

Sustainable recycling of biocomposites reinforced with *Spartium junceum* L. fibres

Održivo recikliranje biokompozita ojačanih vlaknima *Spartium junceum* L.

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Abstract

Sustainable development and the imperative of a circular economy, as well as the growing demand for renewable raw materials, have imposed the need for research into efficient recycling procedures for production and/or consumer waste. This is particularly relevant for new, increasingly prevalent structural materials - biocomposites (composite materials in which at least one constituent, fibre as reinforcement or matrix, is biodegradable or of natural origin). Although biocomposites are considered more environmentally, friendly compared to conventional fibre-reinforced composites, their proper disposal and efficient integration into recycling processes still represents a challenge. Recycling approaches for fibre-reinforced composites include mechanical, chemical, and thermal methods, each with its own advantages as well as limitations. While mechanical recycling is often simpler and less energy-intensive, and thermal recycling enables energy recovery from the material, chemical recycling stands out as a method with the potential for simultaneous recovery of both, fibres and polymer matrix in almost original form, thus enabling their reintegration into the new production process. This paper presents an investigation into the possibility of chemical recycling of a biocomposite made from a PLA (polylactide acid) matrix reinforced with *Spartium junceum* L. fibres, with the aim of defining the most efficient process that ensures satisfactory quality of recovered fibres with minimal environmental impact.

Keywords: biocomposites; sustainability; recycling; chemical recycling

Sažetak

Održivi razvoj i imperativ kružnog gospodarstva kao i sve veća potražnja za obnovljivim sirovinama nametnuli su potrebu istraživanja učinkovitih postupaka recikliranja proizvodnog i/ili potrošačkog otpada. Posebno se to odnosi na nove, sve prisutnije konstrukcijske materijale – biokompozite (kompozitni materijali kod kojih je najmanje jedan konstitutivni dio, vlakno kao ojačalo ili matrica, biorazgradiv ili prirodnog porijekla). Iako se biokompoziti smatraju ekološki prihvatljivijima u usporedbi s konvencionalnim kompozitima ojačanim vlaknima, njihovo pravilno odlaganje i učinkovita integracija u procese recikliranja i dalje predstavlja izazov. pristupi recikliranju vlaknima ojačanih kompozita uključuju mehaničke, kemijske i toplinske metode, od kojih svaka ima svoje prednosti, ali i ograničenja. Dok je mehaničko recikliranje često jednostavnije i energetski manje zahtjevno, a termičko recikliranje omogućuje povrat energije iz materijala, kemijsko recikliranje ističe se kao metoda s potencijalom istodobne uporabe i vlakana i polimerne matrice u gotovo izvornom obliku, čime se omogućuje njihova reintegracija u novi proizvodni proces. Ovaj rad predstavlja istraživanje mogućnosti kemijskog recikliranja biokompozita izrađenog od PLA (polilaktidna kiselina) matrice ojačane vlaknima *Spartium junceum* L., s ciljem definiranja najučinkovitijeg procesa koji osigurava zadovoljavajuću kvalitetu oporabljanih vlakana uz minimalan utjecaj na okoliš.

Ključne riječi: biokompoziti; održivost; recikliranje; kemijsko recikliranje

1. Introduction

With the entry into the 21st century, significant progress within textile was achieved by returning to the usage of natural fibres as renewable raw materials, natural dyes and environmentally friendly finishing materials and processes [1-3]. This was especially evident in the production of fibre-reinforced composites as more and more sought-after structural materials that are designed to the targeted specific purpose and in wide range application [4, 5]. In accordance with the lifelong thinking philosophy, the implementation of eco-design created biocomposites, i.e.

composites in which at least one constituent part (reinforcing fibre or matrix) is based on biological or natural substances [6, 7], and a green composites are noted as a special type of it (Fig. 1) [8]. Namely, a green or eco-composite, is considered more desirable and environmentally friendly, and is defined as a composite material whose all components (both reinforcement and matrix) come from renewable sources while being biodegradable [6, 8-11]. As a result, the global production of biodegradable polymers originating from sustainable natural sources has increased by more than 400% in recent years, and the search for new and/or yet untapped natural fibres has become a challenge [12].

