

Tall oil based rigid polyurethane foams thermal insulation filled with nanofibrillated cellulose^{*)}

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Abstract: Two types of biopolyols based on tall oil were used for the preparation of rigid polyurethane (PUR) foams. High functionality biopolyol was synthesized from tall oil fatty acids by epoxidation and subsequent oxirane ring-opening with trimethylolpropane and tall oil esterification with triethanolamine was carried out to obtain low viscosity biopolyol. The optimal dispergation method with sonication was applied to obtain rigid PUR foams with 0–1.5 wt % of nanofibrillated cellulose. The influence of nanofibrillated cellulose content on the rigid PUR foams' closed-cell content, density, thermal conductivity, compression strength, and compression modulus was evaluated. Addition of NFC fiber into rigid PUR foam structure slightly increased compression strength and Young's modulus.

Keywords: rigid polyurethane foams, nanofibrillated cellulose.

Sztywne pianki poliuretanowe na bazie oleju talowego napełnione nanofibrylną celulozą

Streszczenie: Do przygotowania sztywnych pianek poliuretanowych (PUR) napełnionych nanofibrylną celulozą (NFC) użyto dwa rodzaje biopolioli na bazie oleju talowego. Polioli o dużej funkcjonalności syntetyzowano metodą epoksydacji i otwarcia pierścieni oksiranowych trimetylopropanem, natomiast polioli o małej funkcjonalności otrzymano metodą estyfikacji oleju talowego trietanoloaminą. W celu uzyskania równomiernej dyspersji nanofibrylnej celulozy w sztywnych piankach wykorzystano metodę sonikacji. Zawartość napełniacza wynosiła 0–1.5% mas. Analizowano wpływ dodatku nanofibrylnej celulozy na zawartość komórek zamkniętych, gęstość, przewodność cieplną, wytrzymałość na ścislenie oraz moduł Younga wytworzonych pianek PUR. Stwierdzono że dodatek NFC powoduje nieznaczne zwiększenie wytrzymałości na ścislenie oraz modułu Younga pianek.

Słowa kluczowe: sztywne pianki poliuretanowe, nanofibrylna celuloza.

Bio-based polymers have attracted significant attention over the last decade in scientific community as well as from industrial stakeholders due to environmental concerns and depleting fossil resources [1]. Development of bio-based PUR materials has also been intensively studied, as one of their main component – polyols can be easily derived from renewable feedstock. Polyurethane (PUR) materials are one of the most significant polymers as they are used in a wide range of applications such as, adhesives, coatings, sealants, elastomers as well as flexible and rigid polymer foams [2].

Rigid PUR foams are applied as a thermal insulation material in civil engineering as well as in appliance industries. Rigid PUR foams have an excellent thermal

insulation property due to their morphology where the low thermal conductivity is derived from the closed cells of the material and the blowing agent gas trapped inside the cells.

The majority of bio-based polyol feedstock used for rigid PUR foam development is based on vegetable oils [3, 4], such as soybean oil [5–7], rapeseed oil [8–10], sunflower oil [11], palm oil [12], *etc.* The most of bio-based polyols are synthesised via vegetable oil epoxidation and oxirane-ring opening with different nucleophilic reagents [9, 13, 14]. However, vegetable oil use as a raw material for polymer production has raised a discussion as vegetable oils are also used for food and feed production. An appealing alternative feedstock for bio-based polyols could be tall oil, which is a side stream of cellulose pulping process. Tall oil has also been used to synthesise polyols for PUR material production. Two processes have been explored, the first, esterification of tall oil carboxylic groups with polyfunctional alcohols such as diethanolamine and triethanolamine [15–18] for production of low functionality polyols, and second, epoxy-

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dation of tall oil fatty acids (TOFA) and subsequent oxirane-ring opening and esterification of carboxylic groups with polyfunctional alcohols to synthesise polyols with high OH group functionality [19–21]. Both type of polyols were successfully used to develop good quality rigid PUR foam thermal insulation [21, 22].

An improvement of rigid PUR foam properties can be achieved by development of polymer foam and fiber composite. Different fibers have been used for this purpose such as glass fibers [23], carbon fibers [24], carbon nanotubes [25], flax fibers [26] and wood flour [27]. The addition of bio-based fibers in rigid PUR foams to improve material properties is advisable because it increases renewable material content.

Cellulose micro/nanofibers were successfully used to improve the dimensional stability and mechanical properties of bio-based rigid PUR foams [28]. It has been reported that nanocellulose fibers improve rigid PUR foam compression strength and Young's modulus [29, 30]. Cellulose fiber oxidation with ammonium persulfate is one of the most optimal routes to produce carboxylated cellulose nano/microfibers [31–33].

