

## The role of bondline thickness on mechanical properties of bio-based polyurethane

Paulo Henrique Lixandrão Fernando<sup>1</sup>, Cleber Lucius da Costa<sup>1</sup>,  
Kelly Cristina de Lira Lixandrão<sup>1</sup>, Demetrio Jackson dos Santos<sup>1</sup>

<sup>1</sup>Engineering, Modeling and Applied Social Sciences Center, ABC Federal University (UFABC), Santo André, São Paulo, Brazil.

e-mail: demetrio.santos@ufabc.edu.br

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### ABSTRACT

Bio-based adhesives have been largely applied on several applications in many industrial areas, including automotive and laminated food packaging. Polyurethanes (PU) occupy a leading position among the most used bio-based polymers due to their large range of properties and application versatility. Recent works reported that PU obtained from castor oil and Kraft lignin as polyol developed high mechanical properties and blend miscibility. In spite of its well-known mechanical behavior, additional investigations might support the application of this bio-based PU as adhesive. In this context, our work investigated the effect of adhesive (bondline) thickness variation (size effect) on shear modulus of a bio-based polyurethane under finite deformation and related shear stress distribution. Polyurethane was obtained using a blend of Kraft lignin and castor oil as polyol (20 wt% of Kraft lignin) and applied as adhesive for metal bonding, in which adhesive thickness changed from tens of micrometers up to 220 micrometers. Steel plates were used as substrates and adhesive shear modulus was evaluated using substrates with large thickness (4.76 mm), which minimized the effect of substrate deformation on shear modulus measurement. Single lap joints were uniaxial loaded in order to generate the shear stress on adhesive bondline. Additionally, shear modulus changes were simulated by finite element analysis (FEA), analytical models and compared to experimental data. Results revealed the size effect and pointed to high shear modulus of the PU bondline, justifying its use as an adhesive for structural applications.

**Keywords:** bio-based polyurethane, Kraft lignin, finite element analysis, adhesive.

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### 1. INTRODUCTION

The dependence of adhesive shear modulus ( $G$ ) on bondline thickness, known as size effect, was extensively investigated in the last decade [1,4]. Authors demonstrated that changes of adhesive thickness might affect shear modulus, as a consequence of metallic substrate influence on polymeric structure and properties. In few words, thinner adhesive films are strongly affected by the interface with the metallic surface, in comparison to thicker bondlines for which bulk properties are predominant. Nevertheless, shear stress distribution is also a significant property of adhesively bonded joints subject to shear and combined loadings [5,6].

To the best of our knowledge, the size effect of only isotropic epoxy and polyurethane adhesives were investigated concerning size effect. Shear or effective modulus of these adhesives was usually stabilized for bondline thickness around 200  $\mu\text{m}$  and thicker. In this work we investigated the size effect up 220  $\mu\text{m}$  thickness and shear stress distribution of a bio-based polyurethane adhesive, in which castor oil and Kraft lignin were used as polyol. Kraft lignin is a natural polymer with a complex phenolic structure. It is available at industrial scale as a byproduct of pulp and paper manufacturing [7,9]. An increasing interest in the development of lignin based products has emerged over the last years, triggering its use as a raw material for several polymer products [10,13]. Notwithstanding, the powder state of unmodified lignin restricts its application, due to its inherent poor dispersion in many polymer matrices, including polyurethane [14,15].

The purpose of this work was to investigate if lignin can eliminate or hidden the size effect of lignin-containing polyurethanes. Mechanical tests for size effect investigation were carried out under shear loading, which requires an additional elucidation of shear stress distribution in the adhesive layer [16]. Furthermore, shear stress concentration at edges of single lap joints is a well-known behavior and strongly depends on the following parameters: metallic substrate dimensions and mechanical properties, adhesive properties, bondline

thickness and overlap length. Once size effect was investigated and shear stress distribution was elucidated, finite element method was applied to simulate the mechanical behavior of the adhesive layer.

