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# Influence of flax fibers on network formation of DGEBA/DETA matrix

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## ABSTRACT

Natural fibers and particularly flax fibers have a great potential to replace glass fibers in composite materials. However, the interaction between these fibers and thermoset matrices remains unclear and results in a weak interface affecting the mechanical properties of the composite. This study was carried out to investigate the impact of natural fibers on the chemical reaction between the resin and the hardener, studying the interaction of fibers with each component separately to understand more precisely the phenomena involved. The results show that the contact with the fibers involves a change of the matrix properties that has been attributed to the water absorbed on their surface. On the one hand, water could modify amine functions of the hardener leading to a decrease of 40°C of matrix glass transition temperature ( $T_g$ ). This issue could be corrected by adding a 16% excess of hardener. On the other hand, the water added to the resin could also accelerate the epoxide/amine reaction increasing slightly the  $T_g$  of the matrix and also generating weaker distinct networks of lower  $T_g$  by post-modification of the hardener. Therefore, the control of the water content in flax fibers is a crucial parameter for composite manufacturing.

## KEYWORDS

Curing reaction; flax fibers; composite manufacturing; absorbed water; epoxy resin; amine hardener

## 1. Introduction

In the last decade, natural fibers have shown a great potential for their use in composite materials. In addition to their manifest ecological advantages, these fibers exhibit good specific mechanical properties and low density [1,2]. There is then an obvious interest to use these fibers in the transportation industry because of this low density. Reducing the mass, for example, of an aircraft allows reducing its fuel consumption. This means a reduction of the costs that goes along with a reduction of greenhouse gas emission.

Despite all these advantages, the use of natural fibers in composite materials remains marginal and hardly emerges on the world market. There are still some important technological obstacles to overcome to bring natural fibers on the market. On the one hand, the production of natural fibers is subjected to climatic changes, to various ways

of productions or geographical situation that induce difficulties to provide a constant and repeatable production that the industry needs [1–3]. On the other hand, the complex structure and the inherent properties of natural fibers make the production of biocomposites quite difficult [4]. Indeed, biocomposites are manufactured in the same way as their counterparts made of synthetic fibers while they are totally different. The major issue is the incompatibility between natural fibers and polymeric matrices that directly impacts the manufacturing process and the properties of biocomposites. Natural fibers are mostly hydrophilic while most polymeric matrices are hydrophobic [5,6]. The adhesion between the fibers and the matrix in composite materials is a critical parameter. With a strong adhesion comes a strong composite [7–10]. To overcome this issue, the usual technique is to carry out a treatment on the fibers to modify their structure or the use of a third component, a compatibilizer, to improve adhesion. In the literature, a large number of methods and products to increase the adhesion between fibers and matrices are detailed [11–14]. Physical treatments such as plasma or corona discharge modify the surface of the fibers in order to make them more hydrophobic. These treatments slightly improve the adhesion and the mechanical properties of composites up to 30% for the Young modulus in certain cases [15,16]. Chemical treatments like silanization or acetylation also modify the surface of fibers, improving the mechanical properties of biocomposite as well. However, the treatment of fibers could be discussed. First of all, the choice of a particular treatment has to take in consideration a lot of parameters like the nature of the fibers and of the matrix, the manufacturing process or the properties which need to be improved [10,17]. Secondly, it can be difficult to control and to be sure that all the fibers are homogeneously treated. Also, some treatments can degrade the mechanical properties of the fibers if they are not perfectly controlled [18,19]. Thirdly, the effectiveness of these treatments is studied through the mechanical properties of the composites. This result cannot highlight precisely the improvement of the adhesion between the fibers and the matrix because the phenomena involved are rather complex and can be related to different theories. Finally, the use of an extra step involving chemicals, energy and time is always questionable on an industrial or ecological point of view.

The aim of this study was to understand the mechanisms that occur when natural fibers were put in contact with epoxy thermoset matrices during the manufacturing of a composite. Indeed, the curing of a thermoset matrix like epoxies is based on precise stoichiometry between the resin and the hardener [20]. A small modification on one of these components directly impacts the properties of the thermoset network. Some studies have shown difference between the properties of the matrix in the bulk and the matrix near the fiber called the interphase. The interphase is a tridimensional area between the fibers and the matrix which properties differ from both that can be quite difficult to study [21,22]. In the interphase, a decrease of the glass transition temperature ( $T_g$ ) of the matrix was observed [23]. That has been explained by a local modification of the resin/hardener ratio. These changes can be induced by a reaction between the fibers and one of the components of the matrix. The impact of substrates on amine hardeners has also been investigated [24,25]. Metal substrates, for example, are known to modify or degrade amine functions, and the lack of these functions induces a loss of properties in the final polyepoxy system. Other studies have shown the influence of cellulose nanofibers on the  $T_g$  of composites and describe the reaction between

cellulose and thermoset systems [26,27]. The variation of  $T_g$  is then thought to be induced by the reaction between the resin and the nanofibers.

The water contained in natural fibers could also play a predominant role in resin/hardener reaction. Water can modify the cure kinetics of epoxy-amine thermosets acting as an accelerator or can be detrimental to the reaction in certain conditions [28,29]. The water contained in these fibers is usually seen as an obstacle that can lead to numerous defects such as a bad interphase with the matrix [30,31] or an accelerated ageing [32]. Thus, natural fibers are usually dried before the manufacturing of composites to limit these phenomena. However, the drying of natural fibers such as flax turn out not to be as easy as it seems. Firstly, in certain conditions, the drying step can damage the fibers. It has been shown that drying flax fibers could induce a loss of strength and failure strain by a modification of the fibre structure [30,33,34] which are directly transmitted to composite properties [35]. Secondly, it can be quite difficult to control the water content of natural fibers during the manufacturing of composite due to their hydrophilic nature [36]. When the fibers have been dried and then are exposed to a humid environment, they can absorb a consistent amount of water on a short duration [33]. Flax fibers can reabsorb 25% of the water lost during the drying in only 5 minutes. According to the composite manufacturing process used, natural fibers can be exposed several minutes to their environment and consequently absorb an undefined amount of water depending on the relative humidity in the air. Finally, the drying step requires equipment, energy and time. In this context, it is interesting to study precisely the influence of the water contained in flax fibers on the curing of the matrix and its properties in order to understand the phenomenon involved. This step would help to find way to improve biocomposite properties with a defined water content in the fibers with an easy and controlled manufacturing process.