In this study, bio-based rigid PUR foam and nanofibrillated cellulose (NFC) composites were developed in order to improve material's properties. Different NFC fiber dispersion methods (high shear mixing with and without sonication) into polyols have been studied and the most optimal was selected for composite development.

EXPERIMENTAL PART

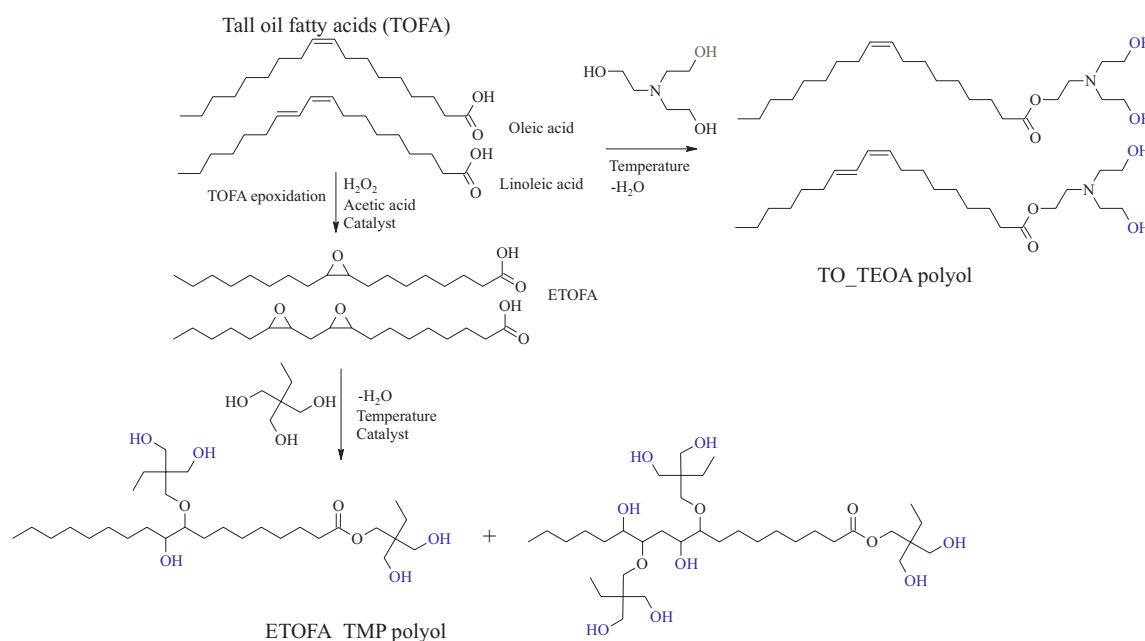
Materials

Following materials for biopolyol synthesis and analysis were used: TOFAs (trade name FOR2) with a high content

of fatty acids (>96%), and low content of rosin acids (1.9%) and unsaponifiables (1.8%) was ordered from Forchem Oyj (Rauma, Finland); hydrogen peroxide, puriss p.a., 35%; glacial acetic acid (EtOOH), puriss 99.8%; 4-(dimethylamino)pyridine (DMAP), reagent plus, 99%; acetanhydride, puriss, 99%; dichloromethane, puriss p.a., ACS reagent; *N,N*-dimethylformamide (DMF), ACS reagent, 99.8%, water content 150 ppm; potassium hydroxide, puriss, 85%; potassium iodide, ACS reagent, 99%; tetraethylammonium bromide, reagent grade, 98%; perchloric acid, ACS reagent, 70%; anhydrous sodium sulfate, puriss; trimethylolpropane (TMP), reagent grade, 97%; lithium perchlorate, ACS reagent, 95.0% were ordered from Sigma-Aldrich (Schnellendorf, Germany). Amberlite IR-120 H, strongly acidic, hydrogen form and sodium thiosulfate fixanal 0.1 M were ordered from Fluka (Bucharest, Romania). Triethanolamine (TEOA) 99.2% (Huntsman, Rotterdam, Netherlands) was used as purchased.

For the production of rigid PUR foams following materials were used as purchased: glycerol – technical grade (Sigma-Aldrich, Germany); tris(1-chloro-2-propyl)phosphate (TCPP) as a flame retardant (Albermarle, UK); tertiary amine-based catalyst PC CAT NP10® and 30 wt % of potassium acetate in diethylene glycol (PC CAT TKA 30®) (Air Products and Chemicals Inc., Netherland); Niax Silicone L-6915 as a surfactant (Momentive Performance Materials Inc., Germany) and *c*-pentane as a physical blowing agent (Sigma-Aldrich, Germany). Desmodur 44V20 L was used as the isocyanate component for all PUR materials. It is a solvent-free product based on 4,4'-diphenylmethane diisocyanate (MDI) and contains oligomers of high functionality (Covestro, Germany). The average functionality f_n of the used isocyanate was 2.8–2.9 and NCO groups content was 31.5 wt %.

