etc. as natural reinforcements in phenolic, unsaturated polyester and epoxies has been reported [7-11]. Natural fibers are not abrasive, cost effective and health safety while handled and they offer interesting balanced properties as potential substitutes of conventional reinforcements [12, 13]. The energy consumption during processing of natural fibers is lower if compared to conventional glass fiber. In addition to this, natural fibers are characterized by low density values so that, specific mechanical properties can be achieved.[14]

With regard to thermoplastic matrices the use of petroleum-based polymers such as polypropylene (PP), polyamides (PA), polyethylene (PE), polycarbonate (PC), etc. has been widely reported in the last years as matrices for composite materials with flax, jute, hemp, etc. processed by conventional extrusion- compounding, injection, hot-press molding, etc.[15-21] Also, new biobased polymers such as polylactic acid (PLA), polyhydroxyalcanoates (PHAs), starch and protein-based polymers, etc. have been reported as matrices with natural fiber reinforcements. [22-27]

Regarding to thermoset matrices, the use of petroleum-based resins such as epoxies, vinylesters, unsaturated polyesters, phenolics, etc. is generalized for composite processing by conventional technologies: hand lay-up, vacuum bagging, autoclave, resin transfer molding (RTM), filament winding, pultrusion, etc. Important efforts are being done in the field of high biobased content resins, both base resin and hardeners. Interesting results have been obtained with phenolic components derived from cashew nut shell liquid industry (CNSL) [28-31] and commercial hardeners such as phenalkamines have been developed and are widely used at industrial level in the coatings' industry. [32, 33] Other cardanol-based epoxy and novolacs resins are commercially available as either base resins or hardeners.[29] Another interesting and promising research field is the use of vegetable oils as base materials for resins and hardeners.[34, 35] The special structure of some fatty acids such as oleic, linoleic, linolenic, etc. with one, two and three carbon-carbon double bonds respectively, allows some chemical modifications to offer a wide variety of resins suitable for the composites industry. In the last years, the use of epoxidized vegetable oils (EVOs) has increased in a remarkable way and nowadays a wide variety of resins from epoxidized linseed oil (ELO), soybean oil (ESBO), castor oil (ECO), etc. can be found.[36-43] On other hand different hardeners synthesized from fatty acids are available as polyamidoamine adducts and they are widely used in the coating industry for ambient cured systems.[44, 45]

In this work we report the use of two commercial (ambient cured) epoxy resins derived from vegetable oils, characterized by high renewable content, as base resins for composite manufacturing with flax fabrics by using conventional vacuum assisted resin transfer molding (VARTM). The curing behavior of these resins is evaluated by differential scanning calorimetry (DSC) and gel time determination. Mechanical

performance of flax-epoxy composites is determined in tensile and flexural tests as well as impact texts. In addition, thermal response of composites is evaluated by Vicat and heat deflection tests.

2. Experimental.

2.1. Materials.

All three epoxy resins were selected in terms of their suitability as easy flow matrices for laminate composites in model making, special effects, outdoor sculptures, etc. and similar applications.

A petroleum-based epoxy commercial resin Epofer EX 401 supplied by Feroca (Comercial Feroca S.A., Madrid, Spain) was used for comparison purposes. This is a resin derived from the reaction between DGEBFA and epychlorohydrin and it is a general purpose cast epoxy resin. It is supplied with an amine hardener Epofer E 432; it can be ambient cured with a resin:hardener stoichiometric ratio of 100:32 (parts by weight) as defined by the provider.

The two eco-friendly epoxy resins were selected in terms of their potential suitability for similar applications to those of the petroleum-based epoxy. Both eco-friendly epoxy resins can also be ambient cured and typical applications provided by the suppliers are similar to the general purpose petroleum-based epoxy resin.

Greenpoxy 55 from Sicomin (Sicomin Epoxy Systems, Châteauneuf les Martigues, France) was supplied by Resineco. This vegetable oil derived epoxy resin is characterized by a high renewable content (> 55%) and it can be ambient cured with a stoichiometric resin:hardener ratio (parts by weight) of 100:40.

The other eco-friendly epoxy resin was EcoPoxy® (EcoPoxy Systems, Providence, USA) which is obtained as a reaction product between DGEBA, alkyl

glycidyl eter and soybean oil. It can also be ambient cured with the reaction product of ethylene amine, bisphenol A (BPA), benzyl alcohol and soybean oil at a resin:hardener stoichiometric ratio (parts by weight) of 100:25.

As reinforcement, a flax fabric supplied by Hilaturas Ferre (Hilaturas Ferre S.A., Banyeres, Spain) with a surface mass of 230 g m^{-2}, was used.

2.2. Chemical characterization of epoxy resins.

The epoxide content was determined by following the ASTM D 1652-97 standard. Samples were titrated with hydrogen bromide (HBr) in glacial acetic acid solution as HBr reacts stoichometrically with epoxide groups. The iodine number was determined by following the guidelines of the ISO 3961:1996 standard. Samples of the different epoxy oils were dissolved in darkness in a solution containing equal parts of cyclohexane, glacial acetic acid and Wijs solution. After one hour potassium iodide and water was added and the resulting solution was titrated with sodium thiosulfate using starch as indicator. With regard to acid number, the UNE 84157:2000 standard was employed using a normalized ethanolic potassium hydroxide solution with phenolphthalein as indicator. Table 1 summarizes the main parameters regarding chemical characterization of the different epoxy resins. Although some differences can be detected in iodine index and acid number values, which are representative for the overall yield of the epoxidizing process (residual non-epoxidized double bonds and free fatty acids respectively), the epoxide is a key parameter and can play a key role on overall behavior or epoxy resins and their composites. All three epoxies are characterized by equivalent epoxide weight (EEW) values higher than 200 g equiv^{-1} but the two eco-friendly epoxy resins have a oxirane oxygen percentage (close to 7.9%) higher than that of the petroleum-based epoxy (6.7%).

