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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 were not 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.

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.

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.

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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
Abrasion to machines	No	Yes
Inhalation health risk	No	Yes
Disposal	Biodegradable	Not biodegradable

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 (24 h)	%	0.02	1.05	0.06	0.02	0.03

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, 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 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., 2012a,b; 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.

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 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 were not 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, BorsodChem, Hungary). The reaction of prepolymerisation was carried out for 2 h at 80 °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 °C for 24 h.

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 min 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*: 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