Carboxylated NFC was produced from total chlorine free bleached birch Kraft pulp by ammonium persulfate



Scheme A. Idealized scheme of biopolyol syntheses from tall oil – adapted from [21]

Table 1. The formulations of rigid PUR foams with different NFC content

Components		Rigid PUR foams with different NFC content, wt %			
		NFC_0%	NFC_0.5%	NFC_1.0%	NFC_1.5%
Polyols	TO_TEOA	10.0	10.0	10.0	10.0
	ETOFA_TMP	85.0	85.0	85.0	85.0
	Glycerol	5.0	5.0	5.0	5.0
NFC		0	1.85	3.73	5.60
Blowing agents	Water	1.9	1.9	1.9	1.9
	c-pentane	15.0	15.0	15.0	15.0
Catalysts	Amine catalysts	3.5	3.5	3.5	3.5
	PC CAT TKA 30®	1.5	1.5	1.5	1.5
Surfactant	L6915	2.5	2.5	2.5	2.5
Flame retardant	TCPP	29.5	29.5	29.5	29.5
Isocyanate	MDI	215.0	215.0	215.0	215.0

oxidation with ultrasonic and mechanical treatment as reported previously by Filipova *et al.* [34]. The diameter of NFC fibrils was 20–300 nm, Zeta potential value of suspension was -26.9 ± 1.8 mV and crystallinity index 74.3% [34].

Biopolyol synthesis

Two types of biopolyols from tall oil were synthesized: tall oil/triethanolamine (TO_TEOA) and ETOFA_TMP polyol. TO_TEOA polyol was obtained by tall oil esterification with TEAO, and ETOFA_TMP – by oxirane ring-opening of epoxidized tall oil fatty acids (ETOFA) and subsequent esterification with trimethylolpropane (TMP). Idealized reaction schemes are given in Scheme A and more detailed polyol syntheses and used materials are described in previous investigations by Cabulis *et al.* and Kirpluks *et al.* [21, 35].

Preparation of NFC dispersion into polyol mixture

The water dispersion of NFC produced by ammonium persulfate method was lyophilized (by Freeze dryer LyoPro3000; refrigeration down to -30°C , drying at 50–100 Pa pressure) and mechanically crushed. The dry mass of NFC is expressly hygroscopic and therefore, before mixing NFC into a mixture of polyols, the moisture content was determined by an infra-red moisture analyzer A&D Weighing MX-50 Moisture Balance. If the moisture content exceeded 6%, the NFC was further dried in a vacuum oven at a temperature of 60°C and pressure of 200 Pa. The water content in the NFC was taken into account in the preparation of the NFC-polyol dispersion.

To prepare NFC-polyol dispersion, the calculated weight of the dry NFC was mixed with ETOFA_TMP polyol for 20 min using a High shear mixer Silverson L-5M-A. The temperature of the dispersion was monitored not to exceed 70°C to avoid NFC degradation. It was cooled in cold water bath. Afterwards dispersion was sonicated for 30 min with the Hielscher ultrasonic processor UP200Ht.

Preparation of rigid PUR foams

An optimized PUR foam formulation was selected from previous investigations [21]. The rigid PUR foams were prepared by free-rising method in a mold at a room temperature. At first, polyol systems according to the formulations presented in Table 1 were mixed in a 0.500 dm^3 plastic beaker. Then NFC was mixed with polyol system with High shear mixer Silverson L-5M-A for 20 min. NFC-polyol system dispersion then was sonicated with the Hielscher ultrasonic processor UP200Ht (6 cycles, 5 min each, power 120 W, amplitude 40%, pulse 70%). Afterwards the isocyanate was added and mixed for 15 s at a speed of 2000 rpm. Then the mixture was quickly poured into an open vertical mold [$30 \times 30 \times 10$ (cm^3)]. The height of prepared PUR foams was ~ 10 cm. The foams were conditioned for 24 h at a room temperature. The samples were named according to the NFC content in foams.

Methods of testing

Biopolyol characterization

The obtained biopolyols were characterized by hydroxyl and acid values that were determined using titrimetric methods according to DIN 53240-2:2007 and DIN 53402:1990 testing standards. The viscosity of polyols was analyzed at 25°C using Thermo Scientific HAAKE (Medium-High Range Rotational Viscometer). The moisture content was determined by Karl Fisher titration using Denver Instrument Model 275KF automatic titrator.

