The use of PLA filled with fibrillar nanocellulose from wastepaper as an expansion joint material

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Abstract: The effect of nanocellulose (3 or 5 wt%) on the PLA properties was investigated. Moreover, the possibility of using such composites as an expansion joint material was considered. Nanocellulose was obtained from wastepaper by mechano-chemical treatment. The structure, impact strength, tensile strength of the composites and the adhesion to the cement were studied. It was observed that with the increasing nanocellulose content, the impact strength and tensile strength decreased because of weak interactions at the interface and formation of agglomerates.

Keywords: PLA, nanocellulose, composites, mechanical properties.

Zastosowanie PLA napełnionego nanocelulozą z makulatury jako materiału dylatacyjnego

Streszczenie: W pracy zbadano wpływ nanocelulozy (3 oraz 5% mas.) na właściwości PLA. Dodatkowo rozważono możliwość zastosowania tego typu kompozytów jako materiału dylatacyjnego. Nanocelulozę otrzymano z makulatury poprzez obróbkę mechano-chemiczną. Zbadano strukturę, udarność i wytrzymałość kompozytów na rozciąganie oraz adhezję do cementu. Zaobserwowano, że wraz ze wzrostem zawartości nanocelulozy udarność i wytrzymałość na rozciąganie zmniejszały się jako efekt słabych oddziaływań na granicy faz i tworzenia się aglomeratów.

Słowa kluczowe: PLA, nanoceluloza, kompozyty, właściwości mechaniczne.

Concerns about sustainability have sparked interest in polymers that are biodegradable, recyclable, and/or made from ecologically benign raw resources. Biomass-based polymers such as polylactic acid (PLA) are one alternative with several sustainability advantages, including decreased reliance on fossil fuel extraction, production from renewable resources, utilization of waste materials, and improved biodegradability. Compared to petroleum-based polymers, the production of PLA requires less fossil energy (about 25–55% less) because the starting materials used to make PLA are derived from renewable resources and not from fossil fuels [1–4].

The CO_2 emissions associated with the production of PLA can range from around 0.8 to 2.7 kg CO_2/kg of PLA. This is lower than the CO_2 emissions associated with the production of most petroleum-based polymers, which can range from around 2 to 5 kg CO_2/kg of polymer. This means that the production of polystyrene can emit 1.5 to 2 times more CO_2 compared to the production of PLA [5].

PLA is brittle compared to other polymers which can make it prone to cracking or breaking under certain types of stress [6]. PLA/nanocellulose composites offer advantages over pure PLA. Nanocellulose (NC) is a renewable, biodegradable, and environmentally friendly material that can be derived from various sources, such as wastepaper, cotton, and wood pulp [7–10].

Nanocellulose has unique properties such as high surface area and surface energy, which enhance the interaction between the nanocellulose and the PLA matrix, leading to improved bonding and dispersion of the nanocellulose particles within the composite. This can result in improved mechanical properties, as well as enhanced thermal and barrier properties. Moreover, nanocellulose can act as a reinforcing filler in PLA composites, increasing the stiffness and strength of the material [11–15]. This can make PLA-nanocellulose composites suitable for applications in the construction industry, such as in expansion joint fillers, where mechanical strength and durability are critical. Adding nanocellulose to PLA can result in a composite material with improved properties

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compared to pure PLA, making it a promising alternative material for bitumen-based expansion joint fillers.

Expansion joints are used in construction to absorb the movement and deformation of building materials due to thermal and structural changes [16,17]. Construction expansion joints are in different shapes and sizes, depending on where they are used and the construction requirements:

– Linear expansion joints – are tiles or strips placed between two sections of sidewalk (for example, between concrete paving or floor slabs). Linear expansion joints are usually rectangular or square in shape, and their dimensions depend on the width of the space they are to fill.

– Angular expansion joints – used where the angle between two parts of the structure is bigger than 90 degrees (for example, in the corner of a building). Angular expansion joints are usually trapezoidal or wedge-shaped.

