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Effect of kenaf fibre modification on morphology and mechanical properties of thermoplastic polyurethane materials

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Abstract

The presented study examined the morphology and mechanical properties of biocomposites obtained from kenaf natural fibre and thermoplastic polyurethane. Kenaf was modified using various methods, namely: acetylation, blocked isocyanate, maleic anhydride and permanganate treatment. Those methods and ways of carrying out of surface modifications weren't studied before on kenaf/thermoplastic polyurethane composites. Different fibre loadings: 10% and 30% (by weight) were applied. The chemical treatments of fibres was confirmed by FTIR. The fibres surface and adhesion of the fibres to matrix was investigated using a Scanning Electron Microscope (SEM). The modulus, tensile strength, elongation at break, hardness, resilience and water absorption were also determined; all results were compared with a untreated kenaf fibre composite. SEM investigations of fibres showed the differences of fibre surface after the chemical treatment. A good adhesion between the polymer matrix and fibres was observed for PU/PMn-KF 30 sample. DMA results indicated that the greatest values exhibited samples with fibre treated by acetylation and permanganate treatment. Increasing the amount of fillers in the polymer matrix leads to higher hardness values and water uptake. Tensile strength and resilience of composites decreased when a higher proportion of kenaf fibre was added. It was observed that the treated fibre composites showed improvement in tensile properties, hardness, resilience and lower water uptake for composites with 10% fibre loading.

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Keywords: thermoplastic polyurethanes; thermoplastic composite; natural fibre; kenaf; fibre modifications

1. Introduction

Design and implementation of new machinery and equipment requires the use of new, original solutions, but also materials that meet the high endurance and performance demands (Pach and Mayer, 2010). Very often, the choice of material is taken into account its impact on the environment and ease of recycling therefore, becoming increasingly popular in the marketing of organic products. Industry is trying to create biodegradable materials and in order to obtain such properties in the case of polymer matrix composites are added e.g. natural fillers (Datta and Głowińska, 2011; Gąsiorowski et al., 2012; Truss, 2011).

Many natural fibres have the potential to replace synthetic fibres and be reinforcement composites. Natural fibres (NF) are introduced to reduce the weight of the composites, what is associated with lower cost than, for example glass fibre. Natural fibres have a lower density (1.2-1.6 g/cm^3) than the glass fibre (2.4 g/cm^3) (Koronis et al., 2013). The main differences between natural and synthetic fibres are shown in Table 1.

Table 1 Comparison between natural and glass fibre (Sreenivasan et al., 2013).

Properties	NF	Glass fibres
Density	Low	Twice that of NF
Cost	Low	Low, but higher than NF
Renewability	Yes	No
Recyclability	Yes	No
Energy consumption	Low	High
CO_2 neutral	Yes	No

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Abrasion to machines	No	Yes
Inhalation Health risk	No	Yes
Disposal	Biodegradable	Not Biodegradable

Natural fibres have many advantages including high specific strength and modulus, low density, renewable nature, biodegradability and absence of health hazards (Mahjoub et al., 2014).

El Shekeil et al. (2012a) studied influence of fibre content on the mechanical and thermal properties of kenaf fibre reinforced thermoplastic polyurethane composites. It was established that 30% fibre loading exhibited the best tensile strength and showed insignificant decrease in impact strength. From other research it is known that tensile strength, modulus, flexural strength increases with fibre loading, whereas tensile strain decreases (El-Shekeil et al., 2014a). Physico-mechanical properties of kenaf fibre reinforced poly(furfuryl alcohol) bioresin composites were examined by Deka et al. (2013). For this green composites the optimal properties were obtained by 20 wt.% of fibre loading. The improvements in mechanical properties were significant (i.e. 310, 123 and 48% increase in the tensile strength, storage modulus and flexural strength, respectively). The green composites showed also good damping behaviour. Researchers believe that these composites are suitable to be used for exterior automotive parts.

However, the main drawbacks of the use of fibres as reinforcement in composites are incompatibility of the hydrophobic polymer matrix, the tendency to form aggregates and poor resistance to moisture (Akil et al, 2011; El-Shekeil et al, 2011). To obtain a good quality composite and to improve the adhesion between the hydrophilic fibre and the hydrophobic matrix, modification of the fibres needs to be made. The most commonly used are chemical treatments. These treatments include i.e. silane treatment, acetylation, mercerisation,

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benzylation, permanganate treatment or isocyanate treatment. The modification is based generally on the use of reagents with functional groups which are able to react with the fibre structure and change their composition. The aim of this operation is to reduce moisture absorption and to ensure better compatibility with the matrix (Kabir et al., 2012; Mahjoub et al., 2014). In general, chemical coupling agents are molecules having two functions. The first of them is to react with the hydroxyl groups of cellulose, and the second is to react with functional groups of the matrix (Li et al., 2007). Fiore et al. (2015) prepared untreated and treated kenaf fibre/epoxy resin composites. The treatment was carried out by fibres immersion in a NaOH solution (6 wt.%) for 48 and 144 h. Kenaf fibres after 48 h were cleaned from impurities whereas after 144 h were damaged. The chemical modification for 48 h improved the mechanical properties of the composite due to the improvement of fibre-matrix compatibility. The effect of chemical treatment on kenaf reinforced thermoplastic polyurethane was studied by El-Shekeil et al. (2012b). The modification of the composite with 4% pMDI had negligible effect on tensile properties, however the treatment with 2% NaOH + 4% pMDI increased the tensile properties by 30 and 42% in tensile strength and modulus, respectively. Błędzki et al. (2008) modified flax fibres by acetylation. Effect of acetylation of flax fibre moisture absorption property is visible. Water absorption is 50% lower than before the acetylation reaction. It was also observed that the moisture absorption is reduced proportionally with the increase in the fibre content of acetyl, due to reduced hydrophilicity of the fibres. They noted that flax fibre morphology changed after acetylation. Thermal stability and mechanical strength increased by 25% compared to the unmodified fibres.

Kenaf (Hibiscus cannabinus) is one of natural fibres (plant) used as a reinforcement in polymer matrix composites. Kenaf fibre is recognised as an important source of cellulose composites and other industrial applications. It is known from the economic and

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environmental benefits, kenaf plant can be harvested 2–3 times a year (Saba et al. 2015). Kenaf bast fibre is used for thermoplastic composites, because of the good mechanical properties, i.e. single kenaf fibre can have a tensile strength and modulus of 11.9 and 60 GPa, respectively (El-Shekeil et al., 2012; Saba et al. 2015). Rowell et al. (1999) studied the potential of kenaf as a reinforcing (or filler) fibre in a polypropylene matrix and compared the mechanical properties with other commonly used composite systems. The results are shown in Table 2.

Table 2 Properties of filled/reinforced polypropylene composites (Rowell et al, 1999).

Filler/reinforcement in PP	Unit	None	Kenaf	Glass	Talk	Mica
Filler by weight	%	0	50	40	40	40
Filler by volume	%	0	39	19	18	18
Specific gravity	-	0.9	10.7	1.23	1.27	1.26
Tensile modulus	GPa	1.7	8.3	9	4	7.6
Tensile strength	MPa	33	65	110	35	39
Flexural modulus	GPa	1.4	7.3	6.2	4.3	6.9
Elongation at break	%	>>10	2.2	2.5	-	2.3
Notched Izod impact	J/m	24	32	107	32	27
Water absorption (24h)	%	0.02	1.05	0.06	0.02	0.03

The mechanical properties of kenaf/PP composites compare favourably to other common fillers in plastics. Since materials are bought in terms of weight, more pieces can be made

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with natural fibres as compared to the same amount in weight of mineral fibres. This can result in significant savings in material costs.

