

## Evaluation of highly filled epoxy composites modified with walnut shell waste filler

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**Abstract** Epoxy composites modified with ground walnut shell used as organic waste fillers were prepared and examined. Post-agricultural waste materials after grinding were characterized by evaluation of grain size distribution and structure observations realized using scanning electron microscope (SEM). The influence of filler addition on the mechanical properties of epoxy-based composites was determined by: static tensile test, Charpy impact test, and ball indentation hardness measurements. Composite samples containing 20, 30, 40, and 50 wt% of walnut shell were characterized by increased stiffness and hardness in comparison to the unmodified resins. Moreover, the incorporation of the filler resulted in a decrease of composite material tensile strength and impact resistance. Thermo-mechanical properties of the composites were investigated by dynamic mechanical thermal analysis (DMTA). Results obtained from DMTA tests showed a growth in the composites' stiffness at elevated temperatures as a function of the increasing natural filler content. The material characterization was supplemented by thermal stability evaluation realized by thermogravimetric analysis (TGA). It was found that the incorporation of ground walnut shell led to an improved thermal stability of composite materials. The analysis of the change in composite material properties, caused

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by natural filler incorporation, was complemented by material microstructure observations.

**Keywords** Composite · Natural filler · Epoxy resin · Walnut shell · Mechanical properties

## Introduction

The purpose of fillers introduced into polymers is to reduce costs, improve the processing properties, and achieve a change in material properties to mention only increase in stiffness and strength [1] as well as improved thermal resistance or conductivity [2, 3]. Polymer composites modified with natural fillers are an alternative to traditional materials, such as wood and its substitutes (chipboard, fiberboard, plywood), as well as so-far used polymer composites modified with inorganic fillers. The unquestionable advantage of natural organic fillers is their availability (the possibility of acquiring raw materials from any part of the locally occurring plants), renewability, and relatively low cost which contributes to a reduced end-product price [4]. It was proved that financial resources necessary to obtain plant material may be twice lower compared with glass fiber, even four times in relation to the aramid fiber, and up to five times to the carbon fiber [5, 6]. Moreover, natural fillers especially powder-like are further characterized by significantly lower energy consumption needed for their manufacturing [7]. Several advantages resulting from the replacement of inorganic and synthetic fillers with organic materials for composite material production should be specified: low density, natural origin, satisfactory mechanical properties, high vibration damping ability, and good thermal insulation [5, 8].

According to the data presented by Nova-Institut GmbH and Asta Eder Composite Consulting, the production of polymer composites modified with natural fillers named wood-plastic composites (WPC) and natural fiber composites (NFC) reached 352,000 t in European Union (EU) in 2012 which represents almost 15% of the European composite market. Natural fillers used as a reinforcement of polymer composites can be extracted from stems, leaves, fruits, as well as lignified parts of plants (seeds, husks, hulls) [5]. Wood flour and cotton fibers, whose share on the European market is 54 and 32% respectively, are the most common natural fillers used in industrial practice [9]. The remaining 14% includes various types of fiber-like fillers of which the most popular are: flax (64% share of the NFC market in the EU with fillers other than wood and cotton), jute (11%), hemp (10%), and sisal (7%) [9, 10]. Various plant fillers used for natural composite production, such as: bamboo, coconut, kenaf, ramie, nettles, abaca, pineapple, sugar cane, rice, and grass, can be found in the literature and industrial applications [10–12]. Except for the specially prepared fiber-like natural fillers (e.g., bamboo, kenaf, jute, and flax), great attention is placed on the incorporation of agricultural waste materials into polymeric matrix. Lignified parts of agricultural plants in the form of various types of shells and husks have become valuable products to be used in composite

modification processes due to their high availability and scarce interest of other industrial sectors i.e., energy and biochemical industry (production of biopolymers) [4, 13, 14]. It is noteworthy that despite the fact that natural composite material production in the EU is third in the world, many NFC products are still imported from the United States and China which are the biggest producers of this kind of assortment [15]. Therefore, finding new low-cost composite materials based on regional natural fillers, especially from agricultural industry, seems more than reasonable. Numerous publications describing composites with the abovementioned fillers are a good proof of the vast applicability of natural composites modified with post-agricultural waste fillers [16–18]. On the basis of economic analysis accounting for its availability and cost of subsequent preparation to be applied as a polymer filler (including grinding and drying), it was found that the price of 1 kg of ground walnut shell obtained in Poland (Central Europe) in 2017 is about 0.12 USD. Therefore, the application of this type of filler in case of low-cost composites can be justified.

The aim of this study is to develop and characterize composites based on epoxy resin highly filled with post-agricultural waste material. Available and inexpensive waste material in the form of ground walnut shell was used as a filler instead of wood flour. It should be underlined that several studies focusing on the application of walnut husks as a filler in thermoplastic and thermoset composites can be found in the literature [19–22]. However, the amount of natural reinforcement used in polymer matrix usually did not exceed 25 wt%. The presented studies include detailed descriptions of filler preparation and characterization, as well as composite production procedure. Composite materials containing different amounts of natural filler were subjected to a series of tests comprising: static tensile test, impact resistance and hardness measurement, dynamic mechanical thermal analysis, as well as thermal stability evaluation. The influence of the filler addition on epoxy composite properties was supplemented by microstructure observations and FT-IR spectroscopic analysis. The main objective of this research was to determine the possible applications and limitations of highly filled thermoset composite materials modified with an organic waste filler coming from the agricultural industry. Attempts were made to determine if and how the features of the ground walnut shell (geometry, chemical constitution, water content) affect the curing process, mechanical and thermo-mechanical properties, and also thermal stability of the composites. To better investigate the relationship between the features of the components and the composites' properties, no additional modifiers and adhesion promoters were incorporated to the mixtures.

