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Research Article

VALORIZATION OF DATE SEEDS WASTES AS REINFORCEMENT FOR STARCH-GRAFTED-POLYPROPYLENE COMPOSITES

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Abstract

Paper discusses the possibility of incorporation of date seed waste as fillers (DSF) into starch-g-PP matrices compared to kenaf fibers (KF with two lengths) based composites. Three starch-g-PP matrices (G906PF, G906PJ and G720PJ) were studied in parallel to a fully PP one. The investigated composites loaded to 20 wt.%, showed differences in performance related, principally, to loading type (DSF, KF) and matrix used. Results showed an improvement of tensile and impact stress at break as well as Shore D hardness of starch-g-PP composites reinforced with date seed fillers (DSF) or kenaf fibers (KF). Further, tensile, storage and loss moduli increased also with loading. Vicat softening point of either KF or DSF/starch-g-PP composites was greater with higher values for KF composites. However, thermal stability of starch-g-PP composites was better when DSF was used.

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The outcome of this work demonstrated that DSF is useful as promising lignocellulosic fillers in manufacturing of bio-composites.

Keywords: Date seed fillers, starch-g-polypropylene, bio-composites, mechanical properties, waste valorization.

1. INTRODUCTION

Vegetal reinforcements has widely received great interest in the past and even more since the development of polymer composites [1]. Some renewable reinforcement such as kenaf, Sisal, flax or wood fibers are cultivated, specially, to meet the needs of composite fields[1, 2]. Increased interest among this class of materials is promoted by the continual research of sustainable and ecological technologies. Furthermore, need to find new outcomes to vegetal origin wastes such as date palm[3], date seed [4], olive husk [5] and coffee husk [6] have stimulated research in this area. For many years, thermoplastics as polypropylene (PP) and polyethylene was considered among thermoplastics with large applications in composite fields. The challenge to those composites based on vegetal reinforcement and polyolefin matrix is the improvement of interfacial adhesion. This is overcome by surface treatment or adding coupling agent that include additive costs [7, 8]. However, because plastics are derived from non-renewable resources, they suffer from cost disruption of the world oil market. In addition to that, their disagreeable impact on the environment inspired some countries to develop a new class of hybrid materials, named also bio-based materials, composed of a conventional thermoplastic (PP, PE) grafted with derivatives starch. Unfortunately, desired performances requires further studies to, properly, orient the material towards new applications other than packaging with respect to new environmental considerations. Few studies exist on this new class of materials focusing on the evaluation of materials performances at the nano or micro scale using natural reinforcement as kenaf fibers[9, 10] or nanoclays[11]. Moreover, no study exist about vegetal waste recovery in bio-based matrices. The present study fits into this perspective and has for goal the valorization of date seeds waste as a reinforcement in bio-based matrices. At the same time, a comparison was done between valorized wastes (date seed fillers) and kenaf fibers-based bio composites. Mechanical tensile and impact properties, viscoelastic behavior by DMTA, Vicat softening point and thermal stability of elaborated composites were then investigated to assess their performances in the presence of various loading type.

2. MATERIALS AND METHODS

2.1.Materials

Four matrices were used in this study. The first was an isotactic homopolymer polypropylene commercialized under the trade name of HP500H by LATI S.p.A (varese, Italy), noted PP. The three others matrices were hybrid polypropylenes commercialized by Roquette S.A (Lestrem, France) and known as G906PF. G906PJ and G720PJ. According to materials technical data sheets density values (ISO 1183) are: 0.9 g/cm^3 (PP) and 1.1 g/cm^3 (G720PJ, G906PF & G906PJ). The MFI (ISO 1133) is 1.8 g/10 min (230°C/ 2.16 Kg) for PP, 1.1 g/10 min (190°C/2.16 Kg) for G906PF, 40 g/10 min (190 °C/ 10 Kg) for G906PJ, and 65 g/10 min (190 °C/ 10 Kg) for G720PJ.

Date seed fillers (DSF) used as reinforcement were extracted from the date palm fruits seeds. Prior to grinding the date fruit seeds was washed several times with cold and hot water and air dried. Then DSF was washed again for several times with acetone solvent. The particle size of the filler selected was less than 40 µm and the composition determined by Van Soest and Wine method gives neutral detergent soluble (NDS) = 25.34 wt % corresponding to the majority of proteins, non-parietal sugars and fatty materials, cellulose = 20.82 wt %, hemicellulose =17.35 wt %, lignin =34.95 wt % and mineral ash=1.54 wt %. The moisture content is 6.46 wt %.

Kenaf fibers (KF) with two different lengths of 11 and 1.5 mm were used in this study, termed respectively, long kenaf fibers (LKF) and short kenaf fibers (SKF), was used as second reinforcement in this study. Kenaf fibers preparation method followed in this work and fiber composition were described in previous studies [9, 10].

2.2.Composites preparation

Composite with 20 wt.% of DSF, SKF or LKF were prepared by melt blending in an internal mixer Rheomix 600 by Thermo Haake® (Karlsruhe. Germany) using rotor speed of 50 rpm. Blending temperature and residence time were 190 °C and 10 min for polypropylene based composites, 175 °C and 7 min for hybrid-polypropylene based composites. Feeding with fibers was done, progressively, after complete melting of polymers to keep fibers length with minimum reduction. Obtained blends were cut down into pellets using a grinder equipped with a set of rotating knifes. Compression molding process in a hydraulic press, at suitable conditions, was used to obtain plates.

2.3.Characterization

Uniaxial tensile tests

All tensile tests were performed on ISO 527-2 type 1BA specimens at room temperatures. In particular, quasi-static uniaxial tensile tests were performed by a Zwick/Roell Z2 tensile testing machine equipped with a 1 kN load cell. Elastic modulus was evaluated deforming specimens up to a strain of 1% at low cross-head speed of 0.25 mm/min. The strain was measured by a resistance extensometer length of 12.5 mm. According to ISO 527 standard, the elastic modulus was evaluated as a secant value between deformation levels of 0.05% and 0.25%. Tensile tests up to fracture were performed at a higher crosshead speed of 10 mm/min. At least 10 specimens were tested for each sample.

Impact tests

Tensile impact tests were performed by an intron CEAST 9050 (Italy) impact pendulum under tensile configuration. The hammer was released from a height selected to reach an impact velocity of 2 m/s with an impact energy of 4.38 J (hammer mass of 2.191 kg). Tests were carried out at room temperature (23 °C) and a minimum of 5 specimens were tested for each sample.

Shore D hardness

Shore D hardness of composites was measured using a digital durometer type Zwick/Roell 3130/3131, following ASTM D2240.

Dynamic mechanical thermal analysis (DMTA)

DMTA measurements were carried out using a TA Instruments (New Castle. DE. USA) DMA Q800 apparatus working in tensile mode. The specimen was a rectangular strip with dimensions of 15 x 5 x 1 mm^3. The measurements were performed at 1Hz and the temperature range was varied between -50 and 150°C with a peak amplitude of 32 and a heating rate of 3°C/min. Storage modulus (E'), loss modulus (E") and loss factor (tan δ) were determined.

Vicat softening temperature

A Vicat softening temperature testing machine HDT-VICAT® Tester Model CEAST HV3-HV6 (Italy) was used to measure the Vicat softening temperature of composites. Tests were carried out following the ASTM D1525-07 A50 standard. The load used was 10 N and the heating rate 50°C/h. Three specimens were tested for each sample and the average value was taken.