– Bridge expansion joints – used in bridge structures to absorb forces due to rotational and sliding movements of the bridge. Bridge expansion joints are rectangular or trapezoidal in shape and usually consist of metal plates.

– Facing expansion joints – used where two structures meet at the end (for example, when connecting walls to the roof). Face expansion joints are usually trapezoidal or wedge-shaped.

The forces that act on construction expansion joints are primarily thermal forces resulting from the expansion and contraction of materials as a function of temperature, as well as forces resulting from static and dynamic loads. Expansion joints must be designed to withstand these forces and prevent damage to the structure. The appropriate size, shape and materials of the expansion joints are selected depending on the type of forces acting on them and the structural requirements. The selection of materials for expansion joints depends on several factors such as the magnitude of movement, exposure to environmental conditions, and the type of structure being built. Some commonly used materials for expansion joints in construction include neoprene, silicone, polyvinyl chloride, polystyrene foam. In the construction industry, the most used material for construction expansion joints is polystyrene foam. However, the use of polystyrene foam has negative impacts on the environment and human health, and alternatives such as biodegradable or recyclable materials should be considered.

Therefore, in accordance with the idea of a circular economy and the principles of sustainable development, fibrillar nanocellulose (NC) from recycled paper was used as a filler for PLA. The effect of nanocellulose (NC) addition (3 or 5 wt.%) on the PLA properties was investigated. Moreover, the possibility of using PLA/NC composites as an expansion material was considered. NC was obtained from wastepaper by mechano-chemical treatment. The structure, impact strength, tensile strength of the composites and the adhesion to the cement were studied.

EXPERIMENTAL PART

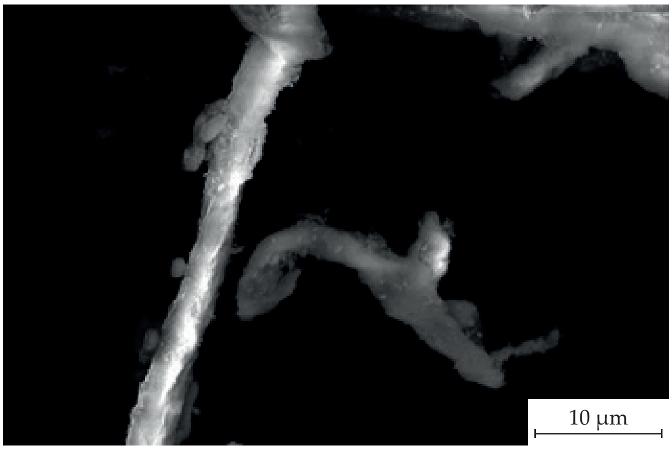
Materials

PLA (Luminy® L175, TotalEnergies Corbion, The Netherlands) in the form of crystalline white pellets with density of 1.24 g/cm^3, MFR = 8 g/10 min (2.16 kg, 210°C) and melting temperature 175°C was used as the polymer matrix.

Nanocellulose preparation and characterization

Contaminants such as staples and plastics were removed from the paper prior to the process. The paper was then shredded and mixed with chemicals in a high-shear mixer (10 min) to break down the cellulosic fibers and remove the non-cellulosic components. The resulting pulp was treated with a sodium hydroxide solution and the process continued in a high-speed ball mill (Pulverisette-5, Fritsch, Germany) to obtain nanofibrillar cellulose (NC). Sonication was used to separate the NC fibers. Figure 1 shows the SEM images of the obtained nanocellulose. Fig. 2a shows cellulose pulp, and Fig. 2b characteristic elongated cellulose fibers forming clusters because of strong agglomeration of particles through hydrogen interactions.

a)



b)