Polyol structure was analyzed by Fourier Transform Infrared (FT-IR) spectrometry data, which were obtained on a Thermo Scientific Nicolet iS50 spectrometer at a resolution of 4 cm^{-1} , 32 scans. The FT-IR data were collected using attenuated total reflectance technique with ZnSe and diamond crystals. Size exclusion chromatography (SEC) from Knauer, equipped with refractive index detector (Detector RI) and polystyrene/divinylbenzene matrix

gel column with a measurement range up to 30 000 Da at tetrahydrofuran (THF) eluent flow of 1.0 cm³/min, was used to analyze the number average molecular weight (M_n), number average functionality (f_n) and polydispersity index (p_d) of the synthesized biopolyols. Poly(methyl methacrylate) standards with molecular mass in-between 102–18 700 Da were used to create a calibration curve. The polyols' f_n was calculated based on hydroxyl values OH_{val} and molecular weight M_n as seen from Eq. (1) [36].

$$f_n = \frac{M_n \cdot \text{OH}_{\text{val}}}{56110} \quad (1)$$

Characterization of NFC dispersion into polyol mixture

Water content of the ready NFC-polyol dispersion was determined by Karl Fischer titration and it was taken into account in the further development of PUR formulations. Microscopic observations of NFC-polyol dispersion before and after sonication were performed by optical microscopy (OM) Leica M8 in polarized light mode. The viscosity of polyol and 1 wt % NFC-polyol dispersion was measured at 25°C temperature with Medium-High Range Rotational Viscometer Thermo Scientific HAAKE.

Rigid PUR foam characterization

The samples of prepared rigid PUR foam blocks for different tests were cut using a band saw and afterwards the samples were conditioned for at least 24 h at a room temperature. The apparent density of obtained PUR foams was tested according to ISO 845:2006 standard and closed cell content – according to ISO 4590:2003 – for specimens with dimension 10 × 3.5 × 3.5 (cm³). The cellular structures of PUR samples were characterized using SEM Tescan TS 5136 MM with secondary electron detector. The samples were coated with gold using sputter coater Emitech K550X (current 25 mA, coating time 2 min). The obtained SEM images and data were processed with VEGA TC computer software. The compression strength and modulus of elasticity parallel and perpendicular to foaming direction of rigid PUR foams were tested according to the requirements of ISO 844:2009 standard on testing machine Zwick/Roell Z100 (maximum load-cell capacity 1 kN, the deformation rate: 10 %/min) for cylinder specimens with diameter and height of ~20 mm. Six specimens were analyzed for each PUR foam formulation. The thermal conductivity coefficient (λ) was tested using Linseis Heat Flow Meter 200 according to ISO 8301:1991 standard

at an average temperature of 10°C [cold plate: 0°C and hot plate: +20°C, sample dimensions: 200 × 200 × 30 (mm³)]. In addition, the sustainable material content was calculated as the total mass of renewable feedstock in rigid PUR foam formulation divided by the total mass of PUR formulation, and result expressed in weight percent (%).

RESULTS AND DISCUSSION

Biopolyol characterization

The chemical structure of biopolyols was investigated by FTIR-ATR, the results are shown in Fig. 1.

In addition, the spectra of TOFA and ETOFA are presented and compared. In ETOFA spectra, the lack of band at 3008 cm⁻¹, that corresponds to the double bond =C-H, is due to the epoxidation. In addition, with appearance of the oxirane ring vibration band at 823 cm⁻¹, these effects confirm that TOFA epoxidation has taken place. After ring-opening with TMP, ETOFA_TMP polyol was obtained. In its FTIR-ATR spectra a broad band at 3400 cm⁻¹ characterizes free hydroxyl –OH groups. The oxirane ring vibration band at 823 cm⁻¹ has disappeared, and the peak of C=O band stretching has changed position from ~1700 cm⁻¹ in TOFA spectra to 1720 cm⁻¹ in ETOFA_TMP spectra. The C=O group peak shift is explained by the ester formation from the free carboxylic acid groups of TOFA with TMP polyfunctional alcohol. In the FTIR-ATR spectra of TO_TEOA polyol, the double bond =C-H remains, but peak at ~1036 cm⁻¹ appears due to the introduction of the tertiary amine group of TEOA.

