Flexible composites based on thermosetting resins and lignocellulosic fibers

Compósitos flexíveis a base de resinas termorrígidas e fibras lignocelulósicas

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ABSTRACT
Flexible thermost resin composites have a wide range of applications, particularly in civil construction, interior design and the automotive industry. The main polymer matrices used for lignocellulosic fiber-based composites are epoxy resin, unsaturated polyester, polybenzoxazine and polyurethane. Many of these resins are synthesized from vegetable oils, whose long chain makes polymers flexible, with the most widely used derived from soybean oil. The main tests applied to demonstrate the flexibility of the composites and resins were dynamic mechanical analysis, thermogravimetry and flexural strength testing.

Keywords: flexibility, thermost, composite, lignocellulosic fiber.

RESUMO
Os compósitos de polímeros termorrígidos com características flexíveis apresentam ampla aplicabilidade, principalmente na área de construção civil, design de interiores e na indústria automobilística. As principais matrizes poliméricas encontradas para tais
compósitos com fibras lignocelulósicas são a resina epoxídica, o poliéster insaturado, a polibenzenoxazina e o poliuretano. Muitas destas resinas são sintetizadas a partir de óleos vegetais, cuja cadeia longa confere flexibilidade ao polímero. Entre tais resinas, a mais comumente utilizada é a resina deriva do óleo de soja. Os principais ensaios utilizados para demonstrar a propriedade flexível dos compósitos e das resinas foram: análise dinâmico-mecânica, termogravimetria e o ensaio de resistência à flexão.

**Palavras chaves:** flexibilidade, termorrígido, compósito, fibra lignocelulósica.

### 1 INTRODUCTION

Flexibility is a physical property commonly present in a number of materials, primarily in plastics and elastomers. It is directly related to the mechanical properties of stress-strain and the molecular characteristics of each material (MANO, 1991).

Among the mechanical properties intrinsically correlated with flexibility are the modulus of elasticity, flexural strength and impact resistance. Toughness is also an interesting trait for flexible materials (MANO, 1991).

Although many thermosetting polymers are known for their poor flexibility (proportional to their degree of reticulation, the higher it is, the lower the flexibility), some may exhibit greater flexibility than their traditional counterparts, depending on the components used for synthesis and curing conditions (MA et al., 2016).

According to the literature, a number of changes have been made to the structure of the main polymer chain to provide thermosetting resins with more flexibility. This is achieved by adding epoxy groups, acrylate or malleate, decreasing the density of reticulations; and/or adding long alkyl chains to the polymer chain (MA et al., 2016; MORENO et. al., 2016; LIU et al., 2016).

Polymer composites are formed by two phases: one termed the matrix phase, whose primary function is to distribute the load through the composite, and the other, the dispersed or reinforcing (filler) phase, responsible for their resistance to the loading forces. For some applications, a thermoset matrix must be used because of the technical requirements, such as greater resistance to temperature, mechanical strength and lower flammability (MANO, 1991; BENINI, 2011; NETO and PARDINI, 2016).

Moreover, some composites make it possible to obtain more rigid or more flexible products, which will supply different niche markets. The flexibility of a composite is associated with the characteristics of its polymer matrix and filler and is a desirable
property in the areas of interior design, civil construction and means of transport, as well as in some airplane and automobile parts (BENINI, 2011; NETO and PARDINI, 2016).

Flexible thermoset polymers can bend without cracking, and lignocellulosic fibers display a high modulus of elasticity. Thermosetting composites can be ductile and deformable after reticulation in ambient temperature, combining processibility and high performance (MANO, 1991; HAMMED et al., 2015).

In general, the most widely studied flexible polymer matrices are polyester resin, epoxy resin, polybenzoxazine and polyurethane. Renewable resins that stand out are epoxy and polyurethane resins, such as acrylated and epoxidized soybean oil (AESO) (LIU et al., 2016; LIU et al., 2019; FEI et al., 2018; TEMMINK et al., 2018) and polyurethane resin derived from vegetable oils: castor oil (MERLINI et al., 2011) and soybean oil (GLOWINSKA et al., 2017).