The aim of the present work was to study the effect of chemical modification on thermoplastic polyurethanes/kenaf composites. Thermoplastic polyurethane was chosen because of its good mechanical properties. We proposed the chemical treatment such as: acetylation, blocked isocyanate, maleic anhydride and potassium permanganate treatment. Those chosen treatments and ways of carrying out of modifications weren't studied before on kenaf/thermoplastic polyurethane composites. The chemical modifications of fibres were carried out in order to improve mechanical properties of composites and adhesion between the fibres and matrix.

2. Experimental

2.1. Synthesis of polyurethane

Thermoplastic polyurethanes were obtained using the prepolymer method. Prepolymer was synthesised from a polyol (poly(tetramethylene ether)glycol) (PTMG, BASF PolyTHF®, 2000, Germany) and 4,4'-diphenylmethane diisocyanate (MDI, Borsod-Chem, Hungary). The reaction of prepolymerisation was carried out for 2 h at 80 ^{o}C. The percentage of free NCO groups in prepolymer was equal to 7.83. In the second step, the prepolymer chains were extended by using 1,4-butanediol (BDO, Sigma Aldrich, Poland); 1,4-diazabicyclo[2.2.2]octane (DABCO, Sigma Aldrich, Poland) was used as a catalyst in amount of 0.3% wt. The scheme of two steps synthesis of polyurethane is shown in Fig. 1. Samples of thermoplastic polyurethane were obtained at the molar ratio of prepolymer [NCO] groups to glycol [OH] groups, namely 1:1. Polyurethane were moulded by gravity casting to the form and, then cured at 100 ^{o}C for 24 h.

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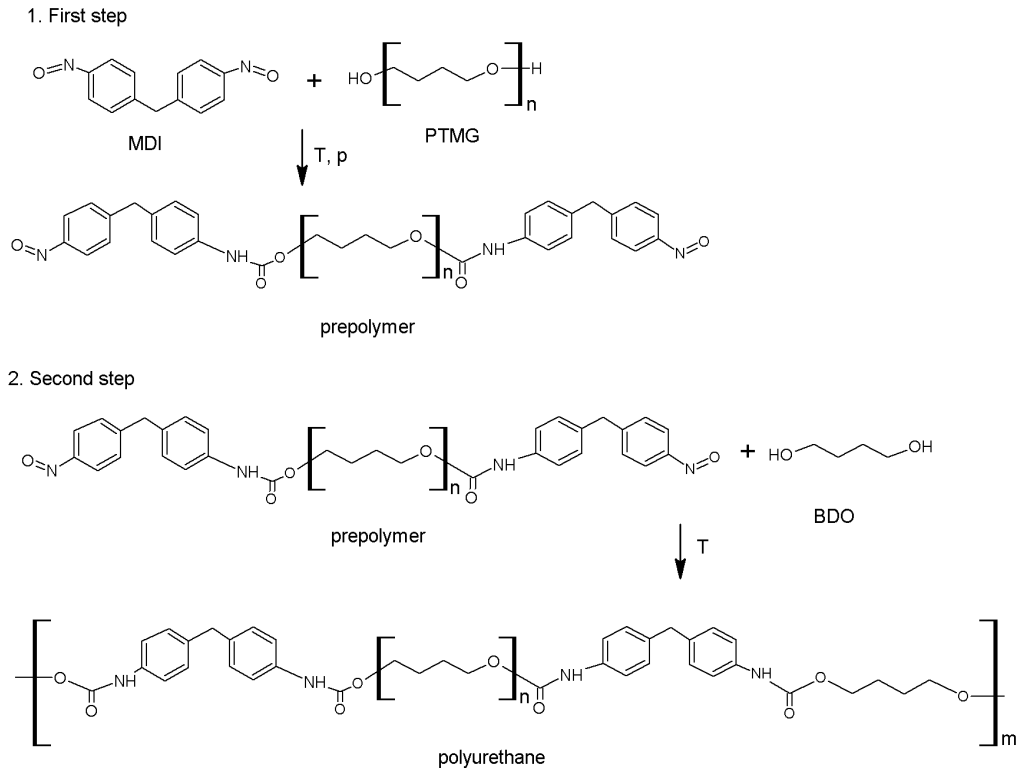

Fig. 1. Scheme of two steps polymerisation of polyurethane. First step is prepolymerisation and second step is extension of prepolymer chain.

2.2.Preparation of kenaf fibre

Kenaf fibres were obtained from Kenaf USA LLC (St. Augustine, Florida). Kenaf fibres were cut into a lengths of about <1-3 mm. The fibres were purified from oils and impurities by soaking in dichloromethane for about 10 minutes and filtered under vacuum. The fibres were dried at about 85 °C for 15 min.

Kenaf fibres were modified in order to improve the adhesion of the fibres to the polymer matrix. Natural fibres were treated using acetic acid, blocked isocyanate, maleic anhydride and potassium permanganate. The detailed procedure of these modifications is described below.

a) Acetylation

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In the first stage the chopped and cleaned fibres were soaked in an aqueous solution of acetic acid (10 wt. % solution of CH_3COOH) for 1 h. Then, in order to reinforce the acetylation was used acetic anhydride. 10 wt. % acetic anhydride solution, with a drop of 96 wt. % sulphuric acid VI was added to the soaked fibres in acetic acid as shown in Fig. 2. Further soaking of the fibres took 1.5 h. Afterwards, the fibres were rinsed with distilled water until natural pH was obtained. The fibres were dried for 48 h at 60 °C. This is based on the modified method described by Mwaikambo (1999).

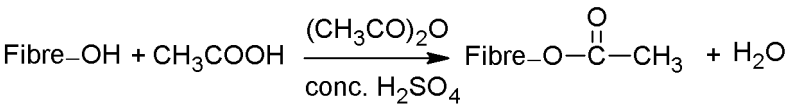

Fig. 2. Scheme of acetylation with an acid catalyst.

b) Modification of a blocked isocyanate

To obtain blocked isocyanate the molten MDI was mixed with methanol in a molar ratio of 1:1 for 30 min to obtain a 20 wt. % solution of MDI and methanol in acetone. Fibres were soaked in this solution for one week. After this time, they were then washed repeatedly with acetone and dried at 100 °C for 2 h. The reaction proceeds as shown below:

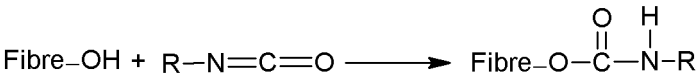

Fig. 3. The reaction between isocyanate agent and fibre.

c) Modification with maleic anhydride

In order to modify fibres using maleic anhydride, 20 wt. % solution of maleic anhydride in acetone was prepared. The fibres were soaked in the solution for 1 h and then cleaned using acetone. In final step fibres were dried in the air for 24 h. The likely reaction between fibre surface and maleic anhydride is shown in **Fig. 4.**

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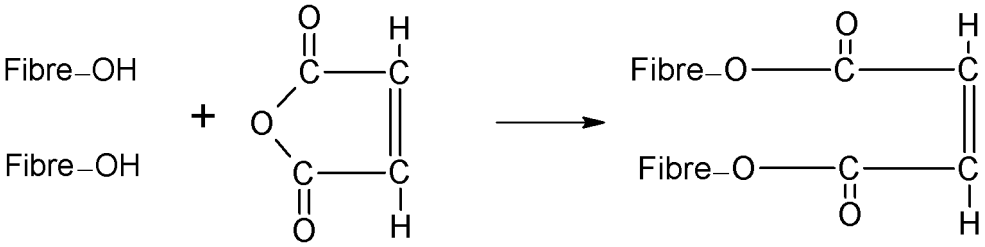

Fig. 4. The reaction between fibre-OH and maleic anhydride.

d) Modification of potassium permanganate

A solution of 0.5 wt. % $KMnO_4$ in acetone was prepared. Kenaf was placed in the solution for 30 min. After this time, kenaf was washed with distilled water and decanted. The fibres were dried in the air for 24 h (Annie Paul et al., 2008). The reaction between fibre–OH group and potassium permanganate is given in **Fig. 5.**

Fig. 5. Permanganate treatment of fibre.