This paper investigates the impact of flax fibers and their absorbed water on the curing and network properties of a DGEBA (Bisphenol A diglycidyl ether)/DETA (Diethylenetriamine) epoxy system. A procedure derived from studies on the influence of metal substrates on epoxy-amine chemistry [24] was set-up to analyze the loss of properties of the network after interaction with the fibers and finally to understand how the fibers could modify the resin/hardener reaction.

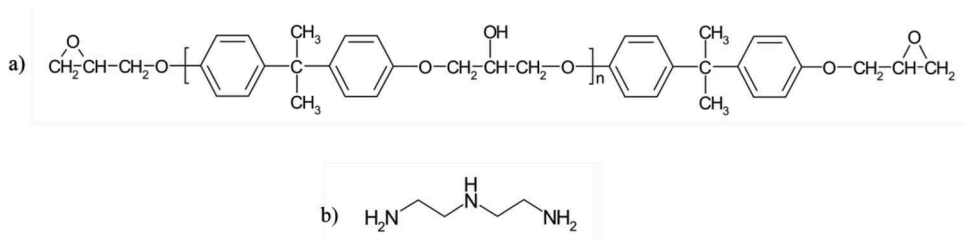
## **2. Materials and methods**

### **2.1. Resin/hardener system**

This study focuses on a DGEBA (Bisphenol A diglycidyl ether)/DETA (Diethylenetriamine) system. This system is well known and is also part of many industrial epoxy systems. DGEBA DER 332 and DETA were provided by Sigma Aldrich (St. Louis, United States of America). DGEBA has a molar mass of 340. 41  $\text{g}\cdot\text{mol}^{-1}$  ( $n = 0.03$ ) with two epoxide functions ( $f_{\text{epoxide}} = 2$ ). DETA has a molar mass of 103  $\text{g}\cdot\text{mol}^{-1}$  and 5 amine functions ( $f_{\text{amine}} = 5$ ). The chemical structures of these components are presented in [Figure 1](#).

### **2.2. Flax fibers**

Woven flax fibers used for this study were provided by Depestele (Le Bocasse, France). It was a 2/2 twill with an area weight of 360  $\text{g}\cdot\text{m}^{-2}$ . The fabric was stored in a climatic chamber at 25°C and 60% of relative humidity (% RH).



**Figure 1.** Chemical structures of (a) DGEBA ( $n = 0.03$ ) and (b) DETA.

The water content of flax fibers was determined by their weight loss after drying. Initially, flax fibers were stored in a climatic chamber at 25°C and 60% RH weighed before drying at 103°C during 24 h in an oven. The fibers were put out of the oven and weighed to measure the weight loss due to the removal of water. Dried fibers were then put in the climatic chamber and weighed at different interval of time to follow their water absorption in a controlled environment as a function of the time. The fibers stored in the chamber had a 7.5% w/w moisture content (%w/w). The fibers dried at 103°C for 24 h had a supposed moisture content of 0%.

## 2.3. Specimens manufacturing

### 2.3.1. Matrices manufacturing

The mixing ratio of DGEBA/DETA system for the different matrices were made using the same stoichiometric ratio  $r$  as shown in Equation 1. A ratio  $r = 1$  corresponds to the stoichiometry where there was as much amine functions as epoxide functions, which corresponded to a mass ratio 100:12.1 of DGEBA and DETA respectively. There is an excess of amine functions or an excess of epoxide functions when  $r > 1$  or  $r < 1$  respectively. For each kind of matrix, several samples were made according to different mixing ratio from  $r = 0.6$  to  $r = 1.4$ . The mix were poured in a silicon mould, cured at 25°C during 12 hours and post cured 1 h in an oven at 160°C in order to reach the maximum glass transition temperature that can be achieved at a theoretical infinite molecular weight called  $T_{g,\infty}$ . It is important to remember that all these samples were made only with the resin and the hardener (modified or not). There were no fibers in the samples analysed which, therefore, were not composites.

$$r = a/e = (f_{\text{amine}} \cdot n_{\text{amine}}) / (f_{\text{epoxide}} \cdot n_{\text{epoxide}}) \quad (1)$$

With  $a$ , the number of moles of amine functions,  $b$ , the number of moles epoxide functions,  $f$ , the functionality of the molecule and  $n$ , the number of moles of molecules.

### 2.3.2. Composites manufacturing

To assess the results obtained from the matrix study, composites specimens were produced by compression molding using 4 layers of woven flax fibers soaked with a mix of DGEBA and DETA for 1 h under 5 bars at 50°C. Then, composite laminates were post cured for 1 h at 150°C in an oven. A plate was made for each studied stoichiometric ratio studied (just as the matrices), i.e., 6 plates for  $r = 0.8$  to 1.3. The

fiber volume fraction was estimated from the difference between the weight of the composite and the weight of fibers used. The fiber volume fraction was 40%. Rectangular test specimens were cut out of the plates using a punch.

## **2.4. Thermal analysis**

$T_g$  was determined using differential scanning calorimetry (DSC) [37]. The reference was an empty pan. The sample and the reference were submitted to a linear variation of temperature in the same oven and the difference of temperature between them was measured. Analyses were realized on a NETZSCH (Selb, Germany) differential scanning calorimeter under inert gas (nitrogen) in order to avoid reactions between the sample and the atmosphere. The temperature scans were: 20°C to 200°C at a rate of 30 °C/min. This rate was chosen because it allowed to make the  $T_g$  more visible. The faster the scan goes, the more visible is the  $T_g$  [38]. For each sample, an amount of 15 mg, weighed with a Mettler Toledo (Columbus, United States) scale with the accuracy of  $\pm 0.1$  mg, was inserted in a 40  $\mu$ l aluminium pan with a pierced lid. For each samples, two consecutive scans were made and the  $T_g$  value was determined using the onset measurement on the second scan to be sure to measure the  $T_{g,\infty}$ . The error was determined by analysing four samples of DGEBA/DETA matrices made at the same mixing ratio  $r$  on four different days and was measured at  $\pm 1$  °C.