## Experimental

### Materials

Epidian 624 epoxy resin, based on bisphenol A (BPA, epoxy number 0.48–0.51 mol/100 g, viscosity 600–800 mPa s, density 1.11 g/cm<sup>3</sup>), and isophorone diamine curing agent (IDA, amine number 250–350 mg KOH/g, viscosity

150–300 mPa s, density 1.02 g/cm<sup>3</sup>), both produced by CIECH Sarzyna S.A.(Poland), were used as polymer matrixes. Composition ingredients were proportioned by weight: 50 wt% of curing agent for 100 wt% of epoxy resin. Pot life of the composition was ca. 50 min. Walnut husk (*Juglans regia* Species, WS) obtained from AGRO Jarosław Seroczyński (Poland) was used as a lingo-cellulosic post-agricultural waste filler.

### Sample preparation

Preparation involved grinding of the filler was carried out on a laboratory mill sieve type MUKF-10 (Młynpol, Chwaszczyno, Poland). During the milling process, sieve mesh with a size of 0.2 mm was used. Next, the drying process was performed using Plus II Incubator (Gallenkamp, Loughborough, Great Britain). The drying time at a temperature of  $40 \pm 2$  °C was 7 days. Additionally, a drying process at a temperature of  $60 \pm 2$  °C and time 24 h was carried out before the production of the composites.

Mixing of the natural components with the resin was carried out using a high-speed mechanical stirrer with a water jacket (CILP-NRI, Warsaw, Poland). Observations conducted during the mixing showed that the solution prevented excessive temperature rise and the maximum temperatures during mixings not exceeded 43 °C. The natural filler of 20–50% by weight was introduced into the epoxy resin and stirring was performed using three rotational speeds: 7000, 10,000, and 17,000 rpm; which were applied for 3, 1.5, and 0.5 min, respectively. Subsequently, the mixture was degassed at a temperature of about 25 °C for 30 min, using a laboratory vacuum dryer Goldbrunn 1450 (GOLDBRUNN THERM, Zielona Góra, Poland). Then, IDA curing agent was added, the components were stirred again for 2 min at a speed of 7000 rpm and degassed in a vacuum dryer for 10 min. Normalized specimens were formed by casting into heated forms coated with a resolving agent. The cast samples were conditioned after curing at room temperature for 7 days.

### Methods

The particle size distribution of ground walnut shell was defined by means of vibratory sieve shaker AS 200 (Retsch GmbH, Haan, Germany), equipped with eight sieves with the following mesh size: 0.02, 0.032, 0.063, 0.071, 0.125, 0.25, 0.5, and 0.8 mm. Measurements were carried out on a loose sample with the mass of 50 g in time of 1 h. The whole of the mechanically fragmented plant raw material was used for the preparation of the composites, without separating the individual fractions.

The evaluation of geometry and surface structure of ground natural fillers were based on scanning electron microscopy SU-8010 (Hitachi High-Technologies Corp., Tokyo, Japan) photographs analysis. Prior to the tests, all specimens were located on the carbon tape and covered with a layer of gold using sputter coater SC7620 (Quorum Technologies Ltd., Lewes, Great Britain). The electron accelerating

voltage of 5 kV was applied and the magnifications of 50×, 1000×, 2000×, and 4500× were used.

The FT-IR measurements were conducted by means of a Fourier transform spectrometer Vertex 70 (Bruker Corp., Billerica, USA) at an ambient temperature (23 °C). To analyze the ground walnut shell, cured epoxy resin and composites' surfaces and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FT-IR) were used. In all cases, a total of 64 scans at a resolution of 1 cm<sup>-1</sup> was used to record the spectra. All spectra, including the CO<sub>2</sub> one, were submitted to weather correction.

Moisture content was determined according to the methodology presented in the ISO 16979 standard, after taking into account the modifications defined in EN 15534-1. Three samples, randomly selected from each batch, weighing about 10 g each, were placed in the laboratory dryer at a temperature of 103 °C (±2 °C) until the difference between subsequent weighings, carried out at an interval of 24 h, exceeded 0.1%. The moisture content of the composites was calculated in accordance with the following equation:

$$H = \frac{m_0 - m_1}{m_1} \times 100$$

where  $m_0$ —is the initial mass of the test piece (g),  $m_1$ —is the mass of the test piece after drying (g).

Mechanical properties of unmodified epoxy resin and epoxy composites were determined in static tensile test according to European standard ISO 527, by means of Zwick Roell Z020 TH ALLround Line universal testing machine (Zwick GmbH & Co.KG, Ulm, Germany) with 20 kN nominal force. Tests were realized with 5 mm/min cross speed. The impact strength of the unnotched samples with 10 × 4 × 15 mm dimensions was measured using Dynstat method (DIN 53453). Hardness evaluation was carried out using Hardness Testing Machine KB 150 R (KB Prüftechnik GmbH, Hochdorf-Assenheim, Germany) in ball indentation hardness test according to ISO 2039 standard. All collected data were statistically elaborated using analysis of variance ANOVA, followed by Scheffe's test using Statistica (data analysis software system) version 10-2011 (StatSoft, Inc., Tulsa, OK, USA).

