

Starch-grafted-polypropylene/kenaf fibres composites. Part 2: thermal stability and dynamic-mechanical response

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Abstract

Kenaf fibres of different aspect ratios (L/D = 30 and 160) were melt compounded in an internal mixer with two types of starch-grafted-polypropylene matrices (G906PF and G906PJ) at various loadings, i.e. 10, 20 and 30 wt%. The compound was then compression-moulded into plaques of 1-mm thickness. Thermal, rheological and dynamic mechanical properties of the composite samples were investigated by several techniques involving differential scanning calorimetry, thermogravimetric analysis, melt flow index, Vicat softening point and dynamic mechanical thermal analysis. The results indicated that both thermal and mechanical properties of the composites were remarkably improved by kenaf fibres. Loss modulus and loss factor showed a shift of peak transitions to higher temperatures. Finally, the properties of the investigated composite materials were not affected by the fibre aspect ratio.

Keywords

Starch-grafted-polypropylene, kenaf fibres, composites, fibre aspect ratio, viscoelastic properties, thermal properties

Introduction

Research studies on composite materials based on thermoplastics and natural fibres have attracted technological and academic interests in recent decades, due to their economical and ecological advantages.¹ Natural fibres exhibit high specific strength and modulus and a relatively higher strain to failure and competitive cost (\$0.44-\$0.55/kg compared to \$2.00-\$3.25/kg for E-glass fibres), which make them potential candidates for replacing traditional reinforcements such as glass fibres which have higher density.² Among these natural fibres, kenaf have found potential applications in various fields, in particular in the automotive industry.^{3,4} However, the widespread applications of natural fibres as reinforcements for polymers are still limited due to the inconsistency in their properties which depend strongly on the conditions of growth, moisture absorption and incompatibility with some polymeric matrices.⁵ The approach commonly followed to overcome these drawbacks is either to modify the fibre surface⁶ or to add compatibilizer and coupling agents such as maleic anhydride, acetic anhydride and silanes^{7–9} to enhance the interfacial interactions between the fillers and the polymer matrices. For many years, polypropylene (PP) was considered among thermoplastics with large applications. But, because plastics are derived from petroleum, they increase country's dependence on oil. It is therefore desirable to find an environment-friendly alternative to these products. The use of biopolymers originated from renewable resources such as polylactic acid (PLA), polyhydroxyalkanoate (PHA) and Nylon 11 (PA11) or thermoplastic starch are of

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strong interest. However, they are often either too expensive or too sensitive to aging and humidity, and not sufficiently resistant to be used in high-performance field (automotive, building and constructions, etc.). Even the efforts to reinforce them with nano or micro filler resulted in materials whose properties/cost ratio is not high enough to replace petroleum-based polymers. Recent investigations have successfully presented a biphasic bio-based matrix composed by a conventional PP grafted with starch (starch-g-PP).^{10,11} However, reaching the desired level of mechanical performance still requires further reinforcement. In the first part of this work,¹² we highlighted the improvement in mechanical performance of starch-g-PP reinforced with kenaf fibres (KF) without using any specific fibre treatment or compatibilizer. In this paper, which is a continuation of our previous work,¹² we focus our attention on understanding the effects of KF content and aspect ratio, on the thermal, rheological and viscoelastic properties of composites. In particular, two types of starch-grafted-polypropylene (starch-g-PP) matrices were selected and reinforced with 10, 20 and 30 wt% of KF with two distinct aspect ratios (length to diameter ratio) of 30 and 160.

Materials and methods

Materials

Starch-g-PP with the trade name of G906PF and G906PJ were used as matrices in this work. The materials were kindly supplied by Roquette S.A (Lestrem, France) in the form of pellets. According to the manufacturer, G906PF resin has a density of 1.1 g/cm^3 (ISO 1183), a melt flow index (MFI) of 1.1 g/cm^3 (ISO 1133 $-190^{\circ}\text{C}/2.16 \text{ kg}$), while G906PJ has an MFI value of 40 g/10 min (ISO 1133 $-190^{\circ}\text{C}/$ 10 kg). According to the technical data sheets provided by the manufacturer, the amount of starch grafted to PP is of 52 wt% for both G906PF and G906PJ products.