## **2.5. Infrared spectrometry**

Analyses of matrices were carried out with a Perkin Elmer (Waltham, United states) FRONTIER FTIR/NIR spectrometer using a CaF<sub>2</sub> beam splitter for a spectral range 15000–1250  $\text{cm}^{-1}$  and a Temperature-stabilized TGS (triglycine sulfate) Near Infrared (NIR) detector. Spectra were analyzed using Spectrum Software. Spectra were recorded on the range 10000–4000  $\text{cm}^{-1}$ . Measurements were done in transmission on specimens with a thickness around 1 mm. The reference spectrum was obtained with the direct beam. Specimens were analyzed considering the phenyl band as reference band at 4623  $\text{cm}^{-1}$ , corresponding to the combination of C = C (1625  $\text{cm}^{-1}$ ) with aromatic - CH (3050  $\text{cm}^{-1}$ ). The epoxide band at 4530  $\text{cm}^{-1}$  is the combination of - CH<sub>2</sub> of epoxide group (1460  $\text{cm}^{-1}$ ) with aromatic - CH (3050  $\text{cm}^{-1}$ ). The band of amine functions (I and II) is the harmonic band of - NH at 6500  $\text{cm}^{-1}$  and the combination of N-H stretching [39,40]. The error was determined by analyzing five samples of DGEBA/DETA on five different areas and was measured at 11%. DGEBA and DETA (modified or not) were analysed in Attenuated Total Reflection (ATR) Spectroscopy on the same apparatus using an OptKBr beamsplitter for a spectral range of 7800–400  $\text{cm}^{-1}$  and TGS MIR detector. Spectra were recorded on the range 4000–400  $\text{cm}^{-1}$ .

## **2.6. 3 points bending tests**

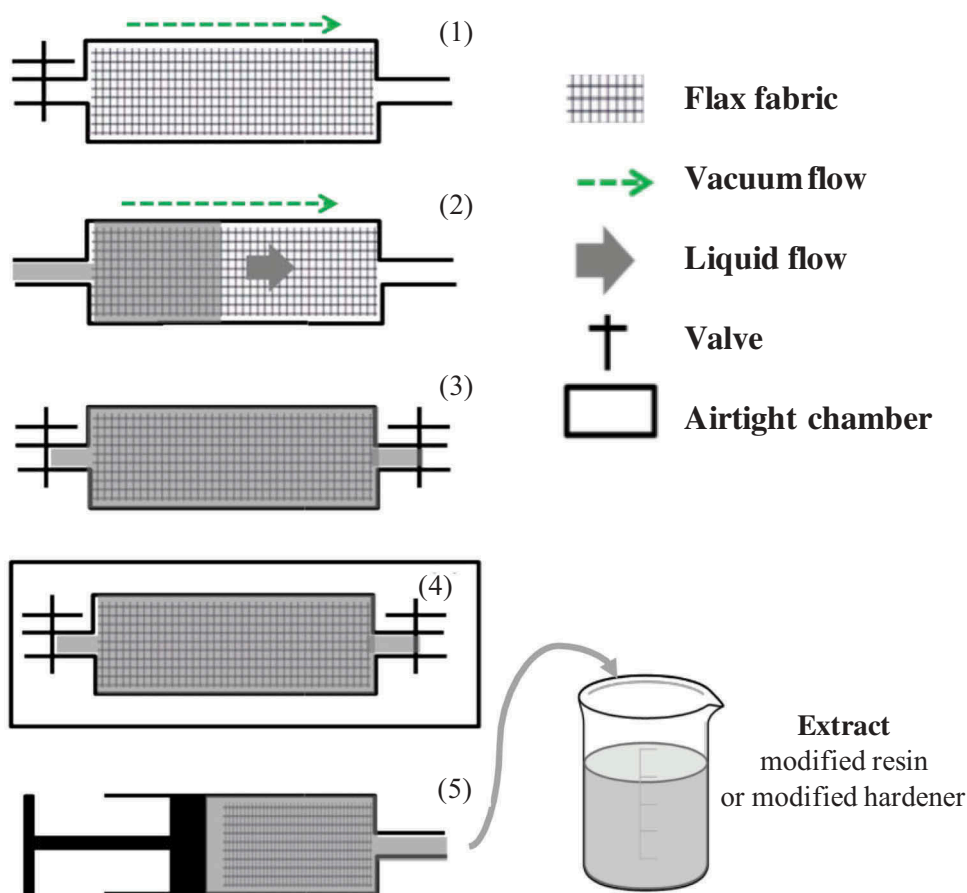
Flexural tests were performed on composite plates specimens (50 mm  $\times$  10 mm  $\times$  2 mm). 4 specimens for each stoichiometric ratio were tested on a Tinus Olsen universal testing machine (Horsham, USA) equipped with a load cell of 500 N. The span length was set to 40 mm. The cross head speed was set to 3 mm/min.

### 3. Results

#### 3.1. Experimental procedure

The aim of this study was to investigate the interactions between flax fibers and the epoxide and amine monomers leading to an epoxy matrix. In the case of the manufacturing of a composite, the resin, the hardener and the fibers are mixed together at the same time. In this configuration, at least three major kind of interactions could happen, namely the resin with the hardener, the resin with the fibers and the hardener with the fibers. The number, the nature and the rates of the different interactions make the investigation quite complicated. Additionally, the interactions between the hardener and the fibers or the resin with the fibers can be physical or chemical. Therefore, in a system in which all the components are mixed together, it is hard to know if a component (the resin or the hardener) is chemically modified by flax fibers or simply absorbed by these. For example, in the case where the hardener is put in contact with flax fibers and later, the resin is added. The addition of resin will act as a quantitative analysis of the remaining amine functions after their reaction with the fibers. If there is a lack of amine functions, it is impossible to determine if it is due to their absorption in the fibers (in a way that they couldn't react with the epoxide functions of the resin) or if it is because of a modification of these functions by the fibers that prevent them reacting with epoxide functions.