Table 1.- Some chemical properties of epoxy resins used as base matrices for flax-epoxy composite laminates processed by VARTM techniques.

Property	Eco-friendly EcoPoxy®	Eco-friendly Greenpoxy 55	Petroleum-based EpoFer EX 401
Epoxide content	0.49	0.49	0.42
Oxirane oxygen (%)	7.9	7.8	6.7
Iodine index	4.0	9.9	3.5
Acid number	0.15	3.3	2.5

2.3. VARTM processing of flax-epoxy composites.

Manufacturing of flax-epoxy composites was carried out by the VARTM (Vacuum Assisted Resin Transfer Molding) process. This consists on an infusion resin process by using vacuum. The reinforcement fabric is placed and shaped onto a mold or surface and the system is sealed with a plastic bag with a resin inlet and an outlet connected to a vacuum pump as it can be observed in Scheme 1. Then the vacuum pump is connected and all the air is removed from the system and once this has occurred, the resin is transferred to the reinforcement by vacuum aid.
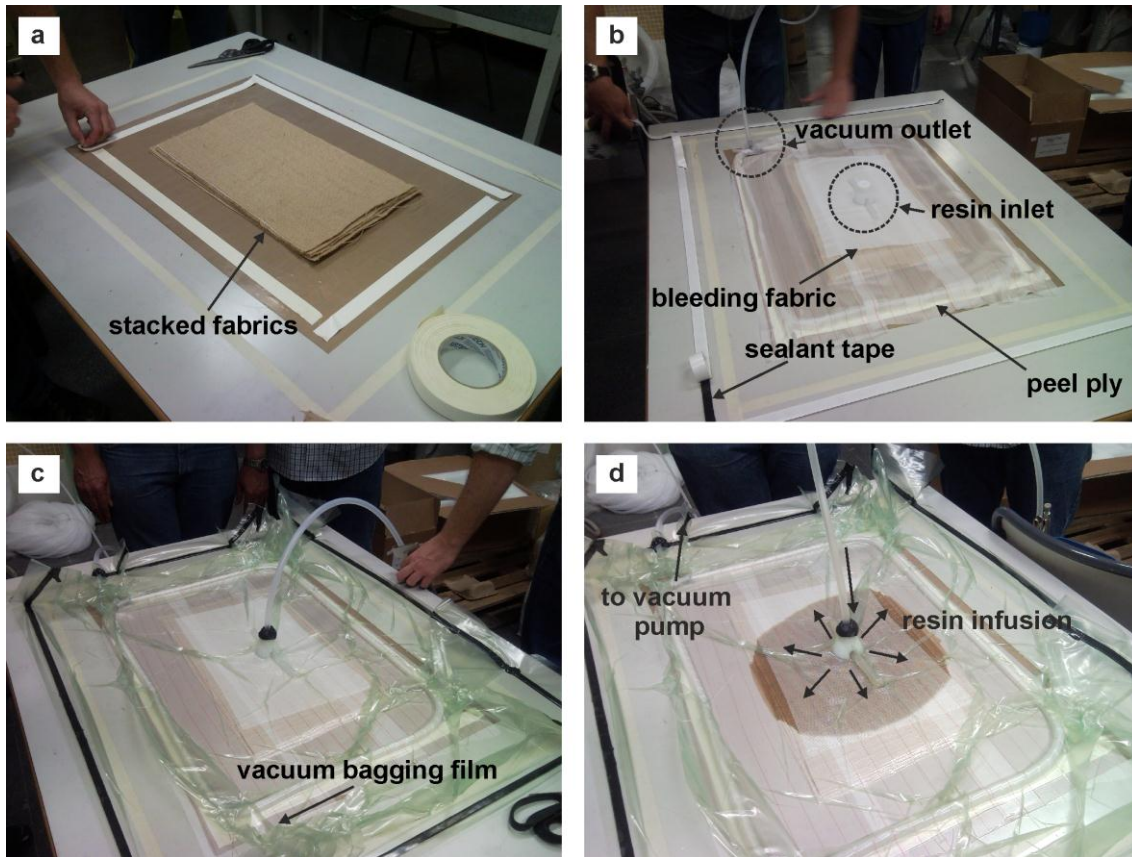
Scheme 1.- Different stages of the vacuum assisted resin transfer molding (VARTM) of composites based on flax fabrics and epoxy resins.

The procedure used for composite preparation is as follows. In a first stage, six flax fabrics were stacked on a table with a polytetrafluorethylene sheet to ensure easy unmolding (Scheme 1a). After this, the peel-ply sheet was placed over the stacked fabrics and following the filter media or bleeding fabric was placed to ensure good resin flow and distribution (Scheme 1b). Finally, the vacuum bag covered all the system and it was sealed with mastic sealing tape (Scheme 1c). Once these stages were completed, the vacuum outlet and the resin inlet were appropriately placed and finally, by using a vacuum pump system, the resin was transferred into the system thus embedding all flax fabrics (Scheme 1d).

2.4. Characterization of the curing behavior.

The curing behavior of the different epoxy resins was followed with differential scanning calorimetry (DSC) in a Mettler Toledo 821 (Mettler-Toledo, Schwerzenbach, Switzerland) with samples sizing 4-6 mg in nitrogen atmosphere (60 mL min^{-1}). The thermal program consisted in a first heating stage from 30 ℃ to 300 ℃ at a heating rate of 10 ℃ min^{-1}, followed by a cooling process up to 30 ℃ at -10 ℃ min^{-1} and subsequent heating up to 350 ℃ at 10 ℃ min^{-1}. The first heating program was used to determine the exothermicity and the second heating stage was used to determine the glass transition temperature (Tg).