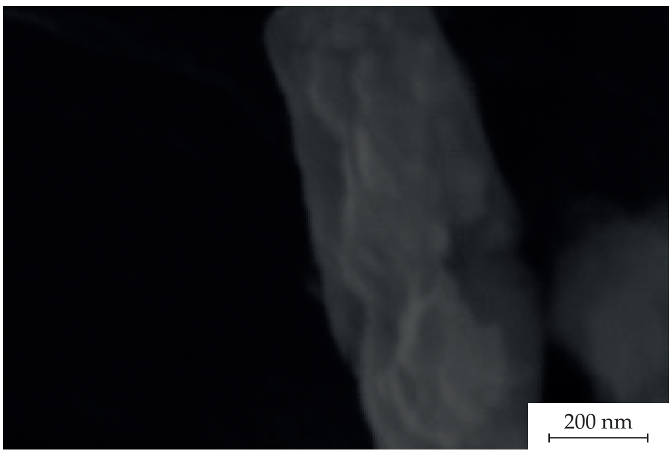


Fig. 1. SEM images of the obtained nanocellulose

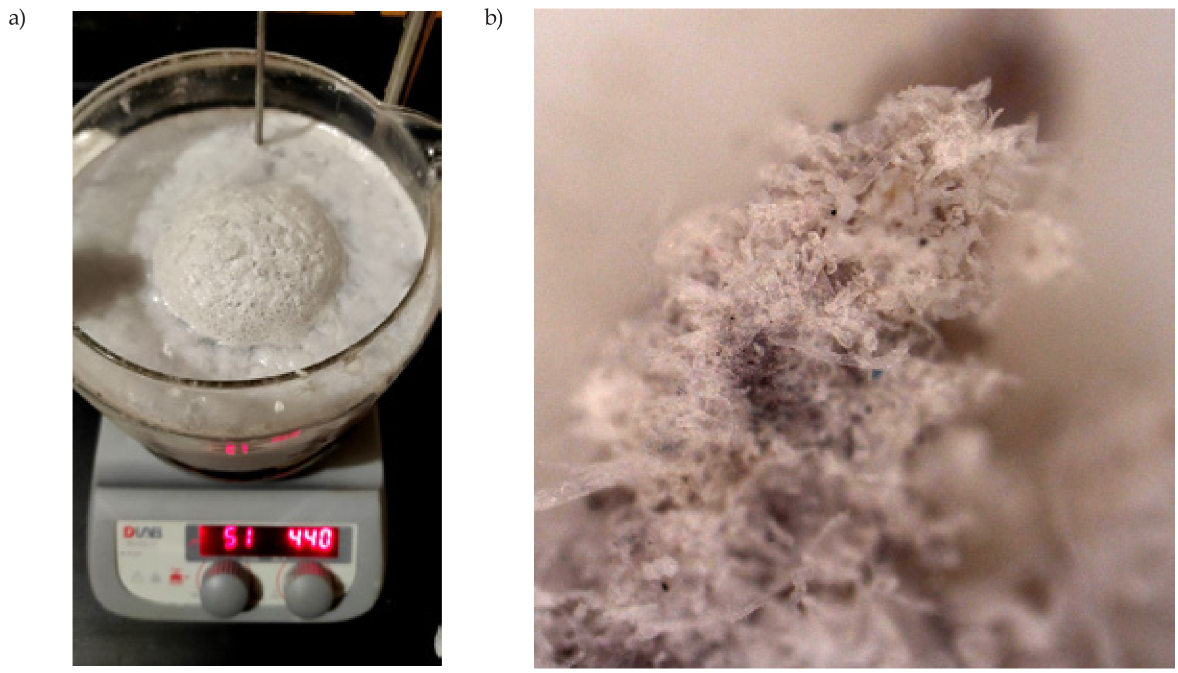


Fig. 2. Cellulose pulp (a), fibrillar nanocellulose (b)

Composites preparation

The homogenization process of PLA with 3 or 5 wt% NC was conducted using a twin-screw extruder (Sline EHP-2X 20, Zamak Mercator) with a screw diameter of 20 mm and a length of 40D. The process was carried out at a temperature of 145–165°C and a screw speed of 700 rpm. Tests specimens were injection molded at 155–175°C using an Arburg 320C single-screw injection machine (Allrounder 320C, Arburg, Loßburg, Germany).