Thermogravimetric analysis (TGA)

Thermal stability of prepared composites and the degradation characteristic were investigated with the use of TGA analysis. Measurements were performed with the use of thermo-gravimetric balance model SDT-Q 600 (Italy). The sample weight is taken about 10 mg. The test were carried out from room temperature to 800 °C with the heating rate of 20°C/min. Measurements were performed under nitrogen atmosphere with 10 mg as an average size of the sample.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry was performed in the control matrices and their composites using TA instrument (Italy) SDT-Q 600 differential scanning calorimeter (DSC), operating under nitrogen flow of 100 ml min^{-1}. Aluminium pans of 40 μm with holes 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. Samples were cooled from 200 to -50 °C for 5 min at -50°C before the second scan to 200°C. The heating and cooling were carried out with the same rate of 10°C min^{-1}. The enthalpy of fusion (ΔHm) was calculated from the endothermic peak normalized to the PP content in matrices. The crystallinity index (Xc) was determined as follows:

$$X_c = \frac{\Delta H_m}{\Delta H^{\circ}_{ref} . W_{PP}} . 100 \quad (1)$$

Where: ΔH_m is the heat of fusion of composites samples. ΔH°_{ref} is the heat of fusion of 100% crystalline isotactic PP (ΔH°_{ref}= 207 J g^{-1}) and W_{PP} is the weight fraction of PP in the composites taking in consideration the real fraction of PP in control matrices.

3. RESULTS AND DISCUSSION

Mechanical properties

Tensile properties. Figure 1 shows elastic moduli of neat PP, neat starch grafted PP matrices noted G906 PF, G906PJ & G720PJ and their respective composites reinforced with 20 wt% DSF, SKF and LKF. As seen from results, neat PP present module value two times greater than that of G720 PJ hybrid matrix and three times more compared to G906PF or G906PJ. With loading addition, elastic moduli values of all neat matrices increased. Values recorded exceeds 100% for G906PF and G906PJ reinforced with DSF and 50% for G720PJ/DSF. When using KF, the improvement was almost by 200% and 100% for, respectively, G906PF & G906PJ and G720PJ. In the opposite, PP composites module values increased by 40% independently from reinforcement used. The increase in elastic moduli is expected for all matrices due to the addition of a rigid reinforcement what is in agreement with literature[5, 9] . Nevertheless, when using two lengths of KF, differences appears in module values thanks to procedure followed in feeding during composite processing that is changed compared to study realized previously [9]. This fact, prevent in some extent fibers length reduction during processing. In case of DSF, which is different from KF in form as well as in chemical composition, it is marked that the gain in elastic moduli values is considerable, even if it isn't of the same order than used kenaf fibers. In his study [5] Hejna et al., found that chemical composition affects the rigidity of composites, in particular, at high filler content. On his side, Essabir et al., [12] have shown that the lower reinforcing effect of coir particles against coir fibers was due to their geometry and lower aspect ratio. Besides, chemical composition owing to the possibility of different stiffness carried by coir particles or fibers affect also composite rigidity.

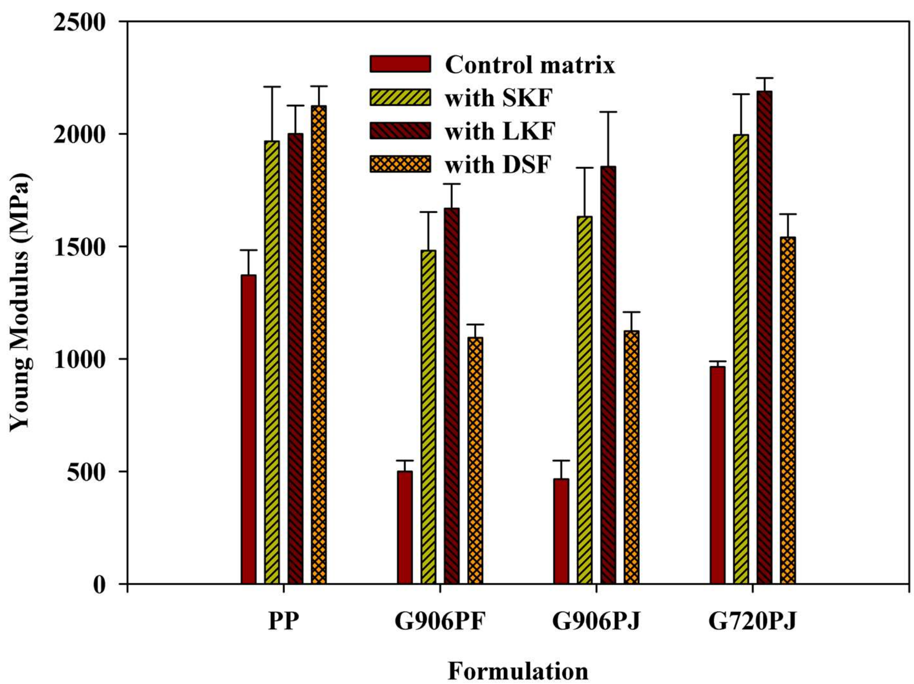


Fig.1. Moduli values of PP, G906PF, G906PJ & G720PJ composites with SKF, LKF and DSF.

Results of tensile strength obtained for neat PP, G906PF, G906PJ & G720PJ and their respective composites with SKF, LKF and DSF were presented in figure 2. For starch-g-PP neat matrices, tensile strength values are weaker than this of neat PP. With matrix reinforcement, tensile strength values of PP composites decrease by almost 20 % compared to the neat matrix. In contrast, loading addition to starch-g-PP matrices induced a considerable increase of tensile strength values compared to neat matrices. In fact, G906PJ composites recorded the highest the gain on tensile strength values estimated to 30%, 81% and 135% with adding 20 wt.% of, respectively, DSF, SKF and LKF. A similar improvement was also marked for G906PF composite. While with G720PJ composites, the gain in tensile strength values was about 21%, 60% and 70% with addition of 20 wt.%, respectively, of DSF, SKF and LKF.

Initially, it is noticed that the decrease in PP composite tensile strength indicated the absence of applied stress transmission from the PP matrix to the cellulosic fillers or fibers. This is well known from different studies based on polyolefin composites that required modification or surface treatment of either matrix or fibers/fillers [1, 7, 8]. Drop in tensile strength was also detected when using biodegradable matrix as PCL filled with date seed or olive husk due to the poor polymer-filler interactions and too big particle size of fillers used [5].

In case of starch-g-PP composites, stress transfer between the matrix and reinforcement used is obvious. This indicates a good interfacial adhesion between both DSF or KF and starch grafted matrices. In fact, these matrices is a complex polymer structure containing polypropylene part grafted to a derivative starch compounds in addition to a mixture of additives as slip agent, plasticizer, anti-UV and antioxidant. The based starch part consist also on a complex homopolymer containing D-glucose units which are hydrophilic groups [13]. The presence of these hydrophilic groups allows starch-g-PP matrices to have good interactions and wettability with vegetal reinforcement as kenaf fibers or DSF. When reinforced with 20 wt.% of kenaf fibers, the tensile strength of the three matrices is improved. These results corroborate with those reported in other studies[9, 14-16]. According to other research [17], kenaf fibers exhibits higher strength values in terms of tensile and flexural properties, as compared to other natural fibers or fillers when reinforcing biodegradable matrix. Other researcher [18] indicates that tensile strength is higher and almost doubled when compared against coir and sisal systems.

When LKF was used as reinforcement for composites, the improvement in tensile strength is higher than that obtained for SKF composite. In a previous work [9], authors highlight that the initial aspect ratio of the fibers only slightly affects the tensile strength of G906PF and G906PJ composites at the lowest fiber content due to fibers shortening during processing. Actual work improved somewhat tensile strength of LKF composites thanks to changing in feeding procedure of melt compounder mainly in residence time of fibers. In the other hand, it is observed that DSF could be a good alternative as reinforcement for some polymers as starch-g-PP one without additional modification, taking advantage of the affinity between these matrices and DSF. When using the fillers, the gain in strength is more than one-third the value gained when KF was used. This is considered for the elaborated composites an acceptable value.

