Chemical technology/modifications

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Modification of cellulosic filler with diisocyanates – volatile organic compounds emission assessment and stability of chemical structure over time

https://doi.org/10.1515/npprj-2020-0104
Received November 25, 2020; accepted December 22, 2020

Abstract: This paper investigated the impact of type and content of diisocyanate on the structure of modified cellulose fillers. Four the most popular isocyanates were applied – isophorone, hexamethylene, toluene and methylene diphenyl diisocyanate – at loadings of 1–15 wt%. Chemical structure, and its short-term storage stability, were investigated for eight weeks. Moreover, the main volatile organic compounds detected during modification, as well as emitted from fillers before and after storage, were identified. The main compounds detected in the air during modifications were terpenes and terpenoids. No diisocyanates were detected, which is very beneficial considering their toxicity. They were emitted from modified fillers at 40 °C, but only from fresh samples. After storage no emissions were noted, which indicated successful modification of fillers, also confirmed by FTIR spectroscopy and changes in polarity of fillers' surface. Observed changes should be considered beneficial for the potential applications of modified fillers in manufacturing of polymer composites.

Keywords: cellulose fillers; diisocyanates; filler modification; storage stability; volatile organic compounds.

Introduction

Cellulose fillers are commonly applied in the manufacturing of different types of polymer composites (Ching et al. 2016, Nie et al. 2020, Trache et al. 2016). Depending on their original form, including, e. g., purity, crystallinity, size of fibers, or particles, they can provide a vast range of properties to the resulting composites. One of the biggest challenges related to the manufacturing of this type of composites, often called wood-polymer composites (WPCs), is the interfacial compatibility between matrix and filler. It is often minimal, due to the differences in the chemical structures between polar lignocellulosic filler and often non-polar polymer matrices. Therefore, different methods of filler modifications were developed, which are often aimed at reducing the polarity of their surface (Joly et al. 1996). These reports are regularly summarized in various review papers by many authors (Kabir et al. 2012, Kalia et al. 2009, Mohit and Arul Mozhi Selvan 2018). The most popular treatments of lignocellulosic fillers include alkali treatment, silanization, acetylation, maleation, acrylation, or modification with permanganate. Moreover, increasingly more attention is focused on other, less popular methods, e. g., benzoylation, modification with fatty acids, triazine, or isocyanates. Recently, we published the review work summarizing the literature reports related to the compatibilization strategies of wood-polymer composites by isocyanates (Hejna et al. 2020).

Modification with isocyanates can be considered as a rather versatile method. In the case of non-polar polymer matrices, grafting of isocyanates onto the surface of lignocellulosic filler reduces its polarity, increasing the compatibility of phases. On the other hand, when polar matrices with functional groups present in their structure are applied, the presence of isocyanates enables covalent bonding at the interphase. Potential reactions of free isocyanate groups with functional groups possibly present on the surface of lignocellulosic fillers or in the polymer backbone, as well as with the moisture, are presented in Figure 1.

Nevertheless, there are a few issues, which should be addressed when isocyanates are applied as a modifier of lignocellulosic fillers. We included them in our recently published review work summarizing the literature reports related to the compatibilization strategies of wood-polymer composites by isocyanates (Hejna et al. 2020).

One of the issues, which should be addressed in the stability of modified fillers during their storage. The rate

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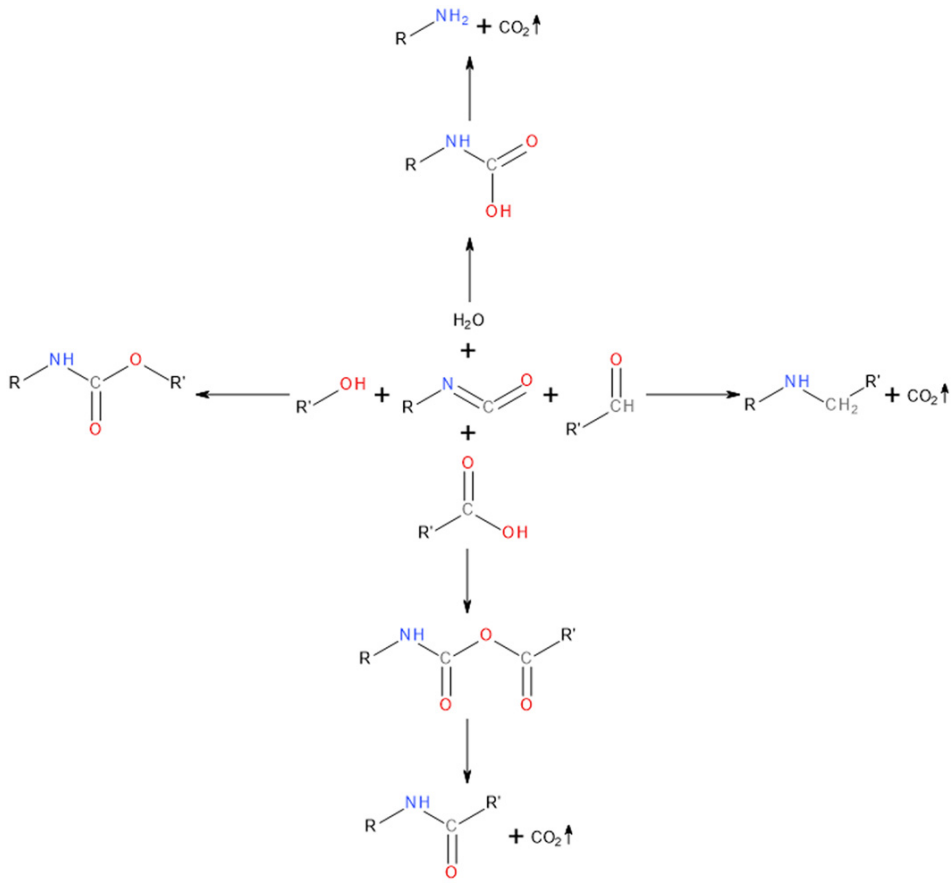


Figure 1: Possible reactions of isocyanates with functional groups of cellulose fillers, and with moisture.

of the reactions mentioned above, when performed without the catalysts (the majority of the reported modification methods did not include catalysts), is rather low compared to the conventional reactions of isocyanates, e. g., during the manufacturing of polyurethanes (Heijkants et al. 2005). Even when catalysts are applied, after 24 or even 48 hours, free isocyanate groups may still be present on the surface of modified fillers, as proven by other researchers (Arjmand et al. 2012, Gómez-Fernández et al. 2017). Therefore, during the storage of these materials, additional reactions would occur, either with functional groups of lignocellulosic fillers or with moisture (Hejna and Kosmela 2020). According to literature data (Vilar 1998), reactions of isocyanate groups with primary hydroxyls and water show similar reaction rates when uncatalyzed at room temperature. They may lead to covalent bonding between filler particles, hence the rise of particle size, or the generation of amine groups on the surface of fillers (see Figure 1). Such reactions would change the properties of modified fillers, so it is important to investigate them. Unfortunately, this issue was not analyzed in previous works of other research groups.

Another aspect related to the use of isocyanates is their toxicity related to the reactivity of free isocyanate groups (Musk et al. 1988). Therefore, it is essential to investigate the emissions of harmful compounds during modification of fillers, as well as from the final products, which could be stored before the introduction into polymer matrices. Various reported modification processes were performed in solution, so the content of isocyanates in generated sewage should be determined (Arjmand et al. 2012, Liew et al. 2018). On the other hand, researchers often performed modifications at elevated temperatures to accelerate the desired reactions (Gómez-Fernández et al. 2017). In such cases, the emissions of volatile organic compounds (VOCs) should be monitored, because due to their toxicity, isocyanates may be harmful even at the relatively low concentrations (Mishra et al. 2008).

In the presented research work, we aimed to investigate the structure, performance, and short-term stability of cellulose filler modified with diisocyanates. We performed the comparative studies for four the most popular isocyanates – isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI)

