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***Development of Composite Materials Based on Natural Fibres
for the Production of SMC Compounds.***

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ABSTRACT

The use of natural fibres as reinforcement for the production of composite materials and the use of adhesively bonded joints are two solutions widely studied to reduce the environmental impact of automotive components. In this study, the mechanical behaviours of a flax-reinforced unsaturated polyester (UP) resin and of three polymeric adhesives were tested.

Because of the intrinsic hygroscopicity of natural fibres, preliminary testing was conducted to measure water content and water regain at varying storage conditions. Successively, the tensile properties of the flax were investigated. The composite material was produced reinforcing the aforementioned UP resin with three different contents (10%, 20% and 30% w/w) of two types of short (20 mm) randomly oriented flax: pre-dried flax and flax as such, stored under variable RH conditions. The material was tested, and the obtained results were compared with a simple theoretical model for composite materials (rule of mixture). The comparison showed that an optimization of the whole production process is required, either to match the theoretical predictions and to enhance the reproducibility of the tensile properties.

Mechanical properties of the three polymeric adhesives were tested at different temperatures. The epoxy adhesive showed the best performances in terms of ultimate strength and failure mode.

SOMMARIO

L'utilizzo di fibre naturali come rinforzo nella produzione di materiali compositi e quello di adesivi all'interno di giunzioni sono due soluzioni ampiamente studiate per ridurre l'impatto ambientale di componenti per il settore automotive. In questo lavoro è stato studiato il comportamento meccanico di una resina poliestere insatura (UP) rinforzata con lino e quello di tre adesivi polimerici.

A causa dell'intrinseca igroscopicità delle fibre naturali, sono stati condotti dei test preliminari per misurare il contenuto di acqua e la velocità di assorbimento al variare delle condizioni di umidità relativa durante lo stoccaggio. Successivamente, sono state testate le proprietà a trazione del lino. Il materiale composito è stato poi prodotto rinforzando la sopracitata resina poliestere con tre differenti quantitativi (10%, 20% e 30% m/m) di due tipi di fibra corta (20 mm) con orientazione casuale: essiccata e stoccata a condizioni di umidità relativa variabile. Il materiale è stato testato e i risultati ottenuti sono stati comparati con un semplice modello teorico per materiali compositi (regola delle miscele). Questa comparazione ha dimostrato come un'ottimizzazione dell'intero processo di produzione sia necessaria per ottenere proprietà meccaniche più vicine a quelle teoriche e per migliorarne la riproducibilità.

Le proprietà meccaniche dei tre adesivi polimerici sono state testate a diverse temperature. L'adesivo epossidico ha mostrato le performance migliori in termini di resistenza massima e meccanismo di rottura.

1. INTRODUCTION

In the last 25 years, global concern towards climate changes and environmental pollution have pushed industry and scientific community in finding new solutions for traditional problems, which guarantee higher sustainability and lower environmental impact. This research has involved all industrial sectors and, among them, also transportation sector, which produces at present 21% of the total GHG emissions (*source: European Environment Agency, 2015*).

In this view, the interest towards natural and bio-based materials has increased exponentially. Natural fibres, in particular, have been widely investigated as a possible alternative to traditional synthetic fibres (glass and carbon, mainly) for the production of composite materials. Cultivation and production of natural fibres, in fact, has a consistently lower environmental impact with respect to production processes of traditional ones.

At the same way, lightening of car components plays a key role in increasing fuel efficiency and, in turn, reducing vehicles emissions. In this sense, the substitution of mechanical joints with adhesive ones is one solution being increasingly investigated.

In this study, carried out in collaboration with Ranger Compositi s.r.l, both aspects, i.e. natural fibres and adhesives, were investigated.

The aim of the company was to exploit their own know-how in Sheet Moulding Compound (SMC) technology to obtain a Natural Fibre Composite material (NFC) for the production of car components. This material, characterized at the same time by low environmental impact and mechanical properties sufficiently high to make it competitive on the market, would be a bio-based epoxy resin reinforced with flax fibre.

Being the development of such a challenging material a complex path, this thesis sets itself as a preliminary step. This study, in fact, was made on a traditional unsaturated polyester (UP) resin reinforced with flax fibres.

Being natural fibres intrinsically highly hygroscopic, one of the main issues was to study the behaviour towards different relative humidity (RH) conditions of two technic flax rovings (NATTEX[®] -by Dehondt- and TEX400 -by Safilin), intended for the production of composite materials. Changes in physical (desorption and regain kinetics) and mechanical (tensile) properties with different RH conditions were evaluated. The results obtained from mechanical testing were used to predict the final properties of the abovementioned composite material.

Actually, at some point of the physical testing, TEX400 was discarded and mechanical testing was performed on NATTEX[®] roving only. Successively, pre-dried NATTEX[®] and NATTEX[®] as such, i.e. exposed to the uncontrolled environment inside the production plant, were used as reinforcements.

Mechanical (tensile) properties of the composite material were tested, and the results compared with predictions. Evaluations on the effect of drying on the final properties were made.

The second goal of this thesis was to compare the performances of three polymeric adhesives when adhesive joints were made bonding traditional GFRPs or bonding NFCs, at different temperatures. Testing on bonded GFRPs only, however, could be made due to technical issues in the production of NFC samples.

2. BACKGROUND

2.1 COMPOSITE MATERIALS IN AUTOMOTIVE INDUSTRY

Since their first development, glass fibre-reinforced (GFR) and carbon fibre-reinforced (CFR) composite materials have been increasingly exploited in transportation and, in turn, automotive industry. In 2018 36% of the European production of GFR plastic was destined to transportation sector, on par with construction and infrastructure one (35%). At the same way, 24% of the global demand of CFR plastic in 2018 came from automotive, overtaken by aviation and aerospace only (36%) (*Source: AVK Market Report, 2018*) [1].

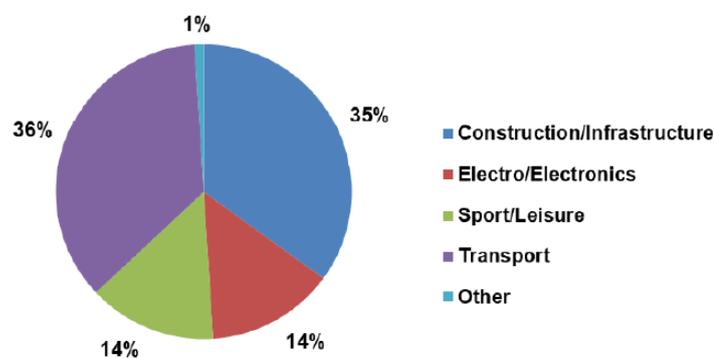


Figure 1. GFR plastic production in Europe by application industry [1].

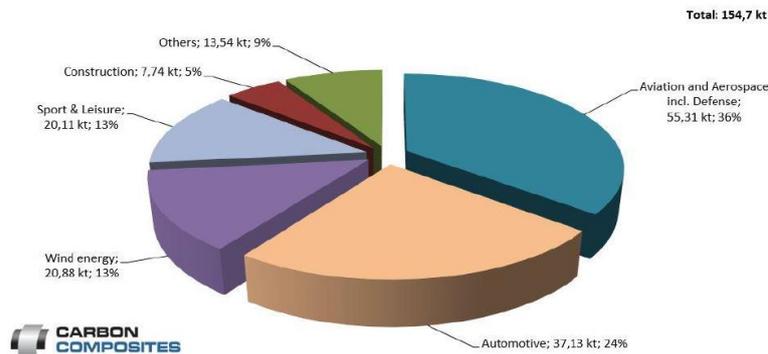


Figure 2. Global CFR plastic demand by application industry [1].

Recent development of hybrid and full-electric cars has further boosted the use of this class of materials, which lightness is fundamental in compensating the overweight coming from the batteries. This, in combination with higher specific mechanical properties with respect to other structural materials and a high durability made composite materials a key element in this sector, where requirements in terms of mechanical properties and sustainability are becoming more and more stringent.

From the point of view of sustainability, actually, issues emerge when life cycle assessments are performed on components in composite materials [2]. The energy consumption of the production process and the environmental impact of the final disposal, in fact, are addressing the scientific community in finding new ways to reduce the carbon footprint of this class of materials.

In this view, the use of bio-based materials, like bio-resins and natural fibres, is one of the most studied solutions [3][4][5][6].

2.1.1 Natural Fibres in Composite Materials

From the point of view of sustainability and reduction of environmental impact, the low carbon footprint, the renewability and the end-of-life scenarios of natural fibres (incineration, for example), made them the first alternative to traditional reinforcement (glass and carbon) in the production of composite materials. At present, 15% of the European composite market is covered by Wood-Plastic Composites (WPC) and Natural

Fibre Composites (NFC), and, since 2012, their production has constantly increased by 3% per year (*Source: nova Institute – GmbH*) [7].

In addition to their lower impact on the environment, natural fibres are characterized by a low specific weight which results in better specific strength and stiffness if compared to glass fibres. They also possess high electrical resistance and good insulating (thermal, acoustic and vibrational) properties. Moreover, from an economical point of view, their processing generates negligible wear of tools and, in general, high production can be obtained with low investment and at low costs [5][6][8].

At the same time, the natural origin makes these fibres highly hygroscopic and subjected to biodeterioration. Hygroscopicity, in particular, results in consistent water absorption from the surrounding environment that, in turn, creates issues in terms of dimensional stability (swelling) and adhesion with the matrix. More, water evaporation during transformation processes can result in the formation of discontinuities (voids or bubbles). This feature, thus, affects mechanical properties of the fibres and, in turn, of their composite materials [9][10][11].

In addition, natural fibres are characterized by a low thermal stability and fire resistance, that in turn, limit the processing temperature range and the variety of matrices. Another intrinsic limit consists in the dependence of the properties of the fibres on the location (and its climatic conditions) of the harvest, on the age of the fibres, on their transportation and storage conditions. Finally, durability and strength (compressive and impact strength, in particular) are lower than those of synthetic fibre-reinforced plastics [5].

By the way, issues coming from hygroscopicity and poor adhesion with the matrix can be strongly reduced with chemical treatments of the fibres. Among them, treatments with alkali (NaOH), acetic anhydride (acetylation), acrylic acid (acrylation), maleated coupling agents (maleic acid), silanes and styrene are the most used [6][12][13][14].

2.1.2 Structure of Flax Fibres

Among the wide variety of natural fibres that are being investigated, flax (*Linum usitatissimum*) is one of the most studied. Flax grows in moderate climates and main producers are China, Canada, France, Belgium and the Netherlands [15][16].

The hierarchical structure of flax cells is very complex. Macroscopically, a flax stem is composed of bark, phloem, xylem and a central void, in order from the outer towards the centre. At a mesoscopic scale, the cross-section of a single bundle is composed of a number (between 10 and 40) of fibres “glued” together by pectin. For what concerns the microstructure of an elementary fibre, it is extremely complex. Each fibre, in fact, is itself made of concentric cell walls, in which the arrangement of the constitutive components changes from wall to wall. At the centre a small open channel, the *lumen*, is present, which contributes to water uptake. The microstructure is shown in Figure 3 [16].

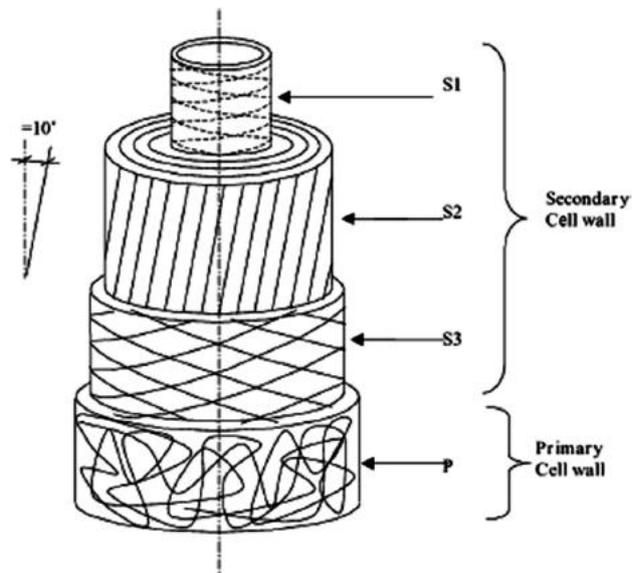


Figure 3. The microstructure of a flax fibre cell [16].

The secondary cell wall (S1 + S2 + S3), which is thicker than the outer primary cell wall, is the one responsible for the strength of the fibre. All the layers are composed of cellulose microfibrils, parallel one to the other that form an angle with the fibre direction. This angle

in S2 wall (the thickest layer) is equal to 10° and is responsible of fibre high tensile strength [16][17].

Finally, at the nanoscale, a microfibril is constituted of cellulose chains, laid down in an oriented, highly crystalline microfibril, embedded in an amorphous matrix made of pectin and hemicellulose. This nanostructure can be seen in final part of Figure 4, where all the structural levels are shown.

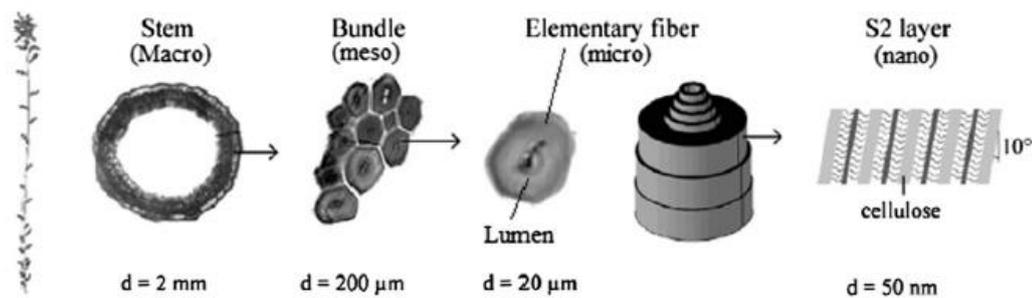


Figure 4. Structure of flax at progressively decreasing scale, from the stem to the nanostructure [16].

Main constituents of flax are thus cellulose, hemi-cellulose and pectin plus lignin and wax, in varying proportions. Cellulose, hemicellulose and lignin are the principal constituents, and it has been shown that mechanical strength of the fibres depends on their relative amounts [15][18]. Cellulose, in particular, which is the strongest and stiffest constituent, represents between 65 and 75% of the total weight of flax fibres [18]. It is a semi-crystalline polysaccharide with a huge amount of hydroxyl group and is the one responsible for the hydrophilic character of flax fibres.

Chemical treatments mentioned in Section 2.1.1 aim to substitute these hydrophilic terminal groups with hydrophobic ones, in order to favour the formation of stronger bonds with the polymeric matrix.

2.2 SHEET MOULDING COMPOUND (SMC) TECHNOLOGY

Many technologies are available for transformation of composite materials. A first distinction can be made between technologies for plastics reinforced with continuous or discontinuous fibres.

For the first class, most common solutions are: lamination (manual, semi-automatic or automatic) followed by treatment with autoclave, filament winding, pultrusion, Resin Transfer Moulding (RTM), vacuum infusion and compression moulding of Long Fibre-reinforced Thermoplastic materials (LFT).

In the second class of technologies we have spray lay-up processes (open mould), injection moulding (closed mould) and compression moulding of sheet-like or bulky semi-finished products (closed mould). These last two technologies are called Sheet Moulding Compounds (SMC) and Bulk Moulding Compounds (BMC), respectively.

In Glass-Reinforced Plastic (GRP) market, in particular, Sheet Moulding Compound is undoubtedly the dominant technology which, in 2018, covered 25% of the European production of GRP (*Source: AVK Market Report, 2018*) [1].

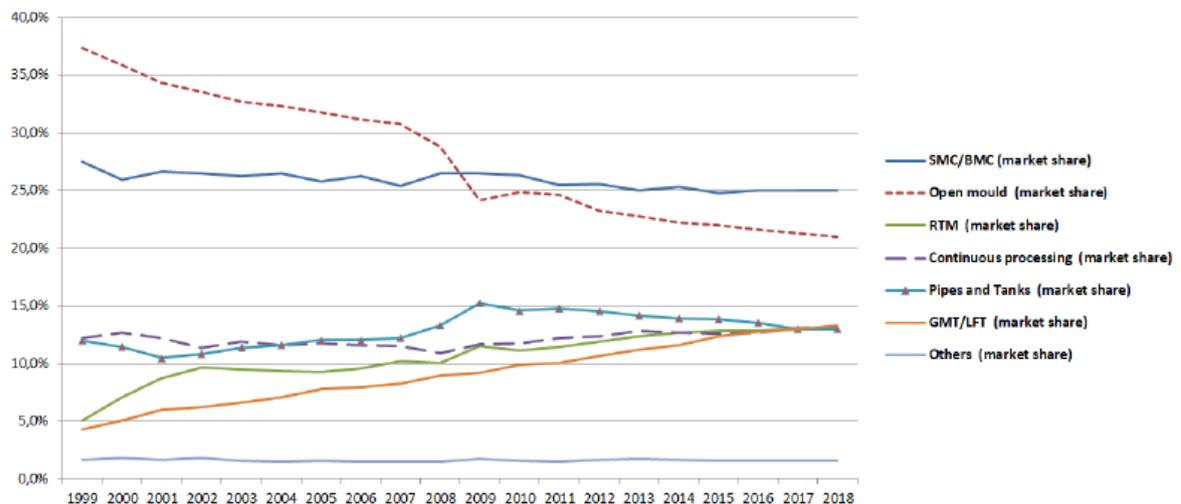


Figure 5. GRP production in Europe by transformation technology [1].

SMC is a two-step transformation process in which a first phase, called “compounding”, is followed by a compression moulding phase. During compounding (Figure 6) a discontinuous fibre-reinforced thermosetting semi-finished product is obtained.

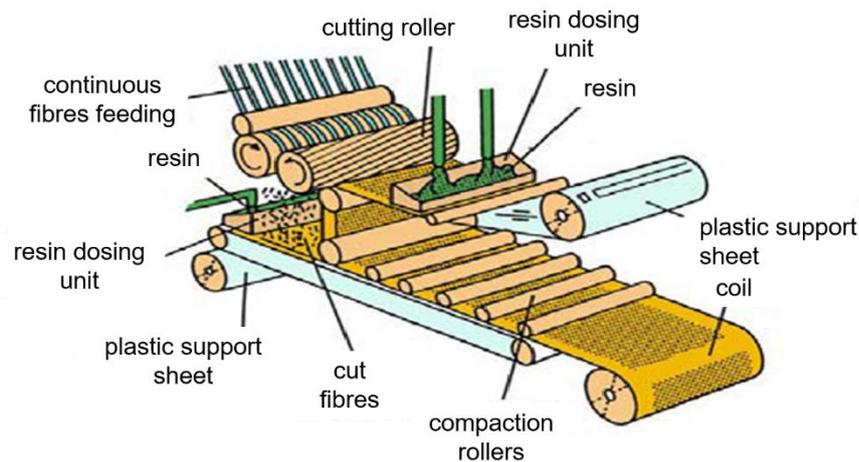


Figure 6. Schematic representation of SMC compounding phase.

As first, continuous glass fibre is fed to a cutting unit from which the cut fibre falls on a plastic (nylon) sheet carrying a layer of unpolymerized matrix, which thickness is uniformed by a dosing unit. Successively, an identical plastic sheet carrying unpolymerized matrix comes from above, “covering” the cut fibres and creating a sort of sandwich. Finally, the material passes through a stage of compaction rolls where the pressure uniform the thickness of the compound and favours the complete impregnation of the fibres. The product is collected in rolls and stored at $T = 30^{\circ}\text{C}$ for 1 – 7 days for maturation.

During compression moulding step a sheet of SMC compound is fed inside the cavity of the mould and thermoformed in the desired shape. If the correct amount of material is used, the material flows filling the whole cavity, imparting the fibres a certain degree of orientation along the flow lines. Anyway, these compounds are still referred to as reinforced with randomly oriented fibres, and their properties are generally considered isotropic.

Main advantage of this technique is the high productivity: complex shapes, in fact, can be obtained in short cycle time. Moreover, a high degree of design freedom can be achieved.

Most common drawbacks are associated to distortions induced by cooling of the material. The addition of a thermoplastic mixture to the matrix formulation is one solution used to limit this effect.

Matrix formulation, in particular, is a crucial aspect. Its viscosity at the unpolymerized state, in fact, must be high enough not to be “squeezed out” by compaction rolls during compounding phase but, at the same time, it must be low enough to ensure correct flow and complete filling inside the cavity during compression moulding phase. The correct behaviour can be obtained by properly tuning the ingredients of the formulation (resin, mineral charge, catalyst, inhibitor, thermoplastic additive). From this “tunability”, the chemical composition of the matrix can be optimized for every type of reinforcement, making this technique even further flexible [19].

Application of this technology to the production of NFC materials has been studied with satisfying results. However, optimizations are needed to shift from a glass fibre-addressed plant to a natural fibre-addressed one [20].

2.3 ADHESIVES IN AUTOMOTIVE INDUSTRY

From the point of view of sustainability, another approach to reduce the environmental impact of vehicles is weight reduction [21]. Lighter components, in fact, help in increasing fuel efficiency and, in turn, in reducing GreenHouse Gas (GHG) emissions. In this view, composite materials are themselves a significant improvement, being lighter than metallic counterparts, but further lightening can be achieved with substitution of mechanical joints with adhesively bonded ones.

In addition to these considerations, the use of fasteners in mechanical joints requires the creation of discontinuities in the components, where stress concentrations are generated. On the contrary, adhesively bonded joints, being continuous, do not create issues in this sense and, in addition, allow for a certain design freedom.

Unfortunately, few theoretical models able to predict the behaviour of adhesives are available, limiting their applicability in primary structures. Moreover, this lack of

mathematical theories often results in an “overdesign” of the structures and advantages in terms of lightening are lost [22][23].

A crucial aspect that must be considered when an adhesive joint is produced is the quality of the surfaces being jointed, as it plays a fundamental role in maximizing the efficiency of the adhesive and, in turn, the final properties of the joint. The presence of defects, dirt and contaminants, in fact, may affect the bonding properties.

At the same way, the efficiency of an adhesive strictly depends on the chemistry of the surfaces and the types of chemical bonds (covalent, mainly, but also ionic and static attractive ones) that can be formed at the adhesive/adherend interface. That’s why an increase in the surface energy and surface roughness of the adherend can be an effective way to promote the formation of strong chemical bonds.

Many surface treatments can be performed to obtain this result. Most used are: surface sanding followed by cleaning with a solvent, chemical etching, cryogenic treatment, laser treatment and plasma treatment [22][24].

