The effect of water on electrical properties of polymer composites with cellulose fibers

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Polymer composites with cellulose fibers are environmental friendly materials with improved mechanical properties. The use of polymer composites with natural fibers in electrotechnics is hindered by the inherent high moisture absorption of cellulose fibers, which determines a reduction of electrical properties of composite material. By appropriate chemical surface treatment of cellulose fibers the effect of water could be diminished. Polypropylene composites with a uniform dispersion of surface treated cellulose fibers were obtained and characterised. The mechanical properties (tensile strength, modulus of elasticity, hardness) and electrical properties (volume and surface resistivity) of polymer composites are reported. Mechanical and electrical tests point out the efficiency of physical and chemical treatment of cellulose fibers. The volume resistivity of polymer composite remains almost unchanged after immersion in water when treated cellulose fibers were used. The treatment with agents capable of creating chemical bonds with cellulose fibers gives the best results.

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1. Introduction

Nanostructured composites from polymers and cellulose fibers are breakthrough materials with a low impact on the environment, improved mechanical properties, low density, reduced tool wear, reduced dermal and respiratory irritation when compared with traditional reinforcing materials [1-6].

The interest of using cellulose fibers for polymer matrix reinforcement is rapidly growing in the last decade because of the above mentioned advantages and because the natural fibers are from annually renewable resources. The influence of water on mechanical properties of polymer-cellulose composites and the influence of environmental aging on the durability of such composites have been the subject of many papers [7-8]. Less work is concerned with the electrical behaviour of polymer-cellulose composites.

The usage of polymer composites with natural fibers in electrotechnics is hindered by the inherent high moisture absorption of cellulose which could determine a reduction of electrical properties: increase of electrical conductivity, dielectric losses and dielectric constant and decrease of the breakdown voltage [9]. By appropriate chemical surface treatment of cellulose fibers the effect of water could be decreased.

The aim of this paper is to present the effects of surface treatment of cellulose fibers on the mechanical and electrical properties of polypropylene-cellulose composites in dry and wet ageing conditions.

2. Experimental

Composite samples were prepared in the following stages:

1. treatment of cellulose fibers from hard wood (beech wood from Romania) by adding the coupling agents (agent 1 – HS(CH₂)₃Si(OCH₃)₃ from Aldrich, agent 2 - H₂N(CH₂)₃Si(OC₂H₅)₂ from Dow Corning) to a 10% cellulose suspension in a 90:10 ethanol/water solution (in volume), stirring for 2 hours, centrifuging and drying 4 hours at 70 °C in an oven with air circulation. The heat treatment consisted of curing at 120 °C for 2 hours with the purpose to realise chemical bonding;

2. mould-pressing at 180 °C for 8-10 min and quenching in cold water.

The samples of polymer composites were cut from the pressed composite materials according to standard procedures. They contain polypropylene and 30% untreated cellulose fibers (PP/CF) or polypropylene and 30% cellulose fibers treated with polypropylene grafted with maleic acid anhydride (PP/CFm) or polypropylene and 30% cellulose fibers treated with agent 1 (PP/CF1) or polypropylene and 30% cellulose fibers treated with agent 2 (PP/CF2).

The composites were investigated from the standpoint of mechanical properties and electrical conductivity. Tensile properties of the composites were determined according to SR EN ISO 527:2000 on specimens type I
with 25 mm/min, modulus of elasticity at ultrasonic frequencies (apparent dynamic modulus) was determined according to ASTM E494 and Shore hardness was determined according to SR EN ISO 868:1995. Conductivity measurements were carried out using a Keithley 6517 electrometer with a measurement cell connected to a PC-Pentium III computer as described in [10].

Sample sheets 150 mm × 150 mm × 1 mm were immersed in distilled water in an immersion tank at room temperature for different periods of time (0, 72, 168, 336, 1800 hours). Samples were positioned on special grids to avoid contact between them. After the immersion, the sample sheets were dried between two sheets of absorbent paper and conditioned at room temperature for 2 hours.

### 3. Results and discussion

#### 3.1. Mechanical properties

The mechanical characteristics of the composite materials from polypropylene and treated and untreated cellulose fibers are presented in Table 1.

The addition of polypropylene grafted with maleic acid anhydride (sample PP/CFm) that determines physical compatibility at polymer-filler interface leads to an increase in the tensile strength, modulus of elasticity and hardness. The addition of curing agents 1 and 2 leads to a significant increase of mechanical strength and hardness (samples PP/CF1 and PP/CF2). This could indicate that a reaction takes place at the interface.

### Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength at break [MPa]</th>
<th>Modulus of elasticity at ultrasonic frequencies [GPa]</th>
<th>Shore hardness [°Sh]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/CF</td>
<td>20</td>
<td>7.1</td>
<td>68</td>
</tr>
<tr>
<td>PP/CFm</td>
<td>26</td>
<td>7.4</td>
<td>71</td>
</tr>
<tr>
<td>PP/CF1</td>
<td>34</td>
<td>7.7</td>
<td>73</td>
</tr>
<tr>
<td>PP/CF2</td>
<td>32</td>
<td>7.7</td>
<td>72</td>
</tr>
</tbody>
</table>

Filler treatment conditions provide the hydrolysis of silane coupling agent, the condensation of silanol and the cellulose fiber surface grafting [2]. The reaction between Si-OH and OH groups of cellulose giving irreversible chemical bonding of the silane onto the cellulose surface (Si-O-Cellulose) was pointed out by FTIR analysis [1]. In the processing conditions of polypropylene-cellulose composites the hydrophobisation introduced by mercapto and amino groups could explain the increase of mechanical properties of PP/CF1 and PP/CF2 composite materials.