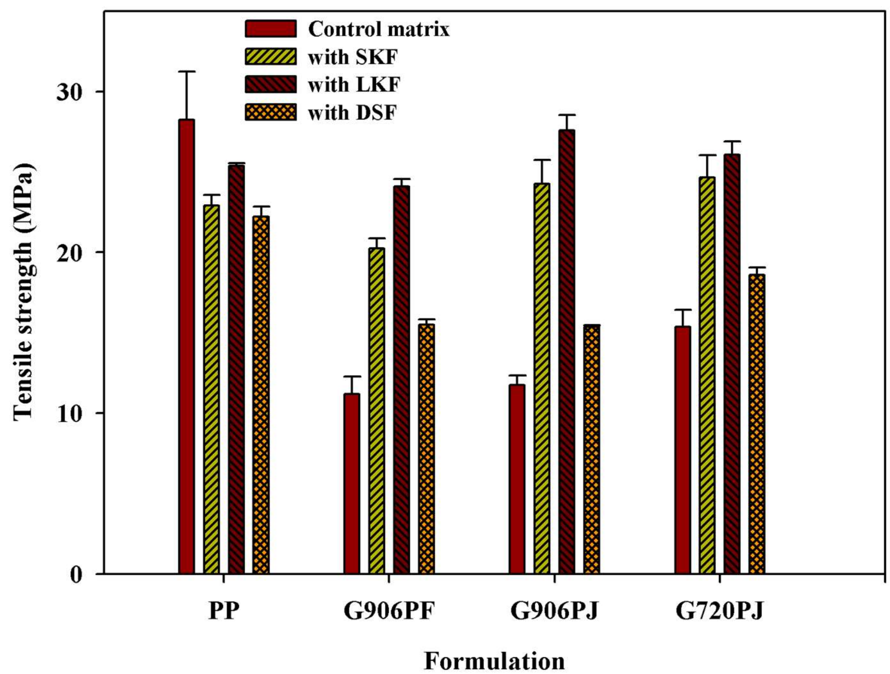


Fig.2. Tensile strength values of PP, G906PF, G906PJ & G720PJ composites based on SKF, LKF and DSF.

The result of tensile strain at break of reinforced PP, G906PF, G906PJ & G720PJ composites with SKF, LKF and DSF are reported in figure 3. Initially it is observed that neat PP present a large strain at break compared to starch-g-PP matrices. In addition to that, G720PJ matrix has the lowest strain at break. This divergence in strain is related to macromolecular chain lengths and crystallinity matrices differences. With loading matrices with KF, a dramatic drop in tensile strain values was recorded for all matrices. For example, deformation reduction of 95% was found with KF composites based on G906PF and G906PJ matrices. While G720PJ/KF composite deformation was reduced by almost 50% against 99% of deformation reduction for PP composites. When DSF were used, strain values decrease by 80% for G906PJ and G906PF composites compared to a reduction of 95% registered for PP composite. In contrast, G720PJ composite tensile strain value remain practically unchanged. When fibers are added to polymeric matrices as PP, G906PF and G906PJ, there is an enhancement of composite stiffness, as seen previously in figure 1, restricting matrix deformation and plasticity domain which leads to a decrease of composite ductility degree [9, 14]. While in case of DSF composites, presence of DSF do not have restriction effect pronounced on macromolecular chains as KF fibers due to the presence of more lignin content than cellulosic one. The ductility decrease has been explained by, the important volume of cellulose that amplifies the contact surface, which results in restricted polymer chain movements. That, is commonly observed as a sharp decline in elongation and has been reported for polymer/plant fiber compositions[19-21]. Further, actual results are also related to particular shape and size of date seed filler used in addition to cellulose content. Thus plastic deformation are largest compared to other composites owing to ductile behavior of concerned composite with DSF. [21] have shown that when using lower content (15%) of pulp rich fraction of olive husk flour in PHBV or PP matrix, the deformation is more important than that of olive flour taken from the core of olive stone. In fact, these fractions diverge in cellulose, lignin and hemicellulose content. The pulp rich fraction of olive husk flour comported higher content in lignin than the other fractions studied in the work of Lammi et al. Other researcher [5] has correlated better deformation at break to the presence of a fraction of proteins in natural fillers that acts as plasticizer, what also decreases tensile strength and elastic module.

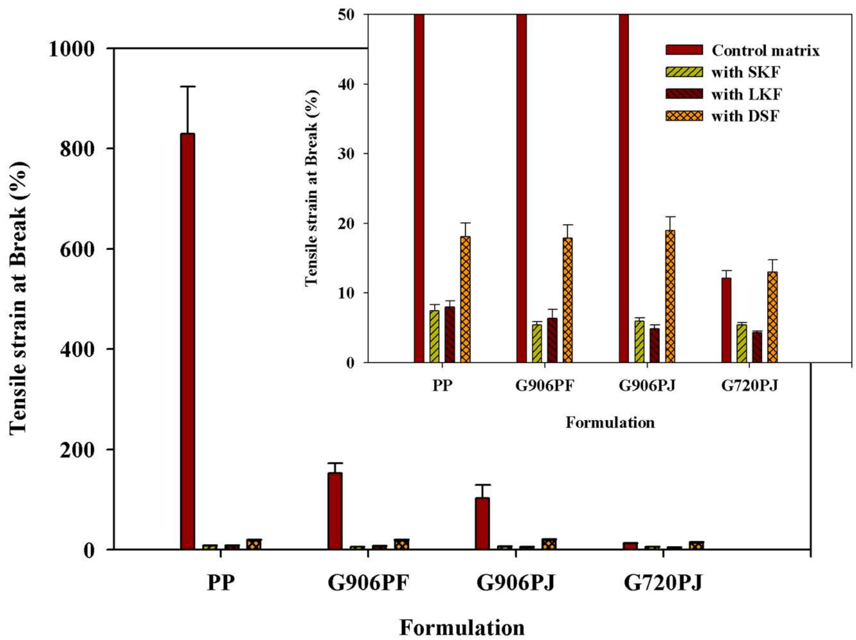


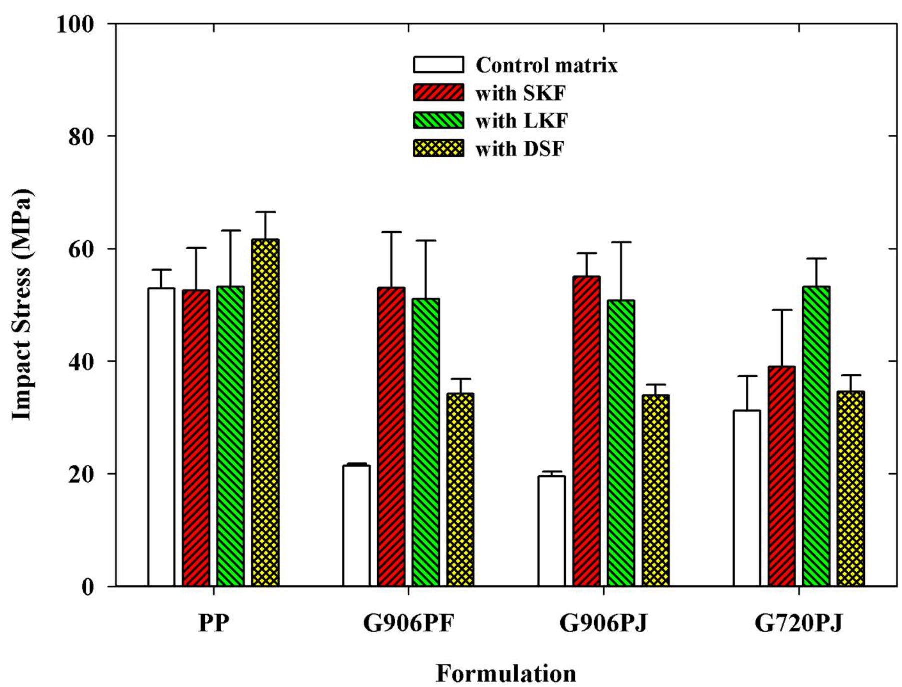
Fig.3. Tensile strain at break values of PP, G906PF, G906PJ & G720PJ composites with SKF, LKF and DSF.

