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Composites & nanocomposites

Sustainable and multifunctional polyurethane green composites with renewable materials

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ABSTRACT

Polyurethane materials are characterised by an ever-expanding range of application possibilities due to their versatility. Currently, the management of leftovers as well as post-production and post-consumer waste for the production of biocomposites is one of the most obvious, effective and profitable solutions. Due to the renewable nature of biofillers such as cellulose, lignin, and chitin, their use to obtain composite polyurethane elastomers is a real perspective for the dissemination of more environmentally friendly materials and, at the same time, contributes to additional economic profit. The key aspect for further development of the polyurethane/biopolymer biocomposite concept is to fulfil of a number of currently functioning industry standards, mainly those regarding functional properties. In the presented research, an attempt to obtain advanced polyurethane elastomers with the addition of biopolymers (cellulose, lignin, and chitin) was conducted for the first time. The innovative biocomposites obtained in this way were characterised by good processing parameters (processing times, density) and improved functional properties compared to the standard without the addition of fillers (abrasion resistance, tensile strength, contact angle, hardness). Due to the above-mentioned facts, the described biocomposites can be successfully used for the production of multifunctional elastomeric materials with a wide range of potential applications. Moreover, it is worth noting that the management of waste materials in this way will reduce production costs while indirectly contributing to the protection of the natural environment.

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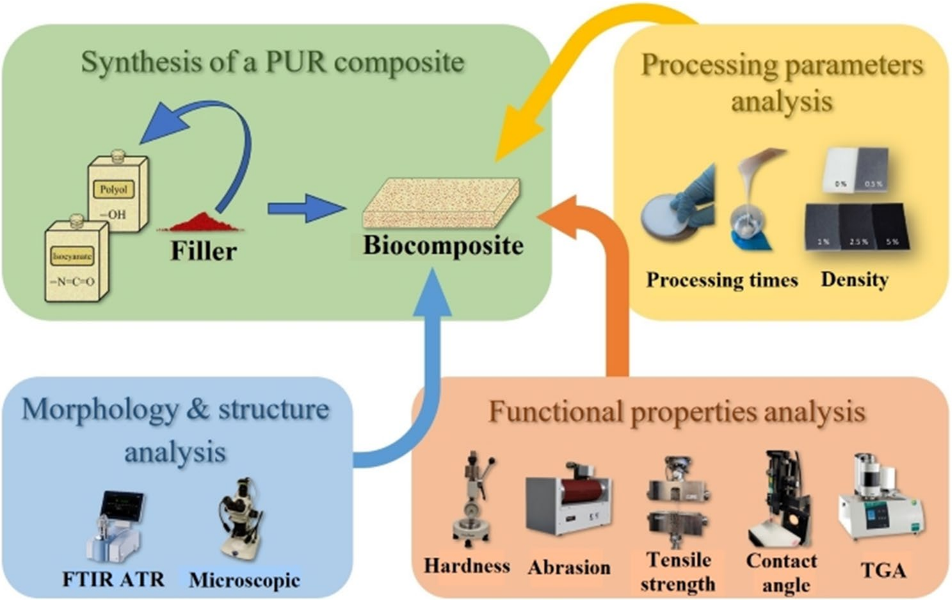
GRAPHICAL ABSTRACT



Introduction

An expansion of ecological awareness can be observed since the begging of the twentieth century. Today, ecology and environmental protection are one of the most frequently discussed topics not only by scientists but also by politicians, mass media, environmental activists, and social media. One of the problems associated with bringing ecological solutions into force is the global dependence on large-scale manufacturing of produce goods. One way to reconcile ecology with mass production is to implement a circular economy approach, namely to minimise waste and maximise the continual use of resources [1–3]. Considering the plastics industry, one of the most obvious and effective solutions to achieving circular economy is the use of post-consumer waste as well as agricultural and post-production waste to produce biocomposites–materials consisting of a polymer matrix and filler of natural origin (biofiller). The most promising biofillers include cellulose, lignin, and chitin, but their potential has not been fully explored yet [4–7].

Cellulose ($(C_6H_{10}O_5)_n$) is a biopolymer and also the most abundant organic material on Earth, which plays a pivotal role in the structural integrity of plant cell walls [8]. It is a polysaccharide made of a linear arrangement of numerous $\beta(1 \rightarrow 4)$ linked D-glucose moieties, which forms chains ranging from several hundred to several thousand units. Cellulose can be obtained, for example, from paper and cardboard waste, agricultural and forest residues, textile wastes, or even from food waste [8, 9]. The effect of the addition of cellulose to the polymer matrix was explored, among others, by scientists from Bucharest (Romania). They added cellulose to a polyethylene matrix. The obtained biocomposite exhibited an increase of the modulus of elasticity, tensile strength, and dynamic modulus. Filler concentration equal to 20% increased the modulus of elasticity 2.5 times [10]. However, scientists from Montreal (Canada) added cellulose to another matrix (polypropylene), which improved the modulus of elasticity—50 phr of cellulose content increased the elastic modulus almost two times [11]. Furthermore, in a research carried out by Alain Dufresne from Grenoble Alpes University (France), the addition of cellulose nanomaterials to poly(styrene-co-butyl acrylate) matrix was analysed. A notable improvement in both the flexibility modulus and thermal stability was observed, even with a low concentration of cellulose nanocrystals [12].

Lignin (the average chemical formula: $C_9H_{10.2}O_{3.4}$) is a complex oxygen-containing aromatic polymer that represents a key component of plant cell walls, along with cellulose and hemicellulose [13]. Lignin exhibits a range of favourable physicochemical characteristics: redox reactivity, remarkable resilience, outstanding heat resistance, antioxidant capabilities and adhesive properties, and it also exhibits antimicrobial behaviour [14]. Lignin is also known to improve the functional properties of polymers. Researchers from Ontario (Canada) added lignin to polybutylene succinate. They found that the addition of this biopolymer improves the tensile, flexural, thermal and thermomechanical properties of composites [15]. Furthermore, scientists from Kanpur (India) added modified lignin to nitrile rubber. The favourable results suggest that the modified lignin may serve as a substitute for more expensive petroleum-derived carbon black in situations when achieving excellent oil and fuel resistance properties is the primary focus, particularly in nitrile rubber applications. The addition of modified lignin led to enhanced thermal stability in vulcanisates, surpassing those achieved with phenolic resin or carbon black [16]. Furthermore, in an experiment conducted by American scientists, the addition of lignin to poly(methyl methacrylate) caused an "extraordinary toughening and strengthening effect" [17].

Chitin ($(C_8H_{13}O_5N)_n$) comprises linear chains of *N*-acetylglucosamine units linked by $\beta(1 \rightarrow 4)$ glycosidic bonds. It is a structural component found abundantly in the exoskeletons of arthropods, the cell walls of fungi, and the beaks of cephalopods [18]. Chitin has also been studied to improve the strength properties of polymers. It was added, among others, to poly(lactic acid). In the study, the mechanical properties of the polymer composites showed a notable improvement compared to pure PLA for all samples [19]. Moreover, researchers from Atlanta (Georgia, USA) conducted a study focused on the addition of chitin nanofibers to poly(ethylene oxide). At 20% of chitin nanofiber loading, the nanocomposites demonstrated approximately a threefold increase in both tensile strength and elastic modulus compared to pure PEO [20]. Additionally, scientists from Joseph Fourier University (Grenoble, France) examined the effect of adding crab shell chitin whiskers to natural rubber. Dynamic mechanical analysis (DMA) revealed a notable enhancement in the rubbery modulus of unvulcanised evaporated natural rubber with the addition of chitin whiskers. In addition to the remarkable improvement in mechanical characteristics, a positive change in the thermal stability of the compound was observed at filler contents greater than 5% by weight, extending up to a temperature of 220–230 °C [21].