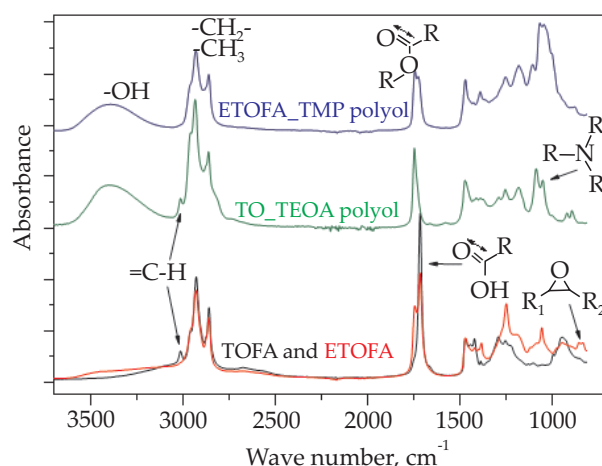


Fig. 1. FT-IR spectra of TOFA, ETOFA and synthesized biopolyols

Table 2. The characteristics of synthesized biopolyols

Polyol	OH_{val} mgKOH/g	Viscosity (25°C), mPa·s	Acid value mgKOH/g	Moisture %	f_n	M_n	p_d
ETOFA_TMP	390 ± 15	77000 ± 1000	7 ± 2	<0.1	9.3	1264	1.59
TO_TEOA	334 ± 10	280 ± 25	5 ± 2	0.24	2.3	391	1.79

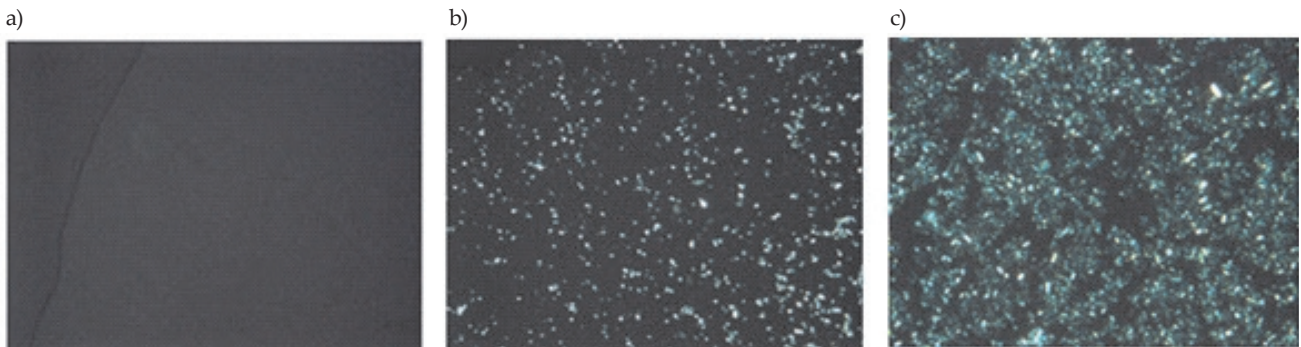


Fig. 2. OM images in polarized light mode at 50× magnification: a) ETOFA_TMP polyol, b) NFC-polyol dispersion mixed with high shear mixer before sonication, c) NFC-polyol dispersion after sonication

The acid numbers, hydroxyl value, water content, viscosity number, average functionality, number average molecular mass and polydispersity index of synthesized polyols are given in Table 2.

The high functionality of ETOFA_TMP ($f_n = 9.3$) allows to employ it as a cross-linking agent in PUR material development. Its relatively high OH value is suitable for rigid PUR foam development. However, the main drawback of ETOFA_TMP polyol might be the high viscosity that complicates polyol processing into up-scaled PUR production. Therefore, TO_TEOA polyol with significantly lower viscosity was introduced in the PUR formulation to decrease the total viscosity of polyol system.

Thus, more effective NFC dispersion and mixing of components of PUR formulation was possible.

NFC-polyol dispersions

To examine the homogeneity of NFC-polyol dispersion, microscopic observations were performed by OM in polarized light mode. The OM images of ETOFA_TMP polyol as well as NFC-polyol dispersion before and after sonication are presented in Fig. 2.

The arrangement of the microparticles on the OM images show that the dispersion becomes more homogeneous and the number of particles increases after sonica-