Impact properties. The evolution of tensile impact stress and tensile impact energy values of PP, G906PF, G906PJ & G720PJ composites based on SKF, LKF and DSF compared to neat matrices are presented, respectively, in figure 4-a & 4-b. From figure 4-a, it is observed that impact stress values of starch-g-PP matrices were lower than that of PP matrix. With adding kenaf fibers, impact stress of starch-g-PP composites (figure 4-a) double or triple values. However, no effect was observed for PP composites. Furthermore, an enhancement in impact stress values was observed for starch-g-PP filled with DSF, which changes by a factor of almost 1.5. Increase in impact stress values is related to tensile strength improvement induced by the good affinity between starch-g-PP matrices and fibers/or fillers added. In addition to that, results confirm the ability of loading to support the applied force.

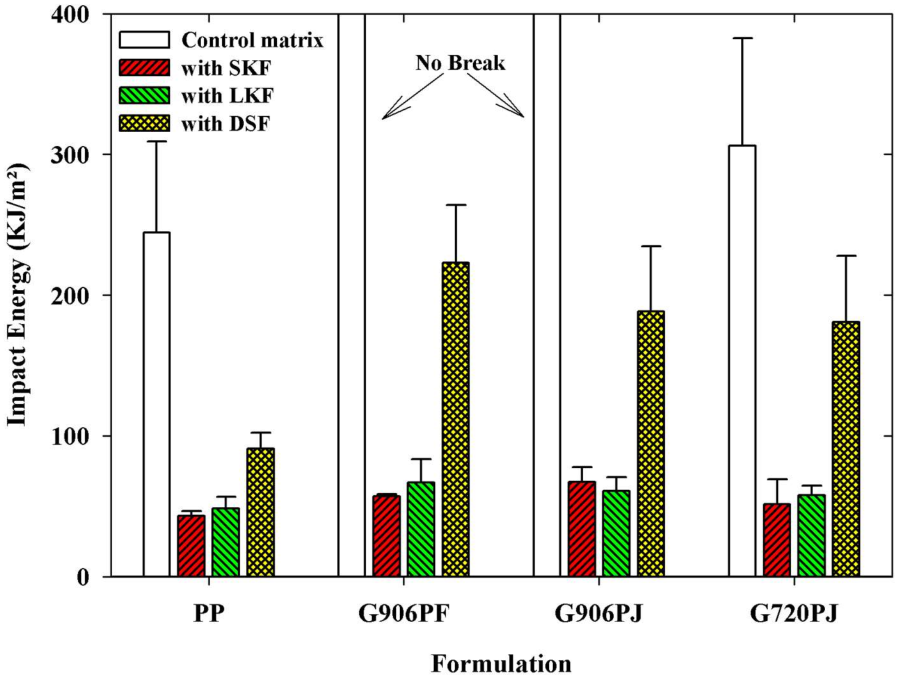
In parallel, impact energy values of studied composites with SKF, LKF and DSF (figure 4-b), have shown same level of impact energy for PP and G720PJ matrices. However, no break was recorded for both G906 PF and G906PJ under selected conditions (figure 4-b). In fact, both matrices revealed ductile failure mode compared to PP and G720PJ one, involving plastic deformation of matrices.

The addition of loading (KF or DSF) induces decreases in impact energy values, which are less pronounced in case of DSF composites. The addition of reinforcement reduced, to different degrees, macromolecular chains mobility of starch-g-PP and PP matrices. This restriction depends on fibers length and loading lignocellulose composition. Consequently, fracture behavior changes from ductile to brittle one.

Some researchers [9, 22, 23] discussed the effect of fibers reinforcement on impact properties of thermoplastics. They agree that matrix loading induces forming stress regions what decreases absorbed energy due to ability of cracks to initiate easily and propagate. In the presence of date stone fillers, bounding behavior between date seed fillers interface and starch-g-PP absorbs larger impact energy due to their smaller size (< 40µm). This induced important interaction surface surrounded by starch-g-PP matrices. Another explanation could be related to plasticization effect of protein extracted from DSF during composite processing under high temperature, evidenced in some studies [5]. This hypothesis could be confirmed by the lowest values found of modules and tensile strength in addition to highest level of deformation compared to KF composites.



(a)



(b)

Fig.4. Tensile impact strength (a) and energy (b) of PP, G906PF, G906PJ & G720PJ composites with SKF, LKF and DSF compared to neat matrices.

Shore D hardness. In figure 5 is presented shore D hardness values of PP, G906PF, G906PJ & G720PJ composites with SKF, LKF and DSF, in comparison to neat matrices. Results displayed higher shore D hardness values of, approximately, 67 and 60 for, respectively, PP and G720PJ. Both G906PF and G906PJ recorded same values that are the lowest compared to previous matrices. As load was added, shore D hardness values increases by 15 for G720PJ and by 45% for both G906PJ and G906PF based composites, while insignificant changes were observed for PP composites. Increase in shore D hardness is related to decrease in flexibility and improvement of composite stiffness with loading. In his study, Verma et al., [7] indicated that the availability of solid particles in the reinforcement and successive chain interconnection results in good hardness in comparison to matrix material.

In addition to that, good dispersion of date stone fillers and either kenaf fibers in starch-g-PP matrices resulted in improvement of composite hardness contrary to values recorded for PP composites. Results are in agreement with literature finding [5] that stated a rise in shore D hardness of composites based on olive husk, wheat brane and date seeds. Authors related the result to the good dispersion of fillers in the matrix and the improvement of physical interactions between matrix and filler phases. Regarding composites with higher filling content, they noted significant dependence of hardness on type of filling. In this work and for the studied filling content, hardness was found to not depend on fibers length and filling type for starch-g-PP composites.