Furthermore an isothermal test was conducted at 60 ℃ for three hours in nitrogen atmosphere (60 mL min^{-1}) to evaluate the curing behavior in isothermal conditions.

2.5. Mechanical characterization of flax-epoxy composite laminates.

Mechanical performance of flax-epoxy composite laminates was evaluated in tensile, flexural and impact conditions. Tensile and flexural tests were conducted on universal test machine Ibertest ELIB 30 (S.A.E. Ibertest, Madrid, Spain) following the guidelines of the ISO 527-5 and ISO 178 respectively with a 5 kN load cell at room temperature. Tensile and flexural samples sized 200 mm x 20 mm and 80 mm x 10 mm respectively with an average thickness close to 4 mm. The crosshead rate was set to 5 mm min^{-1}. At least five different samples were tested and average values for strength, elongation at break and modulus were calculated.

Impact tests were carried out with a Charpy impact pendulum by Metrotec (Metrotec S.A., San Sebastián, Spain). A 6 J Charpy pendulum was used following the

guidelines of the ISO 179 standard. Five different samples were tested and average values were calculated.

2.6. Fracture analysis by microscopic techniques.

Scanning electron microscopy (SEM) was used for surface characterization of flax-epoxy composite laminates with fractured surfaces from impact tests. A scanning electron microscope FEI mod. Phenom (FEI, Oregon, USA) was used. Prior to surface observation, samples were coated with a gold-palladium alloy in a Sputter Coater EMITECH mod. SC7620 (Quorum Technologies Ltd., East Sussex, United Kingdom).

### 2.7. Thermal characterization of flax-epoxy composite laminates.

Heat deflection temperature (HDT) was determined by the ISO 75 standard with an applied force of 75 g and using the B method with a heating rate of 120 ºC h^{-1} on samples sizing 80 x 10 x 4 mm^3. In addition, the Vicat softening temperature (VST) was determined by following the ISO 306:2004 standard with an applied force of 50 N at a heating rate of 50 ºC h^{-1}.

The coefficient of thermal expansion (CTE) was determined with a thermo mechanical analyzer TMA mod. Q 400 (TA Instruments, New Castle, USA) with samples sizing 7x7x3 mm^3. The expansion procedure was used and the heating program was from 0 ºC up to 140 ºC with a heating rate of 2 ºC min^{-1} in nitrogen atmosphere.

3. Results and discussion.

3.1. Characterization of the curing process.

Fig. 1 shows the comparative DSC curves (first and second heating curves) for the petrochemical epoxy resin and the two high renewable content epoxy resins. The first heating program is representative for the exothermicity during the crosslinking which is an important parameter to be considered in ambient cured systems. The second heating program is useful to determine the glass transition temperature (Tg).
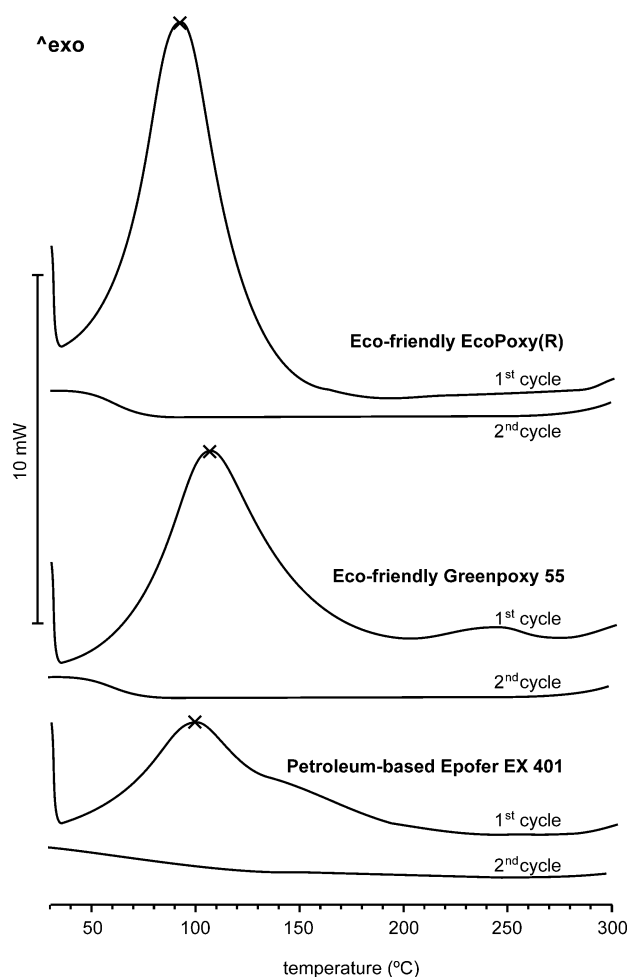
Figure 1.- Comparison of the DSC dynamic curves, first and second heating cycles, for a petroleum-based (Epofer XE 401) and two eco-friendly epoxy resins (EcoPoxy® y Greenpoxy 55).

Table 2 summarizes the main thermal parameters obtained from DSC curves. With regard to the curing process, the peak temperature can be representative for the fastness of the curing reaction. As we can see, the petroleum-based epoxy resin shows a peak temperature close to 100 ºC and the two high biobased content epoxy resins show a peak temperature of 93.1 ºC and 106.3 ºC for EcoPoxy® and Greenpoxy 55 respectively. This indicates that Ecopoxy® curing reaction is slightly faster than Greenpoxy 55 resin and this could be important for processing as this parameter is directly related to viscosity increase due to crosslinking reactions. In addition to this, as it can be observed in Fig.1 the curing peak for EcoPoxy® is more narrow than the curing peak for Greenpoxy 55 and the petroleum-based epoxy thus indicating that EcoPoxy® resin crosslinking is faster than the other two tested epoxy resins. With regard to the exothermicity, the two high renewable content epoxy resins show exothermicity values higher than 300 J g^{-1} while the petroleum–based epoxy resins shows lower exothermicity values close to 200 J g^{-1}; this indicates that the curing process of the petroleum-based epoxy is slower at room temperature than the two eco-friendly resins. It is possible to estimate the glass transition temperature in the second heating curve as a step in the baseline. As we can see in Table 2, the two eco-friendly epoxy resins show Tg values in the 60-70 ºC range which are interesting values for technical applications; nevertheless the petroleum-based epoxy resin does not show a clear Tg value by DSC technique.