In relation to flexible epoxy resin, specifically epoxidized and acrylated soybean oil and its derivatives, the main authors who studied them were Wendi Liu, Tianshun Xie, Renhui Qiu and Ming-en Fei from Faculty of Materials Engineering at University of Agriculture and Forestry in China (LIU et al., 2016; LIU et al., 2018; LIU et al., 2019; FEI et al., 2018).

While flexible composites with polyurethane resins derived from vegetable oils have been studied in Brazil and Poland. Castor oil-derived polyurethane was studied by Claudia Merlini, Valdir Soldi and Guilherme Mariz de Oliveira Barra from Federal University of Santa Catarina (MERLINI et al., 2011). And soy oil-derived polyurethane was studied by Ewa Glowinska, Janusz Datta and Paulina Parcheta-Szwindowska of Gdansk University of Technology (GLOWINSKA et al., 2017).

The lignocellulosic fillers found in flexible thermosetting composites were bamboo fiber (FEI et al., 2018), hemp fiber (LIU et al., 2015), jeans residues (TEMMINK et al., 2018), cellulose nanocrystals (MORENO et al., 2016) and sisal fiber (GLOWINSKA et al., 2017), considering the period in which the bibliographic search was conducted.

2 EXPERIMENTAL

A bibliographic search was carried out of articles published between 2010 and 2020 on thermosetting resin-based flexible composites to determine their main characteristics, as well as thermal and mechanical properties. Greater attention was paid
to the polymer matrices obtained from the reaction with vegetable oils that may result in more flexible and more renewable composites.

Despite also being flexible thermosetting polymers, elastomers were not included in the discussion. This bibliographic search was conducted on Science Direct and Google Scholar websites. The main keywords used in the bibliographic research were: “flexible thermosetting composite”, “flexible thermosetting polymer” and “flexible thermosetting lignocellulosic fiber composite”.

3 RESULTS AND DISCUSSION

Among the flexible epoxy resins found in the published articles, AESO resin and its modified derived resins stand out: isosorbide methacrylated acrilated epoxidized soybean oil (IM-AESO) resin from a mixture of AESO resin and isosorbide methacrylate (IM), and maleinated acrilated epoxidized soybean oil resin (MA-MAESO), from a mixture of AESO resin and anhydride methacrylate (MAA) (LIU et al., 2016; LIU et. al., 2019; FEI et. al., 2018; TEMMINK et. al., 2018).

The flexural modulus values were 1546 MPa for IM-MAESO, 1373 MPa for IM-AESO and 62 MPa for AESO. The reticulation densities were $83.3 \times 10^{-3}$ mol.m$^{-3}$, $75.2 \times 10^{-3}$ mol.m$^{-3}$ and $16 \times 10^{-3}$ mol.m$^{-3}$, respectively. The lower the reticulation density, the higher the resin flexibility (LIU et al., 2016).

Composites of these resins were made with two lignocellulosic fibers (bamboo and hemp fibers) at a resin:fiber ratio of 1:1, in order to compare their effect on the flexibility of a material. In general, all the composites with bamboo fiber were more flexible than those with hemp fiber (LIU et. al., 2019).

As with the composites produced using AESO resin, they also exhibited high flexibility. The flexural modulus was 5.5GPa for the bamboo resin composite and AESO resin, and 9.9 GPa for the bamboo fiber composite with MI-MAESO resin, the least flexible (LIU et. al., 2019).

Among the polyester resins, unsaturated polyester resins (UPE) stand out. These included resins synthesized with N-vinyl-2-pyrrolidone (NVP-UPE) and tri(ethylene glycol divinyl ether (TDE-UPE). Composites were produced using these resins as matrix and hemp fiber as filler (LIU et al., 2015).

The composite produced with TDE-UPE resin showed greater flexibility (flexural modulus of 7GPa, for the composite with 40% resin, and 7.5 GPa for the composite with 50% resin), when compared to composites whose matrix was the NVP-UPE resin. The
greater flexibility is due to the fact that the chemical structure of TDE-UPE is an aliphatic chain, which provides greater mobility to the polymer chain and consequently, to the composite (LIU et al., 2015).

Among the polybenzoxazine class of resins, structural changes in the central portion of the chain make the resin flexible, such as multifunctional diamine-based polybenzoxazines. The higher the number of amine substituents in the central portion of the chain, the greater the flexibility of the resin due to the decline in reticulation density (RIMDUSIT et al., 2013).

