

Water Absorption and Tensile Properties of Hemp Waste and Polyethylene Composites

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Abstract. This research focuses on improving the mechanical properties of linear low density polyethylene (LLDPE) composites reinforced with hemp waste and reducing water absorption. Cross-linking is introduced between the filler and the polymeric matrix. Cleaning the filler surface of dusts with alkali pre-treatment promotes an increase of the aforementioned properties. Hemp waste pre-treatment with TEOS and modified sols decrease composite water absorption and elongation at break, but silanization increase elastic module. The choice of different silanes for the treatment of hemp waste and treatment method affects the properties of composite.

Introduction

The mechanical properties and water absorption are essential properties that limit the use of composites. The properties of the composites are influenced by the components and the manufacturing process.

The usage of hemp fiber producing waste helps to solve the waste disposal problem [1]. Replacing a part of the polymer with fossil resources with the enriched components of biological origin can reduce pollution and produce new materials. The combination of polymeric matrix and natural fibers provide flexibility and have relatively low density and low manufacturing prices [2].

The waste-reinforced composites can be applied in many fields such as automotive, aerospace, packaging, construction, and transportation industries. The choice of polymer as a matrix material is important for the kinds of natural fiber reinforcement. Polyethylene, polystyrene, polylactides, polyvinyl chloride and polypropylene are thermoplastic materials and can be used as matrix materials for composites [3].

This research focuses on mechanical properties and water absorption of composites consisting of linear, low-density polypropylene and hemp waste. The water absorption of composites could be controlled by waste content and treatment methods. Biodegradable fibers are modified by various chemical processes with variable results. Sources often publish data of silanization, mercerization, acetylation, sol-gel method and other treatments, with regard to the effects of natural reinforcing components on the properties of composites [4;5].

The partially degradable composites can be recycled by returning them to the production stream or separating the components and processing individually. The more the composites were recycled, the lower water absorption potential they exhibited by fiber encapsulation, and recycling could lead to the degradation of hemicellulose leaving natural fibers less hydrophilic [6].



Materials and methods

The hemp waste (W) used was supplied from the factory of “Zalers”. Composites with waste content 40 wt% using LLDPE grade 6201XR as matrix (PE) were prepared by two rolls mill ($T=150^{\circ}\text{C}$, $t=10$ min) and pressed for testing.

Table 1. Hemp waste composites

Designation	Waste modification					
	NaOH	ZnO	ZAD	TEOS or APTES	Dipping time	Heating
PE	-	-	-	-	-	-
PE/ZnO	-	-	-	-	-	-
PE/W-NaOH	x	-	-	-	30 min	-
PE/ZnO/W-NaOH	x	-	-	-	30 min	-
PE/W-NaOH-Sol_TEOS	x	-	-	0.14 mol	10 min	120°C
PE/W-NaOH-Sol_TEOS_ZAD	x	-	x	0.9 mol	10 min	120°C
PE/W-NaOH-Sol_TEOS_ZnO	x	x	-	0.9 mol	10 min	120°C
PE/W-NaOH-Sil_TEOS	x	-	-	2 mol	60 min	110°C
PE/W-NaOH-Sil_APTES	x	-	-	2 mol	60 min	110°C

Alkalized waste was prepared using 2 % Sodium hydroxide solution (NaOH). Silanized waste (Sil) was prepared by treated alkalized waste with 2 mol APTES - (3-Aminopropyl) triethoxysilane or TEOS - tetraethyl orthosilicate. Waste dipping time is seen in table 1. Nanosols (Sol) were prepared by a controlled hydrolysis, adding ethanol into TEOS, after adding water and hydrofluoric acid. Solutions were stirred for 30 minutes; the obtained nanosols were homogeneous and then modified with 7.5 wt% zinc acetate dehydrate (ZAD) or zinc oxide (ZnO). The humidity of air was 65 ± 2 % and room temperature was -20 ± 2 °C. The waste samples were then dried and heated.

