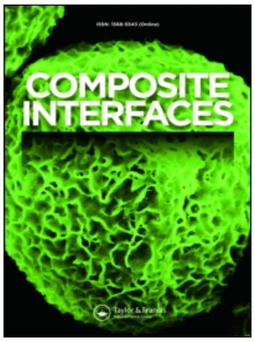

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The thermal and thermomechanical behaviors of Spartium junceum flour reinforced polypropylene composites: effects of treatment and flour content

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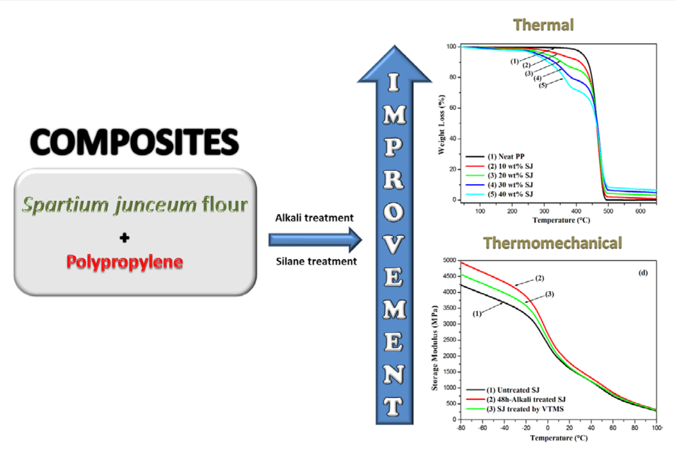
ABSTRACT

The effects of *Spartium junceum* (SJ) flour content, treatment time on the thermal and thermomechanical properties of polypropylene/*Spartium junceum* flour (PP/SJ) composites were studied. In order to improve the interfacial adhesion between the PP matrix and the SJ flour, SJ flour was treated with NaOH (2 wt%) for 8, 24 and 48 h at ambient temperature, respectively, and treated by vinyltrimethoxysilane (VTMS) (5 wt%). The results of thermogravimetric analysis (TGA) of SJ flour shows that the treatment improves the thermal stability of SJ flour. DSC analysis measurements illustrates that the addition of SJ flour increase the degree of crystallinity X_c, which indicate that the SJ flour plays a significant role in heterogeneous nucleating of PP matrix. The chemical treatments significantly affect the storage modulus of composite, where E′ increases for composites with treated flour in comparison to the untreated ones.



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Composites; polypropylene; spartium junceum; alkali treatment; silane coupling agent; thermal stability; interfacial adhesion

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1. Introduction

The development of natural fibers composites have attracted a great attention as realistic alternatives materials in the last few decades and saw a significant growth in the industries as well as academia [1–3]. Combining natural fibers with other resources provides a strategy for producing advanced composite materials that take advantage of the properties of both types of resources [4]. There are ecological and economical reasons in favor of the use of natural fibers as reinforcing fibers for plastics [5]. Theirs abundance combined with the ease of their processability is an attractive feature, which makes them a desirable substitute for synthetic fibers such as glass, carbon and aramid, that are potentially toxic [1–3,6]. Among the reinforcing agents, natural fibers have significant advantages such as their relatively high stiffness, lower density, better recyclability, biodegradability, durability and renewability, less abrasive to processing equipment, lower cost [2–7].

Therefore, current research findings show that in certain composite applications, natural fibers demonstrate competitive performance to glass fibers, and are being utilized commercially in biocomposites in combination with polypropylene for various applications in automotive sector (different interior parts and panels), building structures (for the production of tiles, doors, windows, etc.) [1,3,8,9] and rigid packaging materials [1], aerospace, transportation, sport, and leisure [1,6]. As environmental issues become more stringent, researchers believe that natural fibers are likely to become major components of cars around the world. To reduce vehicle weight, the manufacturers are moving away from steel towards aluminum, plastics and composites. Experts anticipate that in the very near future, polymer and polymer composites will comprise ~15% of total car weight [8–11].

Much work has been done on natural fiber reinforced thermoplastic composites, which have successfully proven their applicability to various fields of technical applications, especially for load-bearing application. Indeed, thermoplastics, such as polyethylene (PE) [12,13], polypropylene (PP) [14–17], polyvinyl chloride (PVC) [18,19], and polystyrene (PS) [20,21], have been compounded with a large number of natural fibers (such as wood, kenaf, flax, hemp, spartium junceum, cotton, sisal, jute, abaca, etc.) to prepare composites.

