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Abstract.

Flax fibers are particularly relevant in composite fabrication due to natural availability and mechanical properties close to glass fibers. We explore flax fiber-containing epoxy-amine (DGEBA/DETA) polymers with wide industrial applicability. Flax fibers impact the glass transition temperature (DSC), with a T_g drop of 67°C at 30 wt.% loading. For deeper insight, we develop here an original mixing calorimetry approach to follow *in situ* DGEBA/fibers and DETA/fibers interphases. DGEBA does not interact quantitatively with flax fibers while DETA/fibers interaction is significantly exothermic and directly related to fibers content. DETA/water interaction only accounts for 25% of total heat effect. Experiments run by contacting DETA with each of the main components of flax fibers (cellulose, hemicelluloses, lignin) point out systematic exothermic effects. Considering their mean proportion in flax fibers, the sum of enthalpy contributions agrees well with the overall effect measured with entire fibers. The main contribution (58%) arises from cellulose. XRD analyses and literature considerations allow concluding on the direct implication of DETA molecules with cellulose chains, resulting in T_g decrease. This work clarifies the chemical role of flax fibers in DGEBA/DETA thermosets, down to the molecular-scale, and highlights that mixing calorimetry is a powerful tool to follow interphase formation *in situ*.

1. Introduction

Bio-based products are increasingly attracting attention worldwide, with the objective to develop ever-more ecological and sustainable added-value materials, for a large number of applications [1-3]. In this context, plant fibers are particularly well suited to enter the composition of composite materials according to their morphology and mechanical properties, with an expected view to allow for mass decrease, lower cost and easier recycling for the manufacture of diversified eco-friendly materials. This is nowadays still not the case as it is often necessary to put at least equivalent or higher masses of flax fabric to obtain equivalent properties to those of glass/thermoset composites. Also, the price of natural fibers is still high due to the huge demand from the garment textile industry but it is expected to decrease in the future [4]. Among such natural sources, hemp, bamboo and flax (linseed) fibers are particularly appealing due to their availability and mechanical inner strength [4, 5]. Therefore, they have been the object of various studies in the field of composites. Flax fibers, arising from *the Linum usitatissimum* plant, may be seen for example as a good alternative to glass fibers, due to their similar mechanical properties, eco-friendly character and lower cost [5-7]. Such fibers may therefore be incorporated in [1] inorganic or organic matrices for improving their mechanical behavior.

Among organic matrices, epoxy-amine mixtures have demonstrated their relevance for a wealth of applicative purposes such as sealants, paints and coatings in diverse strategic industrial sectors such as ground transportation, aeronautics, construction and others.[2,7] They represent indeed an important class of high performance thermosetting polymer precursors. Their major assets are a high Young modulus, resistance to corrosion, thermal stability and low shrinkage under curing. Epoxy thermosets are often obtained by polymerization of epoxide prepolymers with (poly)amine hardeners, ultimately leading to epoxy-amine networks. Such

monomers may be associated to bio-sources fibers with the objective to modulate the physicochemical/mechanical properties of the final product.[2,8] In such composites, the interfacial domain between the fibers and the matrix is thus undoubtedly an important factor in the final characteristics of the material. In fact, since polymerization occurs directly in the presence of the fibers, the interaction of the latter with the epoxide and amine reactants could play a major role in tailoring the final material properties, e.g. mechanical, but also possibly on its durability upon ageing.

Even though this interphase between fibers and epoxide-amine systems likely has a direct impact on the composite properties, it did not receive specific attention to this date, and the type of interaction involved is still unclear. The chemical nature of the natural fibers considered, as well as their humidity could however play an essential role in the interphase formation.[9] Our recent observations indicated that the contact of a common polyamine hardener, namely diethylenetriamine (DETA), with flax fibers led to a shift of the amine-to-epoxide mole ratio r for the Bisphenol A diglycidyl ether (DGEBA)/DETA system.[10] These findings thus highlighted the role of the DETA/flax fibers interaction in the polymerization reaction. It is now interesting to determine the origin of these effects and to quantify them. Better understanding these phenomena could indeed allow controlling these effects and potentially taking advantage of them for further tailoring material properties. Also, because of their hydrophilicity that tends to prevent good adhesion between natural fibers and the matrix, it is common to carry out a treatment on the fibers to overcome this issue, typically involving a "sizing" agents.[11] However, considering the involvement of chemical products and dedicated steps to undergo this treatment, these types of steps remain questionable from an ecological point of view. Better apprehending the role of humidity and fiber chemistry on their interaction with the matrix may help unveil new approaches for fibers handling/engineering.

In this paper, we aimed at exploring in details such flax fibers - amine interphase (using DETA as polyamine), especially by developing an isothermal mixing microcalorimetry strategy

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to follow *in situ* interphase formation and quantify the related interaction energetics, considering a DGEBA/DETA epoxide-amine model matrix for composite manufacturing. DSC experiments confirmed the role played by flax fibers on such matrices thermal properties. To go further, the influence of the chemical components of natural flax fibers (cellulose, hemicelluloses and lignin) as well of water on the interphase properties was explored based on mixing calorimetry and X-ray diffraction (XRD) analyses.

2. Experimental section

2.1. Materials

Flax fibers, in the form of a 2/2 Serge fabric with a surfacic weight of 360 g m^{-2}, were obtained from Depestele (Le Bocasse, France). The constitutive fibers were previously coated with a sizing agent used to facilitate their weaving. The fabric was stored in a climatic chamber at 25°C, 60% HR (relative humidity) until use. To facilitate experiments, it was cut into sections of 5 mm x 3 mm.

To evaluate the effect of several parameters, the fibers were used as such or after specific drying or washing treatments. Drying was operated in an oven preset to 103°C for 24h and the dried fibers were then stored in a desiccator before analysis. The so-called "washing" treatment was undergone to eliminate the sizing agent associated to the fibers. To this aim, the latter were rinsed with ultrapure water several times in a tube until the water became transparent (elimination of the sizing agent leading to a yellowish coloration). Then, the washed fibers were dried at room temperature for one day.

In order to examine one by one the three main components of flax fibers, cellulose (Sigma Aldrich, USA), hemicellulose from corn (Limagrain, France) and lignin from wheat (CIMV, France) were used, in the form of powders.