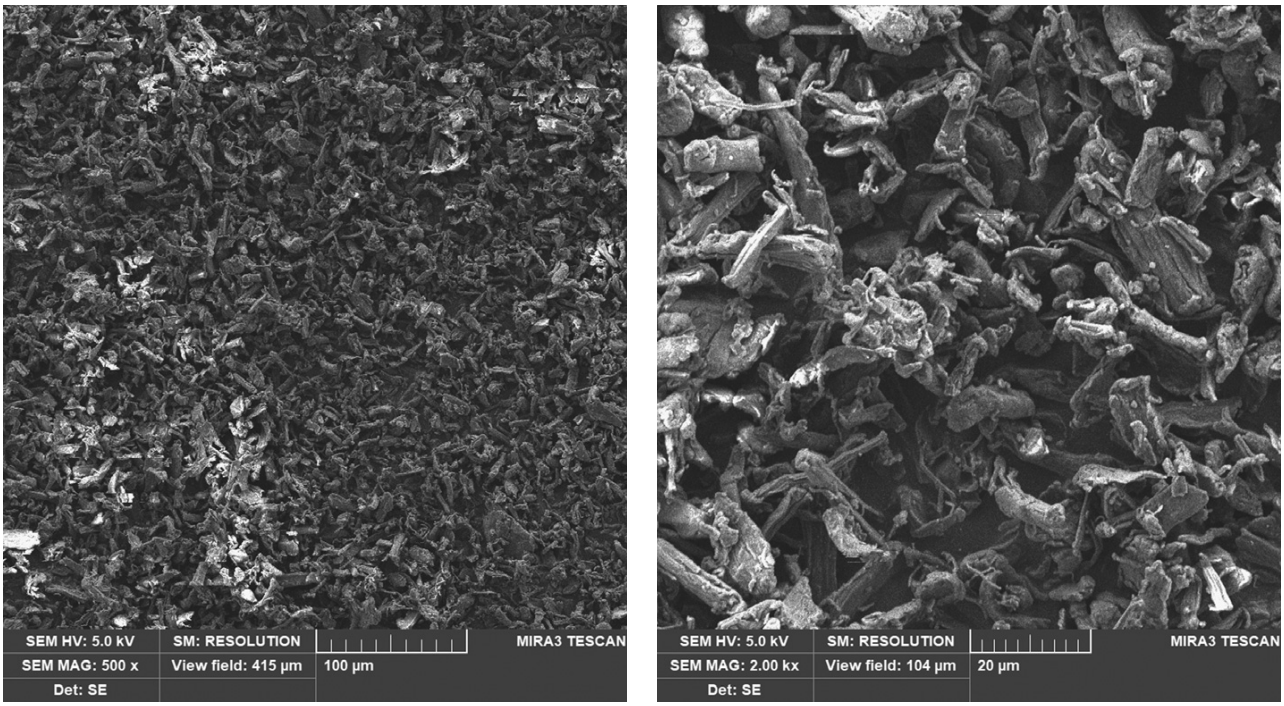


Figure 2: SEM images of UFC100 filler under magnifications of 500× (left) and 2000× (right).

and methylene diphenyl diisocyanate (MDI). Commercially available cellulose filler was modified with 1–15 wt% of diisocyanates, which is higher than in most of the previous works, which usually investigated up to 5 wt%. Changes in the chemical structure of fillers, as a function of type and content of diisocyanate, as well as storage time, were analyzed. Moreover, emissions of volatile organic compounds during modification processes, and from modified fillers were determined.

Materials and methods

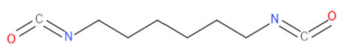
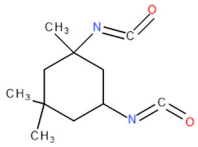
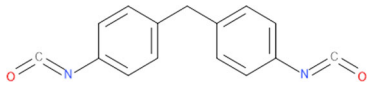
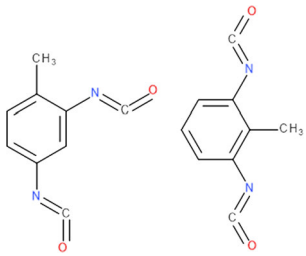
Materials

Commercially available Arbocel® UFC100 filler from JRS J. Rettenmaier & Söhne GmbH (Germany) was used in the presented study. It was characterized by the average particle length of 8 μm, the aspect ratio of 4, bulk density of 160 g/l, and moisture content of 4.84 wt%. In Figure 2, there are presented microscopic images of UFC100 filler obtained with scanning electron microscopy (SEM) under magnifications of 500× and 2000×.

Modifications of cellulose filler were performed with four different isocyanates: hexamethylene diisocyanate, isophorone diisocyanate, methylene diphenyl diisocyanate, and toluene diisocyanate, which were acquired from Sigma Aldrich (Poland). The purity of HDI, IPDI, and MDI was 98 %, 99 %, and 98 %, respectively. TDI mixture of 2,4-TDI and 2,6-TDI in the 80/20 ratio was used. Properties of applied modifiers are presented in Table 1 together with the pictograms according to Globally Harmonized System of Classification and Labelling of Chemicals (GHS), commonly used for classification of chemicals by the risk they pose towards human health and safety (European Parliament and the Council 2008). Except for pictograms, GHS operates with the hazard statements, which are providing more details about the safety of particular chemicals.

As mentioned above, isocyanates are considered very toxic chemicals because of the high reactivity of free isocyanate groups (Musk et al. 1988). According to the GHS standards, applied isocyanates are very irritant towards skin and eyes, so they are listed with statements H315 (Causes skin irritation), H317 (May cause an allergic skin reaction), and H319 (Causes serious eye irritation). Isophorone diisocyanate is also sometimes flagged with statements related not only to irritating effects but damage. Irritation or allergic effects are also observed in the respiratory system (H334 and H335). Depending on the source, applied compounds are classified as harmful, toxic, or even fatal (rarely) if inhaled (statements H332,

Table 1: Structure and properties of diisocyanates applied as modifiers of cellulose filler.

Name	Chemical structure	Molar mass, g/mol	Density, g/cm^3	Melting point, °C	Vapor pressure, Pa	GHS pictograms
HDI		168.2	1.05	−67	7.0	
IPDI		222.3	1.06	−60	$4.0 \cdot 10^{-2}$	
MDI		250.3	1.18	40	$7.0 \cdot 10^{-4}$	
TDI		174.2	1.23	22	4.0	

H331, and H330). However, the most significant threats of diisocyanates are expressed by the statements related to the damage caused to organs (H372 – Causes damage to organs through prolonged or repeated exposure) and cancer (H351 – Suspected of causing cancer). Moreover, IPDI and TDI are sometimes classified as environmental hazards, respectively toxic and harmful to aquatic life with long-lasting effects (statements H411 and H412).

Presented data, once again, motivates to investigate the impact of processes involving diisocyanates towards human health.

Modification of fillers

Fillers were modified using GMF 106/2 Brabender batch mixer at room temperature (varied from 21.1 to 23.1 °C) and rotor speed of 100 rpm. The proper amount of filler was placed in an internal mixer with a calculated amount of diisocyanate, respectively, to the mass of filler. Diisocyanates were introduced in the amounts of 1.0, 2.5, 5.0, 10.0, and 15.0 wt%, relative to the mass of filler. Mixing was performed for 5 minutes, and then samples were put in zipper storage bags.

Room temperature was applied to reduce the possible emissions from applied diisocyanates, which at 20–25 °C show relatively low volatility (see values of vapor pressure in Table 1). At higher temperatures, their volatility is significantly increasing. For example, when the temperature is elevated to 50 °C, the vapor pressure of TDI, IPDI, and MDI is increased 11.9, 22.5, and 33.5 times. Further rise of temperature to 100 °C, increases TDI and MDI vapor pressure by 287 and 3316 times.

Measurements and analytes sampling equipment

The analytical measurements were performed in a two main stages:

First stage – the quality of air on a workplace – studies in enclosed area were carried out employing the Radiello® diffusive passive samplers (Fondazione Salvatore Maugeri, Padova, Italy) at the stage of analyte sampling from the gaseous phase. Mentioned passive sampler was equipped withe a yellow diffusive membrane and the cylindrical container filled with sorption medium Carbograph 4 dedicated for VOCs sampling. Detailed information about the characteristics and working parameters of the Radiello® passive sampler was in detail listed elsewhere (Marć et al. 2014a, 2014b, Plaisance et al. 2008). In brief, the analytical procedure aimed at the qualitative determination of VOCs present in gaseous phase on the studied workplace enclosed the following steps: (i) each time two indepen-

dent Radiello® passive samplers were placed in the studied workplace, at a distance of more than 1 m; (ii) the exposure time of applied passive samplers in studied indoor environment was set up for 4 hours; (iii) sampling devices were placed close to the studied workplace and in the close neighborhood to the materials preparation area; (iv) the temperature was monitored continuously during whole working period and was in the range from 21.1 up to 23.1 °C; (v) after the analytes sampling period, the containers with a sorption medium were removed from the diffusive membrane and placed inside the glass tubes closed with polyethylene nut; (vi) containers with sorption medium were stored in a temperature of 4 °C no longer than 12 hours after sampling.

Second stage – emission studies of chemical compounds – tests were carried out with the application of micro-scale stationary emission chamber system (Markes International Micro-Chamber/Thermal Extractor μ-CTE 250) equipped with four equally stainless steel chambers (single chamber internal volume – 114 cm^3). Detailed information about the working parameters and application area of mentioned stationary emission chambers system was described elsewhere (Marć and Zabiegała 2017, Marć et al. 2017). The studies associated with the estimation of the type of VOCs emitted from studied samples of cellulose filler modified with diisocyanates consist of the following steps: (i) the studied samples of cellulose filler modified with diisocyanates (average mass of sample – 1.2 ± 0.2 g) were placed on a glass Petri dish, put inside a single chamber and tightly sealed; (ii) the operating parameters of applied μ-CTE250 system were set up – seasoning temperature – 40 °C, sampling time – 30 min, inert gas (nitrogen) flow rate – 15 $ml \cdot min^{-1}$, analytes sampling device – stainless steel tube filled with Tenax TA; (iii) after the sampling period the Tenax TA tubes were removed and sealed with a brass long-term storage caps.