In some samples the zinc oxide nanoparticles used in composite manufacturing process as nanofiller in viscous state. Used reagents: sodium hydroxide, ethanol, hydrofluoric acid, APTES and zinc acetate dehydrate were purchased from Sigma Aldrich, TEOS from Alfa Aesar and zinc oxide nanoparticles from Nanjing High Technology Nano Materials Co., Ltd .

Scanning electron microscopy (SEM) was used to examine the nature of the waste surface modification.

The tensile tests were measured on the material testing machine Tinius Olsen 25ST by standard ASTM D 638 M – 3.

Water exposure experiments (according to the standard ASTM D 570-98) were carried out at room temperature ($+23^{\circ}\text{C}$).

Results and discussion

LLDPE elastic module is 69.8 MPa and elongation at break is 21.2 %. The flexibility of the matrix is high, both inorganic and organic ingredients are used to decrease it. ZnO 2wt% nanoparticle filler additive increased elastic module (E_t) to 233.4 MPa, but elongation at break decreases by 26 %, figure 1. The waste pretreated with alkali solution used to clean the waste particles surfaces are applied to all variants under discussion, figure 1. The alkali-treated hemp waste 40 wt% composite (LLDPE/W-NaOH) elastic module (451 MPa) is 7 times higher than the module of net LLDPE, but decreases by 7 % when compared with 40 wt% composite E_t without waste alkali treatment (483.3 MPa) [7]. At the same time elongation at break drops by almost 6 times ($\epsilon_t = 4$ %), figure 1. Samples PE/ZnO/W-NaOH reach elastic module 576 MPa when alkali treated waste combined with ZnO nanofiller in viscous state.

Optional waste treatment with the TEOS based silica sol raises the composite module by 14 % compared with the alkali pre-treated and by only 9 % compared with the waste non-treated variant.

Modules and elongation values of the next three variants are quite close, with an average improvement of 19 % E_t and decrease of 29 % elongation at break compared with the waste non-treated variant ($\epsilon_t = 4.2$ %). The highest E_t obtained using APTES (647 MPa) exceeded the module of non-treated variant by 1.34 times.