2.3.Preparation of TPU/KF composites

Several variants of composites were obtained with the different degree of natural fillers (10 and 30%) and variously modified fibres (without modification after acetylation, the modification: blocked isocyanate, maleic anhydride and potassium permanganate). The codes of composites samples used in the study are given in Table 3.

Table 3 Modifying agents used in the preparation of natural fibre reinforced composites.

Code of the material	Code of the fibre	Modifying agent
PU/KF 10 or 30 wt.%	Untreated	-
PU/Ac-KF 10 or 30 wt.%	Ac	Acetylation

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PU/BIC-KF 10 or 30 wt.%	BIC	Blocked isocyanate
PU/MA-KF 10 or 30 wt.%	MA	Maleic anhydride
PU/PMn-KF 10 or 30 wt.%	PMn	Potassium permanganate

The composites were prepared using melt-mixing method followed by press moulding. 10 and 30 wt. % fibre loadings were applied. The process of homogenisation was carried out at 60 rpm for 20 min at 180 °C. The press moulding process was performed using a hydraulic press under press 4.5-5 MPa for 15 min.

Obtained by the gravity casting thermoplastic polyurethane was processed in the same way as the composite and showed properties as following: the specific gravity was 1.092, the tensile strength was 16.8 MPa, the storage modulus was 491 MPa, the resilience was 36%, the hardness was 84 ^{o}ShA and the water uptake after 504 h was 1.497 wt.%.

2.4.Composite characterisation

2.4.1. Fourier transform infrared spectroscopy

Spectroscopic analysis of kenaf bast fibre was carried out by means of a FTIR Nicolet 8700 spectrophotometer (Thermo Electron Corporation) and ATR technique. The Specac Heated Golden Gate single reflection diamond ATR accessory was used and it operated up to 200 ^{o}C. Spectra were registered at room temperature for wavenumbers ranging from 500 to 4500 cm^{-1}at 4 cm^{-1} nominal resolution with 64 scans. The measurements were performed in the Department of Physical Chemistry, Gdansk University of Technology.

2.4.2. Surface characterization of kenaf fibres and composites

The morphology of the materials was investigated using scanning electron microscopy (SEM). Images of kenaf fibre and the cross-sections of prepared composites were

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carried out under the desktop scanning electron microscope Phenom G2 PRO (Phenom-World) with accelerating voltage of 5 kV.

2.4.3. Dynamic mechanical thermal analysis

Dynamic mechanical analysis (DMA) of thermoplastic composites was performed using DMA Q800 Analyzer (TA Instruments) according to ASTM D6045. Measurements were taken in a temperature range of -60 ^{o}C to +120 ^{o}C at an operating frequency of 10 Hz and heating rate of 4 ^{o}C/min. The samples were 3 mm thick, 10 mm wide and 38 mm long. Storage modulus, loss modulus and glass transition temperature versus temperature were determined.

2.4.4. Mechanical properties

Mechanical analysis in static condition was conducted with a tensile test (tensile strength (TS), elongation at the break (ε)) and performer using Zwick Z020 tensile testing machine. Dumbbell shaped samples with normalised dimensions by PN-ISO 37:1998 were tested. The cross-section of samples was 6.8 x 2.8 mm. Research was executed at 200 mm/min rate. Measurements of the mechanical properties were carried out at the room temperature.

2.4.5. Hardness

Hardness was determined according to PN-EN ISO 868:2005 standard using an electronic durometer type A Zwick/Roell. Shore A durometer perpendicularly applied for 3 seconds.

2.4.6. Resilience

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Elasticity (the rebound resilience) was determinate based on the ISO 4662:2009 standard. This test was carried out with a Schob pendulum. The rebound resilience is determined by a freely falling pendulum hammer that is dropped from a given height, impacts a sample and imparts to it a certain amount of energy. The test result is shown on the pendulum's scale.

2.4.7. Water absorption

Water absorption test was performed according to ASTM 570-98 by long-term immersing. Before immersion in water composite samples were first dried by heating them in an oven ant 50 ^{o}C for 1 h, weighed and then soaked in a bath of distilled water at room temperature. After immersion for specific time intervals until saturation point of water content was reached, the samples were removed from the water, gently dried with a clean cloth and weighed to the nearest 0.001 g. the percentage of water uptake was calculated as followed:

$$WA\ (\%) = \left(\frac{M_1 - M_0}{M_0}\right) x\ 100\%, \qquad (1)$$

where M_0 and M_1 were the dried weight and final weight of the sample, respectively.

3. Results and discussion

3.1. Spectroscopy analysis

The chemical structures of untreated and treated kenaf bast fibre were analysed through FTIR were presented in Fig. 6. This spectra were used to study the shifts in functional groups that occurred as a result of chemical treatments. A strong and broad absorption band in the region 3200-3600 cm^{-1} of O-H stretching vibration is present in all the spectra. However the intensity of this band in case of blocked isocyanate treatment decrease and peak becomes narrower. It is worth noting that the broad band changes also for MA treatment. The difference may indicate that some changes have occurred as a result of the reaction between BIC or MA and hydroxyl groups of kenaf cellulose. Untreated fibre showed the C-H stretching vibration of

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methyl and methylene groups in cellulose and hemicellulose at 2908 cm^{-1} (Haque et al., 2009). In the case of acetylation and PMn treatment, this peak shifted to 2902 and 2895 cm^{-1}, respectively, indicating that part of the cellulose was removed.

The peak in carbonyl region (C=O vibration) near 1722 cm^{-1} for permanganate treatment is shifted to higher frequency (1730 cm^{-1}) and the intensity of peak decreased owing to structural change. In the IR spectrum can be seen the C-O stretching frequency (1716 cm^{-1}) increased upon MA treatment. This is a good evidence for the formation of ester linkages as a result of the reaction between MA and hydroxyl groups on cellulose. 1705 cm^{-1} peak in BIC spectrum corresponds to the stretching vibration of alkylic urethane bonds (NH-CO-O).