Consequently, an experimental procedure, based on a classic vacuum infusion process, was designed to separate these interactions in order to make the investigation as simple as possible and shown in [Figure 2](#). (1) The vacuum was applied in the chamber. The liquid inlet was open. (2) The vacuum let the component (the resin or the hardener) impregnate the flax fabric. Only one component (the resin or the hardener) was put in contact with the fibers at the same time. This allowed to eliminate the polymerization reaction and then only study the reaction between each monomers and the fibers separately. (3) Once the fabric was totally impregnated, the liquid inlet and the vacuum outlet were closed so that the vacuum was maintained in the chamber. (4) The chamber was separated from the assembly and stored 60 min at 50°C. The contact time was set to 60 min because it corresponds to the vitrification time of the DGEBA/DETA system [41,42]. The resin or the hardener were preheated at 50°C before impregnation as compromise. On the one hand, increasing the temperature permitted to reduce the viscosity of DGEBA in order to facilitate the impregnation and promoting the contact between the DGEBA and the fibers and so, promoting the interactions. On the other hand, a too high temperature would have reduced the viscosity but also the vitrification time of the DGEBA/DETA system [42] and thus would have reduced the interaction time between DGEBA or DETA and the fibers in the real case of composite manufacturing. (5) The chamber was then opened and the fabric was compressed using a piston in order to extract the 'modified' component for analysis so the part of the component absorbed by the fibers was not taken into account. This operation allowed to avoid the confusion between an absorbed component (the resin or the hardener) and a modified one as explained above. At this point, after both experiments, respectively for the resin and the hardener, there were two different samples. One is the hardener extracted from the fibers (referred as 'modified hardener') and the other is the resin extracted from the fibers (referred as 'modified resin').



**Figure 2.** Experimental procedure.

In order to quantify the amount of remaining functions for each component after the contact with flax fibers, each sample was mixed with its counterpart. The modified resin was mixed with pure hardener and the modified hardener was mixed with pure resin, both at the stoichiometric ratio  $r = 1$ , to obtain two modified epoxy matrices. A reference was made by mixing pure resin with pure hardener at the same stoichiometric ratio  $r = 1$ . At this point, it is important to notice that only matrices were studied in this part.

The glass transition temperatures of the reference matrix and the pure DGEBA with modified DETA matrix made in various conditions are presented in [Table 1](#). This preliminary study showed that the use of dried fibers and setting the experiment temperature at 25°C, induced a slight decrease of 7°C of the  $T_g$  of the DGEBA/modified DETA system as shown in [Table 1](#). While the same experiment conducted with stabilized fibers (i.e., 7.5%MC) or at a temperature of 50°C exhibited a larger decrease up to 40°C for DGEBA/modified DETA system ([Table 1](#)). These observations led to consider the role of the activity of the water absorbed on flax fibers during the process. It is difficult to control the moisture content of flax fibers when these are dried. Indeed, when the fibers are taken out of the oven, the moisture uptake is really fast. It was measured that in less

**Table 1.** Glass transition temperature of DGEBA/modified DETA matrixes for different experimental conditions.

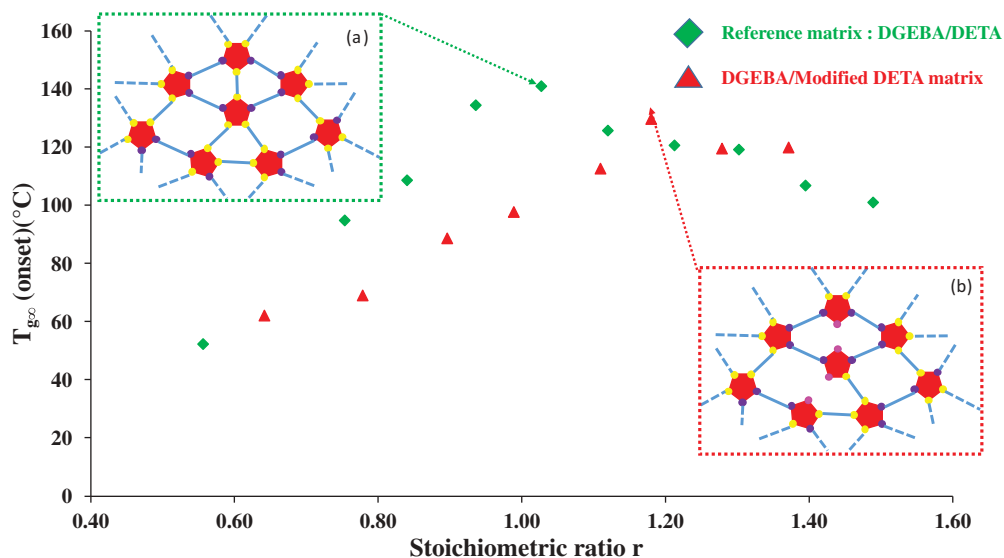
Sample	Fibers moisture content (% w/w)	Temperature (°C)	T <sub>g<sub>onset</sub></sub> (°C)
Pure DGEBA + pure DETA	/	/	141 ± 1
Pure DGEBA + modified DETA	0	25	134 ± 1
	7.5	25	115 ± 1
	7.5	50	98 ± 1

than 10 minutes, the moisture content can increase of 3% (corresponding to 40% of the water content in flax fibers at 25°C and 60%HR). Considering the time needed to set the experiment, it was not possible to know precisely the moisture content of pre-dried fibers at the beginning of the process. It is therefore coherent to use stabilized flax fibers containing absorbed water with an increased temperature. The activity of sorbed water on cellulosic materials varies with the temperature [43] and the transition from 25°C to 50°C can cause a water desorption of 1% of the mass of the fibers (corresponding to 13% of the total water content in flax fibers, i.e., 7.5% w/w). This thermal desorption of water may then be responsible for the T<sub>g</sub> decrease observed at 7.5% w/w and 50°C as the system was prepared and sealed before heating (Table 1). All experiments were then made that way as it better corresponds to the industrial use of such matrices.

### 3.2. Influence of fibers on DETA

DETA was in contact with stabilized flax fibers (containing 7.5% w/w of absorbed water) for one hour at 50°C and then extracted to form a pure DGEBA/modified DETA epoxy matrix with various stoichiometric ratio from  $r = 0.6$  to  $r = 1.4$ . The glass transition temperature of the reference matrix (pure DGEBA and pure DETA) and the pure DGEBA/modified DETA matrix for stoichiometric ratio  $r$  from  $r = 0.6$  to  $r = 1.4$  was measured by DSC and is presented in Figure 3. The reference exhibited a classic bell-shaped behaviour for epoxy matrices with the highest T<sub>g</sub> at 141°C for the stoichiometric mixing ratio  $r = 1.0$  [37,44,45] corresponding to the densest network (Figure 3(a)). The T<sub>g</sub> decreases with an excess of DGEBA or DETA.