The DMTA test was performed using MCR 301 rheometer (Anton Paar GmbH, Ostfildern-Scharnhausen, Germany) equipped with a torsion DMA measuring tool. Investigations were carried out with a constant frequency of 1 Hz and a strain of 0.01%. All samples were evaluated in the temperature range from 20 to 160 °C with a temperature ramp of 2 °C/min.

Thermal stability of the filler, unmodified epoxy resin, and epoxy composites were determined by thermogravimetric analysis realized in the temperature range of 30–900 °C at a heating rate of 10 °C/min under nitrogen atmosphere, using a TG 209 F1 Libra apparatus (Erich NETZSCH GmbH & Co. Holding KG, Selb, Germany). 5 ± 0.1 mg samples were placed on ceramic pans. The initial decomposition temperature  $T_i$  was determined as a temperature at which the weight loss was 5%. Additionally, thermal decompositions at 10 and 50% weight loss were presented. The residual mass ( $\Delta W\%$ ) was defined at 900 °C.

The samples' fractures were examined and digitally captured using a scanning electron microscope Evo 40 (Carl Zeiss Microscopy GmbH, Jena, Germany). The electron accelerating voltage of 12 kV was applied. Prior to the tests, all specimens were sputtered with a layer of gold. The magnification of 400 $\times$  was used.

## Results and discussion

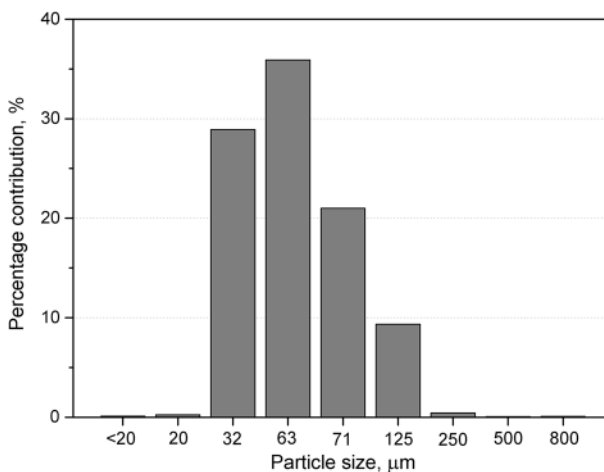
### Natural filler analysis

In Fig. 1, the grain size distribution of ground walnut shell corresponds to the amount of material which remained on a sieve with a specified mesh size. Based on the analysis, it was found that the prepared filler was characterized by a relatively homogeneous size distribution. The analysis of the results allowed to determine that the size of the majority of the constituted particles (95%) was in the range of 32–125  $\mu\text{m}$ .

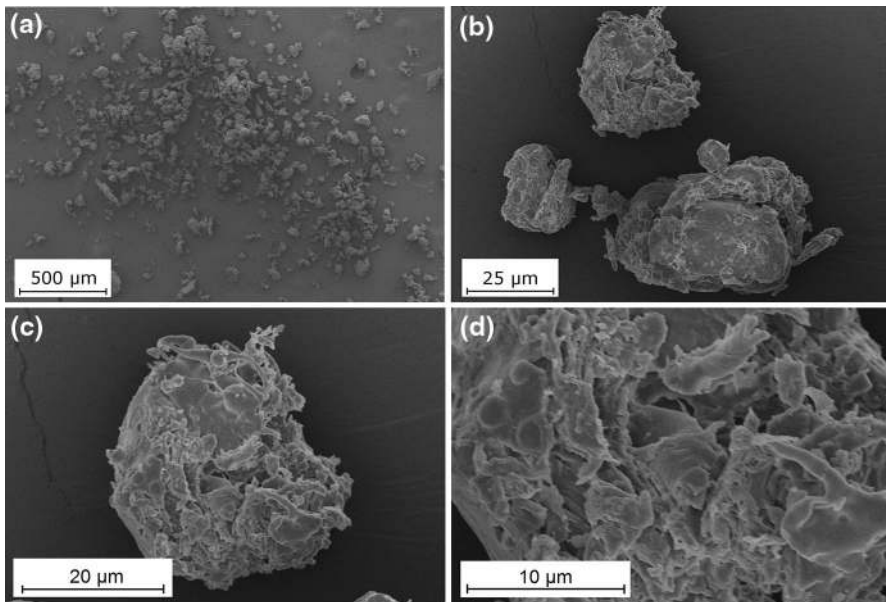
SEM photographs presented in Fig. 2 showed grains of the natural filler applied in this study after the grinding and drying processes. The particles of ground walnut shell differed in size and geometry (Fig. 2a). A considerable number of grains, despite different roughness of the surface (rough or smooth, Fig. 2c), were characterized by similar spherical shape (Fig. 2b). This filler type may be characterized as particle shaped, moreover, most of WS particles were characterized with developed surface (Fig. 2d).

