Properties of Composites Based on Linear Low Density Polyethylene (LLDPE) and by Sol-gel Method Modified Fibres

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Abstract. The influence of sol-gel modified fibres content on the melt flow index (MFI) and water absorption of a linear low density polyethylene was investigated. The fibres were modified with silica xerogel prepared by the sol-gel polymerization of tetraethylorthosilicate (TEOS) under hydrolytic conditions using acid catalysis. Alkali pre-treatment was used for some variants and some composite samples were prepared by adding maleic anhydride grafted polyethylene (MA-g-PE). It was found out that melt flow index increases using sol-gel method for hemp fibres modification with fibres content in composite 40 and 50 wt%. Composite with fibres modified by sol-gel method content 40 wt% water absorption were evaluated in a range from 8.5 to 16.32%, but for composites with 50 wt% - 12.12%.

1. Introduction

Optimal content (30 wt%) of fibres in LLDPE matrix and unmodified hemp fibres reported Solizenko et.al. These composites maintain sufficient fluidity, and they can be processed by traditional polymer processing methods [1]. The fibres content seems relatively small to meet growing necessity of renewable resources integration in materials.

For composites make more environmentally friendly, it is necessary to increase the fibres content and one of the options is chemical treatments like mercerization, acetylation and others. It is important to impart hydrophobicity to the hemp fibres by suitable chemical treatment to develop composites with better mechanical properties and decrease water absorption.

Vihodceva and co-authors reported about sol-gel technology using for the pure cotton textile treatment for imparting of such properties as stable water-repellency, antimicrobial, and UV protection shows a high wear resistant [2].

For composites production with high hemp fibres content is essential such property as a weak water absorption in this research was evaluated the possibility of hemp fibres treatment by mentioned above sol-gel technology with proved water-repellent imparting properties. Hemp fibres, the same as cotton fabrics need to adjust the highest possible heat treatment, which does not damage the fibres and provides the necessary properties of the coating.

In the article the hemp fibres treatment by reported sol synthesis method before composite formation is described to reduce water absorption and measure the sol treatment effect and other treatment combination influence on composite MFI.
2. Materials and Methods

The hemp fibres used in this study were obtained from hemp stems harvested from a trial plot at Agriculture Science Centre of Latgale in Vilani district, Latvia. Hemp fibres of variety ‘Bialobrziesk’ in growing process were cultivated with active nitrogen fertilizer (N30). The harvested hemp stems were left for dew retting on the field 4 weeks.

Content of hemp fibres (length up to 1 mm) in composites was 40 and 50 wt% with pre-processing NaOH (SIA"Enola", ES) 2% solution (4h +23°C) and sol-gel method. Materials used for sol synthesis- C₈H₂₀O₄Si (Alfa Aesar, German), C₂H₅OH and HF (ES (SIA"Enola", ES), deionized water, with or without adding Zn(CH₃COO)₂•2H₂O (Scharlau, Spain) used as the modifier of the sol-gel system and method reported by Vihodceva et.al.

LLDPE grade LL 6201 was used as matrix, MFI = 50g/10min, Tₘₐₜ. = 123°C.

MA-g-PE (Licocene fine grain TP 4351) was used as a coupling agent 5 wt%.

Before mixing, the fibres were dried in an air chamber at +105°C for 24h.

Composites were prepared by mixing of the components on two rolls mill (T=150°C 10 min), then cooled and pressed in 1mm thick sheets. Water exposure experiments (standard ASTM D 570-98) were carried out at room temperature (+23°C). Fluidity was estimated by melt flow index method (MFI) according to the standard ASTM D 1238-90b (T=190°C, P=2.16 kg).

Using Atomic force microscopy composite cross-section surface was investigated. The reference voltage was set to 2.6+/-0.2V, a level that provided clear images. Test operated in Tapping mode, image size 25x25 μm and 20x20 μm with Scan Rate 0,1 Hz. Silicone probe (OTESPA-R3) nominal tip radius, Spring constants and free resonance frequencies were respectively 3.75 μm, 26 N/m and 300kHz.

10 composite samples were prepared with different hemp fibres treatment (Tab 1.).

| Sample | Hemp fibres processing method | Fibres content, wt% |
|--------|-------------------------------|---------------------|
| 2a     | Sol-gel                       | 40                  |
| 2b     | Sol-gel and MA-g-PE 5 wt%     | 40                  |
| 3a     | Sol-gel with Zn(CH₃COO)₂•2H₂O5 wt% | 40 |
| 3b     | Sol-gel with Zn(CH₃COO)₂•2H₂O 5 wt% and MA-g-PE 5 wt% | 40 |
| 4a     | 2% NaOH and Sol-gel           | 40                  |
| 4b     | 2% NaOH and Sol-gel and MA-g-PE 5 wt% | 40 |
| 5a     | 2% NaOH and Sol-gel with 5 wt% Zn(CH₃COO)₂•2H₂O | 40 |
| 5b     | 2% NaOH and Sol-gel with 5 wt% Zn(CH₃COO)₂•2H₂O and MA-g-PE 5wt% | 40 |
| 6      | Without pre-treatment         | 50                  |
| 7a     | Sol-gel                       | 50                  |

3. Results and Discussion

Melt-flow indexes of variants fall in a range from very low (0.1 for samples with un-processed fibres) till very high (24.41 for samples with silica sol pre-treated fibres).