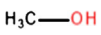
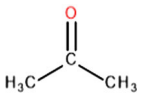
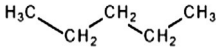
The identification of the main VOCs that occurs in the gaseous phase of studied indoor environment was performed with the use of thermal desorption technique (Unity v.2, Markes International Ltd., Pontyclun, UK), connected with gas chromatography (Agilent Technologies 6890) combined with a mass spectrometer (5873 Network Mass Selective Detector, Agilent Technologies). The cylindrical containers filled with sorption medium were liberated at the temperature of 290 °C by 15 min. During this process, the analytes were transported to the microtrap. Then, the analytes were liberated from the microtrap heating up to 300 °C and maintained by 5 min and transported by the helium flow rate (1.5 $mL \cdot min^{-1}$) to the GC capillary column (Agilent 122-5563, J&W DB-5MS, 60 m × 0.25 mm × 1 μm). The GC oven temperature program was as follows: 50 °C for 1 min, then raised at a rate of 10 $°C \cdot min^{-1}$ up to 280 °C and maintained for 10 min. The temperature of the TD-GC transfer line was set to 150 °C, and the temperature of the GC-MS transfer line was 280 °C. The employed mass spectrometer was working in a SCAN mode. Detailed information about the principals and characteristic of the thermal desorption technique were presented elsewhere (Król et al. 2012, Zabiegała et al. 2007). In order to eliminate signals associated with other processes occurring in the laboratory hall and select only signals related to the performed modification, as well as to ensure the reliability of obtained results, the "background" was also analyzed. Additionally, before each sampling period, the sorption medium placed in the cylindrical tube was conditioned for 30 min at temperature 300 °C. As for the emission studies performed using the μ-CTE 250 system, after the sampling process, the stainless steel tubes were removed and transferred directly to the heating unit of mentioned thermal desorption system connected with GC-MS. The stainless steel tubes filled with Tenax TA were desorbed at the temperature of 285 °C by 12 min. The remaining steps of the procedure associated with analytes liberation, separation and identification were performed under similar conditions as described previously. Before every sampling period, the chambers with the glass Petri dish inlet were baked out at the temperature 100 °C by 30 min, and the blank sample (background value) was measured to ensure the reliability of obtained results. Additionally, before each sampling period, the Tenax TA stainless steel tubes were conditioned for 30 min at temperature 300 °C.

Chemical structure of lignocellulosic fillers' samples was determined using Fourier transform infrared spectroscopy (FTIR) analysis performed by a Nicolet Spectrometer IR200 from Thermo Scientific (USA). The device had ATR attachment with a diamond crystal. Measurements were performed with 1 cm^{-1} resolution in the range from 4000 to 400 cm^{-1} and 64 scans.

The moisture content of prepared cellulosic fillers was analyzed with the Radwag MA 50/1.X2.IC.A Moisture Analyzer. Sample weighting ~1 g was put on the aluminum dish and put inside analyzer at a temperature of 80 °C. The weight of the samples was recorded until the mass loss was lower than 1 mg/25 s.

To evaluate the changes in the fillers' polarity, test for dispersibility of cellulose particles in different solvents was performed. Samples modified with 5 and 15 wt% of diisocyanates were analyzed, as well as neat cellulose. The method was adopted from other research work (Gwon et al. 2018). Specimen of cellulose weighting 1 g was put in a vial, and 20 mL of proper solvent was added. Then, vials

Table 2: Structure and properties of solvents used to evaluate the changes in fillers' polarity.

Compound	Chemical structure	Density, g/cm^3	Dynamic viscosity, mPa·s	Relative polarity
water		0.998	0.8921	1.000
methanol		0.792	0.5480	0.762
acetone		0.789	0.3160	0.355
n-pentane		0.626	0.2224	0.009

were shaken vigorously for one minute, and the sedimentation of cellulose particles was recorded. Photographs were made right after the shaking was stopped, then each minute for five minutes, and after ten minutes. Four solvents were used, which were selected based on their polarity, expressed by the relative polarity index, according to data presented by Reichardt (2003). In Table 2, there are presented properties of the applied solvents.

Analysis of modified fillers' stability

The short-term storage stability of modified fillers' performance was investigated by periodic repetition of analyzes related to the chemical structure, moisture content, and behavior in various solvents. Analyzes were performed after 1, 2, 4, and 8 weeks of sample storage in zipper bags. Moreover, at the end of this period, the emission studies of modified fillers were performed.

Results and discussion

VOCs emission during fillers' modification

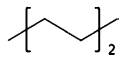
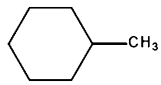
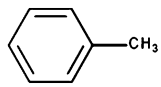
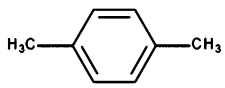
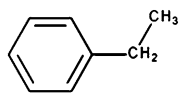
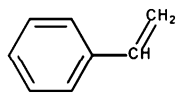
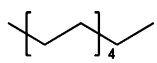
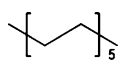
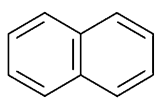
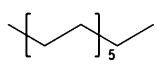
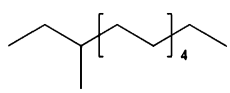
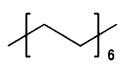
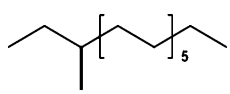
Passive dosimetry was applied in order to evaluate the emission of volatile organic compounds during the modification of cellulosic filler with diisocyanates. According to the Directive 2004/42/CE of the European Parliament and the Council, VOCs are organic compounds with the boiling point lower than or equal to 250 °C, measured at standard atmospheric pressure (European Parliament and the Council 2004). A similar limit is set by the World Health Organization, which also marks out the compounds with a boiling point below 100 °C, as very volatile organic compounds (World Health Organization 1989). On the other hand, volatility is quantitatively expressed by the vapor pressure rather than the boiling point. However, there is no actual value of vapor pressure, which clearly determines if a compound is considered as VOC (Eurofins 2018). Although it is not a strict definition or standard, the United States Environmental Protection Agency exempts solvents in consumer products with a maximum vapor pressure of 0.1 mm Hg at 20 °C. These compounds show little or no volatility, which would not result in significant VOCs emissions (United States Environmental Protection Agency 1998).

Performed screening studies indicated the presence of multiple chemical compounds, which are not associated with the presence of diisocyanates, or cellulose fillers. Therefore, a background check of our laboratory hall was performed, to determine the "baseline" of the emissions, which are related to the other research activities. Among them should be mentioned storage and processing of rubbers, polyurethanes, polyolefins, or polyester resins. In Table 3 there are listed detected compounds, together with their properties and the origin, where: *NR* – natural rubber, *PE* – polyethylene, *PET* – poly(ethylene terephthalate), *Plast* – plasticizers user for various plastics, *PP* – polypropylene, *PR* – polyester resins, *PS* – polystyrene, *PUF* – polyurethane foams, *PVC* – poly(vinyl chloride), *SBR* – styrene-butadiene rubber, *Solv* – solvents, *VA* – vulcanization accelerators. Only compounds with high compliance with the database, exceeding 80 %, were listed. Values of their boiling points and vapor pressures are indicating that these compounds could be considered as VOCs, according to definitions mentioned above.

Except for the compounds listed above, whose presence was attributed to the storage and processing of various polymeric and rubber materials, significant amounts of other VOCs were detected, which can be classified as terpenes and terpenoids. They are hydrocarbons and their derivatives with additional functional groups, usually containing oxygen. Terpenes and terpenoids are significant components of rosins, present in different plants, especially conifers. Therefore they are often present in the cellulosic materials (Gaiolas et al. 2009). In Table 4, there are presented detected terpenes and terpenoids, together with their chemical structures and properties such as boiling point, vapor pressure, and flash point. While the first two are classifying listed compounds as VOCs, flash point is related to their flammability. Moreover, in Table 4, there are presented pictograms according to GHS standards (European Parliament and the Council 2008).

It can be seen that all of the listed compounds are characterized with relatively low flash points, not exceeding 60 °C. Such values implicate that they are flammable

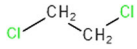
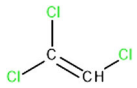
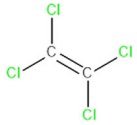
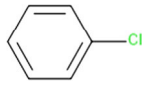
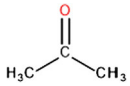
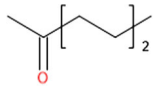
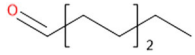
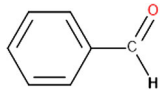
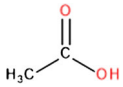
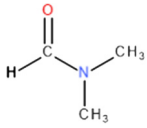
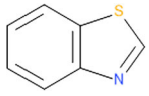
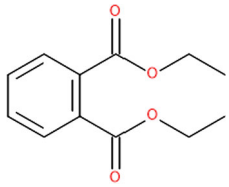
Table 3: Compounds detected in the air during a background check of our laboratory hall.