Many studies revealed that another factor affecting the mechanical properties of adhesive joints is their geometry, in relationship with the type of adhesive used [25][26].

3. EXPERIMENTAL DETAILS

3.1 MATERIALS

3.1.1 Flax

Two flax rovings were initially considered: NATTEX[®], by Dehondt, and Flax Low Twist Roving TEX 400 (from now on referred to as TEX400, for simplicity), by Safilin (Figure 7). Both materials, whose mechanical properties are compared in Table 1, are technic rovings intended for the production of composite materials.

Table 1. Mechanical properties of NATTEX[®] and TEX400 rovings.
Complete datasheets are shown in Appendix A.1 and A.2.

Roving	TEX	Tensile Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
NATTEX [®]	1300	12	115	1.0
TEX400	400	45	500	2.0



Figure 7. NATTEX[®] roving (left) and TEX400 roving (right).

The main difference between the two materials is that TEX400 is twisted (Z40), and thus it assumes the form of a cylindrical yarn. On the contrary, NATTEX® is not twisted and has the form of a flat tow. This can be observed from magnified images shown in Figure 8.

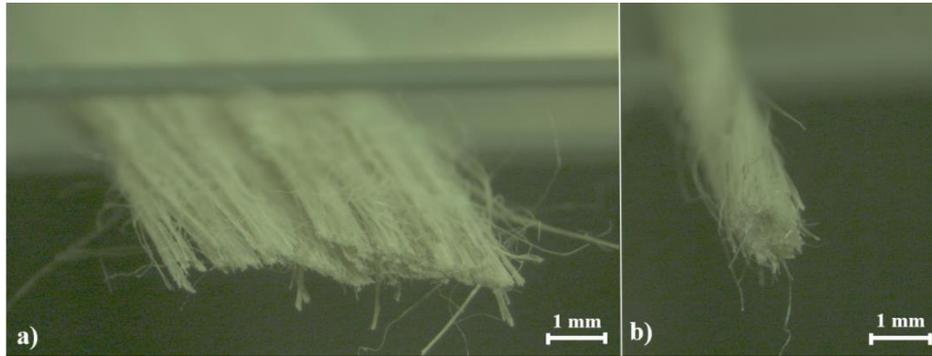


Figure 8. Magnified images of a) NATTEX® and b) TEX400 cross sections.

3.1.2 Matrix

An unsaturated polyester (UP) resin intended for SMC and BMC production was used, Palapreg® P17-02 by Aliancys (complete datasheet is shown in Appendix A.3). This resin is characterized by a viscosity between 1300 and 1500 mPa*s at $T=23^{\circ}\text{C}$, a density of 1300 kg/m^3 and a glass transition temperature of 170°C .

Based on this resin, two matrix formulations with different viscosities were prepared. The first, called V5, was the one with higher viscosity and it was reinforced with 10% and 20% content of flax. The second, called V6, characterized by a lower viscosity, was reinforced with a 30% flax content. Both formulations included: a) UP resin, b) liquid styrene, c) a thermoplastic (TP) mixture of polystyrene and polyvinyl acetate in styrene solution to reduce thermal-induced distortions, d) calcium carbonate (CaCO_3) with two different particle size distributions (5 AV and 2 AV) as mineral charge, e) 1,4-benzoquinone (PBQ) as inhibitor, f) 1,1-Di(t-butylperoxy)-cyclohexane as catalyst, g) MgO as paste thickener and h) zinc stearate as mould release agent.

Details of the two formulations and of the thermoplastic mixture composition are shown in Table 2 and Table 3, respectively.

Table 2. Composition of the two matrix formulations used.

Formulation	UP resin	Styrene	TP mixture	CaCO ₃ (5 AV)	CaCO ₃ (2 AV)	Zinc stearate	Inhibitor	Catalyst	MgO
V5	23.26%	2.58%	14.61%	26.34%	29.82%	1.99%	0.05%	0.75%	0.6%
V6	32.80%	2.58%	14.61%	24.85%	21.67%	2.09%	0.05%	0.75%	0.6%

Table 3. Composition of the thermoplastic mixture used.

Component	Thermoplastic mixture composition
PVA solution	47.6% (Pellets 40% + Liquid styrene 60%)
PS solution	52.4% (Pellets 33% + Liquid styrene 67%)

3.1.3 Adhesives and Glass Fibre-Reinforced Polymers (GFRP)

In this study, the performances of three two-component structural polymeric adhesives were tested:

- epoxy (Araldite[®] 2015-1, by Huntsman), with a 1:1 resin/hardener ratio;
- polyurethane (TS 850F, by Tonsan), with a 1:1 resin/hardener ratio;
- acrylic (TS 828, by Tonsan), with a 10:1 resin/hardener ratio.

Complete datasheets are shown in Appendix A.4, A.5 and A.6, respectively. These adhesives were used to join two different glass fibre-reinforced polymers: Menzolit[®] SMC 1100 NAT and Menzolit[®] SMC 0400 NAT. The former is characterized by higher GF content (36%) and higher mechanical properties, and it is used for structural components. The latter has lower GF content (27%) and lower mechanical properties, and it is used for aesthetic components. Mechanical properties are compared in Table 4.

Table 4. Comparison between mechanical properties of Menzolit[®] SMC 1100 and SMC 0400.

Material	Fibre content (%)	Density (g/cm ³)	Tensile modulus (GPa)	Tensile strength (MPa)	Flexural modulus (GPa)	Flexural strength (MPa)	Impact strength (kJ/m ²)
1100	36	1.80	10	100	11	190	100
0400	27	1.88	9	70	9	160	65

3.2 SAMPLE PRODUCTION

3.2.1 Flax Testing

3.2.1.1 Physical Testing

Desorption and regain testing were made to evaluate quantitatively the entity of the hygroscopicity of flax yarns. Testing was carried out on both NATTEX[®] and TEX400 rovings as such and in the form of carded fibres. A roving sample was obtained by cutting a number of pieces of roving and clipping them together with iron wire (Figure 9a, 9b). A fibre sample was obtained manually carding a number of pieces of cut roving to disentangle the single filaments (Figure 9c, 9d) and, again, clipping them together.

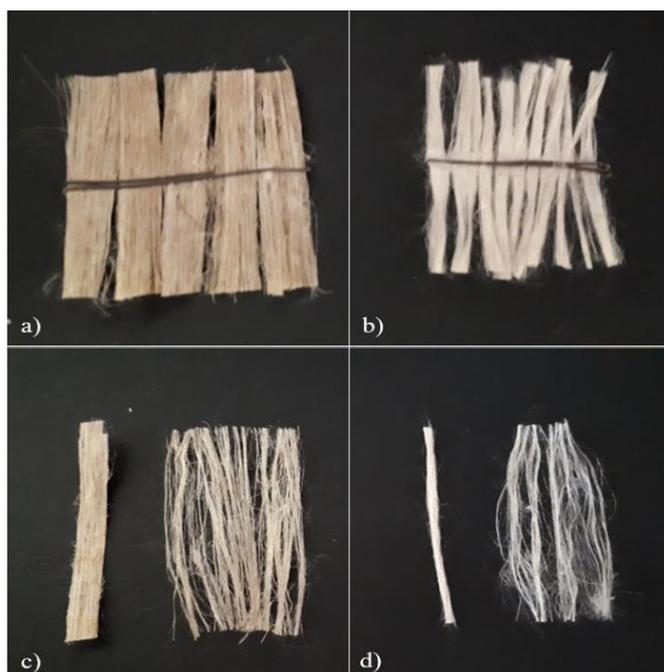


Figure 9. a,b) NATTEX[®] and TEX400 roving samples for desorption and regain testing.
c,d) Comparison between roving as such and carded fibres.

Samples were stored in different conditions of controlled relative humidity for an interval of time long enough to make the mass of the samples reach an equilibrium value. Sample

production and storage were made in a thermostatic chamber at Politecnico di Milano laboratories.

Storage conditions were $25\pm 5\%$, $48\pm 2\%$ and $96\pm 2\%$ RH, while temperature was the one present in the chamber, i.e. $23\pm 2^\circ\text{C}$. The difference in the uncertainties on RH values comes from the different methods used. For storage at $25\pm 5\%$ RH, conditions inside thermostatic chamber were exploited. The other controlled atmospheres were obtained putting supersaturated solutions of water and salts in desiccators and placing the same desiccators inside the thermostatic chamber: magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$) and potassium sulphate (K_2SO_4) were used to obtain $48\pm 2\%$ and $96\pm 2\%$ RH, respectively [27]. Testing at $25\pm 5\%$ and $48\pm 2\%$ RH was made on both materials. Then, TEX400 was discarded and testing at $96\pm 2\%$ RH was made on NATTEX[®] roving only.

3.2.1.2 Tensile Testing

Many studies taken from the literature highlight how the relative humidity of the environment affects the mechanical properties of natural fibre and of their composites. It has been studied how tensile properties are not affected (in some cases even enhanced) when samples are tested at increasing relative humidity conditions [29].

Tensile testing was made on NATTEX[®] roving as such only, stored at different RH values. Storage and sample production were made in the aforementioned thermostatic chamber. As first, roving specimens were cut from the bobbin, at a length of 80 mm. The width and the thickness of the specimen were the one of the roving as such (approx. 7 mm and 0.3 mm, respectively).

Secondly, samples were stored at $50\pm 5\%$, $64\pm 2\%$ and $78\pm 2\%$ RH conditions while temperature was $23\pm 2^\circ\text{C}$. For storage at $50\pm 5\%$, the thermostatic chamber conditions were exploited. This may seem in contradiction with what written in Section 3.2.1.1 (i.e. that RH inside thermostatic chamber was $25\pm 5\%$). The reason is the sensitivity of our thermostatic chamber towards seasonal changes. Differently from the temperature, that can be strictly controlled (at $T=23\pm 2^\circ\text{C}$), for the relative humidity only a maximum value can be fixed (at $50\pm 5\%$ RH). Below this maximum value, the RH depends on the external

environmental conditions. This guarantees a monthly consistency for RH values but discrepancies between different periods of the year.

The relative humidity conditions of $64\pm 2\%$ and $78\pm 2\%$ RH were obtained using supersaturated solutions of water and salts (NaCl and K_2SO_4 , respectively) and placing them in the closed thermal cabinet of the dynamometer used for testing.

According to literature, these solutions should have generated $75\pm 2\%$ and $96\pm 2\%$ RH values. This discrepancy is due to the available experimental setup: a constant relative humidity inside a closed chamber can be achieved only if the height of the chamber is equal to (or lower than) the diameter of the free surface of the supersaturated solution [27]. In our case, the room inside the cabinet was not enough to have a free surface sufficiently high to generate a RH value equal to the theoretical ones.

3.2.2 Composite Testing

The composite material was obtained by reinforcing the matrix formulations described in Section 3.1.2 with three different contents (%m/m) of randomly oriented NATTEX® roving, cut to a length of 20 mm. In details:

- V5 formulation was reinforced with 10% and 20% flax content;
- V6 formulation was reinforced with 30% flax content.

Flax roving used in this stage was stored at Ranger Compositi plant in Verano Brianza (MB), and the production of the composite material was made there too.

Assuming a dependence of the final properties on the moisture content of flax, two series of composite material were produced. The first series, called Dry-Long (DL), was reinforced with flax previously dried for approximately 24 hours in a ventilated oven at $T=80\pm 2^\circ\text{C}$. The second series, called Wet-Long (WL) was reinforced with flax roving stored at uncontrolled environmental conditions (and thus referred to as “wet”) inside the plant. Six different samples were thus obtained and named as shown in Table 5.

Table 5. Nomenclature used for the two different series of samples.

Flax State	10%	20%	30%
Dry Flax (DL)	POLY V5 DL 10	POLY V5 DL 20	POLY V6 DL 30
Wet Flax (WL)	POLY V5 WL 10	POLY V5 WL 20	POLY V6 WL 30

All the flax/matrix mixtures were hand-made, sealed in nylon sheets and left one week at 18°C for maturation. Then, each mixture was transformed by compression moulding at T=145°C and P=185 bar, and 200x200 mm² tiles were obtained. The thickness of each tile is shown in Table 6.

Table 6. Thickness of the tiles obtained for each sample.

Sample	V5 DL 10	V5 WL 10	V5 DL 20	V5 WL 20	V5 DL 30	V5 WL 30
Thickness	4.8 mm	4 mm	4.7 mm	4.8 mm	5.3 mm	5.5 mm

An identical tile was obtained for V5 formulation bare matrix only, with thickness of 5.70. It hasn't been possible to do the same for V6 formulation because of technological limits. Finally, all the tiles were cut to obtain tensile test specimens with size of 20x200 mm². Cutting of the specimens was made at Politecnico di Milano.

3.2.3 Adhesion Testing

In this study, a plasma treatment was used to activate the surfaces. The treatment was performed with Openair[®] technology, by Plasmatreat, and its effectiveness was assessed by spraying a solution with known surface tension on treated and non-treated surfaces, and comparing the patterns obtained. A better wetting of the surface implied an increase in the surface energy of the substrate and, in turn, an effective activation of the substrate. The comparison is shown in Figure 10.

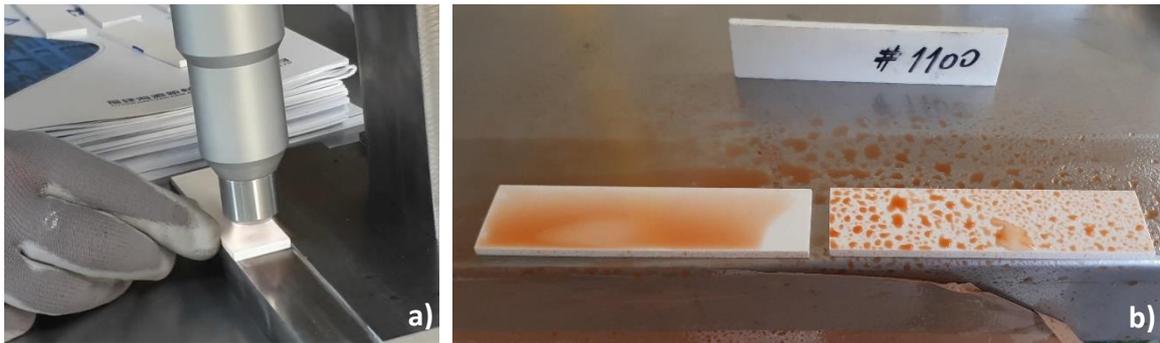


Figure 10. a) Openair® plasma treatment. b) Comparison between activated (left) and non-treated (right) samples sprayed with solution at known surface tension.

The adhesives were then applied, and single-lap-joint specimens for lap-shear testing were obtained. The adhesives were cured for two weeks at room T to ensure a complete development of the mechanical properties (see Appendix A.4, A.5 and A.6).

The geometry of the specimen can be seen in Figure 11.

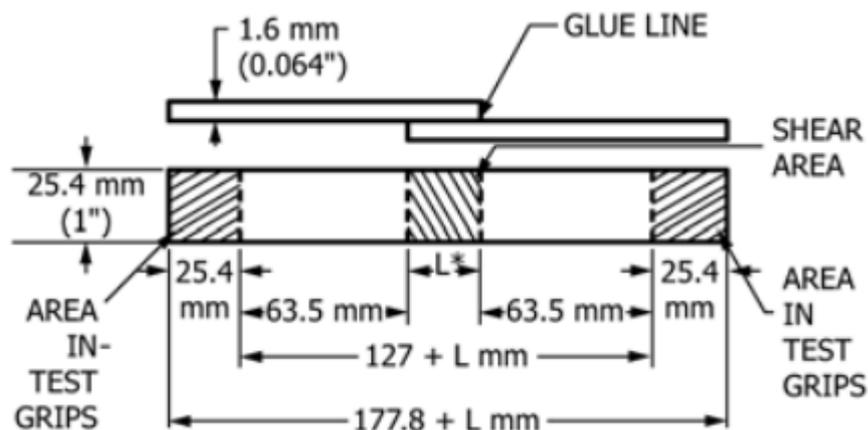


Figure 11. Specimen size for a lap-shear test.[30]

The dimensions for the specimens and for the joint area were chosen according to the relative standard [30]. The excess in polymeric adhesive was removed by machining operation, to avoid differences between real joint surface and nominal one.

Plasma treatment and sample production were made at Ranger Compositi s.r.l. plant in Verano Brianza. Machining was made at Politecnico di Milano laboratories.

3.3 TESTING DETAILS

3.3.1 Flax Preliminary Testing

3.3.1.1 Thermogravimetric Analysis

Thermogravimetry is a thermal analysis which consists in the continuous monitoring of the mass of a sample subjected to a defined thermal history. The variation of the mass can be recorded with respect to time (in case of isothermal analyses) or with respect to temperature (in case of complex thermal histories). A sample of material is put in a small crucible (volume of 110 μL), closed with a lid. The crucible is then placed on a precision balance, that will monitor the mass throughout the whole duration of the analysis. A TGA Q500 TA Instruments was used which, in principle, can operate in two different atmospheres, inert (N_2) or oxidative (air).

In this study, TGA analysis was carried out on flax stored at $25\pm 5\%$ RH. The sample was prepared in thermostatic chamber, and the closed crucible transported to the instrument in a small plastic bag to avoid contaminations from the environment.

An isothermal analysis was made, measuring the variation of the mass in time. A temperature of 80°C was chosen and a temperature ramp of $10^\circ\text{C}/\text{min}$ was used, the duration was 120'. The atmosphere chosen for the analysis was air, to better simulate the operative conditions during the drying step of the production process of the composite material. The applied thermal history can be seen in Figure 12.

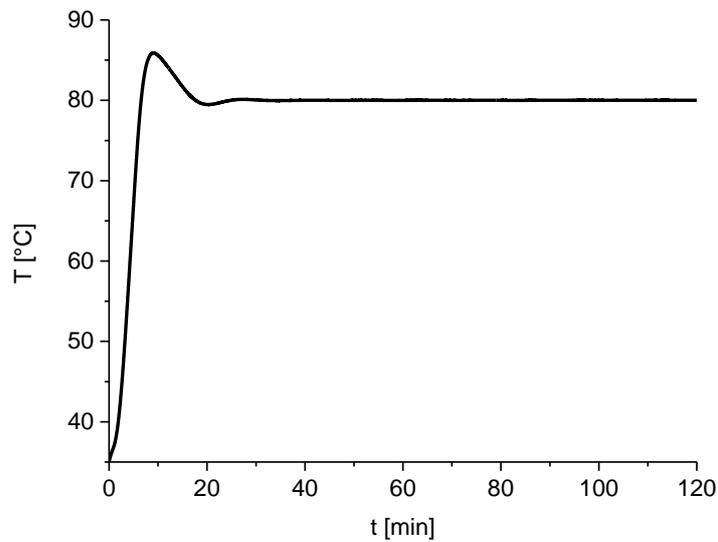


Figure 12. Thermal history applied during thermogravimetric analysis.

Under the reasonable assumption that mass loss was caused by water evaporation only, the equilibrium value for percentage mass variation has been directly related to the equilibrium moisture content of the sample. Percentage mass variation ($\Delta m\%$) was calculated according to Eq. 1.

$$\Delta m(\%) = \frac{m_f - m_i}{m_i} \times 100 = EMC. \quad (3.1)$$

3.3.1.2 ASTM Method for Determination of Amount of Moisture

To assess the equilibrium moisture content of samples stored at a relative humidity of $48 \pm 2\%$ and $96 \pm 2\%$ a standard procedure was followed [32]. The samples used for this testing were the same used for successive physical testing, prepared as described in Section 3.2.1.1.

Each sample was first weighted to measure its “wet” mass, and then put in a sealable glass weighting container, previously weighted too. Weightings were made using a balance, with a readability of 0.1 mg and a repeatability of 0.15 mg.

The uncovered container containing the sample was placed in ventilated oven at $T=105 \pm 2^\circ\text{C}$. The stopper of the container was placed in the oven too, to avoid eventual

problems coming from contractions associated to the successive cooling step. After a certain interval of time, the container was removed from the oven, sealed with the stopper and cooled down in a desiccator with dry atmosphere (Figure 13).

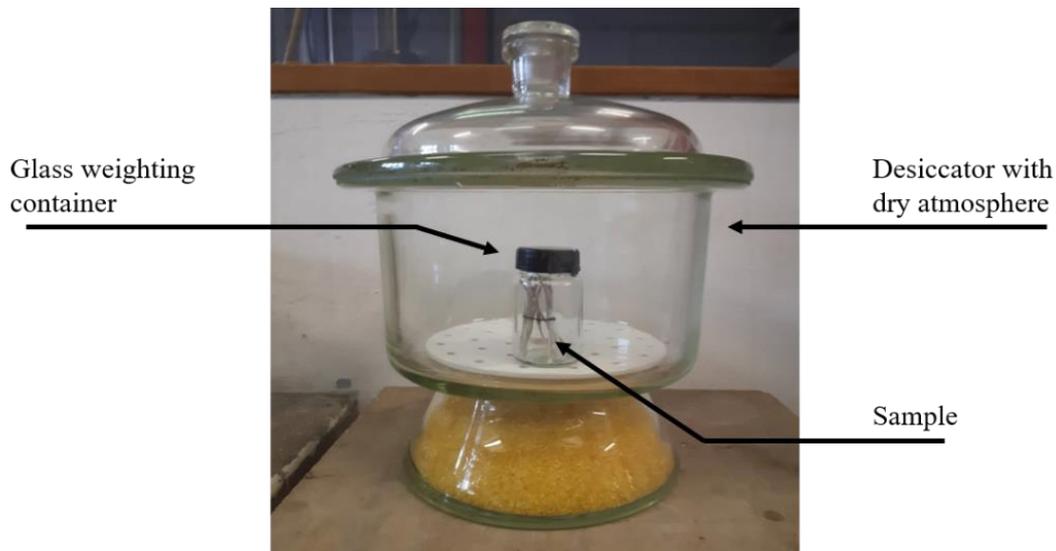


Figure 13. Equipment for ASTM testing.

After cooling, the container with the sample was weighted and the percentage variation in mass with respect to the “wet” value was calculated.

A completely dried sample was said to be obtained when the difference in mass between three weightings was less than 0.1%. The time between these weightings was 20% of the time required for a sample to lose 98% of its total moisture content, as defined by the standard. The procedure was made on roving samples only, repeated on a population of five samples and the results averaged. Testing at $48\pm 2\%$ RH was made on both rovings while testing at $96\pm 2\%$ RH was made on NATTEX[®] roving only.

3.3.1.3 Vacuum Drying Testing

Vacuum drying testing was performed with a dual scope. The first was the validation of the procedure successively used for desorption testing. The samples and the method, in fact, were the same, except for the type of oven used (vacuum oven in this step, ventilated oven during desorption testing).