In spectra of fibre, peak near 1626 cm^{-1} corresponds to adsorbed water in untreated fibre. For acetylated and PMn treatment fibres this peak shifted to 1633 cm^{-1} and 1635 cm^{-1} compared to untreated fibres, respectively. This may indicate the removal of bonded water from the hemicellulose as result of the treatment. Also upon MA treatment this peak was increased and shifted to 1639 cm^{-1}. This may be attributed to the presence of C-C bonds of MA attached on fibre. Upon BIC treatment peak in the spectra is narrow and shifted to 1641 cm^{-1}. The treatment with potassium permanganate led to extensive delignification. As a result the intensity of absorption decreases in the range of 1593-1420 cm^{-1}, which is related to skeleton vibrations of the aromatic ring (De Rosa et al., 2011).

Spectra of blocked isocyanate treatment shows a signal at 1595 cm^{-1} which may associate to the benzene rings of MDI structure and a peak at 1541 cm^{-1} which corresponds to the amide –NH-C=O symmetric stretching vibration.

The characteristic peak at 1421 cm^{-1} and 895 cm^{-1} and is designated as the C-H bending of amorphous and crystalline cellulose. The peak 1363 cm^{-1} is due to the C-OH stretching of the hydrogen bond intensity of crystalline cellulose (Ganan et al., 2008).

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In is known from the literature that after acetylation in IR spectra should show an intensive peak near 1234 cm^{-1}, which would be assigned to ester and C-O bond (Kaczmar et al., 2011). In the Fig. 6. the peak for untreated and acetylated fibre is similar. This situation may be related with to short exposing time in acetylation solution. The very intensive peak is visible after 5 h and 24 h soaking in acetylated mixture (Olaru et al., 2011). The peak at 1028 cm^{-1} is assigned to the aromatic C-H in plane deformation and C-O stretching in primary alcohols of lignin.

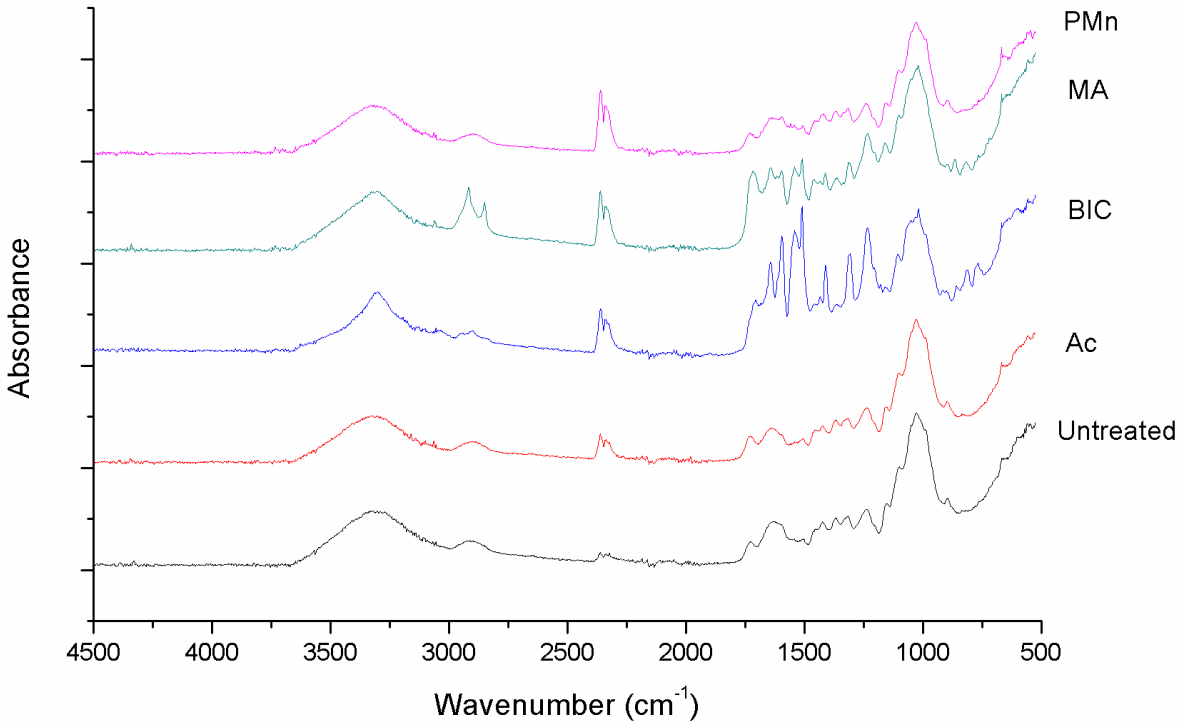

Fig. 6. FTIR spectra of the untreated and treated kenaf fibre.

3.2. Surface characterisation of kenaf fibre

Scanning electron micrographs of untreated and treated kenaf fibres are shown in Fig. 7(a-e). The untreated kenaf fibre (Fig. 7(a)) represents the bundle with relatively smooth surface, although small particles attached to the surface are also seen, suspected to be waxes, oils and impurities. In the Fig. 7(b) are shown the acetylated fibres. The fibres have smooth

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surface and it can be explained by removal of waxy materials (De Rosa et al., 2011). It can be also observed that in the surface are small pores. The fibres after BIC treatment are probably covered with crystals of blocked isocyanate (Fig. 7(c)). In case of maleic anhydride the fibre bundles are clean and quite well separated (Fig. 7(d)). In the Fig. 7(e), the fibres after permanganate treatment look jagged and show very rough and enlarged surface. It may be caused by strong oxidising activity of potassium permanganate.