### Evaluation of composite materials' properties and structure

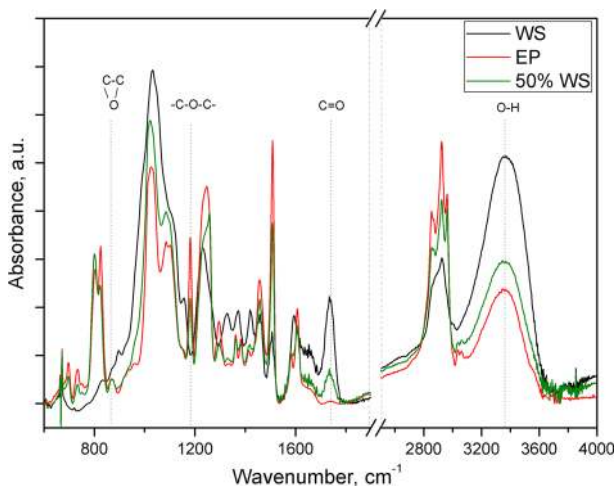
FT-IR spectra of ground walnut shell, the unmodified epoxy resin sample, and the composite containing 50 wt% of the filler, were presented in Fig. 3. At WS spectra,



**Fig. 1** Particle size distribution of ground walnut shell



**Fig. 2** SEM photographs of ground walnut shell, mag.  $\times 50$  (a),  $\times 1000$  (b),  $\times 2000$  (c), and  $\times 4500$  (d)



**Fig. 3** Absorbance FT-IR spectra of ground walnut shell, cured epoxy resin, and composite 50% WS in a wavenumber range from 600 to 4000  $\text{cm}^{-1}$

the broad absorption band at  $3500 \text{ cm}^{-1}$  indicates bonded hydroxyl  $-\text{OH}$  groups existing in the organic filler. Absorption peaks at wavenumbers of around 2900, 1744, and  $1053 \text{ cm}^{-1}$  are assigned to  $-\text{CH}$ ,  $\text{C}=\text{O}$  and  $\text{C}-\text{O}$  stretchings, respectively [23]. Moreover, the observed peak at  $1623 \text{ cm}^{-1}$  corresponds to  $\text{C}=\text{C}$  stretching and confirms the presence of lignin and its aromatic group in the natural filler [24, 25].

At epoxy resin and composite sample spectra, vibration band at  $915\text{ cm}^{-1}$ , resulting from C–O deformation of oxirane group, was recorded. The decrease of this band reflects the development of epoxy groups (a reaction of epoxide rings to form ether linkages). Despite high amount of the filler in the composition, intensities of the unmodified epoxy resin absorbance and of the composite with the highest WS amount were comparable. The increasing peak denoted near  $1200\text{ cm}^{-1}$ , corresponding to C–O–C stretching of aliphatic linear ester, was connected with homopolymerization of epoxy groups. The sample containing 50 wt% of WS showed a strong decrease in absorbance at this intensity, therefore, it can be stated that the curing process was modified by the presence of the organic filler. During epoxy cast curing, epoxide ring opening process is usually accompanied by the occurrence of an increasing peak of the –OH stretching, at  $3500\text{ cm}^{-1}$ . In case of the 50% WS sample, a higher intensity of the absorbance peak (at  $3500\text{ cm}^{-1}$ ) may be observed than for unmodified epoxy resin [26, 27]. This fact may be attributed both to the presence of the organic filler in the composite material, as well as the effect catalytic reaction of the curing process caused by the presence of additional –OH groups originating from the filler [28, 29]. Detailed description of all observed at FT-IR spectra peaks was presented in Table 1.

Moisture testing provides information on the amount of water contained in the material. The presence of water in the composites suggests that, despite the drying process performed, certain amount of water was introduced to the NFC. Unfortunately, to realize complete elimination of the water from the natural fillers, it is necessary to use high temperature drying processes ( $400\text{ }^{\circ}\text{C}$ ), which increases production costs and may cause thermal and hydrolytic decomposition of the hemicellulose material [10]. Preliminary drying of the filler and elevated temperature during curing of the epoxy casts should provide to complete removal of moisture from organic particles, therefore, the absorption of moisture from the air during conditioning of the materials cannot be excluded. This is confirmed by the fact that, under real conditions of use, the moisture content of such composites depends on humidity and is subject to seasonal fluctuations (higher values in the summer months) [12]. In Fig. 4 results of moisture content of pure epoxy and composite materials, determined as the loss of its mass between the time of sampling and state after drying to constant mass at  $103\text{ }^{\circ}\text{C}$ , were presented. Similar values were measured for all composite samples, whereas the highest moisture content was observed for EP. The high values of investigated parameter denoted for unmodified epoxy resin may be attributed to the release of low molecular weight degradation products of the thermoset polymeric matrix. The thermal stability of epoxy resin and epoxy composites was comprehensively described in the part of the article concerning thermogravimetric analysis. Surprisingly, evaluated parameter was almost at the same level for all composite materials. The stabilization effect of the parameter, measured in accordance to ISO 16979 standard, observed for all composite material is a result of simultaneously decreasing amount of low molecular weight products of epoxy resin degradation, as well as increasing amount of hydrophilic natural waste filler.