The T<sub>g</sub> variation of DGEBA/modified DETA matrix had a similar bell-shaped behaviour but with a maximum T<sub>g</sub> of 130°C only and shifted to the right to a ratio  $r = 1.2$ . A plasticizing effect of water could not be responsible for the T<sub>g</sub> depression phenomenon because the T<sub>g</sub> was measured on the second scan of DSC and the water was removed during the first scan. The water absorbed on flax fibers could have been extracted in DETA during the impregnation step of the procedure, especially the amount that has been released by the temperature increase from 25°C to 50°C. But as water is known to accelerate the epoxide-amine reaction when the amount added is relatively small, it should have increased the conversion rate [28]. In this case, the opposite is observed which implied that either the amount of water is too high or amine functions of DETA were modified by water before their reaction with the epoxide functions of DGEBA. Water could then have reacted with DETA during the impregnation to form a large variety of new compounds by protonation of amine functions [46] that could be less reactive and could not lead to the ring opening of epoxide due to the lack of lone pairs of electrons on some nitrogen atoms of DETA.

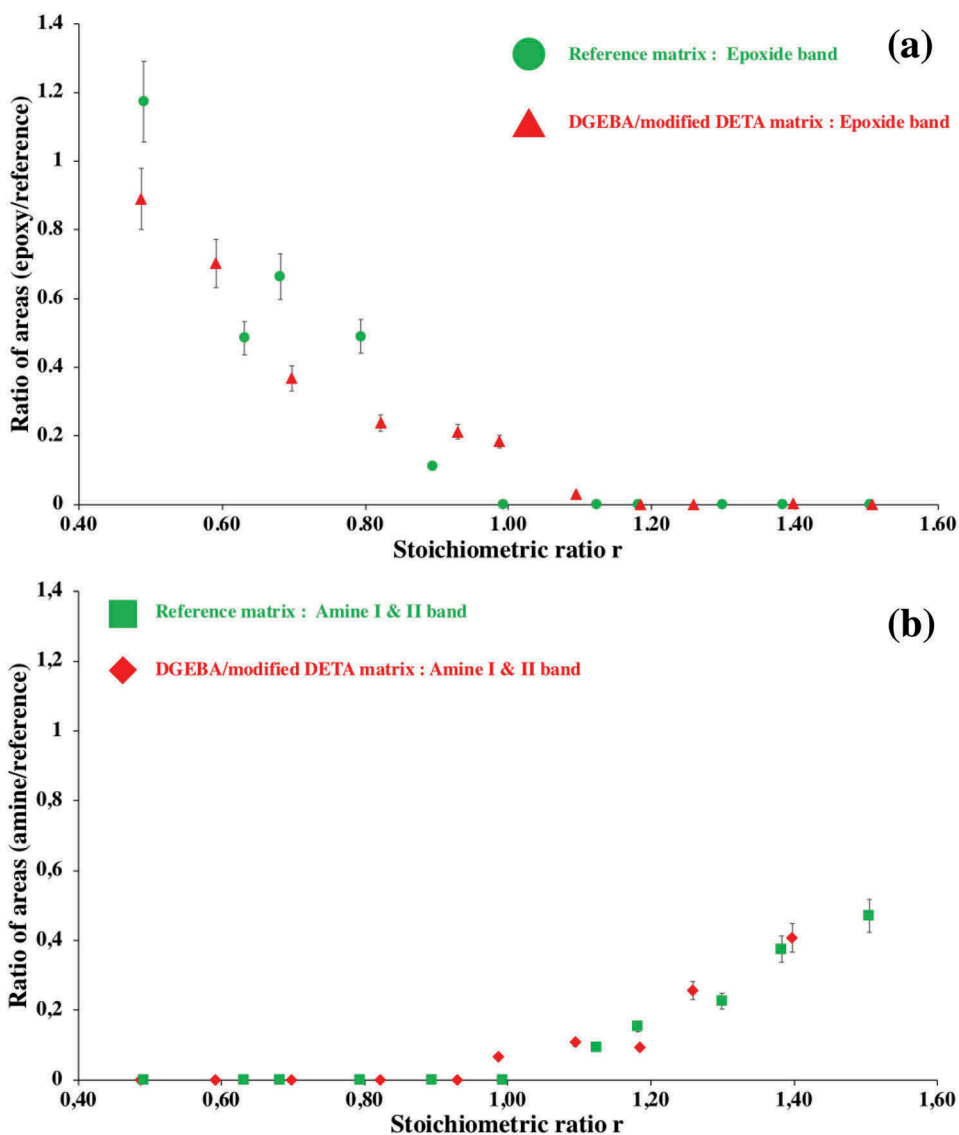


**Figure 3.** Evolution of the  $T_g$  as a function of the ratio  $r$  for the reference matrix (green), the DGEBA/modified DETA matrix (red) and schematic representations of networks for (a) the densest network for the reference matrix at  $r = 1.0$  and (b) the densest network for the DGEBA/modified DETA matrix at  $r = 1.2$ .

The MIR spectra of modified DETA confirmed the absence of extracted water and moreover, the conductivity of modified DETA was higher than the one of pure DETA with conductivities of  $1.1 \mu\text{S}\cdot\text{cm}^{-1}$  and  $12.9 \mu\text{S}\cdot\text{cm}^{-1}$  respectively, which indicated the presence of ions due to the reaction with the fibers during the impregnation step.

The presence of epoxide and amine functions in the matrices for each ratios has been investigated by near infrared spectroscopy and the results are shown in Figure 4. The number of epoxide functions of the reference (pure DGEBA/pure DETA matrix) decreased until they were all consumed by the reaction for  $r = 1.0$ , at the stoichiometry, and remain non-existent for  $r > 1.0$ , as expected [44]. For pure DGEBA/modified DETA matrix, epoxide functions decreased at a slightly lower rate compared to the reference and were totally consumed for  $r = 1.2$  as shown in Figure 4(a). The number of amine functions of the reference was non-existent for  $r < 1.0$  and began to increase after  $r = 1.0$  which is consistent with the total consumption of epoxide functions at the same ratio. The increase of amine functions is directly linked to addition of the excess of DETA. For pure DGEBA/modified DETA matrix, the quantity of amine functions started to appear at  $r = 1.0$ , then remain constant until  $r = 1.2$  where it starts to increase at a rate similar to the reference as shown in Figure 4(b).