Detected compound	Chemical formula	Chemical structure	Boiling point, °C	Vapor pressure, Pa	Origin	Ref.
Hydrocarbons						
Hexane	C_6H_{14}		68	17600	PP	[1,2]
Methylcyclohexane	C_7H_{14}		101	6130	PP	[3]
Benzene	C_6H_6		80	10000	SBR	[3]
Toluene	C_7H_8		111	2800	SBR, *Solv*	[3]
p-Xylene	C_8H_{10}		138	1200	PR, SBR, *Solv*	[4,5]
Ethylbenzene	C_8H_{10}		136	930	PS	[5]
Styrene	C_8H_8		145	670	PS, PR, SBR	[4,5]
Undecane	$C_{11}H_{24}$		196	55	PE, PP	[6]
Dodecane	$C_{12}H_{26}$		216	17	PE, PP, NR	[5,7]
Naphthalene	$C_{10}H_8$		218	11	PVC	[4]
Tridecane	$C_{13}H_{28}$		234	5	PVC, PE	[4]
3-Methyltridecane	$C_{14}H_{30}$		249	5	PR, PE, PP	[4,6]
Tetradecane	$C_{14}H_{30}$		254	2	PR, PE, PP	[4,6]
3-Methylpentadecane	$C_{16}H_{34}$		283	No data	PR, PE, PP	[4,6]

according to GHS standard, which classifies liquids as flammable when the flash point is within the range of 23 and 60 °C. Moreover, chemicals with the flash point up to 93 °C are treated as combustible. However, they are not marked with a special pictogram. Flammability of terpenes and terpenoids is a commonly known issue because of their high content in particular species of wood results in the increased fire threat (Ormeño et al. 2009). Therefore, it is essential to monitor their emissions during various processes, especially if they could be potentially applied on the industrial scale.

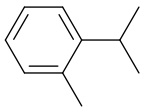
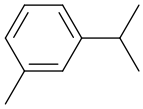
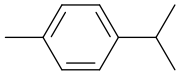
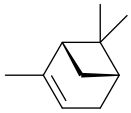
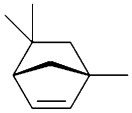
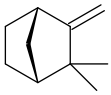
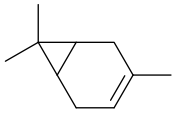
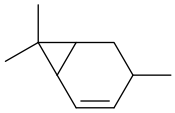
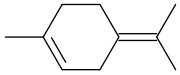
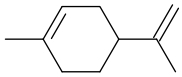
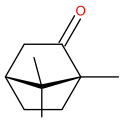
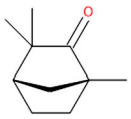
Except for flammability, terpenes and terpenoids may be considered as health and environmental hazards. Regarding the environment, part of them is classified as hazardous to the aquatic environment with acute or long-term hazards – hazard statements H400 and H410–H412. State-

Table 3: (continued)

Detected compound	Chemical formula	Chemical structure	Boiling point, °C	Vapor pressure, Pa	Origin	Ref.
Chlorinated hydrocarbons						
Methylene chloride	CH_2Cl_2		40	57300	PUF, *Solv*	[8]
Trichloromethane	$CHCl_3$		61	26265	*Solv*	[9]
1,2-Dichloroethane	$C_2H_4Cl_2$		84	10530	*Solv*	[10]
Trichloroethylene	C_2HCl_3		87	9200	*Solv*	[9]
Tetrachloroethylene	C_2Cl_4		121	2470	PUF, *Solv*	[8]
Chlorobenzene	C_6H_5Cl		132	1600	PET	[5]
Ketones						
Acetone	C_3H_6O		56	30600	PET, *Solv*	[5]
2-Heptanone	$C_7H_{14}O$		151	510	PE	[11]
Aldehydes						
Heptanal	$C_7H_{14}O$		153	470	PE	[11]
Benzaldehyde	C_7H_6O		178	133	PR	[5]
Others						
Acetic acid	$C_2H_4O_2$		118	1520	NR, PE	[12]
Dimethylformamide	C_3H_7NO		153	516	*Solv*	[13]
Benzothiazole	C_7H_5NS		230	2	VA	[14]
Diethyl phthalate	$C_{12}H_{14}O_4$		302	0.3	*Plast*	[15]

References: 1 – Willoughby et al. 2003, 2 – Wolkoff 1998, 3 – Reingruber et al. 2011, 4 – Yu and Crump 1998, 5 – Curran et al. 2016, 6 – Lattuati-Derieux et al. 2013, 7 – Nielsen et al. 1994, 8 – Hillier et al. 2003, 9 – Stringer and Johnston 2001, 10 – Tsai et al. 2009, 11 – Villberg and Veijanen 2001, 12 – Hoven et al. 2003, 13 – De Vasconcelos et al. 2001, 14 – Reemtsma et al. 1995, 15 – Hauser et al. 2004.

Table 4: The main chemical compounds detected during the modification of lignocellulosic fillers.

Compound	Formula	Chemical structure	Boiling point, °C	Vapor pressure, Pa	Flash point, °C	GHS pictograms
o-Cymene	$C_{10}H_{14}$		178	200	50	
m-Cymene	$C_{10}H_{14}$		175	200	47	
p-Cymene	$C_{10}H_{14}$		177	200	47	
α-Pinene	$C_{10}H_{16}$		156	633	33	
β-fenchene	$C_{10}H_{16}$		157	526	25	
Camphene	$C_{10}H_{16}$		160	333	34	
3-Carene	$C_{10}H_{16}$		170	496	46	
4-Carene	$C_{10}H_{16}$		168	555	38	
Terpinene	$C_{10}H_{16}$		186	99	37	
Limonene	$C_{10}H_{16}$		176	190	50	
Camphor	$C_{10}H_{16}O$		209	27	54	
Fenchone	$C_{10}H_{16}O$		194	109	60	

ments H400 and H410 are associated with high toxicity to aquatic life, related to the lethal concentration LC_{50} are lower than 1 mg/L. For H411 and H412, it is lower than 10 and 100 mg/L, respectively. Moreover, statements H410–H412 are also indicating a long-lasting effect on the aquatic life, expressed by the bioconcentration factor (BCF) higher than 500 (United Nations Economic Commission for Europe 2011).

In terms of health issues, listed terpenes and terpenoids are generally classified as harmful and health

hazards. Depending on the source, different hazard statements are ascribed to particular compounds. However, a couple of them is noted almost for all detected terpenes and terpenoids. One of them is statement H304 – May be fatal if swallowed and enters airways. It refers to the confirmed pulmonary injuries of pneumonia caused by particular chemicals. Regarding skin damages, terpenes are generally classified according to statements H315 and H317, meaning they cause skin irritation and may cause allergic reactions. Some of them are also causing serious eye irritations (H319). Less frequently listed compounds are classified as irritating towards the respiratory system (H335). Camphor and α-pinene are sometimes flagged with H371 (May cause damage to organs) and H372 (Causes damage to organs through prolonged or repeated exposure) statements. Nevertheless, it can be seen that the majority of listed compounds are rather classified as irritating or sometimes allergic than fatal (United Nations Economic Commission for Europe 2011).

Regarding the safety of the analyzed modification processes, it is essential and beneficial that during modification, no traces of applied diisocyanates were detected. Therefore, their relatively low values of vapor pressure at ambient temperature (see Table 1). Such an observation confirms the threshold of 0.1 mm Hg (~13.3 Pa) set by the United States Environmental Protection Agency for solvents, which classifies the compounds like VOCs.

VOCs emission from modified lignocellulosic fillers

In Figure 3 there are presented chromatograms showing the emission of VOCs from prepared samples in a qualitative manner. For the unaged samples, the main detected compounds were terpenes and terpenoids, mainly octanal, 3-carene, *p*-cymene, and limonene, attributed to the peaks for retention times between 12 and 14 minutes. Their share varied for particular samples. However, the most pronounced was the presence of limonene, which is often emitted from lignocellulosic materials (Molhave et al. 2000). After storing the samples for eight weeks, and the completion of reactions between diisocyanates and fillers, the emissions of these compounds were reduced. Nevertheless, limonene was still detected.

However, the most critical insight related to the storage of fillers is the disappearance of signals attributed to the presence of isocyanates used for the modification of fillers. It can be seen that for unaged samples, these signals were powerful. For IPDI, they accounted for over 63 % of the total area under peaks, while for TDI, it was over 83 %. After the aging of samples, these signals were not detected, pointing to the completion of the desired reactions between free isocyanate groups and cellulose fillers (see Figure 1).

Chemical structure

The FTIR spectroscopy determined changes in the chemical structure of UFC100 cellulose filler. In Figure 4 there are presented FTIR spectra of unmodified filler and modified with 15 wt% of different diisocyanates. These spectra were recorded one day after modification. They present the appearance typical for lignocellulosic materials, with additional signals attributed to the isocyanate groups and products of their reactions with cellulose. The broad peaks seen at 3335–3340 cm^{-1} can be attributed to the presence of hydroxyl groups and the stretching vibrations of O–H bonds, as well as to the vibrations of N–H bonds present in amine groups. The magnitude of this peak increased after the modification with isocyanates, which is related to the chemistry of the process, resulting in higher amounts of functional groups (Mullay 1987). Instead of one O–H bond from hydroxyls, there are present two or even three N–H bonds from urethane and amine groups (see Figure 1). Their amount depends on the reaction of the free isocyanate group of diisocyanate particles grafted onto the surface of the filler. If this group reacts with another hydroxyl, it generates a second urethane group (containing one N–H bond). However, in case of reaction with moisture, the terminal amine group with two N–H bonds is obtained. For aliphatic HDI and IPDI, the magnitude of the analyzed peak is 28–30 % higher than for neat cellulose, while for aromatic MDI and TDI, 38 and 46 % increase was noted. Such an effect was related to the higher reactivity of aromatic isocyanates, caused by the high electronegativity of the aromatic ring (Jiao et al. 2013). According to the literature data, rates of these reactions are similar at room temperature without the presence of a catalyst (Vilar 1998). However, the generation of urethane groups should be accompanied by the presence of signals characteristic for C–N and C=O bonds around 1610–1700 cm^{-1}, respectively. It can be seen that for aliphatic diisocyanates, no signals were noted, which suggests the reaction with moisture. Very weak and broad peaks were observed for MDI, while stronger were noted for the most reactive TDI. In the case of aromatic diisocyanates, FTIR spectra indicate their bonding with cellulosic filler. Nevertheless, despite the changes mentioned above, there can still be observed signals around 2300–2350 cm^{-1} attributed to the presence of the unreacted, free isocyanate groups (Jiao et al. 2013).

