Effect of different types of electrospun polyamide 6 nanofibres on the mechanical properties of a carbon fibre/epoxy composites

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• Fibre reinforced epoxy resin composites are widely used in industry, owing to their high strength and stiffness at low weight, and their good corrosion-resistance and fatigue properties.

Fibre reinforced epoxy resin composites:
- Poor impact resistance
- Low fracture toughness
- Poor delamination resistance

Reduction of the resistance and stiffness:
- Most frequent failure mode due to its laminar nature and the fragility of the resins.
- Failure of the structure.

Increase the resistance to delamination:
- Modifying the matrix
  - Thermoplastic materials
  - Nanoparticles
  - Carbonaceous structures
- Interlaminar reinforcement
  - Thermoplastic materials
Electrospun thermoplastic nanofibres veils

Properties
- Great surface/volume ratio
- High porosity
- Low area density
- Adjustable pore size
- Nanoscale fiber diameter
- High mechanical resistance
- High permeability

Advantages
- Thin veils → Their presence do not affect the thickness and weight.
- No need to disperse → No viscosity increase or a non-homogeneous dispersion
- High porosity → not impede the flow of resin

1. INTRODUCTION

Promising technique to toughen laminated composites without deteriorating the mechanical properties

2. OBJECTIVE

The present work studies the effect of the incorporation of electrospun polyamide 6 nanofibre veils coming from two different type of pellets, in the final mechanical properties of carbon fibre epoxy composites with the objective to study the influence of the PA6 mechanical properties and nature in composite material.
3. EXPERIMENTAL PART

Materials

Matrix_Diglycidyl ether of bisphenol A (DGEBA)

Curing agent_4,4’-diaminodiphenylmethane (DDM)

Carbon fibre fabric HT3k

PA6 Ultramid B24 N 03

PA6 Badamid B70

Textile sector

Industrial sector
**3. EXPERIMENTAL PART**

**PA6 nanofibre veils preparation**

- 12 wt% of both types of PA 6 pellets were dissolved in the mixture 2:1 acetic acid:formic acid by stirring during 2 hours at 80ºC.
- The nanofibres were produced using a multijet electrospinning setup Nanospider™, using a high volume spinning tub.
- The solution is poured into the feed unit and a cylindrical electrode formed by six wires is placed in the middle of the solution tank. The upward part has a second wire electrode, which has the opposite charge. The electrical field between the electrodes overcomes the surface tension of the polymer solution, forming thousands of jets than becomes fibres when the solvent is evaporated and they are deposed in the substrate.
PA6 nanofibrous veils characterization

<table>
<thead>
<tr>
<th>System</th>
<th>Fibre diameter (nm)</th>
<th>Areal weight density (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6 Ultramid</td>
<td>60-100</td>
<td>1.94</td>
</tr>
<tr>
<td>PA6 Badamid</td>
<td>60-130</td>
<td>2.23</td>
</tr>
</tbody>
</table>

4. RESULTS AND DISCUSSION

FTIR

TGA

No excess of solvent due to the electrospinning process
PA6 nanofibrous veils characterization

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_f$ (°C)</th>
<th>$\Delta H_f$ (J/g)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultramid pellets</td>
<td>225,1</td>
<td>107,1</td>
<td>46,5</td>
</tr>
<tr>
<td><strong>Ultramid veil</strong></td>
<td>224,3</td>
<td>61,2</td>
<td>26,6</td>
</tr>
<tr>
<td>Badamid pellets</td>
<td>224,1</td>
<td>95,4</td>
<td>41,5</td>
</tr>
<tr>
<td><strong>Badamid veil</strong></td>
<td>225,0</td>
<td>87,8</td>
<td>38,2</td>
</tr>
</tbody>
</table>

% Cristallinity pellets > Veils

% Cristallinity PA6 Badamid > PA6 Ultramid

Thermal characterization (DSC)

4. RESULTS AND DISCUSSION
Composites manufacturing

Two carbon fibre plies interleaved with stand-alone nanofibrous veils were prepared.

For the fracture test (mode I, mode II), composites with 14 layer of carbon fibre and an interlaminar veil in the central axis have been developed also using vacuum infusion technique.
### 4. RESULTS AND DISCUSSION

**Composites characterization**

**Flexure test**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{\text{max}}$ (MPa)</th>
<th>$\Delta \sigma_{\text{max}}$ (%)</th>
<th>$\delta_{\text{max}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>375.5±33.2</td>
<td>2.2±0.2</td>
<td></td>
</tr>
<tr>
<td>1 veil PA6 Ultramid</td>
<td>449.5±10.8</td>
<td>19.7</td>
<td>2.1±0.0</td>
</tr>
<tr>
<td>3 veil PA6 Ultramid</td>
<td>415.4±23.8</td>
<td>10.6</td>
<td>2.1±0.2</td>
</tr>
<tr>
<td>1 veil PA6 Badamid</td>
<td>534.6±28.9</td>
<td>42.4</td>
<td>2.3±0.0</td>
</tr>
<tr>
<td>3 veil PA6 Badamid</td>
<td>502.3±48.5</td>
<td>33.8</td>
<td>2.1±0.1</td>
</tr>
</tbody>
</table>