The major limitations of using natural fibers are poor interfacial adhesion between the polar hydrophilic natural fibers and no polar hydrophobic plastics. Several studies have been carried out to improve the mechanical properties of cellulosic-fiber-filled thermoplastics composites. Also, various treatments have been used to improve the matrix-fiber adhesion in natural-fiber-reinforced composites [22]. Approaches, such as alkali, silane, acetylation, benzoylation, use of maleated coupling agents, peroxide, permanganate, and isocyanate treatment, were considered [9,10,23]. In addition, some research work has shown that the silane coupling agent is effective in improving the interfacial adhesion between Spartium junceum fibers and polypropylene. Nekkaa et al. [16] reported that the use of silane Z-6020 for SJ fibers modification improves the dynamic mechanical properties of PP/SJ fibers composites. Also, the results of water absorption showed that silane treatment reduced the water absorption capacity compared to untreated composites [24]. The chemical process of alkaline treatment is widely used to modify many types of cellulosic fibers. It is a well-known surface treatment for fibers using alkaline solution, prior to composite formation. Most of non-cellulosic components and part of the amorphous cellulose can be removed by the alkali treatment [18].

On the other hand, other factor, such as surface area of fiber has been considered for interfacial adhesion [9], the use of a small particles as well as natural flours increases the specific area and the adhesion between polymer matrix and natural fiber.

Valadez-Gonzalez et al. [13] used a silane coupling agent to promote adhesion between the henequen fibers and a high density polyethylene matrix and have also shown that the adhesion between the natural hard fiber and the matrix played an important role on the final mechanical properties of the composite. Demir et al. [25] studied the effects of coupling agent on the properties of Luffa fiber reinforced polypropylene composites. The results showed increase of the tensile strength and Young's modulus with employment of the coupling agents accompanied by a decrease in water absorption due to the better adhesion between the fiber and the matrix. The thermal behavior jute fiber/polypropylene composites were investigated by Doan et al. [14] in dependence of fiber content, and with or without matrix modifier (maleic anhydride grafted polypropylene: MAH-g-PP). The modification process of PP/jute composites by using 2 wt% MAH-g-PP as a matrix modifier was observed to improve somewhat the thermal resistance. The modified composite was shifted to an approximately 10 °C higher onset temperature than that of non-modified composites. This effect might be due to the stronger interaction between the fiber and matrix caused by the formation of the covalent bond at the interface. Nachtigall et al. [15] assessed the possibility of using polypropylene functionalized with vinyltriethoxysilane as a coupling agent for polypropylene/wood-flour composites. The results indicated that the use of silane increased the interfacial adhesion between the fibers and the polymer matrix. Other authors also show that treatment of the fibers and in particular the alkaline treatment or by silane coupling agent, improves the thermal stability of the composites [12,26]. The thermal and thermomechanical properties of PP and cellulose fiber composites were investigated by Amash et al. [27] where two types of cellulose fiber and a compatibilizer (MAH-g-PP) were used. Calorimetric measurements exhibited an increase in the crystallization temperature and crystallinity of the PP component. This is attributed to the nucleating effects of the fiber surfaces, resulting in the formation of transcrystalline regions. The dynamic mechanical spectra of the composites revealed an increase in the stiffness and a reduction in the damping values with increasing cellulose fiber content.

This study investigates the modification of interfacial adhesion forces between the *Spartium junceum* flour and the polypropylene matrix to increase their compatibility using two different treatment sodium hydroxide (NaOH) and vinyltrimethoxysilane (VTMS). The effective properties of composites prepared with chemically-treated flour will be compared to results obtained from untreated flour composites as well as neat polymer. The composites materials obtained were studied using several analytical techniques, including, thermal stability (TGA, DSC) and the measurement of dynamic mechanical properties (DMA).

2. Experimental

2.1. Materials

The polymer matrix used in this study was Polypropylene commercialized under (PP, Moplen RP241H), having a density (23 °C) of: 0.90 g/cm^3 and a melt flow index (MFI) 1.8 g/10 min at (230 °C/2.16 kg).