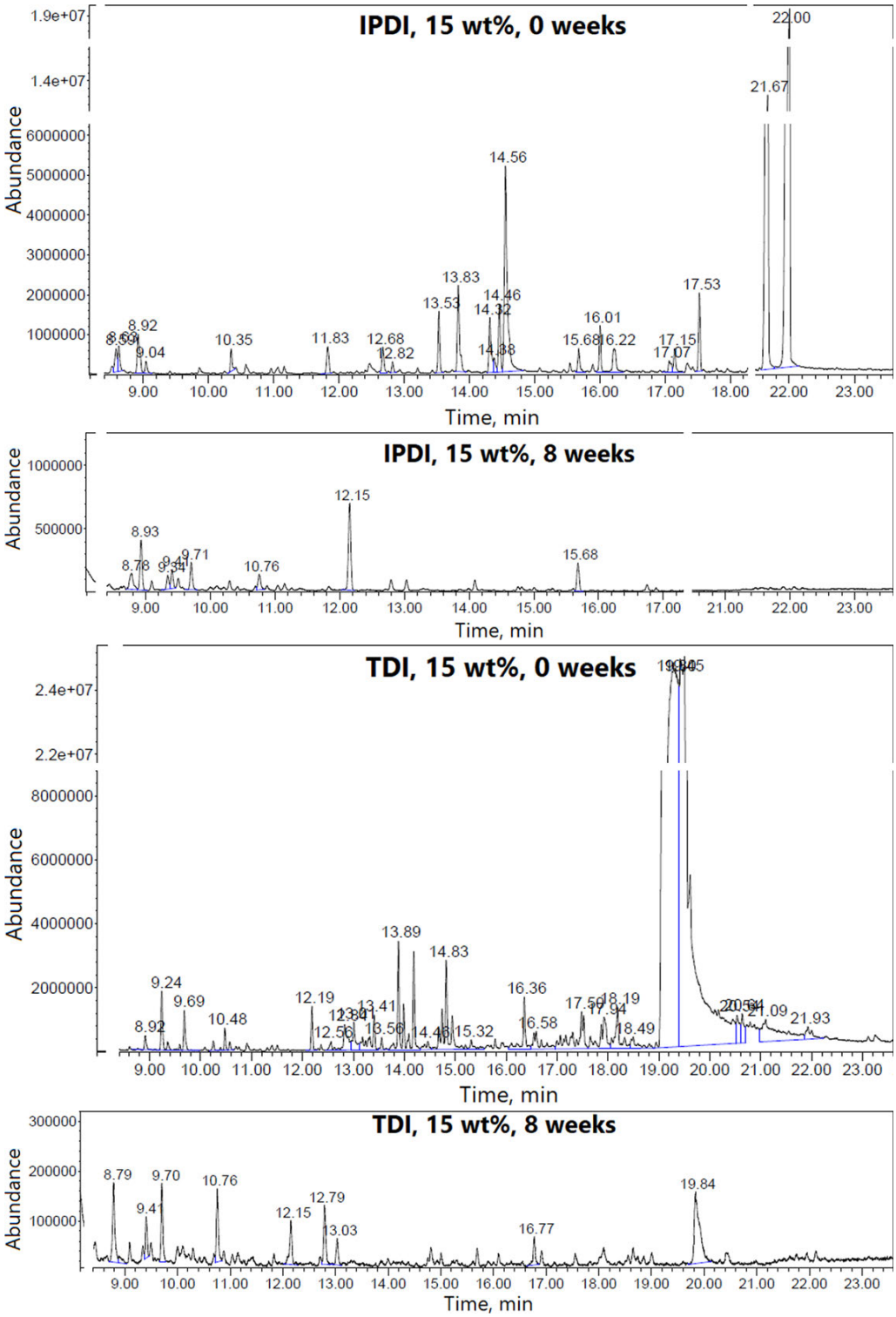


Figure 3: Chromatograms obtained during the μCTE-TD-GC-MS analysis of modified cellulose fillers.

It indicated that desired reactions were not completed during the performed modification process.

Except for signals characteristic for the applied diisocyanates and products of their reactions with cellulose filler also other signals were noted. These in the range of 2840–3000 cm^{-1} were attributed to the symmetric and asymmetric stretching vibrations of C–H bonds. The strength of these signals was hardly affected by the modi-

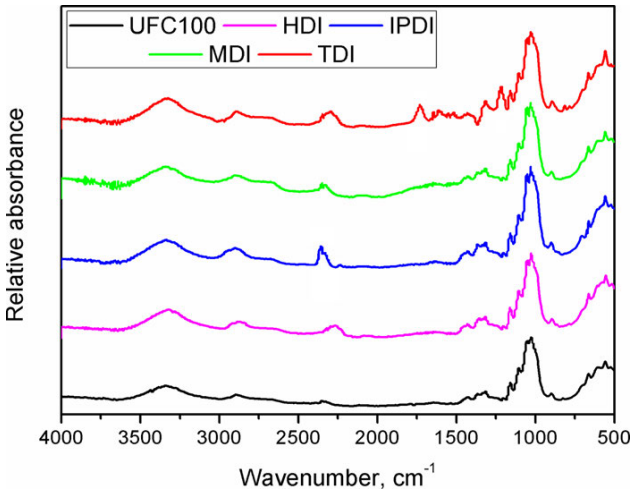


Figure 4: FTIR spectra of UFC100 filler before modification and after treatment with 15 wt% of particular diisocyanates.

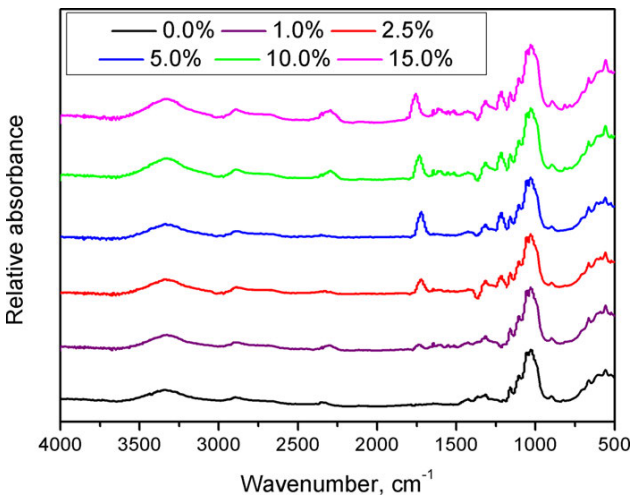


Figure 5: FTIR spectra of UFC100 filler modified with varying content of TDI.

fication of filler. A similar effect was noted for the peaks at 1010–1050 and 1100–1350 cm^{-1}, characteristic for the different types of vibrations of C–C, C–H, C–O, and C–O–C bonds, present in the structure of lignocellulosic materials (Barczewski et al. 2018).

In Figure 5 there are presented FTIR spectra of cellulose fillers modified with varying loading of TDI, which significantly affected their appearance. The magnitude of the peak at 3335–3340 cm^{-1} is increasing with the content of TDI. Modification with 10 and 15 wt% of TDI caused 80, and even 94 % increase, respectively. It was related to the above-mentioned generation of urethane bonds or amine groups during modification. Similar effects were observed for signals attributed to the vibrations of unbonded isocyanate groups and carbonyl bonds included in urethane groups.

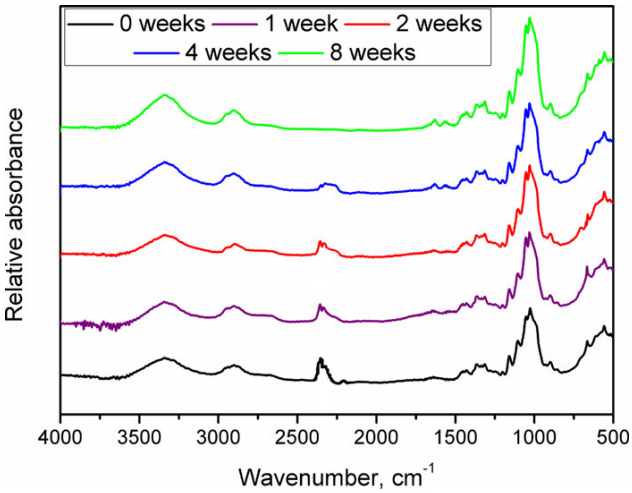


Figure 6: The influence of storage time on the FTIR spectra of cellulose filler modified with 15 wt% of IPDI.