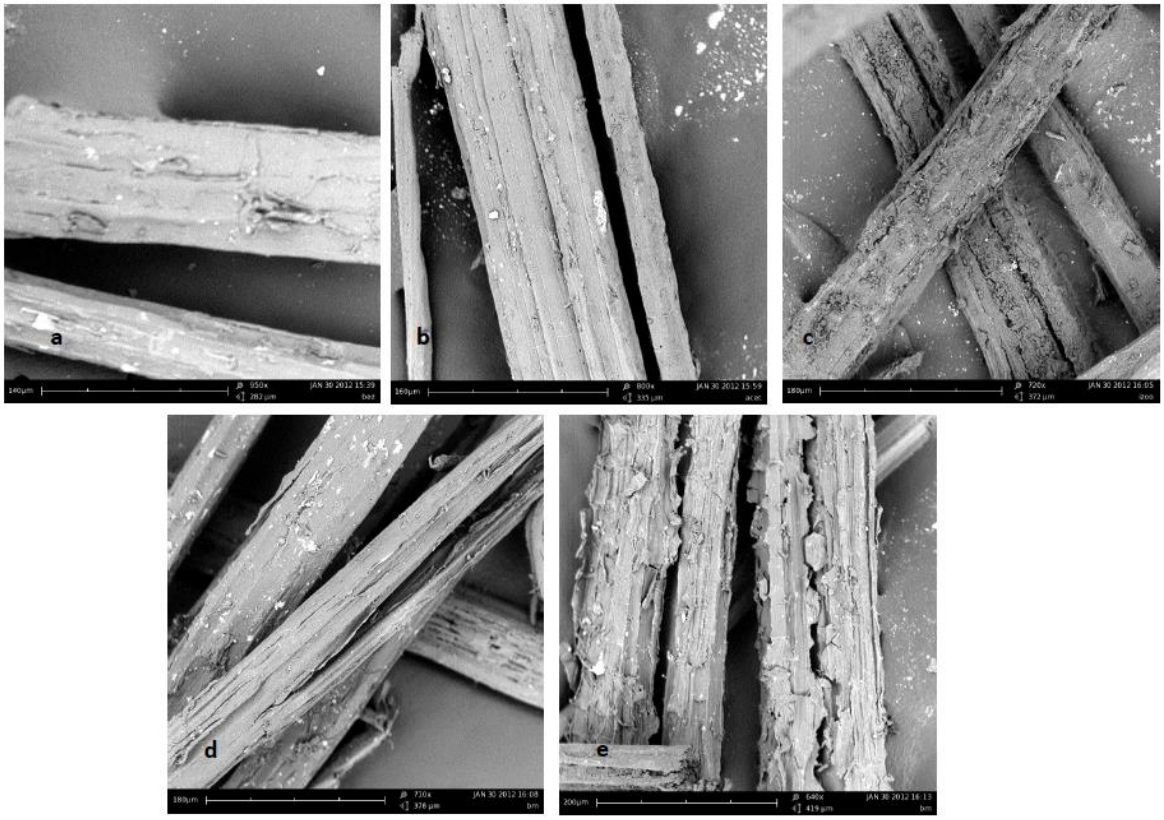

Fig. 7. (a-e) SEM micrograph of untreated and treated kenaf fibre: (a) untreated; (b) acetylated; (c) after block isocyanate treatment; (d) after maleic anhydride treatment; (e) after permanganate treatment.

3.3.SEM morphology

The chemical modification changes the surface of the fibres from smooth to irregular, often porous. Gąsiorowski et al. (2012) observed that the polymer adheres well to the fibres after used the modification, our findings are similar for some of the treatments. Scanning

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electron micrographs of composites are shown in Fig. 8(a-e). Comparing the SEM images of the morphology of composites, it can be concluded that not all composites exhibit good adhesion to the polymer matrix. Fig. 8(b) shows micrograph of composite with acetylated fibres. It is possible to observe a high adhesion between the modified fibre and matrix, but this behaviour is not homogenous, begin that the composites also represents regions of not adherence. In the Fig. 8(c) is shown PU/BIC-KF 30. It is easy to notice gaps between fibres and polymer matrix. Similar situation is visible for PU/MA-KF 30. Hence it can be indicated poor interaction between the treated kenaf fibre and polyurethane matrix. In the Fig. 8(e) it is demonstrated that the fibres, after permanganate treatment are well formulated in the polyurethane matrix. It is related with well-developed surface after modification of fibres. Agglomeration of fibres was also observed, which can cause falling tensile strength. El-Shekeil et al. (2014b) also noticed that additional stress points were created when the population of fibre is increased, leading to a decrease in tensile strength.

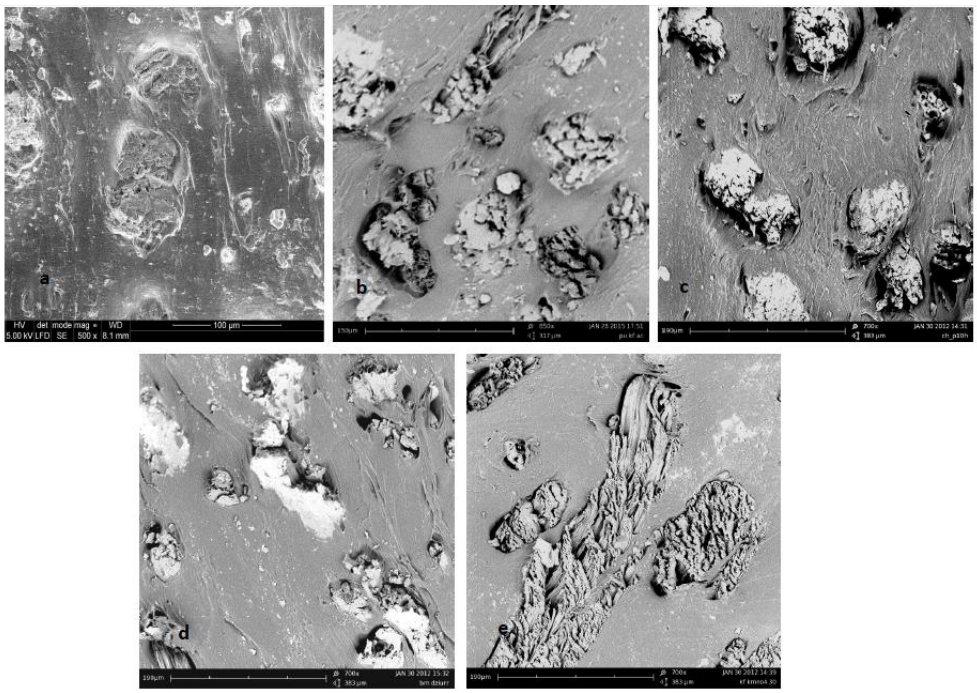

Fig. 8. (a-e) SEM of composites: (a) PU/KF 30 wt.%; (b) PU/Ac-KF 30 wt.%; (c) PU/BIC-KF 30 wt.%; (d) PU/MA-KF 30 wt.%; (e) PU/PMn-KF 30 wt.%.

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3.4. DMA analysis

The storage modulus (E'), specifies the relationship between the phase components of the remaining stress and strain. E' characterises the ability of the material for storing mechanical energy (Prisacanu, 2011). Fig. 9 shows the thermo-mechanical curves recorded during DMA tests. Storage modulus showed one plateau regions, at low temperatures corresponding to glassy state. The storage modulus for PU/KF 30 is equal to 1043 MPa. The best improvement in storage modulus was in the sample with fibres after acetylation, E'=1385 MPa. The most noticeable improvement was observed for the sample, PU/PMn-KF 30. Improvement in case of acetylation and permanganate treatment is in accordance with findings of Vilay et al. (2008) where higher E' value of treated bagasse/unsaturated polyester composites is due to greater interfacial adhesion and bond strength between polyester and fibres. The rest of the treatment did not bring any improvement in the elastic modulus values compared to an unmodified fibres sample. This result suggests that despite successful modification of fibres (Fig. 6), blocked isocyanate and maleic anhydride treatment aren't the best possible choice for chemical treatment of fibres. However, all composite exhibited higher values of storage modulus than polyurethane prepared in the same conditions as the composites (E'=491 MPa).

Variation of tan δ as a function of temperature is shown in the Fig. 9. The tan δ trend is indicative of energy dissipation with regards to the changes in the physical properties. In general for matrix tan δ is seen as a sharp peak, because in an unfilled system the chain segments are unlimited (Pothan et al., 2003). In case of this composites can be observed two tan δ peaks in the curves making the two phases, fibre and matrix. The width of the tan δ peak also becomes broad. The behaviour suggests that there are molecular relaxations in the composite. The molecular motions at the interfacial region generally contribute to the damping of the material apart from those of the constituents. Hence the width of the tan δ

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peak is indicative of the increased volume of the interface (Pothan et al., 2003). The values of tan δ vary between different composites. This results are in accordance to Geethamma et al. (2005). Researchers investigated gum composites with the different treatments of coir. It has appeared that coir/ gum composites showed various values of tan δ, after different treatments. The values of tan δ of all investigated samples were lower than ≥ 0.2, which means that synthesised materials have a high ability to damping capacity (Sobczak et al., 2002).

