

Artificial ageing of composites based on modified cellulose fibres and polyurethane prepolymer

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Composite materials reinforced with natural short fibres have a number of advantages compared to other composites. These materials have high moulding flexibility, lightweight properties and they are environmentally friendly. Through fibre modification, obtained materials have uses in different areas, such as the automotive industry, conductive composites, building construction, etc.

The ultimate goal of this work is to study the properties of produced composite materials. This research focuses on the production of highly-filled polymer composites from short paper fibres from de-inking process and polymer matrix. The properties of these newly created composites are unknown. This is what forms the principle basis for the need for research.

In this work, a method for the use of waste fibres is provided. The fibres were mixed with liquid polyurethane prepolymer to form the composite. The samples were exposed to artificial ageing for 72, 144, 288 and 384 hours at 90°C and 50% RH. Mechanical properties before and after the ageing were studied.

Keywords: Composite materials, Cellulose fibres; Artificial ageing; Mechanical properties; FT-IR.

INTRODUCTION

Wood components are natural polymers and their interface has a large quantity of functional polar groups, in particular the cellulose. Waste wood, waste paper and waste plastics are major components in wood-polymer composites and offer great opportunities as recycled ingredients [1,2].

The paper industry generates a source of waste that can be used in further manufacturing. The waste consists of a mixture of fillers, short fibres and ink.

Bonding at the interface can be achieved by modifying the filler-matrix surface with various surface-active additives or coupling agents [3]. The hydrophilic nature of wood particles and cellulose fibres offers additional advantages, in comparison to inorganic fillers, by readily providing the possibility for the incorporation of different chemical groups on the surface [4].

Several classes of adhesives used in wood bonding involve the use of isocyanates. Isocyanates are widely used due to their reactivity with groups that contain reactive hydrogen, such as amine and alcohol groups at room temperature. Isocyanates are most often used to produce polyurethanes by reacting with liquid diols [5].

A great variety of publications offers results in

the field of artificial ageing of WPC.

In the present investigation, a new prepolymer based on diphenylmethane diisocyanate (MDI) and long chain polyether polyol was obtained and the effect of cellulose fibres as a filler on the mechanical properties after artificial ageing of composites was studied.

EXPERIMENTAL

Materials

The materials used in this study were waste short cellulose fibres, CuSO₄·5H₂O, Na₂S₂O₃·5H₂O (Sigma Aldrich), Desmodur[®] 44 M Flakes (BAYER), Lupranol[®]1000 (BASF), catalyst-Stannous Octoate PC CAT T9 (Performance Chemicals Handels GmbH).

Short cellulose fibres are a waste product from the de-inking process in papermaking. The average value of inorganics in this mixture of fibres, fillers and ink is about 22.06 % ± 0.9.

For the purposes of this study, three different ratios of CuSO₄ and Na₂S₂O₃ were used at hydro modulus 1:6. The goal of fibres modification is obtaining of conductive composites from short fibres [6]. This modification was carried out by the immersion of the fibres in the solution according to Table 1 for 30min at an elevated temperature (80°C). For drying, modified short fibres are kept for 5 hours at a temperature of 105°C.

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Liquid prepolymer was prepared as follows: 0.1 % Stannous octoate is mixed with 1020g Lupranol®1000 (A-component). 350g MDI are melted at 40°C, and then the A-component is added. The process is carried out for 4 hours at 75°C. The isocyanate content was determined using back titration - 9.6%.

Preparation of composites

The composites were obtained by melt blending in a chamber of a Brabender mixer, at 120°C and processed for 30 minutes. After the processing step, each sample was compression moulded at 9.6MPa for 20minutes, at 120°C.

Investigation methods

FT-IR spectra. Infrared Spectroscopy (FT-IR) was applied with Varian 600-IR equipped with a single reflection ATR accessory, at spectrum range- 400-4000cm⁻¹.

Artificial ageing procedure. All composite samples were placed in a laboratory chamber ESPEC PL-2KPH to accelerate the ageing of the samples. According to TAPPI T544 chamber conditions were 90 °C and 50% relative humidity. The samples were removed from the chamber at regular intervals after 72, 144, 288 and 384 hours.

Mechanical properties. Tensile and flexural tests were carried out at room temperature on a Zwick 2000 testing machine equipped with activated grips, according to EN ISO 178:1996 and EN ISO 178:2010.

Every sample has dimensions of 4x10x100mm.

RESULTS & DISCUSSION

Compounding characteristics

Fibres modification was carried out with two component system (Na₂S₂O₃/ CuSO₄) at 120°C for 30 minutes. Ratio between dry mass and liquid in this system was calculated (1:6). Different percentage of modifying agent was used- 20%, 30% and 40%.