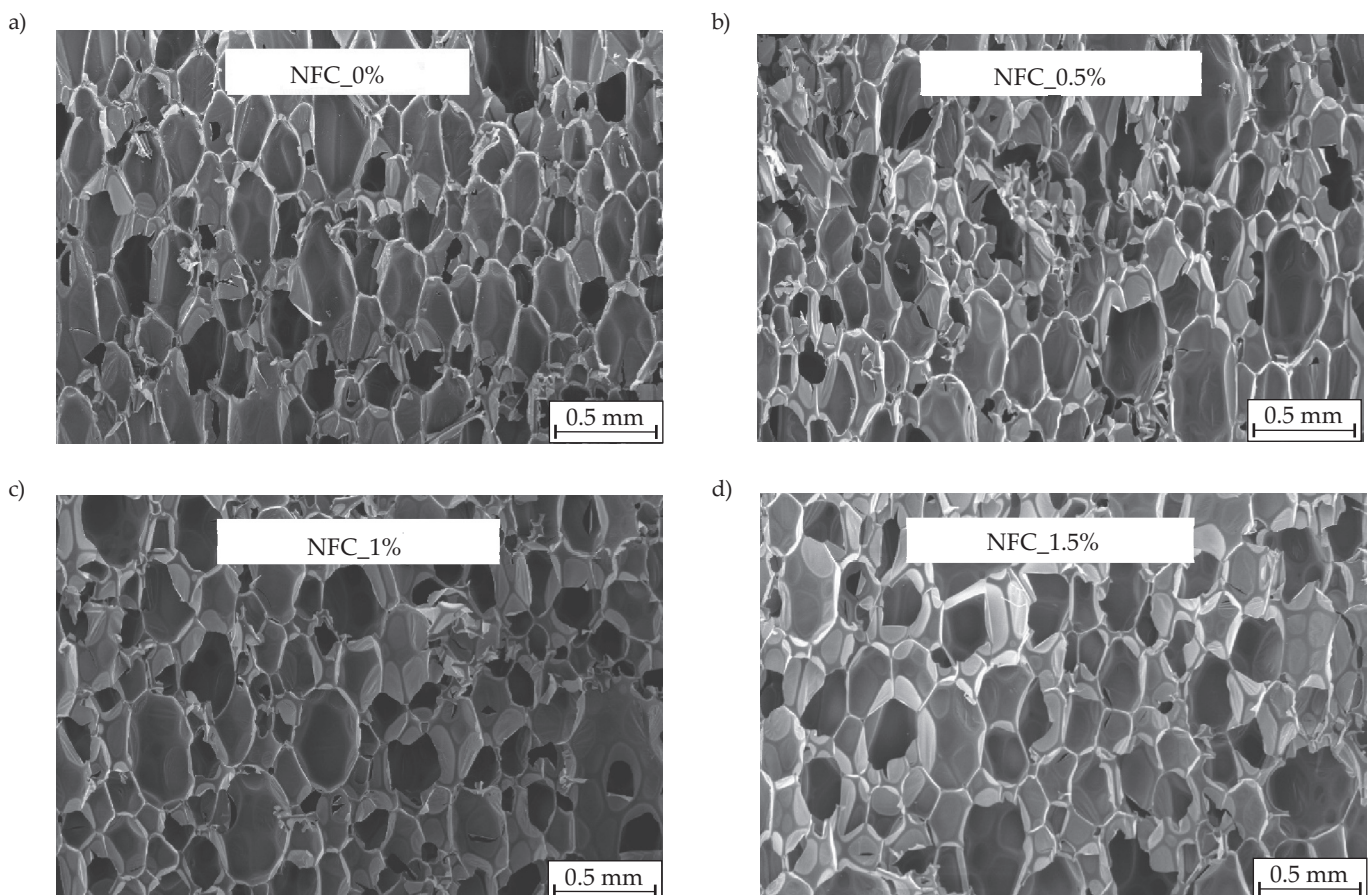
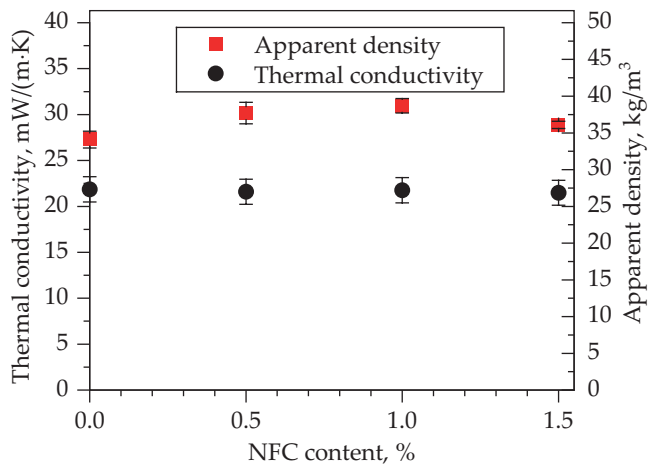


Fig. 3. SEM images of the rigid PUR foams filled with NFC – in foaming direction

Table 3. Closed-cell content and size of cells of rigid PUR foams filled with NFC

Sample	Closed-cell content, %	Cell length μm	Cell width μm	Anisotropy	Sustainable material content, %
NFC_0%	96	397	203	2.0	18.1
NFC_0.5%	95	416	213	2.0	18.5
NFC_1.0%	95	399	238	1.7	18.9
NFC_1.5%	96	415	246	1.7	19.3

**Fig. 4.** Thermal conductivity and apparent density of rigid PUR foams filled with NFC

tion. This indicated that the agglomerates are dissociated into smaller particles. Therefore, sonication is essential for obtaining homogenized polyol and NFC dispersion.