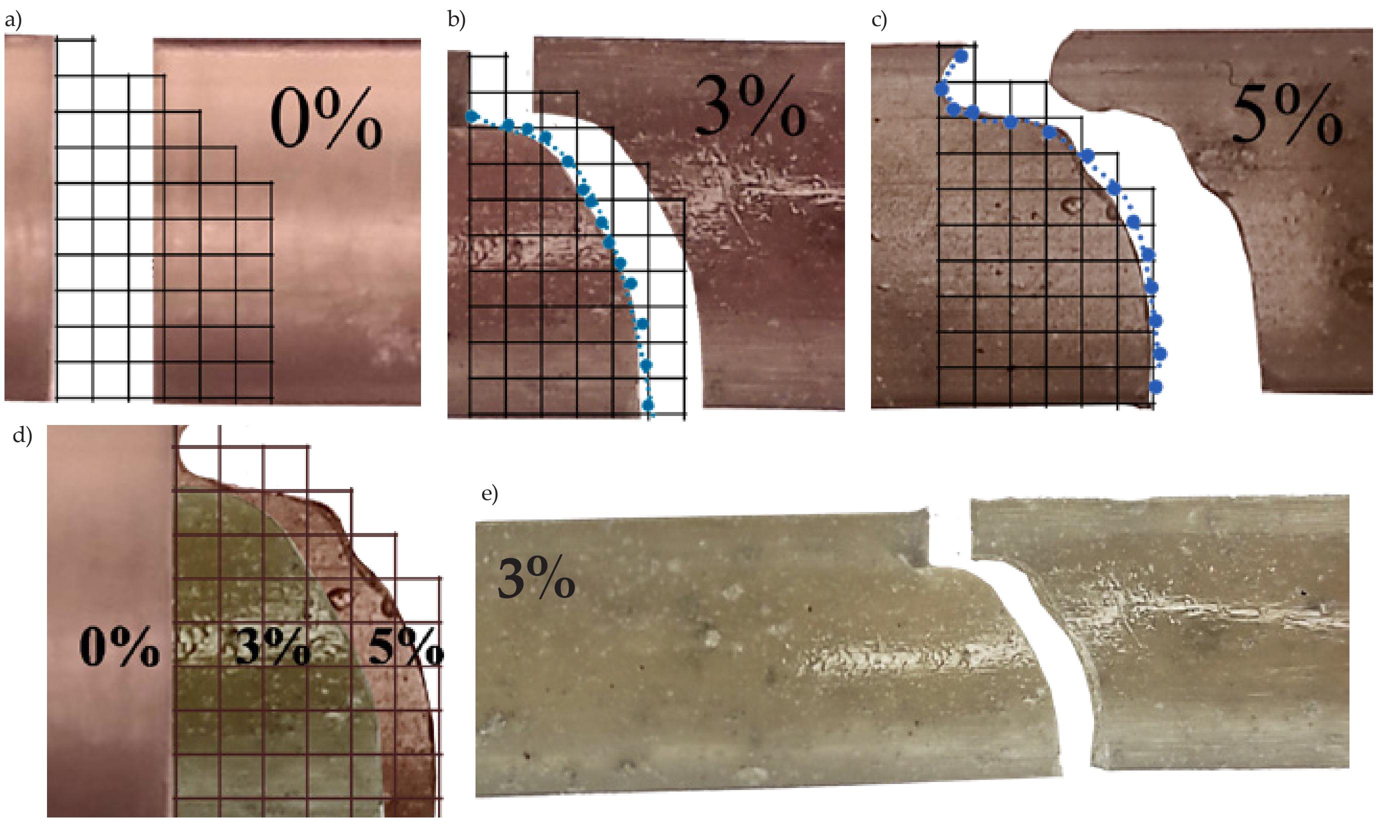


Fig. 3. The method of evaluating PLA/NC impact resistance: a) 0 wt% NC, b) 3 wt% NC, c) 5 wt% NC, d) comparision of all samples, e) 3 wt% NC (the whole sample after the test)