Although the described biopolymers have been used for various polymer matrices, this study describes an attempt to apply them to polyurethane elastomers, which has never been tested before. The results may allow to obtain an innovative material characterised by good processing and functional properties, as well as a favourable price. The use of cellulose, lignin, or chitin for polyurethane elastomers on a large scale may have a positive impact on the environment due to the enormous number of applications of polyurethane elastomers, which include e.g. wheels, rollers, bumpers, pipes, boards, fibres, ski boots, life jackets, a number of vehicle and machinery components (in particular fenders, fascia, trims, interior and exterior vertical panels, doors, chassis fairings, and window surrounds) as well as many other items [22–30].

The present study involved the preparation and analysis of the functional and physicochemical properties of polymeric materials consisting of a matrix in the form of a polyurethane elastomer and fillers of natural origin (biopolymers): cellulose, lignin, and chitin. Such biopolymers were used for the first time for polyurethane elastomers (solid materials), in line with the principles of sustainable development, circular economy, and innovative development of materials with specific functional properties.

Experimental

Chemicals and materials

The following substrates were used for the synthesis of polyurethane elastomers and biocopmosites (Table 1):

Preparation of Polyurethane Biocomposites

The preparation of polyurethane composites was divided into two stages. In the first stage, during the synthesis of the elastomer in the cups, their processing parameters (characteristic times, density). In the second stage, elastomer shapes were obtained (casting method using moulds) to be used for further research (utility properties, morphology, and chemical structure). The synthesis of elastomers on a laboratory scale was performed using a one-step method (scheme is shown in Fig. 1).

The process of obtaining EPUR was started with the polyol being weighed. Then the powdered filler was added in the amount of 0.5; 1; 2.5 or 5% by weight calculated on the weight of the polyol. The whole was mixed using a laboratory mixer (dissolver – ProLab,

Table 1 Reagents used in the research

Polyol component	Polyol Blend: white liquid, viscosity: 350–450 mPa s (25 °C), density 1.06 ± 0.03 g/cm^3 (20 °C)
Isocyanate component	4,4′-methylenediphenyl diisocyanate prepolymer: content of isocyanate groups at the level of 20.2–20.6%, viscosity: 930–980 mPa s (25 °C)
Biofillers	α-chitin—micrometric powder (< 10 µm) (Biosynth, Switzerland) Cellulose—micrometric powder (< 10 µm) (Merck, Germany) Alkali lignin—micrometric powder (< 5 µm) (Merck, Germany)

Poland) equipped with a mechanical stirrer (1800 rpm) at a vacuum of 0.98 ± 0.01 bar for 15 min. The purpose of this was to evenly distribute the filler throughout the entire volume of the system, while eliminating air bubbles that could have a negative impact on the final properties of the material. After mixing and deaeration, the isocyanate component was added in the amount of 40 parts by mass of isocyanate per 100 parts by mass of pure polyol and then the system was immediately mechanically stirred by hand for 30 s.

The obtained liquid elastomer system was used in the first place to test the processing times and density. The remaining elastomer was then poured into two industrial laboratory moulds at room temperature in the amount of 40 and 150 g to obtain fittings for a series of tests. The smaller mould made it possible to obtain fittings for testing tensile strength and elongation at break; the remaining tests were carried out on fittings from a larger mould.

Characterisation of prepared biocomposite materials

The analyses of the biocomposites and biocomposites of the reference sample obtained were divided into three types: processing parameters, functional properties, and evaluation of morphological and chemical structure (Table 2).

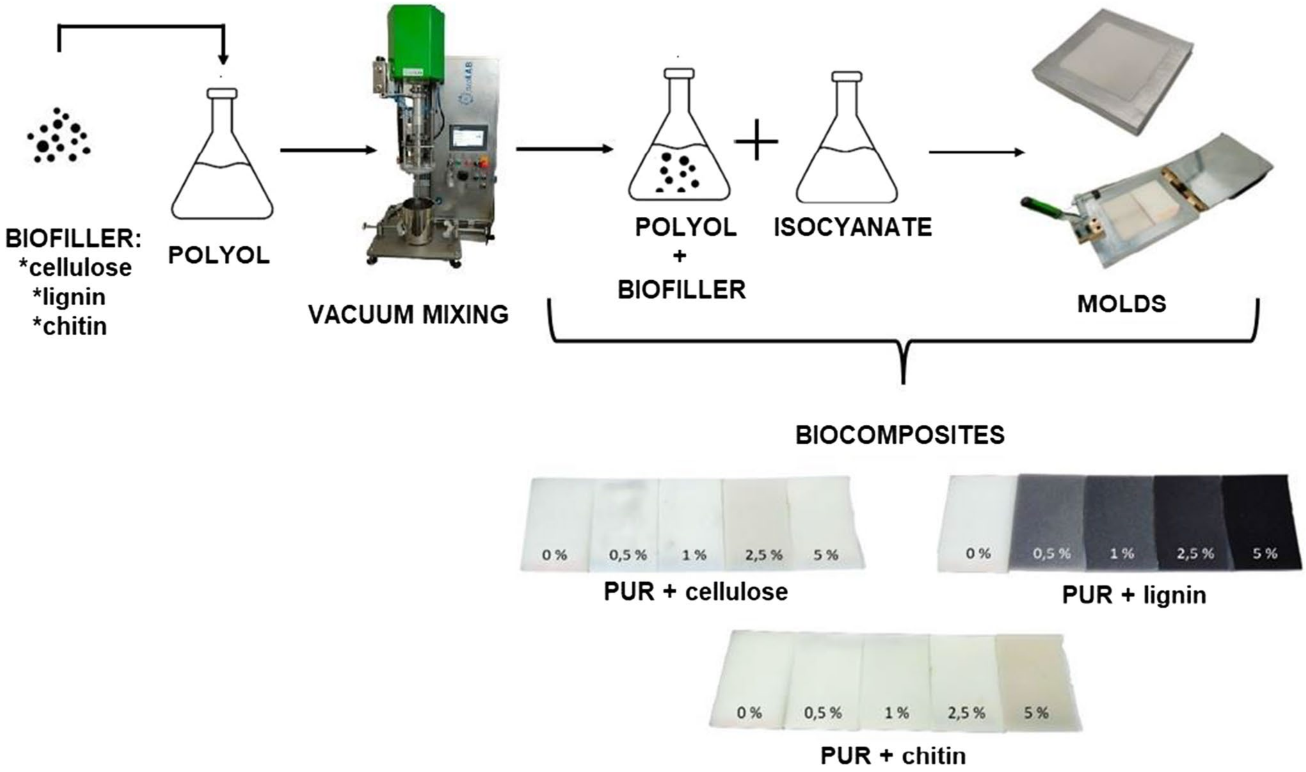


Figure 1 Scheme for obtaining biocomposites based on polyurethane elastomers.