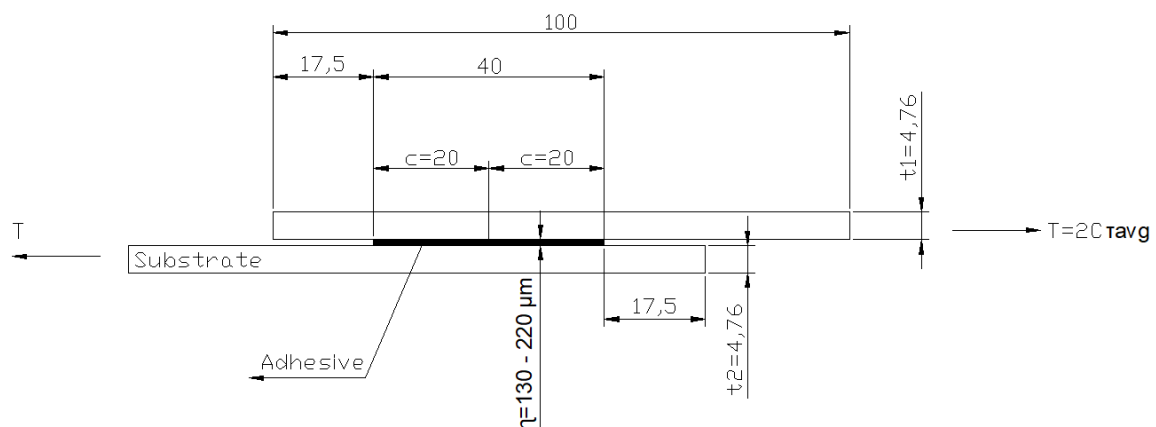
## 2. MATERIALS AND METHODS

### 2.1 Materials

Polyol was obtained by mixing castor oil and Kraft lignin. Kraft lignin was kindly supplied by Suzano Papel e Celulose (Suzano, Brazil), as a byproduct of pulp and paper manufacturing, with pH 8.5, brown color, 255 mg KOH.g<sup>-1</sup> of hydroxyl content and 2.1% of ash content. Castor oil was acquired from A. Azevedo (São Paulo, Brazil) with hydroxyl index of 169 mg KOH.g<sup>-1</sup> and 0.95 mg KOH.g<sup>-1</sup> of acid index. Diphenylmethane diisocyanate (MDI) was purchased from Kalium Chemical (São Paulo, Brazil) for polyurethane synthesis, with NCO content of 31%.

### 2.2 Single lap joints

Steel (SAE 1010) laps with dimensions of 4.76 x 25.4 x 100 mm and Poisson ratio of 0.30 were used as substrates [17,18]. Steel surfaces were mechanically treated in order to control and minimize roughness. Single lap specimens are presented in Figure 1. They were bonded using a polyurethane adhesive to form the adhesively bonded lap shear joint. A blend of Kraft lignin (20 wt%) and castor oil was used as polyol. PU was obtained by mixing the lignin-containing polyol with MDI (molar ratio NCO:OH of 1.2:1). The adhesive was applied on both laps. Parts were put together and kept under constant pressure (grips), generating a bonded length (overlap) of 40 mm. Next, the lap joints were cured for seven days at room temperature. PTFE films were used to control the bondline thickness (130 µm up to 220 µm), whose values are shown in Table 1. Optical microscopy analysis was carried out to measure the adhesive layer thicknesses, after curing.



**Figure 1:** Geometry and materials parameters of the single-lap joint.

**Table 1:** Thickness of adhesive layer (bondline)

A1-B1	A2-B2	A3-B3	A4-B4	A5-B5
130 µm	150 µm	160 µm	180 µm	220 µm

### 2.3 Confocal Laser Scanning Microscopy

Confocal laser scanning microscopy (CLSM) was employed (Olympus LEXT OLS4100) to examine surface topography and determine its roughness. Ten lines with length of 1280 µm were measured on three specimens. Afterwards, the average surface roughness (Ra) was calculated according to ISO 4287/2002 [19].

### 2.4 Single lap shear test

Single lap shear specimens (five specimens) were tested according to ASTM D 1002-99 [20] using an Instron Universal testing machine, model 3369, equipped with a load cell of 50 kN and crosshead speed of 1

$\text{mm}\cdot\text{min}^{-1}$ . High thickness of the steel substrates ensured infinitely higher shear modulus when compared to adhesive shear modulus. This condition allows neglecting substrate deformation under shear and to consider exclusive adhesive deformation.