Untreated hemp fibres composite with 40 wt% practically lost fluidity [3]. Previous experiments 10% solution of acetic anhydride hemp fibres treatment 40 wt% composite MFI increased to 8.47g/10min but 50 wt% composite to 1.81g/10min [4]. Sol-gel method hemp fibres modification shows magnificent fluidity increase, more than 20 times (sample 2a, 2b, 4b) composite with hemp fibres 40 wt% and increasing fibres content to 50 wt% no significant difference (sample 7a), Fig.1.

For better adhesion between by sol-gel method obtained coating and hemp fibres surface some samples used alkali pre-treatment. Previous experiments showed fluidity decrease for about 2 times using 2% NaOH fibres treatment [4]. Combination of alkali pre-treatment with Sol-gel treatment shows 22% fluidity decrease (2a and 4a) compared to only sol-gel treatment. MA-g-PE additive for
sample with alkali pre-treatment showed MFI increase 21% (4a to 4b) and sample with \( \text{Zn(CH}_3\text{COO)}_2\cdot2\text{H}_2\text{O} \) modifier of the sol-gel system MFI increase 52% (5a and 5b).

Samples with Sol-gel modified fibres with \( \text{Zn(CH}_3\text{COO)}_2\cdot2\text{H}_2\text{O} \) modifier of the sol-gel system (3a and 3b) showed lower results but processing of the composites is possible by traditional methods.

Two rolls mill composite processing can pull-off particles from sol layer on hemp fibres surface and could be incorporated into polyethylene matrix. Therefore silica polymer nano-composite nanoparticles can modify matrix and affect some polyethylene properties in the next processing stages. Silica polymer nano-composites agglomerates presence can significantly reduce the silica loading, resulting in reduced thermochemical properties.

Dorigato et. al. reported about linear low density polyethylene/silica nano-composites crosslinking reaction induced by thermal processing (200°C) caused a remarkable increase of the melt viscosity, as revealed by the melt flow index values of both neat matrix and nano-composites [5].

![Figure 1. Melt flow index](image)

At lower temperatures that are used for the hemp fibres thermal treatment (about 120°C) starts partial decomposition of zinc acetate dehydrate and basic zinc compound formation [6]. In the formation of the zinc acetate (\( \text{C}_4\text{H}_6\text{O}_4\text{Zn} \)), silica compounds: \( \text{H}_2\text{Si}_3\text{O}_7(\text{H}_2\text{O}) \) and \( \text{H}_2\text{Si}_{14}\text{O}_{29}•5.4\text{H}_2\text{O} \), and probably from insoluble basic zinc compounds or zinc oxide in amorphous phase can react polymer chains in composite preparing process. Crystalline phase of the ZnO appears starting from the temperature 300°C, in the range of the temperature from 300 to 500°C SiO\(_2\) is also obtained; from the 400°C the formation of the willemite - \( \text{Zn}_2(\text{SiO}_4) \) begins [6], therefore no crystalline phase Zn and Si particles into the matrix possible. Additional studies are required to determine how affects xerogel amorphous phase to the matrix viscosity.

Water sorption after 438h (Fig. 2. and Fig. 3) varies in range 8.5 (40 wt% sample 4b) to 22.16 (50wt% sample 6 with un-processed fibres) and increases with the enhance of the fibres content from 40 to 50 wt%.

Composite water absorption with untreated hemp (40 wt%) fibres varies in range 10.8 to 12.10% (240h) [1].

The highest water resistance showed in the sample 4a was fibres pre-treated with NaOH and then modified fibres surface with sol-gel method. Alkali pre-treatment clean fibres and provides sustainable xerogel coating that is sufficiently stable after insertion in polythene.
But sample 4b with 5 wt% MA-g-PE additive showed one of the lowest water resistance, this indicates that the xerogel coating form chemical bonds with the MA-g-PE as coupling agent and lost the resilience of the fibres. All samples except 4b show higher water resistance with MA-g-PE than without additive.

After 438 hours water exposure for samples of the 3a, 3b, 5a, 5b composite variants equilibrium moisture content established.

Composite water absorption (7a) with silica xerogel treated hemp fibres 50 wt% is 12.12% and it is in the same range as untreated hemp fibres 40 wt% composite water absorption. Hemp fibres (50wt%)/LLDPE composite equilibrium moisture content not established, water uptake is still in process.

In cross section of 50 wt% hemp fibres and LLDPE composite (Fig.4.) are seen compact packed with evenly spread compounds, cannot see cracks and air inclusions. But Fig.5. hemp fibres detached from matrix and not evenly dispersed.
4. Conclusions
The melt flow index increases using sol-gel method for hemp fibres modification with fibres content in composite 40 and 50 wt%. Zn(CH₃COO)₂·2H₂O the modifier of the sol-gel system decrease MFI results but do not give significant improvements in water absorption. MA-g-PE additive increase water resistance but decrease MFI except combination with alkali pre-treatment.

Using sol-gel method for hemp fibres modification in LLDPE composite matrix can increase filler content 50 wt% and more maintaining fluidity and improve water resistance.

The Sol-gel method is suitable to modify hemp fibres hydrophobic surfaces and decrease water absorption and increase MFI.

Future studies need to explore the xerogel coating promising effects on matrix and sol-gel method effect on composite mechanical properties.

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