Table 2 Types of performed analyses of biocomposites

Processing parameters	Functional properties	Morphological and chemical structure
Characteristic **processing times**–time of gelation and demoulding	Shore A **hardness** determination, in accordance with PN-EN ISO 868 **Abrasion resistance**, in accordance with PN-ISO 4649:2007	**Surface wettability angle** using the Owens–Wendt method
Density, determined in accordance with PN-EN ISO 845:2010	**Tensile strength** and **elongation at break,** in accordance with PN-EN ISO 1798:2008 **Thermal stability**–thermogravimetric analysis	**Chemical structure**–Fourier transform infrared spectroscopy **Morphology**–microscopic analysis (optical microscope and SEM)

Processing times were determined for each of the resulting compositions. The start of the measurement of time was taken when all the ingredients started to mix. The measurement was aimed at determining two characteristic stages of obtaining polyurethane elastomer materials:

- Gel time—as a result of mixing the components, new chemical bonds are formed. This process leads to the formation of increasingly longer polymer chains and bonds between individual chains (cross-linking). As a result, the viscosity of the system increases until a solid form is obtained. This moment was considered to be the end of the gel time during the measurement.
- Demoulding time, the processes of polymerisation, cross-linking, and maturation of the polyurethane elastomer increase the cohesion and decrease the adhesion of the material. This allows the received element to be removed from the mould without permanent tearing or deflection. The time after which it was possible to perform such an action was considered as the demoulding time.

The determination of **hardness** on the Shore A scale (intended for soft materials) was carried out by pressing with the use of a hardness tester (ZwickRoell 3115, Germany). The results obtained are the arithmetic mean of five measurements taken at different locations on the surface of the elastomeric materials.

When determining the **abrasion resistance**, the volume loss of the sample was determined as a result of its abrasion with an abrasive cloth with a certain degree of granularity (NOSELAB ATS abrasion tester, Germany). The result of the tests was to obtain numerical values of the abrasion indexes (K_S) [mm^3] for all the samples obtained. The results obtained are the arithmetic mean of five measurements taken of the elastomeric materials.

Tensile strength and break **elongation** were performed using a ZwickRoell Allround-Line Z020 TEW (Germany) testing machine. The samples were cut so that they were characterised by the lack of visible structure defects, one of the standardised shapes using punching dies. The results obtained are the arithmetic mean of five measurements taken of the elastomeric materials.

The **thermal stability** of composite polyurethane elastomers was assessed using thermogravimetric analysis (TGA). The weight loss of the station in the set temperature range was displayed using the Jupiter STA 449 F3 analyser from Netzsch (Germany). Testing of the temperature stability in the range of 30–560 °C, reaching the temperature $\Delta T = 10$ °C/min, in the nitrogen atmosphere.

Subsequently, a study was carried out to determine the **surface wettability** of the obtained composites by measuring the wettability angle using two types of liquid: polar (distilled water) and non-polar (poly(ethylene glycol)—PEG) − Goniometer (OCA 20, Data Physics Instruments, Germany). Using FTIR analysis, the characteristic functional groups (**chemical structure**) present in the bicomposites were determined (Bruker Vertex 70 Spectrophotometer, Germany). **Morphological** evaluation was performed using the optical microscope (Optika SN 576408, Italy) and a Tescan MIRA3 scanning electron microscope (Princeton Gamma-Tech, USA).

Results and discussion

The following part of the study is focused on the presentation and interpretation of the obtained results. For this purpose, it was divided into three parts. The first presents the results of measurements of processing parameters (characteristic times and free density). They constitute the basis for a further detailed analysis of composites, providing information regarding the correct course of key chemical reactions. The second part contains an analysis of the results of functional properties tests (abrasion resistance, tensile strength, wetting angle and hardness), which play a key role in the process of assessing the application potential of the obtained materials. The third, last part is focused on the results of morphology and structure research, the most important goal of which is to explain the causes of the obtained results and the phenomena described earlier.

Processing parameters

Obtaining EPUR with appropriate specificity and characteristic processing times is a basic and indispensable aspect for the proper conduct of the production process. An elastomer with excessively fast polymerisation kinetics may pose a challenge to obtain the desired shape and lead to a number of defects in the structure of the product. In turn, if the deformation time is too long, there is a risk that pulling the shape out of the mould will result in irreversible demoulding of the product. This will result in an obvious waste of time and raw materials. It may even be necessary to extend the production cycle, resulting in reduced production volume and efficiency, which are key indicators.

Based on the data presented in Fig. 2a, a clear correlation should be noted between the quantitative addition of filler and the gelation time of the system. The shortest gelation time was recorded for the standard sample (139 s), and the longest for the sample containing 5% chitin (185 s). Increase of the filler content (lignin, chitin and cellulose) results in an extension of the gelation time, which is the expected effect due to the increased viscosity of the system and thus hindered migration and diffusion of the reacting components (Table 3). After a further analysis of Fig. 2a, it can be seen that the amount of filler rather than its type has a greater impact on the gelation stage, because the results for individual additives (in analogous percentage amounts) are very similar.

The results presented in Fig. 2b illustrate the clear impact of the used fillers on the demoulding time of the system, which amounted to 410 s for the reference sample. The addition of 0.5 wt.% chitin contributed to the lowest effect on this final stage (475 s), whereas the longest time after which demoulding was possible for the composite was observed for samples with the

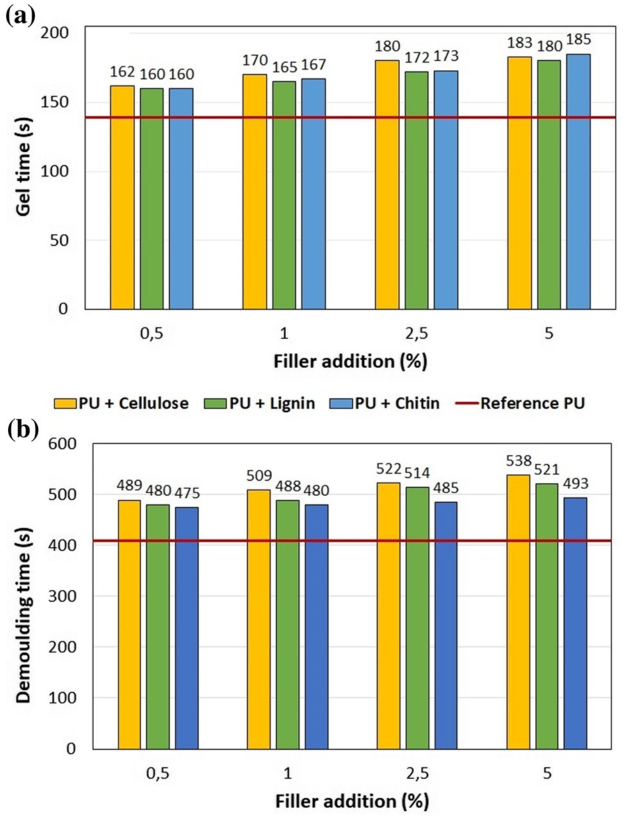


Figure 2 Dependences of characteristic times on the type and amount of filler addition: gel time (**a**) and demoulding time (**b**).