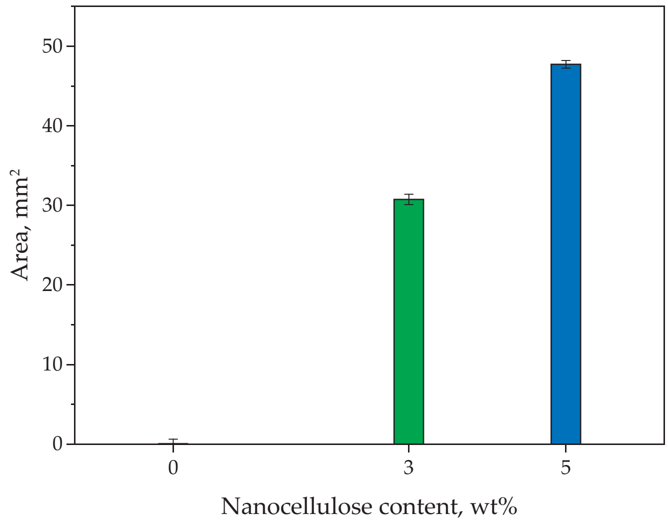


Fig. 4. Calculated damage fields of PLA/NC composites

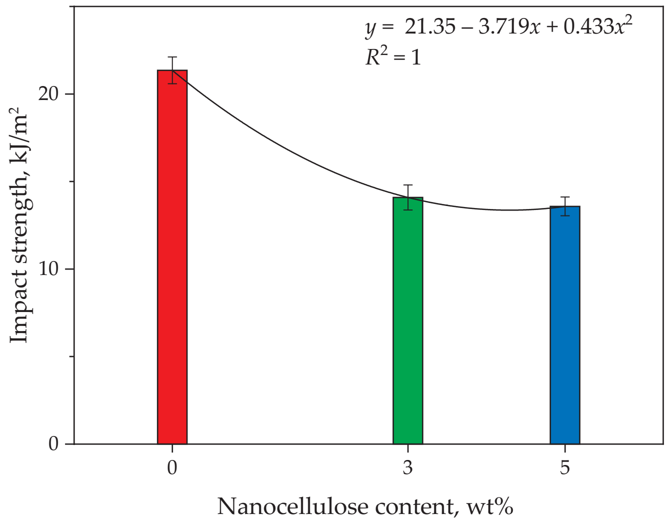


Fig. 5. Impact strength of PLA/NC composites

Methods

The composites morphology was conducted using a scanning electron microscope (SEM, Phenom ProX, Phenom-World Holding B.V, The Netherlands) operating at 10 kV. The nanocellulose structure was characterized using NovaNanoSem 450 (FEI Europe, The Netherlands) scanning electron microscope. The samples were covered with gold.

Tensile properties were determined using a universal testing machine (Z010, Zwick/Roell, Ulm, Germany) in accordance with PN-EN ISO 527. During this test, specimens with a length of 150 mm, a width of 10 mm, and a thickness of 4 mm were subjected to tension as specified in the mentioned standard. Measurements were made at a transverse movement speed of 50 mm/min using a 5 kN load cell.

Unnotched impact strength was measured using a Charpy hammer according to PN-EN ISO 8256 standard.

To assess the adhesion of the cement slurry to the PLA-nanocellulose composite, the pull-off test was used, consisting in applying a tensile force to the cement-PLA-nanocellulose contact sample until failure occurred. The force required to break the sample is proportional to the strength of the bond between the two materials.