The second goal was to assess any difference in the behaviour of the two materials when studied in the form of roving as such and in the form of carded fibres. This testing, in fact, was made on samples of NATTEX[®] and TEX400 stored at 25±5% RH, in form of roving as such and in the form of carded fibre.

As first the samples were weighted to record their initial “wet” mass. Then, they were put in a vacuum oven at $T = 80 \pm 2^\circ\text{C}$ and repeatedly taken out to be weighted. Weighting was made at different times, depending on which material was being tested (NATTEX[®] or TEX400) and in which form (roving or carded fibre). In this way, the percentage variation of mass ($\Delta m\%$) in time was monitored, and desorption curves were obtained. This testing was made until an equilibrium value for the mass of the samples was reached.

Equilibrium values of $\Delta m\%$ were compared with equilibrium moisture content values acquired from previous TGA analysis. Being the values comparable, the procedure used for desorption testing was validated.

Lastly comparisons were made between behaviours of rovings as such and carded fibres.

3.3.2 Flax Physical Testing

3.3.2.1 Desorption Testing

Desorption testing was made on samples prepared as described in Section 3.2.1.1, to evaluate the drying time, i.e. the time required for the flax to be free from absorbed moisture. This was important to validate the duration of the drying step during the production of the composite material (Section 3.2.2).

To perform this testing, a procedure identical to the one described for vacuum drying was followed, using now a ventilated oven, again at $T=80 \pm 2^\circ\text{C}$. Testing lasted until an equilibrium value for the mass of the samples was reached and this value was directly correlated to the equilibrium moisture content.

Desorption testing from 25±5% RH were made on NATTEX[®] and TEX400 in both forms of roving as such and of carded fibres. Results were compared with ones coming from previous vacuum drying testing. Consistency was assessed, further validating the

procedure used, independently from the type of oven. Again, comparisons between behaviours of roving as such and the carded fibres were made for each material.

Desorption testing from $48\pm 2\%$ RH were made on both materials in the form of roving as such only, while testing from $96\pm 2\%$ RH was made on NATTEX[®] roving as such, only. Testing was repeated on populations of 5 specimens and the results averaged. Comparisons between results obtained at different RH were made.

3.3.2.2 Regain Testing

Regain testing was made on dried samples to calculate how the regain rate, i.e. the amount of moisture absorbed in time, changed when dried flax was exposed to different RH conditions. This parameter was used to predict the amount of water absorbed when flax was taken out from the oven during the production of the composite material. Considerations on the diffusion coefficient and its dependence on the RH were also made. Regain testing was performed exposing dried samples to atmospheres with $25\pm 5\%$, $48\pm 2\%$ and $96\pm 2\%$ RH and weighting them at different times, depending on which material, and at which RH, was being tested (NATTEX[®] or TEX400). This testing was performed on roving samples only.

Each test lasted ≈ 24 h, independently from whether the samples had reached an equilibrium moisture content or not. This choice is strictly related to the aim of these testing. Since exposure to the environment during the production process lasted few minutes at most, there was no need for this testing to last more than 1 day. Testing was repeated on populations of 5 specimens and the results averaged.

3.3.3 Flax Mechanical Testing

For this testing, an Instron 5967 dynamometer equipped with a thermal cabinet was used. Bare roving samples were prepared as described in Section 3.2.1.2. The cabinet was used to obtain a closed environment in which the different storage conditions were created. In so doing, consistency between storage and testing conditions was guaranteed.

Five values for thickness and width were taken at different points of the sample to calculate five local cross section values. From these values, an average cross section was calculated.

Tensile testing parameters were chosen according to the relative standard [33]. A rate of extension of 2 mm/min was used and a distance between clamps of 20 mm was chosen, to match the average length of the flax roving inside the composite material. The geometry of the specimens is shown in Figure 14.

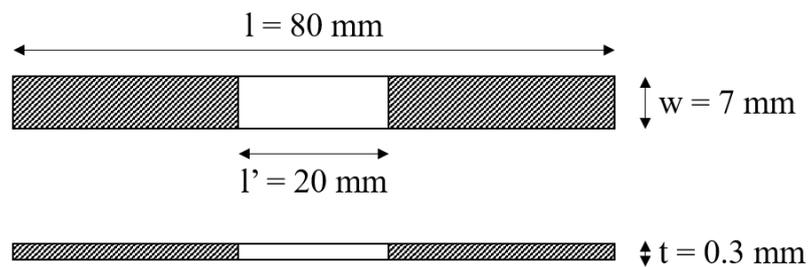


Figure 14. Tensile specimen for fibre testing.

Force-displacement curves were recorded and converted into stress-strain curves. A population of 5 samples was used and for each sample tensile strength, tensile modulus and elongation at break were calculated. The results were averaged.

3.3.4 Matrix and Composite Mechanical Testing

For this testing, an Instron 1185 dynamometer was used. Bare matrix and composite material samples were obtained as described in section 3.2.2.

Five values for thickness and width were taken at different points of the sample to calculate five local cross section values. From these values, an average cross section was calculated.

Tensile testing parameters were chosen according to the relative standard [34]. A rate of extension of 2 mm/min was used and a distance between clamps of 10 cm was chosen.

Force-displacement curves were recorded and converted into stress-strain curves. A population of 9 samples was used and for each sample tensile strength, tensile modulus

and elongation at break were taken. The results were averaged. The geometry of the specimens is shown in Figure 15.

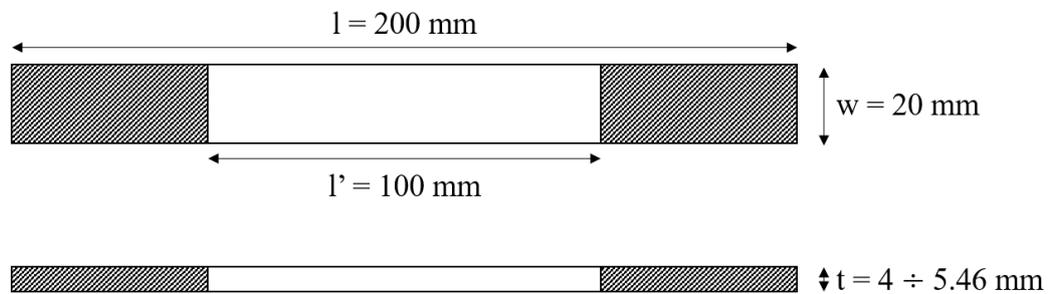


Figure 15. Tensile specimen for matrix and composite testing.

3.3.5 Adhesion Testing

Lap-shear testing was made to evaluate the apparent shear strength of the three adhesives and compare their behaviour at different temperatures. A sketch of single-lap shear test is shown in Figure 16.

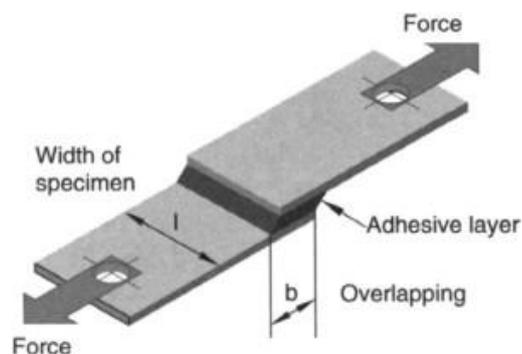


Figure 16. Typical deformation in a single-lap specimen.[35]

Because of the geometry of single-lap specimens, the tensile load applied along the axis of the specimen generates both shear and peel stresses in the joint. As a result, a non-uniform stress distribution is generated (Figure 17).

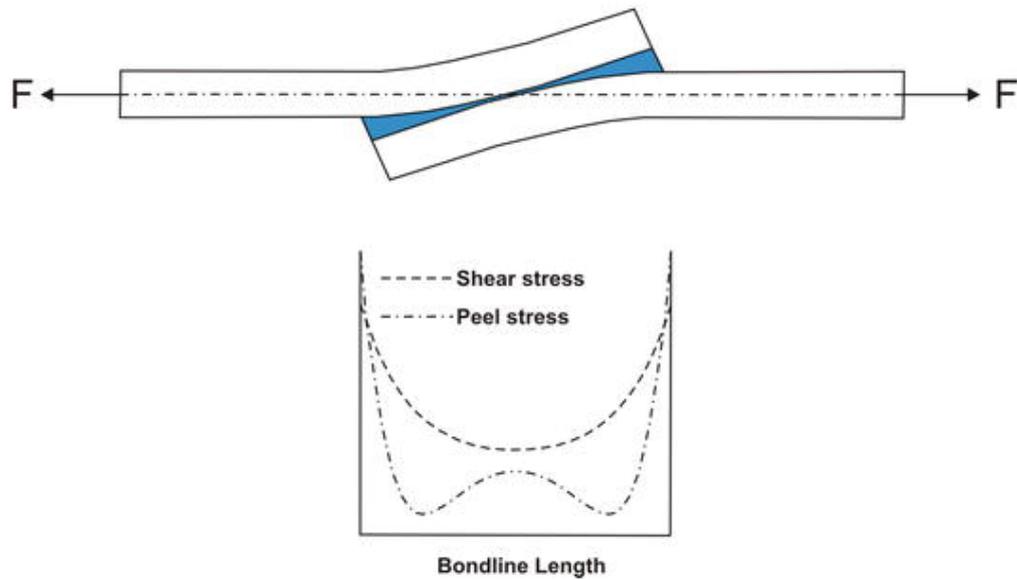


Figure 17. Stress distribution in a single-lap adhesive joint.[36]

An Instron 1185 dynamometer equipped with a thermal cabinet was used and testing was made at temperatures of: $-40\pm 2^{\circ}\text{C}$, $23\pm 2^{\circ}\text{C}$ and $80\pm 2^{\circ}\text{C}$. Before testing, the samples were conditioned inside the oven at the testing temperature for 24h. A loading rate of 1.3 mm/min was used, according to the standard [30]. Force-displacement curves were recorded and converted into stress-strain curves. A variable number of samples was tested for each adhesive at each temperature, because of limitations in the availability of the samples. The number of tested specimens are shown in Table 7.

Table 7. Number of tested specimens for each adhesive at each temperature.

Adhesive	$-40\pm 2^{\circ}\text{C}$	$23\pm 2^{\circ}\text{C}$	$80\pm 2^{\circ}\text{C}$
Epoxy	3	5	7
Acrylate	0	3	5
Polyurethane	3	4	4

For each sample the ultimate tensile strength was taken, and the results averaged. The type of failure was evaluated, too.

4. RESULTS AND DISCUSSION

4.1 FLAX PRELIMINARY TESTING

4.1.1 TGA and ASTM Method for Determination of Amount of Moisture

The results of thermogravimetric analysis carried out on both materials stored at $25\pm 5\%$ RH are shown in Figure 18 and Figure 19 for NATTEX[®] and TEX400, respectively. Desorption curves were obtained plotting percentage mass variation with respect to time (in minutes).

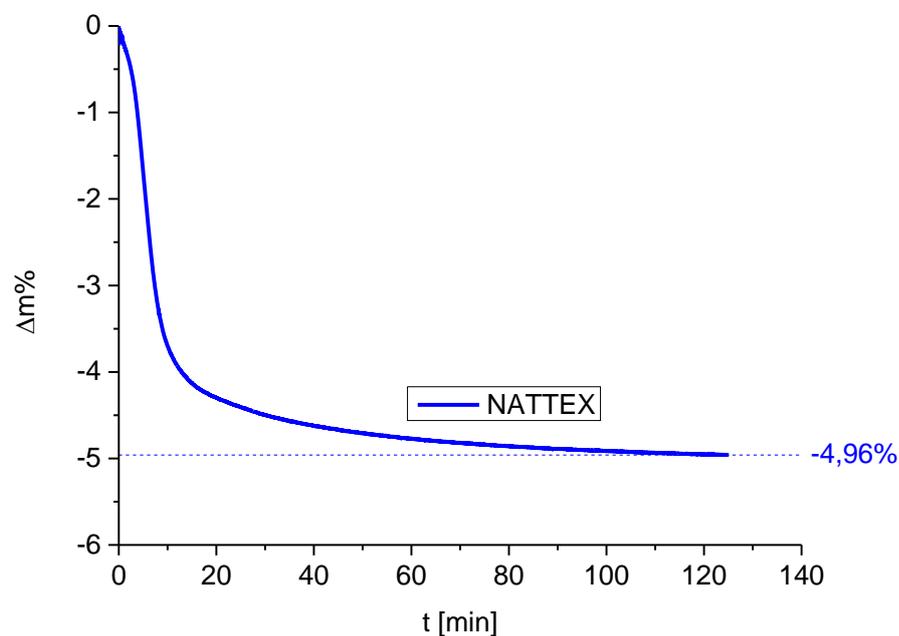


Figure 18. TGA curve for NATTEX[®].

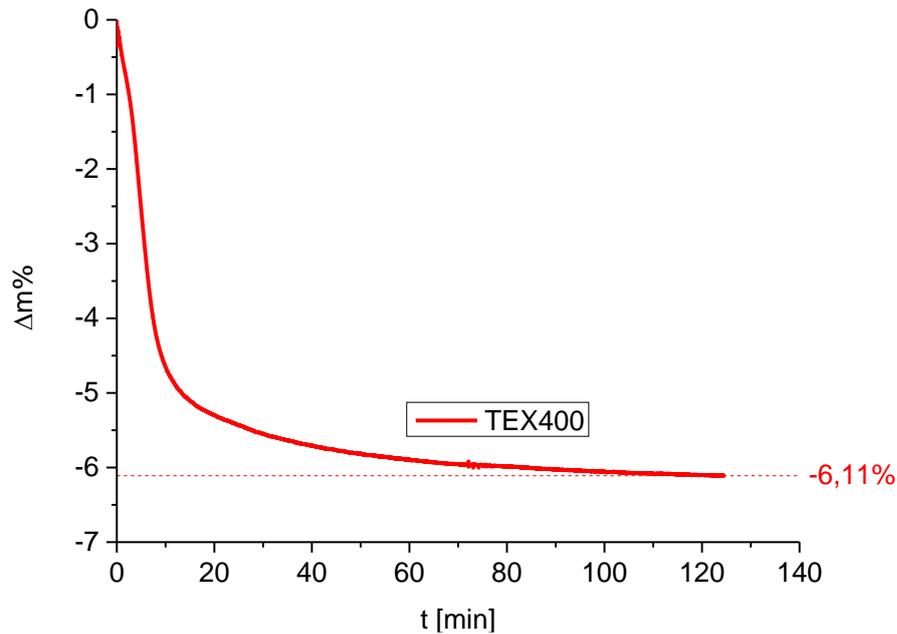


Figure 19. TGA curve for TEX400.

For what concerns preliminary ASTM testing carried out on samples stored at $48\pm 2\%$ and $96\pm 2\%$ RH, no desorption curves were obtained, but Equilibrium Moisture Content (EMC) values only. Results are shown in Table 8.

Table 8. Equilibrium moisture content for samples stored at $25\pm 5\%$, $48\pm 2\%$ and $96\pm 2\%$ RH.

Material	$25\pm 5\%$ RH (TGA)	$48\pm 2\%$ RH (ASTM)	$96\pm 2\%$ RH (ASTM)
NATTEX [®]	4.96%	6.50%	21.0%
TEX400	6.11%	6.42%	

Equilibrium moisture content on TEX400 stored at $96\pm 2\%$ RH is not shown because, by the time testing at these conditions was made, the material had been already discarded.

For storage at $25\pm 5\%$ RH, TEX400 results being more hygroscopic. On the contrary, when comparing EMC values for samples stored at $48\pm 2\%$ no differences are seen. More, the equilibrium moisture contents for TEX400 stored at $25\pm 5\%$ and $48\pm 2\%$ seem very similar.

Both oddities may be explained by the different forms in which the material is tested during TGA and ASTM analysis. In the first case, in fact, the sample is little enough for the material to lose its roving form and acquire the form of carded fibre. ASTM analysis, on the

contrary, are carried out on roving as such. This hypothesis will be confirmed by following vacuum drying testing.

4.1.2 Vacuum Drying Testing

Following the hypothesis formulated in previous section, vacuum drying testing was initially made on the two materials in the form of carded fibre. The times at which samples were taken out from vacuum oven to be weighted are shown in Table 9.

Table 9. Weighting times for vacuum drying testing on fibre samples.

Fibre	t ₁	t ₂	t ₃	t ₄	t ₅	t ₆	t ₇	t ₈
NATTEX®	5'	9'	20'	45'	90'	135'	375'	1295'
TEX400	5'	20'	80'	200'	320'	1295'		

Desorption curves ($\Delta m\%$ vs time) obtained are plotted in Figure 20 and Figure 21 for NATTEX® and TEX400, respectively.

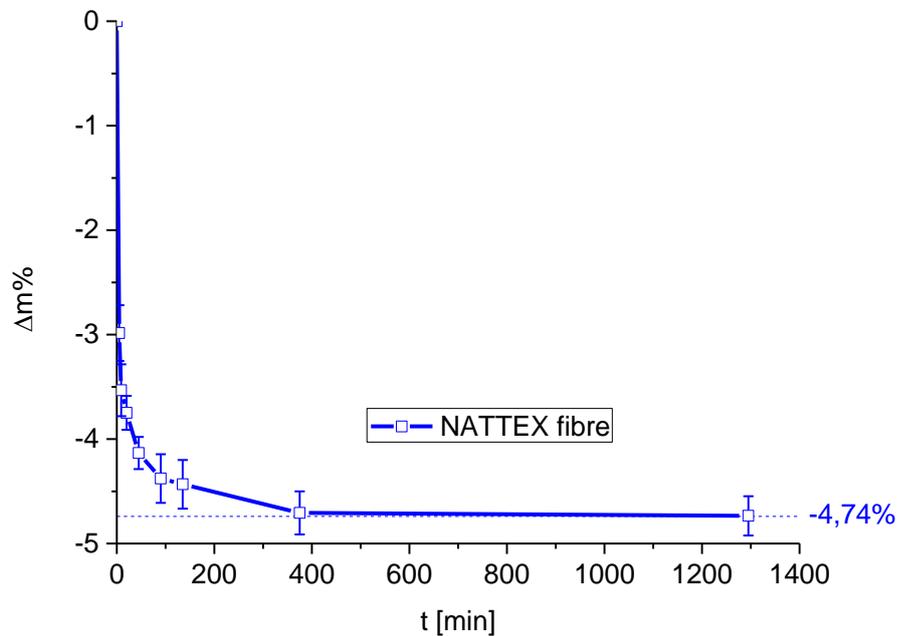


Figure 20. Desorption curve obtained by vacuum drying for NATTEX® carded fibre.

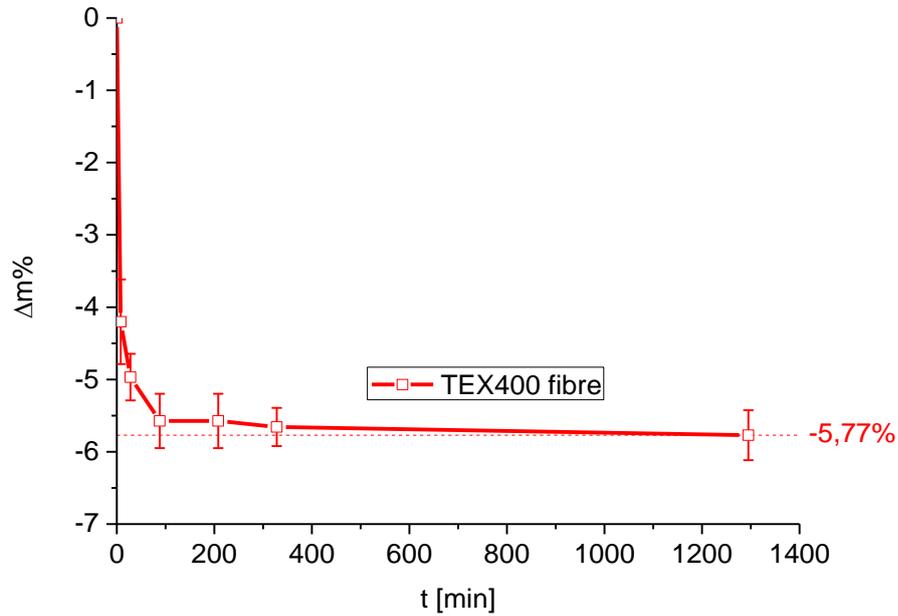


Figure 21. Desorption curve obtained by vacuum drying for TEX400 carded fibre.

Comparison between equilibrium moisture content obtained by TGA analysis and vacuum drying is shown in Table 10.

Table 10. Comparison between EMC found by TGA analysis and vacuum drying for NATTEX® and TEX400 carded fibres.

Material	TGA ANALYSIS	VACUUM DRYING
NATTEX® fibre	4.96%	4.74%
TEX400 fibre	6.11%	5.77%

Consistency between the results validated desorption testing procedure.

Successively, the same procedure was repeated on roving samples. Times at which roving samples were taken out to be weighted are shown in Table 11.

Table 11. Weighting times for vacuum drying testing on roving samples.

Roving	t ₁	t ₂	t ₃	t ₄	t ₅	t ₆	t ₇	t ₈	t ₉
NATTEX®	10'	20'	40'	60'	90'	145'	210'	300'	1295'
TEX400	10'	20'	35'	55'	85'	145'	235'	1295'	

Desorption curves obtained for both rovings as such, are shown in Figure 22 and Figure 23.

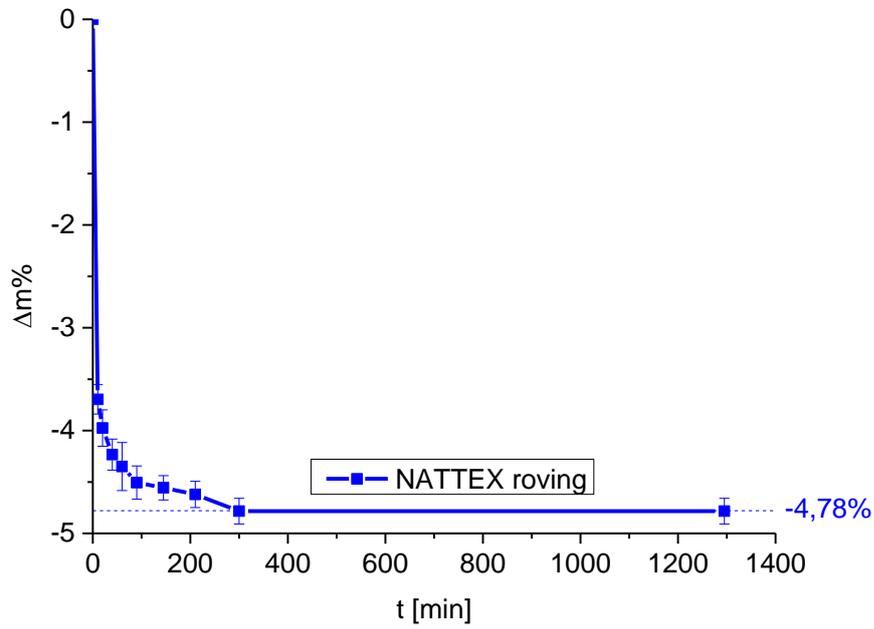


Figure 22. Desorption curve obtained by vacuum drying for NATTEX® roving.