The influence of the storage time on the chemical structure of cellulose fillers is presented in Figure 6 on the example of the sample modified with 15 wt% of IPDI. Noticeable differences can be seen between particular spectra. The signal at 3335–3340 cm^{-1} attributed to the stretching vibrations of hydroxyl and amine groups is increasing with storage time. Its rise by 3, 8, 23, and 61 % was noted, respectively, after 1, 2, 4, and 8 weeks. Such an effect was associated with the progress of the isocyanate reactions with functional groups of the filler and with moisture (see Figure 1). It was also confirmed by the increase of the magnitude of small peaks around 1610–1700 cm^{-1}, characteristic for vibrations C–N and C=O bonds (even 204 % increase for eight weeks of storage), pointing to the generation of urethanes. Also, signals at 1010–1050, and 1100–1350 cm^{-1} were slightly increased. These changes were also correlated with the disappearance of the peak characteristic for the presence of free isocyanate groups, pointing to the changes in the chemical structure of fillers' surface resulting from performed modifications.

Moisture content

In Figure 7 there are presented changes in the moisture content of modified cellulose filler, as a function of type and content of diisocyanate. It can be seen that regardless of the type of modifier, the moisture content of fillers is decreasing after treatment, which is associated with the reduced polarity of fillers' surface. Such an effect is related

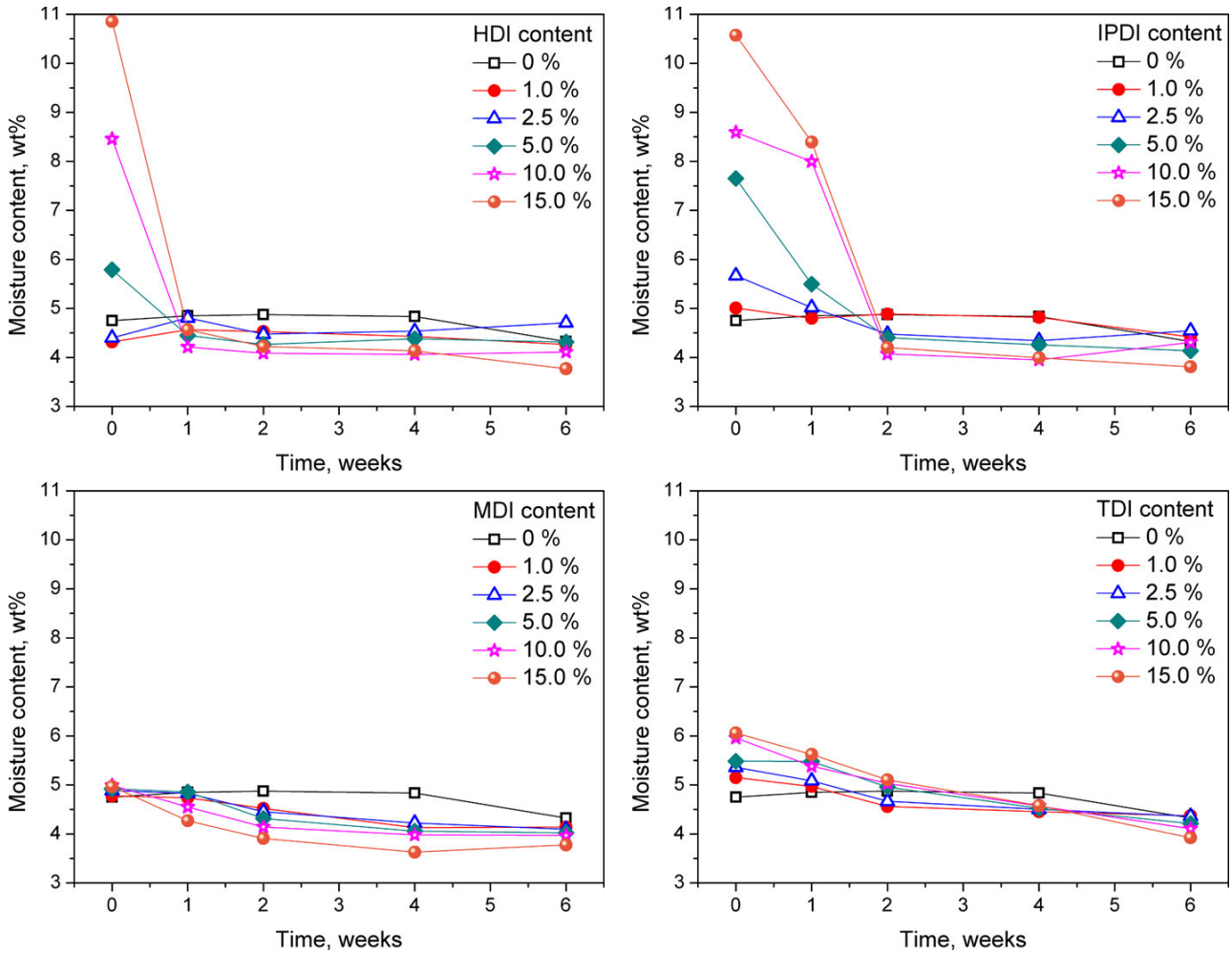


Figure 7: Changes in the moisture content of modified fillers over time as a function of type and content of modifier.

to the changes in the chemical structure occurring during modification. As mentioned above, two main reactions may take place during isocyanate treatment of filler – the reaction of free isocyanate group of modifier with moisture or with hydroxyl groups present on the filler surface (see Figure 1). As a result, after treatment and sufficient storage time, when all reactions are completed, hydroxyl groups may be replaced by amine groups or hydrocarbon part of diisocyanate (when one particle react with two hydroxyl groups of cellulose). Also, the diisocyanate particles may react with two water particles, generating diamine, which can be deposited on the surface of filler and linked via hydrogen bonds. Independently of the outcome, investigated treatment with diisocyanates results in the reduction of fillers' polarity, hence the ability to bond moisture (Yew et al. 2005).

It can be seen that for the fillers modified with aliphatic diisocyanates, the initial values of moisture content were significantly higher than for aromatic ones. Such an effect can be associated with the hygroscopic character of isocyanates, and lower reactivity of aliphatic diisocyanates, due to the higher electronegativity of aromatics (Vilar 1998). Therefore, aliphatic diisocyanates are absorbing more water, when they are unbound because the reaction with functional groups of cellulose filler occurs slower. It can be seen that for modification with HDI, moisture content of filler has significantly dropped after one week, indicating that the desired reactions took place, for IPDI changes were slower, which is associated with the presence of hexane ring and resulting steric hindrance, limiting the reactivity of the isocyanate group attached to a secondary carbon (Randall and Lee 2002). A particle of HDI, due to the six-carbon chain, is significantly more flexible and contains two equally reactive isocyanate groups. A similar effect can be noted for MDI and TDI. In MDI, both isocyanate groups are equally reactive because they

are linked to different aromatic rings. In TDI, the reactivity of the two groups differs also depending on the isomer. In case of 2,4-TDI, after reaction of the first, a more reactive group in the para position relative to the methyl group (assume its reactivity factor is 100), the reactivity of the second one is considered to be over eight times lower (reactivity factor 12) (Vilar 1998). When 2,6-TDI is used, both isocyanate groups are equally reactive, and the reactivity of the second group is over three times lower (reactivity factor 17). However, their initial reactivity is almost two times lower comparing to para-group in 2,4-TDI (reactivity factor 56) (Vilar 1998). In the presented work, the 80/20 mixture of 2,4-TDI and 2,6-TDI was applied. Therefore, changes in the modified fillers hydrophilicity, hence also their water absorption was slower than for MDI. Nevertheless, it can be seen that for the majority of investigated modifications, after two weeks, hardly any changes in moisture content were noted.

Changes in surface polarity

From the physical point of view, the rate of sedimentation of solid particles depends on their concentration, differences in density between particles and fluid, the viscosity of the fluid, and particle-particle interactions (Garrido et al. 2003). Nevertheless, for micrometric particles, especially with high surface area, the solid-liquid interactions also play a critical role (Azema 2006). Therefore, the type of applied liquid and modifications, which are changing the hydrophilicity of fillers' surface, have a significant impact on sedimentation behavior. In order to evaluate changes in fillers' polarity after modification processes, suspensions of fillers in different solvents were prepared, and the sedimentation behavior was investigated. In Tables 5–7, the presented photographs are showing the behavior of neat and modified fillers in applied solvents. In all photographs, the solvents are ordered in the following manner – water, methanol, acetone, *n*-pentane (from left to right).

Table 5 shows the influence of the diisocyanate type on the behavior of modified fillers. It can be seen that unmodified UFC100 filler creates relatively stable suspensions in polar solvents – distilled water and methanol. In acetone, and especially, *n*-pentane, cellulose particles are falling significantly faster. Such an effect is associated with lower densities of these solvents, but also with the differences in polarity. Performed modifications noticeably affected the behavior of fillers, indicating changes in surfaces' polarity. The most significant change was noted for water, which was related to the chemical reactions between free isocyanate groups and solvent particles. As a result, cellulose particles were hardly sinking to the bottom of flasks. Instead, the porous layer was observed on top of the solvent. Its porous structure was related to the presence of carbon dioxide generated in the reactions between isocyanate groups and water (see Figure 1).