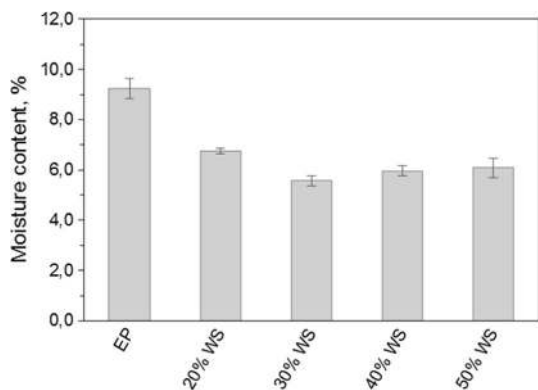
Tensile strength and Young's modulus were measured by means of static tensile experiment to assess the influence of an organic filler addition on epoxy composites'



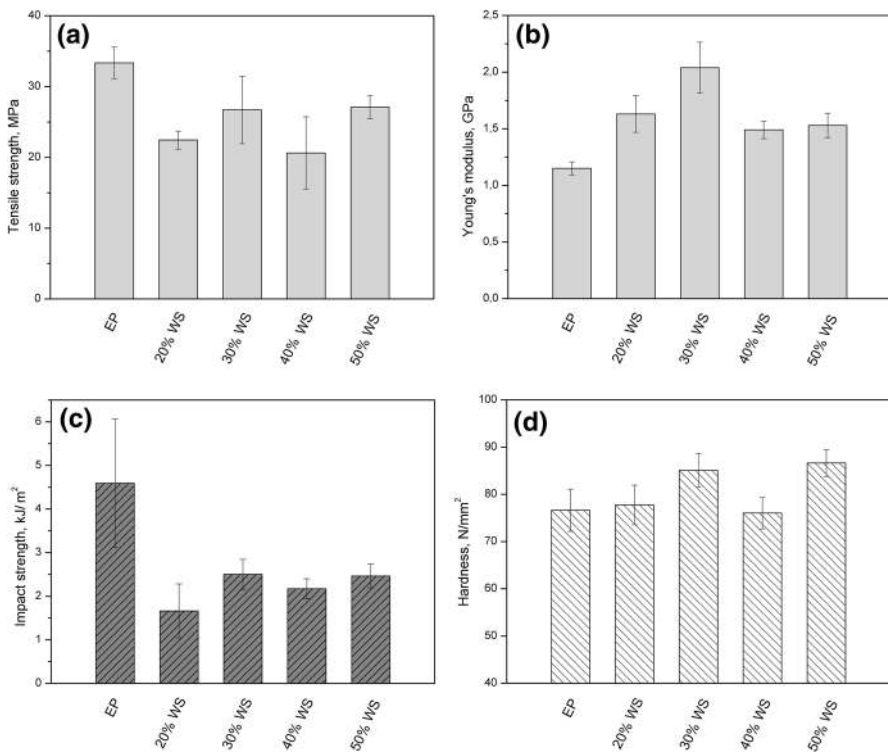
**Table 1** Detailed information about characteristic vibrations observed at FT-IR spectra of ground walnut shell [23–25] and epoxy resin [26–34]

Material	Band (cm <sup>-1</sup> )	Assignment
Walnut shell	3356	O–H stretching
	2932	C–H stretch in methyl and methylene groups
	1733	C=O stretch in unconjugated ketone, carbonyl and in ester groups
	1623	C=C stretching in aromatic group
	1593	Aromatic skeletal vibrations C=O stretch
	1506	Aromatic skeletal vibrations
	1458	C-H asymmetrical deformations in –CH <sub>3</sub> and –CH <sub>2</sub> –
	1421	Aromatic skeletal vibrations combined with C–H in-plane deform
	1371	Aliphatic C–H stretch in CH <sub>3</sub>
	1230	C–C, C–O and C=O stretching
	1031	Aromatic C–H in-plane deformation, C–O deform in primary alcohols and C=O stretch
Epoxy resin	3369	O–H stretching
	3062	Stretching of C–H of the oxirane ring
	2923, 2854	Bending vibration of –C–H in methylene group
	1606, 1180	Stretching vibration of –C=C in benzene ring
	1508	C–O–C stretching
	1456	C=C stretching in aromatic ring
	1296	Stretching vibration of C–N
	1245	Asymmetrical stretching vibration of C–O– $\phi$
	1026	Stretching C–O–C of ethers
	915	Stretching C–O of oxirane group
825	Out-of-plane bending vibration of –CH <sub>2</sub> in epoxide group	

$\phi$  benzene ring

**Fig. 4** Moisture content of pure epoxy resin (EP) and composite samples (WS)

properties. Figure 5a, b showed variations of those two mechanical properties describing samples' behavior as a function of filler amount. The organic filler incorporation into polymeric matrix caused a decrease of tensile strength in comparison to the unmodified polymer. Simultaneously, the values of Young's modulus measured for the samples made of composite materials were significantly higher in comparison to unmodified epoxy resin. Gradual improvement of the sample stiffness was observed for samples containing 20 and 30 wt%. For composite samples modified with 30 wt% of the filler, the Young's modulus value, mainly 2.0 GPa, was almost twice higher in comparison to the reference-unmodified epoxy sample, which reached 1.2 GPa ( $p < 0.00001$ ). However, in case of higher amount of the filler, i.e., above 30 wt%, the elasticity modulus-measured values were lower in comparison to the sample containing 20 wt% of the filler. Description of NFC for which a fall in the Young's modulus was recorded after exceeding the optimum filler content 50 wt% can be found in the literature [35]. It can be stated that the improved elasticity modulus is a result of epoxy resin curing process modification. It is well known that any incorporation of a filler, with a surface rich in hydroxyl –OH groups, may cause an additional catalytic effect resulting in the creation of additional segments of curing network [28]. Therefore, the improved stiffness of the composites containing lower amount of ground walnut shell is