Table 3 Viscosity of polyol systems and density of polyurethane elastomers

Filler addition		Viscosity of the system (mPa s)	Density (kg m^{-3})
Reference sample		370	1022
Cellulose	0.5	389	1023
	1.0	405	1026
	2.5	450	1029
	5.0	489	1032
Lignin	0.5	378	1023
	1.0	382	1024
	2.5	395	1026
	5.0	437	1029
Chitin	0.5	379	1023
	1.0	389	1025
	2.5	411	1028
	5.0	492	1031

addition of 5% cellulose (538 s). The range of fillers used according to the extension of the demoulding time can be presented as follows: chitin < lignin < cellulose. The probable cause is a larger number of available hydroxyl groups compared to other fillers (in chitin some – OH groups in its structure are replaced by *N*-acetylamino groups, in the case of lignin there are numerous steric hindrances). The presented analysis of the results confirms that the addition of the used fillers affects the reactivity of the system and, consequently, also the polymerisation process. During the initial polymerisation (gelation stage), no significant differences were observed in terms of the type of filler used. The differences are only visible at the stage of cross-linking and initial maturation of the polymer—e.g. demoulding time. It should be noted that all observed values are within the limits accepted by industrial practice.

The density of polyurethane elastomers is one of the most important physicochemical properties. Therefore, this was the next stage of the research. The obtained results are presented in Table 3. As expected, an increase in the density of all composite shapes was observed compared to the reference sample (1023 kg m^{-3}). The density increased with the increasing content of biofillers, which were added in the form of powdered solids (density in the range of 1300—500 kg m^{-3}). On average, the highest increase in density was observed with the addition of cellulose (maximum 1032 kg m^{-3}), and the lowest with the addition of lignin (maximum 1029 kg m^{-3}). It should be emphasised that the lack of reduction in the density of the obtained composites compared to the standard indicates the practical absence of water in the used fillers. When solid materials are obtained such as polyurethane elastomers, it is important that they have a compact and uniform structure. The presence of water in the fillers would result in a reaction with the isocyanate. As a result, carbon dioxide would be produced, which would lead to the effect of foaming (obtaining an undesirable cellular structure). The formation of a cellular structure (foaming) translates into a decrease in the density of elastomers. This fact, in turn, leads to the conclusion that the differences observed in functional properties result from unique matrix-filler interactions rather than the reaction of the isocyanate component with water, which is absent in the reference formulation.

The current state of knowledge confirms the correlation between density and functional properties of polyurethane materials, in particular the hardness of the materials. Research by Włoch and Landowska [31] analysed the density of composites and their functional properties. Grinded buckwheat husks were used as a thermoplastic poly(ester-urethane) filler. With the increase in the amount of filler, an increase in the density of the composites was observed (1234–1301 kg m^{-3}) compared to the reference sample (1224 kg m^{-3}). Thus, it had a direct impact on the hardness value obtained from the polymer materials. With increasing density, the composites were characterised by higher hardness. The results obtained were indirectly correlated with tensile strength. The density of polyurethane materials can affect the hardness of the materials (direct relationship). The hardness of composites is discussed in detail in the next chapter.

Functional properties

Shore hardness is a characteristic parameter for elastomers and elastomer-based composites, which influences the range of their potential applications. The hardness values of the obtained elastomers on the Shore A scale are presented in Fig. 3a. The hardness chart that shows the materials as a function of filler type and quantity reveals a trend in which the addition of cellulose, chitin and lignin results in a slight increase in the hardness of the polyurethane elastomer compared to the reference sample (63.6°ShA). The only exception is the composite with 0.5% lignin addition, which exhibits a hardness of approximately 62.9°ShA. However, considering the measurement error, this result does not disrupt the overall trend. This increase can be attributed to the higher hardness of the filler particles compared to the reference elastomer as well as the relationship between the hardness of the elastomers and their density. Furthermore, it can be observed that an increase of the filler content leads to a slight increase in the hardness of the resulting material (except chitin). The results of the hardness measurement for the biocomposites with cellulose and lignin additives show some correlation with the observed demoulding times (elongation of a given stage with increased biopolymer addition). On this basis, it can be speculated that the increased presence of these biopolymers in the PUE structure translates to a higher number of functional groups participating in the cross-linking process. However, this correlation does not apply to materials obtained with chitin addition, as their hardness

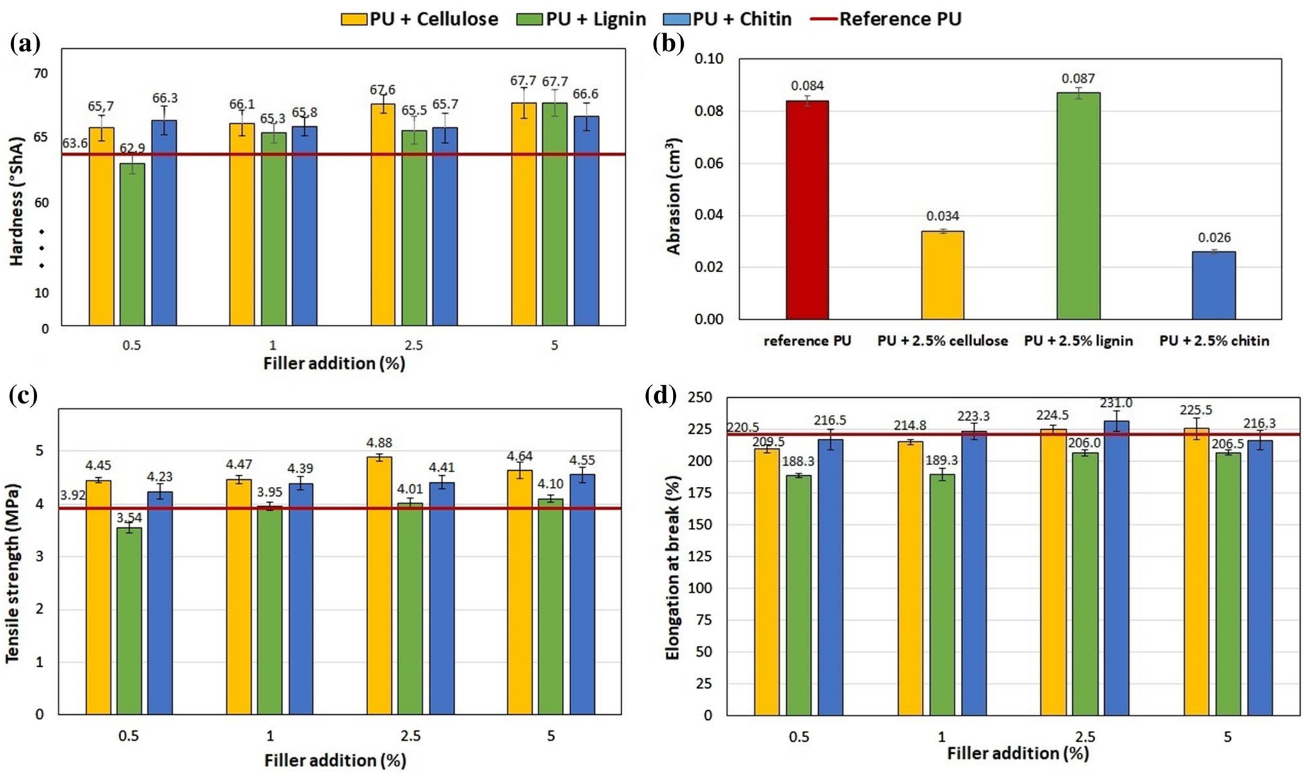


Figure 3 Performance properties of the polyurethane obtained elastomers: hardness (**a**), abrasion resistance (**b**), tensile strength (**c**) and break elongation (**d**).

values range from 65.7 to 66.6°ShA (differences within the statistical error limit) without showing any noticeable trend.