Liquid prepolymer DesLu2.8-1 was synthesized and subsequently studied by means of FT-IR. This process was carried out for approximately 4 hours. The samples were collected for 5 minute periods and the changes in OH-group's absorption peak at ~3500 cm⁻¹ was used to study kinetic reactions.

Several infrared vibrations, typical of polyurethane systems, could be assigned:

- N-H stretching mode assigned at ~3365 cm⁻¹;
- Carbonyl assigned between ~1780 cm⁻¹ and ~1600 cm⁻¹ (Amide I);

The low intensity of the vibration at ~1643 cm⁻¹ (urea carbonyl) compared with that of the overlapped vibration at ~1732 cm⁻¹ (urethane carbonyl) indicates that, under the synthesis conditions used, -NH formation is favoured.

- Amide II ~1556 cm⁻¹ and amide III ~1244 cm⁻¹ vibration modes;
- C- H stretching vibrations are assigned at ~2950 cm⁻¹ and ~2880 cm⁻¹;
- ~2270 cm⁻¹ NCO consumption;
- ~3500 cm⁻¹ OH-consumption, ~3365 cm⁻¹ – NH formation.

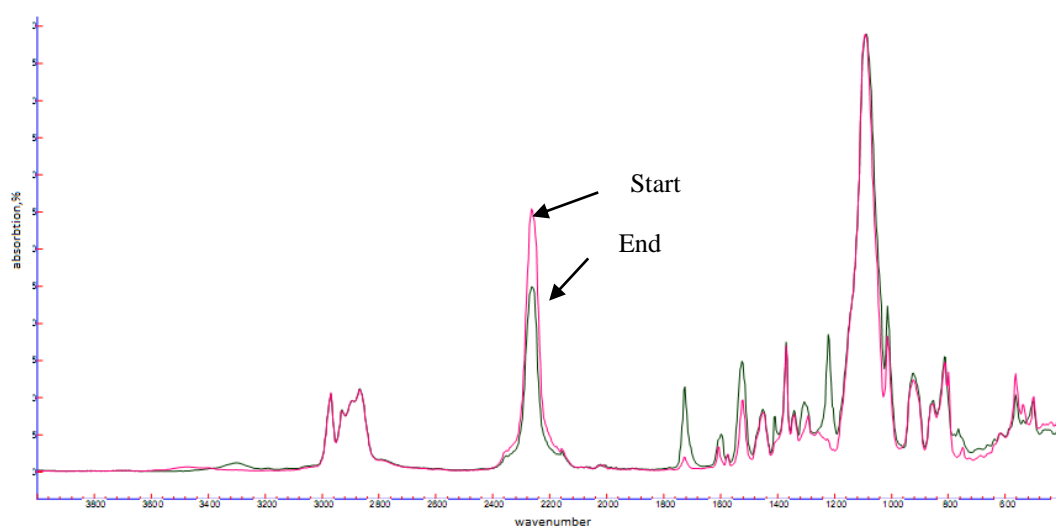


Fig.1: FT-IR spectrum of polyurethane prepolymer DesLu2.8-1 (reaction start and end)

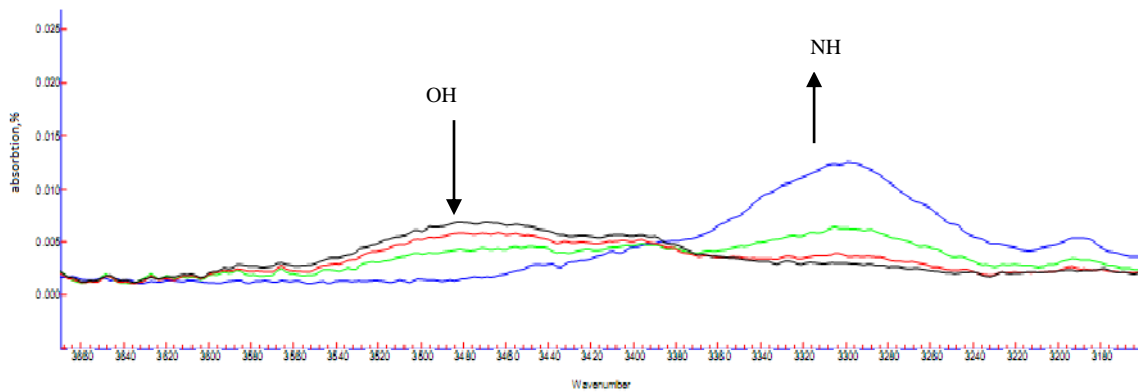


Fig.2: FT-IR characteristic spectrum OH-consumption and –NH formation (DesLu2.8-1, 5min, 10min, 15min, 50min)