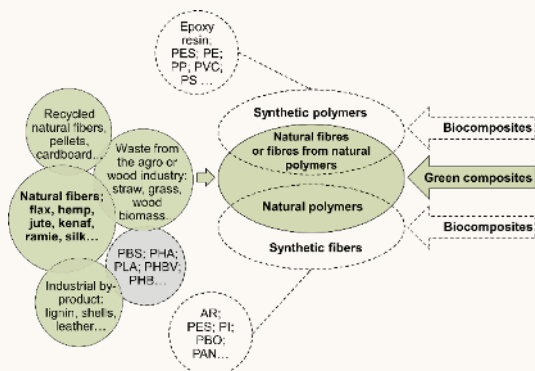


Figure 1. Biocomposites – by origin and composition

Although in general, biocomposites and especially green composites are considered more environmentally friendly compared to conventional fibre-reinforced composites, their proper disposal or efficient integration into recycling processes still represents a challenge. Namely, biodegradation irreversibly destroys fibrous and matrix raw materials, which may pose a problem in the future due to increasing urbanization, Earth's population, demand for food, etc. The imperative of a circular economy, as well as the growing demand for raw materials, have imposed the need for research into efficient recycling procedures for biocomposite waste materials. Recycling approaches for fibre-reinforced composites include mechanical, chemical, and thermal methods, each with its own advantages as well as limitations [13, 14].

Mechanical recycling refers to the mechanical shredding or grinding of waste composites. Despite the simplicity of this process, its main disadvantage is that the long fibres of the original composite are broken and degraded during the grinding process and therefore, the most valuable component of composite i.e. fibres cannot be reused for the same purpose [15, 16]. Almost the same is with thermal recycling of waste composites. While the fibres irreversibly degrade and cannot be used further, energy recovery from waste material is possible. Since chemical recycling converts composite waste back into secondary raw materials or recycled feedstocks, reduces the need for virgin resources [17] and stands out as a method with the potential for simultaneous recovery of both, fibres and polymer matrix in almost original form thus enabling their reintegration into the new production process (Fig. 2), all of which is in line with EU Green Deal [18] and circular economy.

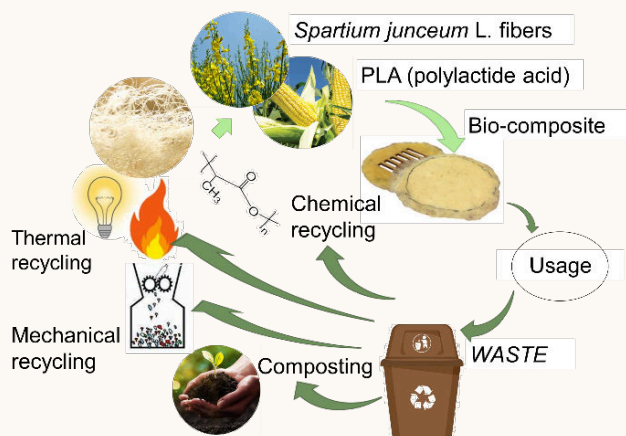


Figure 2. Possibilities of biocomposite recycling

2. Experimental part

Composting as one of the proven successful methods for sustainable biocomposite waste disposal at the end of their life cycle, also results in the loss of valuable raw materials. In order to overcome this, researchers are increasingly focused on alternative waste management strategies,

with particular emphasis on developing innovative and/or efficient recycling methods for waste biocomposites. The method that stands out for its ability to fully recover the fibrous raw material in its approximately original form and states is chemical recycling. Thus, the aim of this study is to investigate the possibility and applicability of chemical recycling of biocomposites made by reinforcing PLA as a matrix with *Spartium junceum* L. fibres. The research focuses on preserving the quality of the recovered *Spartium junceum* L. fibres after their extraction from the composite, and to ensure that the recycled fibres can be reused for the same or less demanding applications.