Modifications of fillers with diisocyanates also changed their behavior in less polar solvents. Suspensions in the least polar *n*-pentane were also unstable for all samples, slight enhancement was noted for modification with MDI. However, significant differences were noted for acetone. For HDI, MDI, and TDI, the most stable suspensions were noted for this solvent. Considering the values of the relative polarity of water and acetone (1.000 and 0.355, respectively), it indicates a substantial change in surface polarity. For TDI modification, the stability of suspensions was quite similar for methanol and acetone, which points to the slower changes of surface polarity compared to MDI, confirming the results of moisture content analysis.

Table 6 presents the influence of storage time on the behavior of cellulose filler modified with 15 wt% of TDI in solvents. It can be seen that the polarity of the filler surface is changing with time. Initially, particles were creating relatively stable suspensions in methanol and acetone, indicating moderate changes compared to neat cellulose. However, after one week, the polarity of filler changed as a result of the greater extent of desired reactions between filler and modifier. Elongation of storage time resulted in a decrease of filler polarity, which was expressed by the lower suspension stability in methanol and slightly higher in *n*-pentane. When storage time was higher than two weeks, hardly any changes were noted. A similar effect was observed for other diisocyanates.

Table 7 also presents the influence of diisocyanate content on the fillers' behavior in particular solvents. The increase of hydrophobicity was noted, particularly pronounced for MDI. For samples stored for a month, an increase of MDI content led to the more stable suspension in *n*-pentane, while for acetone, and especially methanol, the result was the opposite. For other modifiers, the effect was smaller, which is in line with the results of fillers' moisture content, which are very similar for stored samples.

Conclusions

Presented paper aimed to investigate the impact of type and content of diisocyanate on the structure of modified cellulose filler. Four the most popular isocyanates

Table 5: The influence of the diisocyanate type on the behavior of modified fillers in particular solvents (from left to right – water, methanol, acetone, *n*-pentane).

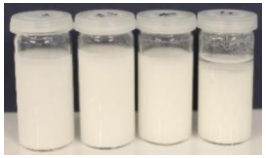
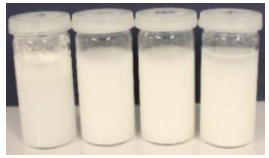
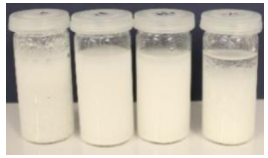
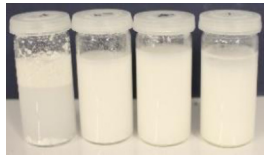
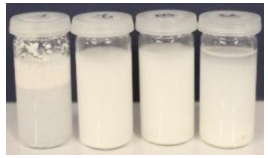
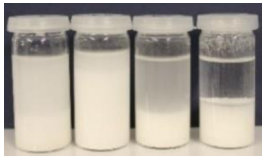
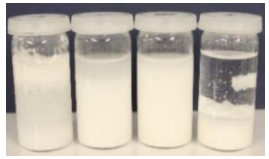
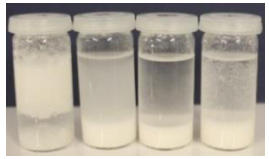
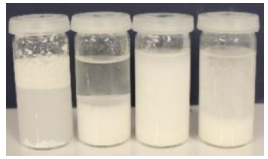
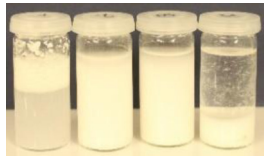
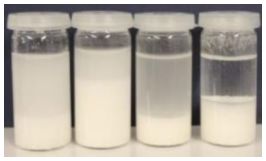
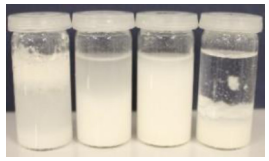
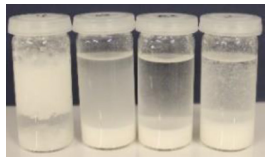
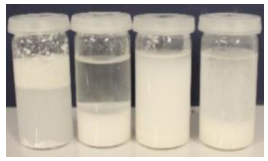
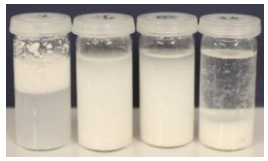
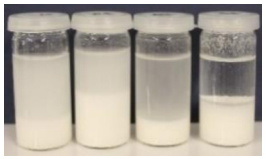
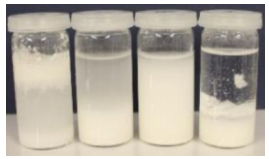
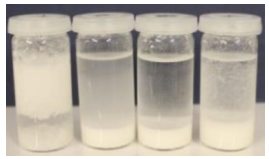
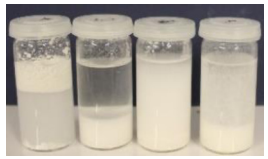
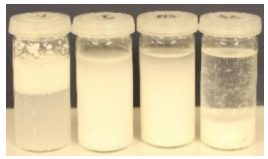
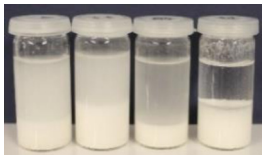
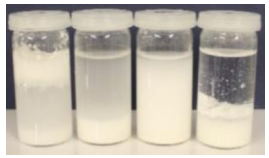
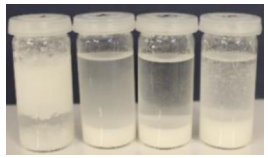
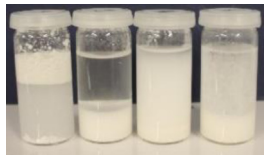
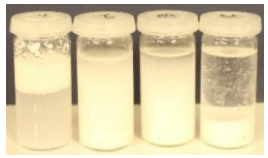
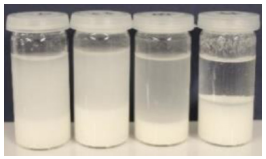
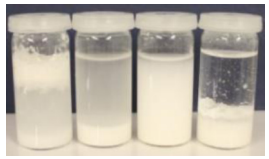
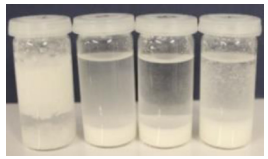
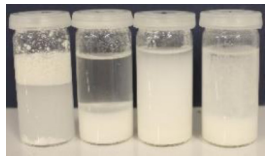
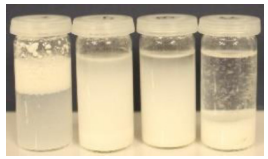
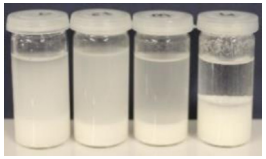
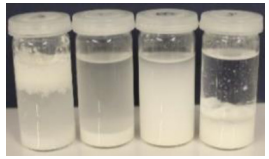
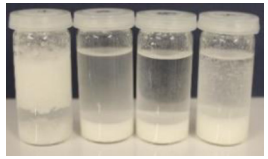
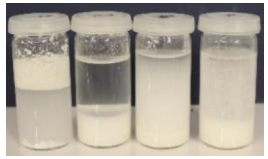
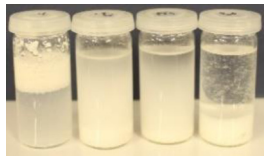
Time, minutes	Sample				
	Neat cellulose filler	HDI, 15 %, 0 weeks	IDPI, 15 %, 0 weeks	MDI, 15 %, 0 weeks	TDI, 15 %, 0 weeks
0					
1					
2					
3					
4					
5					
10					

Table 6: The influence of storage time on the behavior of filler modified with 15 wt% of TDI in particular solvents (water, methanol, acetone, *n*-pentane).