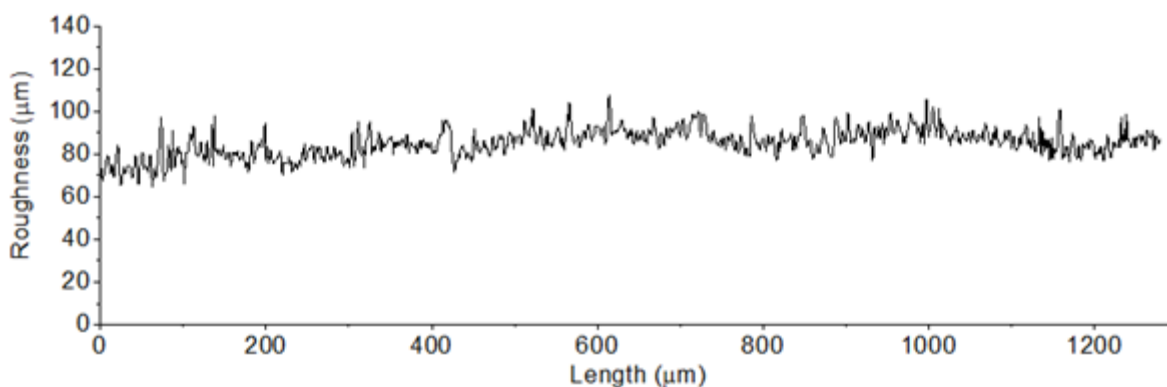
### 2.5 Simulation of the adhesive layer behavior

Firstly, adhesive behavior (under shear loading) was simulated with a ANSYS finite element software [21]. The adhesive layer was considered isotropic and modeled using an 8-node mesh, with three degrees of freedom (DOF) and 30184 elements. Secondly, traditional models (Volkersen, Gosland and Reissner) were applied for comparison with FEM and experimental results [22, 23].

## 3. RESULTS AND DISCUSSION

### 3.1 Confocal Laser Scanning Microscopy

Figure 2 shows a roughness profile of the treated steel surface obtained by CLSM. An average roughness of  $2.987\ \mu\text{m}$  ( $R_a$ ) was determined. This value cannot be taken as significant, since the thinnest adhesive layer presented  $130\ \mu\text{m}$  of thickness. Thus, the substrate roughness is too low in comparison to the adhesive layer thickness. Based on the low roughness and homogeneous topography, we can assume that irregularities of metallic substrate do not affect the results of the mechanical tests.

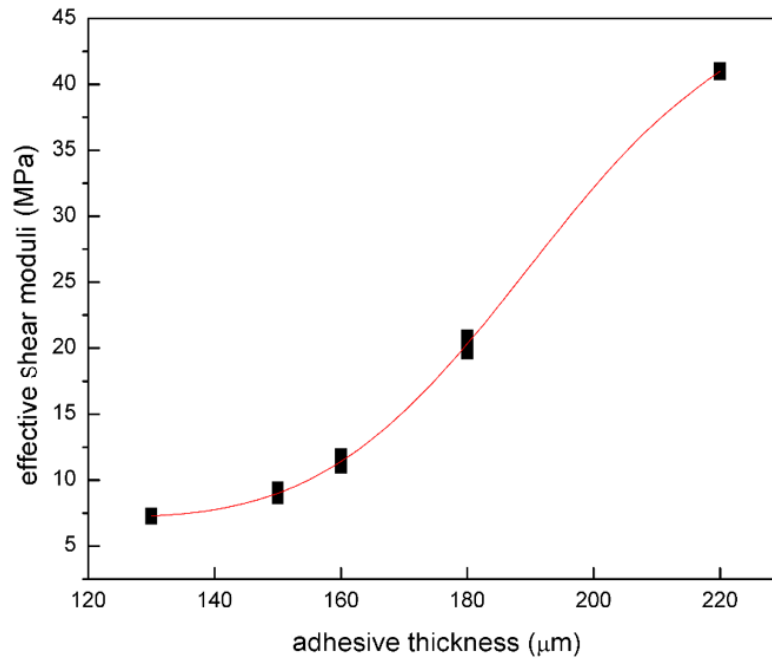


**Figure 2:** Representative roughness profile of the steel surface (adherent).

### 3.2 Experimental results

As previously mentioned, size effect refers to effective modulus changes (shear modulus) as a consequence of varying adhesive layer thickness [1]. Assuming shear modulus as a material property, it could be contradictory to consider it as thickness dependent. By contrast, the influence of metallic substrates on chemical state of polyurethanes and epoxies is established. It is well-known that native metal surfaces affect the chemical states of the adhesive in the region close to substrate/adhesive interphase [24, 25]. Based on this scenario, it is quite acceptable to propose a chemical state gradient of the adhesive layer as a function of the proximity to the steel surface. Likewise, thicker adhesive layers tend to be less affected by this chemical state gradient (adhesive).