Głowińska and Datta [32] analysed biocomposites composed of a polyurethane matrix and a microcrystalline cellulose filler. Samples with a biopolymer addition in the range of 5 ÷ 20% by weight were examined. The hardness values were found to increase with an increasing content of biofiller (at the highest filler content, the hardness increased from 83.2 to 90.5°ShA, which corresponds to an 8.7% increase). According to the researchers, this suggests a stronger interaction between cellulose and the polyurethane matrix, resulting from the accumulation of hydrogen bonds and the increased hardness of the filler itself [32]. Another confirmation of the influence of biopolymers on increasing the surface hardness of polyurethane materials is provided by research conducted by the team of Veigel [33]. After an analysis of coating materials composed of a PU matrix and a nanocrystalline cellulose filler, it was observed that increasing the biopolymer content in the range of 0 ÷ 2% by weight resulted in an increase in the hardness of the obtained coating [33].

By definition, abrasion resistance refers to the ability of a material to withstand mechanical actions such as friction, scraping, or erosion, which gradually remove material from its surface. The abrasion resistance of polyurethane elastomers is their key advantage. Polyurethane is used for this reason in applications where significant wear occurs due to friction. Examples include bushings, bearings, wheels, and wear liners. In applications that are particularly prone to severe wear over time, polyurethane often outperforms rubber, other synthetic materials, and metals. In many applications, this specific abrasion resistance allows manufacturers to produce polyurethane products using less material than other elastomers would require. The results of abrasion resistance obtained for the materials are presented in Fig. 3b. The obtained results indicate diversification of this key property among the studied materials. The addition of 2.5% by weight of lignin caused a slight deterioration in the resistance to abrasion (higher wear values by 3.6% compared to the reference), while the addition of cellulose and chitin resulted in a significant improvement (lower wear values by 59.5% and 69.0%, respectively, compared to the reference sample). This represents a crucial achievement in terms of enhancing the mechanical properties. The improvement of mechanical properties may result from the structure of the used biopolymers. When cellulose is added, it contributes to the presence of hydroxyl groups. These groups are capable of forming hydrogen bonds between themselves and fragments of polyol molecules already present in the final polyurethane structure. Such bonds may affect the compact internal structure. In the case of chitin, it is noticeable that it can act as a chain extender by forming covalent bonds. As a result, flexible segments are created. This is noticeable during elongation analyses. The direct results of the tear strength tests correlate with the results of the abrasion tests.

The presented results demonstrate the exceptional nature of the obtained materials in light of existing scientific reports. Previous literature reports described a deterioration of this parameter after the use of renewable fillers. Diestel and Krause [34] examined the influence of addition of wood flour on the abrasion resistance of the thermoplastic polyurethane elastomer. For both polyether-based and polyester-based polyurethanes, the best abrasion resistance was achieved for the unfilled elastomer, indicating a deterioration of this property due to the addition of powdered biofiller (absolute values of the Taber wear index (TWI_{1000}) ranged from 55.18 to 510.67 mg, indicating an eightfold increase in abrasion) [34].

Similar results were presented by the research team led by Mengeloğlu [35]. thermoplastic elastomers incorporating 15% and 30% fillers of natural origin, such as teakwood flour, rice husk, and microcrystalline cellulose, were obtained by injection moulding. Abrasion resistance, expressed as TWI_{1000} index values, ranged from 72 to 254 mg. The lowest and highest wear indices were obtained in the unfilled TPUR and the 30% rice husk-filled elastomer, respectively. Regardless of the type of filler, the addition of fillers significantly affected the susceptibility of the material to wear [35].

Shimpi et al. [36] have demonstrated that it is possible to improve the abrasion resistance of polyurethane elastomers by adding powdered fillers (mineral/inorganic). The percentage values of abrasion resistance for nanocomposites based on polyurethane elastomer and 0.5% and 2% by weight of $Mg(OH)_2$ nanoparticles were equal to 2.14% and 1.7%, respectively, while the addition of 2.5% nanoparticles resulted in a value of 2.34%. For the pure elastomer, the abrasion resistance index was 3.34%. Therefore, the results of the composites indicated an improving trend of abrasion resistance by $Mg(OH)_2$ nanoparticles up to a maximum of 2% addition, beyond which this trend reversed. According to the authors, the initial improvement was attributed to the hard surface of the PUE composites with a uniform distribution of the nanoparticles, which caused an alignment of the polymer chain arrangement. Subsequent decrease in properties was due to nanoparticle agglomeration within the elastomer matrix [36].

It should be noted that although the possibility of improving the abrasion resistance of polyurethane elastomers, for example, through the use of $Mg(OH)_2$ nanoparticles, has previously been demonstrated, the composites with biopolymers obtained in this study exhibit even better properties while having greater environmental potential. Nanoscale $Mg(OH)_2$ requires a specific synthesis using highly pure chemical reagents and cannot be aligned with the concept of utilising waste materials, unlike cellulose and chitin.

Typical applications of polyurethane elastomers stem from their exceptional mechanical properties, with particular emphasis on tensile strength and elongation at break. Currently, industrially produced materials exhibit a satisfactory range of these properties for the vast majority of customers. Therefore, the priority of this study was to achieve composites with mechanical properties that would not be inferior to those of the reference, and any improvement would be an additional advantage. The obtained results are presented in Fig. 3c and d.

The data shown in the accompanying graphs indicate a significant difference in the mechanical properties of the obtained materials. It should be noted that the relatively low standard deviation of the obtained results demonstrates good filler dispersion throughout the composite volume. After an analysis of the results presented in Fig. 3c, a tendency of increasing tensile strength with the increase in the amount of a specific filler can be observed. The only exception is the addition of 5% cellulose, which resulted in a decrease of tensile strength from 4.88 to 4.64 MPa (compared to the composite with a 2.5% addition). This result is correlated with the results of the measurements of the water contact angle, gelation time, and elongation at break, in case of which an increase in cellulose content from 2.5 to 5% caused a reversal or at least a visible inhibition of similar trends. Averaging the results for different filler quantities, biocomposites with cellulose additives exhibited the highest tensile strength (up to 4.88 MPa), while those containing lignin as a filler showed the lowest result (up to 4.10 MPa). Only the sample with 0.5% lignin exhibited a lower tensile strength (3.54 MPa) compared to the reference sample (3.92 MPa). The other samples showed improvement in this aspect, which is a positive outcome.