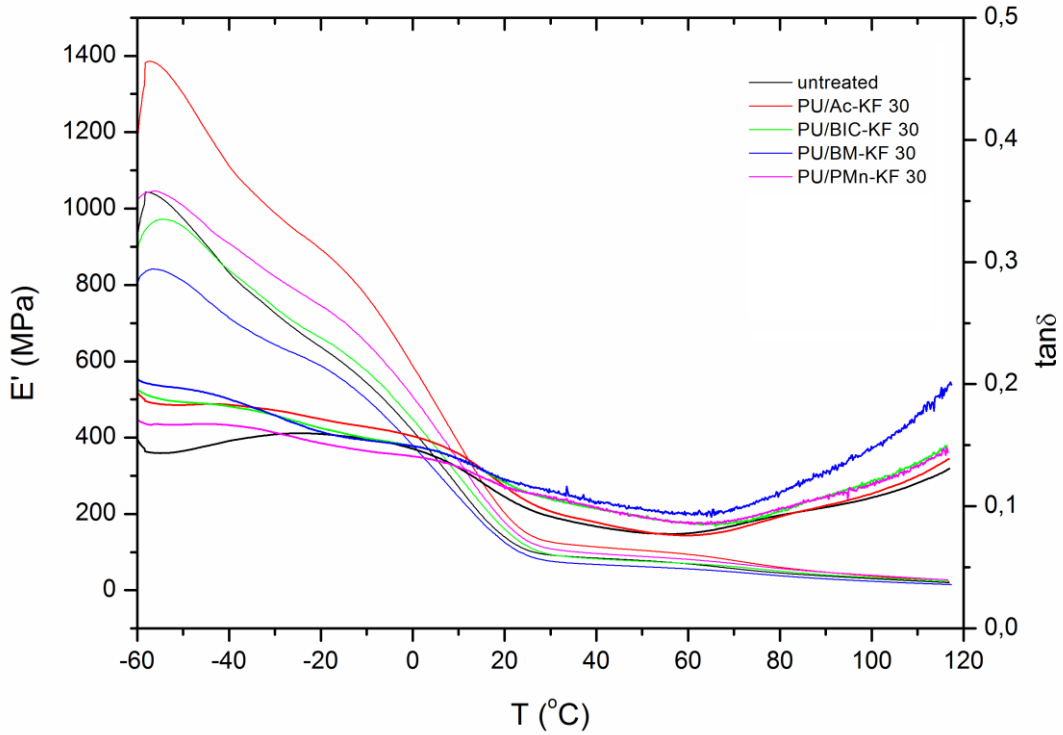

Fig. 9. Storage modulus (E') and tan δ as a function of temperature for prepared composite.

The loss modulus (E") determines the relationship between the phase-shifted components of the stress and strain. It is characterised by the body's ability to irreversible viscoelastic dissipation of mechanical energy (Prisacanu, 2011). The value of loss modulus and the glass transition temperature (T_g) are presented in Table 4. T_g is derived from loss modulus curves, usually interpreted as the peak of the E" curves obtained during DMA tests (Huda et al., 2006). The glass transition temperatures of all composites are ranging from -58

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to -56 ^{o}C, which shows a similar construction of the composites. The shifting of T_g to higher temperatures can be related with decreasing mobility of the matrix chains. Such values are characteristic for elastomeric materials (Datta and Głowińska, 2014). This glass transition temperature was T_g values of the treated fibres composites are lower than untreated composites (besides PU/Ac-KF), therefore, it can be deduced that the interfaces were changed by the fibres treatments.

Table 4 Summary of DMA results of TPU/kenaf composites.

Composite type	E'(MPa)	E''(MPa)	Tan δ	T_g (^{o}C)
PU/KF 30	1043	151	0.16	-58.2
PU/Ac-KF 30	1385	257	0.18	-58.2
PU/BIC-KF 30	972	182	0.18	-56.0
PU/MA-KF 30	842	168	0.19	-57.4
PU/ PMn-KF 30	1046	175	0.16	-56.2

3.5.Tensile properties

Strength of the composites depends on several factors, such as, strengths of fibres and matrix, fibre volume fraction and fibre-matrix interfacial bonding (Ozturk, 2010). The results in Table 5 show a comparison of the tensile strength and elongation at break of the prepared composites. Low values of tensile strength can be attributed to the lack of the fibres ability to transfer the load to one another. This means that with low fibres content, the effect of crack initiation was more dominant as compared to the effect of crack inhibition (Wirawan et al. 2011). As we can see in Table 5, with higher content of fibres in polyurethane matrix,

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tensile strength decreases. This behaviour can be related to the increase population of fibres, which in turn leads to agglomeration and stress transfer gets blocked (Jacob et al., 2004; Ozturk, 2010). Elongation at break decreases when increasing fibre loading. This is a typical effect of the increase fibres volume which, is having a low strain (Kenaf strain is 1.6%) (Bismarck et al., 2005).

The modification of kenaf fibres improves the tensile strength and elongation. The use of maleic anhydride does not give a significant improvement compared to the sample with unmodified fibres. Acetylation, blocked isocyanates and potassium permanganate treatment improves the values of both stress and strain. The stress of the sample PU/Ac-KF 10, PU/BIC-KF 10, PU/PMn-KF 10 compared with a sample of PU/KF 10 increased by 9%, 16%, 15% respectively, and strain 35%, 47%, 62% respectively. This result can confirm, that conducted treatments of fibres improved mechanical properties of composites with fibres loading 10 wt.% With higher content of fibres in polyurethane matrix, tensile strength decrease, probably due to agglomeration and for some of the samples poor adhesion the fibres to the matrix (Fig. 8(c, d)). The sample PU/PMn-KF 30 shows a noticeable improvement in strength properties by 14%, it associates with successful permanganate treatment of kenaf (Figs. 7(e) and 8(e)). Our findings are similar with that of the results from Sreekumar et al. (2009). They examined influence of the fibres surface modification on the tensile properties of sisal/polyester composites. It was demonstrated that the tensile strength and modulus of polyester treated sisal fibres composites were improved. In the case of alkali treatment, modified fibre reinforced composites showed 36% and 53% increase in tensile strength and in Young's modulus, respectively.

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Table 5 Comparing the tensile strength (TS) and elongation at break (ε) of composites containing 10 and 30 wt. % fibres.

Fibre content (%)	Properties	PU/KF	PU/Ac-KF	PU/BIC-KF	PU/MA-KF	PU/PMn-KF
10	TS (MPa)	9.4 ±0.2	10.2 ±0.1	10.9 ±0.2	9.6 ±0.3	10.9 ±0.3
	ε (%)	131.2 ±26.6	177.4 ± 14.4	193.3 ±25.1	131.8 ±35.7	212.9 ±14.0
30	TS (MPa)	9.9 ±2.0	9.8 ±0.9	8.3 ±0.8	7.6 ±0.3	11.3 ±0.8
	ε (%)	40.7 ±5.2	40.7 ±5.2	27.3 ±1.5	44.0 ±2.8	39.8 ±0.8

3.6.Hardness

Hardness of a particular sample refers to its stiffness or resistance to being broken in turn leading to its shape being changed permanently when load is applied to it. Hardness of a composite depends on the distribution of the filler into the matrix (Jamal et al., 2006; Premlal et al., 2002).