Table 1. Chemical composition of Spartium junceum.

Composition	Cellulose	Lignin	Hemicellulose	Pectin	Ash	Waxes
%	44.5 ± 0.2	18.5 ± 0.3	16.3 ± 0.1	13.3 ± 0.1	4.0 ± 0.2	3.4 ± 0.1

Spartium junceum flour was prepared in our laboratory, from fibers obtained from local resources. The shurb can be cultivated manually, then and the fiber was cleaned and crushed. The dimension average particle size was (D < 100 µm). The chemical composition of Spartium junceum according to Gabriele et al. [28] is reported in the Table 1 near here.

2.2. Pretreatment

The SJ flour was pretreated to remove undesired waxes and lignin in a mixture toluene/ethanol with the ratios of (2:1 v/v), at room temperature for 2 days. Subsequently, the flour was washed with distilled water, and then dried. The de-waxed flour was used for chemical modifications such as alkali and silane treatments.

2.3. Treatment of Spartium junceum flour

2.3.1. Alkali treatment

The flour was treated with sodium hydroxide (NaOH) aqueous solution (2 wt%) for 8, 24, and 48 h at ambient temperature (22 °C), respectively. Then, it was washed with distilled water until all the sodium hydroxide was eliminated, and the washing water pH was neutral. Subsequently, flour was dried at 60 °C until constant weight was found.

2.3.2. Silane treatment

Vinyltrimethoxysilane (VTMS) was dissolved in a 60/40 v/v solution of ethanol and water, 5 wt% VTMS was used. The pH of the solution was adjusted to 4 with acetic acid and stirred continuously for 15 min. Next, the flours were soaked in the solution for 30 min at ambient temperature. Then the flour was dried at 60 °C for 12 h to initiate the chemical reaction between SJ flour and silane coupling agent. The SJ flour was then rinsed several times with distilled water. Lastly, the flour was oven dried at 60 °C for 24 h.

2.4. Composites and plates preparation

The composite materials PP/SJ were prepared by mixing the polymer matrix and the flour in a two-roll mixer 'SCHWABENTHAN/BERLIN' at a temperature of 180 °C and a mixing rate of 17 rpm/min for 10 min. Different composites PP/SJ flour were prepared; the untreated and treated SJ flour amounts added were 10, 20, 30 and 40wt%. The resulting sheets were cut into small pieces, and then were subjected to mechanical grinding. A rectangular plates having dimensions of ($100 \times 60 \times 2$ mm^3) were molded using an hydraulic press 'CARVER 3856CE' at 190 °C under 44 kPa for 10 min.

2.5. Characterization

2.5.1. Thermogravimetric analysis (TGA)

The pyrolysis characteristics of SJ flour and composites were analyzed using a thermogravimetric analyzer Perkin Elmer TGA 4000. The samples, weighing between 10 and 15 mg were stacked in an open platinum sample pan and the experiment was conducted in N_2 atmosphere under a purge rate of 20 cm^3/min. TGA were measured from 30 to 500 °C for SJ flour and from 30 to 700 °C for composites, at the heating rate of 10 °C/min.

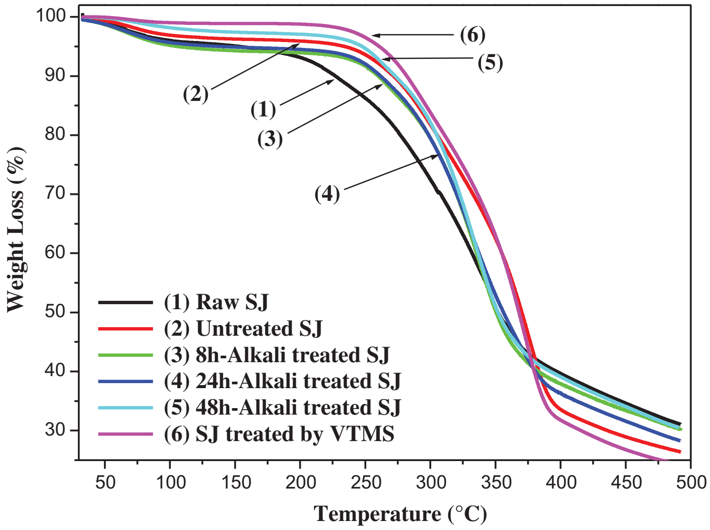

Figure 1. TG Thermograms of Spartium junceum flour.