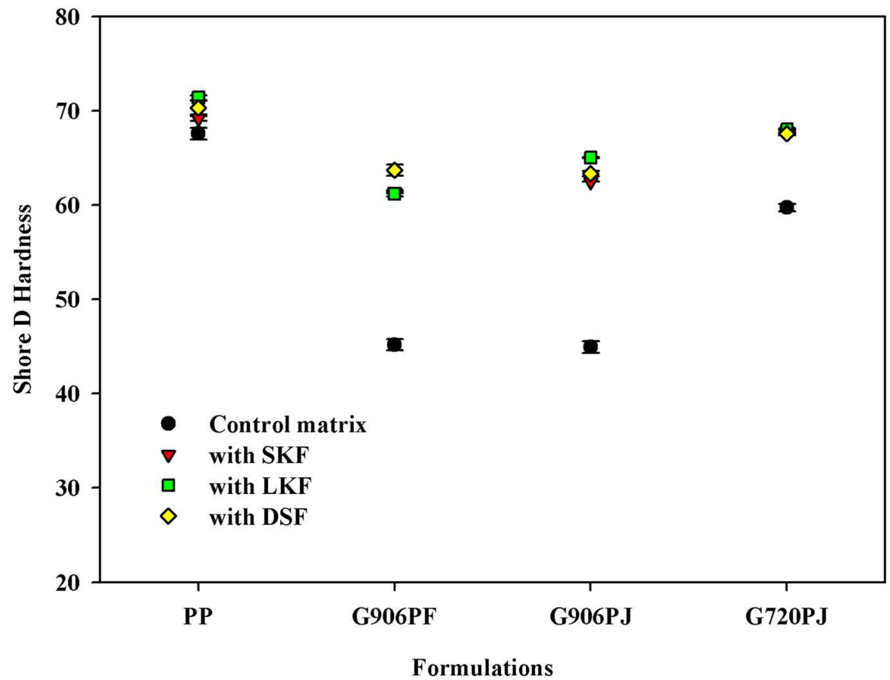


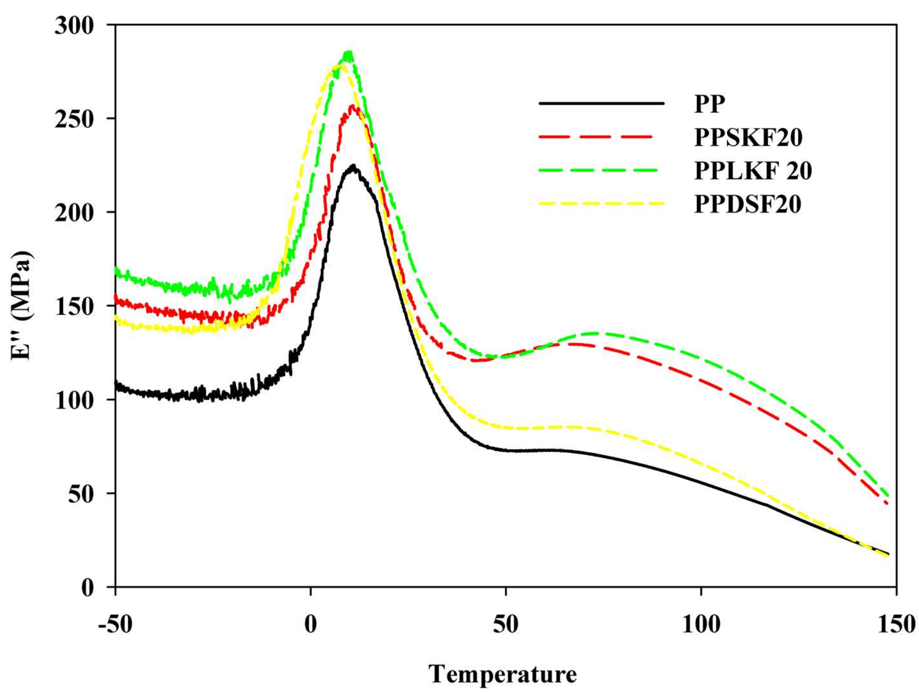
Fig.5. Shore D hardness values of PP, G906PF, G906PJ & G720PJ composites filled with SKF, LKF and DSF compared to unfilled matrices.

Thermo-mechanical properties by DMTA analysis. Dynamic mechanical experiment was done to confirm the mechanical behavior of composites and provide information about the relaxation mechanisms associated and molecular chain dynamics of reinforced polymers. Storage modules (E') taken at various temperatures of studied matrices and their respective composites was summarized in Table 1. From results, major difference between the starch-g-PP polymers and PP one is noted. This confirms static mechanical test attesting on the high rigidity of PP compared to starch-g-PP matrices that exhibit a ductile behavior. Besides, it can be seen that with addition of 20 wt.% of KF or DSF, storage module increases considerably. For instance, at 25°C, storage module values E' increased by an average value of 200 %, 170% and 70 % for, respectively, G906PF, G906PJ and G720PJ based KF composites. For DSF based ones, the increase in E' values at 25 °C exceeds 100 % with G906 PJ and G906PF matrices and 30 % with G720PJ. These results are due to the increase in stored energy needed in each cycle. In fact, when reinforcement was added to polymers, the mobility of macromolecular chains is restricted and thereby increased the storage module of composites. Besides that, the DMTA analysis reveals important trends in reinforcing efficiency of DSF and KF with both lengths. This effect is predominant for starch-g-PP matrices based on long kenaf fibers compared to composites based on short kenaf fibers and date seed fillers. In addition to that, composites based on G906PJ and G906PF polymers recorded a considerable improvement in storage modules compared to G720PJ based one. These findings are confirming the quasi-static tensile module values reported previously.

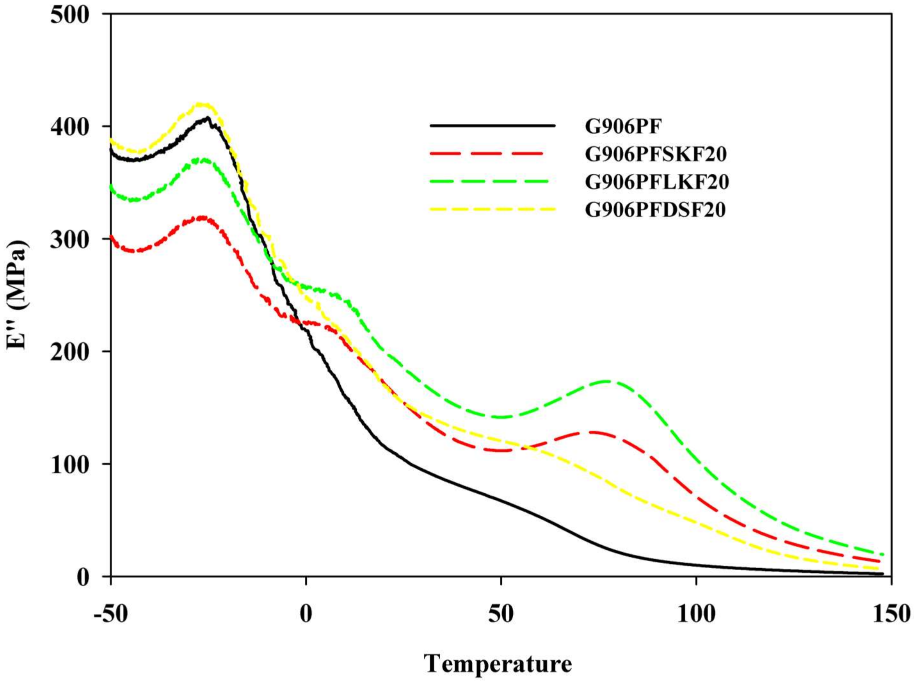
Table 1. Storage module at various temperatures of neat PP, G906PF, G906PJ & G720PJ and their respective composites with SKF, LKF and DSF.

Formulations	**Storage module E' (MPa)**				
	-25 °C	**0°C**	**25°C**	**50°C**	**75 °C**
PP	4764.40	4058.9	2242.77	1537.82	894.97
PP/SKF	5791.05	4997.88	2973.50	2221.68	1442.52
PP/LKF	6276.95	5336.63	3209.71	2413.37	1595.15
PP/DSF	5532.53	4265.80	2280.16	1547.99	1058.96
G906PF	4087.10	1789.97	718.08	329.96	127.39
G906PF/SKF	5095.24	3293.52	2001.33	1391.10	768.52
G906PF/LKF	5779.38	3814.64	2291.37	1642.95	959.02
G906PF/DSF	5405.66	3108.16	1608.58	1014.54	449.58
G906PJ	4018.60	1786.61	751.49	372.77	130.58
G906PJ/SKF	5360.31	3403.06	1931.12	1331.69	686.49
G906PJ/LKF	5394.85	3331.21	2068.78	1433.02	701.34
G906PJ/DSF	5387.83	3091.81	1506.08	941.02	432.70
G720PJ	4593.1	2847.66	1562.67	1087.74	577.12
G720PJ/SKF	5597.09	3699.03	2414.30	1689.95	1045.75
G720PJ/LKF	6379.50	4290.13	2885.30	2094.19	1507.21
G720PJ/DSF	5180.18	3371.41	2042.92	1434.42	839.16

Loss moduli of studied composites was illustrated in figure 6. As seen, similar trend as storage modules was obtained for the loss module in the rubbery region, with the addition of 20 wt.% KF or DSF. The rise in E" values is prominent and seem to be dependent on reinforcement type and length. In addition to that, a shift of α relaxation temperature toward higher values was observed. Results suggested an increase in composite damping properties and the presence of additional viscous dissipation when reinforcements were added to matrices. In the presence of DSF, the energy lost was less significant and the interfacial friction between fillers and bio-based matrices, under the action of outside oscillation load, was lower than that of kenaf fibers. In some literature[12, 24] they found also an increase in storage and loss moduli after polymer reinforcement that was explained by the restriction in macromolecular chains upon addition of loading. Other authors [19] ascribed increases in loss and storage moduli upon addition of cellulosic fillers to the good filler dispersion and existing reinforcement network through the whole composite and good load-bearing properties. They have shown that enhancement of composite loss module is a result of cellulosic particule-particule slippage when cellulose fillers were used as reinforcement. Thus, fillers and polymer matrix dissipated more heat than pure matrix. In their study, Platnieks et al [19] demonstrate also that higher is the rigidity of fillers used, better is the rise in the damping properties and storage module proving the reinforcement network.