In accordance with the aim of this study, the investigation of the biocomposites chemical recycling potential is organized into several parts, as shown in Figure 3.

Before implementing a chemical recycling process, which aims to preserve the quality and quantity of fibres, it is necessary to select the most effective solvent for the matrix (which will not have a negative effect on the fibres), as well as the most efficient and environmentally friendly process. Therefore, the research in this study included the following procedures:

- preliminary investigations, which explored the dissolution potential of the PLA matrix in various solvents under different processing conditions;
- optimization of the chemical recycling process using the selected solvent to improve time and energy efficiency, and
- evaluation of fibres quality extracted from biocomposites, with the aim of determining their mechanical properties after the recycling process

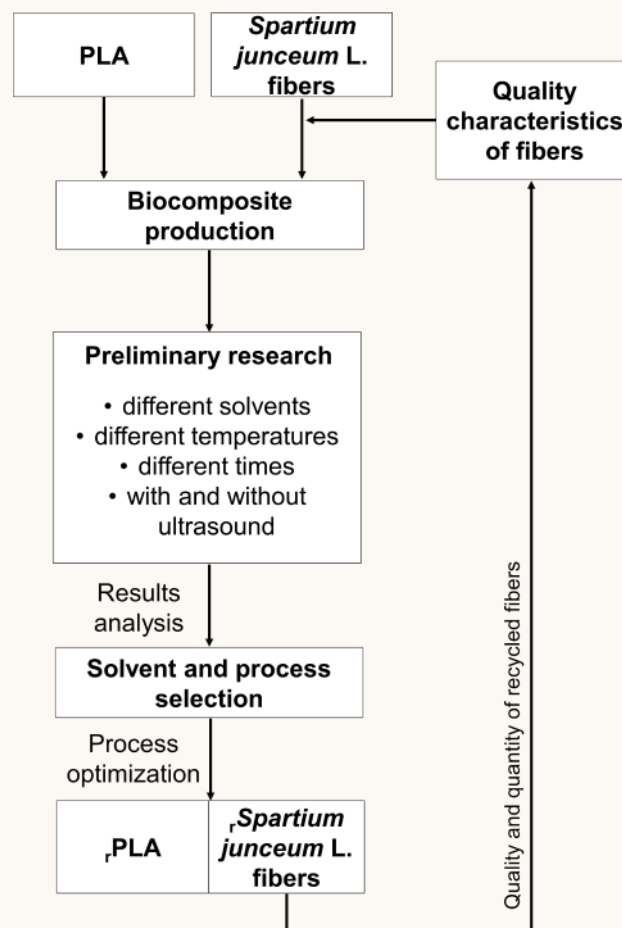


Figure 3. Research plan

2.1. Materials

For the purposes of this study, a unidirectional biocomposite was produced consisting of 20% by mass of *Spartium junceum* L. fibres embedded in a polylactic acid (PLA) matrix using a compression moulding process. The reinforcing fibres were extracted from broom plants harvested in the vicinity of Šibenik (Croatia), while for the matrix PLA Ingeo 6201D granules were used, with their physical properties shown in Table 1.

Table 1. Physical properties of PLA Ingeo 6201D

Specific gravity [g/cm ³]	Relative viscosity	Melting index [g/10 min]	Melt density [g/cm ³]
1.24	3.1	15 – 30	1.08

2.2. Chemical recycling process – matrix dissolution

Preliminary investigations - were primarily conducted to select most suitable/effective solvent for the PLA matrix and the method for performing the chemical recycling process of the biocomposite reinforced with *Spartium junceum* L. fibres. Five solvents (Fig. 4) were used, selected based on literature data, efficiency, cost-effectiveness, availability, and potential harmfulness. The conditions of temperature, time, and mechanical movement of the biocomposite sample in the solvent were varied during the process.