**Fig. 5** Mechanical properties of pure epoxy resin (EP) and epoxy composite (WS) samples

probably caused simultaneously by stiff filler structures' presence, as well as increased cross-linking density of epoxy matrix. The reason for lowering Young's modulus values for composites containing 40 and 50 wt% of fine ground walnut shell, as compared to the samples which reveal the highest elasticity modulus values, i.e., 30 wt% WS, could be a random arrangement of filler particles and a hindered degassing of highly viscous compositions. Moreover, it should be mentioned that volumetric share of organic waste filler in polymer matrix was significantly higher than amount calculated by weight. It may be stated that for composites containing more than 30 wt% of the filler some particles were in a mutual contact. This phenomenon provides to local variations of stress transfer, which caused lowered values of whole composite material elasticity modulus. Lower values of mechanical properties obtained for the composites with the highest share of the filler suggest that the incorporation of high amount of fine ground walnut shell may be reasonable only in case of fabrication of the products that will not be highly loaded during their exploitation. It cannot be excluded that natural rigidity and ability to transfer mechanical loads, resulting from the walnut shell structure, were lost because of the significant level of its fragmentation. The rigidity of polymer composites depends on the shape of the filler. If value of aspect ratio of the filler is close to one, as in the case of a applied ground walnut shell, the amount and elasticity of incorporated filler as well as elasticity of polymeric matrix gain in significance [35, 36].

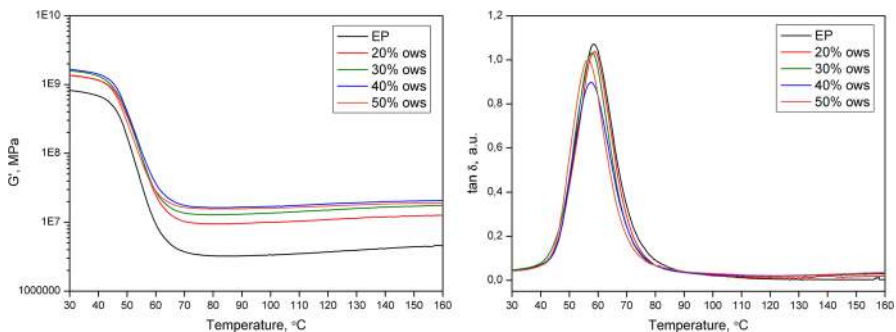
In Fig. 5c the results of the impact strength of epoxy resin and composite materials were depicted. Natural filler incorporation caused a decrease in the impact strength of the composites in comparison to the unmodified polymeric matrix. The lowest impact strength, equal to 1.66 kJ/m<sup>2</sup>, was observed for the sample containing 20 wt% of the WS, while for unmodified epoxy resin, the value was 4.6 kJ/m<sup>2</sup> ( $p < 0.001$ ). This phenomenon is typical for polymeric composites modified by a particle-shaped filler and its insufficient dispersion in polymer matrix [37]. Moreover, it cannot be excluded that residual moisture present in the filler and incorporated to composite material provided micropores that acted as notch during abrupt load in the course of Charpy experiment. It should be mentioned that the measured values of impact strength were not corresponding to higher amount of the filler in composite material.

Hardness measurement results for epoxy resin and composite materials were presented in Fig. 5d. It can be observed that the incorporation of ground walnut shell led to an improvement in the composites' hardness in comparison to the unmodified thermoset polymer. The highest value of HB hardness was denoted for the composite containing 50 wt% of the filler, mainly 86.6 N/mm<sup>2</sup>, while for unmodified epoxy resin, the value was 76.6 N/mm<sup>2</sup> ( $p < 0.01$ ). However, the lack of a distinct relationship between the filler amount and the composites' hardness may be attributed both to the low hardness of walnut shell itself (2.5–3.5 in Mosh scale), as well as insufficient dispersion in epoxy matrix. According to our previously published results, the hardness of the natural fiber composites with ground sunflower husks and pistachio shell depends on the size of the particles and decreased with increasing fillers content [38]. Moreover, the lack of correlation between the amount of incorporated into polymeric matrix natural filler and

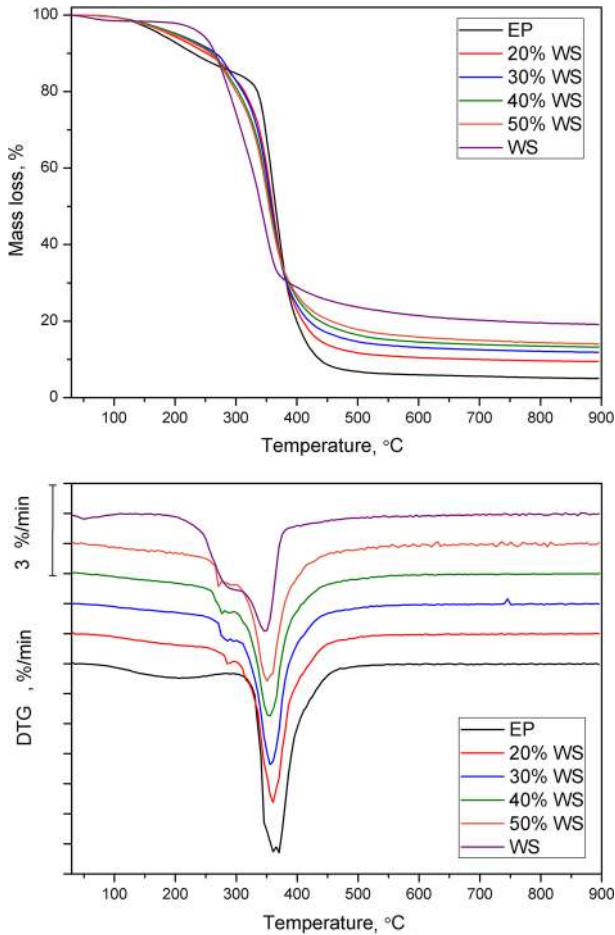
mechanical properties of the composites was observed also in the case of polyethylene filled with hazelnut shell [39].