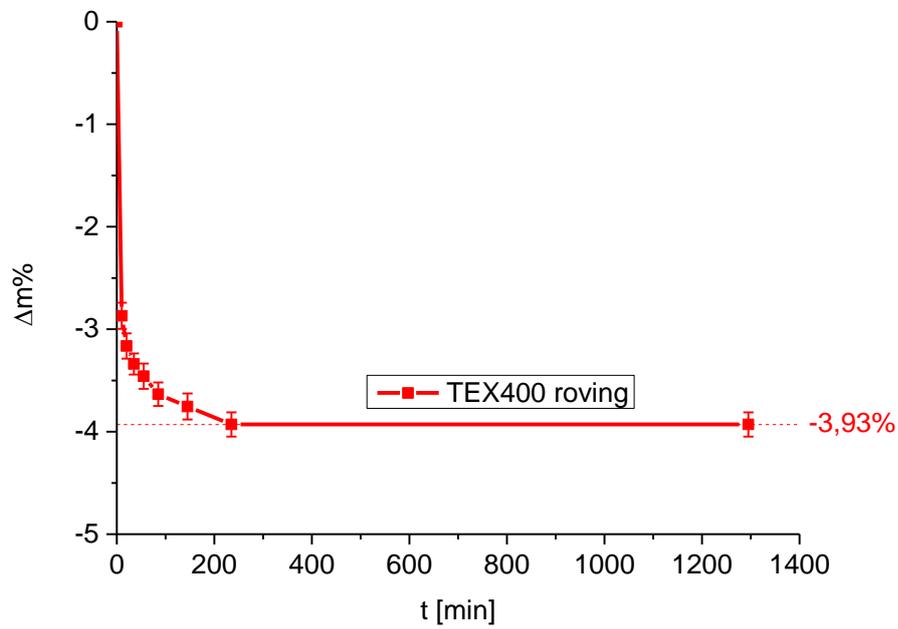


Figure 23. Desorption curve obtained by vacuum drying for TEX400 roving.

Comparison between equilibrium moisture contents of rovings as such and carded fibres is presented in Table 12.

Table 12. Comparison between equilibrium moisture contents obtained by vacuum drying for NATTEX® and TEX400 in the forms of roving as such and carded fibre.

Vacuum drying	Roving as such	Carded fibre
NATTEX®	4.78%	4.74%
TEX400	3.93%	5.77%

From the results it can be said that behaviour of NATTEX® does not change significantly when carded. On the contrary, for TEX400, the EMC increases when passing from the roving as such form to the carded fibre form. In particular, TEX400 results being less hygroscopic than NATTEX® when rovings as such are considered. This trend is inverted when carded fibres are compared, with TEX400 being more hygroscopic.

This can be explained by the different shapes of the two materials. Being NATTEX® a tow, we didn't expect a significant change in the behaviour when passing from the roving to the carded fibre. On the contrary, carding operation makes TEX400 lose its twist and its cylindrical shape, increasing more significantly its contact surface with the environment and, consequently, the amount of moisture absorbed.

These considerations confirmed the hypothesis made in Section 4.1.1, for which differences in the behaviour during TGA and ASTM preliminary testing may be due to the different forms in which the materials were tested (carded fibres during TGA, and rovings as such during ASTM procedure).

4.2 FLAX PHYSICAL TESTING

4.2.1 Desorption Testing at 25±5% RH

Once validated by previous vacuum drying, desorption testing procedure was carried out on NATTEX® and TEX400 stored at 25±5% RH, again in both forms of rovings as such and carded fibres. Times at which roving and carded fibre samples were taken out from ventilated oven to be weighted are shown in Table 13 and Table 14, respectively.

Table 13. Weighting times for desorption testing on roving samples stored at 25±5% RH.

Roving	t ₁	t ₂	t ₃	t ₄	t ₅	t ₆	t ₇	t ₈	t ₉	t ₁₀	t ₁₁
NATTEX®	5'	10'	20'	30'	45'	65'	100'	160'	240'	335'	1295'
TEX400	5'	10'	20'	30'	45'	65'	95'	155'	215	335	1295

Table 14. Weighting times for desorption testing on carded fibres samples stored at 25±5% RH.

Fibres	t ₁	t ₂	t ₃	t ₄	t ₅	t ₆	t ₇	t ₈	t ₉	t ₁₀	t ₁₁
NATTEX®	5'	10'	20'	30'	45'	65'	100'	155'	215'	335'	1295'
TEX400	5'	10'	30'	45'	65'	95'	155'	215'	335'	1295'	

Results for NATTEX® and TEX400 are plotted in Figure 24 and Figure 25, respectively.

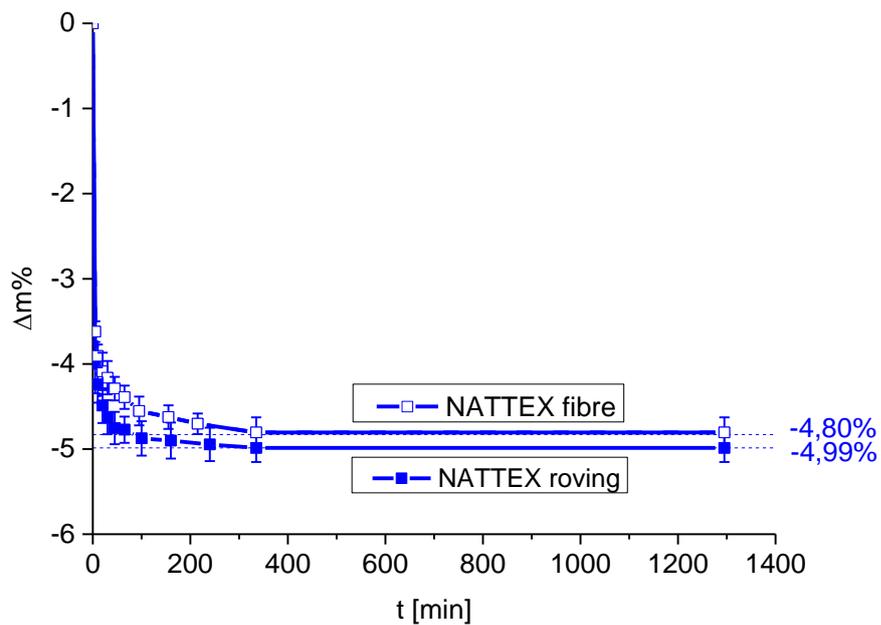


Figure 24. Desorption curves obtained for NATTEX® roving as such (solid) and its carded fibres (empty), stored at 25±5% RH.

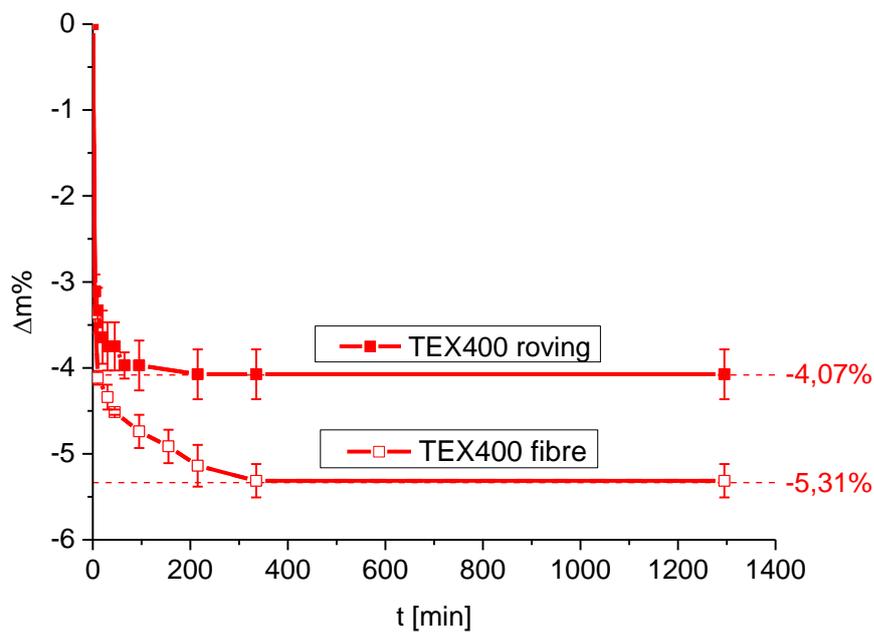


Figure 25. Desorption curve obtained for TEX400 roving as such (solid) and its carded fibres (empty), stored at 25±5% RH.

The equilibrium moisture contents obtained for each material in both forms are shown in Table 15. Comparison with values acquired during vacuum drying are shown, too.

Table 15. Comparison between EMC obtained by vacuum drying and desorption testing for NATTEX® and TEX400 in both forms of roving as such and carded fibre.

Material	Form	Air drying	Vacuum drying
NATTEX®	<i>Roving</i>	4.99%	4.78%
	<i>Fibre</i>	4.80%	4.74%
TEX400	<i>Roving</i>	4.07%	3.93%
	<i>Fibre</i>	5.31%	5.77%

From the values in the table we can say that no clear differences arise when using vacuum oven during vacuum drying testing or ventilated oven during desorption testing. Thus, ventilated oven was used for further testing.

From the point of view of drying time, intended as the time required for a sample to be completely dried, a time of ≈ 300 minutes was said to be satisfactorily enough for both materials in both forms.

4.2.2 Desorption Testing at $48\pm 2\%$ and $96\pm 2\%$ RH

The same procedure was repeated on samples stored at $48\pm 2\%$ and $96\pm 2\%$ RH. Being the difference in the behaviour between rovings and carded fibres already assessed, at this point samples of rovings as such were tested, only. Times at which rovings were taken out from the oven and weighted were the same and are shown in Table 16.

Table 16. Weighting times for desorption testing on roving samples stored at $48\pm 2\%$ RH.

Times	t ₁	t ₂	t ₃	t ₄	t ₅	t ₆	t ₇	t ₈	t ₉	t ₁₀	t ₁₁
	5'	10'	20'	30'	45'	65'	95'	155'	215'	335'	1295'

Comparisons between the plots obtained for the two materials and EMC values obtained by preliminary ASTM procedure are made in Figure 26 and Figure 27 for NATTEX® and TEX400, respectively.

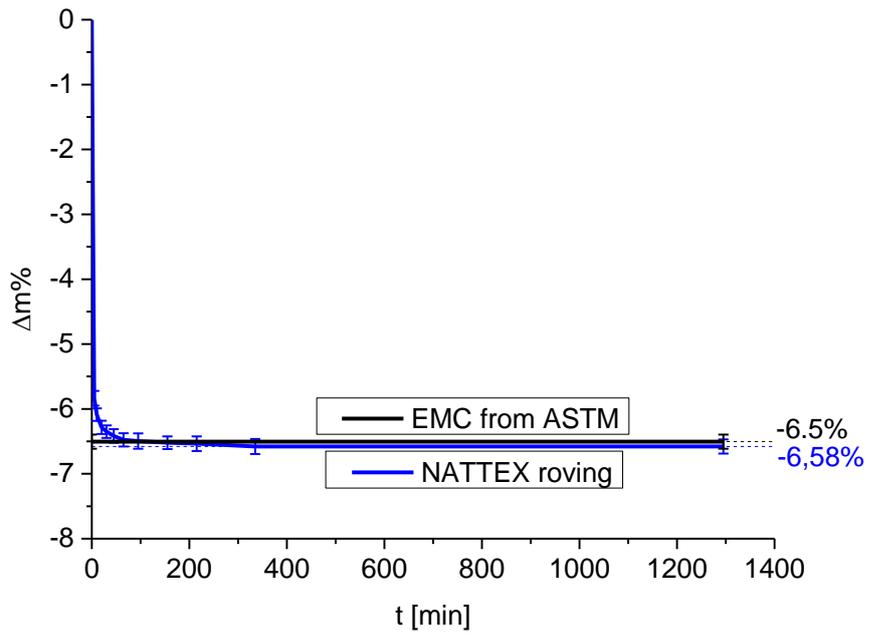


Figure 26. Comparison between desorption curve obtained for NATTEX® roving stored at 48±2% and EMC value obtained by preliminary ASTM analysis.

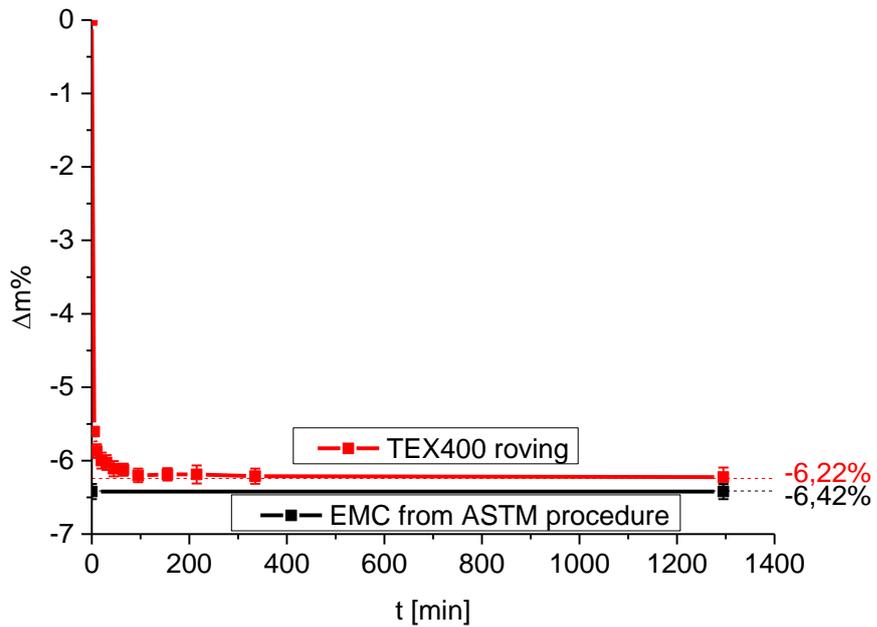


Figure 27. Comparison between desorption curve obtained for TEX400 roving stored at 48±2% and EMC value obtained by preliminary ASTM analysis.

At this point, TEX400 was discarded. Thus, testing on samples stored at 96±2% RH was performed on NATTEX® roving, only. Weighting times were identical to those used in

previous testing from $48\pm 2\%$ RH, shown in Table 16. Comparison with EMC value obtained by ASTM procedure is shown in Figure 28.

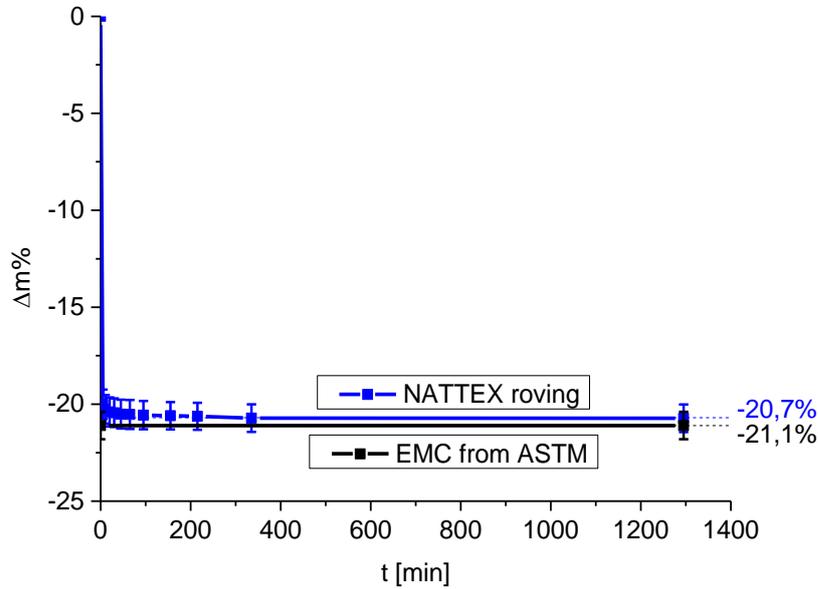


Figure 28. Comparison between desorption curve obtained for NATTEX[®] roving stored at $96\pm 2\%$ and EMC value obtained by preliminary ASTM analysis.

The results obtained by desorption testing are consistent with EMC values previously obtained by ASTM procedure for both testing at $48\pm 2\%$ and $96\pm 2\%$ RH.

EMC and drying times for both rovings stored at different RH are summarized in Table 17.

Table 17. Comparison between EMC and drying times for NATTEX[®] roving samples stored at different RH conditions.

Material	Storage conditions	EMC	Drying time
NATTEX [®]	<i>25±5% RH</i>	4.99%	300'
	<i>48±2% RH</i>	6.58%	300'
	<i>96±2% RH</i>	20.7%	300'
TEX400	<i>25±5% RH</i>	4.07%	300'
	<i>48±2% RH</i>	6.22%	300'

From the table is evident that EMC increases with increasing RH of storage conditions, as expected, and the obtained results are consistent with values taken from literature [37].

For what concerns the drying time, again, a time of ≈ 300 minutes was enough for the samples to be considered dried, independently from the storage conditions.

4.2.3 Regain Testing

Regain testing was performed exposing dried samples of both rovings to controlled atmospheres with $25\pm 5\%$, $48\pm 2\%$ and $96\pm 2\%$ relative humidity. Conditioning was made using thermostatic chamber and desiccators with controlled atmospheres.

Samples were weighted immediately when taken out from the oven to record their “dry” mass. Then, for regain testing at $25\pm 5\%$ RH, they were weighted after: 15”, 30”, 1’, 3’, 5’, 7.5’, 10’, 15’, 20’, 25’, 30’, 40’, 55’, 80’, 130’, 210’, 330’, 1390’.

Regain curves ($\Delta m\%$ vs time) obtained for NATTEX[®] and TEX400 rovings at $25\pm 5\%$ RH are shown in Figure 29 and Figure 30, respectively.

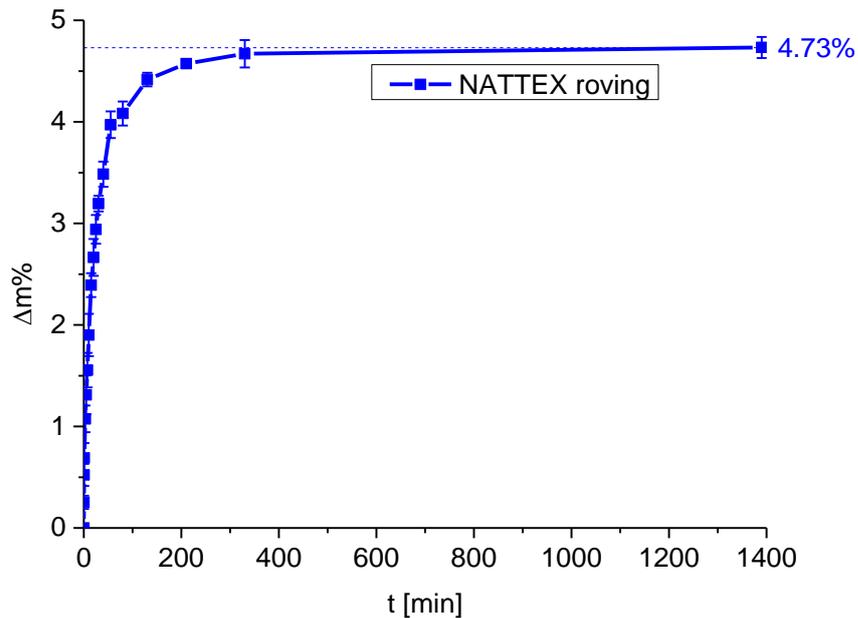


Figure 29. Regain curve obtained for NATTEX[®] roving as such, at $25\pm 5\%$ RH.

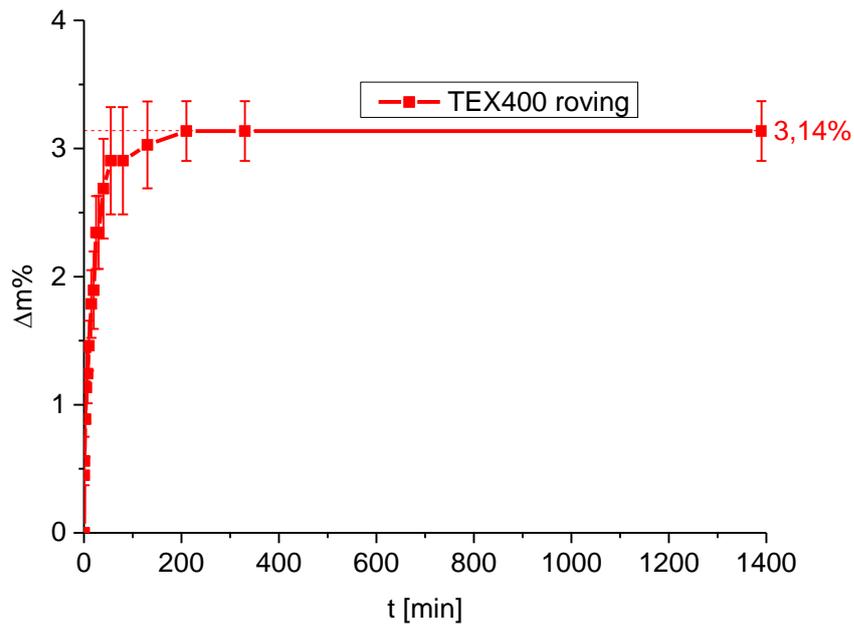


Figure 30. Regain curve obtained for TEX400 roving as such, at 25±5% RH.

For regain testing at 48±2% and 96±2% samples were weighted after 30'', 1', 3', 7', 12', 20', 30', 60', 90', 120', 180', 240', 360', 1390'. Regain curves obtained for NATTEX® and TEX400 rovings at 48±2% RH are shown in Figure 31 and Figure 32, respectively.