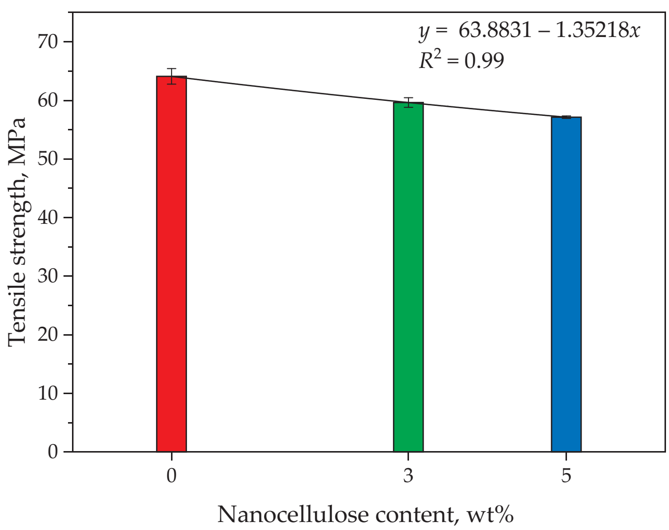


Fig. 6. Tensile strength of PLA/NC composites

RESULTS AND DISCUSSION

The method of evaluating PLA/NC composites impact resistance is shown in Fig. 3.

Comparing the destruction fields for all samples (Fig. 3d), it can be seen that it depends on the NC content. For PLA, the area of the destruction field was 0. This field increased with the increase of the NC content in PLA. Based on the measurements, the equations of the curves describing the sample break were developed, equation 1 for 3 wt% NC and equation 2 for 5 wt% NC. Calculated damage fields of PLA/NC composites are presented in Fig. 4.

$$\int_0^x (-0.0097x^6 + 0.1479x^5 - 0.8257x^4 + 1.9675x^3 - 1.16717x^2 + \\ -0.4289x + 8.9666)dx + \int_0^{x_1} (0.7982\ln x + 10.285)dx \quad (1)$$

$$\int_0^x (-0.1185x^3 + 0.4186x \ -0.733x + 8.2054)dx \quad (2)$$

The pattern of forces acting on the expansion joint material is similar to the forces generated during the impact test. Such a test can show how the material will behave in real conditions. The impact strength of samples with 3 and 5 wt% NC content decreased by 34% and 36%, respectively, compared to pure PLA (Fig. 5). The reduction in impact strength may be due to the formation of NC agglomerates because of poor adhesion between PLA and NC. Further research should focus on increasing interactions at the matrix-filler interface by using a compatibilizer, e.g. maleated PLA [12].

Attention should also be paid to the destruction scheme of samples with 3 wt% and 5 wt% NC content. As can be seen, the PLA/NC composites did not have a "straight line of destruction" (Fig. 3). This can be advantageous if a PLA/NC