The treatment with agents capable of creating chemical bonds with cellulose fibers gives the best results in improving mechanical properties.

#### 3.2. Electrical properties

DC electrical measurements were performed by applying a voltage of 500 V for 2 hours on samples of 100 mm × 100 mm × 2 mm before and after water immersion. The time of 2 hour voltage application were established after the first series of experiments. Differences between the values of volume (or surface) resistivity after 1 hour (3600 s) and 2 hours (7200 s) are significant (Table 2).

### Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before immersion t [s]</th>
<th>ρs [Ωm]</th>
<th>t [s]</th>
<th>ρf [Ω]</th>
<th>After immersion 72 h t [s]</th>
<th>ρs [Ωm]</th>
<th>t [s]</th>
<th>ρf [Ω]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/CF</td>
<td>1812</td>
<td>5.01×10^4</td>
<td>1805</td>
<td>3.18×10^16</td>
<td>1812</td>
<td>1.23×10^15</td>
<td>1810</td>
<td>1.28×10^14</td>
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<tr>
<td></td>
<td>3608</td>
<td>6.61×10^4</td>
<td>3610</td>
<td>3.08×10^16</td>
<td>3603</td>
<td>1.89×10^15</td>
<td>3602</td>
<td>2.32×10^15</td>
</tr>
<tr>
<td></td>
<td>7206</td>
<td>8.00×10^4</td>
<td>7208</td>
<td>3.18×10^16</td>
<td>7202</td>
<td>3.87×10^13</td>
<td>7209</td>
<td>4.51×10^13</td>
</tr>
<tr>
<td>PP/CFm</td>
<td>1802</td>
<td>4.05×10^4</td>
<td>1811</td>
<td>1.39×10^16</td>
<td>1801</td>
<td>1.55×10^14</td>
<td>1803</td>
<td>2.18×10^15</td>
</tr>
<tr>
<td></td>
<td>3600</td>
<td>5.88×10^4</td>
<td>3610</td>
<td>1.79×10^16</td>
<td>3613</td>
<td>2.08×10^14</td>
<td>3608</td>
<td>3.06×10^15</td>
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<tr>
<td></td>
<td>7033</td>
<td>7.91×10^4</td>
<td>7210</td>
<td>1.68×10^16</td>
<td>7205</td>
<td>2.75×10^14</td>
<td>7202</td>
<td>5.75×10^16</td>
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<td>PP/CF1</td>
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<td>3.35×10^4</td>
<td>1800</td>
<td>2.18×10^17</td>
<td>1805</td>
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<td>3607</td>
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<td>3602</td>
<td>3.69×10^17</td>
<td>3200</td>
<td>2.97×10^14</td>
<td>3602</td>
<td>5.24×10^15</td>
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<tr>
<td></td>
<td>7033</td>
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<td>7209</td>
<td>6.16×10^17</td>
<td>7202</td>
<td>4.95×10^14</td>
<td>7213</td>
<td>1.17×10^16</td>
</tr>
<tr>
<td>PP/CF2</td>
<td>1801</td>
<td>4.75×10^4</td>
<td>1801</td>
<td>1.81×10^16</td>
<td>1812</td>
<td>2.3×10^14</td>
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<td>3603</td>
<td>6.43×10^4</td>
<td>3603</td>
<td>2.61×10^16</td>
<td>3611</td>
<td>3.63×10^14</td>
<td>3604</td>
<td>7.21×10^15</td>
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<td></td>
<td>7207</td>
<td>8.26×10^4</td>
<td>7210</td>
<td>4.08×10^16</td>
<td>7205</td>
<td>5.51×10^14</td>
<td>7208</td>
<td>1.36×10^16</td>
</tr>
</tbody>
</table>
Volume and especially surface resistivity of PP/CF composites, which contain untreated cellulose fibers, decrease with more than an order after 72 hours of water immersion. Polymer composites with treated fibers (physical or chemical treatment) present similar values for volume and surface resistivity before and after water immersion (Table 1). The results of electrical measurements on composite samples before and after immersion in water different periods of time are presented in Fig. 1 and 2.

The treatment with agents capable of creating chemical bonds with cellulose fibers gives the best results in improving electrical properties: PP/CF2 sample presents the greatest surface (Fig. 1) and volume resistivity (Fig. 2) after water immersion of all tested samples.

4. Conclusions

The treatment of cellulose fibers is essential for improving mechanical properties (tensile strength, modulus of elasticity, hardness) of polymer composites. The treatment with agents capable of creating chemical bonds with cellulose fibers gives better results in improving mechanical properties.

The immersion in water of polymer composite samples affects the electrical behaviour of composites. The samples of polymer composites with treated cellulose fibers keep better resistivity values after immersion in water.

The treatment of cellulose fibers with agents capable of creating chemical bonds (especially with amino groups) improves mechanical and chemical properties of polymer composites immersed in water.

References


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