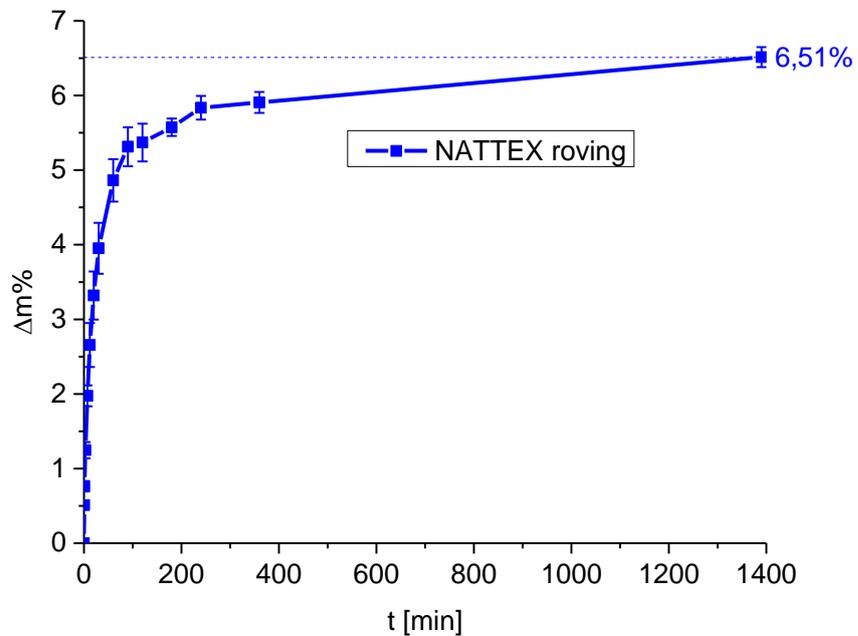


Figure 31. Regain curve obtained for NATTEX® roving as such, stored at 48±2% RH.

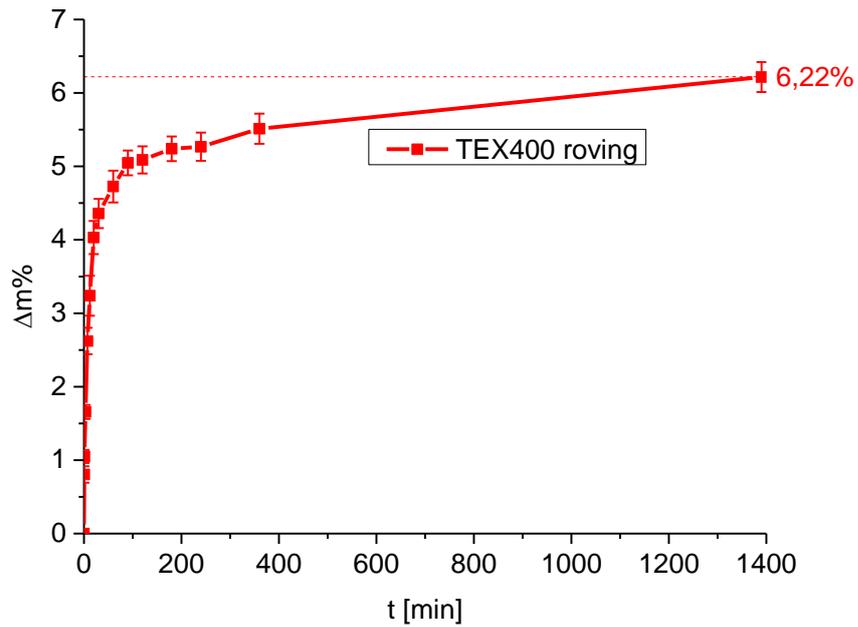


Figure 32. Regain curve obtained for TEX400 roving as such, stored at $48\pm 2\%$ RH.

Regain curve obtained for NATTEX[®] roving at $96\pm 2\%$ RH, is shown in Figure 33.

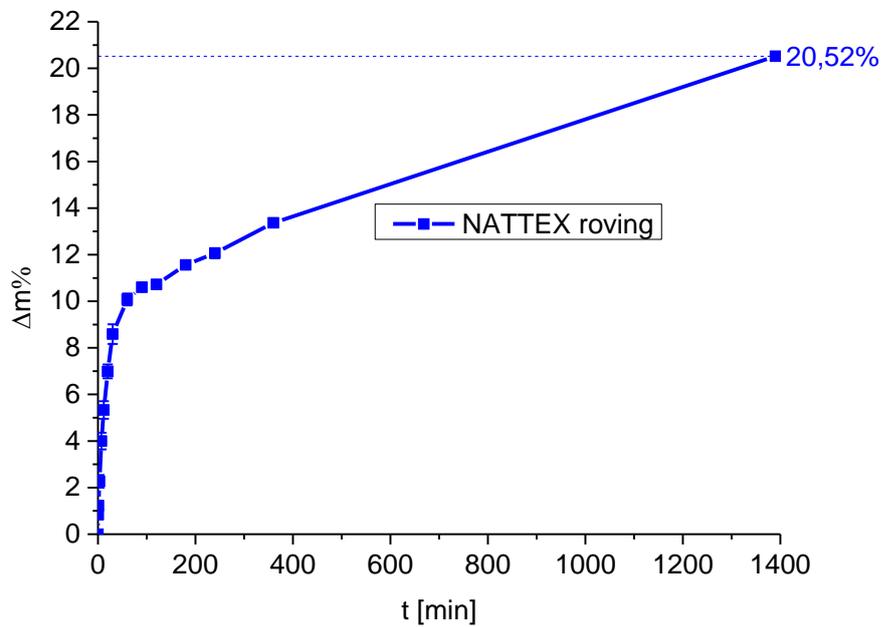


Figure 33. Regain curve obtained for NATTEX[®] roving as such, stored at $96\pm 2\%$ RH.

An interval of time of 10 minutes was selected as a reasonable estimation of the exposure time of dried flax to the environment during the production of the composite material.

The amount of moisture absorbed by flax rovings after this time was taken directly from regain curves. Results are shown in Table 18.

Table 18. Regain ($\Delta m\%$) of NATTEX® and TEX400 rovings after 10 minutes of exposure to different RH conditions.

RH %	NATTEX®	TEX400
25±5%	1.90%	1.46%
48±2%	2.66%	3.24%
96±2%	5.33%	

It is important to underline that, because of the procedure used during the production process, this regain is inevitable.

From a theoretical point of view, regain process is based on diffusion phenomena and, thus, it can be described by Fick's second law of diffusion [38]:

$$\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

According to Crank, for the case of a plane sheet with both surfaces exposed to the same concentration of diffusing species, Fick's equation can be rewritten as [39]:

$$\frac{M_t}{M_f} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \{-D(2n+1)^2 \pi^2 t / 4l^2\} \quad (3)$$

that, at initial stages, i.e. when $M_t/M_f \leq 0,5$, can be further simplified to:

$$\frac{M_t}{M_f} = \left(\frac{4}{L\sqrt{\pi}} \sqrt{D} \right) \sqrt{t}. \quad (4)$$

being M_t the amount of moisture absorbed after time t , M_f moisture absorbed at infinite time, L the thickness of the specimen and D the diffusion coefficient [39][40].

Within 10 minutes, the simplification given by Eq. 4 is always valid, for every regain test performed. Regain plots were thus converted into M_t/M_f versus square root of time (in $s^{0.5}$) plots for the calculation of the diffusion coefficient. In first approximation, final values of each regain plot was used as M_f value. The portion of graph with $t < 10'$ was isolated and fitted with a linear function. Comparisons were made and are shown in Figure 34 and Figure 35, for NATTEX® and TEX400 respectively.

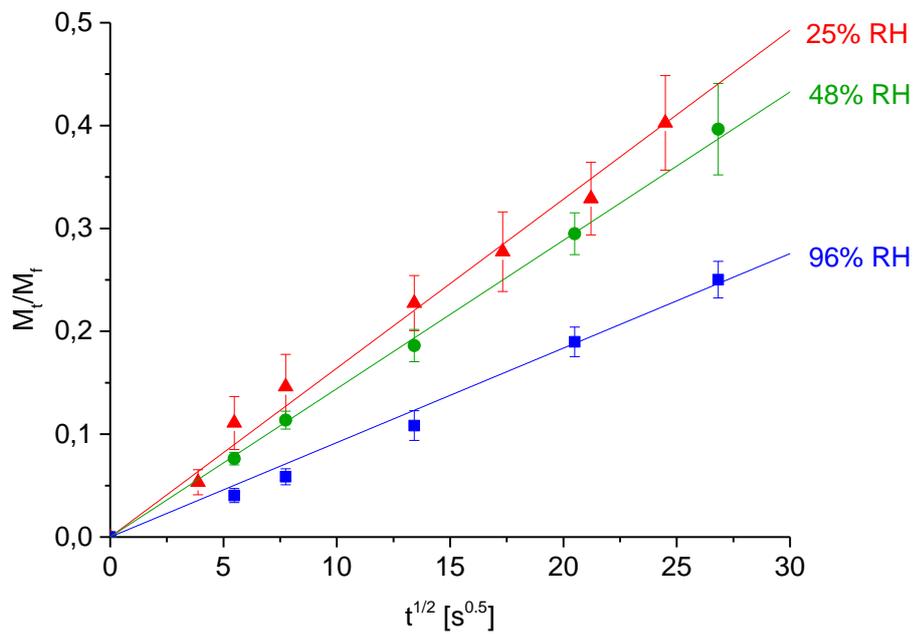


Figure 34. Comparison between regain curves obtained for NATTEX® roving at different RH. M_t/M_f vs square root of time is plotted.

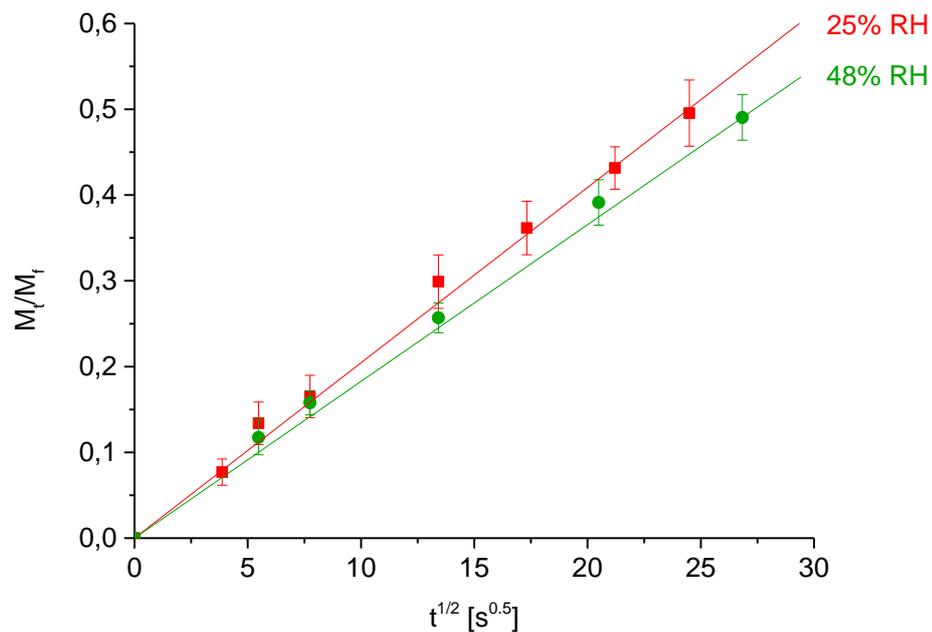


Figure 35. Comparison between regain curves obtained for TEX400 roving at different RH. M_t/M_i vs square root of time is plotted.

The accuracy of the fitting confirms a linear dependence of the regain on the square root of time. From Eq. 4, diffusion coefficient for both materials at each RH condition can be calculated, starting from the slopes of the linear fitting. Results are shown in Table 19.

Table 19. Diffusion coefficients [cm^2/s] of NATTEX[®] and TEX400 rovings at different RH value.

RH %	NATTEX [®]	TEX400
25±5%	$2.33 \cdot 10^{-7}$	$3.57 \cdot 10^{-7}$
48±2%	$1.78 \cdot 10^{-7}$	$2.85 \cdot 10^{-7}$
96±2%	$7.20 \cdot 10^{-8}$	

The values obtained for the diffusion coefficients are in accordance with values taken from literature [41]. From the table is evident that diffusion coefficient does not change significantly when comparing testing performed at 25±5% and at 48±2% RH. On the contrary, diffusion coefficient for NATTEX[®] decreases by one order of magnitude when tested at 96±2% RH. This result may be explained by the occurrence of an inhibition effect caused by already absorbed moisture, that slows down further absorption of water [41]. Another contribution to this effect may come from the microstructure of flax fibre cells.

As described in Section 2.1.2, flax fibres are characterized by a hollow cylindrical shape. Water absorbed inside the central cavity, called “lumen”, can cause swelling effects, that inhibit the absorption process. It is reasonable to think that, at very high relative humidity, this effect may be more consistent, reducing the diffusivity of water inside the material [41]. The full understanding of this phenomenon was beyond the scope of this study.

4.3 FLAX MECHANICAL TESTING

Tensile testing was carried out on NATTEX[®] roving only, stored at 50±5%, 64±2% and 78±2% RH. Being the roving made of many parallel fibres, its nominal cross section (calculated as the average width of the roving multiplied by its average thickness) couldn't be considered as continuous and homogeneous. The real cross section was calculated manually by carding a number of samples and counting the individual fibres. Then, the average size of a single fibre was measured with an optical microscope and the real cross section calculated. The two cross sections (nominal and real) differed by one order of magnitude. Results from tensile testing are shown in Figure 36.

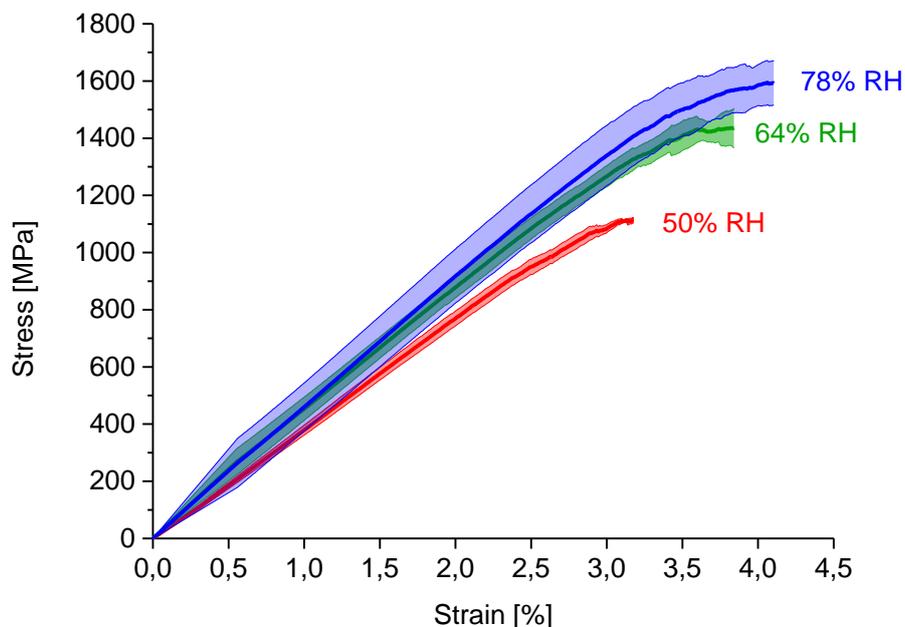


Figure 36. Stress-strain curves of NATTEX[®] roving stored and tested at different RH conditions.

Comparison between mechanical properties at varying RH are made in Figure 37, Figure 38 and Figure 39 for tensile modulus, tensile strength and elongation at break, respectively.

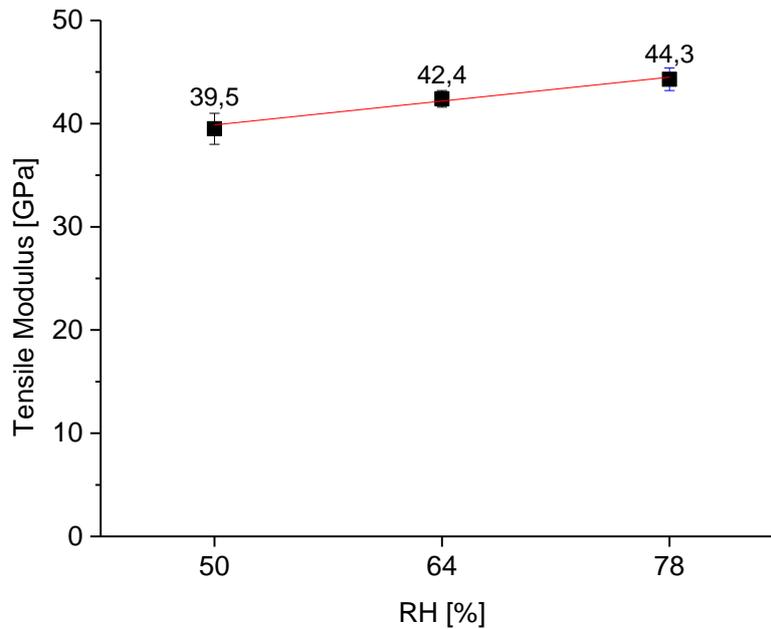


Figure 37. Variation of tensile modulus [GPa] of NATTEX® roving at varying RH conditions.

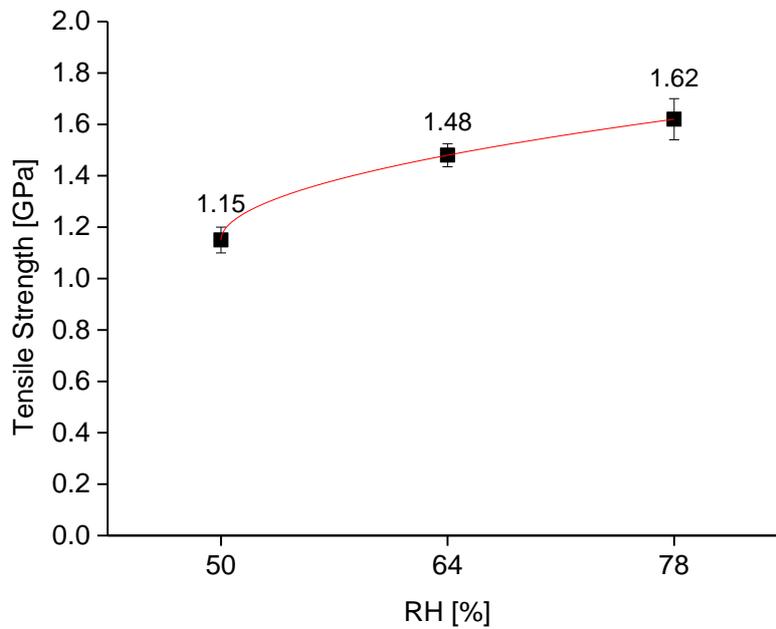


Figure 38. Variation of tensile strength [GPa] of NATTEX® roving at varying RH conditions.

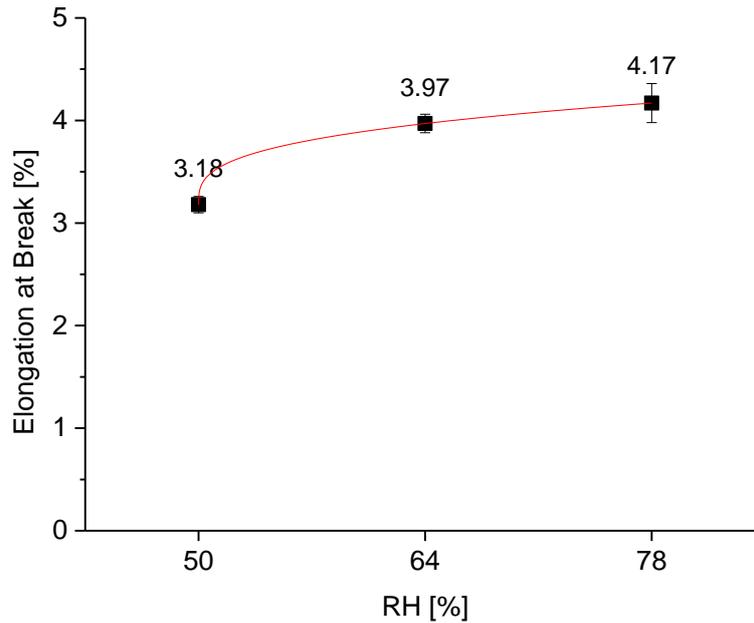


Figure 39. Variation of elongation at break [%] of NATTEX® roving at varying RH conditions.

Tensile properties increased with RH conditions. Tensile modulus increased linearly, by 7.5% from 50% RH to 64% RH and by 15.1% from 50% to 78% RH. Tensile strength increased by 29% at 50% RH and by 39.8% at 78% RH. Elongation at break increased by 24.6% at 64% RH and by 31.1% at 78% RH.

These results are in agreement with results taken from literature [29][41]. This effect is associated to plasticization effects caused by absorbed water molecules. When moisture is absorbed, hydrogen bonds are formed between water molecules and hydroxyl groups present on the cellulose macromolecules constituting flax cell walls, favouring relative motion between the same macromolecules [42][43].

4.4 MATRIX AND COMPOSITE MECHANICAL TESTING

For the calculation of theoretical values for tensile modulus, the rule of mixture for thin composites reinforced with random short fibre was used:

$$E_1 = \eta_0 \eta_l v_f E_{1f} + v_m E_m. \quad (5)$$

In Eq. 5 η_0 is an efficiency factor that takes into account the random orientation of fibres in a thin composite material, and it is equal to $3/8$. η_l is a second efficiency factor depending on the fibre aspect ratio, that can be calculated from graph shown in Figure 40.

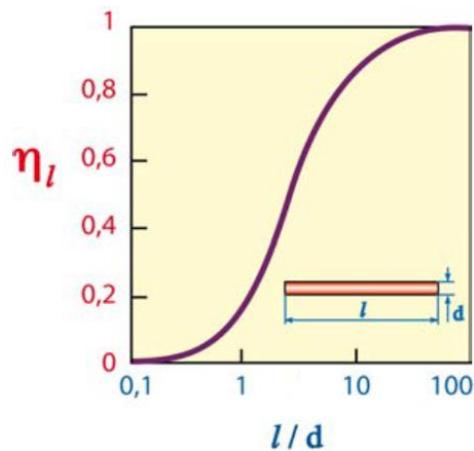


Figure 40. Graph for the calculation of the aspect ratio efficiency factor.

The average length of the reinforcement is 20 mm and the mean equivalent diameter is equal to 0.67 mm², giving a value for η_l equal to 0.98. Finally, v_i and E_i are, respectively, the volume fraction and the tensile modulus of each phase (Fibre or Matrix).