Kenaf fibres (KF) were provided by Kenaf Natural Fibre Industries Sdn. Bhd (KFI), Malaysia. In this work KF with two different aspect ratios (length/ diameter = L/D) were used: short KF (SKF: L/D \approx 30) and long KF (LKF: L/D \approx 160). According to previous analyses, they are composed by 45–57 wt% of cellulose, 21.5 wt% of hemicelluloses, 8–13 wt% of lignin and 3–5 wt% of pectin and the average density is 1.4 g/cm³.^{3,13}

Preparation of composite samples

Before compounding all raw materials were properly dried as described in Hamma et al.¹² Composite materials containing 10, 20 and 30 wt% of both SKF and

LKF were prepared by melt compounding in an internal mixer Rheomix 600 by Thermo Haake[®] (Karlsruhe, Germany). Compounding was performed at 175°C with a rotor speed of 60 rpm during 7 min. Plates of about 1mm thickness were obtained by compression moulding in a Carver[®] hydraulic press at 170°C. Specimens were cut from plates for all tests.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) measurements were carried out using a TG50 thermobalance linked to a TC10A thermal analysis system by Mettler-Toledo (Columbus, OH) on samples weighing about 40 mg. Samples were heated from 30 to 750°C at 10°C/min under a nitrogen flow of 100 ml/min. Differential thermogravimetric (DTG) curves were determined by the Mettler software.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) tests were performed through a DSC30 measuring module by Mettler-Toledo (Columbus, OH, USA). Aluminium pans of 40 µm were used and the sample weight was approximately 15 mg. All samples were first heated from -50 to 200°C and then maintained for 5 min to erase their thermal histories and tested under a nitrogen flow of 100 ml/min. Samples were then cooled from 200 to -50°C and kept for 5 min at -50°C before a second heating scan up to 200°C. Heating and cooling steps were carried out with the same rate of 10°C/min. The melting and crystallization temperatures (T_m and T_c) were determined at the maximum endothermic and exothermic peaks, respectively. The enthalpy of fusion (ΔH_m) and crystallization (ΔH_c) were calculated from the endothermic and exothermic peaks normalized to the PP content in matrices, respectively. The crystallinity content (X_C) was determined according to equation (1)

$$X_{\rm C} = \frac{\Delta H_{\rm m}}{\Delta H_{\rm ref} W_{\rm PP}} \tag{1}$$

where ΔH_m is the heat of fusion of composite samples, ΔH_{ref} is the heat of fusion of 100% crystalline isotactic PP ($\Delta H_{ref} = 207 \text{ J.g}^{-1}$)¹⁴ and W_{PP} is the weight fraction of PP in the composites estimated taking the real fraction of PP in neat matrices into consideration.

Vicat softening point

A HDT-VICAT[®] Tester MP/3 by ATS FAAR (Milano, Italy) was used to measure the Vicat softening temperature of composites. Tests were carried out following the ASTM D1525-07 A50 standard. A 10 N

load was used and the heating rate was fixed to 50° C/h. Three specimens were tested for each sample.

MFI

MFI measurements were carried out by a melt flow indexer Polymer Test Model 4003DE by Dynisco (Franklin, MA, USA). Measurements were performed according to ASTM D 1238/79 standard at 190°C and 10 kg. Ten measurements were performed for each sample.

Rheological measurements

Rheological measurements were carried out using a MCR301 Anton Paar GmbH rheometer (Seelze, Germany) in a plate-plate configuration with a 25mm diameter for the upper plate. Tests were performed at a temperature of 170°C on disc samples of 25 mm in diameter with a set up gap of 1 mm between plates. Frequency sweep tests were carried out with a constant strain at 1% to ensure the linear viscoelastic zone in a frequency range between 0.01 and 100 rad/s. The average time for scan measurement was 90 min.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) measurements were carried out using a DMAQ800 apparatus by TA Instruments (New Castle, DE, USA) working under tensile mode. The specimen was a rectangular strip with dimensions of $15 \times 5 \times 1 \text{ mm}^3$. The measurements were performed at 1 Hz in the temperature range of $-50 \text{ to} + 150^{\circ}\text{C}$ with a peak amplitude of $32\mu\text{m}$ and a heating rate of 3°C/min . Storage modulus (E'), loss modulus (E'') and loss factor (tan δ) were determined.