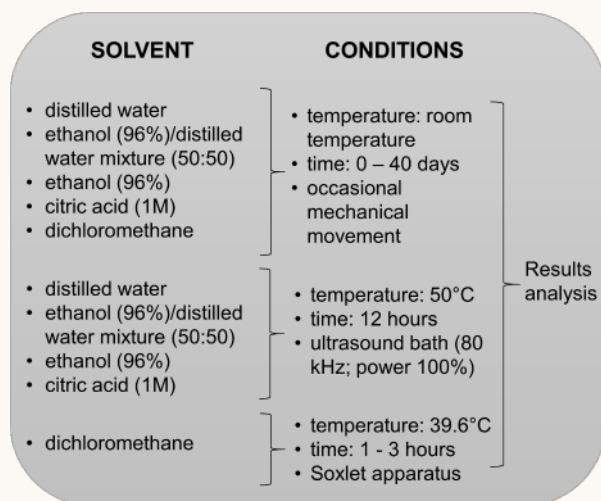


Figure 4. The matrix dissolution process of the researched biocomposite sample

*Extraction of *Spartium junceum* L. fibres using dichloromethane* - was carried out in two ways: at room temperature and with heating. The room temperature extraction lasted for two hours, with occasional mixing of the samples in the solvent at 10-minute intervals. The heated extraction process was conducted using a Soxhlet apparatus for periods of 1 hour (8 cycles), 2 hours (16 cycles), and 3 hours (24 cycles). After both processes and removal of the fibres from the solution, PLA matrix was separated from the solvent by solvent pre-distillation.

Process optimization - the efficiency of each chemical recycling process was determined through the following:

- measurement of the mass change of the tested samples in each solvent and the proportion of individual components;
- macroscopic surface analysis of the samples using a Dino-Lite Pro AM413T digital microscope with a magnification range of x20 to x230;

- microscopic analysis of the extracted fibres using an Olympus CH20 microscope upgraded with Dino-Eye digital camera;
- determination of the breaking force and elongation at break of the extracted fibres in accordance with the HRN EN ISO 5079:2020 standard [19], using a Vibrodyne 400 dynamometer by Lenzing;
- determination of the fineness of the extracted fibres in accordance with the HRN EN ISO 1973:2021 standard [20], using a Vibroscope 400 device by Lenzing.

3. Results and discussion

3.1. Chemical recycling of biocomposites – dissolution of the PLA matrix

Since one of the possible and relatively cost-effective methods of fibre-reinforced composites' chemical recycling is matrix dissolution, the possibility of dissolving the PLA matrix in various solvents was primarily investigated. Although PLA polymer is soluble in solvents such as acetone, benzene, chloroform, ethyl acetate, etc. [21], the primary factor in choosing solvents was their low toxicity, ease of handling, potential for regeneration, and their known non-destructive behaviour towards fibres. Table 2 shows the results of PLA matrix dissolution in different solvents and for various processing conditions.

Table 2. Dissolution of the PLA matrix in different solvents and under different conditions

Conditions: room temperature; occasional mechanical movement of the sample			
Solvent	Time	Mass change [%]	Observation
Distilled water	40 days	- 7.0	Apparently partial dissolution; sample softening
Ethanol (96%) / distilled water mixture (50:50)	40 days	- 7.3	Apparently partial dissolution; sample softening
Ethanol (96%)	40 days	- 7.8	Apparently partial dissolution; sample softening
Citric acid (1M)	7 days	/	Sample degradation
Dichloromethane	2 hours	- 78.2	Almost complete Dissolution of PLA

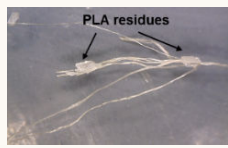

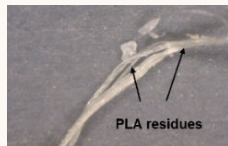

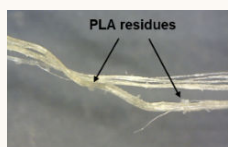

(frequency 80 kHz; power 100%)			
Solvent	Time	Mass change [%]	Observation
Distilled water	12 hours	- 1.5	Minimal dissolution; sample colour change
Ethanol (96%) / distilled water mixture (50:50)	12 hours	- 1.1	Minimal dissolution; sample colour change
Ethanol (96%)	12 hours	- 2.4	Minimal dissolution; sample colour change
Citric acid (1M)	12 hours	+ 3.6	Surface erosion of the composite
Conditions: temperature 39,6°C; Soxhlet apparatus			
Solvent	Time	Mass change [%]	Observation
Dichloromethane	1 hour	- 71.1	Almost complete Dissolution of PLA
	2 hours	- 73.8	Almost complete Dissolution of PLA
	3 hours	- 77.4	Almost complete Dissolution of PLA