2.5.2. Differential scanning calorimetry (DSC)

DSC was carried out using a TA Instrument (DSC Q 1000) with 3–5 mg of the manufactured composites at the designated time points. Each sample was scanned in dynamic mode from 30 to 160 °C at a heating rate of 10 °C/min followed by cooling at the same rate under a nitrogen atmosphere (a purge rate of 20 cm^3/min). The melting (T_m), and crystallization (T_c) temperature were determined from the first and the second scan, respectively.

2.5.3. Dynamical mechanical analysis (DMA)

The storage modulus and loss modulus were measured at a frequency of 1 Hz, a strain rate of 0.1%, and a heating rate of 5 °C/min over −80 to 100 °C. A TA Instruments dynamic mechanical analyzer (DMA Q800, V21.1 Build 51) working in the tensile mode on rectangular samples of (20 × 6 × 2 mm^3) cut from the molded plates.

3. Results and discussion

3.1. Thermogravimetric analysis (TGA)

3.1.1. Characterization of Spartium junceum flour

Figure 1 depicts the weight loss as a function of temperature for the raw Spartium junceum flour, untreated, treated with NaOH at different treatment time and treated by VTMS, respectively. The thermal degradation of Spartium junceum flour can be represented as the sum of thermal degradation reactions of the individual components, namely cellulose, hemicellulose and lignin. It can be deduced that cellulose and hemicellulose components of Spartium junceum are the major contributors to decomposition between 200 °C and 350 °C (stage 1), whereas lignin is mainly responsible for char formation of the Spartium junceum at 350 °C and above (stage 2). The thermal degradation of cellulose occurs in the temperature range from 310 °C at around 350 °C. Hemicelluloses are less thermally stable than celluloses. The hemicelluloses degrade at temperatures from 200 °C to around 260 °C. Aliphatic side

Table 2. Thermal degradation kinetic parameters of SJ flour.

Materials	T_{Onset} (°C)	T (°C) at 10 wt%	T (°C) at 50 wt%	T_{dmax} (°C)	Residual (wt%) at T = 475 °C
Raw SJ	256	226	353	348	32
Untreated SJ	291	272	370	377	27
8 h-Alkali treated SJ	285	259	351	341	32
24 h-Alkali treated SJ	276	262	357	334	29
48 h-Alkali treated SJ	298	273	353	336	32
SJ treated by VTMS	310	282	368	372	25

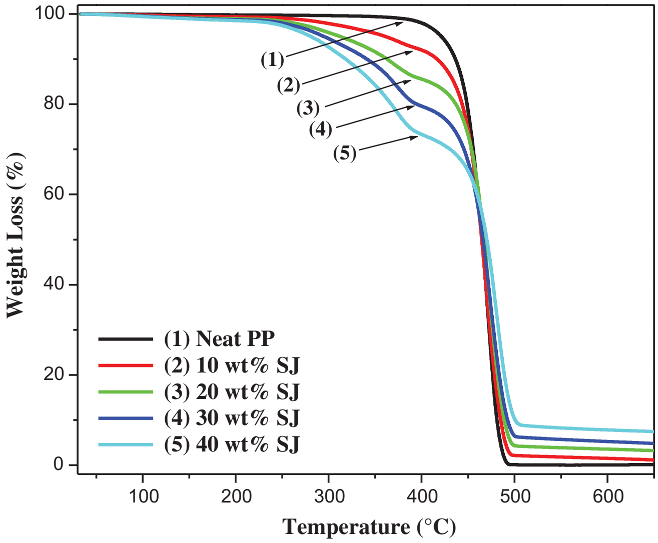

Figure 2. TG Thermograms of neat PP and PP/Untreated SJ flour composites.

chains start splitting off from aromatic rings at 300 °C. Finally, the carbon-carbon linkage between lignin structural units is cleaved at 370 and 400 °C. The final degradation reaction of lignin occurs at high temperatures (550 °C) [24,29–31].