Table 2.- Thermal characteristics of the curing (1st heating cycle) and cured (2nd heating cycle) epoxy resins from different sources obtained by DSC analysis.

Base resin for flax-epoxy composite laminates	1st heating		2nd heating
	Peak temperature (ºC)	Enthalpy (J g^{-1})	Glass transition temperature (ºC)
Petroleum-based Epofer EX 401	99.7	196.8	not clear
Eco-friendly EcoPoxy®	93.1	332.5	66.9
Eco-friendly Greenpoxy 55	106.3	305.9	65.4

Fig. 2 shows the DSC curves for the isothermal curing of the different epoxy resins at 60 ºC. All DSC curves are similar in shape as they start from a peak temperature and the released heat decreases as the time increases until an asymptotic stable horizontal baseline is achieved which is representative for the end of the curing process. As it can be observed in Fig. 2, the EcoPoxy® resin needs a curing time of about 21 min to reach a fully cured material. With regard to the Greenpoxy 55 resin, the minimum time to reach a fully cured material is nearly 40 min while the petroleum-based epoxy resin needs intermediate curing times around 33 min to fully cure. This calorimetric information is in total agreement with gel time values at 60 ºC as the eco-friendly EcoPoxy® resin shows a gel time of about 1 min 10 s while the other resins, petroleum-based Epofer EX 401 and eco-friendly Greenpoxy 55 show higher gel time values of about 19 min 30 s and 8 min 31 s respectively. As these resins can be ambient cured, the gel time at room temperature can give useful information for VARTM processing; therefore, the gel time value is 10 min 51 s for the fast eco-friendly

EcoPoxy® while Epofer EX 401 and Greenpoxy 55 show similar gel times of 3 h 22 min 50 s and 3h 11 min 50 s respectively. So that we can observe similar reactivity for Epofer EX 401 and Greenpoxy 55 at room temperature while the other eco-friendly epoxy resin (EcoPoxy®) shows faster curing process.
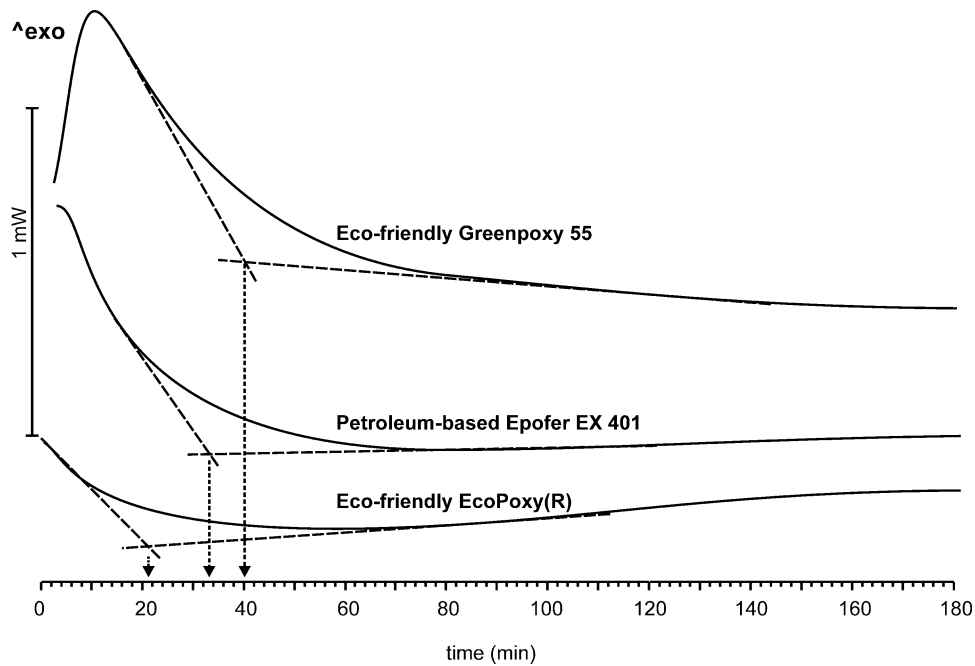

Figure 2.- Comparison of the DSC curves for the isothermal curing of a petroleum-based (Epofer XE 401) and two eco-friendly epoxy resins (EcoPoxy® y Greenpoxy 55) at 60 °C.