In Fig. 6, storage modulus ( $G'$ ) and loss factor ( $\tan\delta$ ) curves were presented as a function of temperature ( $T$ ). It can be clearly observed that the natural waste filler incorporation caused an increase in  $G'$  in the considered temperature range. The denoted improvement in  $G'$  value after adding 50% of WS was equal to 100 and 403% measured at 30 and 80 °C, respectively, in comparison to unmodified epoxy resin. This means that composite materials reveal a higher ability to maintain mechanical loading with recoverable viscoelastic deformation than unmodified epoxy resin, also in elevated temperature [26, 40]. Changes observed for resin modified with walnut shell particles on the  $G'$  vs.  $T$  curves are in good agreement with the static tensile test results and may be assigned to the improved stiffness of composite materials. However, it should be mentioned that for samples containing more than 20 wt% of the organic filler, the differences between measured storage modulus values were negligible. In Fig. 6b, loss factor changes were depicted. The unmodified epoxy sample revealed the highest value of  $\tan\delta$ . With the increasing amount of natural filler particles, the maximum measured loss factor was slightly reduced. This phenomenon is comprehensible because of the incorporation of filler stiff domains which acted as a steric hindrance reducing material attenuation. The glass transition temperature ( $T_g$ ) measured as a peak of  $\tan\delta$  vs.  $T$  curve was lowered with a higher content of the filler. It is probable that residual fat in ground walnut shell plasticized composite materials [41]. However, this effect was not accompanied by  $G'$  decrease, therefore, it may be stated that the used filler did not modify the curing process in the entire polymer material but only led to a modification of the cross-link density near the organic particles' surface.

Thermal stability of highly filled epoxy composites was evaluated by thermogravimetric analysis to complement the characteristics and to define a potential temperature usability range of final products. The results of TG measurements realized in inert atmosphere are presented in Fig. 7. The additional data on the degradation process, including: 5, 10, and 50% mass loss temperatures, residual mass, and information on maximum intensity of degradation read from DTG curves for all measured samples, are summarized in Table 2. Based on the change in mass,



**Fig. 6** DMTA curves of  $G'$  and  $\tan\delta$  vs. temperature of unmodified epoxy resin (EP) and epoxy composite (WS) samples



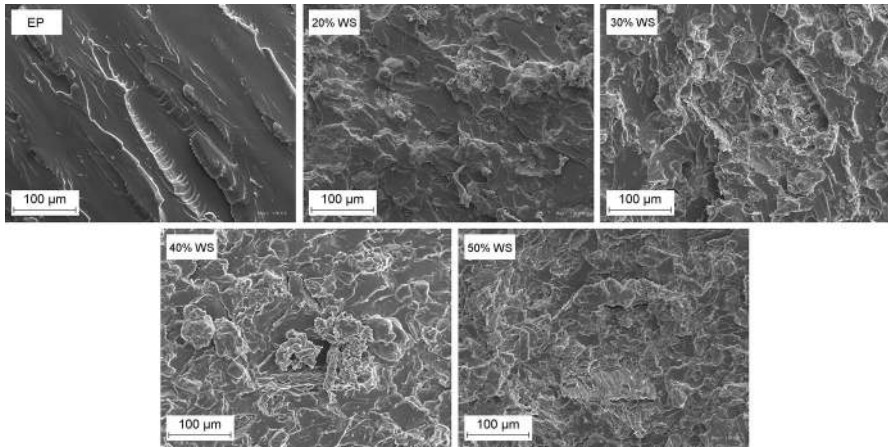
**Fig. 7** TG and DTG curves of epoxy resin (EP), epoxy composites (WS), and natural filler

**Table 2** TG and DTG data of epoxy resin (EP) and epoxy composites (WS) investigated under nitrogen atmosphere

Material	5% mass loss (°C)	10% mass loss	50% mass loss	Residual mass (%)	DTG (°C; %/min)
EP	177	231	365	5.00	371; -12.6
20% WS	192	252	360	9.44	361; -11.25
30% WS	204	267	358	11.88	356; -10.7
40% WS	203	262	356	13.23	356; -9.47
50% WS	197	258	354	14.06	351; -9.15
WS	244	266	341	19.13	345; -7.83