(a)


500
400
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200
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0
-50
0
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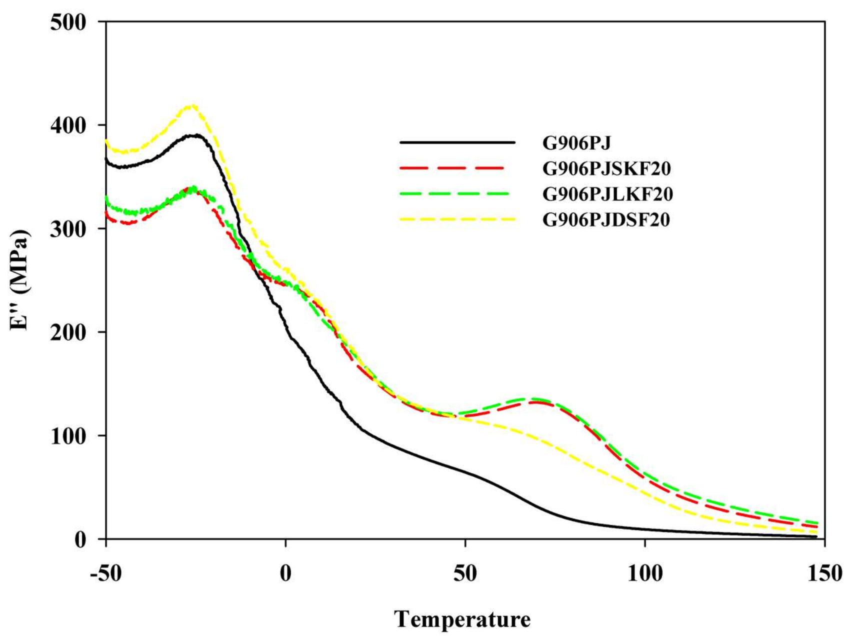
E'' (MPa)
Temperature
G906PF
G906PFSKF20
G906PFLKF20
G906PFDSF20

(b)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G906PJSKF20
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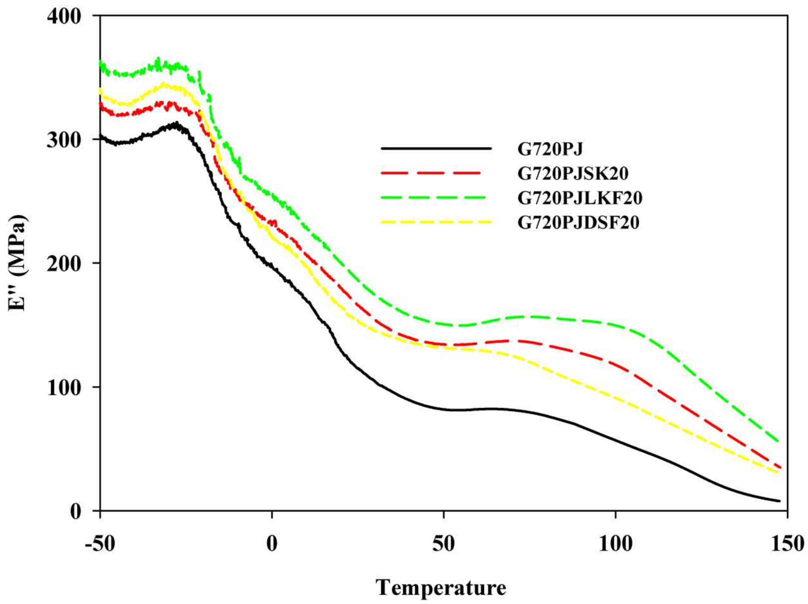
G906PJDSF20

(c)



(b)

Fig.6. Temperature dependence of loss module of (a)-PP, (b)-G906PF, (c)-G906PJ & (d)-G720PJ composites with SKF, LKF and DSF compared to neat matrices.

Brittleness and composite performance factor evaluation. For a general description of the obtained results in static and dynamical mechanical tests, two multifactorial coefficients were compared to obtain a more specific result of the analysis. The first factor is the composite performance factor "C-factor", determined using equation (2) [25-27].

$$C - factor = \frac{(E'_g/E'_r)_{composite}}{(E'_g/E'_r)_{matrix}} \quad \text{..........(2)}$$

Where the E'_g and E'_r are storage module values in, respectively, glassy and rubbery region taken at (-50 °C) and (100 °C).

The second factor taken in account in this study is materials brittleness B, which is calculated following equation (3) [25-27].

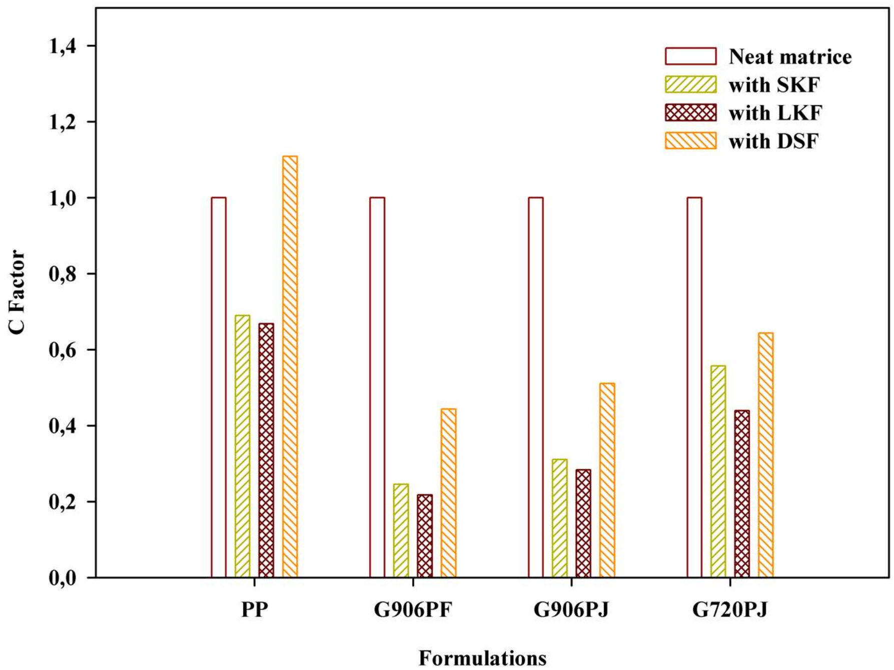
$$B = \frac{1}{\varepsilon_b . E'} \quad \text{..........(3)}$$

Where ε_b refers to the value of elongation at break taken from the static tensile measurement, while E' represents the value of storage module at room temperature taken from the dynamical mechanical analysis.