The results of thermogravimetric analysis of Spartium junceum flour untreated and treated are represented in Table 2 near here. As is shown, the decomposition temperature (T_{Onset}) was determined at the starting point of severe weight loss. The results of Table 2 show an increase of decomposition temperature of treated flour. The use of the silane coupling agent (VTMS) improves the thermal stability of SJ flour much as the alkali treated SJ flour which is more stable than the untreated SJ flour and the raw ones. Silane coupling agent improve T_{Onset} of the SJ flour more than that treated with NaOH, this is due to grafting of the silane onto the cellulosic chain.

3.1.2. Characterization of PP/SJ flour composites

The thermal stability of natural fibers can be considered as one of the limiting factors in their use as reinforcement in composite structures [32].

Figures 2–6 show the TG thermograms of neat PP and the different PP/SJ flour composites, respectively. The thermal degradation of polypropylene begins at about 400 °C due to the rupture of the C-C bonds of the main chain [14,15], this temperature is higher than that of SJ flour. The neat PP has a decomposition process in a single step, while the composite

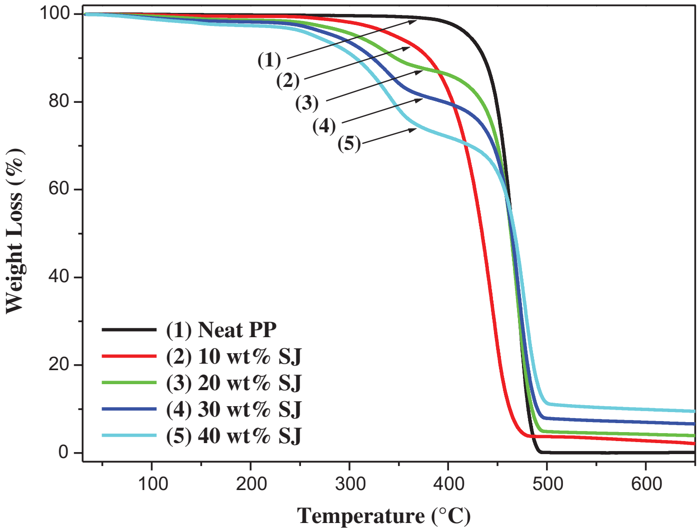

Figure 3. TG Thermograms of neat PP and PP/8 h-Alkali treated SJ flour composites.

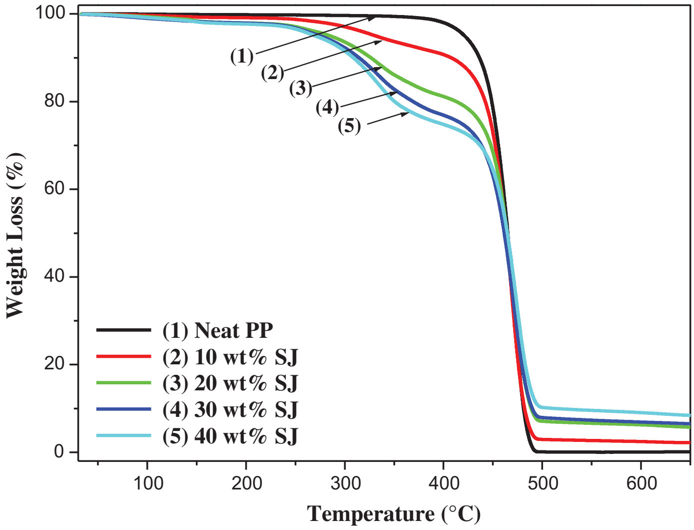

Figure 4. TG Thermograms of neat PP and PP/24 h-Alkali treated SJ flour composites.

clearly show a two step process. The first step is the decomposition of the SJ flour between 235 and 400 °C (decomposition of the cellulose), and the second step corresponds to that of the PP matrix (between 400 and 507 °C). The composites exhibit a thermal stability intermediate between that of flour and that of the matrix. Adding SJ flour therefore reduces the thermal stability of the PP.

In general, the addition of flour decreases the thermal stability of the composite as the thermal stability of the flour being lower than that of the PP, the degradation of the flour can accelerate the decomposition of the polypropylene [14].