Results and discussion

Resistance to thermal degradation

TGA thermograms of KF, G906PF and G906PJ matrices are reported in Figure 1. The TGA curve of KF presents an initial mass loss of almost 4 wt% up to almost 150°C followed by a strong mass loss (of about 73 wt%) between 150 and 400°C. The first mass loss is attributed to the evaporation of the moisture absorbed by the fibres. However, in the second step and according to the literature,^{6,15–17} the mass loss is due to the degradation of hemicelluloses, cellulose and lignin, which take place in the temperature ranges of 220-320°C, 250-380°C and 282-502°C, respectively. The maximum thermal decomposition temperature (T_{max}) of KF determined on DTG curves occurred at approximately 363°C, which is related to cellulose and lignin degradation, representing the main constituents of natural fibres.

The TGA thermograms of the two investigated starch-g-PP matrices are quite similar and exhibit three main mass loss steps, i.e. a first one below



Figure 1. TGA and DTG curves of kenaf fibres, G906PFand G906PJ matrixes.



Figure 2. TGA and DTG thermograms of G906PFcomposites reinforced with (a) short (SKF) and (b) long (LKF) kenaf fibers.



Figure 3. TGA and DTG thermograms of G906PJ composites reinforced with (a) short (SKF) and (b) long (LKF) kenaf fibers.

200°C; a second one located between 250 and 360°C and the last one occurs beyond 360°C. As reported by some authors,^{18,19} the mass loss below 200°C is due to the evaporation of adsorbed water and plasticizers contained in the thermoplastic starch. The second mass loss is attributed to the degradation of starch compounds corresponding to a maximum degradation temperature of 318°C.¹⁸ The main degradation products of starch result mainly from crosslinking of glycosidic units after dehydration leading to unzipping of chains and formation of laevoglucosan, which further decomposes predominantly into furfural, formic acid and formaldehyde and also to other volatile products at low concentration.^{15,20,21} The last degradation step is relative to the decomposition of the PP phase contained in both starch-g-PP matrices, with T_{max} at around 468°C. As a result, aliphatic saturated and unsaturated

products are generated involving dienes, alkanes (C_{12} , C13 and C14) and alkenes without any formation of char.²² Figures 2 and 3 show TG and DTG thermograms of G906PF and G906PJ matrices reinforced with both SKF and LKF, respectively. Further, Table 1 provides the values of the mean degradation temperature of both neat matrices and composite materials. It is observed that the incorporation of KF in starch-g-PP matrices decreases the values of $T_{10\%}$ and $T_{50\%}$ corresponding to the degradation temperature at 10 and 50% mass loss, respectively. This can be explained by the lower stability of KF compared to the matrices, due to the presence of hemicelluloses that are very sensitive thermal degradation at low temperature.¹⁷ to Furthermore, the decrease in the degradation temperature at T_{50%} appears to be dependent on both KF content and aspect ratio for G906PF composites. The

					T _{max.rate} (°C) I st /2 nd /3 rd	Char (wt%)
SKF content (wt%)		T _{10%} (°C)	T _{50%} (°C)	T _{75%} (°C)	DTG peak	at 550°C
G906PF/SKF	0	284	420	462	318/466.5	6.3
	10	260	400	460	324/366/468	6.5
	20	259	374	464	326/366/468	7.9
	30	268	370	464	326/366/469	9.5
G906PJ/SKF	0	283	430	467	(318/468)	6.5
	10	262	408	468	(325/366/470)	6.2
	20	260	375	466	(326/366/469)	8.0
	30	270	371	466	(326/366/471)	9.6
KF		286	359	382	303/363	16.3
LKF content (wt%)						
G906PF/LKF	0	264	403	466	324/367/467	6.6
	10	262	386	466	325/367/470	7.0
	20	265	375	465	326/367/468	8.2
	30	264	403	466	324/367/467	6.6
G906PJ/LKF	0	283	430	467	(318/468)	6.5
	10	258	401	465	325/367/467	6.6
	20	260	376	465	326/367/467	7.4
	30	269	372	466	326/367/471	9.3
KF		286	359	382	303/363	16.3

Table 1. TGA characterization of neat starch-g-PP filled with short (SKF) and long (LKF) kenaf fibers.

