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INTERFACE FORMATION MECHANISMS IN FIBRE REINFORCED THERMOPLASTIC TAPES

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Abstract

Composite materials future relies on achieving lighter parts through integrating sustainable materials, with bio-based and/or circular materials in reinforced thermoplastics. To meet the requirements of various industrial applications, Poly Ether Ether Ketone (PEEK) and biodegradable PolyLactic Acid (PLA) matrices can be reinforced by reclaimed carbon fibers and biodegradable flax fibers. However, the mechanical behavior of composites is heavily influenced by the quality of the interface and the presence of defects and voids, this would imply a required control at the stage of composite manufacturing. Despite their significance, mechanisms governing interface and void formation at the microscales and mesoscales remain insufficiently explored and understood.

The adhesion phenomena at the fiber / matrix interface depends on different properties of the constituents. The most influent ones still must be identified. Moreover, the effect of temperature should be considered since the polymer can be exposed to high temperatures during the interface formation. Furthermore, the crystallinity and the induced mechanical properties of the produced fiber / matrix interface will be studied.

The DUINTACOS project aims to address this gap by allowing a deep understanding of interface formation in fiber-reinforced thermoplastic tapes, seeking to minimize micro voids, that is a requirement to obtain a high-quality composite structure.

1. Introduction

Continuous fiber composite tapes are nowadays increasingly employed in the transportation industry, since they allow manufacturing of lightweight structures with complex shapes using high-performance materials, such as carbon fiber-reinforced poly (ether ether ketone) (PEEK), that is widely used in aerospace applications [1]. Alongside, several types of tapes incorporating various reinforcements, including bio-based alternatives [2], and different matrices, involving thermoplastics and thermosets, are utilized. Research delves into process steps at the composite scale, including automated tape laying, composite molding, and consolidation, aimed at minimizing defects and porosity in composite parts to maximize their mechanical properties. The quality of the fiber / matrix interface, crucial for mechanical behavior of composite parts, is greatly influenced by these defects [3].

At the mesoscopic scale of tape, where micro-voids are observable, the quality of the fiber / matrix interface remains relatively difficult to predict. Although these porosities are characterized, the mechanisms behind micro-void formation are not yet fully understood. Within the field of fiber-reinforced thermoplastic tape, the impregnation of fibers by molten polymer is driven by the capillary forces and viscous effects that occur at the mesoscale [4]. Despite this, the theory of capillary phenomena

in composite manufacturing, particularly with molten polymers, still presents theoretical gaps and experimental data remain unfitted by the existing models [5]. Adhesion phenomena at the local fiber / matrix interface are known to depend on various constituent properties, including surface energies and fiber roughness, yet questions persist regarding which parameters are critical in affecting adhesion. Additionally, the impact of temperature is crucial, as the polymer is exposed to elevated temperatures during the interface formation [5], [6]. Thus, the first objective of this study is to deeply understand the fiber / matrix adhesion phenomena depending on the properties of the fibers and the matrix as a function of temperature. This study is a part of a research project funded by ANR (ANR JCJC DUINTACOS). Another factor that must be studied is the dynamic wetting during the polymer flow on and between fibers. This phenomenon occurs with temperature depending on the properties of the constituents, the interaction between fluid and fibers during the flow at microscopic scale, and on the morphology of fibers in the yarn at the mesoscopic scale. There is, at the moment, no reported methodology in literature to study and deeply understand the fiber impregnation phenomena as a function of temperature [7]. That will be the second objective of this work, by developing reliable methods and predictive models to characterize these phenomena.

Furthermore, after wetting of fibers by molten polymer is completed, there arises a need to characterize polymer crystallization and the resulting microstructure at the local fiber / matrix interface [8]. While some experimental studies and models on polymer crystallization are emerging in literature [8], further advancements in this area, particularly concerning the fiber / polymer interface, will be pursued within the framework of the DUINTACOS project, and this will be the third objective.

Moreover, after consolidation, it is important to estimate mechanical properties induced at the interface [9]. Then, the fourth and the final objective of this project is to deeply understand the induced mechanical properties in the produced interface.