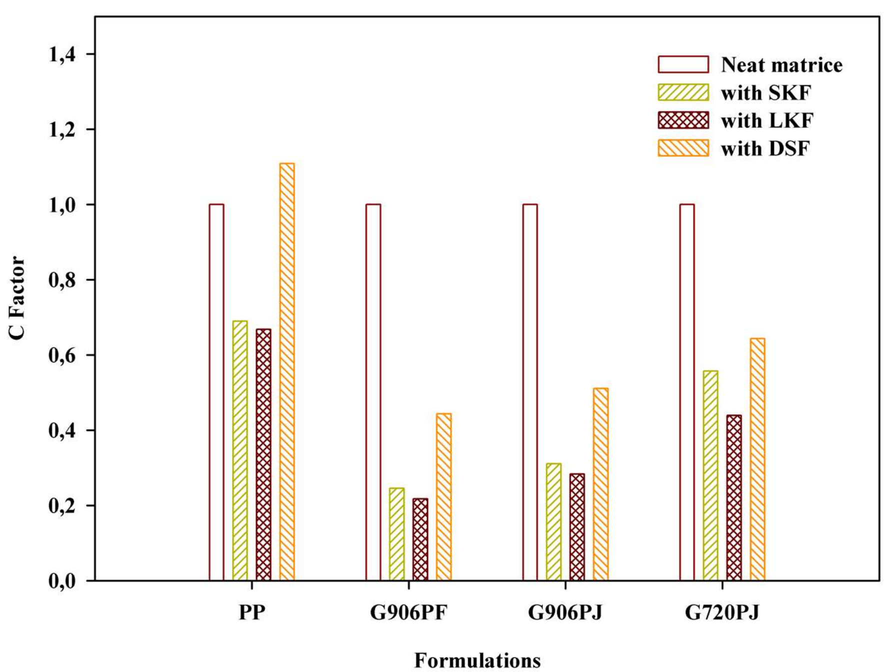
The values of both parameters for PP, G906PF, G906PJ and G720PJ composites with SKF, LKF and DSF are summarized in figure 7-(a, b). It is seen that C-factor values of starch-g-PP based composites decreased compared to neat matrices suggesting a reinforcement effect with addition of the different loads. While it is evident that C-factor values depends much on type of load. In our case, addition of DSF induces the lowest reinforcing effect with G720PJ, without considering PP composite needing interface modification. However, the highest reinforcing effect was observed with G906PF/KF.

In turn, brittleness coefficient of composites showed higher values compared to neat matrices except for G720PJ/DSF. Increase in B coefficient with loading matrices suggests unfavorable cracking mechanism for the considered composites, especially, when using kenaf fibers as reinforcement. In contrast with DSF loading, it is clear that brittleness is lesser, in particular, for G720PJ/DSF composite. When brittleness is lower, dimensional stability of elaborated composites is affected positively in service life in the repetitive loading, as reported by some literature [28].

Andrzejewski et al [27] reported that C-factor and brittleness values are affected by both the loading content as well as the loading nature. Accordingly, trends obtained during the study, indicates the typically physical nature of interactions occurring at the filler-matrix interface in the composite. In addition to that, it depends also on the matrix crystallinity and associated changes in the mechanical properties of composite matrix.


Neat matrice
with SKF
with LKF
with DSF
C Factor
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
PP
G906PF
G906PJ
G720PJ
Formulations

(a)


Neat matrice
with SKF
with LKF
with DSF
C Factor
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
PP
G906PF
G906PJ
G720PJ
Formulations

(b)

Fig.7. Evaluation of a) C-factor and b) Brittleness of PP, G906PF, G906PJ & G720PJ composites with SKF, LKF and DSF.

Resistance to thermal degradation, Vicat softening point (VSP) and crystallinity. Table 2 regroup typical degradation temperatures and char obtained from TGA/DTG analysis for PP, G906PF, G906PJ & G720PJ composites with SKF, LKF and DSF, in addition to VSP values and crystallinity index obtained by DSC. As seen, it is clear that adding of 20 wt.% of KF shift decomposition temperatures to lower values and decrease thermal stability of composites independently from fibers length. In the opposite, thermal stability of starch-g-PP composites was affected by the nature of reinforcement used. It means when DSF were used as reinforcement, thermal stability of composites was somewhat better than that of starch-g-PP/KF. Different factors could contribute to that. The first one is the fact that during DSF composite decomposition, there is formation of char which is increasing what contribute to the protection of remained composite from further degradation. In addition to that, high content of lignin in DSF could be another reason to the formation of higher content of char. It could also due to diffusion of some extractives from DSF upon particle size reduction with processing. These extractives have played a role in increasing thermal stability of composite.

Vicat softening point of neat matrices G906PF and G906PJ, shown in table 2, displayed lowest values followed by G720PJ then PP that has the highest value. With addition of 20 wt. % of load (KF, DSF), noticeable changes were observed on VSP starch-g-PP composites values. The improvement in the stability at high temperature for starch-g-PP composites exceed 20 % and it is dependent on fiber length and its nature for the studied content. As KF length increased, VSP reached higher values, whereas, incorporation of DSF to matrices induces the lowest values. In this study DS fillers used have irregular shapes between particular to elongated forms with maximum diameter of 40 μm and high lignin content contrary to kenaf that are in form of short or long fibers with approximately a length of 1.5 and 11 mm and high content of cellulose. In general, an increase in VSP with load adding could be a result of an increase of Tg or crystallinity of the polymer matrix, or also stiffening effect due to restriction of the polymer mobility. In the present case, crystallinity values evaluated by DSC (table 2) clearly indicate either a decrease for G906PF & G720PJ composites or no changes for PP and G906PJ ones. Thus, suggesting that the improvement in heat resistance could be rather due to the reinforcement effect of fibers or fillers, which causes a restriction in the mobility of polymer chains in the amorphous phase thus reducing the composite deformation under load.

Table 2. Decomposition temperatures, char wt. %, VSP and crystallinity index of PP, G906PF, G906PJ & G720PJ composites with SKF, LKF and DSF.

Formulations	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{75\%}$ (°C)	$T_{max.rate}$ (°C) 1st/2nd/3rd DTG peak	Char (wt.%) at 650 °C	VSP (°C)	X_c (%)
PP	*411*	*450*	*462*	*461*	*0*	166.63 ± 0.60	49.95
PP/SKF	357	448	464	352/463	2.11	167.75 ± 0.50	50.38
PP/LKF	357	456	468	352/464	2.43	168.89 ± 0.21	48.34
PP/DSF	310	456	468	294/464	2.74	165.04 ± 0.52	50.30
G906PF	*298*	*439*	*472*	*324/475*	*5.64*	96.79 ± 0.36	34.00
G906PF/SKF	280	402	465	327/367/475	5.74	121.80 ± 2.82	32.24
G906PF/LKF	280	402	468	327/367/475	5.87	134.14 ± 0.86	31.37
G906PF/DSF	286	411	472	324/475	8.56	112.97 ± 1.22	30.56
G906PJ	*291*	*435*	*470*	*324/475*	*0*	96.43 ± 3.30	30.29
G906PJ/SKF	284	386	449	324/367/439	6.26	128.32 ± 3.46	30.76
G906PJ/LKF	284	386	469	324/367/475	6.94	134.24 ± 0.89	32.08
G906PJ/DSF	285	412	472	324/475	9.05	115.92 ± 2.60	31.77
G720PJ	*304*	*441*	*476*	*317/475*	*0*	115.90 ± 0.37	26.34
G720PJ/SKF	299	399	467	324/360/475	7.94	148.84 ± 2.73	22.50
G720PJ/LKF	299	399	467	324/360/475	7.95	149.58 ± 1.04	22.04
G720PJ/DSF	291	417	473	317/475	9.75	142.32 ± 1.57	23.40

4. CONCLUSION

This manuscript presents the possibility of incorporation of DSF and KF into starch-g-PP matrices compared to fully PP one. Taking in account the mechanical properties it is clearly seen that the addition of DSF as well as KF led to a significant improvement in the tensile strength and impact stress without any modification of starch-g-PP composites contrary to the fully PP one needing treatment. The affinity between starch-g-matrices and loading and their good dispersion in matrices was also demonstrated by the rise in shore D hardness values. The addition of DSF and KF to starch-g-PP matrices enhanced considerably the tensile and storage module of elaborated composites due to chain mobility restriction by stiffed loading. The improvement in previous properties depends on loading composition, form and size in addition to the strach-g-PP matrix used. Accordingly, with kenaf fibers containing less lignin and more cellulose fraction than date seed fillers, the elastic, storage and loss modules, tensile and impact stress at break of strach-g-PP based composites doubled or tripled values against lower values for DSF based composites. With long Kenaf fibers, the effect on tensile stress at break, storage and loss modules was more pronounced. The evaluation of composite performance factor and brittleness revealed that values depend much on type of load and matrix used. Addition of DSF induced the lowest reinforcing effect and brittleness with G720PJ matrix thus the dimensional stability of such composite is better in-service life in the repetitive loading. In the other hand, it was found that DSF and KF incorporation to starch-g-PP composites increased, significantly, VSP values. In addition to that, an improvement of thermal stability of composites based on DSF was obtained.