DTG: Differential thermogravimetric.

temperature at maximum rate of degradation ($T_{max.rate}$) is shifted to higher temperature for the composite materials. The first degradation temperature referred to starch decomposition shifts also to higher temperature by almost 5 and 8°C for composites reinforced with a KF fraction of 10 and 30 wt%, respectively. This is an indication of good compatibility between both matrices and KF.¹⁹ Another factor that is also responsible for a reduction in the thermal degradation rate is the formation of char, which increases with KF content. As established, the char may act as barrier between the composite and the heat source.¹⁵

Thermal properties and Vicat softening temperature

The thermal properties of starch-g-PP/KF composites were investigated by DSC to analyse the combined effects of fibre content and aspect ratio on crystalline index (Xc), melting temperature and enthalpy (T_m and ΔH_m), crystallization temperature and enthalpy (T_c and ΔH_c) of the composites. The data are summarized in Table 2.

Both matrices display almost the same values of melting and crystallization temperatures located at about 161 and 120°C, respectively. Further, in composites reinforced with 30 wt% of KF it can be observed that the two matrices exhibit a very small decrease in

the melting and crystallizations peaks of almost 1 and 3°C, respectively. The aspect ratio of KF seems, however, do not play any effect on melting and crystallization temperatures of the composite materials. According to the literature, 7,23 a decrease in melting temperature can be explained as a result of a disturbing effect of the fibres on the crystalline phase of PP chains. Consequently, the density of crystalline nuclei decreases and the diffusion of PP chains to the surface of crystal-line nuclei can be hindered.^{24,25} The slight decrease in crystallization temperature as a result of the low crystallization rate of PP chains in the composite samples indicates that KF do not play a nucleating effect. In addition, a decrease in the crystallization enthalpy of all composite samples is observed. The DSC data also indicate that for both matrices, the values of melting enthalpy of the composites decrease regularly with increasing the content of KF. This is obviously due to the reduction of matrix content when fibres are added. However, a deep analysis of the corrected ΔH_m values based on the effective matrix content in the composite samples highlights two different trends. In case of G906PF composites, ΔH_m values follow a decreasing trend as the content of KF increases. However, in case of G906PJ composites, an increasing trend is observed. Similar behaviour is noticed for the crystallinity as illustrated in Figure 4, which is in agreement with the

Composition (wt%	5 of SKF)	T _m (°C)	$\Delta H_{m \text{ composite}}$ (J/g)	$\Delta H_{m PP}$ (J/g)	T _c (°C)	ΔH_{c} (J/g)	X _c (%)
G906PF/SKF	0	161.2	33.51	67.0	119.6	58.0	32.38
	10	161.3	26.87	59.7	119.3	58.5	28.85
	20	160.2	25.12	62.8	117.2	59.0	30.34
	30	160.3	20.27	57.9	117.0	56.2	27.98
G906PJ/SKF	0	161.7	30.74	61.5	119.6	57.4	29.70
	10	160.0	28.25	62.8	120.5	56.I	30.33
	20	160.3	24.96	62.4	117.5	55.7	30.14
	30	159.4	22.77	65.0	117.7	56.8	31.43
Composition (wt%	of LKF)						
G906PF/LKF	Ó	161.2	33.51	67.0	119.6	58.0	32.38
	10	160.2	27.07	60.2	119.7	57.2	29.70
	20	160.3	24.01	60.0	118.0	54.8	29.00
	30	160.3	19.15	54.7	116.8	55.7	26.43
G906PJ/LKF	0	161.7	30.74	61.5	119.6	57.4	29.70
	10	160.0	28.28	62.8	120.2	56.0	30.36
	20	160.0	25.37	63.4	117.4	55.6	30.64
	30	159.6	22.39	64.0	117.4	56.4	30.90

 Table 2. DSC temperatures and heat of transition for G906PF and G906PJ matrices reinforced with short (SKF) and long (LKF) kenaf fibers.

DSC: Differential scanning calorimetry.



Figure 4. Evolution of crystallinity of starch-g-polypropylene composites reinforced with kenaf fibres.



Figure 5. Effect of kenaf fibres contents and aspect ratio on Vicat softening temperature of starch-g-polypropylene composites.

literature data.^{26,27} In contrast, the fibre aspect ratio has no significant effect on the thermal properties of the composite samples.