To summarize the four main objectives, the aim of the DUINTACOS project is to achieve deep understanding of interface formation in fiber reinforced thermoplastic tapes, considering high temperatures and the consequent cooling, at the microscopic and mesoscopic scales, to reduce voids and obtain high quality composite structures. A schematic drawing presenting the overall concept of the project, related to the different objectives, is shown in Figure 1.

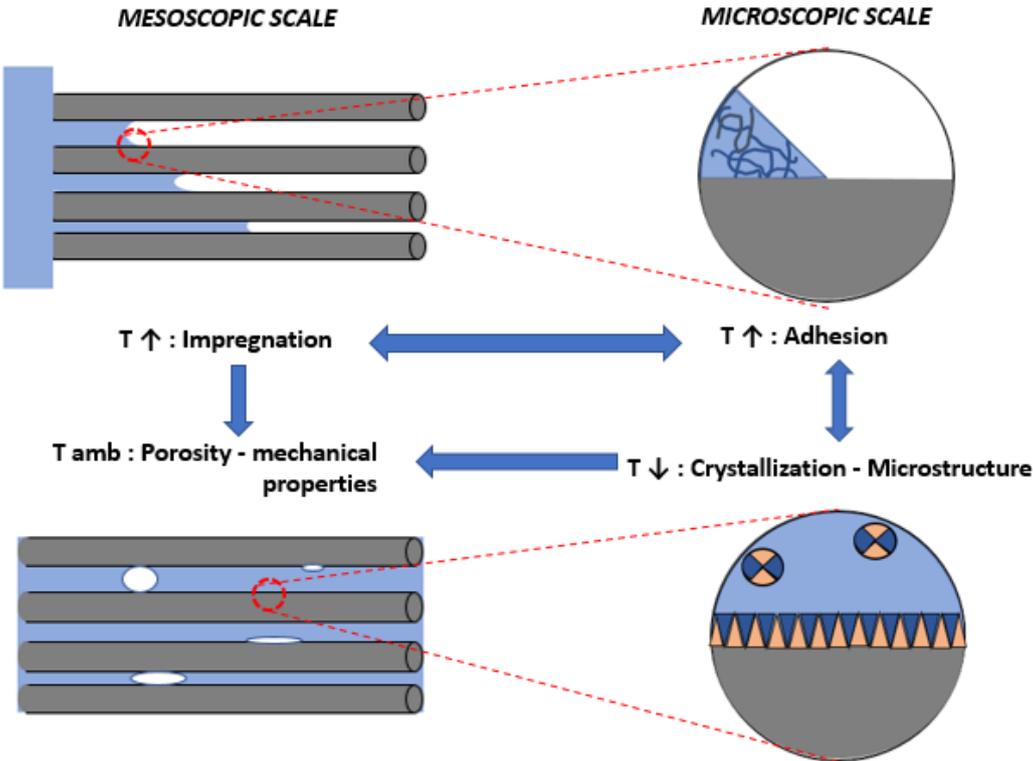


Figure 1 Schematic drawing of DUINTACOS project concept.

The present work focuses on the determination of surface tension of polymers as a function of temperature. First, a reliable and reproducible procedure on the goniometer using the pendant drop method is set, to obtain reliable and repeatable surface tension measurements at room temperature using some known liquids, before moving with the surface tension determination at elevated temperatures. Then, the obtained surface tension results will be compared with the results obtained from tensiometric tests. After that, we will be working on determining the surface tension components (polar and dispersive), then moving forward with the spontaneous and dynamic wetting on fibers.

2. Materials and Methods

2.1. Materials

The materials that are studied can be divided into two categories: test liquids and fibers. The first category concerns water, silicon oil, polyethylene glycol, n-Hexane, and diiodomethane. These liquids are used to validate experimental methods. The second category is the fibers to be tested: Carbon fiber, recycled Carbon fiber, Flax fibers (sized and unsized), and basalt fibers (sized and unsized).