The nominal volume fraction of the matrix was calculated backwards starting from the mass of the tiles and the mass fraction of the matrix. The density of the matrix was first calculated on the basis of the Archimedes' principle and a value of 1700 kg/m³ was obtained. Then the volume fraction was calculated and, consequently, expectation values for the modulus of the composite material.

For what concerns tensile modulus of the matrix, it was calculated from tensile testing on the bare matrix. Successively, testing was carried out on the six different composite materials produced (see Table 5 in Section 3.2.2). Results obtained for tensile modulus are shown in Figure 41, in which %v/v is reported on the horizontal axis. The line representing the rule of mixture is also plotted, for visual comparison (black line).

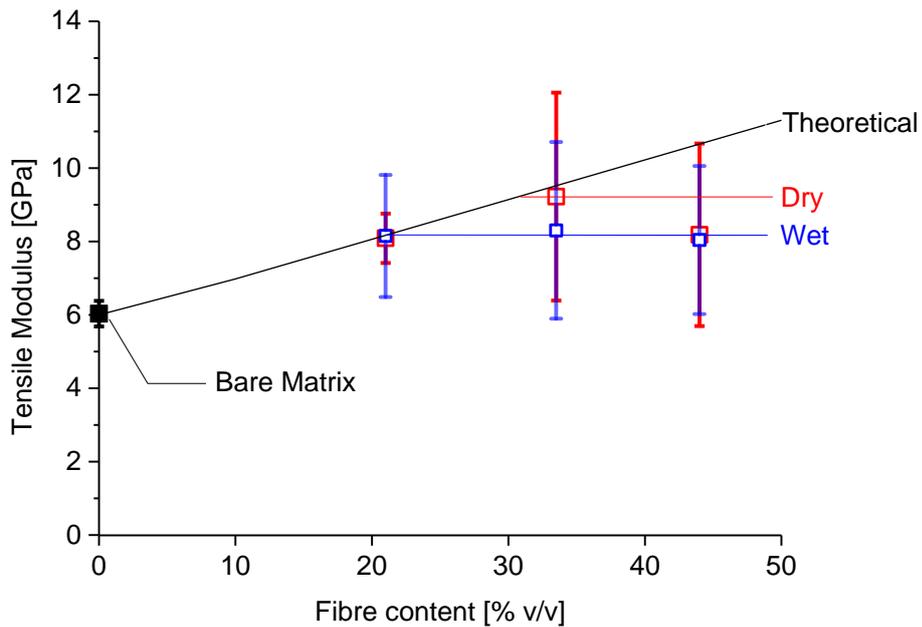


Figure 41. Variation of tensile modulus [GPa] of composite material at varying fibre content [%v/v] and fibre conditions (dry or wet). Value of the bare matrix is also shown.

From the graph a slight increase from the value of 6 GPa for the bare matrix to an average value of ≈ 8 GPa for the reinforced matrix is seen. It is also evident that, apart from the material obtained with 20% content of dried flax, an increase in the fibre content does not correspond to an increase in mechanical properties. Moreover, no difference can be seen between materials reinforced with dried and non-dried flax.

When experimental values are compared with theoretical values, not perfect agreement arises. This disagreement is highlighted by the horizontal lines.

For what concerns composite materials reinforced with dry flax, an acceptable agreement can be seen up to flax content of 20% w/w. At 30% flax content the experimental tensile modulus is 25% lower than the theoretical value.

For what concerns composite materials reinforced with wet flax, a worse agreement can be seen. At 20% flax content the experimental value is 15% lower than the theoretical one while at 30% flax content this difference increases up to 25%.

For both reinforcements, the error bars of points at 30% flax content lie entirely below the black line, making the disagreement statistically more relevant.

Finally, a bad reproducibility, highlighted by consistent error bars, is evident for all the materials.

Both issues, disagreement and lack of reproducibility, can be due to the method used during the production of the composite material (i.e. manual mixing), that resulted in a poor distribution and a poor wetting of the reinforcement inside the composite material. Results for tensile strength and elongation at break are shown in Figure 42 and Figure 43, in which %w/w is reported on the horizontal axis.

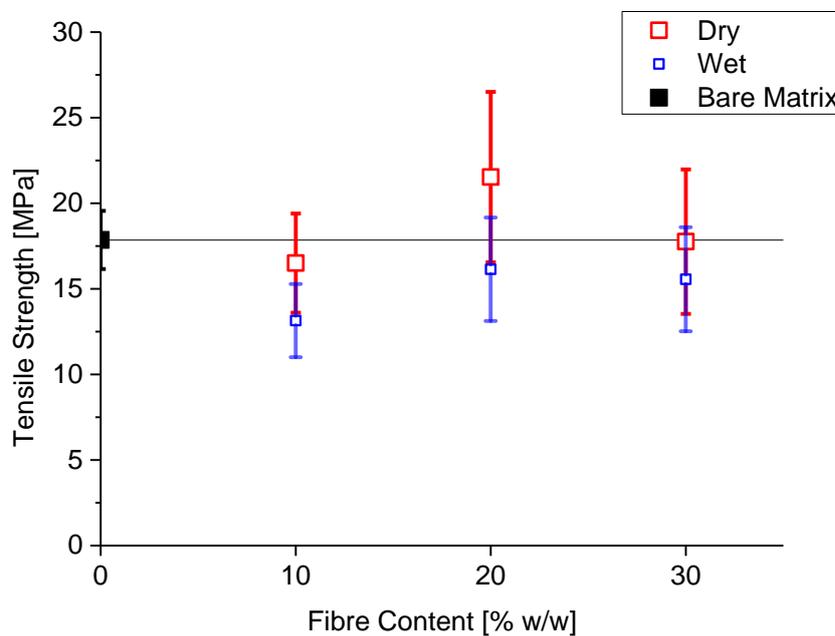


Figure 42. Variation of tensile strength [MPa] of composite material at varying fibre content [%w/w] and fibre conditions (dry or wet). Value of the bare matrix is also shown.

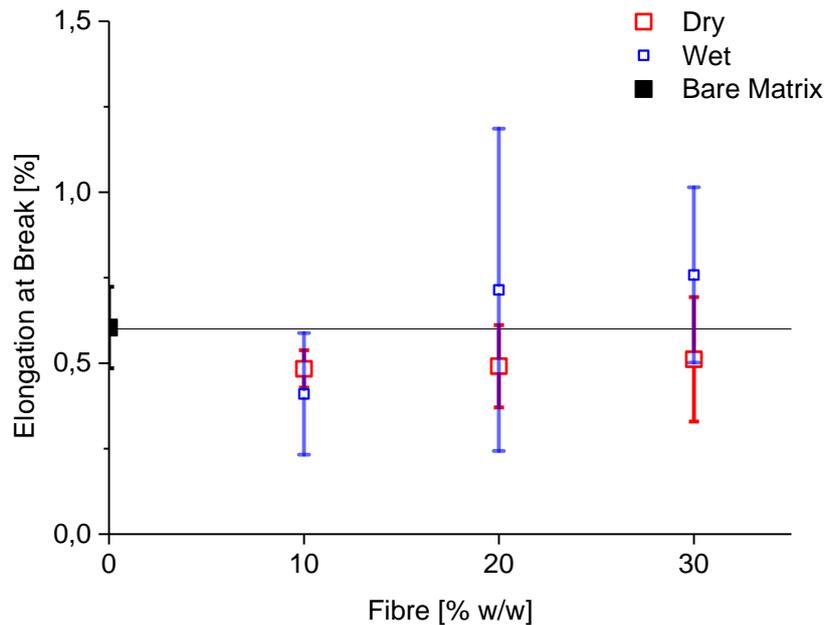


Figure 43. Variation of elongation at break [%] of composite material at varying fibre content [%w/w] and fibre conditions (dry or wet). Value of the bare matrix is also shown.

Considering, again, the substantiality of the error bars, it can be said that no differences can be seen between the performances of the bare matrix and the performances of the composite materials, independently on the type of flax (dry or wet) used. For what concerns tensile strength, an increase in the flax content does not result in an increase in the mechanical properties of the composite.

Again, this can be explained by the poor distribution and the poor wetting of the reinforcement inside the composite material.

4.5 ADHESION TESTING

Adhesion testing was performed on three polymeric adhesives at $-40\pm 2^{\circ}\text{C}$, $23\pm 2^{\circ}\text{C}$ and $80\pm 2^{\circ}\text{C}$.

Ultimate tensile strength and type of failure were considered. Results are shown in Table 20, Table 21 and Table 22, in which, for each adhesive, samples are grouped according to their type of failure (A = Adhesive failure, S = Substrate failure, C = Cohesive failure, M = Mixed failure). Average ultimate strength was calculated for each group.

Table 20. Ultimate tensile strength and type of failure of adhesives tested at 23°C.

Adhesive	Sample	τ_{max} [MPa]	Failure mode	Average τ_{max} [MPa]	Std. Dev.
Acrylate	#1	1.73	A	1.88	0.15
	#2	2.03			
	#3	3.55	M	3.55	
Epoxy	#4	3.56	A	3.62	0.06
	#8	3.67			
	#5	3.47	S	3.76	0.23
	#6	3.77			
	#7	4.03			
PU	#9	2.76	A	2.59	0.17
	#10	2.42			
	#11	2.24	C	2.24	
	#12	3.93	M	3.93	

Table 21. Ultimate tensile strength and type of failure of adhesives tested at 80°C.

Adhesive	Sample	τ_{max} [MPa]	Failure mode	Average τ_{max} [MPa]	Std. Dev.
Acrylate	#1	1.95	A	1.66	0.17
	#2	1.62	A		
	#3	1.55	A		
	#5	1.52	A		
	#4	2.11	M	2.11	
Epoxy	#7	2.77	S	2.81	0.13
	#8	2.83	S		
	#9	2.97	S		
	EXTRA1	2.87	S		
	EXTRA2	2.59	S		
	#10	2.30	A	2.30	
	#6	3.61	M	3.61	
PU	#11	1.30	A	1.26	0.20
	#12	1.56	A		
	#13	1.07	A		
	#14	1.10	A		

Table 22. Ultimate tensile strength and type of failure of adhesives tested at -40°C.

Adhesive	Sample	τ_{\max} [MPa]	Failure mode	Average τ_{\max} [MPa]	Std. Dev.
Epoxy	#1	4.19	S	4.56	0.27
	#2	4.85	S		
	#3	4.63	S		
PU	#4	3.13	A	3.19	0.13
	#5	3.07	A		
	#6	3.37	A		

Examples for each type of failure are shown in Figure 44.

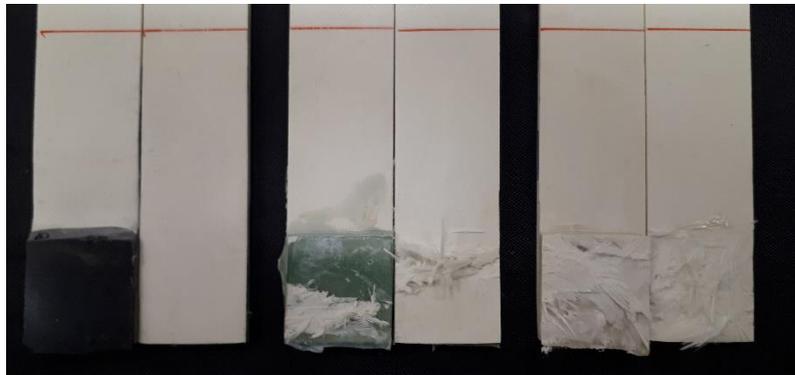


Figure 44. Example of adhesive failure (left), mixed mode (middle) and substrate failure (right).

For each adhesive, comparison between average tensile strength depending on type of failure and temperature were made in Table 23. Probability of occurrence for each type of failure is also shown.

Table 23. Comparison between shear strength of adhesives for each failure mode at varying testing temperature.

		-40°C		23°C		80°C	
		Occurrence (%)	$\bar{\tau}_{max}$ (MPa)	Occurrence (%)	$\bar{\tau}_{max}$ (MPa)	Occurrence (%)	$\bar{\tau}_{max}$ (MPa)
Acrylate	AF	N.A.		67%	1.88	80%	1.66
	MM			33%	3.55	20%	2.11
	SF						
Epoxy	AF			40%	3.62	14.3%	2.30
	MM					14.3%	3.61
	SF	100%	4.56	60%	3.76	71.4%	2.81
PU	AF	100%	3.19	67%	2.59	100%	1.26
	MM			33%	3.93		
	SF						

As first, an overall increase in tensile strength with decreasing testing temperature can be seen, as expected, independently from the type of adhesive and the type of failure. This trend is explained by an increase in stiffness associated to a reduction in temperature. Comparing average ultimate tensile strength values, epoxy was the adhesive for which highest values were recorded.

Secondly, the probability of occurrence of substrate failure (S) mode is highest for the epoxy adhesive. For acrylate and polyurethane ones, adhesive failure is the predominant mechanism, suggesting a poor chemical adhesion between the two materials. Only in few cases a mixed mode was observed for these two materials, but the overall probability of occurrence is too low to make it statistically relevant.

No trends were observed when correlating probability of occurrence of a certain type of failure with different testing temperatures.

From these considerations, considering both ultimate tensile strength and most probable type of failure, epoxy adhesive was the one that gave the best results.

5. CONCLUSIONS

Results of physical and mechanical testing on the two rovings were found to be consistent with results from literature: an increase in the EMC was seen when the materials were stored at increasing RH conditions. Moreover, a decrease in diffusion coefficient due to a transition from Fickian to non-Fickian absorption behaviour was seen. Tensile properties improved at increasing RH storage and testing conditions, too.

For what concerns the composite material, in general, a low level of reproducibility was observed, probably due to poor wetting and poor distribution of the reinforcement.

This also explained why, apart from POLY V5 DL 20%, an increase in the volume fraction of reinforcement did not correspond to an increase in tensile modulus and why no differences could be seen between the properties of the matrix and those of the composite, in terms of tensile strength and elongation at break. However, an improvement in tensile modulus due to the addition of flax fibres was observed as compared to the bare matrix.

These results show that improvements are required to enhance mechanical properties.

A different method for the mixture of the matrix with flax (automatic, for example) could be a first solution to improve distribution of the reinforcement and uniformity in the composite.

A better control on the conditions during the whole process could be achieved by means of environmental chamber, to avoid moisture regain by dried flax.

The use of coupling agents could help in enhancing the matrix-flax adhesion and interface.

For what concerns testing performed on polymeric adhesives, epoxy showed the best results in terms of mechanical properties and failure mechanism, as expected from literature.

Ringraziamenti

Otto anni sono tanti, tantissimi. Ma, più di tutto, questi otto anni sono stati lunghissimi, quasi interminabili. Se faccio mente locale su com'era il mondo quando ho iniziato, sembra passata 'na vita (pensa te che Instagram esisteva da un anno).

Però dai, se alzo un po' lo sguardo da tutte 'ste cose (più o meno come facevo a lezione, quando dall'ultima fila allungavo la testa per riuscire a far finta di prendere appunti), la vista non è poi così male, anzi.

Una vista piena di momenti, emozioni, fatiche seguite (ogni tanto) da gratificazioni. Una vista piena anche di momenti non facili, ma che comunque hanno contribuito a farmi arrivare fin qui. Ma soprattutto, una vista piena di Persone, di quelle belle dentro. E quante che ce ne sono state in questo lungo cammino.

A partire dagli amici di sempre, compagni di squadra e non, che sono sempre stati il mio momento di "stacco", la valvola di sfogo, quando l'atmosfera universitaria si appesantiva. Passando da chi ho conosciuto proprio all'interno di quella stessa atmosfera universitaria o tra i banchi (leggasi banconi, quelli dei bar) di quelle biblioteche che mi hanno accolto quando l'ansia pre-esame raggiungeva auree potentissime.

Quante partite a carte (leggasi madonne, visto il mio carattere da "era così tranquillo, salutava sempre" in certi frangenti), quante pause caffè (di cui ora sono dipendente, ma vabbè), quanto freddo inutile preso durante le vostre pause sigaretta (che in realtà io manco fumo, ma sticazzi, ogni scusa era buona per fare pausa), quanti appunti "scroccati" (ah, a tal proposito, ho già fatto partire tre o quattro processi di beatificazione).

Arrivando poi agli ultimi arrivati, solo in ordine di tempo, chiaramente.

I miei compagni di laboratorio, (tesisti, dottorandi, tecnici e professori – anche se questi ultimi chiaramente esulano un pelo da questa definizione un po' "confidenziale", ma

tant'è), con cui ho avuto modo di condividere questa ultima parte di carriera universitaria, sempre pronti nel darmi una mano ogni qualvolta io ne avessi bisogno (nonostante le mie battute vergognose e il mio essere un pizzico logorroico - ve ne sarete accorti, giunti a questo punto).

Il mio relatore, il professor Frassine, che ha sempre trovato il tempo per rispondere ad ogni mia domanda, dubbio e perplessità (ancora un po' e gli avrei chiesto pure di che colore convenisse fare la copertina della tesi), e che mi ha accompagnato passo passo in questo "travagliato" percorso di tesi, sempre orientandomi senza mai vincolarmi.

Il mio tutor, Simone, e Ranger tutta, che mi hanno sempre fatto sentire uno di famiglia.

Nel mezzo tantissime altre Persone che hanno toccato la mia vita, a volte in maniera leggera, altre volte lasciando il segno.

(Di sicuro ho tralasciato qualcuno, ma tanto non ho messo nomi, quindi si noterà di meno.)

A tutte queste Persone, con cui ho condiviso tanto e che mi hanno dato davvero tanto. A queste Persone, su cui ho sempre potuto contare quando avevo bisogno di parlare, di staccare, o anche solo di una spalla su cui appoggiarmi un attimo, giusto per riprendere fiato 'n attimo e ripartire. A tutti loro va il mio più sentito "Grazie davvero, di tutto".

Chiaramente tutto questo non sarebbe stato possibile se alle spalle non avessi avuto la mia Famiglia (tutta, comprensiva di zii, cugini, nonne, vicini di casa e mettiamoci pure il gatto Virgola), che mai ha mancato di darmi supporto, di spronarmi, ma anche di cazziarmi quando ce ne fosse stato bisogno. Mamma, Papà, Gaia ed Ema, anche se sapete che faccio sempre una fatica enorme a dirlo, vi voglio bene e oggi non sarei qui se voi non aveste sopportato ogni mio sbalzo d'umore (giusto quei 4 o 5 all'ora) e se, semplicemente, non foste quello che siete. Nel bene e nel male (questo ho dovuto aggiungerlo prima che vi montiate troppo la testa). E quindi grazie, grazie e grazie ancora. Per tutto quello che mi avete trasmesso ed insegnato (oltre all'avermi mantenuto fino ad oggi, chiaramente).

Ed ora, come direbbe un mio Amico, "con la testa, si pensa alla prossima partita".

È finita.

APPENDIX – TECHNICAL DATASHEET

A.1 NATTEX® Roving



PRODUCTS NATTEX® Roving

Semi-finished product in natural fibre in the form of continuous technical flax fibres



Characteristics	Data
Titration	1 g/m à 10 g/m
Length of bobbins	200 to > 1000 m
Mechanical properties (XP T 25 501 -2)	
• Tensile strength	500 MPa
• Tensile module (Young)	45 GPa
• Tensile elongation	2%
Presence of reactives	Sizing
Thermal degradation	> 230°C
Packaging	Cardboard core Ø 75 mm

A.2 Flax Low Twist Roving TEX400



FLAX LOW TWIST ROVING TEX 400

Technical Datasheet

SPECIFICATIONS

GENERAL PARAMETERS

LINEAR DENSITY:	TEX	400	COLOR:	NATURAL
	Nm	2.5	FLAX CONTENT:	100%
TORSION:	tpm	40	FLAX ORIGIN:	EU non-EU

FIBER TREATMENTS

WASHING:	YES	NONE	Alkali washing
BLEACHING:	YES	NONE	
SIZING:	YES	NONE	
ADDITIVES:	YES	NONE	
OTHER:	YES	NONE	

STANDARD BOBBIN CONDITIONING

CORE:	WEAVING CONE
TYPE:	CONIC
WEIGHT:	1.1 kg
DIAMETER:	N/A
WIDTH:	180 mm
LENGTH:	~2750 m
HUMIDITY:	~9 %

STORAGE

Recommended low humidity storage (< 50% R.H.); limited exposure to sunlight

DRY FLAX ROVING PARAMETERS

BREAKING STRENGTH	TENACITY	CV BREAKING	ELONGATION	RKM	RKM	RKM	RKM	Um
(N)	(cN/TEX)	STRENGTH (%)	(%)	min	3 points min	max	medium	(%)
32,0	8,00	20,2	1,0	4,8	5,3	13,4	8,5	14,8

CVm	Points g							
(%)	(-40%)	(-50%)	(+35%)	(+50%)	(+70%)	(+100%)	(+200%)	(+400%)
18,6	802,3	71,1	609,8	107,9	8,0	1,5	10,5	0,8

data obtained according to Uster specification for natural fibers

PARAMETERS	UNITS	VALUES
TENSILE STRENGTH	MPa	115
TENSILE MODULUS	GPa	12.0
TENSILE ELONGATION	%	1.0
DENSITY OF FLAX FIBERS	g/cm ³	1.44

A.3 Palapreg® P17-02

PRODUCT DATA SHEET

DATE OF ISSUE: NOVEMBER 2015 VERSION: 000352/2.0

PALAPREG® P17-02

CHEMICAL/PHYSICAL NATURE

Palapreg® P17-02 is an unsaturated polyester resin derived from orthophthalic acid and standard glycols, dissolved in styrene. Palapreg® P17-02 is of medium viscosity and high reactivity.

MAJOR APPLICATIONS

Palapreg P17-02 is intended for SMC and BMC production. It is mainly used together with Palapreg high polymer components for low shrink or low profile SMC / BMC applications. The resin can be readily thickened with magnesium oxide.