Figure 3 presents the shear modulus for each tested condition of adhesive layer thickness. Effective moduli (shear moduli) were obtained from shear stress x strain curves at 0.5% strain. Thinnest adhesive layer presented the lowest value of shear modulus. Increased adhesive thickness lead to increasing of shear modulus, in accordance with reported results by JOHLITZ [1]. Our results revealed, therefore, the size effect for this lignin-containing polyurethane. Additionally, all samples presented cohesive failure.



**Figure 3:** Effective modulus as function of bondline thickness.

Although shear modulus values were obtained at 0.5% strain under finite deformation to investigate the size effect, single lap shear experiments were carried out until specimen rupture. Average shear stresses are reported in Table 2. Since the shear stress distribution may not be constant over the entire overlap length, the measured value (experimental) represents in fact the average shear stress (the average strength of the adhesively bonded joints). The maximum shear stress followed the same trend observed for the shear modulus, increasing with the bondline thickness.

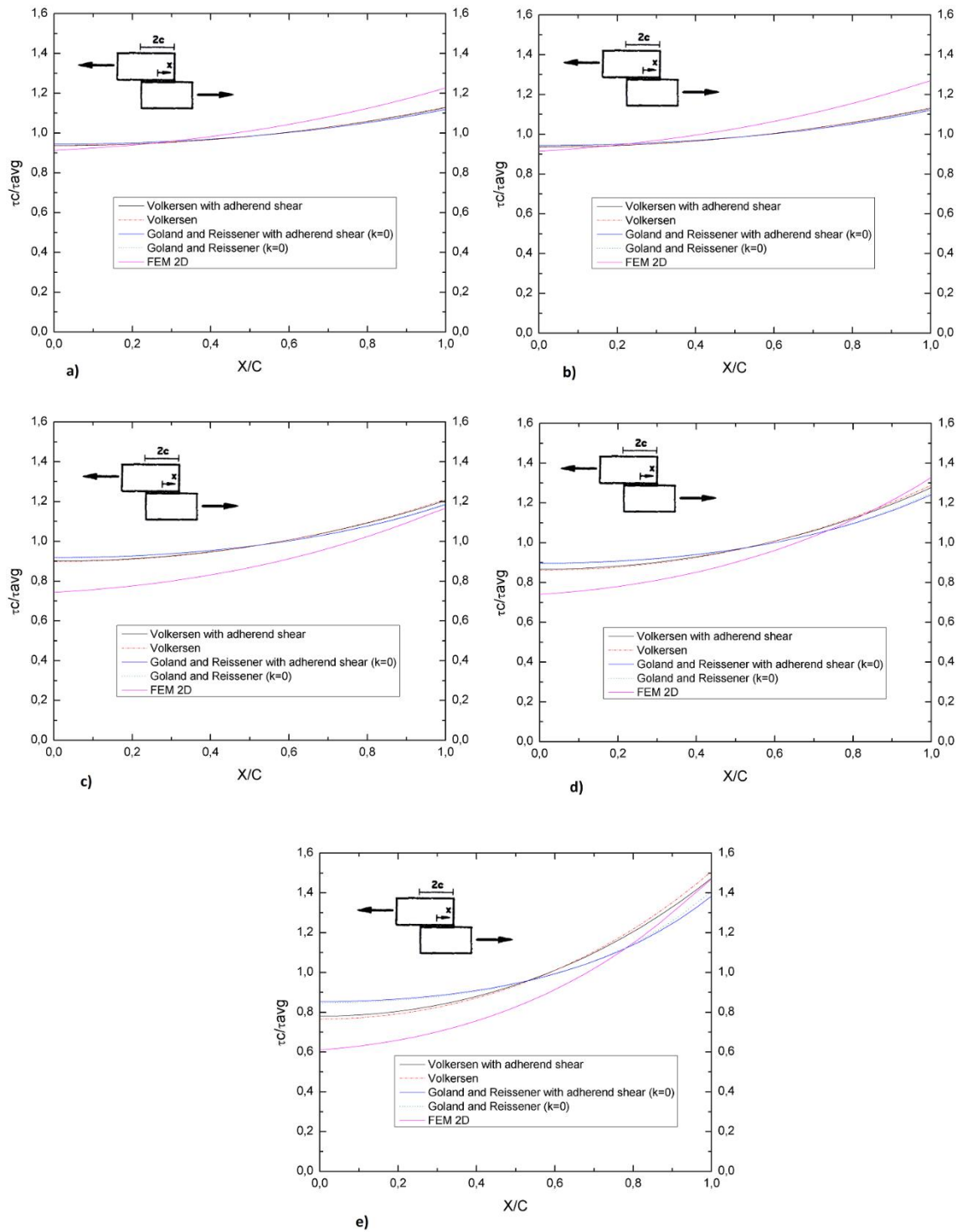
**Table 2:** Measured maximum (average) shear stress.