The viscosity measurements of polyol and NFC-polyol dispersions were performed. The viscosity of 1 wt % NFC-polyol dispersion ($\mu = 187\,700$ mPa·s at 25°C) was almost 2.5 times higher than viscosity of neat ETOFA_TMP polyol.

NFC influence on rigid PUR foam morphology

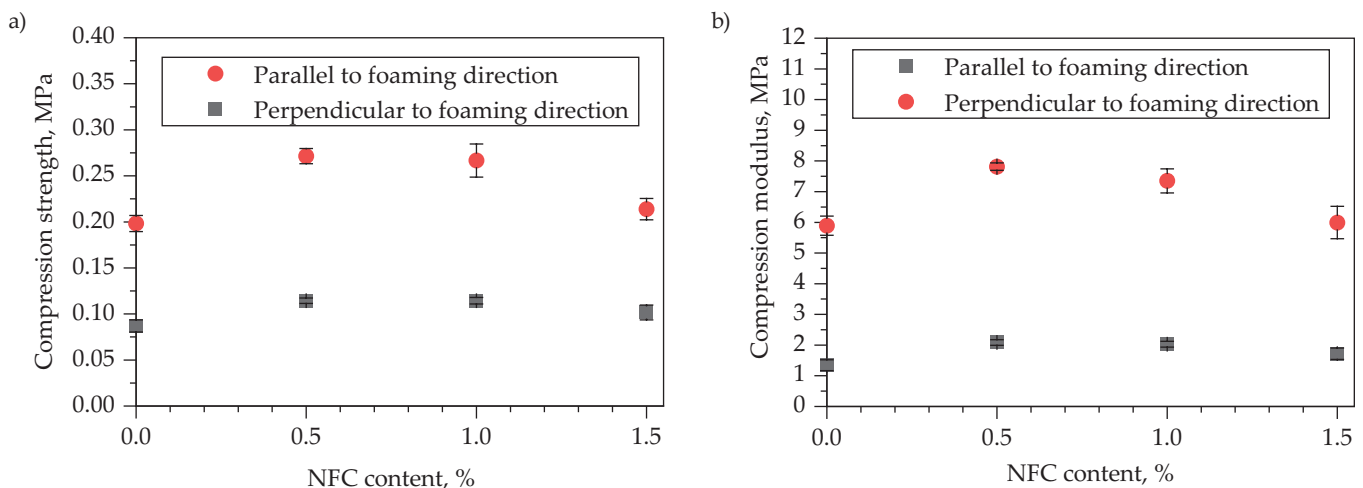
SEM images of rigid PUR foams with and without NFC (Fig. 3) were acquired to study morphology of foams and to measure size of cells (Table 3).

Although fillers usually act as a nucleating agent to give a smaller cell size [37, 38], no significant impact of NFC to the size of cells was observed. The high polyol viscosity that results in insufficient homogeneity of NFC-polyol dispersion could be the reason. NFC addition of at least 1% into rigid PUR foams slightly increased width of cells and decreased the anisotropy coefficient from 2.0 to 1.7.

Closed-cell content was not affected by the addition of NFC, and it was >95 vol % for all samples. The closed-cell content value correlates with the typical value for rigid PUR foam thermal insulation material. The addition of 1.5 wt % of NFC in rigid PUR foam allowed to achieve 19.3% of sustainable material content which can be considered relatively high.

NFC influence on the thermal conductivity of rigid PUR foams

To be able to study NFC influence on the apparent density of rigid PUR foams, rigid PUR foams filled with NFC contained the same amount of foaming catalysts and blowing agents as neat PUR foam formulations. NFC increased the density of PUR foams from 34 to 39 kg/m³ which was explained by the increase of the viscosity of the overall reacting PUR mass. All samples showed similar thermal conductivity ~21.7 mW/(m·K) and the increase in the apparent density did not significantly disrupt the thermal insulation properties of the composite (Fig. 4). A similar finding that addition of micro/nanocellulose to PUR foams do not affect foams thermal conductivity is reported [39].