3.2. Mechanical characterization of flax-epoxy composite laminates.

Firstly, mechanical behavior of ambient cured flax-epoxy composite laminates in tensile conditions is described. Fig. 3 shows a comparative plot of tensile strength and modulus of flax-epoxy composite laminates obtained by VARTM with petroleum-based epoxy and the two ambient cured eco-friendly resins. We can see that tensile strength and modulus of petroleum-based laminates are similar to those obtained with

the use of the eco-friendly epoxy EcoPoxy® although tensile strength is slightly higher for composites with EcoPoxy® resin while the modulus is close to 1.0 GPa for composite laminates with both resins. With regard to the eco-friendly resin Greenpoxy 55, it is important to remark that composite laminates obtained with it, show higher tensile strength values (close to 80 MPa) and slightly higher tensile modulus, around 1.2 GPa. These results are in agreement with previous results about chemical characterization of all three epoxy resins. As we have described in Table 1, the epoxide content of the bio-based epoxy resins is close to 0.49 which represents an oxirane oxygen percentage of 7.8% and 7.9% for Greenpoxy 55 and EcoPoxy® respectively while the petroleum-based epoxy resin is characterized by a slightly lower epoxide content of 0.42 which leads to oxirane oxygen percentage of 6.7%. Higher oxirane oxygen percentages are directly related to formation of more interlock points during the curing reaction and this leads to higher mechanical resistance properties as detected in Fig. 3. In general terms, tensile behavior of composite laminates obtained with the two eco-friendly resins is higher to that offered by a multi-purpose cost-effective petroleum-based epoxy due to higher oxirane oxygen percentages for eco-friendly epoxy resins.
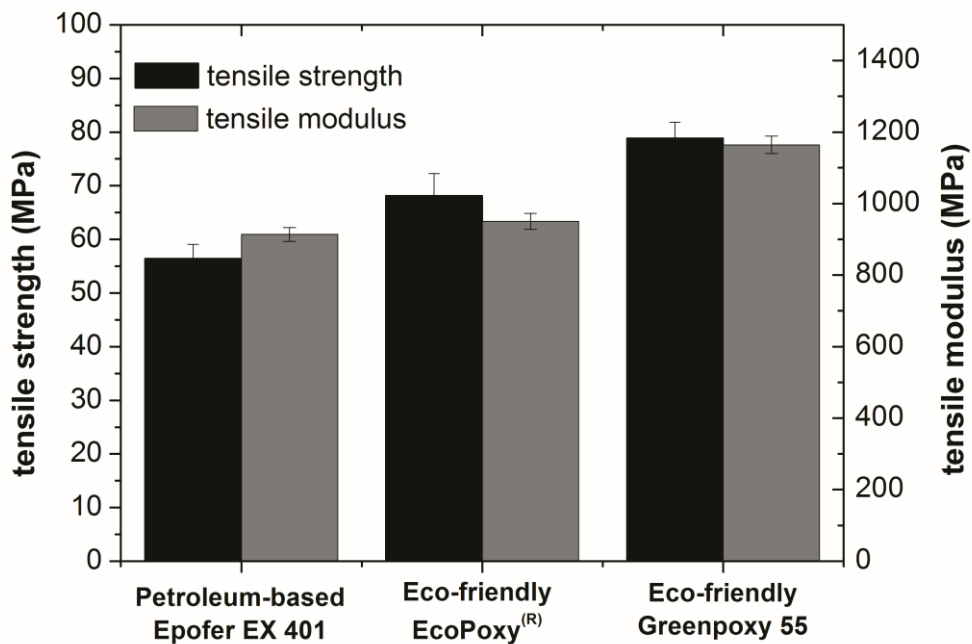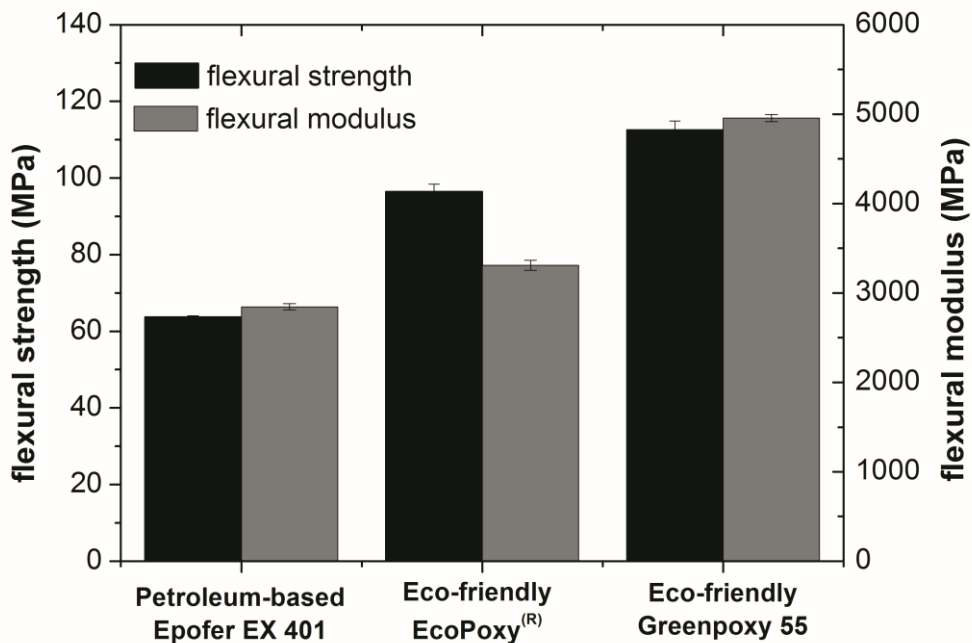
Figure 3.- Comparative bar plot for tensile strength and modulus of ambient cured flax composite laminates processed by VARTM with a petroleum-based (Epofer XE 401) and two eco-friendly epoxy resins (EcoPoxy® y Greenpoxy 55).

Similar tendency is observed for flax-epoxy composite laminates in flexural conditions with the three tested ambient cured epoxy resins (Fig. 4). Flexural modulus for composite laminates with petroleum-based epoxy is close to 2.8 GPa and higher values for flexural modulus are obtained for the two eco-friendly epoxy resins (3.3 GPa and 4.9 GPa for EcoPoxy® and Greenpoxy 55 respectively). Once again, we observe a direct relationship between the oxirane oxygen percentage of the tested epoxies and mechanical performance of composites derived from them, thus indicating that the epoxide content is a key parameter to be considered if we need high performance composite materials. Similar tendency can be detected with regard to flexural strength; the petroleum-based epoxy resin with an oxirane number of 6.7% is lower (63.8 MPa) than the values corresponding to the two eco-friendly epoxy resins (96.5 MPa and 112.6

MPa for EcoPoxy® and Greenpoxy 55 respectively) with higher oxirane numbers (>7.8%). Once again, mechanical performance of composite laminates obtained with eco-friendly resin Greenpoxy 55 is the best if compared to the other resins tested in this work.