2.2. Methods and Primary Results

The DUINTACOS Project started in January 2024 and is currently in its early stages. First steps are focused on determining surface tension for known liquids at room temperature to establish a robust procedure. This initial phase involves using a goniometer to determine surface tension, with subsequent validation using a tensiometer [6]. Our goal is to refine these methods for application with both known liquids and at varying temperatures, then for molten polymers.

2.2.1 Pendant Drop Analysis:

Drop shape techniques are powerful techniques in determining the surface and interfacial tension of liquids, since it requires only small amount of the tested liquids, and the results are not related to contact angles or another empirical value [10].

The setup required for the experiment is relatively simple, where it requires a syringe, a needle, a camera, and a light source [11].

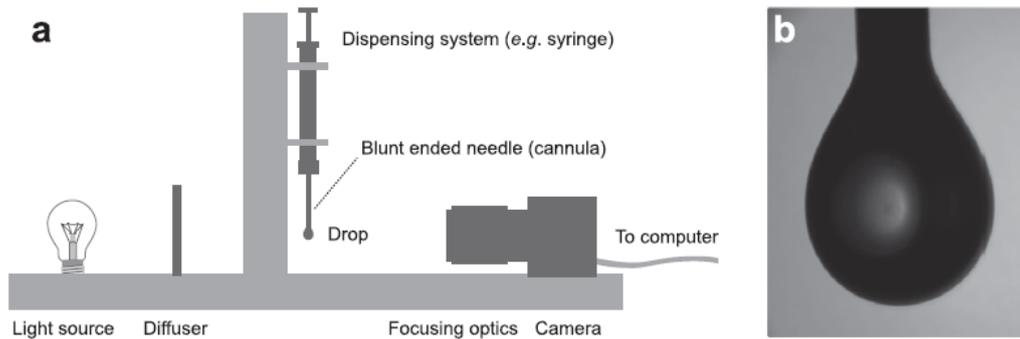


Figure 2 Schematic representation of the pendant drop setup (a) and the pendant drop (b) [11].

At equilibrium, the pendant drop obeys the Young-Laplace equation that relates the pressure difference across a liquid-fluid interface to the curvature of the interface and surface tension:

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P \equiv \Delta P_0 - \Delta \rho g z \quad (1)$$

where R_1 and R_2 are the principal radii of curvature, γ is the liquid surface tension, and $\Delta \rho g z$ is the hydrostatic pressure, ΔP is the pressure difference between the pressure inside the drop and the pressure of the surrounding medium, and ΔP_0 is the pressure difference at a reference plane that is set at the drop apex.

At the Centre des Matériaux des Mines d'Alès (C2MA), there are two setups for pendant drop testing.

The first setup is the DigiDrop from GBX, which is a relatively old setup (from the 90's), and there is a more advanced setup, the Drop Shape Analyzer DSA30 that is provided by Kruss.

Currently experiments are done at room temperature on well-known liquids such as water, polyethylene glycol (PEG 300), silicone oil, n-Hexane, and diiodomethane.

The captured images are post treated through two different software's that are OpenDrop software and the Pendant Drop plugin in the ImageJ software.

The OpenDrop software does the fitting of the detected drop contour with the theoretical model by varying a set of parameters by utilizing the Levenberg–Marquardt–Fletcher automated optimization (LMF–AO) algorithm. One of these parameters is the Bond number (B_o), that is used to calculate the surface tension of the tested liquid [11]:

$$B_o = \frac{\Delta\rho g R_0^2}{\gamma} \quad (2)$$

$\Delta\rho$ is the density difference between the tested liquid and the surrounding liquid, g is the gravity, R_0 is the radius of curvature at the drop apex.

The pendant drop plugin in ImageJ works on a similar way, but the surface tension is measured according to the obtained value of the capillary length [12]:

$$\gamma = \Delta\rho g l_c^2 \quad (3)$$

where l_c is the capillary length.

Throughout the measurements that we are performing, we are varying basically two main parameters that are the drop volume and the needle size.