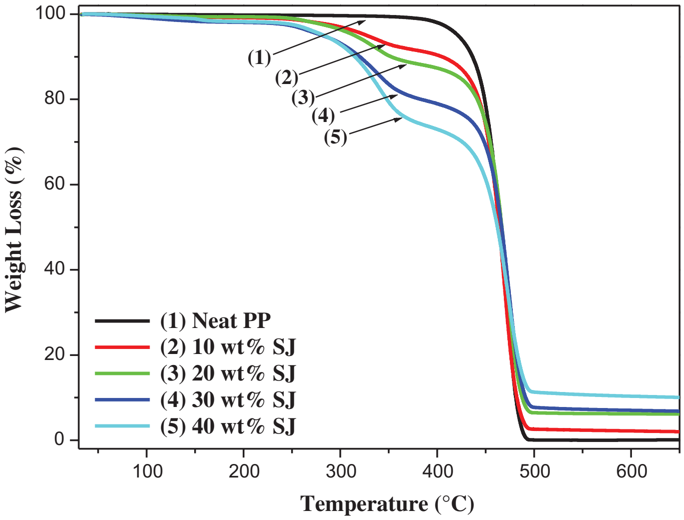

Figure 5. TG Thermograms of neat PP and PP/48 h-Alkali treated SJ flour composites.

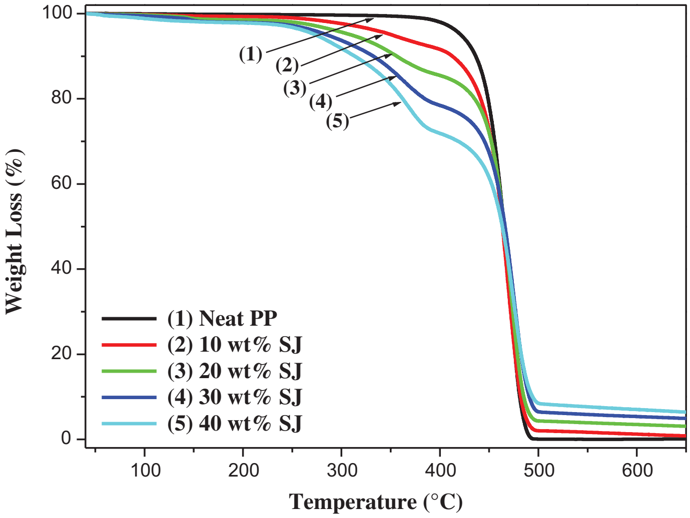

Figure 6. TG Thermograms of neat PP and PP/VTMS-Treated SJ flour composites.

3.1.3. Characterization of PP/30 wt% SJ flour composites

Figure 7 shows the effect of SJ flour treatment on the thermal stability of the PP/30 wt% SJ flour composites. We find that the SJ flour treated by mercerization for longer time is most effective in reducing the thermal decomposition of composites. On the other hand, treatment by VTMS makes them more stable composites, which results an increase of T_{Onset}, as well as reducing the degradation rate. The results of the thermal degradation of PP/30 wt% SJ flour composites are represented in the Table 3 below.