Table 2. Composite samples

Composite material	Fibres		Prepolymer, %
	Modification	%	
1-90F10P	Chem1 (60/40)	90	10
1-80F20P	Chem1 (60/40)	80	20
1-70F30P	Chem1 (60/40)	70	30
2-90F10P	Chem2 (70/30)	90	10
2-80F20P	Chem2 (70/30)	80	20
2-70F30P	Chem2 (70/30)	70	30
3-90F10P	Chem3 (80/20)	90	10
3-80F20P	Chem3 (80/20)	80	20
3-70F30P	Chem3 (80/20)	70	30

The peak that occurs at $\sim 3500\text{ cm}^{-1}$ corresponds to the OH-groups of the long chain polyether polyol and the peak at $\sim 3365\text{ cm}^{-1}$ corresponds to the NH-groups of the polyurethane prepolymer. As the reaction takes place the hydroxyl groups of the polyol are reduced in order to form polyurethane groups of the prepolymer. The two characteristic peaks at $\sim 1720\text{ cm}^{-1}$ and $\sim 1530\text{ cm}^{-1}$ proved formation of urethane structures. Non-modified fibres were used for reference samples preparation (Table 2).

Table 1. Reference composite samples

Composite	Fibres, %	Prepolymer, %
0-90F10P	90	10
0-80F20P	80	20
0-70F30P	70	30

Composites from modified fibres and liquid prepolymer were obtained. All specimens were artificially aged in a chamber under controlled

conditions. For the conditioned samples FT-IR was applied.

A significant difference in FT-IR spectra of modified and non-modified composites was observed. Figure 3 shows that a peak at $\sim 1428\text{ cm}^{-1}$ occurs. This peak is close to the peak of poly(ethyl acrylate) – a component of ink formulation. This component has a boiling point of 99°C and processing the fibres at temperature of 120°C for 30 minutes leads to poly(ethyl acrylate) evaporation.

Mechanical properties

Figure 4 presents the normal behaviour of the fibres after artificial ageing. Non-modified fibres have no significant changes in tensile properties but for the series with modified fibres a collapse in the values was observed. This can be explained with the heat exposure by fibre modification followed by another heat exposure by compression moulding.

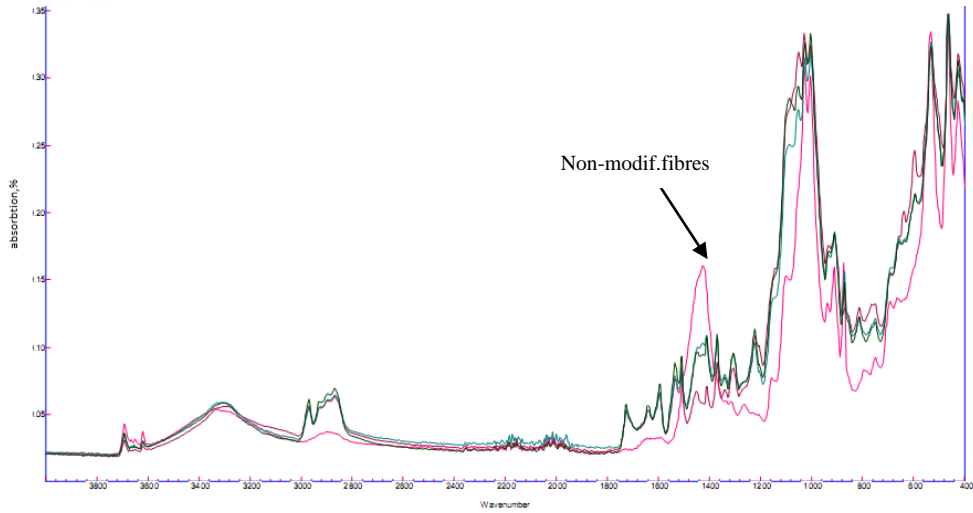


Fig.3. FTIR of composites containing non-modified and modified short fibres.