The epoxide monomer used was Bisphenol A diglycidyl ether (DGEBA), reference DER 332 from Sigma Aldrich (molecular weight 348.52 g mol^{-1}), with a functionality of 2 (i.e. two epoxide terminal groups per DGEBA molecule). The selected amine hardener, acting as a curing agent for the DGEBA epoxide compound, was diethylenetriamine (DETA) from Sigma Aldrich (molecular weight 103.17 g mol^{-1}) with a functionality of 5 protons, arising from 2 primary amines and 1 secondary amine. **Figure S1** (Supporting Information) reports the chemical formulas of these two monomers and the calculation relationship for the stoichiometry ratio r, taking into account the amine and epoxide functionalities. In order to target complete reticulation of the epoxy matrix, stoichiometric proportions of reactants ($r = 1$) were used throughout this work for the preparation of DGEBA/DETA samples. This ratio was indeed selected to offer the most favorable conditions of analysis, as it allows the final thermoset polymer to reach the maximal glass transition temperature, $T_{g\infty}$. Polymerization of the DGEBA/DETA mixtures was undergone at 140°C for 1h, after a first period at room temperature for 3h, starting from 10 g DGEBA and 1.18 g DETA. In the case of DGEBA/DETA/flax fibers composites, the procedure followed is depicted in **Figure 1**, starting from 3 g DGEBA, 0.35 g DETA and 1.5 g fibers (~ 30 wt.% fiber content).
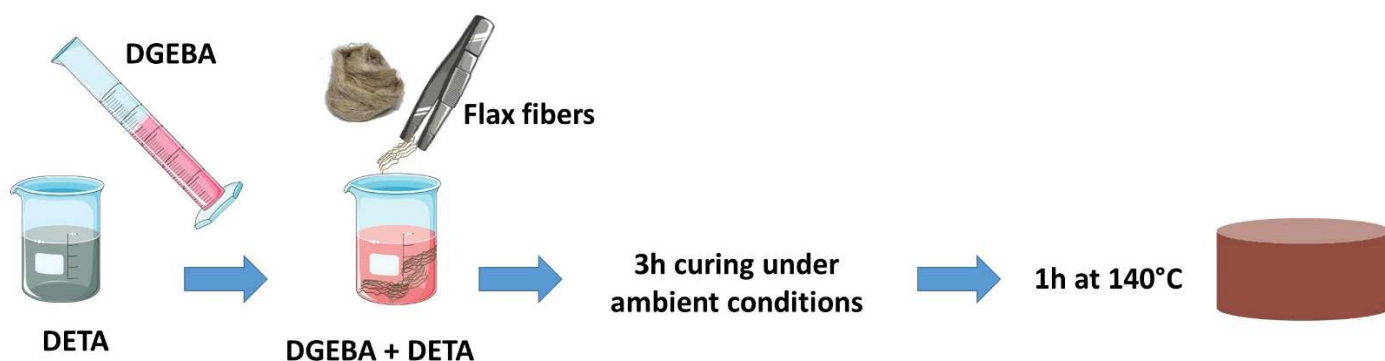
Figure 1. Procedure for DGEBA/DETA/flax fibers composite preparation

2.2. Mixing calorimetry

The interaction between DGEBA and DETA monomers and flax fibers was followed, and quantified from an enthalpy point of view, using isothermal mixing microcalorimetry (C80 Setaram, France). The measuring calorimeter cell made of Hastelloy® consists in two compartments separated by a Teflon® membrane. The calorimeter internal temperature was set to either 25°C (common temperature for composite preparation) or 50°C (to increase DGEBA fluidity and facilitate infusion processes),[12] as specified in the text. After temperature equilibration and start of baseline recording, the membrane is punctured thanks to the lowering of a piercing helix-shaped device inside the cell, thus allowing contact between the upper and lower compartment contents. In this work, the upper compartment typically contained liquid DETA or DGEBA (1.5 g) while the lower compartment contained the flax fiber sections or their individual chemical components as powders in proportions indicated in the text, typically up to 0.4 g. Upon contact, the corresponding heat flow is measured via a thermopile (3D sensor technology surrounding the measurement cell) composed of 19 superimposed thermo-elements, each thermo-element containing 38 thermocouples. The heat flow measurement is made relatively to an identical but empty reference cell (containing only the membrane) included in a second parallel thermopile, connected in opposition to the measurement one. Based on the calibration of the calorimeter (heat flow resolution: 0.10 µW, temperature accuracy: ± 0.1°C), integration of the heat flow signal over time, using the Calisto® software, leads to the enthalpy

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of the reaction/interaction studied. Potassium chloride (KCl, Merck) dissolution in water was used as regular checks for calibration. After each experiment, a blank experiment was carried out after return of the baseline to its stabilized level, to take into account the eventual asymmetry of the calorimeter setup. The obtained ΔH_{blank} enthalpy value was then subtracted from the raw measured enthalpy to determine the corrected reaction enthalpy that will be considered (ΔH_R). Note that, in this work, all the given ΔH_R values refer to interaction of the several types of compounds (fibers, water, cellulose, hemicelluloses or lignin) with a fixed mass of 1.5 g of DGEBA or DETA, respectively.

2.3. Physicochemical characterization

Differential scanning calorimetry (DSC) was used for the determination of glass transition temperature (T_g) of the various epoxide-amine-based networks prepared in this work, as indicated in the text. DSC runs were acquired on a Netzsch 204 apparatus, and data processing was performed using the Proteus® software. Calibration was checked with indium fusion. The samples were placed in pierced aluminum crucibles and the mass was measured with the accuracy of $\pm$ 0.1 mg. Three runs were programmed, from -70 °C to 180 °C, typically at a heating rate of 50 K min^{-1}. Between two cycles, an isothermal step of 5 min was integrated. This increase in heating rate was intended to facilitate determination of T_g. Note that the T_g values reported in this manuscript refer to the "midpoint" ones obtained at the second run.

X-ray diffraction (XRD) was used to analyze flax fibers before and after contact with DETA. To this aim, XRD patterns were acquired using an Equinox 100 diffractometer (INEL, France) equipped with a cobalt anticathode (λ_{Co} =1.78897 Å). The whole 2θ range was recorded simultaneously using a curved detector, for 2h acquisitions.

Scanning electron microscopy (SEM) images were recorded on a FEI Quanta 450 microscope operated at 10 kV and under low vacuum (typically around 100 Pa of water vapor).