Only four of the twelve investigated composite systems exhibited higher elongation at break than the reference sample (220.5%). These were elastomers with 0.5% and 1% chitin additions, as well as 2.5% and 5% cellulose additions (the elongation at break measurements resulted in 223.3%, 231%, 224.5%, and 225%, respectively). In the remaining cases, the elongation at break deteriorated. It has been reported in the literature that an increased filler content leads to a greater restriction of the molecular motion of macromolecules. Therefore, the addition of more filler causes resistance to flow and ultimately increases susceptibility to tearing [32]. The results shown in Fig. 3d exhibit the opposite trend, as an increase of the filler content leads to an increase in elongation at break. However, it should be noted that beyond a 2.5% addition this trend slows significantly and, in the case of chitin, it is reversed. Based on this, it can be assumed that a 2.5% weight addition represents an optimal filler content in the used polymer matrix.

Particular attention should be given to composite materials characterised by an improvement in both tensile strength and elongation at break. In the present study, these are the systems with 1% and 2.5% chitin additions, as well as 2.5% and 5% cellulose additions. The remaining composites exhibited higher stiffness compared to the unfilled material, which means that the tensile strength increased while the elongation at break decreased. The probable cause is associated with excessive cross-linking of the polymer structure due to the addition of biopolymers in specific quantities, resulting in a higher proportion of rigid segments.

The research results published by Głowińska and Datta [32] confirm some of these assumptions. The tensile strength of the obtained polyurethane composite increases with increasing microcrystalline cellulose (MCC) content. As predicted, the materials also exhibited reduced elongation at break compared to the reference sample. The elongation at break decreased from 454 to 153% with an increase in the MCC content. According to the researchers, the reinforcement effect of the polyurethane matrix by the biopolymer may arise from hydrogen bonding between the hydroxyl groups of the fillers and the urethane group. Additionally, cellulose acts as a multifunctional cross-linking agent, reducing the mobility of polymer segments [32].

The results of the study conducted by Włoch and Landowska [31] provide another example that increasing the amount of biofiller in the form of solid particles in composites results in decreased elongation at break. The addition of 10% powdered rice husk to polyurethane elastomer caused a decrease in elongation at break from 404.1 to 107.2%. Modification of the filler led to higher elongation at break values, however they were still significantly below the reference value (288.4%) [31]. According to the authors, this is a commonly observed trend, which confirms the exceptional properties of the materials obtained in this study.

The resistance of the material to high temperatures is a particularly important parameter in the case of polyurethane elastomers. Elements of mining machinery, pump rotors, conveyor belts, various rollers and wheels—in all these applications they are exposed to increased temperatures resulting from friction forces. The results of thermal analysis using thermogravimetry are shown in Fig. 4a.

Based on the above graph, it can be seen that all of the resulting composites are completely thermally stable at temperatures below 215 ℃. Above this threshold, the sample containing added lignin began to degrade first, while the others remained thermally stable up to approximately 280 ℃. The presented results show that for the lignin biocomposite there are two main stages of thermal degradation: the first one in the range of 215–290 °C and the second one at 290–410 °C. The existence of this difference compared to other systems can be attributed to the fact that phenolic compounds containing an aromatic ring, hydroxyl and alkyl groups are released from the lignin structure at a temperature of about 270 °C [37]. In most cases, the main thermal degradation stage, accounting for more than 50% of the mass loss, is found to be related to the decomposition of urethane bonds, while the remaining stages are usually related to the decomposition of thermally resistant fractions [38]. Most likely, for this reason, at a temperature of approximately 410 °C, only 5% of the original mass remained from the sample of the reference material, while composites with lignin, chitin or cellulose in a similar situation retained 15%, 9% and 10% of the sample mass. The thermal decomposition curve for biocomposites with the addition of cellulose and chitin is close to the standard curve (PUR elastomer without the addition). In the case of

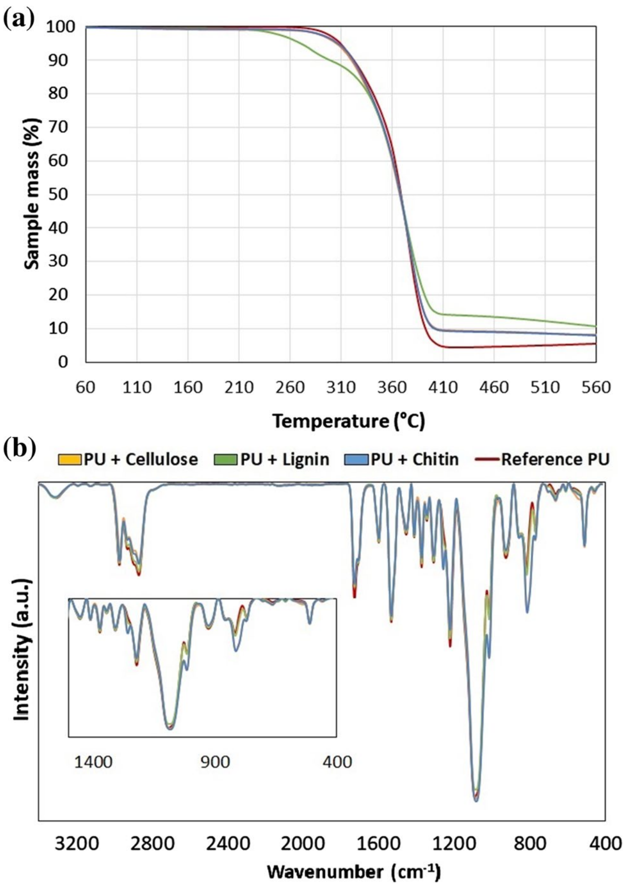


Figure 4 Thermogram (**a**) and FTIR spectrum (**b**) of the obtained polyurethane elastomers.

a biocomposite with the addition of lignin, significant differences can be seen. One of the reasons that may influence this is the structure of the biofillers themselves. Cellulose and chitin have crystalline (ordered) phases in their structure [39, 40]. Due to the presence of strong intermolecular interactions between polysaccharide macromolecules, cellulose and chitin are characterised by greater thermal resistance than amorphous lignin.

Finally, each of the obtained composites is characterised by exemplary resistance and thermal stability, making them ideal materials for the applications mentioned above. The addition of less heat-resistant fillers of natural origin did not reduce the heat resistance of polyurethane materials.

Morphological and chemical structure

Fourier transform infrared spectroscopy analysis was also performed. The aim was to identify specific bonds and functional groups present in the obtained materials. Although the characteristic bands appearing in the spectra are very similar, some variations are noticeable, which allowed for a more accurate interpretation of the obtained results. The results of the FTIR analysis for the standard elastomer and its modified form owing to the addition of fillers are shown in Fig. 4b. The FTIR spectrum confirms the presence of groups characteristic for polyurethane elastomers in the tested material samples. The broad band that occurs at approx. 3300 cm^{-1} was created as a result of stretching vibrations originating from O–H and N–H bonds. The obtained spectra show shifts and demoulding of the stretching bands of the hydroxyl group and the amide band, the probable cause of which is the formation of hydrogen bonds between the rigid segments of the elastomer.

The distinct band occurring in the wave numbers range of 1740–1700 cm^{-1} results from stretching vibrations of the C = O bonds of the urethane group (1740 cm^{-1}) and the ketone and amide groups (1700 cm^{-1}) in the case of the elastomer with the addition of lignin and chitin. The band at 1530 cm^{-1} is the result of stretching vibrations of the C = C bond of the aromatic skeleton, which is an element of the diisocyanate structure. The lack of a band at approx. 2300 cm^{-1}, which is usually a consequence of the presence of an unreacted isocyanate group (− N = C = O), in this case proves that it is practically completely bound by hydroxyl groups coming from the polyol component and the groups competing with them in this respect, included in the used composition fillers.