Vicat softening point (VSP) is one of the thermal characteristic to assess the heat stability in terms of maximum service temperature of plastics. From Figure 5, it can be noticed that increasing the KF content leads to a remarkable increase of VSP. Indeed, the value of VSP increases from 96°C for the control matrices to 147°C after addition of 30 wt% of KF. The observed beneficial effect of KF does not depend on their aspect ratio. In general, an increase in VSP with fibre addition could be the result of various factors, which may be related to an increase of T_g or crystallinity of the polymer matrix, or a stiffening effect due to restriction of the polymer mobility. In the present case the DSC data clearly indicate that the crystallinity is not changed by the presence of KF, thus suggesting that the improvement in heat resistance could be rather due to the reinforcement effect of KF which causes a restriction in the mobility of polymer chains in the amorphous phase thus reducing the composite deformation under load.

MFI and rheological behaviour

Figure 6 summarizes the MFI values as a function of the fibre content. It can be observed that MFI values decrease as the KF content increases indicating a rise in the material viscosity. This result is typical for most filled thermoplastics and it is attributed to the rigid nature of the fibres, which may restrict the mobility of the polymer melt.^{28,29} However, the incorporation of LKF with higher aspect ratio (L/D = 160) into starch-g-PP induces a more pronounced decrease in the MFI values compared to those obtained with SKF (L/D=30), irrespective of the fibre content. These results are in good agreement with those found by Viksne et al.,²⁹ La Mantia et al.³⁰ and Kumari et al.,³¹ who documented how the incorporation of fillers of lower aspect ratio induces a slight increase in viscosity. The difference in viscosity values of composites based on SKF or LKF reduced at high amount of fibres. This is due to the high fibre breakage during processing which is more pronounced at higher fibre contents.³⁰ This is explained as a result of processing conditions: in fact, the aspect ratio of LKF loaded at 30 wt% was observed to decrease more sharply with respect to that of SKF.¹²

The rheological measurements were performed in the linear viscoelastic region at a constant temperature of 170°C. The effects of LKF on the complex viscosity, storage and loss moduli of G906PJ- and G906PF-based composites are presented in Figures 7 and 8 as a function of frequency.

From Figure 7(a), it is observed that the complex viscosity of both polymeric matrices decreases with the frequency, indicating a shear thinning behaviour



Figure 6. Evolution of melt flow index of starch-g-polypropylene composite with kenaf fibres contents and aspect ratio.



Figure 7. Complex viscosity of (a) Control matrixes, (b) G906PJ-LKF and (c) G906PF-LKF as a function of frequency, for various fibres loading rates.



Figure 8. Storage and shear modules of (a) Control matrixes, (b) G906PJ-LKF and (c) G906PF-LKF as a function of frequency, for various fibres loading rates. G' curves refer to the lower x-axis scale, G'' curves refer to the upper x-axis scale.

of G906PJ and G906PF matrices within the investigated frequency range. This behaviour is typical of plasticized starch contained in the matrices.¹¹ Furthermore, it is also noticed that the complex viscosity of G906PJ is higher than that of G906PF. With the incorporation of KF into G906PJ and G906PF matrices, similar shear thinning behaviour is observed for both of them as illustrated in Figure 7(b) and (c), respectively. According to Pardo et al.,³² this behaviour indicates a greater degree of fibre/matrix interaction requiring higher shear stress and longer relaxation time to flow. However, Krácãlík et al.³³ reported that this phenomenon could be attributed to the orientation of the fibres in the flow direction. Compared to the control matrices, the composite samples showed higher complex viscosity, increasing with the fibre content with more pronounced difference at low frequency. This result is typical of filled polymer melts in

agreement with the literature data.^{34,35} The high value of complex viscosity reflects the viscoelastic resistance of the polymer melt against flow. Hence, the incorporation of the rigid KF disturbs and creates obstructions to flow and subsequently, chain segment mobility is hindered as the internal friction in the molten polymer increases.^{32,36,37}

From Figure 8(a), an increase of storage (G') and shear modulus (G") with increasing the frequency for G906PJ and G906PF matrices can be observed. The elastic and viscous response of the two matrices shows the same order of magnitude except at higher frequency, where G906PJ and G906PF exhibit gel behaviour. Furthermore, the values of modulus of G906PJ are always higher than those of G906PF in the investigated frequency range. A comparison between the loss and storage modulus of the composite samples and control matrices is illustrated in



Figure 9. Temperature dependence of (a) storage modulus, (b) loss modulus and (c) tan δ of G906PF composites at different short kenaf fibres loading.