3. Results and discussion

One of the key parameters describing a thermosetting polymer network is its glass transition temperature (T_g). The T_g value measured for the polymerized DGEBA/DETA "reference" system at stoichiometry was measured to 146 ± 5 °C (midpoint). In contrast, the addition of flax fibers (30 wt.%) prior to polymerization drastically decreased this value down to 79 ± 5 °C (**Figure 2a**). This decrease of 67°C is evidence of a clear interaction between the polymeric network and the flax fibers, but it is impossible to know if the interaction between the hardener and the fibers or the resin with the fibers is physical or chemical as the fibers may absorb the monomers as by a sponge-like effect and/or react with them. Indeed, in thermosets, T_g depends on the crosslinking density as chain mobility is constrained by the network structure.[13] The occurrence of a chemical reaction seems corroborated by analyses performed in a previous study, evidencing a shift in the stoichiometric ratio r between amine and epoxide functions available for polymerization.[10] Interestingly, repetition of this DSC experiment with washed fibers – to eliminate the sizing agent as described in the experimental section – led to a very similar T_g drop to 74 ± 5 °C (**Figure 2b**); therefore the observed T_g decrease cannot be assigned to the sizing agent itself. Apart from the latter, water is also known to be naturally associated to flax fibers, with a mean content of 8 wt.%,[5] and could play a role in the observed phenomenon. Effects of water addition on epoxide-amine polymerization were indeed reported, at least on the kinetic parameters:[9,14] water added to the system up to 2-3 wt.% was typically shown to accelerate the polymerization reaction, probably by helping the opening of the epoxide endgroups, thus promoting the reaction with amines.[9] Beyond this amount, water was shown to play instead a negative role on epoxide-amine polymerization by forming a secondary phase with dissolved amine, making it less prone to react with epoxide groups. To check the possible influence of the water content included in raw fibers, a DSC analysis was carried out on a

DGEBA/DETA/fibers composite prepared with dried fibers (24h at 103°C, NF ISO 6496 2011 standard). SEM observations allowed checking the retained general shape and morphology of the fibers despite this treatment without noticeable degradation (**Figure 3**). In this case, the T_g value was lowered to 114 ± 5 °C (**Figure 2b**). This intermediate T_g value between the reference and the composite formed with raw (humid) fibers indicates that water indeed plays a role in the T_g drop, but that water alone cannot explain the drastic modification of T_g measured for raw fibers. Therefore, the organic components of the fibers likely impact the quality of the DGEBA/DETA polymer network upon curing. These observations are likely related to interfacial processes occurring between the monomer(s) and the fibers and/or water.
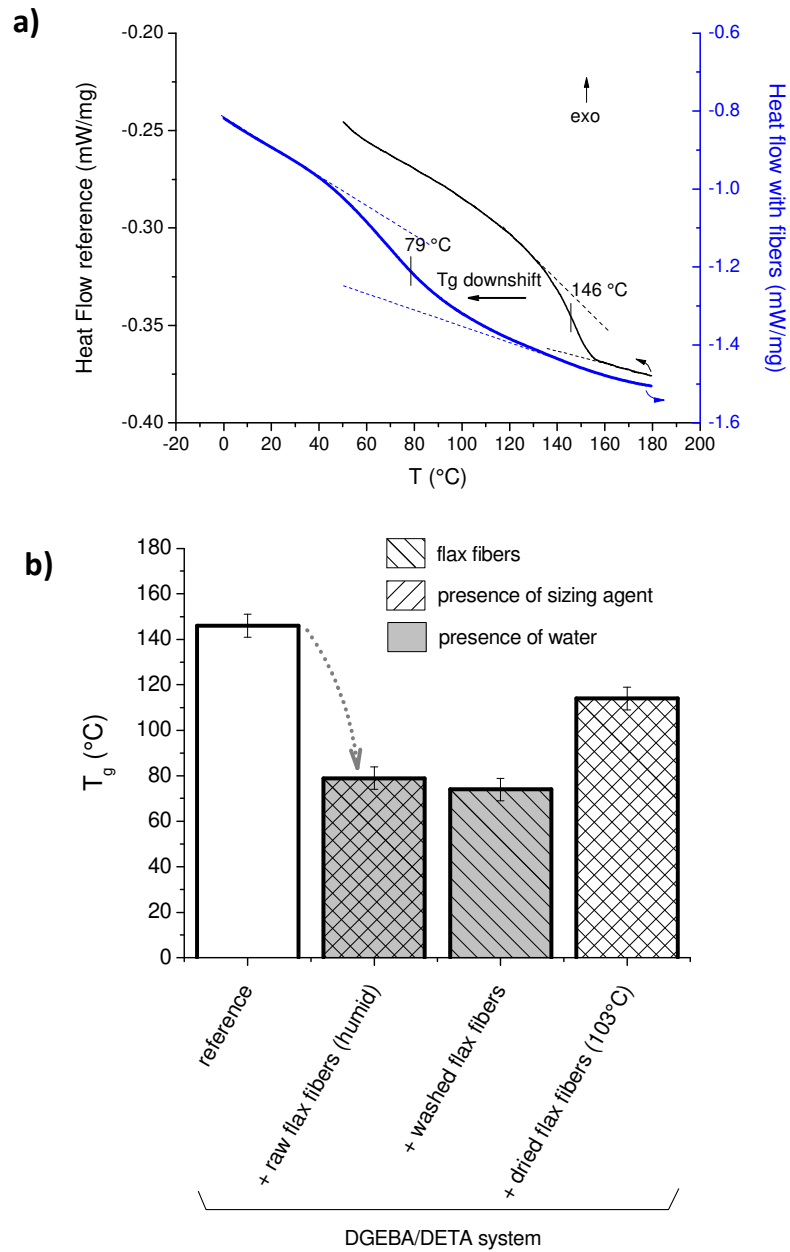
Figure 2. a) Evidence of T_g downshift for the DGEBA/DETA system in the presence of flax fibers (30 wt.%), b) Measured T_g values for the DGEBA/DETA system in different conditions: reference and in the presence of flax fibers (raw, washed, or dried at 103°C / 24 h)
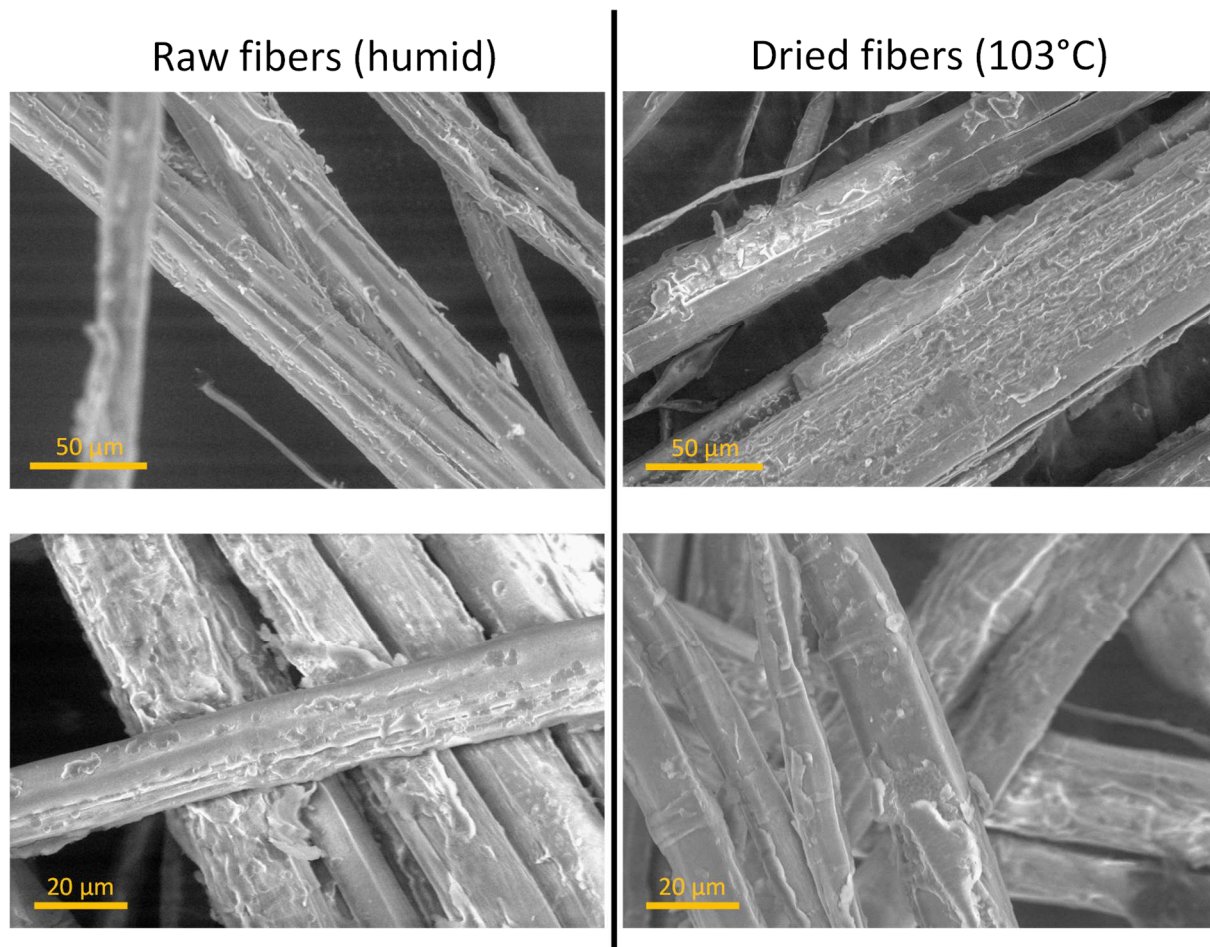
Figure 3. SEM observations of raw (humid) and dried (103°C) flax fibers