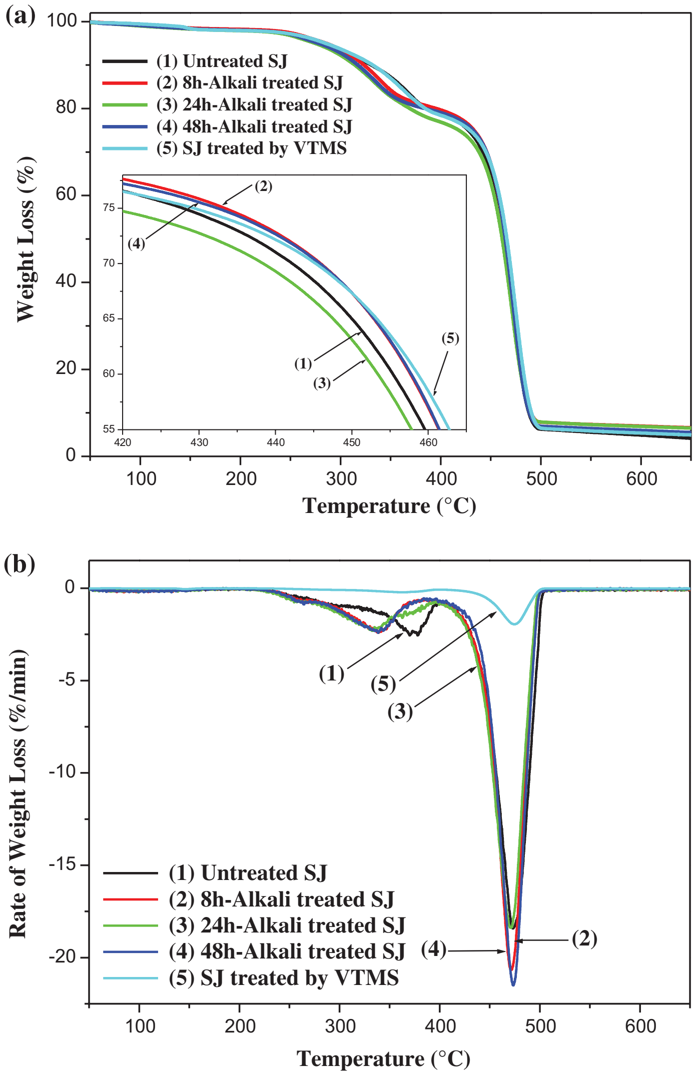

Figure 7. TG-DTG Thermograms of PP/30 wt% SJ flour composites: (a) TG; (b) DTG.

Table 3. Thermal degradation kinetic parameters of PP/ 30 wt% SJ flour composites.

Materials	T_{Onset} (°C)	T (°C) at 10 wt%	T (°C) at 50 wt%	T_{dmax} (°C)	Residual (wt%) at $T = 650$ °C
Untreated SJ	302.85/450.24	340.44	465.75	370.51/473.49	4.88
8 h-Alkali treated SJ	288.13/450.44	322.42	464.71	339.23/471.72	6.78
24 h-Alkali treated SJ	277.14/448.98	313.46	462.19	333.91/471.16	6.57
48 h-Alkali treated SJ	283.58/454.91	320.74	466.40	338.67/473.96	6.98
SJ treated by VTMS	261.25/ 456.13	332.64	465.89	362.89/474.61	4.78

Table 4. The thermal properties of neat PP and PP/SJ flour composites.

	Cycle 1 (heating)		Cycle 2 (cooling)		
Materials	ΔH_m (J/g)	T_m (°C)	ΔH_c (J/g)	T_c (°C)	X_c (%)
Neat PP	49	130/144	−62	117	36
PP/10 wt% Untreated SJ	58	131/143	−61	115	47
PP/20 wt% Untreated SJ	39	131/143	−50	115	35
PP/30 wt% Untreated SJ	32	142	−45	115	33
PP/40 wt% Untreated SJ	18	141	−34	114	22
PP/10 wt% 48 h-Alkali treated SJ	55	131/143	−62	115	44
PP/20 wt% 48 h-Alkali treated SJ	46	131/143	−52	115	42
PP/30 wt% 48 h-Alkali treated SJ	33	130/142	−43	115	34
PP/40 wt% 48 h-Alkali treated SJ	20	143	−33	114	24
PP/10 wt% SJ treated by VTMS	61	131/144	−64	115	49
PP/20 wt% SJ treated by VTMS	40	142	−50	115	36
PP/30 wt% SJ treated by VTMS	34	130/142	−49	115	35
PP/40 wt% SJ treated by VTMS	26	130/143	−42	115	31

3.2. Differential scanning calorimetry (DSC)

The melting (T_m), and crystallization (T_c) temperatures, the melting (ΔH_m) and crystallization (ΔH_c) heats, and the crystallinity (X_c), which were determined and calculated from the DSC thermograms, are summarized in Table 4. The flour content is given as weight percentage. The crystallinity of the PP component was determined by using the Equation (1):

$$X_c(\%) = \frac{\Delta H_m}{w.\Delta H_m^0} \times 100 \tag{1}$$

where ΔH_m is the melting heat of the PP, and PP/SJ flour composites, ΔH_m^0 is the melting heat for the 100% crystalline PP (= 138 J/g), and $\boldsymbol{w}$ is the weight fraction for PP in the composites [24,33].