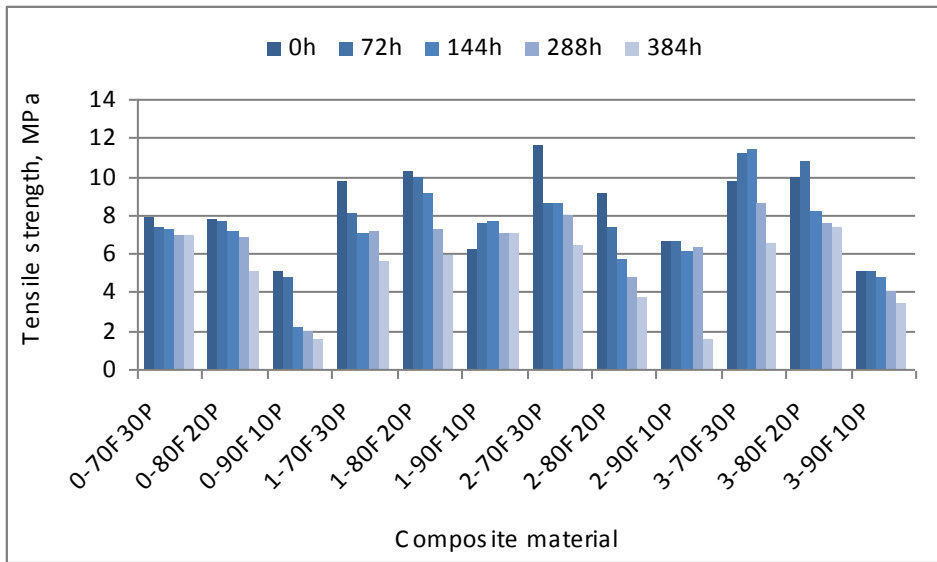


Fig.4. Tensile strength of the composites.

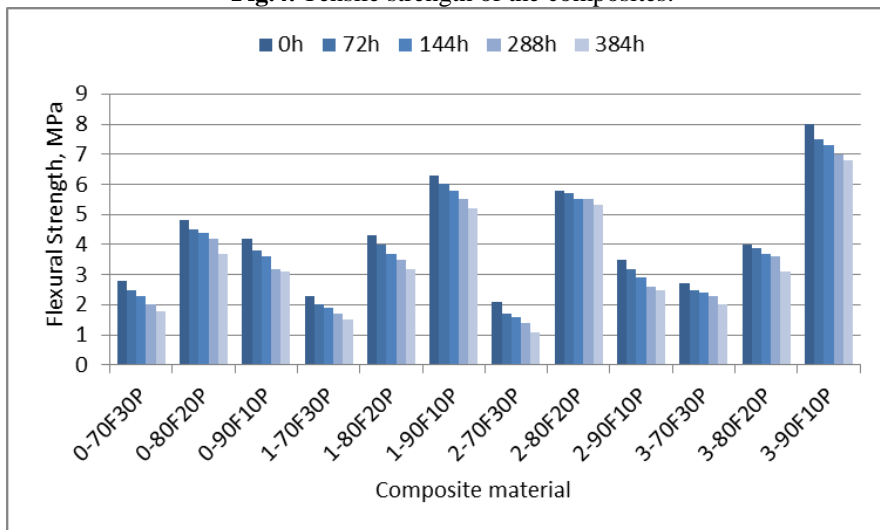


Fig. 5. Flexural strength (ϵ_B , MPa) of the composites

The modulus of short-fibre-reinforced composites depends in general on the length of fibres and their uniform dispersion in the matrix. A difference is observed by fibre content of 90%, which means higher fibre content and a greater level of ageing.

After the artificial ageing only 3 to 4% collapse in flexural strength values are observed.

It is seen that water affects the strength properties of the composites, but the degree of this influence depends on the compounding process. The absorbed water molecules reduce bonding between the short fibres and establish hydrogen bonds between short fibres and water molecules.

CONCLUSIONS

Polyurethane/Modified cellulose fibres composites were prepared by melt mixing and their behaviour upon controlled weathering was investigated. The influence of artificial ageing on the mechanical properties of short fibres

composites was observed. Significant changes at σ_M after ageing were observed by a sample prepared from 90% fibres and 10% prepolymer. The composites with 20-30 wt% prepolymer recorded a small decrease in mechanical properties after artificial ageing.

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ИЗКУСТВЕНО СТАРЕЕНЕ НА КОМПОЗИТНИ МАТЕРИАЛИ, ПОЛУЧЕНИ ОТ МОДИФИЦИРАНИ ЦЕЛУЛОЗНИ ВЛАКНА И ПОЛИУРЕТАНОВ ПРЕПОЛИМЕР

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(Резюме)

Композитните материали, усилен с къси природни влакна, имат редица предимства в сравнение с останалите познати композити. Тези композити притежават еластичност, ниско тегло и не вредят на околната среда. Чрез модифицирането на влакната, получените материали придобиват специфични свойства, приложими в различни технически области- автомобилна и строителна индустрия, производство на проводими материали и др.

Целта на изследванията е да се изучат свойствата на тези нови композитни материали. Работата е насочена към получаването на високо напълнени полимерни композити от къси целулозни влакна, които са отпадъчен материал при обезмастиляване на хартията и последващото им комбиниране с полимерна матрица. Свойствата на този нов тип композити не са известни, което налага провеждане на обширни изследвания в тази насока.

В процеса на работа са използвани отпадъчни целулозни влакна, които се смесват с течен полиуретанов преполимер за получаване на композитен материал. Композитните образци са подложени на изкуствено стареене в продължение на 72, 144, 288 и 384 часа при 90°C и 50% относителна влажност на въздуха. Изследвани са механичните свойства преди и след стареене на материалите.