In order to shed light on these observations, to explore underlying mechanisms, and to verify if the fibers-monomers interaction is either chemical or physical (simple differential adsorption), we developed – for the first time on such fiber-reinforced composites – an *in situ* analysis approach based on mixing microcalorimetry. This strategy was inspired from our recently reported works developed on other systems, essentially to follow DETA-metal interactions, which unveiled the relevance of the mixing microcalorimetry tool for exploring interphase formations *in situ*.[15]

In a first stage, we investigated the possible interaction between the DGEBA epoxide monomer and flax fibers (1.5 g DGEBA, 0.1 g fibers). The measured enthalpy of interaction, at the typical temperature of 50°C, was found to be negligible ($\Delta H_{R\ DGEBA/fibers}$ = +29 mJ

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corresponding to +0.29 J g^{-1} of fibers) by being lower than the absolute value of the blank experiment (159 mJ). Absence of a detectable heat of interaction in these conditions strongly suggests that DGEBA does not interact significantly with the fibers. This result is interesting as it is counter-intuitive regarding the possible chemical reactivity of epoxide cycles e.g. in the presence of OH-exposing organic compounds,[16] and thus highlights the relevance of direct calorimetry measurements.

In a second stage, we examined the interaction between DETA and flax fibers. A typical example of evolution of the heat flow versus time is depicted in **Figure 4a** (50°C, 1.5 g DETA, 0.1 g fibers), and **Figure S2** reports as additional illustration the full thermogram obtained at 25°C. The effect of a variation of fibers content (1.5 g DETA, fiber mass from 0 to 0.4 g) was followed at both 25 and 50°C, as reported in **Figure 4b**. In this case, in contrast to DGEBA, a noticeable exothermic phenomenon was systematically recorded, with a measured ΔH_R typically ranging between 0 and -65 J. This led to $\Delta H_{R\ DETA/fibers}$ = -210 ± 2 J g^{-1} of fibers at 25°C and $\Delta H_{R\ DETA/fibers}$ = -180 ± 5 J g^{-1} of fibers at 50°C. These findings thus suggest the existence of significant interaction between DETA molecules and flax fibers; and this interaction likely plays a key role in the T_g decrease evidenced previously by DSC.