Figure 8(b) and (c). An increase in G' and G" is observed for the composite samples compared to the control matrices. This may be attributed to the KF, which restrict the deformation of the composites. However, at low frequency, i.e. below 0.1 rads⁻¹, G' is higher than G", and it is not dependent on frequency, which is a characteristic of a solid-like behaviour.³⁸ This is generally due to the formation of interconnected fibres network structure within the matrix.³⁴

DMTA

The thermograms describing the variation of storage modulus (E') with temperature measured at 1 Hz at various KF contents for both G906PF and G906PJ composites are shown in Figures 9(a) and 10(a), respectively. In the whole temperature range, an increase in E' values of the composite samples with

the KF content can be observed. Indeed at room temperature the values of E' increase by two, three and four times when the fibre content is 10, 20 and 30 wt%, respectively. These results are consistent with the trend in the quasi-static tensile modulus reported in the Part 1 of the present investigation.¹²

Thermograms of the loss modulus and the loss tangent are presented in Figure 9(b) and (c), respectively, for composites based on G906PF matrix reinforced with SKF and Figure 10(b) and (c), for those based on G906PJ. From these figures, three transition peaks can be detected. The one at about 60°C represents the α transition in the control matrices, which is related to the relaxation of restricted amorphous chains in the crystalline phase of PP and also to a lamellar slip mechanism and rotation in the crystalline phase.^{39,40} Oromiehie et al.⁴¹ assigned this transition to the overlap of α transition of PP chains and β transition of plasticized starch. In fact, according to the literature,⁴²



Figure 10. Temperature dependence of (a) storage modulus, (b) loss modulus and (c) tan δ of G906PJ composites at different short kenaf fibres loading.

PP has two transitions: β relaxation around -10 to 10° C and α relaxation at about 60–100°C. On the contrary, unplasticized starch has an unique relaxation α taken also as T_g at around 50°C.⁴¹ As it was recently shown by Lendvai et al.,⁴³ it is assumed that the position and number of relaxations of plasticized starch depends on the concentration and nature of plasticizer used. For glycerol plasticized starch two relaxations could be generally observed. The first one is located in the range from -40 to -70° C corresponding to the relaxation of plasticizer or starch-poor phase, and the second one is around 40 to 60°C and it is related to the starch-rich phase relaxation.44-46 However, other plasticizers such as sorbitol, xylitol, maltitol, show a unique relaxation peak.⁴⁶ In Figures 9(c) and 10(c), the temperature dependence of loss tangent of composites is reported. The stiffening effect played by KF is clearly manifested in a translation of the peak toward higher temperatures, which is determined by an increase of the glass transition temperature.

The main effect at room temperature is a remarkable decrease of the loss factor induced by the presence of KF.

The contribution of KF with different lengths can be evaluated by looking at the thermograms of Figure 11(a) and (b), where DMTA curves of the storage modulus and loss factor of G906PJ composites reinforced with SKF and LKF are compared. It is observed that longer fibres induce only a moderate increase in the storage modulus values over shorter ones, which is consistent with the data of tensile modulus reported in the Part 1 of this work.¹² On the other hand, a negligible effect is played by the fibre length on the loss factor of the investigated materials.

Conclusions

In this study, physical, thermal and thermo-mechanical properties of starch-g-PP/KF composites at various filler aspect ratios and contents were investigated



Figure 11. Temperature dependence of (a) storage modulus and (b) tan δ of G906PJ composites at different kenaf aspect ratio.

and the following conclusions can be drawn. DMTA analysis indicated the existence of interactions between the polymeric matrix and fibres through the evolution of transition temperatures. Further, storage modulus (E'), VSP, complex viscosity and shear modules of the composites increased considerably with increasing the fibre content due to the reinforcing effect of KF. On the other hand, MFI and loss modulus of the composite materials decreased. The study showed also that the thermal stability of the composites was improved by the addition of KF. No noticeable effect of variation fibres aspect ratio was found on the thermal and thermo-mechanical properties of investigated composites.