Figure 4.- Comparative bar plot for flexural strength and modulus of ambient cured flax composite laminates processed by VARTM with a petroleum-based (Epofer XE 401) and two eco-friendly epoxy resins (EcoPoxy® y Greenpoxy 55).

Both strength and modulus are considered as resistant mechanical properties. A mechanical property representative for ductile behavior can be the absorbed energy under impact conditions which is a useful parameter for selecting the appropriate material for a particular application. Table 3 summarizes the results obtained in the Charpy impact test for composite laminates with the petroleum-based and the two eco-friendly epoxy resins. As expected, ductile properties have opposite tendency since high mechanical strength and modulus are related to high stiffness and this indicates low

deformation capacity (directly related to oxirane oxygen percentage). As energy absorption is directly related to deformation capacity thereby, high strength and modulus would lead to low ductile properties. As we can see in Table 3, the absorbed impact energy for the petroleum-based resin is the highest for the three resins tested in this work, reaching values of about 33 KJ m^{-2} while the absorbed energy under impact conditions is remarkably decreased up to values of 23 KJ m^{-2} and 19 KJ m^{-2} for eco-friendly resins EcoPoxy® and Greenpoxy 55 respectively.

Table 3.- Absorbed energy under impact conditions obtained in the Charpy impact test of ambient cured flax composite laminates obtained by VARTM with a petroleum-based (Epofer EX 401) and two eco-friendly epoxy resins (EcoPoxy® y Greenpoxy 55).

Base resin for flax-epoxy composite laminates	Impact energy (KJ m^{-2})	SD
Petroleum-based Epofer EX 401	32.6	0.88
Eco-friendly EcoPoxy®	22.5	0.07
Eco-friendly Greenpoxy 55	18.7	0.96

In addition to mechanical characterization, a SEM study on fractured surfaces from impact tests was carried out in order to know the extent of fiber-matrix interactions (Fig. 5). As shown in Fig. 5a and 5b, poor fiber-matrix interaction is detected in fractured composite laminates obtained with petro-based epoxy resin Epofer EX 401 as a clearly evident gap between fiber and matrix is observed. This is in total agreement with previous mechanical properties as described before since tensile and flexural strength are highly sensitive to fiber-matrix interactions. Low interactions are

responsible to stress concentration effects and this promotes early fracture with relatively low strength values. On other hand, if strong fiber-matrix interactions are achieved in composite laminates, the polymeric matrix can easily transfer stress to fibers by shear and this results in high strength values. This situation can be observed for fractured composite laminates with eco-friendly EcoPoxy® resin (Fig. 5c and 5d) and Greenpoxy 55 (Fig. 5e and 5f). Fractured surfaces of composite laminates with EcoPoxy® show a small gap between fiber and matrix and this is representative for more intense interactions which lead to higher tensile and flexural strength values as described previously. With regard to composites with Greenpoxy 55 as matrix, the gap between fiber and matrix is still smaller thus having a positive effect on mechanical resistant properties such as strength and modulus.
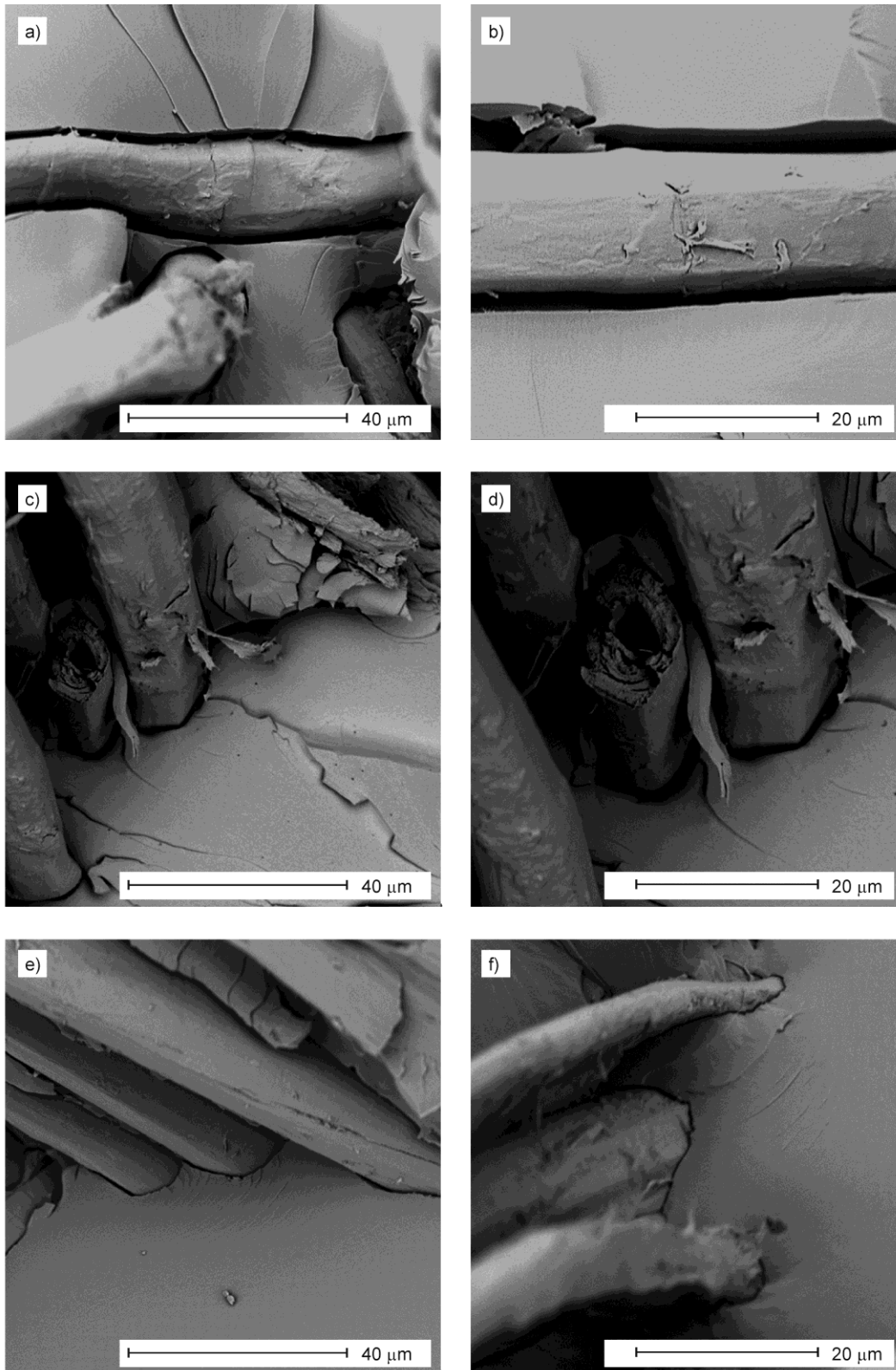
Figure 5.- SEM images of fractured surfaces from Charpy impact test of ambient cured flax composite laminates processed by VARTM with a petroleum-based (Epofer XE 401) and two eco-friendly epoxy resins (EcoPoxy® y Greenpoxy 55).