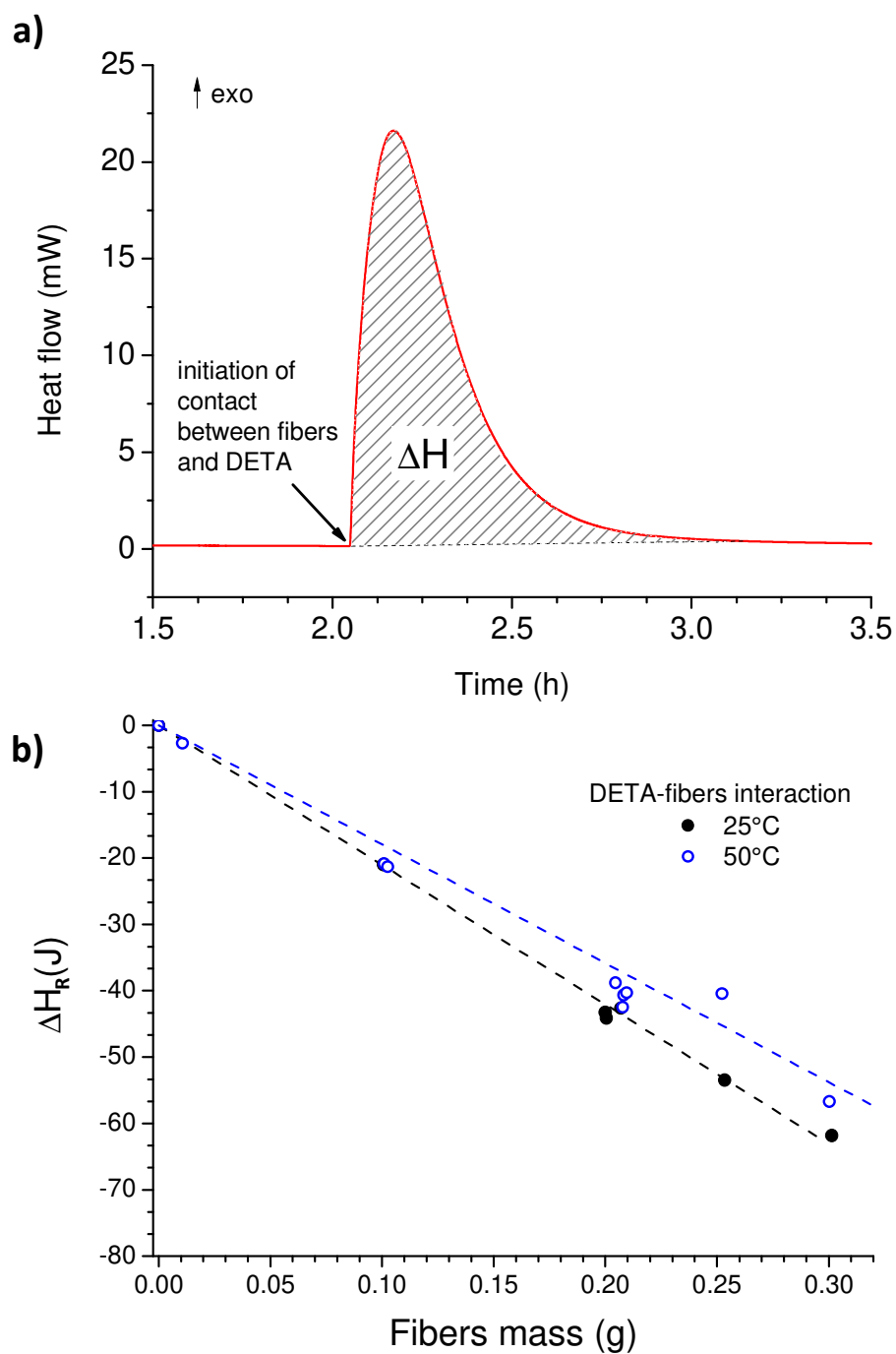
Figure 4. a) Example of thermogram (mixing calorimetry) obtained by contacting DETA with flax fibers, at 50°C (the raw value ΔH leads to the interaction enthalpy ΔH_R after subtraction of the blank), b) evolution of $\Delta H_{R\ \text{DETA/flax fibers}}$ versus fiber mass, at 25°C and 50°C

Since flax fibers contain, however, a non-negligible amount of water (mean of 8 wt.%,[5] as illustrated by TG analysis on **Figure S3**), the potential impact of the presence of water in the ΔH_R values measured deserves specific attention. To this aim, series of experiments were

carried out, at both 25 and 50°C, by simply mixing DETA with increasing amounts of water (diamond symbols, plotted versus the water/DETA mole ratio, **Figure 5**). Such DETA/water interaction was found to be exothermic. If recalculated per gram of water, this led to the very similar enthalpy values of $\Delta H_{R\ DETA/water} = -632 \pm 11$ J g^{-1} of water at 25°C and -636 ± 13 J g^{-1} of water at 50°C. Considering the mean 8 wt.% humidity of the fibers, the equivalent mass of water associated to the fibers was determined to evaluate the contribution of the DETA/water interaction in the global exothermic effect observed in the DETA/fibers system. Results have been added in **Figure 5** (circle symbols). For both temperatures, leading to rather similar outcomes, comparison of the DETA/fibers and DETA/water systems allowed us to evaluate a factor of nearly 4 (precisely 4.2 at 25°C and 3.5 at 50°C) between the two sets of data; DETA/fibers being systematically the most exothermic system. Therefore, water molecules associated to the fibers in their natural (humid) state may only explain about one-fourth of the global exothermic effect detected with the humid fibers, thus confirming the DSC results and showing that the (organic) fibers themselves interact strongly with DETA.
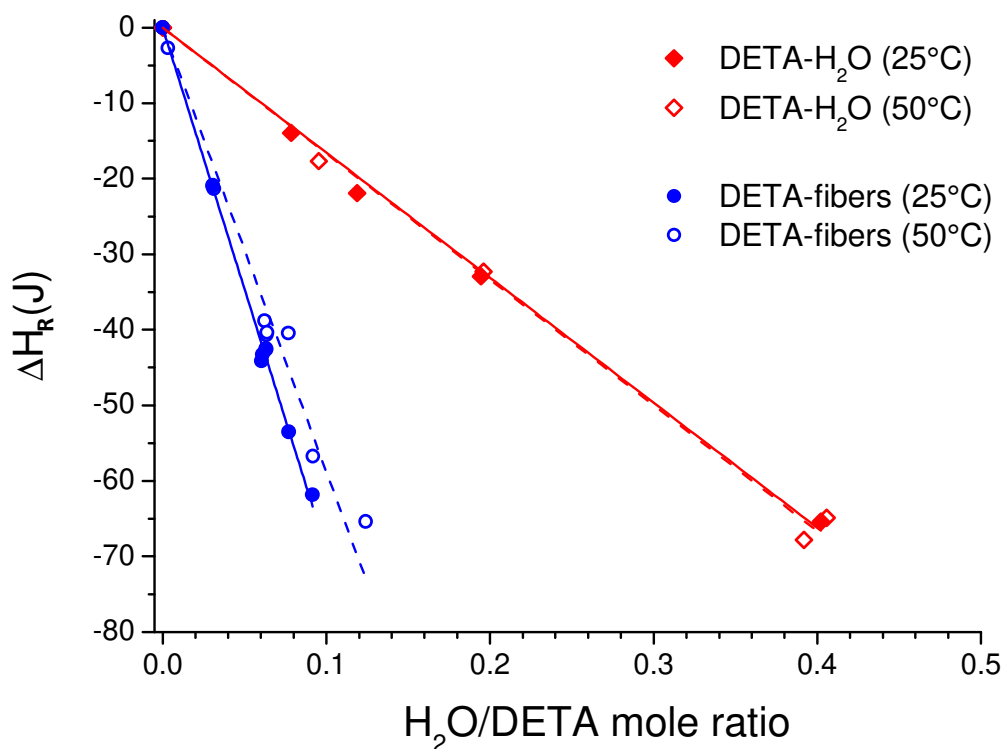
Figure 5. Evolution of ΔH_R for the DETA/flax fibers and DETA/water systems upon increasing water content, at 25°C and 50°C