The presented results point out the possibility of use of date seed wastes as an alternative reinforcement for starch-g-PP polymers, taking advantage of the low price of this waste and the affinity between both composite compounds.

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DISCLOSURE STATEMENT

No potential conflict of interest was reported by the authors.

REFERENCES

[1] L. Mohammed, M.N.M. Ansari, G. Pua, M. Jawaid, M.S. Islam, A Review on Natural Fiber Reinforced Polymer Composite and Its Applications, International Journal of Polymer Science, 2015 (2015) 243-947.

[2] J. Bachmann, C. Hidalgo, S. Bricout, Environmental analysis of innovative sustainable composites with potential use in aviation sector—A life cycle assessment review, Science China Technological Sciences, 60 (2017) 1301-1317.

[3] T. Alsaeed, B.F. Yousif, H. Ku, The potential of using date palm fibres as reinforcement for polymeric composites, Materials & Design, 43 (2013) 177-184.

[4] A. Hamma, M. Kaci, A. Pegoretti, Polypropylene/date stone flour composites: Effects of filler contents and EBAGMA compatibilizer on morphology, thermal, and mechanical properties, Journal of Applied Polymer Science, 128 (2013) 4314-4321.

[5] A. Hejna, M. Sulyman, M. Przybysz, M.R. Saeb, M. Klein, K. Formela, On the Correlation of Lignocellulosic Filler Composition with the Performance Properties of Poly(ε-Caprolactone) Based Biocomposites, Waste and Biomass Valorization, 11 (2020) 1467-1479.

[6] N. Bellili, H. Djidjelli, A. Boukerrou, B. Dairi, R. Bendib, A Study on the Effect of Acetylation on Composite Materials Based on Polypropylene/Coffee Husk Waste, Composites: Mechanics, Computations, Applications: An International Journal 11 (2020) 309-322.

[7] D. Verma, K.L. Goh, V. Vimal, Interfacial Studies of Natural Fiber-Reinforced Particulate Thermoplastic Composites and Their Mechanical Properties, Journal of Natural Fibers, (2020) 1-28.

[8] A. Ali, K. Shaker, Y. Nawab, M. Jabbar, T. Hussain, J. Militky, V. Baheti, Hydrophobic treatment of natural fibers and their composites—A review, Journal of Industrial Textiles, 47 (2016) 2153-2183.

[9] A. Hamma, M. Kaci, Z.A. Mohd Ishak, A. Pegoretti, Starch-grafted-polypropylene/kenaf fibres composites. Part 1: Mechanical performances and viscoelastic behaviour, Composites Part A: Applied Science and Manufacturing, 56 (2014) 328-335.

[10] A. Hamma, Kaci, M., Mohd Ishak, Z., Ceccato, R., & Pegoretti, A. , Starch-grafted-polypropylene/kenaf fibres composites. Part 2: thermal stability and dynamic-mechanical response. , Journal of Reinforced Plastics and Composites, 34 (2015) 2045–2058.

[11] R. Tessier, E. Lafranche, P. Krawczak, Development of novel melt-compounded starch-grafted polypropylene/polypropylene-grafted maleic anhydride/organoclay ternary hybrids, Express Polymer Letters, 6 (2012) 937-952.

[12] H. Essabir, M.O. Bensalah, D. Rodrigue, R. Bouhfid, A. Qaiss, Structural, mechanical and thermal properties of bio-based hybrid composites from waste coir residues: Fibers and shell particles, Mechanics of Materials, 93 (2016) 134-144.

[13] M. Akay, D. Barkley, Fiber orientation and mechanical behavior in reinforced thermoplastic injection moldings, Journal of Materials Science, 26 (1991) 2731-2742.

[14] N. Sarifuddin, H. Ismail, Z. Ahmad, Effect of fiber loading on properties of thermoplastics sago starch/kenaf core fiber biocomposites, Bioresources, 7 (2012) 4294-4306.

[15] N.H. Eszer, Z.A.M. Ishak, Effect of compatibilizer on morphological, thermal and mechanical properties of Starch-Grafted-Polypropylene/Kenaf fibers composites, IOP Conference Series: Materials Science and Engineering, 368 (2018) 012-017.

[16] Y.J. Phua, A. Pegoretti, Z.A.M. Ishak, Experimental analysis and theoretical modeling of the mechanical behavior of starch-grafted-polypropylene/kenaf fibers composites, Polymer Composites, 39 (2018) 3289-3299.

[17] S. Ochi, Mechanical properties of kenaf fibers and kenaf/PLA composites, Mechanics of Materials, 40 (2008) 446-452.

[18] M. Zampaloni, F. Pourboghrat, S.A. Yankovich, B.N. Rodgers, J. Moore, L.T. Drzal, A.K. Mohanty, M. Misra, Kenaf natural fiber reinforced polypropylene composites: A discussion on manufacturing problems and solutions, Composites Part a-Applied Science and Manufacturing, 38 (2007) 1569-1580.

[19] O. Platnieks, S. Gaidukovs, A. Barkane, A. Sereda, G. Gaidukova, L. Grase, V.K. Thakur, I. Filipova, V. Fridrihsone, M. Skute, M. Laka, Bio-Based Poly(butylene succinate)/Microcrystalline Cellulose/Nanofibrillated Cellulose-Based Sustainable Polymer Composites: Thermo-Mechanical and Biodegradation Studies, Polymers, 12 (2020) 1472.

[20] J. Kajaks, K. Kalnins, R. Naburgs, Wood plastic composites (WPC) based on high-density polyethylene and birch wood plywood production residues, International Wood Products Journal, 9 (2018) 15-21.

[21] S. Lammi, N. Le Moigne, D. Djenane, N. Gontard, H. Angellier-Coussy, Dry fractionation of olive pomace for the development of food packaging biocomposites, Industrial Crops and Products, 120 (2018) 250-261.

[22] T.T. Law, Z.A.M. Ishak, Water absorption and dimensional stability of short kenaf fiber-filled polypropylene composites treated with maleated polypropylene, Journal of Applied Polymer Science, 120 (2011) 563-572.

[23] Y.A. El-Shekeil, S.M. Sapuan, K. Abdan, E.S. Zainudin, Influence of fiber content on the mechanical and thermal properties of Kenaf fiber reinforced thermoplastic polyurethane composites, Materials & Design, 40 (2012) 299-303.

[24] M.J. John, C. Bellmann, R.D. Anandjiwala, Kenaf–polypropylene composites: Effect of amphiphilic coupling agent on surface properties of fibres and composites, Carbohydrate Polymers, 82 (2010) 549-554.

[25] W. Brostow, H.E. Hagg Lobland, Survey of relations of chemical constituents in polymer based materials with brittleness and its associated properties Chemistry & Chemical Technology, 10 (2016).

[26] W. Brostow, H.E. Hagg Lobland, S. Khoja, Brittleness and toughness of polymers and other materials, Materials Letters, 159 (2015) 478-480.

[27] J. Andrzejewski, M. Szostak, M. Barczewski, P. Łuczak, Cork-wood hybrid filler system for polypropylene and poly(lactic acid) based injection molded composites. Structure evaluation and mechanical performance, Composites Part B: Engineering, 163 (2019) 655-668.

[28] W. Brostow, H.E. Hagg Lobland, Brittleness of materials: implications for composites and a relation to impact strength, Journal of Materials Science, 45 (2010) 242-250.

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