The band clearly visible at 1260 cm^{-1} only for the spectra of samples with the addition of chitin and cellulose originates from the C–O–C bond between glucoside rings (cellulose) or.

N-acetylglucosamine (chitin). Such bonds do not occur in the structure of lignin and the elastomer itself. The band visible at 1220 cm^{-1} is the effect of stretching vibrations of the C–N bond of the urethane group. The broad band, characterised by particular intensity and occurring at the wave number of 1090 cm^{-1}, is the result of asymmetric stretching vibrations of the C–O–C bond system (Fig. 4b). It confirms the presence of flexible fragments of the polymer chain and originates from the polyetherols used for the synthesis. In the case of the distinctive band around 810 cm^{-1} for the addition of chitin and cellulose, it is difficult to clearly indicate its origin. This region is known in the literature as the "backbone region". As the name suggests, bands in this range are associated with vibrations of the carbohydrate skeleton. Unfortunately, accurate and unambiguous information regarding the structure of polysaccharides in this area is limited and rarely discussed [41].

The observed differences in the intensity of the remaining bands may be caused by differences in the chemical structures of the fillers used and the resulting additional interference or band shifts. Apart from the mentioned changes in the intensity of individual bands, no significant changes were observed compared to those of the reference elastomer. This should be considered a positive phenomenon, because it suggests that the biofillers used do not interfere with the key chemical reactions that lead to the formation of the polyurethane elastomer.

Polyurethanes are a group of generally polar polymers with free surface energy values (SFE) typically not exceeding 40 mN/m. Increased hydrophobicity of elastomers is required in applications that involve prolonged contact with water, such as footwear soles, tyre treads on forklifts, or outdoor mining machinery components. The hydrophobic properties of polyurethane surfaces were characterised using the contact angle measurement. The results are presented in Table 4. On analysis of the accompanying graph, it can be observed that considering the contact angle values for water and the standard deviations of these averaged values, the hydrophobicity of samples with filler additions did not change drastically compared to the reference sample. The reference value was 105.1°, and the lowest and highest calculated values were 100.6° for the addition of 5% cellulose and 108.3° for the addition 5% chitin, respectively. Averaging the results for different quantitative additions of the same filler showed that the composites containing cellulose exhibited the lowest water contact angles, while those with chitin addition showed the highest values. This phenomenon may be attributed to the fact that chitin itself is a crystalline polysaccharide with minimal affinity to water.

According to the research team led by Qi [42], this intriguing behaviour can be interpreted by considering, on the one hand, that the contact angle is influenced by the presence of strong hydrophobic groups in lignin and its rigid aromatic structure. The phenolic hydroxyl groups in lignin can act as cross-linking agents, reducing the free spaces between polymer chains and thereby limiting their mobility. As a result, the composites become more cross-linked, which hinders water penetration and limits surface wetting. However, when the addition of lignin exceeded a certain threshold, partial agglomeration occurred, ultimately increasing the free surface energy [42].

According to Table 4, the most pronounced changes caused by filler additions are evident compared to water. Almost all samples exhibited a higher average contact angle value for PEG relative to the reference, which had a contact angle of 74.0°. The only exception is the composite with 5% lignin addition, which resulted in a contact angle of 73.0°. The highest value was also recorded for the composite with lignin, at a 2.5% addition. In general, it can

Table 4 Average contact angle for the obtained samples in the case of water and PEG

Tested sample	Medium used			
	Water		PEG	
	Average contact angle (°)	Standard deviation (°)	Average contact angle (°)	Standard deviation (°)
Reference sample	105.1	2.1	74.0	1.1
PU + 0.5% cellulose	102.4	2.9	75.0	1.1
PU + 2.5% cellulose	103.7	2.4	74.9	4.4
PU + 5% cellulose	100.6	3.2	78.7	2.7
PU + 0.5% lignin	106.1	2.1	76.7	2.6
PU + 2.5% lignin	107.2	1.4	82.6	2.8
PU + 5% lignin	102.3	2.4	73.0	2.5
PU + 0.5% chitin	107.0	1.5	76.4	1.8
PU + 2.5% chitin	105.5	1.4	78.7	0.6
PU + 5% chitin	108.3	3.2	77.1	0.8

be stated that the affinity of the composite materials toward PEG increased compared to that of the conventional elastomer. Zia et al. [43] synthesized chitin-based polyurethane materials and examined their surface properties. Contact angle measurements demonstrated that as the chitin content increased, the hydrophobicity also increased. The hypothesis was put forward that the hydroxyl groups present in the chitin structure participate in intramolecular hydrogen bonding, enhancing the crystallinity of the polymer matrix. This, in turn, may limit the swelling ability of the polymer. Therefore, it was shown that the introduction of chitin into the polyurethane structure without agglomeration leads to increased surface hydrophobicity [43].

Images of all elastomer samples were taken using an optical microscope and scanning electron microscope (in order to better present the structure of composites). The aim was to visually assess the occurrence of filler agglomeration in the structure of composites and to outline the scale of this phenomenon if it was noticed. Figures 5 and 6 include photographs of a reference sample of elastomer and composites, which is the basis for determining the changes that occur in the obtained samples. Based on Figs. 5a and 6a, it can be seen that even samples without the addition of fillers may contain some structural imperfections in the form of single air bubbles. Their occurrence is completely expected and acceptable when casting fittings using the "manual" method, not using low-pressure units.

Optical and SEM images of composite samples with the addition of cellulose presented in Figs. 5b, c and 6b, c are largely similar to those with the addition of chitin. As in their case, the addition of 5% by weight significantly modifies the appearance of the sample cross section. Figures 5f, g and 6f, g show a gradual increase in the amount and degree of imperfections in the composite structure with an increase in the content of chitin as a filler. The addition of 0.5% does not cause such visible changes in the sample cross section. When using 5.0% filler, single filler clusters can be noticed, which significantly change the appearance of the cross section. It is also possible to see numerous clusters of filler particles within the image (it is marked in yellow in SEM photographs—Fig. 6). These results are correlated with the observed mechanical test results. The addition of 2.5% chitin resulted in an improvement in both tensile strength and elongation at break, while the addition of 5% resulted in a deterioration of these properties or at least inhibition of the positive trend.