In order to explore further the underlying mechanism of interaction between the organic components of the flax fibers and DETA, we have performed calorimetry experiments by selecting, one by one, each of the three main components of flax, namely cellulose (representing 61-71 wt.% of the total mass), hemicelluloses (18.6-20.6 wt.%) and lignin (1.8-5.7 wt.%).[17] Indeed, in short, the flax fiber structure may be described as a hemicelluloses/lignin matrix reinforced by embedded cellulosic microfibrils. Several analyses were conducted here using 0.2 g of each component separately and 1.5 g of DETA. Since all trends identified in this study were systematically observed at both calorimeter temperatures, these additional experiments were run at the temperature of 50°C that is particularly suited for infusion processes for composite fabrication. Every component of the fibers was found to react significantly and in an exothermic way with DETA. The ΔH_R value found for each organic moiety (per gram) was

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-178 ± 10 J g^{-1}, -125 ± 3 J g^{-1} and -236 ± 10 J g^{-1} respectively for cellulose, hemicelluloses and lignin. Considering the mean proportion of each component in flax (i.e. 66 wt.% cellulose, 19.6 wt.% hemicelluloses, 3.7 wt.% lignin), it was then possible to evaluate the enthalpy contribution of each of these three substances, as well as that of water (8 wt.%) to calculate a global $\Delta H_{R\ calc}$ value corresponding to the composition of the natural (humid) fibers (**Figure 6** and **Table 1**). The resulting calculation, $\Delta H_{R\ calc}$ = -203 ± 7 J g^{-1}, is in rather good agreement (within 12%) with the experimental value obtained with the fibers, $\Delta H_{R\ DETA/fibers}$ = -180 ± 5 J g^{-1}, reported above from the analysis of **Figure 4b**. The difference observed here remains limited, and may arise from several factors: *i)* in actual fibers the three components are organized in a three-dimensional structure providing some degree of confinement (thus limiting somewhat accessibility to the liquid phase), *ii)* some degree of hydration may be associated with the organic moieties (easy equilibration with atmospheric humidity once exposed to air) and *iii)* slight variations may exist in the composition of the organic moieties compared to their counterparts in actual flax fibers. Nevertheless, these findings show a good general correspondence in terms of global enthalpy of interaction, thus validating that the exothermic peak observed with flax fibers may be decomposed into four main components related (per order of importance) to cellulose, water, hemicelluloses and lignin.
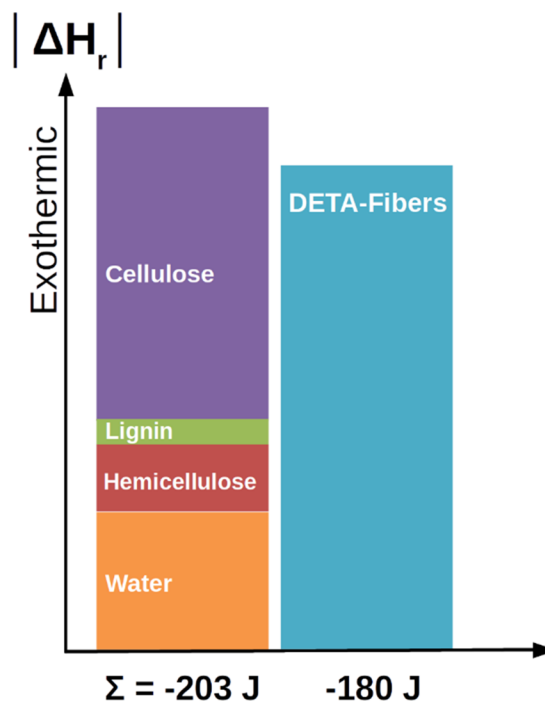
Figure 6. Schematic overview of enthalpy contributions (exothermic, absolute values) of each component of flax fibers in interaction with 1.5 g DETA (50°C), in comparison to 1 g of full fibers

Table 1. Distribution of the enthalpy contributions of each component of flax fibers in interaction with 1.5 g DETA (50°C)

Components	Mean proportion in flax fibers [wt.%]	ΔH_R DETA/component [J g^{-1}]	ΔH_R DETA/fibers [J g^{-1}]
Initial fibers (natural, 8 wt.% humidity)	-		-180 ± 5
		ΔH_R DETA/component [J g^{-1}]	Equivalent ΔH_R contribution in fibers [J g^{-1}]
Cellulose	66	-178 ± 10	-118 ± 7
Hemicellulose	19.6	-125 ± 3	-25 ± 1
Lignin	3.7	-236 ± 10	-9 ± 0.4
Water	8	-636 ± 13	-51 ± 1
		Sum of contributions:	**-203 ± 7**