According to tests using water, it has been seen that when the drop volume is small, the results are not accurate and that is because the interfacial tension dominates the gravitational effect, and as the volume increases, the accuracy of the results are increased [11]. Thus, we decided to move with other liquids as close as possible to the maximum drop volume but taking into consideration obtaining an equilibrium state.

Figure 3 shows the obtained surface tension of water at different drop volumes using a 1mm diameter needle. The maximum drop volume that this needle was able to withstand was around 18 μL . The maximum volume studied was 17.5 μL to make sure that equilibrium was obtained. At each volume, 5 droplets were formed and post treated. The average surface tension was calculated at each volume and the results were used to plot the graph shown in *Figure 3*. It was seen that when the drop volume is below 15 μL , the measured average surface tension of water is not comparable to the theoretical surface tension of water (72.67 mN/m at 22.5°C), and it was seen that the standard deviation is high. While as the drop volume ranges between 15 and 17.5 μL , the obtained results are comparable to the theoretical surface tension with minimal deviation.

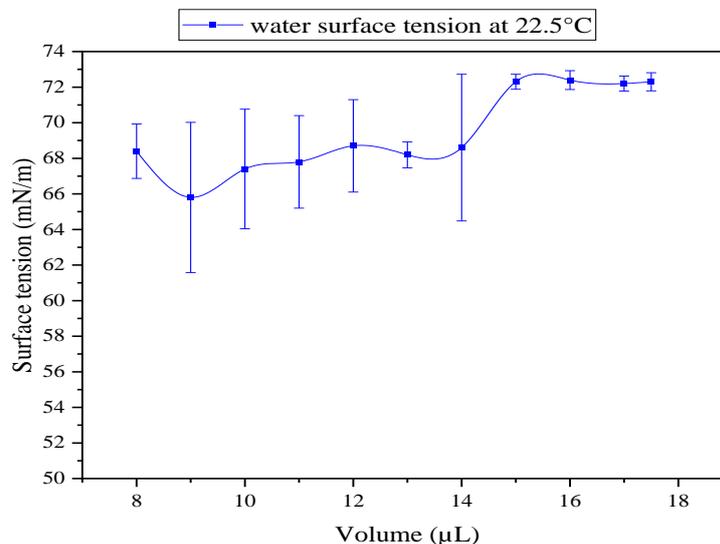


Figure 3 Experimental results of water surface tension as a function of pendant drop volume.

On the other hand, experiments have been performed with varying needle sizes, measuring the surface tension of the liquid at around the maximum volume that the needle can provide. So far, it has been seen that the needle size also had an influence on the determined results. It was seen that some needles are not optimum for some liquids, where we have seen liquid climbing effect and fast detachment of the drop with specifically small needle sizes (0.5 mm diameter needle).

The objective of these measurements at room temperature is to obtain a reliable method that would provide accurate and reproducible results, that would prepare the study with temperature and polymers. Noting that the surface tension determination depends on the density of the liquid. At elevated temperatures the sessile drop technique will be used to determine the volume of the drop, along with the weight measured using a balance, so that we can obtain the density of the liquid at a specific temperature [13]. It is important to note that the interfacial tension will also be determined following the pendant drop method, using a cuvette will be filled with a liquid with known properties and a drop of the studied liquid will be formed into the container. After that, the polar and dispersive components can be determined as explained in section 2.2.2 (equations 4 and 5).

2.2.2 Tensiometric Analysis:

A reliable method was developed in a previous work to assess the surface tension of liquids as well as their dispersive and polar components [6]. This method discussed below will be adopted for the study of molten thermoplastics, and to compare the results with the ones obtained by the pendant drop analysis. The process goes as follows in the developed method. First, Archimedes principle on Wilhelmy plate is recorded when the plate is immersed in n-hexane, which is a well-known totally dispersive liquid. Then the surface tension of the tested liquid γ_R is measured through the measurement of the meniscus weight formed between Wilhelmy's plate and the liquid. Then the interfacial tension γ_{RL} between the well-known liquid (n-hexane) and the tested liquid can be measured (Figure 4).