All these observations indicated that the contact of DETA with the fibers led to a shift of the stoichiometric ratio from  $r = 1.0$  to  $r = 1.2$  paired with a  $T_g$  depression of  $11^\circ\text{C}$  between the reference matrix and the DGEBA/modified DETA matrix for stoichiometric ratios  $r = 1.0$  and  $r = 1.2$  respectively. This ratio appeared to be the closest to the stoichiometric mix ratio that led to the densest network for the system pure DGEBA/modified DETA. This indicates that this system needs an extra amount of DETA, and so of amine functions, in order to have a quasi-complete reaction. This observation implied



**Figure 4.** Evolution of ratio of areas of peaks of (a) epoxide functions or (b) amine functions on reference areas as a function of the ratio  $r$  for the reference matrix (green) and DGEBA/modified DETA (red).

that modified DETA had about 16% of amine functions that could not react with epoxide functions, functions that may have been modified during the impregnation process. NIR analysis showed that this shift was not caused by a simple elimination of amine functions because amine functions coexisted with epoxide functions at  $r = 1.0$  and  $r = 1.1$ . The presence of both functions indicates that the reactivity of at least one of them has been modified in a way that prevents them to react together and thus support the modification of amine functions by the water absorbed on fibers surface. The modification of one or

more amine functions on DETA led to the formation of a looser network (Figure 3(b)) explaining the lower  $T_g$  in comparison to the reference.

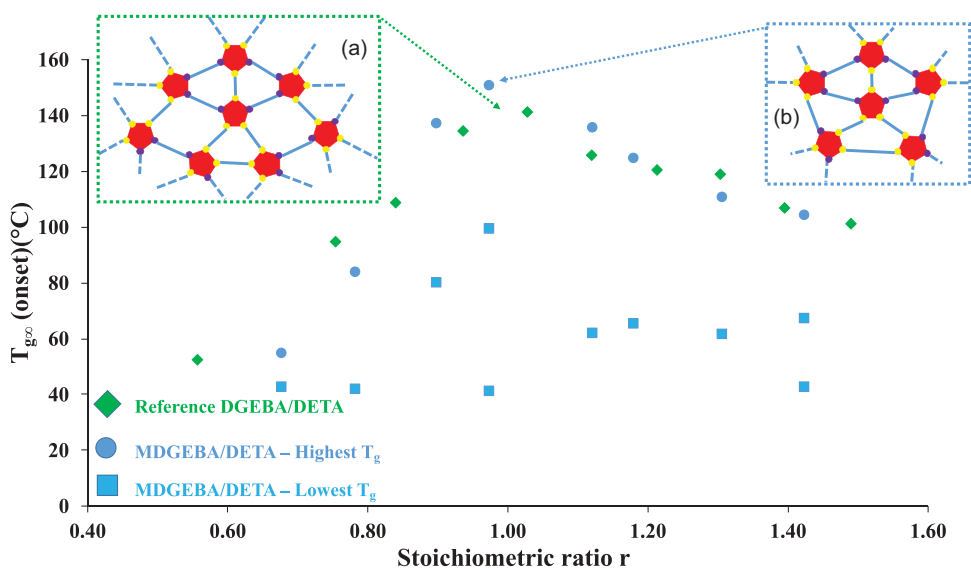
### 3.3. Influence of fibers on DGEBA

In the same manner, samples made with modified DGEBA (DGEBA in contact with stabilize flax fibers for one hour at 50°C) were analyzed by DSC in order to compare their glass transition temperature to the ones of the reference with various stoichiometric ratio  $r$ . The Figure 5 shows the results of this analysis: the reference curve is the same as the one presented in Figure 3.

First of all, DGEBA modified samples exhibited more than one  $T_g$  while the reference had only one. This means that different distinct networks coexist within the matrix for each stoichiometric ratio  $r$ . The highest  $T_g$  value for each ratio seemed to be slightly increased compared to the value of the  $T_g$  of the reference corresponding to a quasi-non modified network while the other  $T_g$ , significantly lower, corresponded to depressed networks within the matrix. The highest  $T_g$  value was obtained for  $r = 1.0$  as for the reference which indicated that the contact with water did not modify the stoichiometry of the epoxide/amine reaction.

This increase of maximal  $T_g$  could be explained by the solubilization of some free water originally absorbed on the fibers in DGEBA during the impregnation step. Epoxy resin can solubilize a certain amount of water close to 3% even if it is hydrophobic. Under this saturation limit, the water is intimately mixed with the resin and above, the water exists in a separated phase [28].

The presence of water in modified DGEBA has been investigated by MIR spectroscopy. The spectrum of modified DGEBA was compared to the ones of pure DGEBA,

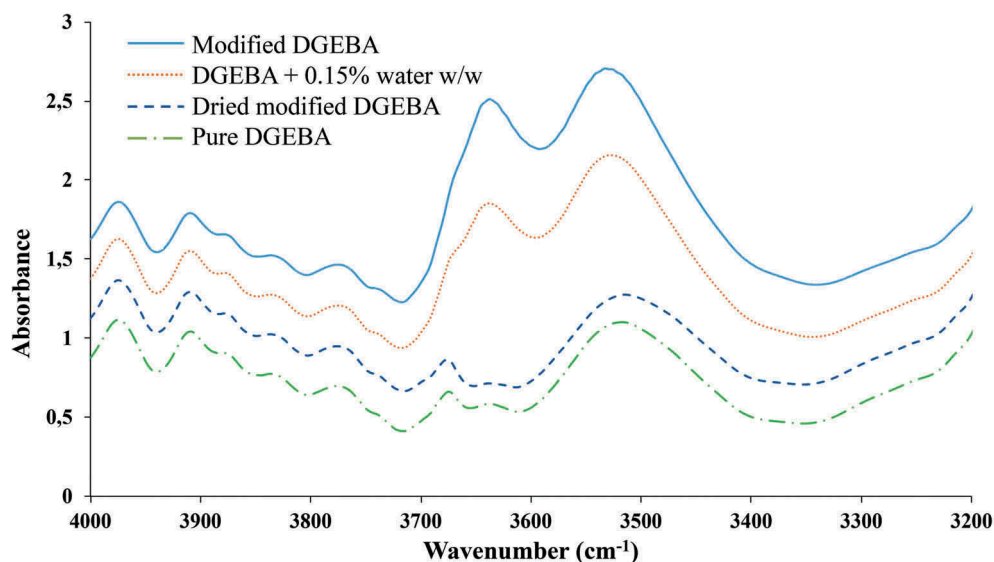


**Figure 5.** Evolution of the  $T_g$  as a function of the ratio  $r$  for the reference matrix (green), the modified DGEBA/DETA matrix (blue) and schematic representations of networks for (a) the densest network for the reference matrix at  $r = 1.0$  and (b) the densest network for the modified DGEBA/DETA matrix at  $r = 1.0$ .