The existence of a heat of interaction upon contacting the DETA triamine with H_2O molecules appears rather unsurprising, as at least hydrogen bonds may be expected to form. In contrast, interaction of DETA with the lignocellulosic components was less obvious. Finally, from these mixing calorimetry results, it may be inferred that the main contribution (58%) in the DETA/fibers exothermic interaction concerns the cellulose component of the fibers. This discovery was not especially expected, as cellulose is the most crystalline organic moiety contained in flax fibers. The existence of an interaction between cellulose and epoxy-amine systems has been reported in the literature by measuring curing heat-flow curves by DSC.[18] In the present work, we highlight the direct interaction between cellulose (alone or as a component of flax fibers) and the DETA polyamine, and our findings underline again the high potential of (poly)amines such as DETA to chemically interact with a variety of substrates, as we showed previously in the case of metal (hydr)oxidized surfaces.[15] Additional calorimetry experiments were carried out here in order to reach deeper understanding of the DETA/cellulose interaction. In this view, a first hypothesis could lie in the highly alkaline character of DETA, which may provide a local concentration of OH^- ions upon interaction with water molecules enclosed in the organic moiety. To test this hypothesis, cellulose was subjected to a sodium hydroxide solution in replacement for DETA in the upper compartment of the calorimetry setup. A NaOH concentration of 0.1 M was selected so as to approach the pH reached when 1.5 g DETA is contacted with few drops of water (pH ~ 13). Measurement with the mixing calorimeter showed that cellulose (0.2 g) reacted exothermically with sodium hydroxide 0.1 M (1.5 g) with an interaction enthalpy $\Delta H_{R\ NaOH/cellulose}$ = -18 J g^{-1} of cellulose. Such an effect can likely be assigned to partial dissolution of cellulose under alkaline pH.[19] However, this value is 10 times lower than the one obtained for cellulose reaction with DETA; therefore interaction with the only ions OH^- cannot explain the high exothermic enthalpy contribution measured with DETA. Instead, a special role of the DETA molecule itself needs to be implied.

Earlier research explored the chemical influence of DETA on cellulose by DRX analysis.[20] The authors concluded that, upon contact, a rearrangement of the chains occurred, with the separation of adjacent cellulose chains from the crystalline regions and DETA intercalation toward cross-linking to form a cellulose-DETA complex, involving the secondary amine as well as one primary amine (the other amino group being suggested to form additional hydrogen bonds). Cellulose being poly-hydroxylated, the involvement of –OH groups in this type of interaction may be postulated. To identify similar modifications when subjecting flax fibers to DETA, we performed X-ray diffraction analyses (XRD). To this aim, few sections of flax fibers were soaked in DETA for 10 min. The sample was then analyzed by XRD (cobalt source) and compared to the XRD pattern of initial flax fibers, as shown in **Figure 7**. Clear differences may be detected between the two patterns. The pattern of initial flax fibers (red upper curve) shows a main peak around $2\theta = 26.5°$ and a doublet around 17 and 19° (also see **Figure S4** for peak positioning). After contact with DETA (green lower curve), the main peak was shifted toward lower angles, the doublet disappeared, and a new peak appeared at low angles around 7°. These results strongly remind those obtained by Segal and Loeb on cellulose/DETA interaction,[20] as evidenced graphically in **Figure 7** by the superimposed black-and-white patterns (note that Segal and Loeb used a copper source for XRD analyses, which was taken into account for the superimposition). While the main features discussed above for initial flax (upper red curve) are indicative of a high amount of cellulose polymorph I,[21] the pattern obtained after contact with DETA becomes closer to the crystallographic features of the DETA-cellulose complex as described by Segal and Loeb.[20] Based on this XRD analysis, it thus confirms that at least the cellulosic component of flax fibers undergo a chemical interaction with DETA, likely involving cellulose-DETA complexes as reported by Segal and Loeb. Since this transformation directly involves DETA molecules, it may thus explain the significant decrease of T_g observed by DSC after polymerization, by considering that part of the DETA amino functions are associated to the organic component(s) of flax fibers and will not readily react with epoxide groups.
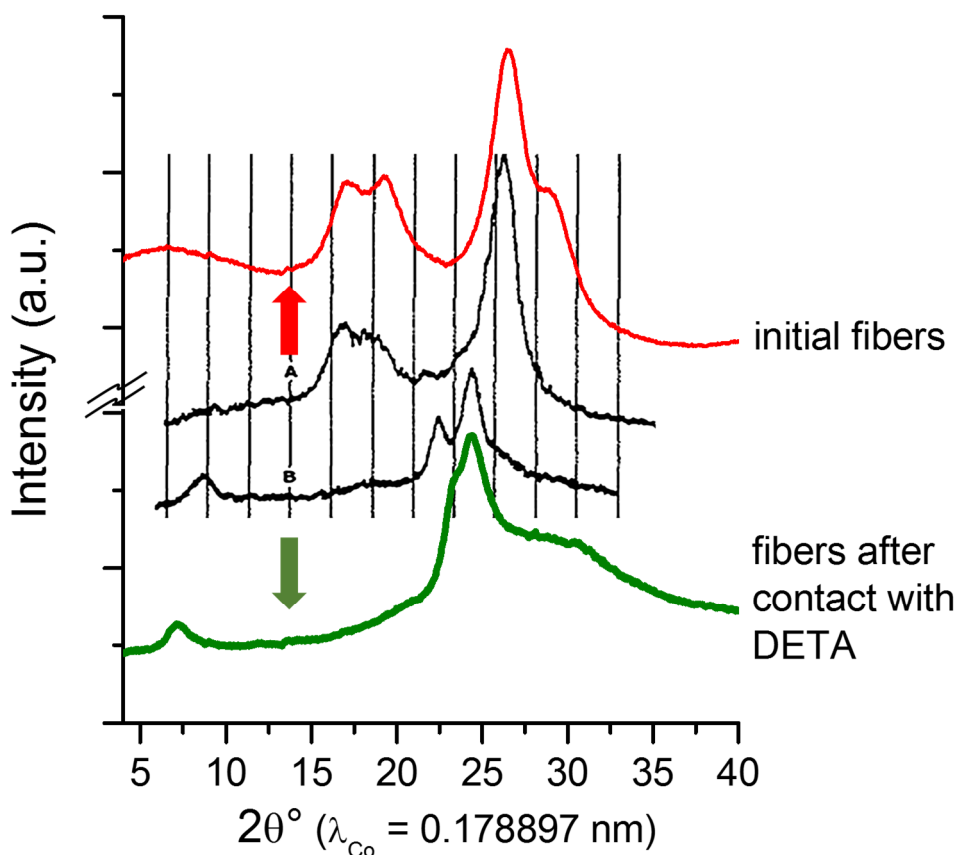
Figure 7. XRD patterns of initial and DETA-soaked flax fibers. The black-and-white superimposed inlet is reproduced with permission,[20] 1960, Wiley). Note: the two maxima at 22.5 and 14.7° from this reference paper, relative to an XRD copper source, become respectively positioned at 26.2 and 17.1 in relation to the cobalt source used here

Since this transformation directly involves DETA molecules, it may thus explain the significant decrease of T_g observed by DSC after polymerization, by considering that part of the DETA amino functions are associated to the organic component(s) of flax fibers and will not readily react with epoxide groups. Such a decrease of T_g could be found useful, as for the use of plasticizers. On the other hand, if this decrease is not suitable, an increase of initial amount of hardener in the reacting mixture (leading to an excess of initial amine functions) may offset the lack of reactive functions, as described previously [10].