Chemical recycling of the biocomposite reinforced with *Spartium junceum* L. fibers through the dissolution of the PLA matrix in various solvents showed that distilled water, ethanol, and their mixture were not suitable solvents for the PLA matrix. Although PLA can degrade in water over time, it does not dissolve under normal conditions, but instead slowly hydrolyses, especially in a heated environment.

The conducted research revealed that even with extended dissolution times (40 days), there was no significant mass loss of the biocomposite (mass loss of 7.0–7.8%), and thus no dissolution of the PLA matrix, although there was noticeable softening of the composite sample. The softened sample allowed mechanical extraction of some fibres from the tested composite through crushing and rolling. However, residual PLA matrix was still present on the extracted fibres (Tab. 3).

The highest amount of matrix residue was observed on the *Spartium junceum* L. fibres extracted after biocomposite exposure to distilled water, and the lowest amount was found on the fibres extracted from samples exposed to a 50:50 mixture of ethanol and distilled water. This indicates the need for additional cleaning of the fibres.

Table 3. Macroscopic and microscopic images of recycled *Spartium junceum* L. fibres after mechanical extraction

Solvent	Macroscopic image	Microscopic image
Distilled water		
Ethanol (96%) / distilled water mixture (50:50)		
Ethanol (96%)		

The use of citric acid (1M) as a solvent for the PLA matrix (at room temperature with occasional mechanical movement over a period of 7 days, Tab. 2) resulted in the destruction of the sample (Fig. 5.a) and degradation of the fibres (Fig. 5.b). This indicates that citric acid is either unsuitable for dissolving the PLA matrix or that a lower concentration of citric acid should be used.







Figure 5. Samples exposed to citric acid in period of 7 days: a) destruction of biocomposite and b) destruction of fibre

Dichloromethane proved to be the most effective solvent for the PLA matrix under the specified conditions (room temperature and occasional mechanical movement) since the matrix was almost completely dissolved within two hours. Specifically, the mass loss of the initial biocomposite was 78.2%, which is approximately equal to the mass fraction of the PLA matrix in the investigated composite (80% PLA matrix). This result indicates the need for additional extraction of the fibres after removing them from the PLA and dichloromethane solution. Therefore, in accordance with the standard procedure for extracting preparations from fibres, the investigated biocomposite was subjected to dissolution (extraction) of the PLA matrix using dichloromethane at elevated temperature in a Soxhlet apparatus. The results (Tab. 2) indicate that complete dissolution of the PLA matrix was not achieved during the extraction process, even after a duration of one to three hours at an elevated temperature (39.6°C). The mass loss after three hours was 77.4%, suggesting the need for prolonged extraction time. This is further supported by the partial residual presence of PLA on the fibres.

Since dichloromethane is an extremely harmful chemical for the environment and humans (bio-accumulative/toxic/carcinogenic) [22], and thus undesirable regarding sustainable development guidelines, an attempt was made to increase the solubility of PLA in the investigated solvents, which are more suitable for handling, by changing the dissolution conditions. Research on the dissolution of the PLA matrix in