PRODUCT SPECIFICATIONS UPON DELIVERY

Property	Range	Unit	TM
Viscosity, 23°C	1300 - 1500	mPas	2013
Color, APHA	0 - 140	-	2017
Solids content, IR	63 - 66	%	2033
Appearance	clear	-	2265
Water content	0.04-0.07	%	2350
Acid value, as such	15-19	mg KOH/g	2401
Viscosity	450000 – 900000	mPas	2914A
Gel time, 130°C	65 - 110	seconds	2261
Peak time	110 - 155	seconds	2261
Peak temperature	265 - 290	°C	2261

REMARKS

Viscosity: Z2/100/23°C

Reactivity determined with 1 g TBPB added to 100 g resin
Typical Values Refractive Index
(23°C - TM 2150) = 1.523 - 1.527

PROPERTIES OF THE LIQUID RESIN (TYPICAL VALUES)

Property	Value	Unit	TM
Density, 20°C	1100	kg/m ³	2160
Flash point	33	°C	2800
Stability, no init., dark, 25°C	3	months	-

PROPERTIES OF CAST UNFILLED RESIN (TYPICAL VALUES)

Property	Value	Unit	TM
Density, 20°C	1200	kg/m ³	DIN 53479
Flexural strength	100	MPa	ISO 178
Flexural modulus	3.8	GPa	ISO 178
Outer fiber strain	2.8	%	ISO 178
Tensile strength	60	MPa	ISO 527-2
Mod. of elasticity in tension	3.8	GPa	ISO 527-2
Elongation at break	1.7	%	ISO 527-2
Impact res. - unnotched sp.	8	kJ/m ²	ISO 179
Heat deflection temp. (HDT)	140	°C	ISO 75-A
Glass transition temp. (T _g)	170	°C	ISO 537

PROPERTIES OF SMC-MOULDED (TYPICAL VALUES)

Property	Value	Unit	TM
Glass content	30	%	-
Density, 20°C	1700	kg/m ³	DIN 53479
Flexural strength	200	MPa	ISO 178
Flexural modulus	13	GPa	ISO 178
Outer fibre strain	2.7	%	ISO 178
Tensile strength	100	MPa	ISO 527-2
Mod. of elasticity in tension	11	GPa	ISO 527-2
Elongation at break	1.9	%	ISO 527-2
Impact res. - unnotched sp.	110	kJ/m ²	ISO 179
Moulding shrinkage	0.25	%	DIN 53464
Glass transition temp. (T _g)	200	°C	DIN 53445
Coefficient of linear thermal expansion (0-60°C)	23·10 ⁻⁶	K ⁻¹	DIN 53752/A
Volume resistivity	10 ¹⁴	A · cm	DIN 53482
Surface resistance	10 ¹²	A	DIN 53482
Comparative tracking index	CTI 600	-	DIN IEC 112



PROPERTIES OF SMC-MOULDINGS (TYPICAL VALUES)

Component	Weight
Palapreg® P 17-02	100
TBpB	1.5
Styrene	5
Polyethylene powder	5
Calcium carbonate	150
Zinc stearate	4
MgO-paste (35% MgO)	3

PROCESSING

Palapreg® P17-02 is usually processed into standard SMC / BMC, or together with Palapreg® high polymer solutions into low shrink / low profile SMC and BMC. As a rule, the ratio of Palapreg® P17-02 and high polymer solution is 60:40, but it can be varied if necessary. Depending on the size of the molded part it is recommended to add 300 to 600 ppm p-benzoquinone to the system (calculated on UP-resin plus thermoplastic solution).

STORAGE GUIDELINES

The resin should be stored indoors in the original, unopened and undamaged packaging, in a dry place at temperatures between 5°C and 30°C and the properties might change during storage. Shelf life is reduced at higher temperatures and the properties of the resin might change during storage. The shelf life of styrene containing unsaturated polyesters will be significantly reduced when exposed to light. Store in dark and in 100% light tight containers only.

MATERIAL SAFETY

A Material Safety Data Sheet of this product is available on request.

TEST METHODS

Test methods (TM) referred to in the table(s) are available on request.

Aliancys is a leading global company active in the sales of Quality Resins for composite applications. Together with its customers, Aliancys is pushing the limits of both composite part manufacturing and performance. Taking an integral approach to new product development, Aliancys is using its full expertise in resin chemistry, material science, and component manufacturing for shaping new applications in composites. So let's talk and increase our mutual business success, both today and tomorrow. More information on www.aliancys.com

[PRODUCT INQUIRY? PLEASE CLICK HERE](#)

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A.4 Araldite® 2015-1

HUNTSMAN

Enriching lives through innovation

Advanced Materials

Araldite® 2015-1

Structural Adhesives

TECHNICAL DATASHEET

Araldite® 2015-1 Two component epoxy paste adhesive

Key properties

- Toughened paste
- Ideal for bonding GRP, SMC and dissimilar substrates
- Gap filling, non-sagging up to 10mm thickness
- Good resistance to weathering

Description

Araldite® 2015-1 is a two component, room temperature curing paste adhesive giving a resilient bond. It is thixotropic and non sagging up to 10mm thickness. It is particularly suitable for SMC and GRP bonding.

Product data

Property	Araldite® 2015-1 Resin	Araldite® 2015-1 Hardener	Mixed Adhesive
Colour - visual (A112)*	grey soft paste	beige soft paste	grey paste
Specific gravity	1.4	1.4	1.4
Viscosity at 25°C (Pas)	thixotropic	thixotropic	thixotropic
Lap shear strength at 25°C (A501)*	-	-	> 15 MPa
Pot Life (100 gm at 25°C)	-	-	45 - 55 minutes

Specified data are on a regular basis analysed. Data which is described in this document as 'typical' is not analysed on a regular basis and is given for information purposes only. Data values are not guaranteed or warranted unless if specifically mentioned.

Processing

Pre-treatment

The strength and durability of a bonded joint are dependent on proper treatment of the surfaces to be bonded. At the very least, joint surfaces should be cleaned with a good degreasing agent such as acetone, iso-propanol (for plastics) or other proprietary degreasing agents in order to remove all traces of oil, grease and dirt. Low grade alcohol, gasoline (petrol) or paint thinners should never be used. The strongest and most durable joints are obtained by either mechanically abrading or chemically etching ("pickling") the degreased surfaces. Abrading should be followed by a second degreasing treatment.

Mix ratio	Parts by weight	Parts by volume
Araldite® 2015-1 Resin	100	100
Araldite® 2015-1 Hardener	100	100

Application of adhesive

The resin/hardener mix may be applied manually or robotically to the pretreated and dry joint surfaces. Huntsman's technical support group can assist the user in the selection of a suitable application method as well as suggest a variety of reputable companies that manufacture and service adhesive dispensing equipment.

A layer of adhesive 0.05 to 0.10 mm thick will normally impart the greatest lap shear strength to the joint. Huntsman stresses that proper adhesive joint design is also critical for a durable bond. The joint components should be assembled and secured in a fixed position as soon as the adhesive has been applied.

For more detailed explanations regarding surface preparation and pretreatment, adhesive joint design, and the dual syringe dispensing system, visit www.aralditeadhesives.com.

Equipment maintenance

All tools should be cleaned with hot water and soap before adhesives residues have had time to cure. The removal of cured residues is a difficult and time-consuming operation.

If solvents such as acetone are used for cleaning, operatives should take the appropriate precautions and, in addition, avoid skin and eye contact.

Typical times to minimum shear strength

Temperature	°C	10	15	23	40	60	100
Cure time to reach	hours	10	6	4	1	-	-
LSS > 1MPa	minutes	-	-	-	-	20	3
Cure time to reach	hours	20	15	8	3	-	-
LSS > 10MPa	minutes	-	-	-	-	40	5

LSS = Lap shear strength.

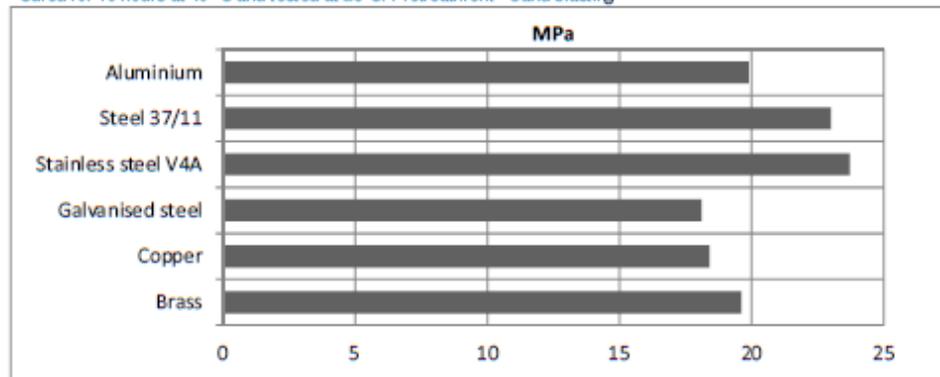
Typical cured properties

The figures were determined with typical production batches using standard testing methods. They are provided solely as technical information and do not constitute a product specification.

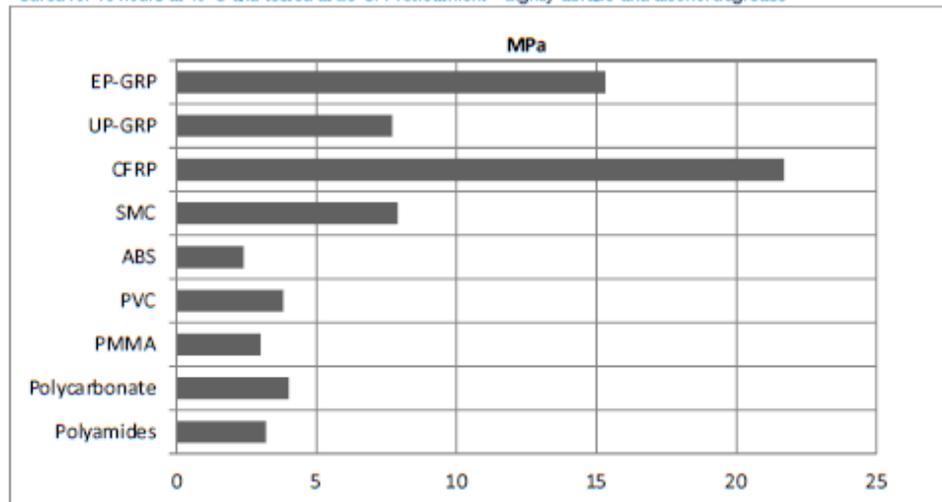
Unless otherwise stated, the figures given below were all determined by testing standard specimens made by lap-jointing 114 x 25 x 1.6 mm strips of aluminium alloy. The joint area was 12.5 x 25 mm in each case.

Average lap shear strengths of typical metal-to-metal joints (ISO 4587) (typical average values)

Cured for 16 hours at 40°C and tested at 23°C. Pretreatment - Sand blasting



Average lap shear strengths of typical plastic-to-plastic joints (ISO 4587) (typical average values)
 Cured for 16 hours at 40°C and tested at 23°C. Pretreatment – Lightly abrade and alcohol degrease

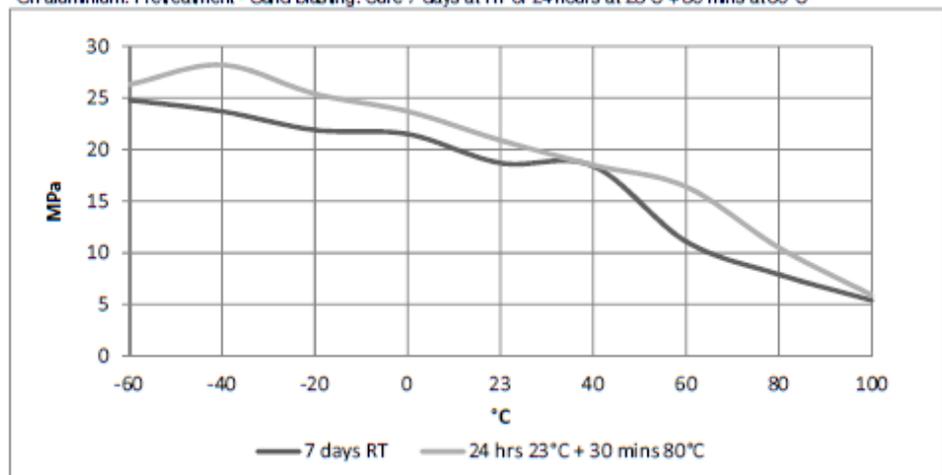


Tensile properties (ISO 527). Cure 16hrs at 40°C (typical average values)- tested at 23°C

Tensile strength	31 MPa
Tensile modulus	1.6 GPa
Elongation at break	4.2%

Lap shear strength versus temperature (ISO 4587) (typical average values)

On aluminium. Pretreatment - Sand blasting. Cure 7 days at RT or 24 hours at 23°C + 30 mins at 80°C



Glass transition temperature (typical average values)

Cure: 1 hour at 80°C

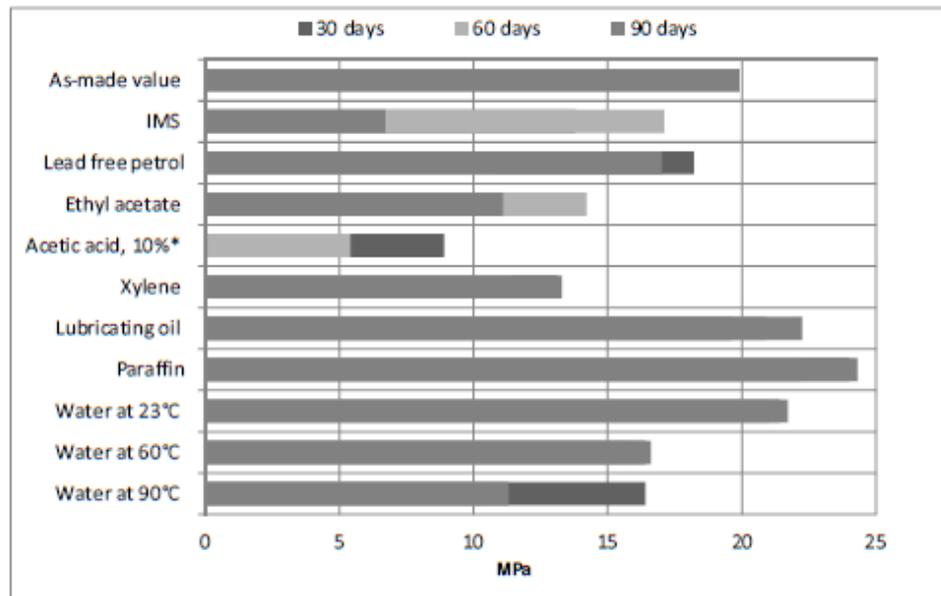
78°C by DMA

Lap shear strength versus immersion in various media (ISO 4587) (typical average values)

On aluminium, cured for 16 hours at 40°C and tested at 23°C. Pretreatment - Sand blasting

Unless otherwise stated, L.S.S. was determined after immersion for 30, 60 and 90 days at 23°C

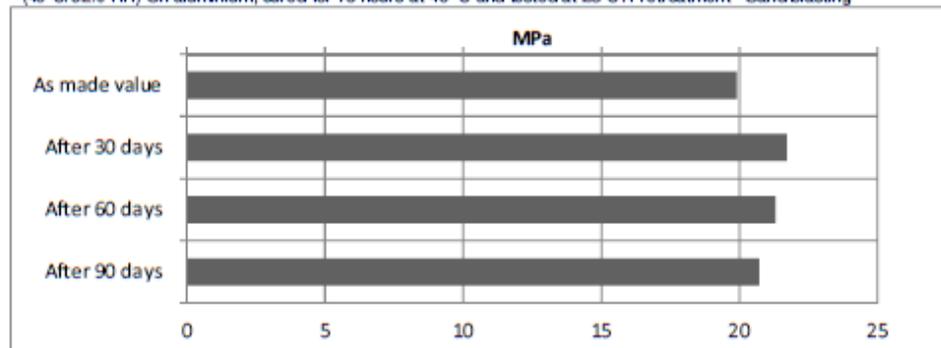
Cure 16 hours 40°C



*: degraded in acetic acid after 90 day

Lap shear strength versus tropical weathering (ISO 4587) (typical average values)

(40°C/92% RH) On aluminium, cured for 16 hours at 40°C and tested at 23°C. Pretreatment - Sand blasting



DMA Shear modulus G' (ISO 6721) (typical average values).

Cure: 1 hour at 80°C

Temperature	G'
-50°C	1.8 GPa
0°C	1 GPa
20°C	900 MPa
50°C	540 MPa
75°C	61 MPa
100°C	12 MPa

Flexural Properties (ISO 178) (typical average values).

Cure 16 hours at 40°C , tested at 23°C

Flexural Strength

43 MPa

Flexural Modulus

1800 MPa

Tensile Properties (ISO 178) (typical average values).

Cure 16 hours at 40°C , tested at 23°C

Tensile Strength

31 MPa

Tensile Modulus

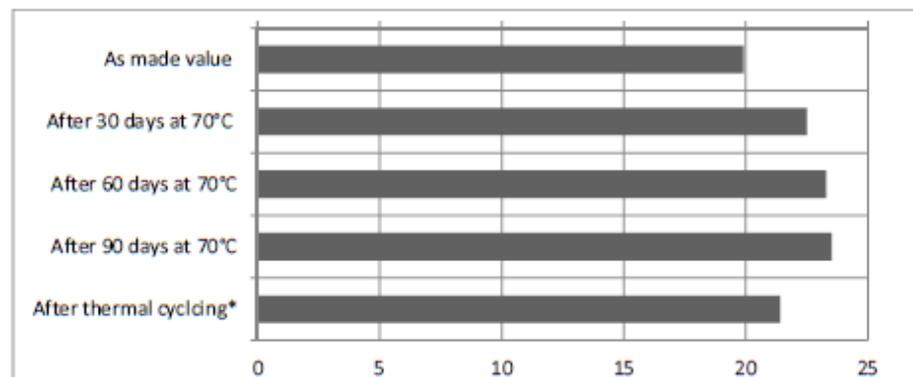
1600 MPa

Elongation at break

4.2%

Lap shear strength versus heat aging (ISO 4587) (typical average values)

On aluminium, cured for 16 hours at 40°C and tested at 23°C. Pretreatment - Sandblasting



* Thermal cycling: 25 cycles of 6 hours duration from -30°C to 70°C

Storage Araldite® 2015-1 must be stored at room temperature provided the components are stored in sealed containers. The expiry date is indicated on the label.

Handling precautions **Caution**

Our products are generally quite harmless to handle provided that certain precautions normally taken when handling chemicals are observed. The uncured materials must not, for instance, be allowed to come into contact with foodstuffs or food utensils, and measures should be taken to prevent the uncured materials from coming in contact with the skin, since people with particularly sensitive skin may be affected. The wearing of impervious rubber or plastic gloves will normally be necessary; likewise the use of eye protection. The skin should be thoroughly cleansed at the end of each working period by washing with soap and warm water. The use of solvents is to be avoided. Disposable paper - not cloth towels - should be used to dry the skin. Adequate ventilation of the working area is recommended. These precautions are described in greater detail in the Material Safety Data sheets for the individual products and should be referred to for fuller information.



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A.5 TS 850F



March 2015

TS 850F PU Structure Adhesive

TECHNICAL DATA SHEET

PRODUCT DESCRIPTION

TS 850F is a two-component structure adhesive based on polyurethane, with high toughness and high strength, which cures at room temperature. The work time and curing times are dependent on temperature. By increasing the temperature these times can be reduced; low temperature retard the process.

UNCURED PROPERTIES

Chemical base	Polyurethane
Colours	A-yellow B-black
Odour	odourless
Consistency	pasty,thixotropic
Density	A-approx. 1.4g/cm ³ B-approx. 1.1g/cm ³
Solids	≥98%
Mix ratio by volume	1:1

CURED PROPERTIES

Work time	approx. 5-10 mins*
Tack-free time	approx. 10-30 mins*
Shore D hardness (GB/T 531)	approx. 55*
Tensile shear strength(GB/T 7124)	≥13 MPa*
Application temperature	5°C to 40°C
In service temperature range	-40°C to 80°C
Short exposure	120°C

*:standard climate: 23°C,50% relative air humidity

Characteristics

- < 1% VOC
- odourless
- Non-corrosive
- Excellent adhesion on many substrates
- High performance mechanical properties
- Paintable

APPLICATIONS

Structure bonding of metals and thermoset composites (BMC, SMC, RTM, etc)

APPLYING METHOD

Proper surface preparation is essential to the success of any polyurethane application. In all cases the surface should be clean, dry, free from oils, and rough.

- a) Clean and abrade application surface. Sandblast or grind is needed.
- b) All abrasive preparation should be followed by another cleaning to remove any remnants from that process.
- c) Mix 2 parts, and insure no liquid inflow on the surface.
- d) Cover mixed material over the prepared surface firmly to ensure maximum surface contact.

Application from 600ml dual cartridges is made with the corresponding hand gun or air pressure pistols. The two components are mixed through the mixer nozzle.

PAINTABILITY

TS 850F may be over-painted, however due to the large number of paints and varnishes. We strongly recommend a compatibility test before application.

STORAGE

Recommended storage temp. 5-25°C
Shelf-life 12 months in original packaging

PACKAGING

600ml 1:1 Dual Cartridges
55 Gallon

ORDERING INFORMATION

Stock No. 08501205/black

Stock No. 08501209/black

A.6 TS 828

PRODUCT DESCRIPTION

TS828 High Performance Structural Adhesive is a 10:1 two components acrylic structure adhesive with the property of heat-setting and high strength after curing. Cured layer has high toughness and good resistance to peeling off. Fixture time is 5-9 minutes at room temperature, 80% of the final strength can be reached in 20 minutes. TS828 High Performance Structural Adhesive is especially suitable for bonding plastic and metal with a minimum of surface preparation.