Hardness of the produced composites is in the range of 85-91 ^{o}Sh. Those values are higher than for neat polymer and it implies that adding fibres leads to higher stiffness of material. As it is shown in the Fig. 10, the addition of fibres to the polyurethane matrix increases hardness values. With a higher content of kenaf, hardness increase (about 5%). Samples with modified fibres have a higher hardness values than those with unmodified fibres. The best results are obtained by using acetylation, a blocked isocyanate and potassium permanganate treatment. The use of maleic anhydride as a modifier of natural fibre does not contribute to a significant improvement in hardness of the samples. It associates with better adhesion of composites (besides PU/MA-KF). These results are in concurrence with Islam et al. (2010). They examined the Rockwell hardness of untreated and benzene diazonium salt

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treated coir/polypropylene composites. Higher values of hardness were observed in modified coir/polypropylene composites in comparison to unmodified coir/polypropylene composites.

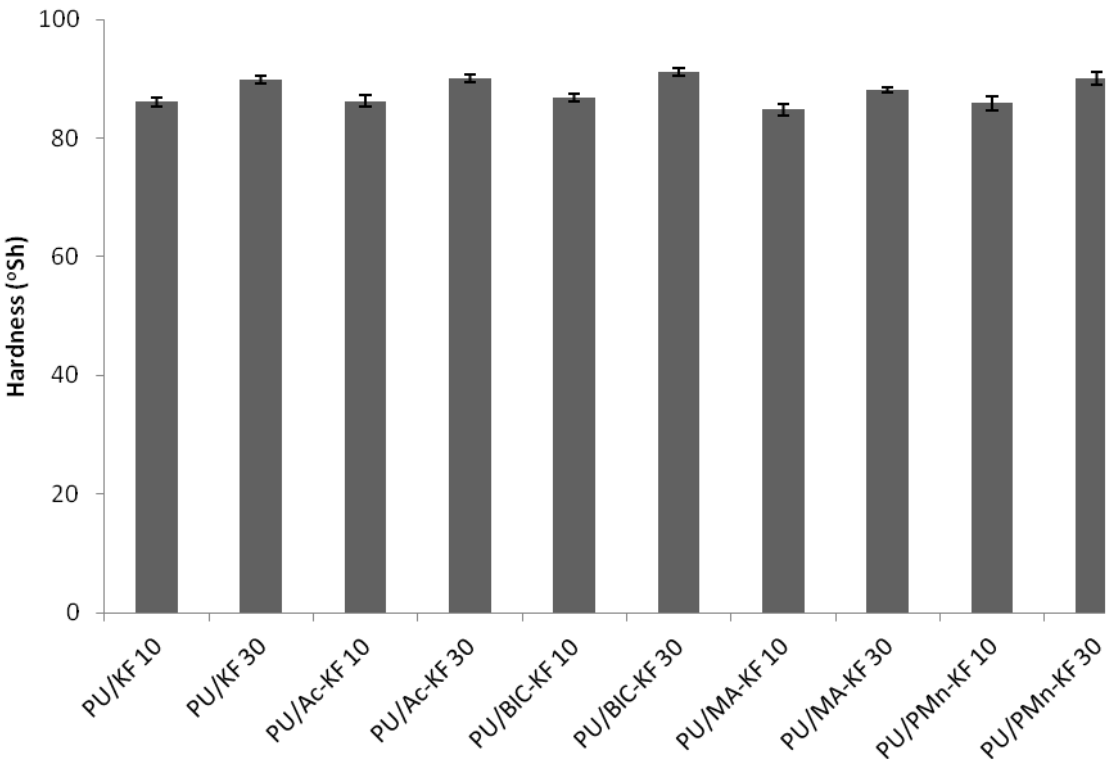

Fig. 10. Comparing the hardness of composites containing 10 and 30 wt.% fibres.

3.7.Resilience

Fig. 11 shows the results of flexibility for composites filled with 10% and 30% of fibres. The flexibility of the reflection depends on the amount of fibre added to the polymer matrix. Increase in natural fibre content in turn decreased the elasticity values. The reason for the observed relationship is stiffening of the composites with filler. These results are similar to findings of Głowińska et al. (2013), where they analysed elasticity of sisal/biopolyurethane composites. Resilience of the biocomposites decreased with a higher content of sisal fibre.

Resilience increased by 9, 10, 8 and 12% for samples PU/Ac-KF 10, PU/BIC-KF 10, PU/MA-KF 10 and PU/PMn -KF 10, respectively. The use of modifiers improves the elasticity of the samples, which contain 30% of fibres, in the range of 8% - 20%, depending on the modification. The best results were obtained using blocked isocyanate and potassium permanganate treatment. Those values are in accordance to conducted tests. The greatest

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improvement is visible for permanganate treated fibres reinforced composite which associates with very good adhesion fibres to matrix.

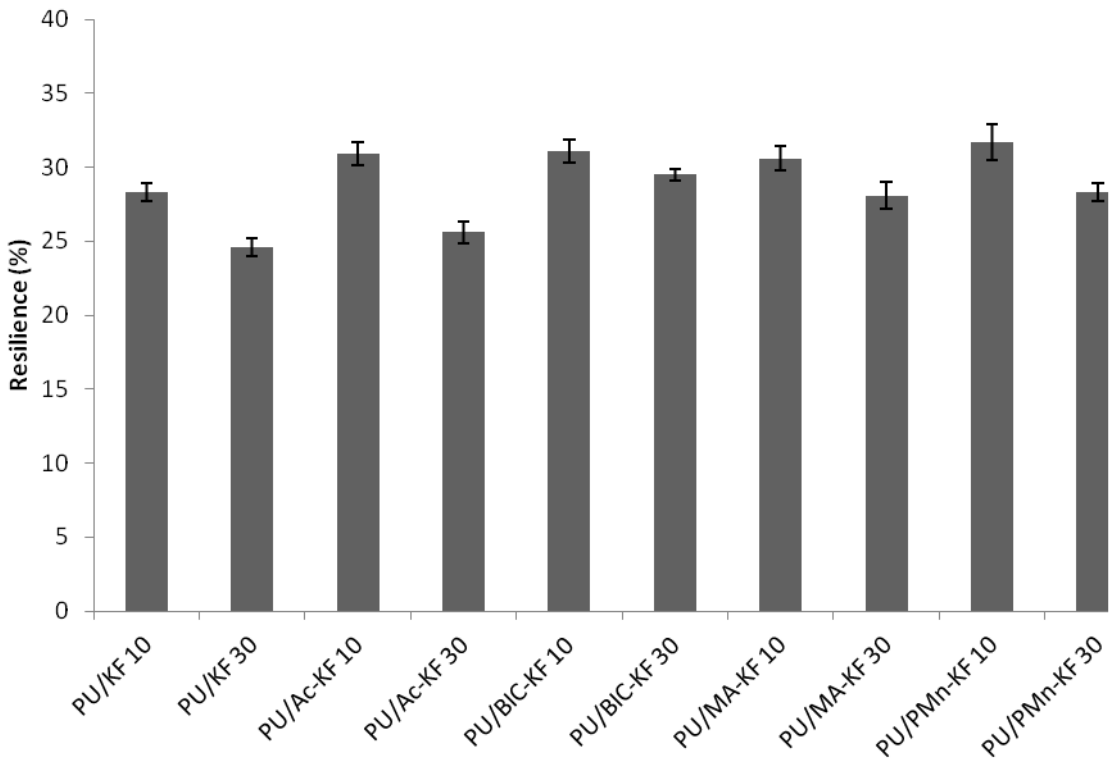

Fig. 11. Comparing the resilience of composites containing 10 and 30 wt.% fibres.