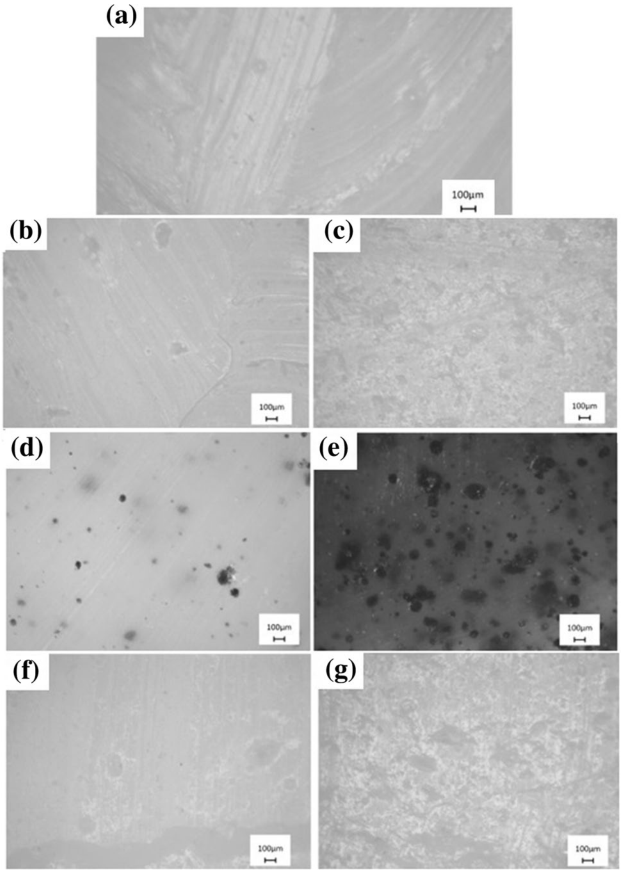


Figure 5 Microscopic photographs of the reference sample (**a**) and polyurethane elastomer composites with the addition of cellulose: 0.5% (**b**) and 5.0% (**c**), lignin: 0.5% (**d**) and 5.0% (**e**), chitin: 0.5% (**f**) and 5.0% (**g**).

Analogously to the above-mentioned addition of chitin, cellulose improves the mechanical properties typical of elastomers. The reasons for such numerous coherences between composites with the addition of chitin and cellulose are probably associated with the high degree of similarity of their chemical structures. Both are linear polymers belonging to the group of polysaccharides, but chitin additionally possesses *N*-acetylamino groups in the unit structure, unlike cellulose, which contains only hydroxyl groups. In turn, significantly different observations regarding composites with the addition of lignin can be explained due to the high degree of chain branching and the presence of aromatic rings.

The best examples for observing changes in the spatial distribution of filler particles (optical images) are Fig. 5d, e. The dark lignin particles contrast with the white colour of the polyurethane matrix, allowing the observation of the distribution (dispersion) of the

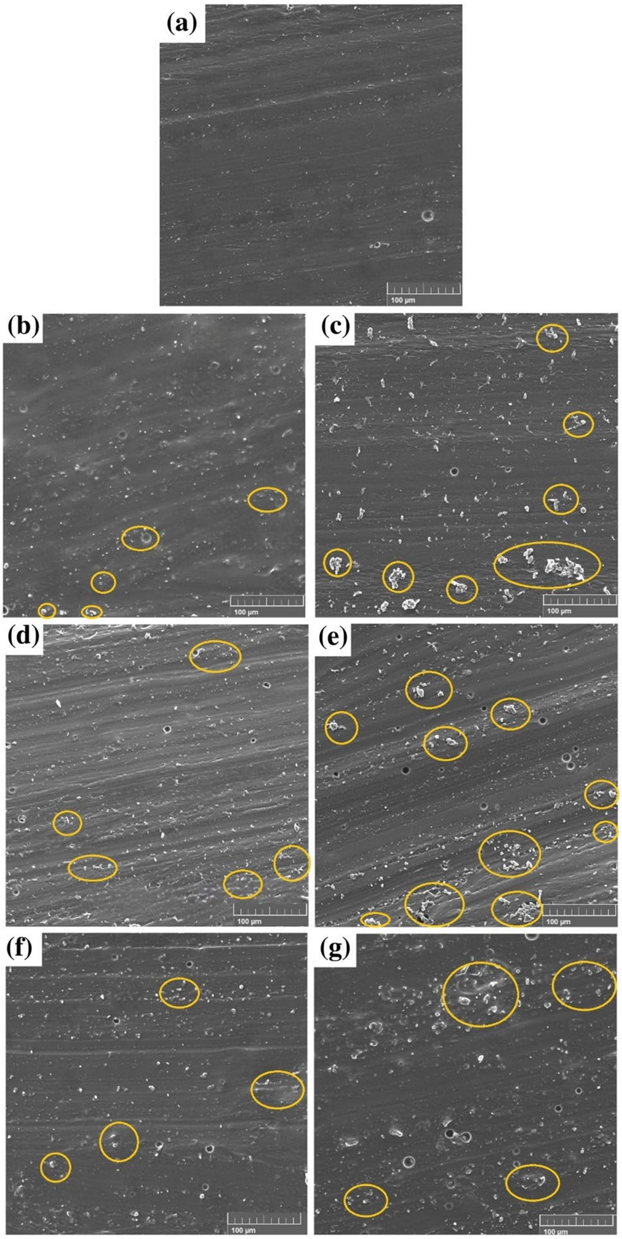


Figure 6 SEM photographs of the reference sample (**a**) and polyurethane elastomer composites with the addition of cellulose: 0.5% (**b**) and 5.0% (**c**), lignin: 0.5% (**d**) and 5.0% (**e**), chitin: 0.5% (**f**) and 5.0% (**g**).

filler on the surface and partially inside the sample. In particular, the heterogeneous structure (agglomerations and bubbles or defects) is confirmed by Fig. 6d, e. Because of this, it is possible to observe that only the addition of 5% biopolymer by weight results in the local occurrence of agglomeration of filler particles. This phenomenon is the probable reason for stopping the trend to increase the tensile strength of the obtained composites.

Conclusions

After an analysis of the obtained results, it can be concluded that the addition of biopolymers in the form of cellulose, chitin and lignin is an innovative solution for obtaining multifunctional polyurethane elastomers.

The addition of the above-mentioned fillers to the reference reaction mixture resulted in shapes with a slightly higher density than that of the reference sample (without the addition of fillers). The influence of fillers on functional properties, mechanical properties in particular, turned out to be an extremely important aspect. The addition of cellulose and chitin significantly improved abrasion resistance. This parameter is very important for solid materials and difficult to achieve. It is worth mentioning that the two mentioned biofillers also improved the tensile strength. In the case of the addition of chitin, an increase in elasticity can be observed and, consequently, an increase in elongation during stretching. This is an extremely important achievement in the preparation of biocomposites. When lignin was added, the mechanical properties did not improve. In the case of both composites (PUR + cellulose or chitin), there was a significant improvement in functional properties without significant deterioration of the processing parameters. This fact determines the significant application potential of the described materials.

FTIR analysis confirmed the presence of bonds and functional groups in the structure of the obtained materials, which are characteristic for polyurethane elastomers. This means that the addition of the used fillers does not disturb the processes and reactions necessary to obtain polyurethane elastomers. Microscopic photographs indicate the occurrence of structural defects and local agglomeration of filler particles in case of 5% addition, which was reflected in some of the results of functional properties. This shows a clear correlation between these two phenomena and the properties of the obtained materials.

Polyurethane elastomers with the addition of biopolymer fillers were successfully obtained and thoroughly analysed. The results obtained in the framework of this research indicate the significant potential for applications of these materials. Their introduction on a large industrial scale would not only be economically justified but would also have an indirect positive impact on the natural environment.

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Author contributions

PB contributed to conceptualisation, methodology, formal analysis, investigation, writing—original draft, writing—review & editing, visualisation; KS contributed to validation, formal analysis, investigation; MT contributed to formal analysis and investigation; and SB contributed to writing—review & editing, supervision, funding acquisition.

Data availability

Data supporting the results of this study are available upon request from the corresponding author.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical approval Not applicable.

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