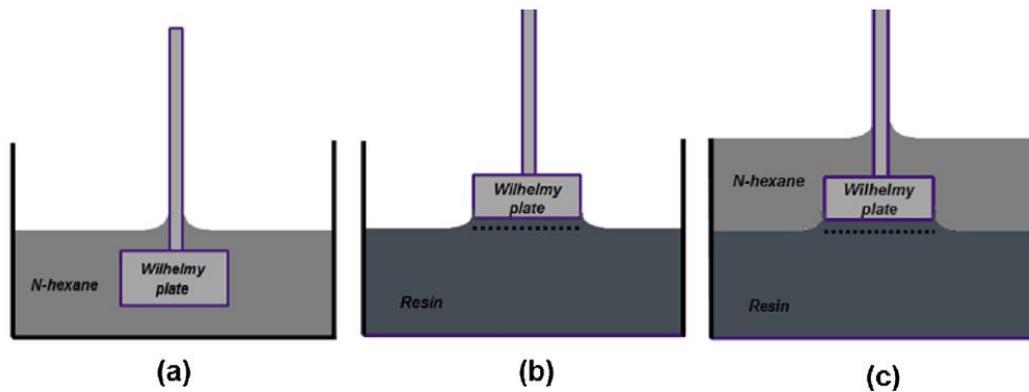


Figure 4 (a) Archimedes force measurement for n-Hexane. (b) Surface tension measurement of the tested liquid (resin). (c) Interfacial tension measurement between resin and n-hexane[6].

Finally, according to equation 4, the dispersive component (γ_R^d) of the tested liquid can be determined, and using equation 5, the polar component (γ_R^p) can be determined [6].

$$\gamma_R^d = \frac{\gamma_L^d + \gamma_R - \gamma_{RL}}{4\gamma_L^d} \quad (4)$$

$$\gamma_R = \gamma_R^d + \gamma_R^p \quad (5)$$

The idea here is to use this protocol to find the surface tension, polar and dispersive components of well-known liquids at room temperature and at higher temperatures. This protocol will be applied on both tensiometric tests and pendant drop tests. It will be beneficial to obtain results from two different setups, where a comparison will be made to prove repeatability and accuracy of the measurements. On the other hand, when moving with molten thermoplastics, there are some limitations with the tensiometric tests.

Indeed, a maximum temperature that could be reached by the tensiometer is an obstacle since it would not be sufficient to melt the tested thermoplastic polymer. Another limitation is the relatively big amount of molten thermoplastic required to perform the test, which requires a long waiting time for the thermoplastic polymer to melt completely.

The aim of this protocol is to be able to study thermoplastic polymers at elevated temperatures and obtain accurate surface tension measurements as well as the polar and dispersive components. The effect of temperature on the surface tension and components of the studied thermoplastic polymer will thus be assessed, which is for now not reported in literature. Once these data will be obtained, this will ease the way to study the dynamic wetting and surface energy of fibers, to assess the impregnation during tape manufacturing and adhesion phenomena of the generated fiber-matrix interface.

3. Conclusions

To conclude, in this paper, the DUINTACOS project was introduced. As a primary result of the pendant drop tests, it was seen that the volume of the drop plays a major role in the accuracy of the measured value of the surface tension. It was proved in *Figure 3* that the accuracy of the surface tension is the best around the maximum volume that the used needle can withstand.

In addition, pendant drop and tensiometric methods were discussed in detail, to determine at the first step the surface tension of known liquids at room temperature and at elevated temperatures. Then we will move on to interfacial tension characterization to determine the polar and dispersive components of the tested liquids. A comparison of the obtained results between the two different setups used will be made to ensure accuracy and repeatability of the adopted protocol. Finally, this protocol will be applied to thermoplastic polymers used for tapes, to determine their surface tension and components at elevated temperatures, that are essential, coupled to fiber surface energy, to study the dynamic wetting on fibers, and deeply understand the impregnation and the adhesion phenomena between the fiber and the matrix.

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