Specimen	A1-B1	A2-B2	A3-B3	A4-B4	A5-B5
Thickness (μm)	130	150	160	180	220
$\tau_{avg}$ (MPa)	$(3.32 \pm 0.45)$	$(3.47 \pm 0.46)$	$(3.68 \pm 0.59)$	$(4.61 \pm 0.43)$	$(4.73 \pm 0.40)$

### 3.3 Simulated mechanical behavior

Figure 4 shows simulated shear stress distribution for adhesive layers, based on several models: 2D FEM, Volkersen and Goland-Reissner models. Measured shear stress and shear modulus were used as input parameters. The Poisson's ratio of the adhesive was assumed as 0.37 [26]. Volkersen and Goland-Reissner models consider the following parameters for stress distribution determination: adhesive and substrate dimensions, mechanical properties. These models are described in details elsewhere [21]. Results presented normalized shear stress as function of overlap length, for which  $X/C=0$  is the middle point of the total overlap (40 mm). Likewise,  $X/C= 1.0$  represents the edges of the bonded length. Moreover, normalized shear stress was obtained as a ratio of average shear stress ( $\tau_{avg}$ ) and local shear stress ( $\tau_c$ ).

Volkersen and Goland-Reissner simulations were carried out in two conditions: i. Considering the shear modulus ( $G_a$ ) as infinitely high, i.e., substrate is not affected by the applied shear loading (constant  $k=1$ ) and; ii. Assuming the engineering adherent shear modulus ( $k=0$ ), where  $k$  is a model parameter related to the substrate shear modulus. In this context, Figure 4a-b revealed a complete convergence between simulations using Volkersen and Goland-Reissner models. In contrast, FEM simulation suggests a higher shear stress concentration at overlap ends in comparison to analytical models.



**Figure 4:** Normalized adhesive shear stress distributions of thick-adherend single-lap joint predicted by 1-D bar model (Volkersen), 1-D beam model (Goland and Reissner), the present 1-D bar model (Volkersen with adherend shear), the present 1-D beam model (Goland and Reissner with adherend shear) and 3-D finite element model (FEM). a) 130  $\mu\text{m}$ , b) 150  $\mu\text{m}$ , c) 160  $\mu\text{m}$ , d) 180  $\mu\text{m}$ , and e) 220  $\mu\text{m}$ .

Simulations of adhesive layers with thickness of 160  $\mu\text{m}$  and higher (Figure 4 c-e) developed similar levels of local shear stress at overlap edges. Mechanical behavior of thicker adhesive layers is governed by bulk properties, as the thickness of affected bondline (interphase with metal) is insignificant in comparison with the total thickness of the adhesive. In this sense, simulations considering material isotropy seem to be more effective for thicker adhesive layers. The mechanical behavior of adhesively bonded joint was simulated. Simulations based on analytical models were in agreement, considering or even neglecting substrate de-

formation, indicating that substrates (steel plates with high thickness) provided infinitely high shear modulus when compared to adhesive shear modulus.

#### 4. CONCLUSIONS

Size effect was verified for lignin-containing polyurethane adhesive, in spite of its multiphase composition, since shear modulus of lignin-containing was affected by the thickness of the adhesive layer. Thicker adhesive layers presented higher average shear strength. Simulated results converge with experimental ones for thicker adhesive layers, for which bulk properties are predominant. Thinner adhesive layers are strongly affected by the steel surface and are not well represented by isotropic continuum simulations. Results can support further investigations and technological applications of lignin-containing adhesives.

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## ORCID

Paulo Henrique Lixandrão Fernando <https://orcid.org/0000-0002-2460-5878>

Cleber Lucius da Costa <https://orcid.org/0000-0002-9349-0541>

Kelly Cristina de Lira Lixandrão <https://orcid.org/0000-0003-1969-7402>

Demetrio Jackson dos Santos <https://orcid.org/0000-0002-4707-2285>