*3.3. Thermal characterization of flax-epoxy composite laminates.*

In this section, some thermal properties of flax-epoxy composite laminates are described. Table 4 shows the heat deflection temperature (HDT) and Vicat softening temperature (VST) values of flax-epoxy composites with a petroleum-based and two eco-friendly epoxy resins. The evolution of these thermo-mechanical properties is similar to that observed for mechanical strength and modulus as these thermal properties are directly related to mechanical response. Therefore, flax composite laminates based on the epoxy resin with lower strength and modulus (petroleum-based epoxy Epofer EX 401) in the previous section shows the lowest HDT and VST values, located at 50.1 ℃ and 97.8 ℃ respectively. With regard to flax composites with eco-friendly epoxy resins, as they show higher mechanical properties, HDT and VST values are also higher. So that, the HDT values are close to 55.6 ℃ and 57.5 ℃ for eco-friendly EcoPoxy® and Greenpoxy 55 resins respectively. Therefore, we can observe some differences in thermal response for the three considered epoxy resins. With regard to Vicat softening temperature (VST), the differences are even higher and composites with eco-friendly EcoPoxy® resins offer VST values about 20 ℃ higher to that offered by petroleum-based epoxy. In the case of composites with Greenpoxy 55, the VST increase is still higher (+55 ℃ if compared to petroleum-based epoxy). These differences in thermal response can be attributable to the matrix resin as all three composites possess the same reinforcement type and amount. Higher VST and HDT values are related to highly crosslinked structures which restrict chain mobility. As we have described previously, the oxirane oxygen is a key parameter since it determines the crosslinking density that can be achieved during the curing process. The two eco-friendly epoxy resins are characterized by higher oxirane number values (>7.8%) than the petroleum-based epoxy resin (around 6.7%) and this is directly related to the higher

thermal performance of the two eco-friendly resins if compared to the petroleum-based epoxy.

Table 4.- Heat deflection temperature (HDT) and Vicat softening temperature (VST) values for ambient cured flax composite laminates obtained by VARTM with a petroleum-based (Epofer XE 401) and two eco-friendly epoxy resins (EcoPoxy® y Greenpoxy 55).

Base resin for flax-epoxy composite laminates	HDT (ºC)		VST (ºC)	
	average	SD	average	SD
Petroleum-based Epofer EX 401	50.1	1.79	97.8	5.65
Eco-friendly EcoPoxy®	55.6	2.78	117.2	6.43
Eco-friendly Greenpoxy 55	57.5	2.04	152.9	3.25