3.8. Water absorption

Water absorption experiments were carried out due to changes in the shape caused by absorption, deboning or loss of strength in products regularly exposed to moisture (Tserki et al., 2006). The effects of kenaf fibre loading and treatment on the water uptake of kenaf/TPU composites are shown in Fig. 12. In the initial stage of absorption process, the kinetic of uptake is fast and then the increasing rates slow down and finally reach plateau. With the incorporation of kenaf fibres, water absorption capacity of PU/KF composites increased. The composites showed app. 3-5.5% and 8.5-11% water uptake with the loading 10 and 30%, respectively. The rise of water absorption can be attributed to the hydrophilic nature of natural fibres due to the presence of hydroxyl groups, which can react with water molecules, contrary

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to the hydrophobic polyurethane matrix (Sarifuddin et al., 2013). There are also noticeable differences between untreated and treated fibres filled composites. For composites with loading 10 wt. % of fibres, sample PU/KF 10 absorbed the highest amount of water. It can be seen that composites with treated fibre indicate lower amounts of water uptake, the lowest water uptake is found for PU/BIC-KF 10 sample. However this trend changes for composites with loading 30 wt.% of fibres. Composite after permanganate treatment absorbed over 11 wt.% , whereas for untreated fibre composite this value is 10.4 wt.%. Such higher values, than for other treated composites can be associated with very rough surface of permanganate treated fibre (Fig. 7(e)). In general, chemical treatments of fibre provide to decreasing of water uptake in composites. Such an effect confirms that modifications reduce the hydrophilic character of the fibre and suggests better adhesion with hydrophobic matrix, which results in better mechanical properties (De Rosa et al., 2011).

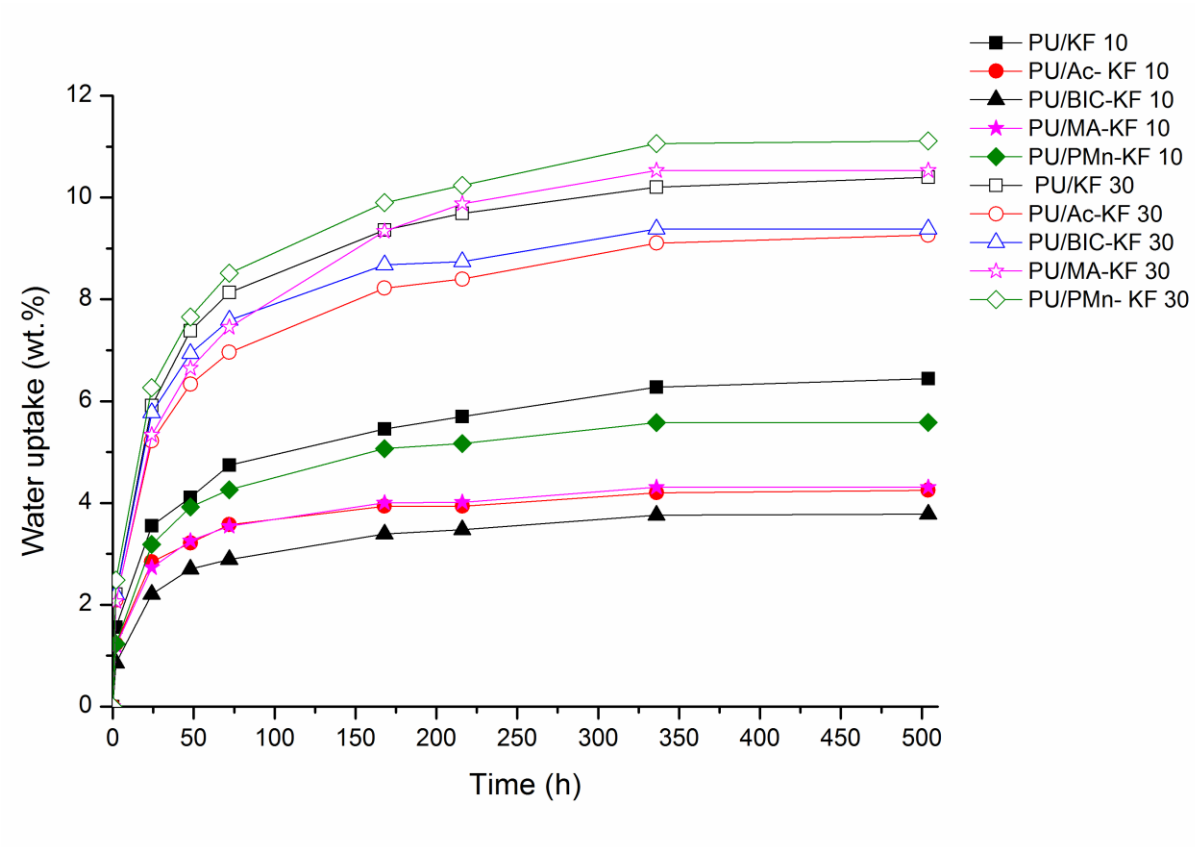

Fig. 12. Water absorption of untreated and treated kenaf fibre composites.

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4. Conclusions

In this paper were examined materials with increased amounts of natural component. The effect of different fibre treatments such as acetylation, blocked isocyanate, maleic anhydride and permanganate on morphology and mechanical properties of kenaf/polyurethane composites were investigated as a function of fibre loading. The conducted treatments of fibres were confirmed by FTIR spectra and SEM micrographs. A good adhesion between polyurethane and fibre could be seen for PU/PMn-KF 30 (Fig. 8(e)) due to the increased surface the fibre after permanganate treatment (Fig. 7(e)). For other composites there are region with high and poor (visible gaps) adhesion. Agglomeration of fibres was also observed, causing a decrease of tensile strength. In the cases of acetylation and permanganate treatment, the modulus were improved. The greatest increase (about 33%) of modulus was obtained for PU/Ac-KF 30, although the acetyl treatment wasn't carried out with high efficiency (lack of peak near 1240 cm^{-1}). The rest of the treatment did not bring any improvement in the elastic modulus values compared to untreated fibre reinforced composite. The composites have high ability to damping capacity, because all samples exhibited tan δ lower than 0.2. The glass transition temperature ranges from -58 to -56 ^{o}C. The mechanical properties (in dynamic and static condition) and structure of thermoplastic polyurethane/kenaf composites were influenced with the modification of kenaf fibres. It was found that natural fibre treatments changed the mechanical properties of composites. Improvement of the tensile strength was for all prepared composites with modified short kenaf fibres (besides maleic anhydride treatment) in comparison to composites with untreated fibres. Use of maleic anhydride as a modifying agent did not give significant improvement in tensile strength. Decrease in elongation at break was demonstrated when increasing the content of kenaf fibre, however elongation at break values were greater after the conducted treatments. The best mechanical properties in static conditions indicated permanganate treated fibre reinforced composites. It was establish that

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higher content of fibres in composites caused increase in hardness and decrease in resilience values. Higher values of mentioned properties were observed for treated fibres. Water absorption of biocomposites increased approximately two times with incorporation of kenaf fibres. Most of treatments affect water uptake in a good way (especially for 10% of fibres loading), which means that those values are lower than for untreated fibre reinforced composite. In the case of higher content of fibre in composite, the greatest water uptake exhibited PU/PMn-KF 30, which can be caused due to changed and rough surface of fibres.

It seem seems that the materials can have a broad technical applications and be used in automotive or light industry.

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