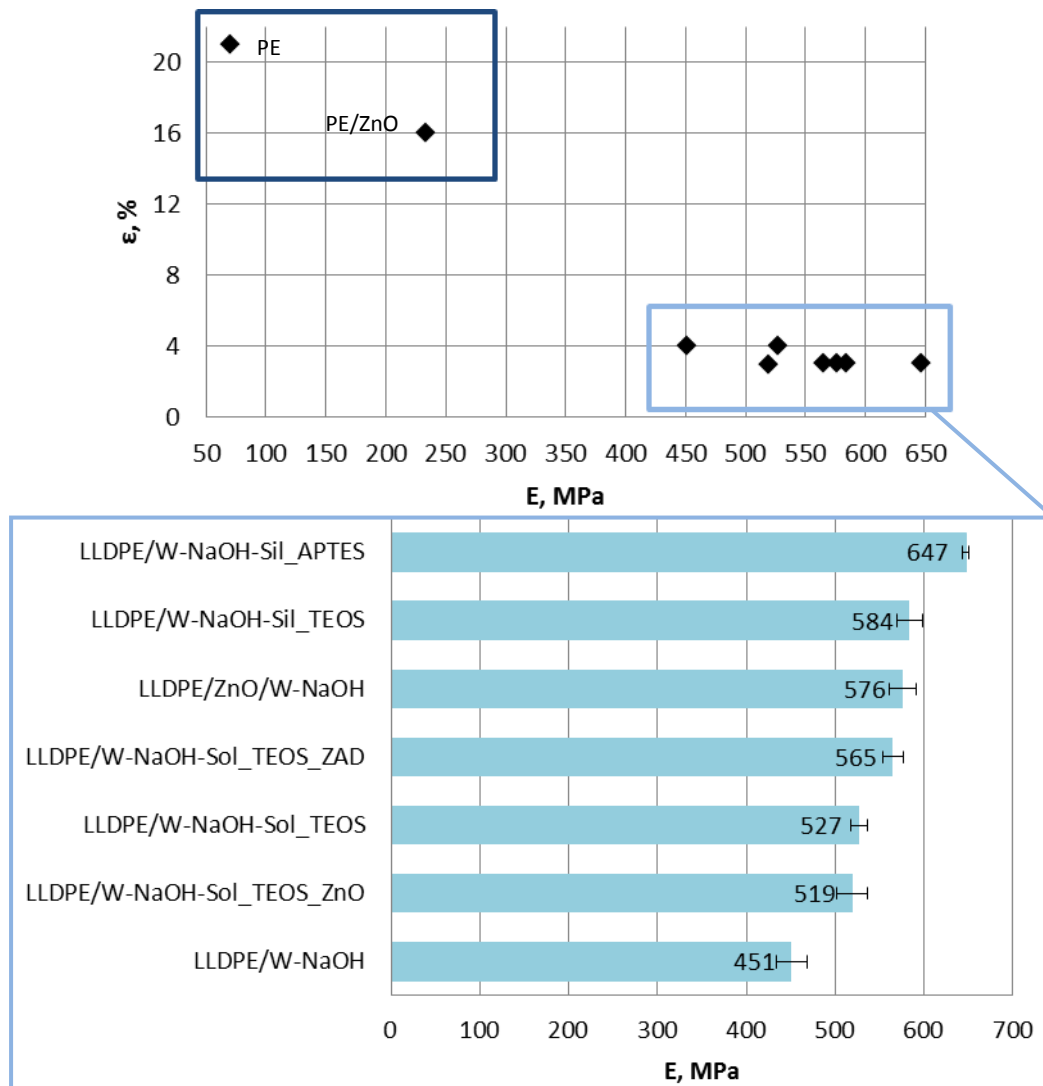


Figure 1. Composites elastic module and elongation at break

LLDPE does not absorb water, LLDPE/ZnO composite absorbs 0.6% water due to air inclusions occurring in the manufacturing process, which serves as a way of penetrating water. Untreated hemp waste composite water absorption is 13.6 % [8]. Water absorption of 40 wt% alkali-treated hemp waste composite is 13.7 %. It is substantially (by 26%) increased if the waste is subsequently subjected to the several pre-treatments as in variant LLDPE/W-NaOH-sil_TEOS (figure 2) indicating that the fibers are damaged and silanisation with TEOS is not suitable for hemp waste.

It seems that in the case of several pre-treatments, it is very important to choose the proper combination. The combination of when TEOS based sol treatment follows after 2 wt% alkali treatment (composite LLDPE/W-NaOH-sol_TEOS) with very low saturation moisture content (5.2 %) works excellently. Composite samples of variants LLDPE/W-NaOH- TEOS_ZAD and LLDPE/W-NaOH-Sol_TEOS_ZnO (7.5 % and 7.4 % respectively) show equal absorption disposition in waste pre-treated with sol containing Zn compounds (figure 2).