DGEBA with added water and modified DGEBA that has been dried 12 h at 100°C and are presented in Figure 6. Pure DGEBA and dried modified DGEBA exhibited the same bands. The band at 3500 cm<sup>-1</sup>, corresponding to the O-H stretching of hydroxyl groups, indicated the presence of dimers (or higher molecular weight species) [47]. Modified DGEBA and DGEBA with added water showed the same band at 3500 cm<sup>-1</sup> but more intense and a second one at 3635 cm<sup>-1</sup> also corresponding to the O-H stretching of hydroxyl groups [48]. The presence of additional hydroxyl groups in modified DGEBA, the similarity of its spectrum with the one of DGEBA with added water and the disappearance of the O-H stretching band at 3635 cm<sup>-1</sup> when modified DGEBA was dried confirmed the presence of water in modified DGEBA and thus its extraction from the fibers during the impregnation step.

It has been shown that a small amount of water, lower than 3%, can accelerate the reaction between the resin and the hardener by ring opening reaction of epoxide functions [29]. Moreover, this phenomenon could improve the flexural load and the flexural storage modulus of the matrix [28,29] by increasing the final conversion giving a denser network as shown in Figure 5(b).

DSC measurements also showed the formation of other distinct networks for the modified DGEBA matrix samples with a lower T<sub>g</sub>. The formation of double networks in epoxy systems has been studied in the literature. Usually, the formation of double networks is the results of the use of a blend of curing agents with different reactivities [49]. In this case, there was only one curing agent and only DGEBA was modified. An explanation would then be that a part of the extracted water would have acted as an accelerator for the reaction while the remaining water would have made amine functions less reactive (as described in part 3.3.) resulting in distinct networks. The absence of



**Figure 6.** ATR spectra (from top to bottom): Modified DGEBA, pure DGEBA mixed with 0.15% of water w/w, Modified DGEBA dried for 12 h at 100°C and pure DGEBA. Spectra were shifted parallel to the y-axis for clarity.

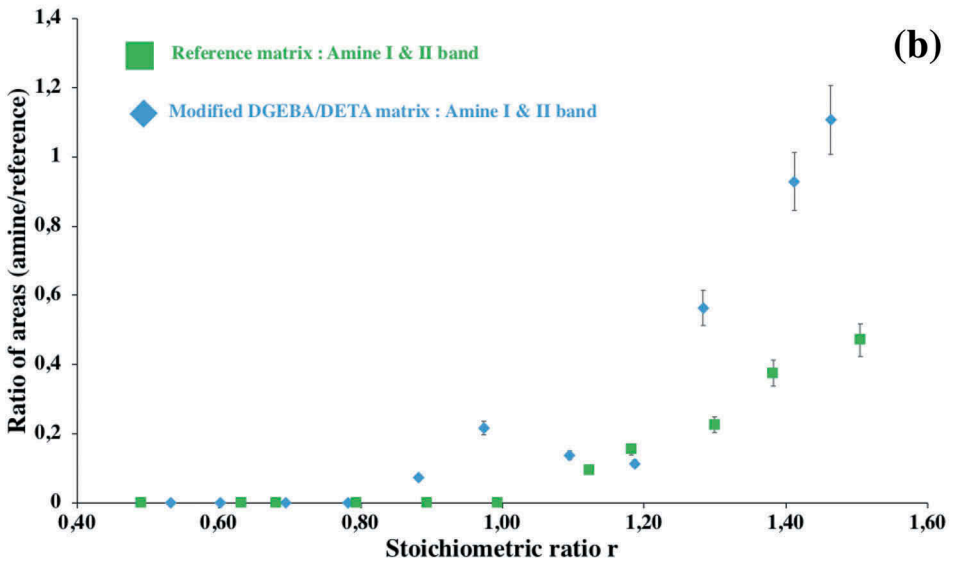
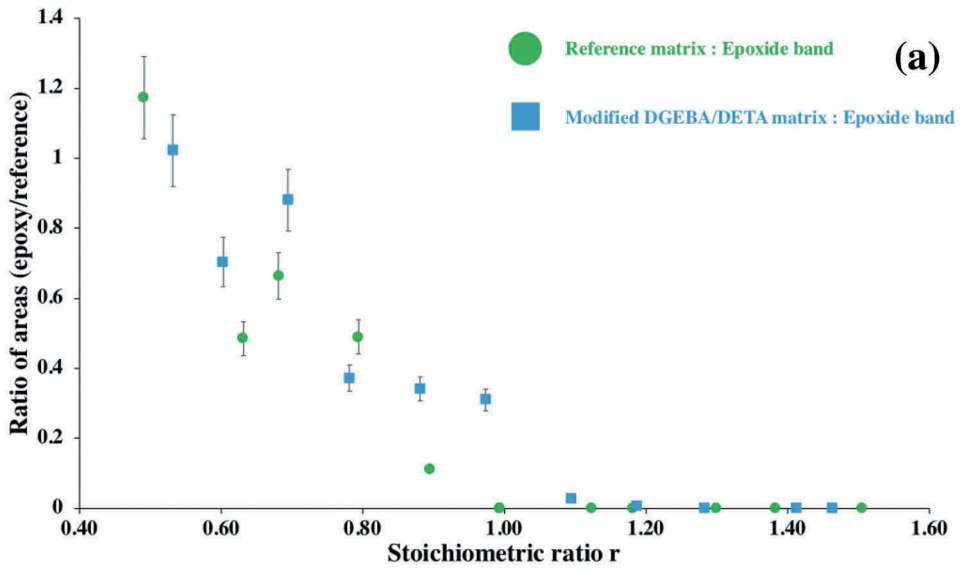
stoichiometric shift could be explained by the variation of water content in the reaction compared to the amount of DETA for each ratio  $r$ . For modified DETA experiment, all the DETA was in contact with a certain amount of water of the fibers, so the ratio DETA/water remained the same for each stoichiometric ratio. In this case, DGEBA extracted a certain amount of water which was constant for all stoichiometric ratios while the quantity of DETA varied. This could have an effect on the acceleration and the conversion of the polymerization and the modification of DETA. Also in this experiment, the extracted water in DGEBA was put in contact with DETA at the same time as the DGEBA was put in contact with the DETA so both reactions occurred simultaneously with most probably different rates. Furthermore, the modified DGEBA has been analyzed alone in DSC with two scans in order to determine if there was a reaction of homopolymerization during the contact with fibers. The DSC analysis showed that unmodified and modified DGEBA have the same  $T_g$  around  $-20^\circ\text{C}$  measured on the second scan. It confirms that DGEBA homopolymerization reaction in presence of fibers is very limited even non-existent, as this was already demonstrated with cellulose nanofibers [27]. The extraction of passive compounds from the fibers that could interfere with the reaction during the DGEBA/DETA mix could not explain these results. The experiments on DETA have shown that DETA seems to extract more compounds from the fibers, and still, there is only one network for modified DETA samples (Figure 3).