On other hand, thermo-mechanical analysis has been used to evaluate the thermal stability of flax composite laminates. In particular, the glass transition temperature (Tg) and the coefficient of thermal expansion (CTE) before and after the glass transition have been determined. Fig. 6 shows comparative TMA curves for flax composite laminates with a petro-based and the two eco-friendly epoxy resins. As we can see, we can detect a slope change for all systems and this is directly related to the glass transition temperature. The coefficients of thermal expansion (CTE), before and after the glass transition have been calculated as the line slopes and summarized values are presented in Table 6. Once again, higher oxirane number values are directly related to higher Tg values as more interlock points are obtained during the curing process.
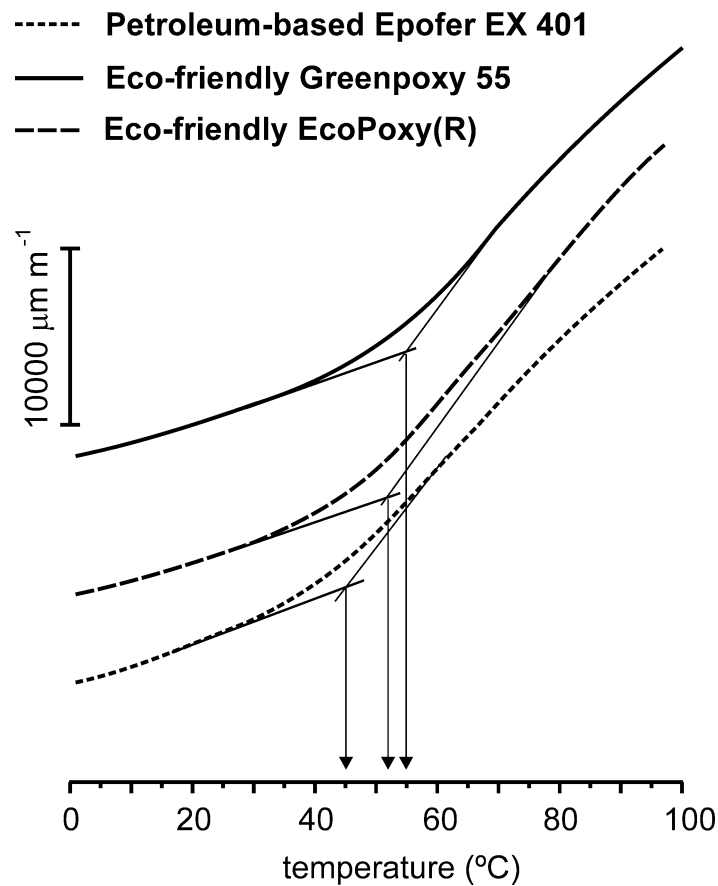
Figure 6.- Comparison of the thermo-mechanical (TMA) curves corresponding to ambient cured flax composite laminates processed by VARTM with a petroleum-based (Epofer XE 401) and two eco-friendly epoxy resins (EcoPoxy® y Greenpoxy 55).

The glass transition temperatures obtained by TMA analysis slightly differ from values obtained with DSC analysis but the tendency is maintained. Therefore, flax composites with eco-friendly resins show glass transition temperatures of 52.3 ℃ and 52.1 ℃ for EcoPoxy® and Greenpoxy 55 respectively. These values are in accordance to those obtained by DSC analysis on individual resins. With regard to the petroleum-based composites, the glass transition temperature is close to 45.4 ℃, slightly lower than the eco-friendly systems. These results are in accordance to the general mechanical performance described previously. In general terms, systems with lower Tg values allow more deformation so that ductile properties are higher than mechanical resistant

properties such as strength and modulus. Additionally, the coefficient of thermal expansion (CTE) before the glass transition temperature follows opposite tendency as observed for mechanical resistant properties as the CTE is directly related to deformation ability (Table 5). Therefore, the CTE for flax composites with petroleum-based epoxy is about $1.18 \cdot 10^{-4}$ μm (m ºC)$^{-1}$ while CTE for flax composites with eco-friendly epoxy resins are slightly lower: $1.14 \cdot 10^{-4}$ μm (m ºC)$^{-1}$ and $1.10 \cdot 10^{-4}$ μm (m ºC)$^{-1}$ for EcoPoxy® and Greenpoxy 55 respectively. With regard to the CTE over the glass transition temperature, it is important to remark that higher values are obtained for all systems and no significant differences are detected with values close to $4.0 \cdot 10^{-4}$ μm (m ºC)$^{-1}$.

Table 5.- Glass transition temperature and coefficient of thermal expansion (CTE) obtained by TMA analysis, for ambient cured flax composite laminates obtained by VARTM with a petroleum-based (Epofer EX 401) and two eco-friendly epoxy resins (EcoPoxy® y Greenpoxy 55).

Base resin for flax-epoxy composite laminates	Tg (ºC)	CTE (below Tg) [μm (m ºC)$^{-1}$]	CTE (over Tg) [μm (m ºC)$^{-1}$]
Petroleum-based Epofer EX 401	45.4	$1.18 \cdot 10^{-4}$	$3.70 \cdot 10^{-4}$
Eco-friendly EcoPoxy®	52.3	$1.14 \cdot 10^{-4}$	$4.14 \cdot 10^{-4}$
Eco-friendly Greenpoxy 55	55.1	$1.10 \cdot 10^{-4}$	$3.70 \cdot 10^{-4}$

4. Conclusions.

In this work, the potential of two new commercially available eco-friendly epoxy resins is evaluated in comparison to a conventional petroleum-based epoxy resin for general purposes. All three systems can be ambient cured and the calorimetric study has revealed similar behavior of all three systems in dynamic curing. In addition, curing behavior in isothermal conditions at 60 ºC reveals low curing times for all systems. So that, it is possible to conclude that the curing behavior of the petroleum-based epoxy resin and the two eco-friendly epoxy resins is similar so that they can be used in similar applications.

These epoxy resins have been used as base resins for VARTM processing with flax fabrics to obtain composite laminates. Mechanical characterization of these composite laminates reveals that the best mechanical resistant properties (tensile and flexural strength and modulus) are obtained with the two eco-friendly epoxy resins (EcoPoxy® and Greenpoxy 55) and this is related to good fiber-matrix interactions as small gaps between fibers and the epoxy matrix are observed in the SEM study. The petroleum-based epoxy Epofer EX 401 offers lower mechanical performance but, in contrast, maximum ductile properties are obtained under impact conditions which is representative for energy absorption.

Thermal response of flax composite laminates made with different epoxies are in total agreement with mechanical performance as eco-friendly epoxy resins lead to flax laminates with higher thermal stability. With regard to thermal isolation properties, all three epoxy resins lead to flax composite laminates with low thermal conductivity which is an important property for using these composite laminates in technical sectors.

Finally we can conclude that new commercially available epoxy resins characterized by high renewable content offer good balanced behavior in terms of

ambient curing conditions, VARTM processing, mechanical performance and thermal stability of composite laminates with flax fibers if compared to conventional petroleum-based epoxies. Nevertheless petroleum-based epoxies are still cost-effective if compared to eco-friendly resins and this is the main restriction to a wide use at industrial level of eco-friendly epoxies.

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