FEATURES

- 5-9 minutes for Fixture time
- Superior impact and peel strength
- Excellent heat resistance properties
- Little or no surface preparation
- Offers excellent tolerance to off-ratio mixing
- 100% reactive
- Excellent environmental resistance

TYPICAL APPLICATIONS

- Metals
- Plastics
- Leathers
- Rubbers
- Wood

UNCURED PROPERTIES

	Part A	Part B	Mixed (20g)
Open time (min)	—	—	4-6
Fixture time (min)	—	—	5-9
Color	Ivory White Paste	Blue Paste	Light Blue Paste(After mixing) Green Solid(After curing)
Viscosity (mPa*s)	380,000	50,000	—
	~	~	
Special Gravity	600,000	220,000	1.00
Mix Ratio	0.986	1.098	
By weight	10	1	
By volume	9	1	—

CURED PROPERTIES

Operating Temperature Range.....	-60-150°C
Lap-shear Strength (MPa) GB/T 7124-2008 (Carbon Steel)	32.3 CF
Lap-shear Strength (MPa) GB/T 7124-2008 (Stainless Steel)	32.6 C80
Lap-shear Strength (MPa) GB/T 7124-2008 (Al 2024 A 5T3)	22.6 CF

Lap-shear Strength (MPa) GB/T 7124-2008 (FRP)	12.3 SF
Lap-shear Strength (MPa) GB/T 7124-2008 (PVC)	2.65 SF
Lap-shear Strength (MPa) GB/T 7124-2008 (PMMA)	5.45 SF
Lap-shear Strength (MPa) GB/T 7124-2008 (ABS)	5.87 SF
Lap-shear Strength (MPa) GB/T 7124-2008 (PC)	12.3 SF
Tensile Strength (MPa) GB/T 6329-1996.....	36.2 CF
Peel Strength (N/cm) GB/T 2791-1995.....	82.5 CF
Cured Shrinkage (cm/cm)	0.01

NOTE: SF = Substrate Failure/Break/Yield

CF = Cohesive Failure

AF = Adhesive Failure

MM = Mixed (Mode of AF and CF)

HEAT RESISTANCE

Lap-shear Strength at 60°C (MPa) GB/T 7124-2008.....	18.6 CF
Lap-shear Strength at 80°C (MPa) GB/T 7124-2008.....	14.1 CF
Lap-shear Strength at 100°C (MPa) GB/T 7124-2008.....	8.5 CF
Lap-shear Strength at 120°C (MPa) GB/T 7124-2008.....	5.8 CF
Lap-shear Strength at 150°C (MPa) GB/T 7124-2008.....	2.8 MM

NOTE: All strengths are lap-shear strength. All substrates are 45#carbon steel.

SF = Substrate Failure/Break/Yield

CF = Cohesive Failure

AF = Adhesive Failure

MM = Mixed (Mode of AF and CF)

ENVIRONMENTAL RESISTANCE

Lap-shear Strength (Water)	27.6 CF
Lap-shear Strength (5% Sodium Chloride Solution)	26.4 CF
Lap-shear Strength (10% NaOH Solution)	25.2 CF
Lap-shear Strength (Alcohol)	26.8 CF
Lap-shear Strength (46# Antiwear Hydraulic Oil)	31.5 CF
Lap-shear Strength (TOTAL-35% Antifreezing Solution)	28.7 CF
Lap-shear Strength (5W-40 Lubricating Oil)	29.8 CF
Lap-shear Strength (10% Acetic Solution)	24.9 CF

NOTE: Environmental & Chemical Exposure Test on 45#carbon steel. All strength are lap-shear strength. All Exposure Times 7 Days Unless Otherwise Noted. All Temperatures are 23±2°C Unless Otherwise Noted

SF = Substrate Failure/Break/Yield

CF = Cohesive Failure

AF = Adhesive Failure

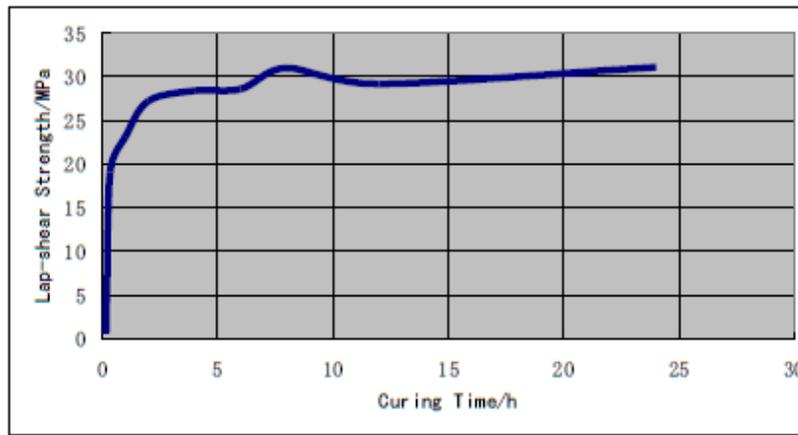
MM = Mixed (Mode of AF and CF)

HEAT AGING (1000H)

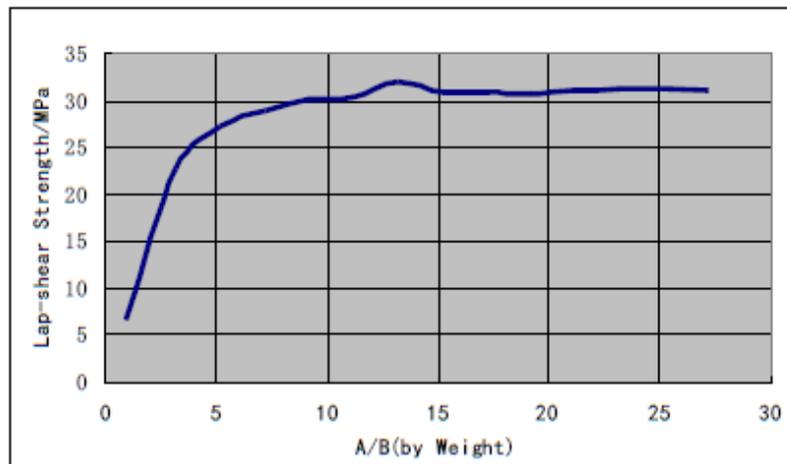
Lap-shear Strength after 120°C for 1000h (MPa) GB/T 7124-2008.....33.0 CF

Lap-shear Strength after 150°C for 1000h (MPa) GB/T 7124-2008.....31.6 CF

DEVELOPMENT OF BOND STRENGTH



LAP-SHEAR STRENGTH FOR DIFFERENT A/B



NOTE TO APPLICATION

- For best performance bond surfaces should be clean and free of grease. Extensive surface preparation is not required.
- Mixing part A and part B in the correct ratio and mix thoroughly. Once mixed, it should achieve a uniform color. It is recommended that either meter mix equipment or cartridges with static mix nozzles be used to properly

ratio and dispense the adhesive.

- To assure maximum bond strength, surfaces must be mated within the adhesive's open time. Use enough material to completely fill the joint when parts are clamped.
- Do not return unused material to container as it would result in contamination and/or premature hardening of contents.
- Heat buildup during and after mixing is normal. To reduce the likelihood of exothermic reaction or excessive heat buildup, mix less than 100 grams at a time. Mixing smaller amounts will minimize heat build up.

STORAGE AND SHELF LIFE

Store between 8°C and 25°C. Continuous storage above 25°C reduces the shelf life of the materials. DO NOT FREEZE. shelf life is 9 months.

CAUTION

TS828 High Performance Structural Adhesive is an eye irritant and may also irritate skin. They contain no solvents or aggressive adhesive agents. Skin should be washed after contact with these products. In case of eye contact, flush with water and seek medical attention. Keep away from heat, sparks, and open flames and keep out of the reach of children.

For complete safe handling information, please refer to the appropriate Material Safety Data Sheets prior to using this product.

For technical assistance, please call +86-10-88795588.

ORDERING INFORMATION

Stock No.	Unit Size
08280205	490ml(PP cartridge)
08280207	490ml(PBT cartridge)

Note

The data provided herein are typical values for the purpose of technical reference only, should not be considered as the product specification or acceptance standard. All the information is believed by Tonsan Adhesive Inc. ("Tonsan") to be accurate and reliable, but due to the differences in the application conditions, substrate surfaces and/or curing conditions, Tonsan strongly recommends that the user should perform necessary tests before any purchase or practice, to determine the suitability of our product for the intended use. Furthermore, the storage and shipping conditions could also affect the stability, physical and mechanical properties of the product. Tonsan will not assume the responsibility for the results obtained by the user or any third parties, from the methods out of Tonsan's control.

Tonsan Adhesive, Inc.

5 Shuangyuan Rd. Badachu High-Tech Zone, 100041, Beijing, China

A.7 Menzolit® SMC 1100 NAT



Priliminary Data Sheet

Menzolit® SMC 1100 NAT

Formulation:

02145

Product identification

Date:

2019-4-29

Menzolit® SMC 1100 NAT is a sheet moulding compound based on unsaturated polyester resin. The product is glass fibre reinforced and contains mineral fillers. In case of fire the product doesn't melt, neither does it form droplets nor is smoke generation excessive. The material is compression moulded in heated steel moulds. It is recommended to work with chrome plated tools. The product contains no halogens or heavy metals nor any candidates from the REACH SVHC list.

Product description

Menzolit® SMC 1100 NAT is a special vinyl ester SMC for high strength applications. The reinforcement has been put to a level that combines mouldability with high strength and stiffness properties. The specific resin and a higher amount of glass fibers results in high mechanical strength. Durability is improved as well. Even without a specific fire retardant, the fire retardancy level HB according UL 94 is achieved. Typical applications are structural components within the automotive industry or mechanical engineering. It is suitable for load carrying applications or fast moving and accelerated components.

Physical properties

	Standard	Units	
Glass Fiber Content	EN ISO 1172	%	36
Density	ISO 1183	g/cm ³	1.80
Shrinkage	ISO 2577	%	-0.01
Heat Distortion Temp	EN ISO 75-2	°C	>200
Tensile Strength	EN ISO 527-4	MPa	100
Young's Modulus	EN ISO 527-4	GPa	10
Flexural Strength	EN ISO 14125	MPa	190
Flexural Modulus	EN ISO 14125	GPa	11
Impact Strength	EN ISO 179	kJ/m ²	100
shear Modulus	ASTM D4065	GPa	5
Barcol	ASTM D2583	Hba	50
Poisson's Ratio	M		0.3-0.7
Fire Retardancy	UL94	mm&level	3mm,HB
Water absorption	ISO62	%	<0.7

Menzolit® SMC 1100 BLK is produced in a standard width of 1200/1500mm. It is folded and packaged in cardboard / wooden boxes. In any case, a styrene barrier film wrapping is being used. For alternative packaging please contact our technical service team. Each packaging container is marked with the date by which the material should be used. This date refers to material stored indoors in a dry place, shaded from direct sunlight, in the original packaging at a temperature less than 25 degrees C.

menzolit is a registered trademark |

Note: Properties given are the mean value of test results, and taken from non pigmented, compression moulded panels at room temperature. All data here can not be used as testing requirements/limitations. Our products are manufactured according to ISO 9001 standards, a Safety Data Sheet according to GHS/REACH is available. We make no warranty or representation as to the suitability of the product or information herein for any particular application. The determination of the suitability of the above information for any particular use is solely the responsibility of the user. For further information please contact your local Menzolit Technical Service Team for assistance or see www.menzolit.com

A.8 Menzolit® SMC 0400 NAT



Priliminary Data Sheet

Menzolit® SMC 0400 NAT

Formulation: 01150

Product identification

Date: 2018-12-18

Menzolit® SMC 0400 NAT is a sheet moulding compound based on unsaturated polyester resin. The product is glass fiber reinforced and contains mineral fillers. In case of fire, the product doesn't melt, neither does it form droplets nor is smoke generation excessive. The material is compression moulded in heated steel moulds. It is must to work with chrome plated tools. It does not contain any halogenes, nor heavy metals nor any candidates from the REACH SVHC list.

Product description

Menzolit® SMC 0400 NAT is a standard class A SMC material. These compounds mould to parts with good up to excellent surface quality. Surface defects like waviness, fiber patterns and orange peel do not occur with this products. To achieve the highest surface quality, we recommend that tool surfaces are mirror polished. To ease demoulding we highly recommend chrome-plating of tool surfaces.

Physical properties

Physical properties	Standard	Units	
Glass Fiber Content	EN ISO 1172	%	27
Fiber Length	M	mm	25
Unit Weight	M	g/m ²	4750
Density	ISO 1183	g/cm ³	1.88
Shrinkage	ISO 2577	%	-0.05
Heat Distortion Temp	EN ISO 75-2	°C	>200
Glass Transition Temp	ISO 11357-2	°C	200
Continuous Service Temp	M	°C	165
Tensile Modulus	EN ISO 527-4	GPa	9
Tensile Strength	EN ISO 527-4	MPa	70
Flexural Modulus	EN ISO 14125	GPa	9
Flexural Strength	EN ISO 14125	MPa	160
Impact Strength	EN ISO 179	kJ/m ²	65
Fire retardancy	UL 94	mm & Level	HB 3.0mm
Surface Resistivity	IEC 60093	Ohm	1.00 E+12
Volume Resistivity	IEC 60093	Ohm.cm	1.00 E+15
Comparative Tracking Resistance	IEC 60112	Level	CTI 600
Water absorption	ISO 62	%	≤ 0.50

Menzolit® SMC 0400 NAT is produced in a standard width of 1200/1500mm. It is packaged in cardboard / wooden boxes. In any case, a styrene barrier film wrapping is being used. For alternative packaging please contact our technical service team. Each packaging container is marked with the date by which the material should be used. This date refers to material stored indoors in a dry place, shaded from direct sunlight, in the original packaging at a temperature between 10 and 25 degrees C.

menzolit is a registered trademark |

Note: Properties given are the mean value of test results, and taken from non pigmented, compression moulded panels at room temperature. All data here can not be used as testing requirements/limitations. Our products are manufactured according to ISO 9001 standards, a Safety Data Sheet according to GHS/REACH is available. We make no warranty or representation as to the suitability of the product or information herein for any particular application. The determination of the suitability of the above information for any particular use is solely the responsibility of the user. For further information please contact your local Menzolit Technical Service Team for assistance or see www.menzolit.com.

BIBLIOGRAPHY

- [1] E. Witten, V. Mathes, M. Sauer, and M. Kühnel, "AVK Composites market report 2018 - Market developments, trends, outlooks and challenges," 2018.
- [2] S. Das, "Life cycle assessment of carbon fiber-reinforced polymer composites," *Int. J. Life Cycle Assess.*, vol. 16, no. 3, pp. 268–282, 2011.
- [3] D. . S. S. Ray, "Thermosetting bioresins as matrix for biocomposites," 2017, pp. 57–80.
- [4] J. M. Raquez, M. Deléglise, M. F. Lacrampe, and P. Krawczak, "Thermosetting (bio)materials derived from renewable resources: A critical review," *Prog. Polym. Sci.*, vol. 35, no. 4, pp. 487–509, 2010.
- [5] M. R. Sanjay, S. Siengchin, J. Parameswaranpillai, M. Jawaid, C. I. Pruncu, and A. Khan, "A comprehensive review of techniques for natural fibers as reinforcement in composites: Preparation, processing and characterization," *Carbohydr. Polym.*, vol. 207, no. November 2018, pp. 108–121, 2019.
- [6] K. L. Pickering, M. G. A. Efendy, and T. M. Le, "A review of recent developments in natural fibre composites and their mechanical performance," *Compos. Part A Appl. Sci. Manuf.*, vol. 83, pp. 98–112, 2016.
- [7] Nova-Institute, "Natural fibre-reinforced plastics: Establishment and growth in niche markets," *JEC Compos. Mag.*, vol. 55, no. 118, pp. 23–24, 2018.
- [8] W. W. M. Ali, L. E. Ooi, and Z. A. M. Ishak, "Sound and Vibration Damping Properties of Nonwoven Flax Reinforced Acrylic Based Polyester Composites," *MATEC Web Conf.*, vol. 217, 2018.
- [9] A. Moudood *et al.*, "Effect of Moisture in Flax Fibres on the Quality of their Composites Effect of Moisture in Flax Fibres on the Quality of their Composites," *J.*

- Nat. Fibers*, vol. 16, no. 2, pp. 209–224, 2019.
- [10] C. A. Fuentes *et al.*, “Effect of humidity during manufacturing on the interfacial strength of non-pre-dried flax fibre/unsaturated polyester composites,” *Compos. Part A Appl. Sci. Manuf.*, vol. 84, pp. 209–215, 2016.
- [11] A. le Duigou, J. Merotte, A. Bourmaud, P. Davies, K. Belhouli, and C. Baley, “Hygroscopic expansion: A key point to describe natural fibre/polymer matrix interface bond strength,” *Compos. Sci. Technol.*, vol. 151, pp. 228–233, 2017.
- [12] S. Alix, E. Philippe, A. Bessadok, L. Lebrun, C. Morvan, and S. Marais, “Effect of chemical treatments on water sorption and mechanical properties of flax fibres,” *Bioresour. Technol.*, vol. 100, no. 20, pp. 4742–4749, 2009.
- [13] X. Li, L. G. Tabil, and S. Panigrahi, “Chemical treatments of natural fiber for use in natural fiber-reinforced composites: A review,” *J. Polym. Environ.*, vol. 15, no. 1, pp. 25–33, 2007.
- [14] S. Reich, A. El Sabbagh, and L. Steuernagel, “Improvement of fibre-matrix-adhesion of natural fibres by chemical treatment,” *Macromol. Symp.*, vol. 262, no. 1, pp. 170–181, 2008.
- [15] M. Ramesh, “Flax (*Linum usitatissimum* L.) fibre reinforced polymer composite materials: A review on preparation, properties and prospects,” *Prog. Mater. Sci.*, vol. 102, no. December 2018, pp. 109–166, 2019.
- [16] L. Yan, N. Chouw, and K. Jayaraman, “Flax fibre and its composites - A review,” *Compos. Part B Eng.*, vol. 56, pp. 296–317, 2014.
- [17] C. Baley, C. Morvan, and Y. Grohens, “Influence of the absorbed water on the tensile strength of flax fibers,” *Macromol. Symp.*, vol. 222, pp. 195–201, 2005.
- [18] A. Lefeuvre, A. Le Duigou, A. Bourmaud, A. Kervoelen, C. Morvan, and C. Baley, “Analysis of the role of the main constitutive polysaccharides in the flax fibre mechanical behaviour,” *Ind. Crops Prod.*, vol. 76, pp. 1039–1048, 2015.
- [19] L. Orgèas and P. J. J. Dumont, “Sheet molding compounds ’,” *Wiley Online Libr.*, pp. 2683–2718, 2012.
- [20] B. Van Voorn, H. H. G. Smit, R. J. Sinke, and B. De Klerk, “Natural fibre reinforced

- sheet moulding compound,” *Compos. Part A Appl. Sci. Manuf.*, vol. 32, pp. 1271–1279, 2001.
- [21] M. Akhshik, S. Panthapulakkal, J. Tjong, and M. Sain, “The effect of lightweighting on greenhouse gas emissions and life cycle energy for automotive composite parts,” *Clean Technol. Environ. Policy*, vol. 21, no. 3, pp. 625–636, 2019.
- [22] M. D. Banea and L. F. M. Da Silva, “Adhesively bonded joints in composite materials: An overview,” *Proc. Inst. Mech. Eng. Part L J. Mater. Des. Appl.*, vol. 223, no. 1, pp. 1–18, 2009.
- [23] S. Pantelakis and K. I. Tserpes, “Adhesive bonding of composite aircraft structures: Challenges and recent developments,” *Sci. China Physics, Mech. Astron.*, vol. 57, no. 1, pp. 2–11, 2014.
- [24] E. S. . E. C., *Surface Treatment of Materials for Adhesive Bonding: Second Edition*. 2013.
- [25] P. I. Chen, K. Y. Wang, and H. H. Huang, “Strength and failure modes of adhesively bonded composite joints with easily fabricated nonflat interfaces,” *Compos. Struct.*, vol. 225, no. March, p. 111162, 2019.
- [26] N. G. C. Barbosa, R. D. S. G. Campilho, F. J. G. Silva, and R. D. F. Moreira, “Comparison of different adhesively-bonded joint types for mechanical structures,” *Appl. Adhes. Sci.*, vol. 6, no. 1, pp. 1–19, 2018.
- [27] B. ISO Standard, “Plastics - Small enclosures for conditioning and testing using aqueous solutions to maintain the humidity at constant value. BS EN ISO 483:2005.,” *Int. Organ. Stand. Geneva, Switzerland.*, vol. 483, p. 12, 2005.
- [28] D. Zhang, N. R. Milanovic, Y. Zhang, F. Su, and M. Miao, “Effects of humidity conditions at fabrication on the interfacial shear strength of flax/unsaturated polyester composites,” *Compos. Part B*, vol. 60, pp. 186–192, 2014.
- [29] M. Gomina, “Effects of the hygrothermal environment on the mechanical properties of flax fibres,” *J. Compos. Mater.*, vol. 48, no. 12, pp. 1699–1707, 2014.
- [30] ASTM International, “Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading (Metal-to-

- Metal). ASTM D1002 - 10," *Annu. B. ASTM Stand.*, vol. 10, pp. 1–5, 2005.
- [31] ASTM International, "Standard Terminology Relating to Wood and Wood-Based Products. ASTM D9 - 12," *Annu. B. ASTM Stand.*, pp. 1–12, 2019.
- [32] ASTM International, "Tentative Methods of Test for Amount of Moisture in Textile Materials. ASTM D 2654 - 67 T," *Standards*, pp. 590–601, 2016.
- [33] ASTM International, "Standard Test Method for Tensile Properties of Single Textile Fibers. ASTM D3822/D3822M - 14," *Standards*, pp. 1–10, 2014.
- [34] ASTM standard, "Standard test method for tensile properties of polymer matrix composite materials. ASTM D3039M - 08," *Annu. B. ASTM Stand.*, pp. 1–13, 2013.
- [35] B. R. Burchardt and P. W. Merz, "Elastic Bonding and Sealing in Industry," *Handb. Adhes. Sealants*, vol. 2, pp. 355–xliv, Jan. 2006.
- [36] H. Özer, "Applied Adhesive Bonding in Science and Technology - Introductory Chapter," *IntechOpen*, pp. 3–10, 2018.
- [37] H. J. E. Brandenburg N. R., "Equilibrium moisture content of fiber flax," *USDA Tech. Bull.*, p. TB 1200, 1959.
- [38] S. Noorolahi, J. Khazaei, and S. Jafari, "Modeling Cyclic Water Absorption and Desorption Characteristics of Three Varieties of Wood," in *IAALD AFITA WCCA2008*, 2008, pp. 113–122.
- [39] J. Crank, *The Mathematics of Diffusion - Second Edition*. 1975.
- [40] M. Assarar, D. Scida, A. El Mahi, C. Poilâne, and R. Ayad, "Influence of water ageing on mechanical properties and damage events of two reinforced composite materials: Flax-fibres and glass-fibres," *Mater. Des.*, vol. 32, no. 2, pp. 788–795, 2011.
- [41] A. Stamboulis, C. A. Baillie, and T. Peijs, "Effects of environmental conditions on mechanical and physical properties of flax fibers," *Compos. Part A*, vol. 32, pp. 1105–1115, 2001.
- [42] A. Mustata and F. S. C. Mustata, "Moisture absorption and desorption in flax and hemp fibres and yarns," *Fibres Text. East. Eur.*, vol. 99, no. 3, pp. 26–30, 2013.
- [43] V. Placet, O. Cisse, and M. L. Boubakar, "Influence of environmental relative

humidity on the tensile and rotational behaviour of hemp fibres," *J. Mater. Sci.*, vol. 47, no. 7, pp. 3435–3446, 2012.