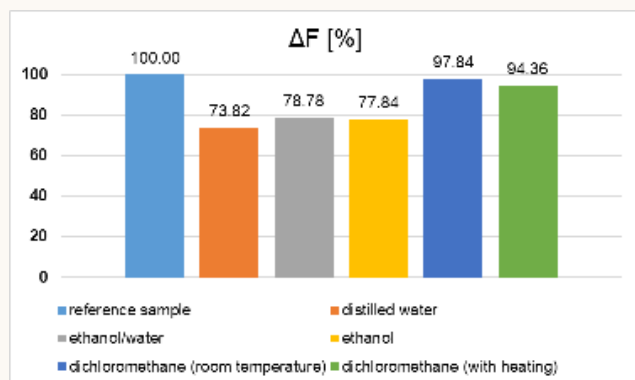
various solvents at a temperature of 50°C using an ultrasonic bath (frequency 80 kHz; power 100%) revealed minimal dissolution of the PLA matrix over 12 hours (the maximum continuous operating time of the ultrasonic bath). The observed mass reduction of the biocomposite samples ranged from 1.2% to 2.4% in distilled water, an ethanol and water mixture, and ethanol. Conversely, the use of 1M citric acid resulted in an unexpected mass increase of 3.6%. Additionally, exposure to the ultrasonic bath caused a colour change in samples treated with distilled water, the ethanol/water mixture, and ethanol, while the composite sample treated with 1M citric acid showed a surface change, i.e. surface erosion (Tab. 4).

Table 4. Macroscopic images of biocomposites after exposure to the ultrasonic bath

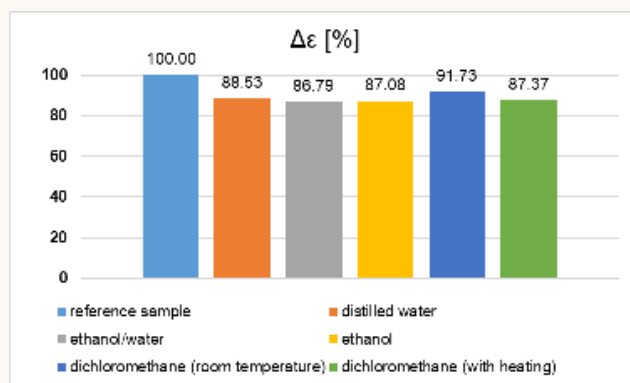
Solvent	Macroscopic image	Observation
Distilled water		color change
Mixture of ethanol (96%)/distilled water (50:50)		color change
Ethanol (96%)		color change
Citric acid		surface erosion

3.2. Chemical recycling of biocomposites – the quality of *Spartium junceum* L. fiber

On the recovered fibres obtained from the previously described processes, the breaking force and breaking elongation were determined. These included fibres extracted after matrix dissolution in dichloromethane (at room temperature and with heating), and fibres separated by mechanical process after exposure of the samples to distilled water, ethanol and water mixture and ethanol for a period of 40 days at room temperature with occasional mechanical movement. The results of the aforementioned tests are shown in Figure 6.



a)



b)

Figure 6. Quality of recovered fibres expressed through: a) breaking force and b) breaking elongation

From the graphs shown in Figure 6, it can be seen that the quality of the recovered *Spartium junceum* L. fibres, i.e. their mechanical properties, is best preserved by dissolving the PLA matrix using dichloromethane without heating (the smallest decrease in strength compared to the original fibres, which was 2.16%). A more significant reduction in breaking force (from 21.22% to 26.18%) was observed in fibres recovered after subjecting biocomposite samples to distilled water, ethanol and distilled water mixture, and ethanol. Although these solvents do not damage the fibres, the observed reduction in strength can be explained by damage incurred during the mechanical separation of fibres from the treated composite, i.e. the softened matrix, which damaged the integrity of the *Spartium junceum* L. technical fibres.

According to the research conducted on the possibility of dissolving the PLA matrix using different solvents and under various processing conditions, it can be concluded that dichloromethane is the most effective solvent for dissolving the PLA matrix of the tested biocomposite. Furthermore, the chemical recycling process is most suitably performed at room temperature with occasional mechanical movement for several reasons:

- dissolving PLA using dichloromethane at room temperature required a significantly shorter time (2 h) compared to other solvents used under the same conditions, which makes this process more time-efficient;
- heating is unnecessary, as a greater amount of PLA dissolves at room temperature compared to elevated temperatures, and in a shorter time, thereby improving energy efficiency;
- the quality of the recovered fibres is significantly higher than that of fibres recovered with other PLA solvents, as the process does not require additional mechanical separation, which could severely impact fibre quality; and
- the use of dichloromethane enables the recovery of both fibres and the PLA polymer.