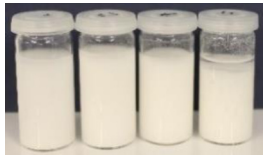
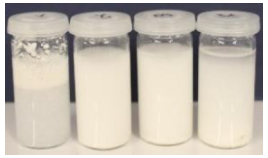
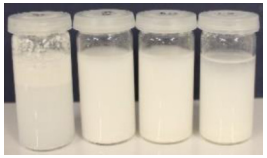
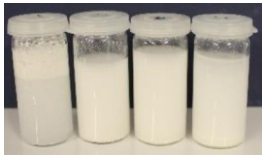
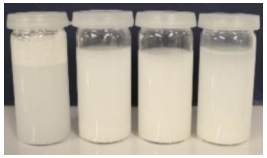
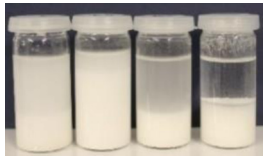
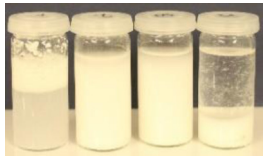
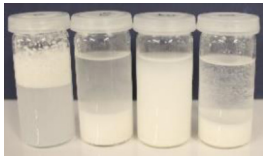
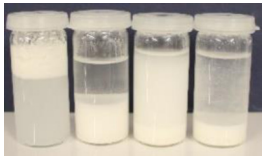
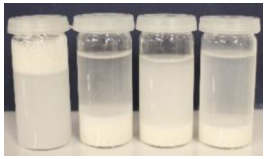
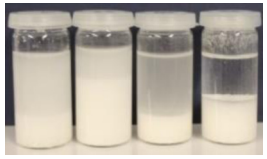
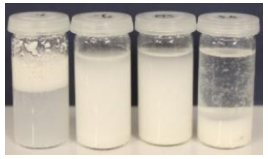
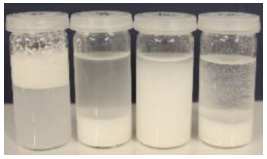
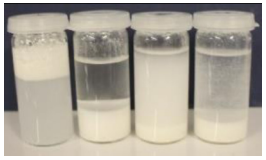
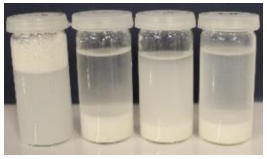
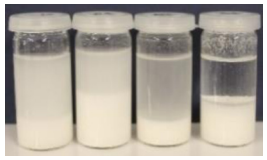
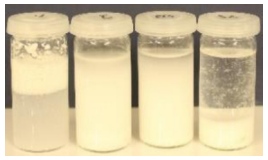
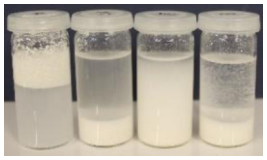
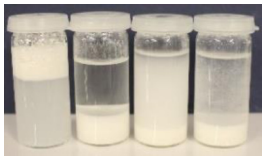
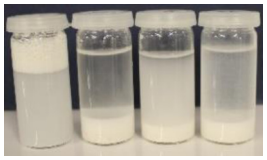
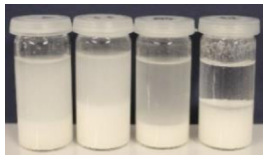
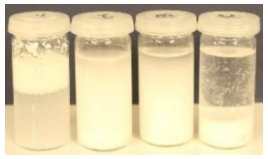
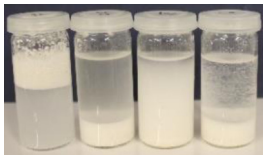
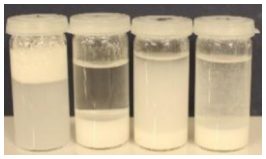
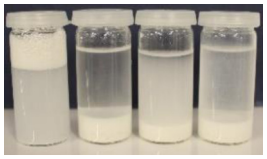
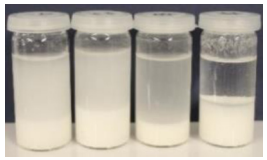
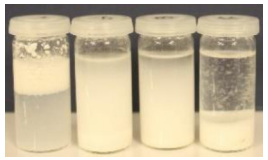
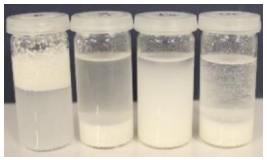
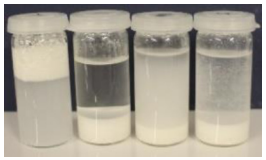
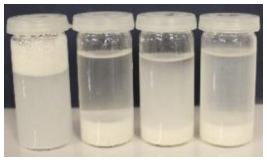
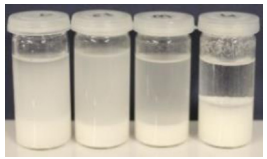
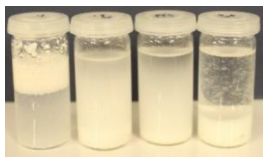
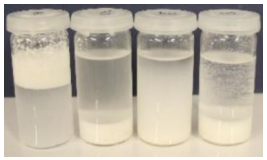
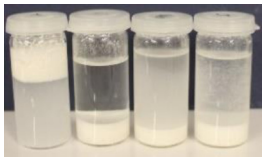
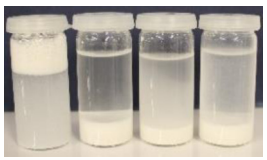
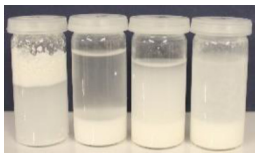
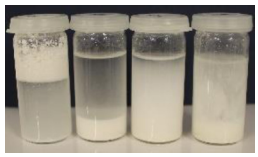
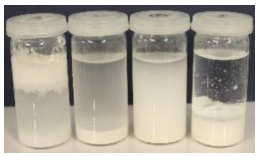
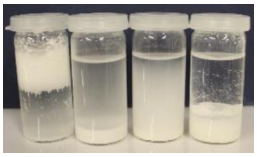
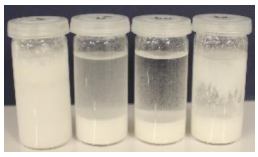
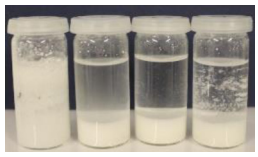
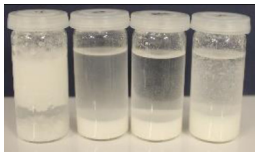
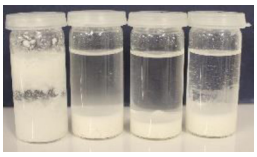
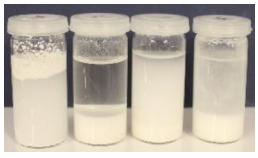
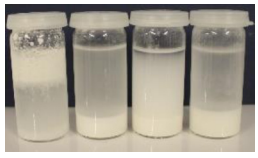
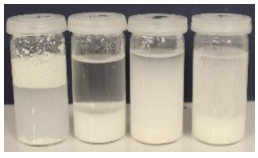
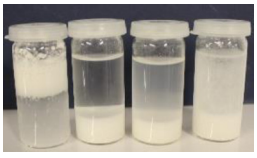
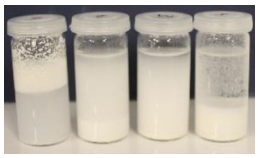
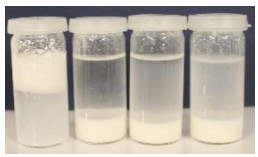
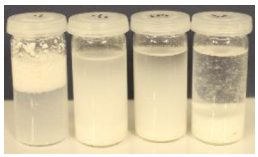
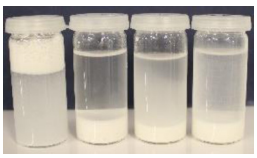
Time, minutes	Sample				
	Neat cellulose filler	TDI, 15 %, 0 weeks	TDI, 15 %, 1 week	TDI, 15 %, 2 weeks	TDI, 15 %, 4 weeks
0					
1					
2					
3					
4					
5					
10					

Table 7: The behavior of unaged and aged modified fillers in solvents depending on the type and content of the modifier.

Modifier	Diisocyanate content, wt%			
	5		15	
	Storage time, weeks			
	0	4	0	4
HDI				
IPDI				
MDI				
TDI				

were applied – isophorone, hexamethylene, toluene and methylene diphenyl diisocyanate – in the amount of 1 to 15 wt%. Chemical structure, and its short-term storage stability, were investigated over a period of eight weeks. Moreover, the main volatile organic compounds detected during modification, as well as emitted from modified fillers before and after storage, were identified.

The main compounds detected during modification were terpenes and terpenoids, which can show the irritating and allergic character, according to Globally Harmonized System of Classification and Labelling of Chemicals. Moreover, some of them are characterized by relatively low values of flash point, even below 40 °C. Therefore, their emissions during modification of cellulose materials should be carefully monitored and proper precautions need to be taken. It should be also considered as very beneficial that during modification of cellulose fillers, diisocyanates were not detected in the enclosed area at ambient temperature (21–23 °C), which was related to their relatively low values of vapor pressure.

At a slightly elevated temperature of 40 °C, diisocyanates were detected among VOCs emitted from modified fillers (vapor pressure of diisocyanates significantly increases with temperature). It suggests that applied modifiers did not react with cellulose fillers immediately and in some part were only deposited on the surface of material. Such an assumption was also confirmed by the FTIR tests and analysis of fillers' behavior in solvents. Nevertheless, during storage of modified fillers desired reactions took place. As a result, after eight weeks, diisocyanates were not detected among VOCs emitted from modified fillers. Successful modification was also indicated by FTIR analysis. Reduction of signals related to the free isocyanate group was noted, while peaks characteristic for urethane and amine groups increased their magnitude. Changes in the chemical structure resulted in the change of the character of fillers' surface from hydrophilic to more hydrophobic. It was confirmed by the reduction in moisture content after modification, which was proportional to the diisocyanate content and elongation of storage time. Changes in polarity were also confirmed by the analysis of fillers' behavior in different solvents. After modification they created more stable suspensions with less polar solvents such as acetone and *n*-pentane, which indicated increased hydrophobicity of surface. This changes should be considered as very beneficial for the potential applications of modified fillers in manufacturing of polymer composites.

Generally, presented paper provided valuable insights into the issue of isocyanate modifications of cellulosic fillers and what is important, in contrast to the majority

of the papers, not only focused on properties of modified fillers, but also their stability over certain storage time and impact of modified fillers on human health and the surrounding environment.

Funding: This work was supported by the National Science Centre (NCN, Poland) in the frame of SONATINA 2 project 2018/28/C/ST8/00187 – *Structure and properties of lignocellulosic fillers modified in situ during reactive extrusion*.

Conflict of interest: The authors declare no conflicts of interest.

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