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Declaration of Conflicting Interests

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References

- Sgriccia N, Hawley MC and Misra M. Characterization of natural fiber surfaces and natural fiber composites. *Compos A Appl Sci Manuf* 2008; 39: 1632–1637.
- Wambua P, Ivens J and Verpoest I. Natural fibres: can they replace glass in fibre reinforced plastics? *Compos Sci Technol* 2003; 63: 1259–1264.
- Akil HM, Omar MF, Mazuki AAM, et al. Kenaf fiber reinforced composites: a review. *Mater Design* 2011; 32: 4107–4121.
- Koronis G, Silva A and Fontul M. Green composites: a review of adequate materials for automotive applications. *Compos B Eng* 2013; 44: 120–127.
- Ok Han S, Karevan M, Na Sim I, et al. Understanding the reinforcing mechanisms in kenaf fiber/PLA and kenaf fiber/PP composites: a comparative study. *Int J Polym Sci* 2012; 1–8.
- Han YH, Han SO, Cho D, et al. Kenaf/polypropylene biocomposites: effects of electron beam irradiation and alkali treatment on kenaf natural fibers. *Compos Interf* 2007; 14: 559–578.
- Feng D, Caulfield DF and Sanadi AR. Effect of compatibilizer on the structure-property relationships of kenaffibre/polypropylene composites. *Polym Compos* 2001; 22: 506–517.
- Law TT and MIZ A. Water absorption and dimensional stability of short kenaf fiber-filled polypropylene composites treated with maleated polypropylene. *J Appl Polym Sci* 2011; 120: 563–572.

- Pracella M, Haque MM-U and Alvarez V. Functionalization, compatibilization and properties of polyolefin composites with natural fibers. *Polymers* 2010; 2: 554–574.
- Khanna ND, Kaur I and Kumar A. Starch-grafted polypropylene: synthesis and characterization. J Appl Polym Sci 2011; 119: 602–612.
- Tessier R, Lafranche E and Krawczak P. Development of novel melt-compounded starch-grafted polypropylene/polypropylene-grafted maleic anhydride/ organoclay ternary hybrids. *Express Polym Lett* 2012; 6: 937–952.
- Hamma A, Kaci M, Mohd Ishak ZA, et al. Starchgrafted-polypropylene/kenaf fibers composites. Part 1: mechanical performances and viscoelastic behaviour. *Compos Part A Appl S* 2014; 56: 328–335.
- Zampaloni M, Pourboghrat F, Yankovich SA, et al. Kenaf natural fiber reinforced polypropylene composites: a discussion on manufacturing problems and solutions. *Compos Part A Appl S* 2007; 38: 1569–1580.
- 14. Mark J. *Polymer data handbook*, 2nd ed. New York: Oxford University Press, 1999.
- Craig L and Beyler MMH. Thermal decomposition of polymers. SFPE handbook of fire protection engineering book. 1988. 1 ed. Section one: 110–31.
- Ogbomo SM, Chapman K, Webber C, et al. Benefits of low kenaf loading in biobased composites of poly(L-lactide) and kenaf fiber. J Appl Polym Sci 2009; 112: 1294–1301.
- Yussuf AA, Massoumi I and Hassan A. Comparison of polylactic acid/kenaf and polylactic acid/rise husk composites: the influence of the natural fibers on the mechanical, thermal and biodegradability properties. *J Polym Environ* 2010; 18: 422–429.
- Mano JF, Koniarova D and Reis RL. Thermal properties of thermoplastic starch/synthetic polymer blends with potential biomedical applicability. J Mater Sci Mater Med 2003; 14: 127–135.
- Tomé LC, Fernandes SCM, Sadocco P, et al. Antibacterial thermoplastic starch chitosan based materials prepared by melt mixing. *BioResources* 2012; 7: 3398–3409.
- Bryce DJ and Greenwood CT. The thermal degradation of starch Part III. The formation of decomposition products from starch and related materials at temperatures between 175°C and 400°C. *Starch-Stärke* 1963; 15: 359–363.
- Bryce DJ and Greenwood CT. The thermal degradation of starch. Part II. The identification by gas chromatography of the minor volatile products produced at 300°C. *Starch - Stärke* 1963; 15: 285–290.
- Bockhorn H, Hornung A, Hornung U, et al. Kinetic study on the thermal degradation of polypropylene and polyethylene. *J Anal Appl Pyrolysis* 1999; 48: 93–109.
- Roy SB, Ramaraj B, Shit SC, et al. Polypropylene and potato starch biocomposites: physicomechanical and thermal properties. *J Appl Polym Sci* 2011; 120: 3078–3086.