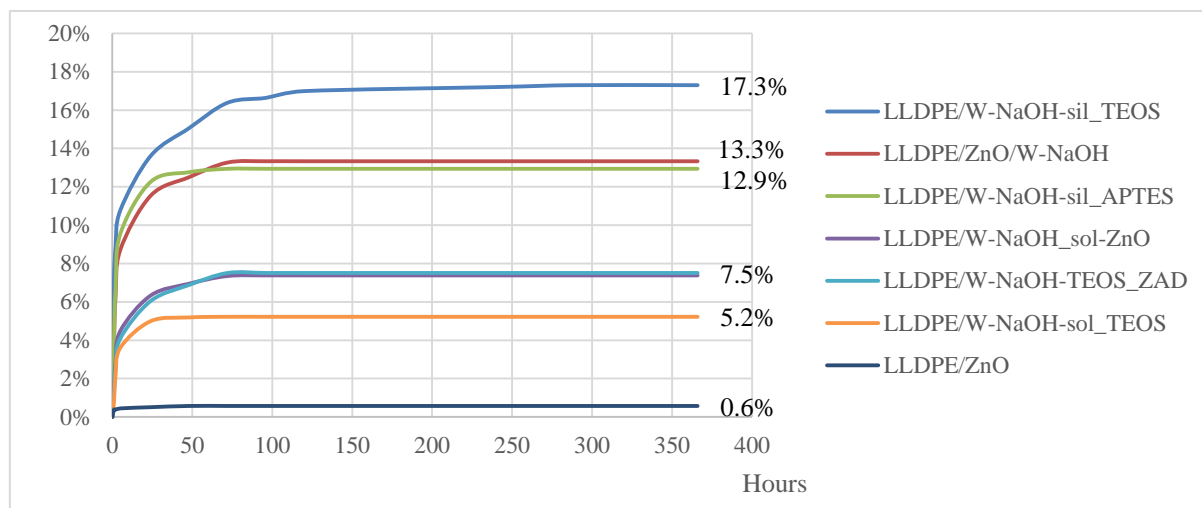


Figure 2. Composites water absorption kinetics

Composites rapidly absorb water in the first 24 hours and reach a point of equilibrium within 72 hours except composite LLDPE/W-NaOH-Sil_TEOS.

As we can see, the untreated hemp waste surface is rough with small dust particles, but alkali treatment cleans the surface which means that a part of the hemicellulose and another water soluble components are washed out together with dust, figures 3 and 4. Clean waste surfaces promote a more durable coating after treatment with silane.

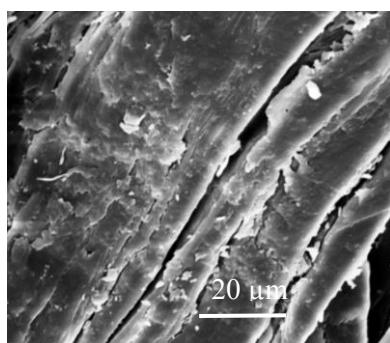


Figure 3. Untreated hemp waste

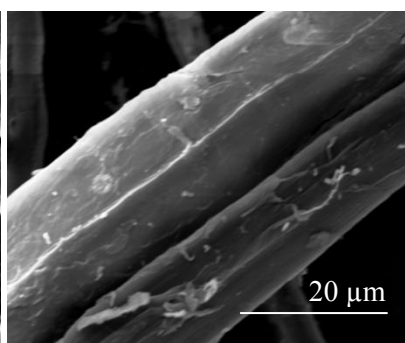


Figure 4. Hemp waste with 2 % NaOH solution treatment

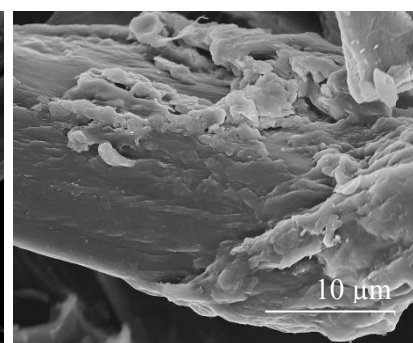


Figure 5. Hemp waste with 2 % NaOH treatment and silanized with 2 mol APTES

The hemp waste surface modified with sol-gel method forms a silica coating on the surface, but silanization also penetrates into some deeper layers and creates a smooth surface (figure 5).

Summary

The highest elastic module and the lowest elongation at break, from all eight composites, shows that composites with alkali pre-treatment and waste silanization are effective for hemp waste treatment to increase composite mechanical properties. The high elastic module and low elongation at break also show composites with alkali treated waste and ZnO 2 wt% additive.

To decrease hemp waste reinforced composite water absorption, alkali pre-treatment could be combined with the sol-gel technology. The composites with the lowest water absorption are made from hemp waste pre-treated sequentially with 2 wt% alkali and 0.14 mol. TEOS sol. Waste pre-

treatment with 0.09 mol. TEOS and 7.5 wt% Zn acetate dehydrate precursor sol moderate increase water sorption still not exceeding 8 %, at the same time elastic module of composite increase too; these composites are suitable for outdoor use. Waste silanization leads to the water absorption capability increase above 12 wt% of LLDPE composites with the hemp waste content 40 wt%, and this treatment can't be recommended to reduce moisture absorption.

As we can see, it is not possible to achieve high mechanical composite properties and low water absorption with the same waste treatment methods, therefore, the purpose of using composites and the use of the most suitable processing combinations should be considered.

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