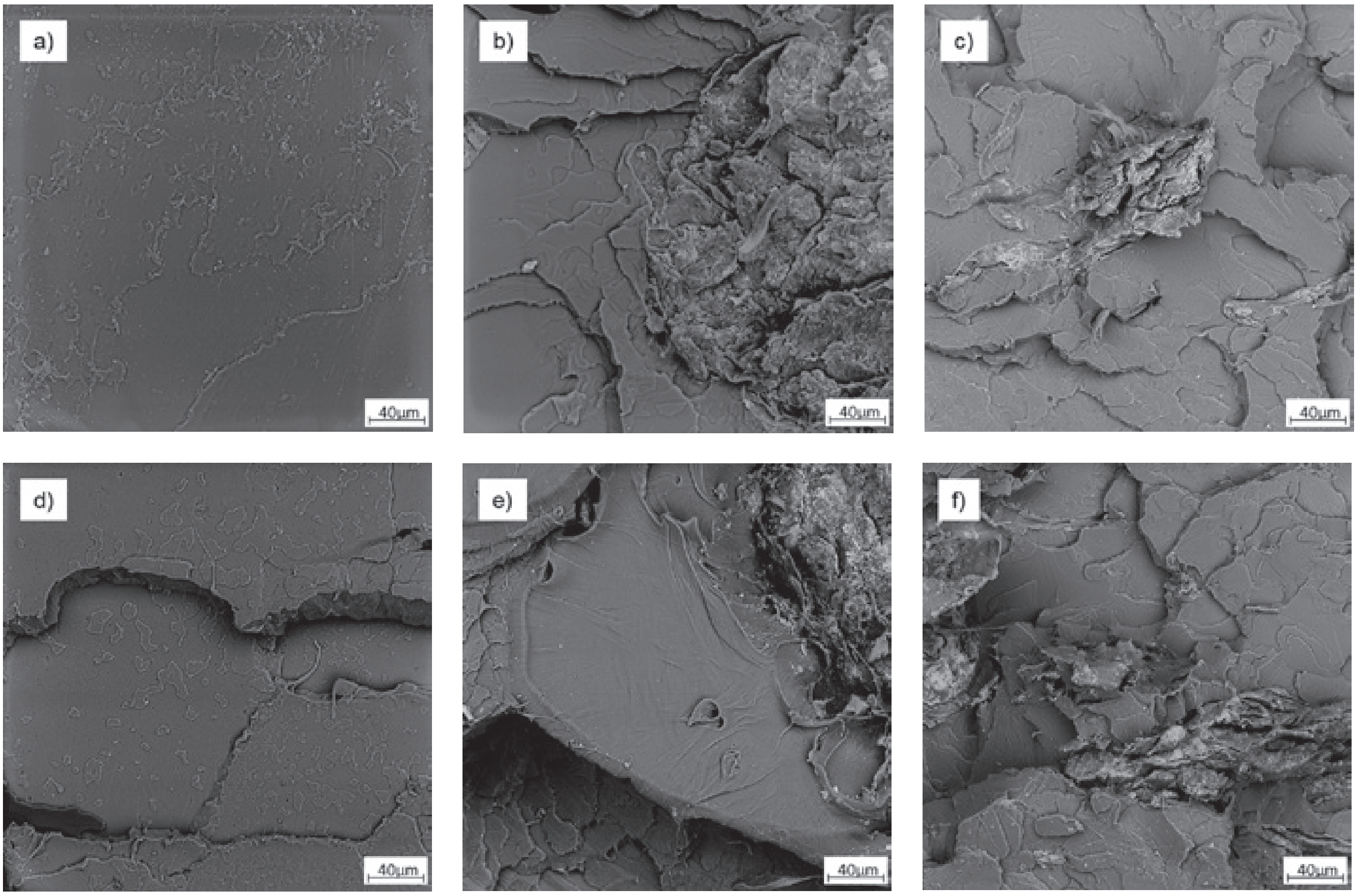


Fig. 7. SEM images of PLA/NC composites after impact test: a) 0 wt%NC, b) 3 wt% NC, c) 5 wt% NC, and after tensile test: d) 0 wt% NC, e) 3 wt% NC, f) 5 wt% NC

composite was used as the expansion joint material, because it will not be destroyed immediately, but it can work with the structure, which can contribute to a longer life of the material. It is also worth looking at the impact strength trendline. With a content of 10 wt% NC impact strength is approx. 28 kJ/m^2 (29% increase compared to pure PLA).

The effect of the NC addition on the tensile strength of PLA/NC composites is shown in Fig. 6. The tensile strength decreases with the increase in the NC content by 7% and 11%, respectively. This behavior can be explained by the poor distribution of nanocellulose in the PLA matrix as well as the formation of nanocellulose clusters. In addition, the nanocellulose content may also be too low. According to other studies, the tensile strength of PLA/NC composites increased after adding 10–30 wt% NC [18, 19]. Therefore, future research should

a)
b)