- Anuar H and Zuraida A. Thermal properties of injection moulded polylactic acid – kenaf fibre biocomposite. *Malaysian Polym J* 2011; 6: 51–57.
- Wanjun Liu Y-JW and Sun Zhenhua. Crystallization behavior of starch-filled polypropylene. J Appl Polym Sci 2004; 92: 484–492.
- Amash A and Zugenmaier P. Morphology and properties of isotropic and oriented samples of cellulose fibre–polypropylene composites. *Polymer* 2000; 41: 1589–1596.
- Wulin Qiu FZ, Takashi Endo and Takahiro Hirotsu. Preparation and characteristics of composites of highcrystalline cellulose with polypropylene: effects of maleated polypropylene and cellulose content. J Appl Polym Sci 2003; 87: 337–345.
- Caraschi JC and Lopes Leão A. Woodflour as reinforcement of polypropylene. *Mater Res* 2002; 5: 405–409.
- Viksne A, Berzina R, Andersone I, et al. Study of plastic compounds containing polypropylene and wood derived fillers from waste of different origin. J Appl Polym Sci 2010; 117: 368–377.
- La Mantia FP, Morreale M and Mohd Ishak ZA. Processing and mechanical properties of organic fillerpolypropylene composites. *J Appl Polym Sci* 2005; 96: 1906–1913.
- Kumari R, Ito H, Takatani M, et al. Fundamental studies on wood/cellulose-plastic composites: effects of composition and cellulose dimension on the properties of cellulose/PP composite. J Wood Sci 2007; 53: 470–80.
- Pardo SG, Bernal C, Ares A, et al. Rheological, thermal, and mechanical characterization of fly ash-thermoplastic composites with different coupling agents. *Polym Compos* 2010; 31: 1722–1730.
- Kráčalík M, Pospíšil L, Šlouf M, et al. Effect of glass fibers on rheology, thermal and mechanical properties of recycled PET. *Polym Compos* 2008; 29: 915–921.
- Ares A, Bouza R, Pardo SG, et al. Rheological, mechanical and thermal behaviour of wood polymer composites based on recycled polypropylene. *J Polym Environ* 2010; 18: 318–325.
- Luan L, Wu W and Wagner MH. Rheological behavior of lubricating systems in polypropylene/seaweed composites. J Appl Polym Sci 2011; 121: 2143–2148.
- Ghasemi I, Azizi H and Naeimian N. Rheological behaviour of polypropylene/Kenaf fibre/wood flour hybrid. Composite. *Iran Polym J* 2008; 17: 191–198.
- Twite-Kabamba E, Mechraoui A and Rodrigue D. Rheological properties of polypropylene/hemp fiber composites. *Polym Compos* 2009; 30: 1401–1417.
- Teyssandier F. Formulation et morphologies de mélanges de polymères thermoplastiques à base d'amidon. *INSA de Lyon*. Lyon, France2011.
- Awal A, Ghosh SB and Sain M. Thermal properties and spectral characterization of wood pulp reinforced biocomposite fibers. *J Thermal Anal Calorimetry* 2009; 99: 695–701.

- Hristov V and Vasileva S. Dynamic mechanical and thermal properties of modified poly(propylene) wood fiber composites. *Macromol Mater Eng* 2003; 288: 798–806.
- 41. Oromiehie AR, Taherzadehlari T and Rabiee A. Physical and thermal mechanical properties of corn starch/LDPE composites. *J Appl Polym Sci* 2012; 127: 1128–1134.
- McCrum NG, Read BE and Williams G. Anelastic and dielectric effects in polymeric solids. New York: Dover Publications Inc., 1991.
- 43. Lendvai L, Karger-Kocsis J, KmettyÁ, et al. Production and characterization of microfibrillated cellulose-

reinforced thermoplastic starch composites. J Appl Polym Sci 2015; 132: 42397.

- 44. Avérous L, Fringant C and Moro L. Plasticized starchcellulose interactions in polysaccharide composites. *Polymer* 2001; 42: 6565–6572.
- 45. Curvelo AAS, de Carvalho AJF and Agnelli JAM. Thermoplastic starch–cellulosic fibers composites: preliminary results. *Carbohydr Polym* 2001; 45: 183–188.
- 46. Mathew AP and Dufresne A. Plasticized waxy maize starch: effect of polyols and relative humidity on material properties. *Biomacromolecules* 2002; 3: 1101–1108.