Based on the previous findings, chemical recycling of the biocomposite made from *Spartium junceum* L. fibres and PLA matrix was conducted using dichloromethane at room temperature with occasional mechanical movement over a period of 2 hours on three parallel samples. The aim of this process was to determine the quantities of recovered fibres and matrix (shown in Tab. 5), as well as to evaluate fibre fineness and tensile strength (shown in Tab. 6).

Table 5. The proportion of reclaimed fibres and the PLA polymer (relative to their initial amounts incorporated into the manufactured biocomposite)

Sample	Proportion of <i>rSpartium junceum</i> L. fibres [%]	Proportion of rPLA [%]
1	99.3	99.7
2	100.1	99.0
3	99.0	99.8
Xs	99.5	99.5

Table 6. Results of determining the fineness and mechanical properties of virgin and reclaimed *Spartium junceum* L. fibres

	Reference sample			
	Fineness	Breaking strength	Elongation at break	Work of rupture
	Tt [dtex]	σ [cN/tex]	ϵ [%]	W [cNcm]
Xs	33.90	65.19	6.89	4.12
CV [%]	23.74	25.42	21.27	55.09
	<i>rSpartium junceum</i> L. fibres			
	Fineness	Breaking strength	Elongation at break	Work of rupture
	Tt [dtex]	σ [cN/tex]	ϵ [%]	W [cNcm]
Xs	33.82	54.74	5.51	2.70
CV [%]	26.90	26.65	21.33	51.64

Based on the obtained results, shown in Table 5, it can be concluded that the proportion of reclaimed fibres and PLA polymer is almost complete, which indicates the exceptional material efficiency of this recycling process. The process enables almost 100% recovery of the main components of the composite, further confirming its sustainability and environmental friendliness in terms of waste reduction and efficient resource utilization.

The presented results of the fibre fineness (Tab. 6) indicate that the fineness of recycled fibres is almost completely preserved, with a minimal increase of only 0.2% compared to the fineness of the original raw material. Given the high fineness variability of natural fibres, this change should generally not be considered significant.

As for the breaking strength (Tab. 6), the recycled fibres exhibit a 16.0% decrease compared to the reference sample, while elongation is reduced by 20%. Although these results differ slightly from the preliminary findings, it can still be concluded that the recycled fibres maintain an acceptable level of quality for their reuse, potentially even for the same application. However, their reuse is certainly appropriate in less demanding applications.

4. Conclusions

Sustainable development has imposed numerous demands on raw material producers and modern construction materials (composites / biocomposites). This is particularly evident in the increasingly stringent and demanding approaches to sustainable waste management. While biocomposites, through composting, were initially seen as a primary response to this issue, the potential future lack of raw materials and the imperative of a circular economy even for renewable resources have driven research into the recycling of biocomposites and/or recovery of their components. This has been especially highlighted in the field of natural fibre reinforced polymers, which are becoming increasingly prevalent in various application areas.

The conducted research within this study has demonstrated that by selecting the appropriate solvent (dichloromethane), optimizing the dissolution process (room temperature; occasional mild mechanical movement; two-hour duration of process), and solvent regeneration (solvent separation by extraction in a closed system), the investigated biocomposite (20% *Spartium junceum* L. fibre and 80% PLA polymer) can be suitably managed at the end of its life cycle through the renewal of its constituent components (*Spartium junceum* L. fibres and PLA polymer) in a high percentage (over 90%) and with satisfactory quality of reclaimed fibres. Although the proposed recycling method is efficient in terms of time, energy, and material efficiency, the toxicity of the selected solvent present a potential threat to both, human health and the environment. Therefore, it is essential to adhere to all safety precautions and closely monitor their implementation.

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