4. Conclusion

In this work, by way of DSC analyses, we showed the direct effect of flax fibers on the thermal properties of epoxy-amine systems, and in particular a drop of their glass transition temperature T_g. This effect was then scrutinized in details by mixing microcalorimetry to determine whether the resin or the hardener was chemically modified by flax fibers or simply absorbed by them. We first evidenced that the DGEBA component did not interact quantitatively with flax fibers. In contrast, DETA/fibers interaction led to a significant exothermic effect, which was quantified and directly linked to the fibers content. Thanks to additional calorimetry experiments involving each of the three main components of flax fibers – namely cellulose, hemicellulose and lignin – as well as water, we then showed that each of these moieties reacted exothermically with DETA. Taking into account the proportions of each of these compounds in flax fibers, the sum of enthalpy effects was then found in good accordance with the overall exothermic effect measured with the whole fibers. The main contribution was that of cellulose, responsible for 58% of the global heat effect, despite its partial crystallized state. With the help of XRD analyses and other considerations from cellulose literature, we finally concluded on the direct implication of DETA molecules with cellulosic chains in the formation of DETA/cellulose complexes, thus limiting the amount of "reactive" amino functions of DETA in view of subsequent polymerization with DGEBA, hence explaining the decreased T_g values. This work sheds light on the chemical role of flax fibers in epoxy-amine thermosets, down to the molecular-scale, and highlights the relevance of the mixing calorimetry approach to follow *in situ* interphase formation.

Conflict of interest

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The authors declare no conflict of interest.

Acknowledgements

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Antoine Rouilly is Assistant Professor at the University of Toulouse in the Laboratory of Agro-Industrial Chemistry (UMR Toulouse INP/INRAE 1010). His field of expertise concerns biopolymer processing mainly for non-food applications and the role of water in the physical-chemical properties of biopolymers. He has been working on various biopolymers such as protein (storage and structural), starch and cellulose but also on complex systems such as lignocellulosic fibers or agricultural by-products. He is since 2012 the leader of a team of his lab dedicated to agro-materials and biopolymer processing.

Christophe Drouet is a CNRS Senior Scientist (*eq*. Prof) at the University of Toulouse, in the CIRIMAT laboratory. PhD in materials science, major research fields address the physico- and thermo- chemistry of natural and synthetic compounds, their characterization and surface reactivity. Key milestones include 3 years as Research Associate in Prof. A. Navrotsky's group (Thermochemistry Facility) at UC Davis, USA, for calorimetry studies. C. Drouet received the *honorary Racquel Legeros Award* in 2013 and the *ISCM Excellence Award* in 2016 for his contribution to the field of biomaterials research. Listed in the 2021 Stanford survey on Highly Cited Researchers. https://www.christophedrouet.com

Maëlenn Aufray is Assistant Professor at the University of Toulouse, in the engineering school INP-ENSIACET and the CIRIMAT Laboratory (UMR CNRS 5085) since February 2008. Her expertise lays in adherence measurements and the investigation of chemical reactions at interfaces leading to interphase formation. She has developed in the lab mechanical test setups as a reproducible 3-point bending test. M. Aufray has more than twenty years of experience in the field of polymers and practical adhesion. In addition, she recurrently works at the interface of several teams, as her research area is highly transversal.

Table of contents text:

We develop a mixing calorimetry approach to follow *in situ* interphase formation between flax fibers and DGEBA or DETA. DETA/fibers interaction is particularly exothermic. Each component of flax fibers leads to exothermic effects, cellulose giving the most prominent enthalpy contribution. DETA interacts with cellulosic chains, which limits the amount of "reactive" amino functions for polymerization and decreases the T_g value.

N. Canavy, A. Rouilly, C. Drouet, C. Thouron, M. Aufray*

Influence of Flax Fibers on Epoxide-Amine Composites: Energetics of Interphase Formation

ToC figure:
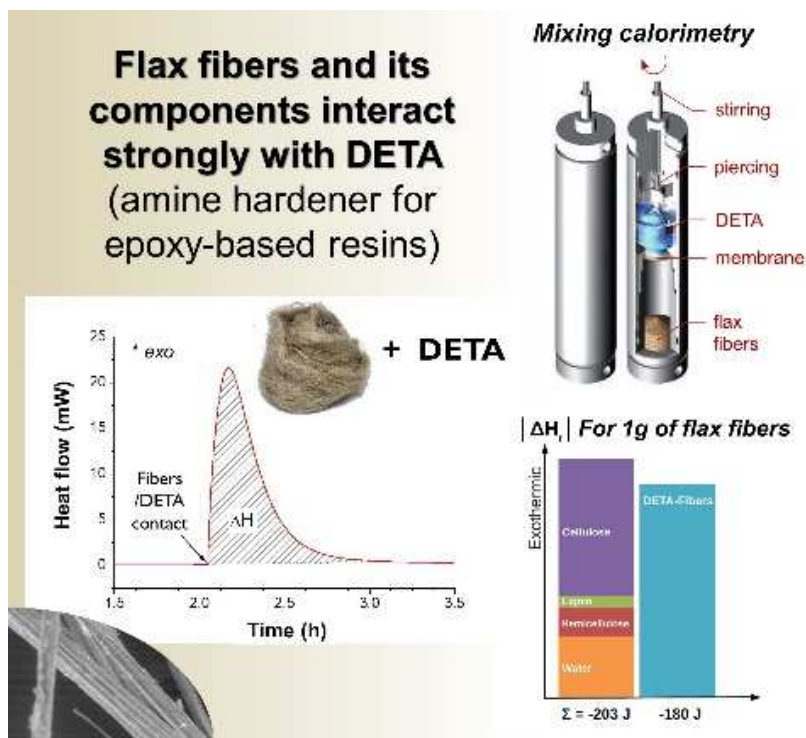
Highlights

- Addition of flax fibers in epoxy-amine mixture leads to T_g decrease (67 characters)
- Mixing microcalorimetry does not show interaction between DGEBA and flax fibers (84 characters)
- DETA/fibers interaction is significantly exothermic (63 characters)
- Cellulose, hemicellulose, lignin and water reacted exothermically with DETA (76 characters)
- Cellulose is responsible for 58% of the heat effect despite its crystallized state (83 characters)