Composites of bisphenol A-aniline based benzoxazine with hemp fibers treated with NaOH and cured with 25% v/v THF content promoted oxazine ring opening at lower curing temperatures and improved adhesion between fiber and matrix, showing an increase on the flexural modulus by 1.3 GPa. The highest flexural modulus found was for the composite with the ratio of 80:20 (v/v) benzoxazine based on bisphenol A-aniline (BA-a) with hemp fiber (5.5 GPa) (DAYO et al., 2017).

Disregarding foams and elastomers, which are known to be flexible, polyurethane resins containing vegetable oils show greater flexibility (SILVA et al., 2019; MERLINI, et al., 2011; GLOWINSKA et al., 2017; ATIGAH et al., 2017; MILEO et al., 2010; MILEO et al., 2011).

Polyurethane composites derived from castor oil and short fibers from the trunk of the banana plant displayed modulus of elasticity of 14 MPa and 44 MPa, respectively, for composites with 5 and 15% fiber, respectively (MERLINI et al., 2011).

Another example is polyurethane composites prepared from the dispersion of soybean oil and ethylene glycol in 5% and 15% by mass of sisal fiber. Composites were obtained with untreated fiber and with silane treated fiber (MILEO et al., 2010).

The results of dynamic-mechanical analysis (DMA) tests allowed to correlate the physical property of flexibility with the glass transition temperature (Tg), from the analysis of the Tan delta curve. The highest value of glass passage temperature (-36°C) was found in the composite with 5% by mass of untreated sisal fiber. While the lowest glass transition value (-42°C) was found for the composite with 15% by mass of untreated sisal fiber (MILEO et al., 2010).

Table 1 shows the flexural modulus and modulus of elasticity values of the most flexible composites found in the bibliographic search for this study.
Table 1. Properties of thermosetting resin composites with lignocellulosic fillers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Composite and composition (m/m)</th>
<th>Flexural modulus (GPa)</th>
<th>Modulus of elasticity (MPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin</td>
<td>AESO/ Bamboo fiber: 1:1</td>
<td>5.5</td>
<td>-</td>
<td>(LIU et al., 2019)</td>
</tr>
<tr>
<td>Polyester</td>
<td>TDE-UPE/hemp fiber:2:3</td>
<td>7.0</td>
<td>-</td>
<td>(LIU et al., 2015)</td>
</tr>
<tr>
<td>Polybenzoxazine</td>
<td>Bisphenol A/ Hemp fiber: 80:20*</td>
<td>5.5</td>
<td>-</td>
<td>(DAYO et al., 2017)</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>PU derived from castor oil/short banana fiber 85:15</td>
<td>-</td>
<td>14</td>
<td>(MERLINI et al., 2011)</td>
</tr>
</tbody>
</table>

* Percentage by volume (v/v)

The composite formed by bisphenol A and hemp fiber shows greater flexibility, since it exhibits a low flexural modulus. However, most of the articles on thermosetting resin composites and lignocellulosic load involve epoxy resin, especially epoxidated and acrylated soybean oil resin and polyurethane resins. The most widely used lignocellulosic fibers reported in articles for the formation of these composites are bamboo and hemp fiber.

Flexible thermoset composites were also found, but without lignocellulosic fillers. These include epoxy resin with graphene (LI et al., 2021), barium oxide glass powder and polyhedral oligomeric silsesquioxanes (POSS) (WU et al., 2010).

4 CONCLUSIONS

The most widely studied thermosetting resins in flexible thermoset composites observed in the bibliographic review conducted between 2010 and 2020 were polyurethane resin (5 articles) and epoxy resin (5 articles). Fewer articles on flexible composites were found for polybenzoxazine class resins (2 articles) and unsaturated polyester (1 article). This review demonstrates the potential of these resin classes for use in composites with lignocellulosic fillers to provide flexibility and toughness.

These composites exhibit unique properties and a wide range of applications, such as in automobile parts and interior design, in addition to adding value to agribusiness waste, which would otherwise be discarded. Furthermore, it can be observed that most of such flexible composites are produced from bioresins and lignocellulosic materials, which make them more sustainable composites and help to protect and (or) reduce negative impacts on the environment.
REFERENCES