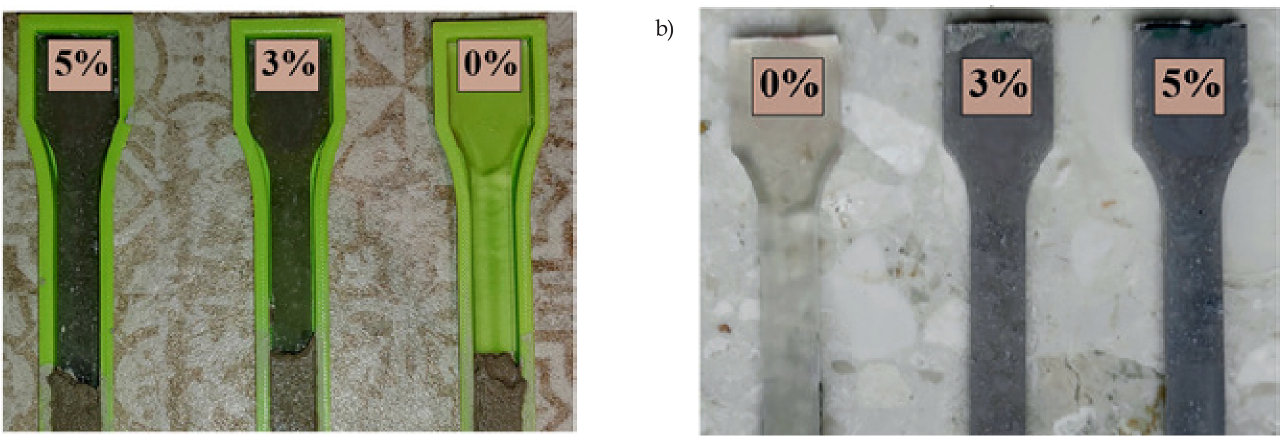


Fig. 8. Appearance of the samples before (a) and after (b) the adhesion test

focus on increasing the NC content and its effect on the mechanical properties of PLA.

The fracture surfaces after tensile and impact tests were analyzed by scanning electron microscopy. It was noticed that the addition of nanocellulose to PLA affects the cracking mechanism (Fig. 7). PLA exhibits brittle fracture with smooth surface. On the other hand, the fracture surface of PLA/NC composites is rougher, and the roughness increases with increasing NC content. Ramps and beams were observed on the fractured surface. As indicated in the literature, they are oriented parallel to the direction of global crack propagation [20]. The fracture surfaces of the composites with nanocellulose (Fig. 7) after the impact and tensile tests indicate a lack of compatibility between the fiber and the matrix and the formation of NC clusters and agglomerates. The presence of small voids and drawn polymer fibers was observed. The lack of compatibility may cause some kind of microcracks, which is beneficial from the energy consumption point of view [21]. Further research should focus on improving the dispersion of nanocellulose in the matrix to avoid the formation of nanocellulose clusters.

The adhesion of cement to biocomposites is a key factor in the development of sustainable and environmentally friendly building materials. The pull-off test was used to evaluate the adhesion of cement paste to PLA/NC composites. The tensile force required to break the cement-PLA/NC bond is a measure of the adhesion between materials. The lack of adhesion between the PLA/NC composite and cement paste was observed, which may be an advantage when using it as a dilatation material (Fig. 8). The cement paste can be easily removed from the composite surface. This can be particularly useful during processes where it is desired to remove excess cement mortar or its residues. If the cement mortar does not adhere to the composite, cracking and damage are less likely.

CONCLUSIONS

The effect of NC on the structure, mechanical properties and adhesion to cement was investigated. With the increase in the content of nanocellulose, the impact strength and tensile strength decreased, which is the result of the incompatibility of the filler with the polymer matrix and the formation of agglomerates. The lack of adhesion of the PLA/NC to cement can be an advantage in applications where it is necessary to remove excess cement or its residue from the surface of the material without damage. PLA/NC composites as dilatation materials can replace the commonly used polystyrene as more environmentally friendly and sustainability materials.

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