ranging from ambient temperature to 130 °C, it was found that despite the drying process the content of water in the shell reached 1.58%. It is possible that in filler-remained water, which was constantly linked with hydrophilic fiber components by chemical bonds. Natural filler decomposition occurred in the course of a two-step process, while the unmodified epoxy resin took place in a single-step way. The first mass loss of the TG curve observed for walnut shell sample was up to 130 °C and corresponded to the evaporation of the moisture which was present in the organic material. The next mass loss observed at the natural filler TG and DTG curves began at about 190 °C, rose to the maximum decomposition rate at 345 °C, and finished at about 390 °C. The courses of the WS thermogravimetric curves are similar to those presented in the literature and correspond to decomposition of the three main components of walnut shell: hemicellulose (210–325 °C),  $\alpha$ -cellulose (310–400 °C), and lignin (160–500 °C) [42–45]. Passive pyrolysis of the natural filler occurs above 470 °C. All composite materials containing walnut shell undergo a two-step decomposition with an increasing intensity during the first step, adequate to the increasing content of ground walnut shell. Because of the possibility of ligno-cellulose fiber decomposition, due to the temperature increase during the manufacture of the composites, the degradation temperature of the filler ( $T_{dmax}$ ) was determined.  $T_{dmax}$ , corresponding to a weight loss of 1% at temperatures above 150 °C, in presented study reached 215 °C and was at a similar level to the literature data [18]. A comparison of the values shown in Table 2 allows to ascertain that the natural filler has a significantly higher thermal stability in the range of 10% mass loss than unmodified epoxy resin. Therefore, it is comprehensible that composite materials containing walnut shell particles have higher thermal stability in a temperature range up to 355 °C. The sample containing 30 wt% of ground walnut shell revealed the highest thermal stability based on 5 and 10% mass loss. The difference between composite materials with various amounts of WS results from higher natural filler amount in comparison to the 20% WS sample, and better dispersion in comparison to samples filled with 40 and 50 wt% of ground walnut shell. It should be mentioned that thermal degradation of all composite materials was significantly suppressed. The lowest improvement in thermal stability, measured as temperature of 5% mass loss, was 15 °C, while the highest was 27 °C for samples containing 20 and 30 wt% of the filler, respectively. At a measuring point recorded at 50% mass loss, a different tendency may be observed. The highest temperature was denoted for epoxy resin, whereas the increasing content of WS caused a gradual decrease of 50% mass loss temperature. Measured at 900 °C, the sample residual mass grew with the increasing content of the organic filler. DTG data indicate that composite decomposition rate was lower than for unmodified epoxy resin, however, the maximum intensity temperature of composite thermal degradation decreased as a function of an increasing organic filler content.

The analysis of epoxy composites' structures was carried out on the basis of the scanning electron microscope photographs. Images of sample fractures taken at 400 $\times$  magnification were summarized in Fig. 8. The microstructure of composites containing various amounts of the filler allowed to observe a good saturation of organic particles' surface by polymeric matrix. The application of thermoset material characterized by a relatively low molecular weight favorably influenced the



**Fig. 8** SEM photographs of pure epoxy resin (EP) and epoxy composite (WS) breakthroughs, mag.  $\times 40$

wettability of the filler particles' surface and increased interfacial adhesion between polymer and reinforcement. This phenomenon may be confirmed by the observation of fractured fragments of walnut shell particles instead of entire ones in polymeric matrix. The fractures are caused by a pull-out effect occurring when there are limited interactions in the interface. It should also be noted that the amount of voids resulting from the contact between the resin and the filler was small. The voids were distributed mainly in the polymeric matrix which may be an effect of a hindered degassing of the highly viscous compositions. SEM photographs allowed to observe the filler particles with size of several dozens to more than 100  $\mu\text{m}$  in the case of the material containing the highest amount of the WS. It cannot be unequivocally stated that large grain sizes predominate in the case of high-filled composites, since a fragment of the shell of approximately 100  $\mu\text{m}$  can be found in the photographs of the WS 30%. The occurrence of varied sizes and shapes of grains is adequate to the SEM photographs of the filler before it is introduced into the polymer. It can be presumed that the method of mixing the components did not cause further shredding of the shells. SEM analysis allowed to ascertain that the previously described negative effect of the natural filler incorporation on the mechanical properties of the composites may be attributed to a random arrangement of filler particles.

## Conclusions

Post-agricultural organic waste was applied as a filler to modify epoxy resin composites. The incorporation of ground walnut shell into polymeric matrix resulted in a complex modification of mechanical and thermo-mechanical properties of the composites. Epoxy composites containing natural fillers showed significantly improved stiffness and hardness together with a decreased tensile and impact

strength. The use of thermoset epoxy resin as composite matrix had a beneficial effect on the wettability of the organic filler surface which resulted in a better adhesion of the components, as confirmed by the microstructure analysis carried out with scanning electron microscopy. The improved stiffness and hardness of the composites were related to the reinforcing effect caused by the presence of ground walnut stiff domains, as well as to the modified curing process of epoxy composites. Measurements carried out in the course of dynamic mechanical thermal analysis showed an improved thermo-mechanical stability of the composite materials within the complete temperature range (30–140 °C). Moreover, the ground walnut shell incorporation led to an increase in thermal stability of the composites in comparison to unmodified epoxy resin, which was found after thermogravimetric analysis had been carried out.

To summarize, it was proved that the incorporation of high amounts of finely ground walnut shell into thermoset polymer allows to prepare low-cost composites with acceptable mechanical and thermo-mechanical properties and make them applicable as materials for low-demanding parts and applications. In reference to changes of mechanical properties and thermal stability, the most favorable filler content for developed epoxy-based composites was 30 wt%. However, with regard to economic considerations, it also seems reasonable to manufacture high-filled composites containing 50 wt% of a ground walnut shell, especially in the case of non-structural applications.

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