Both, PA6 Ultramid and PA6 Badamid nanofibrous veils, toughen composite laminates considerably

$$\sigma_{\text{max}} \text{ 1 Veil > } \sigma_{\text{max}} \text{ 3 Veils}$$

The outer veils do not contribute positively to the improvement flexural mechanical properties.
Composites characterization

4. RESULTS AND DISCUSSION

Fractographic SEM analysis

1 Veil PA6 Ultramid
## Composites characterization

### Flexure test

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<tr>
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<th>Δσ\text{max} (%)</th>
<th>δ\text{max} (%)</th>
</tr>
</thead>
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</table>

σ\text{max}\text{Badamid veil} > σ\text{max}\text{Ultramid Veil}
**Composites characterization**

Fracture waves of the resin end in the veil
The veils prevent the propagation of the crack through the polymeric matrix

Reference

1 Veil PA6 Ultramid Interlaminar Veil

12 μm

1 Veil PA6 Badamid Interlaminar Veil

11 μm

PA6 Badamid

- Better integration of the veil
- Better intrinsic properties
- Greater crystallinity
Composites characterization

While the interlaminar veil clearly stops the crack propagation, the outer veils do not seem to contribute to avoid it

A difference in the position of the outer veils is appreciated

The infusion process can result in composite materials with a very thin external face of resin or an outer face formed by the resin impregnated veil
## Composites characterization

Fracture Mode I test

<table>
<thead>
<tr>
<th>Sample</th>
<th>Load (N/mm)</th>
<th>Δ%</th>
<th>Energy (J/m)</th>
<th>Δ%</th>
<th>$G_{IC}$ (J/m²)</th>
<th>Δ%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>6.6±0.8</td>
<td></td>
<td>62.7</td>
<td></td>
<td>389±12.8</td>
<td></td>
</tr>
<tr>
<td>PA6 Ultramid</td>
<td>2.5±0.1</td>
<td>62.9</td>
<td>68.1</td>
<td>8.6</td>
<td>466±73.0</td>
<td>20.0</td>
</tr>
<tr>
<td>PA6 Badamid</td>
<td>6.4±0.1</td>
<td>2.6</td>
<td>72.0</td>
<td>14.8</td>
<td>560±72.3</td>
<td>44.0</td>
</tr>
</tbody>
</table>

The presence of the veil tends to impede the propagation of the crack.
**Composites characterization**

**Fracture Mode II test**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Load (N/mm)</th>
<th>Δ%</th>
<th>$G_{IIc}$ (J/m²)</th>
<th>Δ%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>22.7±2.7</td>
<td></td>
<td>2536.8±257.7</td>
<td></td>
</tr>
<tr>
<td>PA6 Ultramid</td>
<td>22.1±1.4</td>
<td>2.6</td>
<td>2544.0±304.0</td>
<td>0.3</td>
</tr>
<tr>
<td>PA6 Badamid</td>
<td>22.6±0.4</td>
<td>0.4</td>
<td>2970.9±526.0</td>
<td>16.8</td>
</tr>
</tbody>
</table>

The maximum load reached is similar. No significant improvement is reached.
Composites characterization

The surface of the veils remains in both sides of the composite specimen and the crack propagates partially between the carbon fibre and the veil.
Composites characterization

Dynamic mechanical thermal analysis (DMTA)

\( T_{g\infty} \) Increase
5. CONCLUSIONS

• The incorporation of polyamide nanofibre veils increase their mechanical properties.

• For composites with one PA6 nanofibre veil between the carbon fibre plies, the stress at failure during the flexural mechanical tests increased 19.7% and 42.4% for composites modified with PA6 Ultramid and PA6 Badamid, respectively.

• The analysis of the fractured surfaces, carried out by SEM, indicated that the veil hindered the crack propagation in the composites.

• The veils from Badamid, with higher crystallinity, conduct to better results than the veils from Ultramid.

• The fracture toughness analysis showed that \( G_{IC} \) value increased 20 and 44% for composites modified with a veil of PA6 Ultramid and PA6 Badamid, respectively, whereas \( G_{IIIC} \) values only increase slightly for the composite modified with the veil of PA6 Badamid. This increment is due to the crack propagation across the PA6 veil, which result in a high energy absorption of the veil.

The inclusion of electrospun polyamide 6 nanofibre veils on the carbon fibre/epoxy composites resulted in a significant improvement in mechanical properties, both flexural and fracture toughness, without an increase in laminate thickness, weight and maintaining or slightly increasing the glass transition temperature of the composite.
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