However, there was a slight difference between the NIR spectra of the reference matrix and of the modified DGEBA/pure DETA matrix, as shown on Figure 7. Epoxide functions decreased at a lowest rate than the reference and a certain amount remained for  $r = 1.0$  at the supposed stoichiometry (Figure 7(a)). It was the same for amine functions with an abnormal amount for  $r = 1.0$ . There was approximately the same amount of both functions which implies that the network formed is the result of an almost stoichiometric ratio and could explain why the  $T_g$  for  $r = 1.0$  was the highest. After  $r = 1.0$ , the increase rate of amine is faster than the reference as shown on Figure 7(b). This higher rate could be explained by the excess of modified non-reacted amine functions in the networks with the lowest  $T_g$ .

### **3.4. Mechanical properties of flax fibers composites**

Composite laminates were tested in 3 points bending tests for different stoichiometric ratio from  $r = 0.8$  to  $1.3$  in order to assess the impact of flax fibers on the polymerization of the matrix in the real case of composite manufacturing. Figure 8 reports the flexural modulus and maximum stress obtained for the different specimens tested. The value of the flexural modulus of the composites varied according to the mixing ratio between DGEBA and DETA. The lowest value was obtained for  $r = 0.8$  (i.e., 10.5 GPa) and the highest value for  $r = 1.2$  (i.e., 13.2 GPa). Moreover, the value of the modulus increased with the ratio  $r$  from  $0.8$  to  $1.2$  and then decreased for  $r = 1.3$ . The value of the maximum stress remains more or less the same, around 140 MPa, despite the modification of the stoichiometric ratio  $r$ .

The pattern observed for the values of the flexural modulus corresponded to the results obtained in DSC with modified DETA matrices (Figure 3). This seems to indicate that there is a direct link between the modification of DETA by flax fibers and the value of the modulus of the composite laminate. It appeared that, even formerly mixed with DGEBA, the DETA could be modified by the water contained in flax fibers during composite manufacturing. Consequently, an addition of DETA is needed in order to

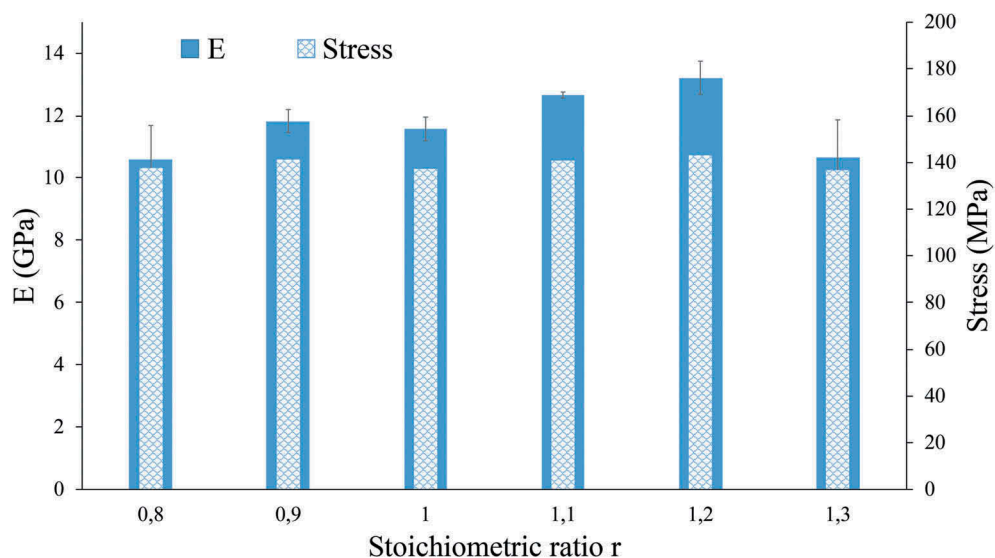


**Figure 7.** Evolution of ratio of areas of peaks of (a) epoxide functions or (b) amine functions on reference areas as a function of the ratio  $r$  for the reference matrix (green) and modified DGEBA/DETA (blue).

obtain the densest matrix (as presented in 3.2). Shifting the mixing ratio from  $r = 1.0$  to  $r = 1.2$  led to a 15% increase of the flexural modulus of the composite.

#### 4. Conclusions

Studying the influence of natural fibers (i.e., flax fibers) on network formation of DGEBA/DETA matrix, absorbed water appeared to be the key parameter. The water



**Figure 8.** Modulus and stress of flax fibers composites, for different stoichiometric ratios  $r$  (matrix) obtained in 3 points bending test.

absorbed on natural fibers is a key parameter in composite manufacturing. Water has a different impact on the resin and the hardener and several phenomena could be involved. The amine functions of the hardener could be modified by water and become less reactive. An excess of hardener is then required to offset the lack of reactive functions. In the case of modified resin, it seems that the water did not react with DGEBA during the impregnation phase and is only extracted. Then, when put in contact with DETA, the water may act both as an accelerator that lead to an improvement of the network and react with the DETA leading to some distinct looser networks. Flexural tests on composite laminates showed that even in the real case of composite manufacturing, the modification of DETA could still occur leading to a shift of stoichiometry. Moreover, a simple addition of DETA in the mixing ratio ( $r = 1.2$  instead of  $r = 1.0$ ) led to a 15% increase of the flexural modulus of the composite. Therefore, the water content in flax fibers is a major parameter to be taken into account especially as the complete removal of this water cannot be a solution. These reactions should be investigated by isothermal microcalorimetry (IMC) to improve the understanding of the phenomena involved.

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