**Fig. 5.** a) Compression strength, b) compression modulus of rigid PUR foams filled with NFC

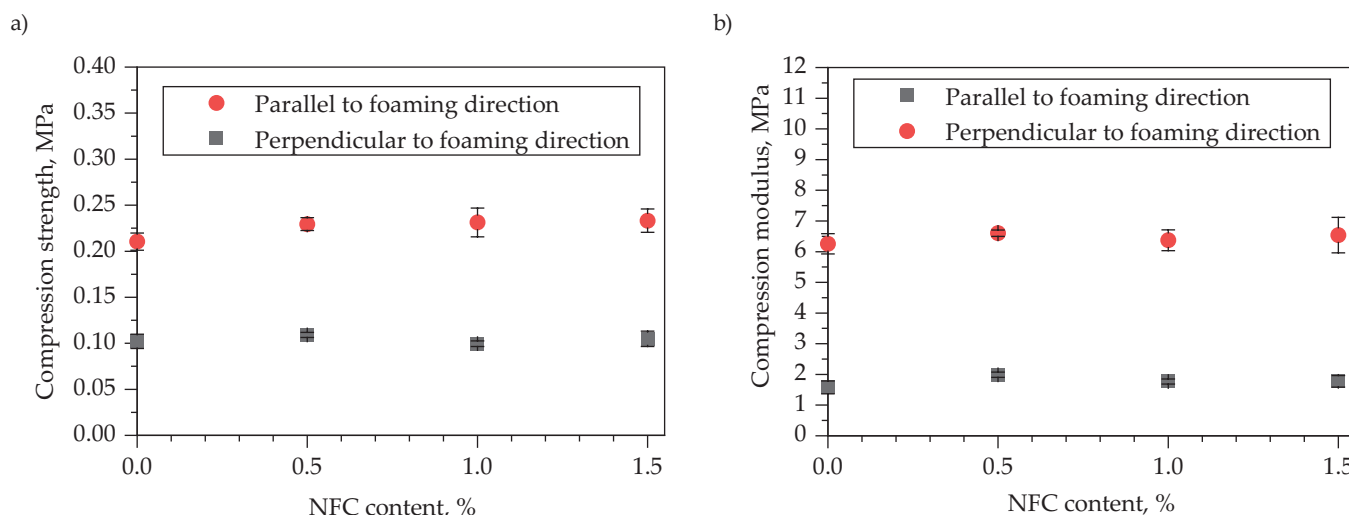


Fig. 6. The influence of NFC on normalized: a) compression strength, b) compression modulus of rigid PUR foam to average apparent density of 40 kg/m^3

Compression strength of rigid PUR foams filled with NFC

The compression strength of rigid PUR foams filled with NFC was measured parallel and perpendicular to foaming direction. Results are presented in Fig. 5.

The sample with 0.5 wt % of NFC showed the highest compression strength ($0.27 \pm 0.01 \text{ MPa}$ and $0.11 \pm 0.01 \text{ MPa}$, parallel and perpendicular to foaming direction, respectively) and the highest compression modulus ($7.8 \pm 0.1 \text{ MPa}$ and $2.1 \pm 0.1 \text{ MPa}$, parallel and perpendicular to foaming direction, respectively). That was ~ 1.3 times higher than the rigid PUR foams without the NFC. In the literature, increase of compression strength of PUR foams by adding NFC has been explained due to such reasons as smaller cell size [29], favorable matrix–nanocellulose interactions arising from efficient dispersion of nanocellulose in polyurethane [40] and even nanocellulose acting as crosslinking agent [29]. The higher density might also be related to higher compression strength. Therefore compression results were normalized to average apparent density of 40 kg/m^3 according to equations by Hawkins *et al.* and Kirpluks *et al.* [41, 42]. Results are shown in Fig. 6.

The results are more equal after normalization, only a slight increase in compression strength can be observed when NFC content is increased. This difference is negligible; hence it can be concluded that the difference in compression strength shown in Fig. 5 is mainly due to the difference in the apparent density.

CONCLUSIONS

Two types of biopolyols based on tall oil were synthesized. High functionality biopolyol was synthesized from tall oil fatty acids by epoxidation and subsequent oxirane ring-opening with trimethylolpropane. Low functionality and low viscosity biopolyol was synthesized by tall

oil esterification with triethanolamine. Both biopolyols showed appropriate characteristics (OH value, acid value, moisture content, and functionality) to be used in rigid PUR foam production.

Carboxylated nanofibrillated cellulose with 20–300 nm fibrils was produced from total chlorine free bleached birch Kraft pulp by ammonium persulfate oxidation with ultrasonic and mechanical treatment. Nanofibrillated cellulose-polyol dispersion was prepared by mixing with high shear mixer and with/without sonication afterwards. It was determined that sonication is essential for obtaining homogenized dispersion. It was found that the highest increase of compression strength of rigid PUR foams was observed when 0.5 wt % of nanofibrillated cellulose was introduced into foams. This effect was mainly due to the difference of apparent density as the compression results normalized to equal density between rigid PUR foam samples with different content of nanofibrillated cellulose did not show significant differences.

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