3.2.1. Effect of SJ flour content

Figures 8–10 show an example of thermograms of DSC first and second curves of neat PP and PP/SJ flour composites, which are their endothermic T_m peaks and exothermic T_c peaks in the DSC curves respectively. The polypropylene used in the present study was a copolymer with 7% of ethylene. The melting range of the polymer is visible as an endothermic peak. It exhibit two melting peaks: first the polyethylene peak at about 130 °C, whose size is proportional to the amount of ethylene bloc in the copolymer, and then the main melting peak at about 144 °C.

On the other hand, it was noticed that the incorporation of Spartium junceum flour in the polymeric matrix has no significant impact on the value nor on the shape of the melting or crystallization peaks. Luz et al. [34] showed that the incorporation of sugarcane fiber in PP caused apparent T_c and ΔH_c increases. The researchers attributed this effect to fibers that act as nucleating sites for the crystallization of the polymer. Quan et al. [35] reported that the presence of nucleating sites on the surface of the fiber affects the crystallization and the natural cellulosic fibers having abundant nucleation sites on the surface induce transcrystallization in PP. Joseph et al. [36] found that as the amount of the added sisal fiber into PP increases the crystallization temperature and

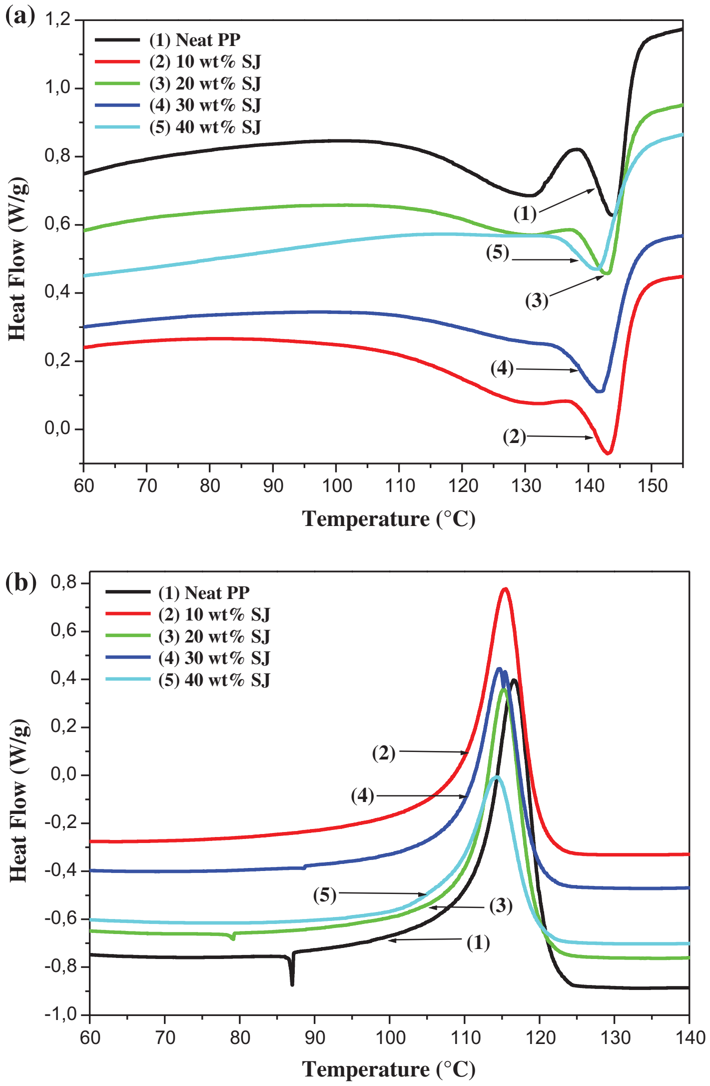

Figure 8. DSC thermograms of neat PP and PP/Untreated SJ flour composites: heating; (b) cooling.

the crystallization heat also was found to increase, indicating that fibers accelerate the crystallization process.

From the results of the Table 4 below, it is observed that the degree of the crystallinity X_c increases with addition of SJ flour, but no consistent trend was observed. For some composites (containing less than 20 wt% of SJ flour), the X_c was higher than the PP matrix. In the other composites, the X_c values were similar or smaller indicated that the SJ flour plays a significant role in heterogeneous nucleating of PP. This can be explained by the nucleating ability of the cellulosic filler, which alter the kinetics of crystallization of the PP matrix [34,37,38]. Nekkaa et al. [24] mentioned that the incorporation of SJ fiber in PP caused an

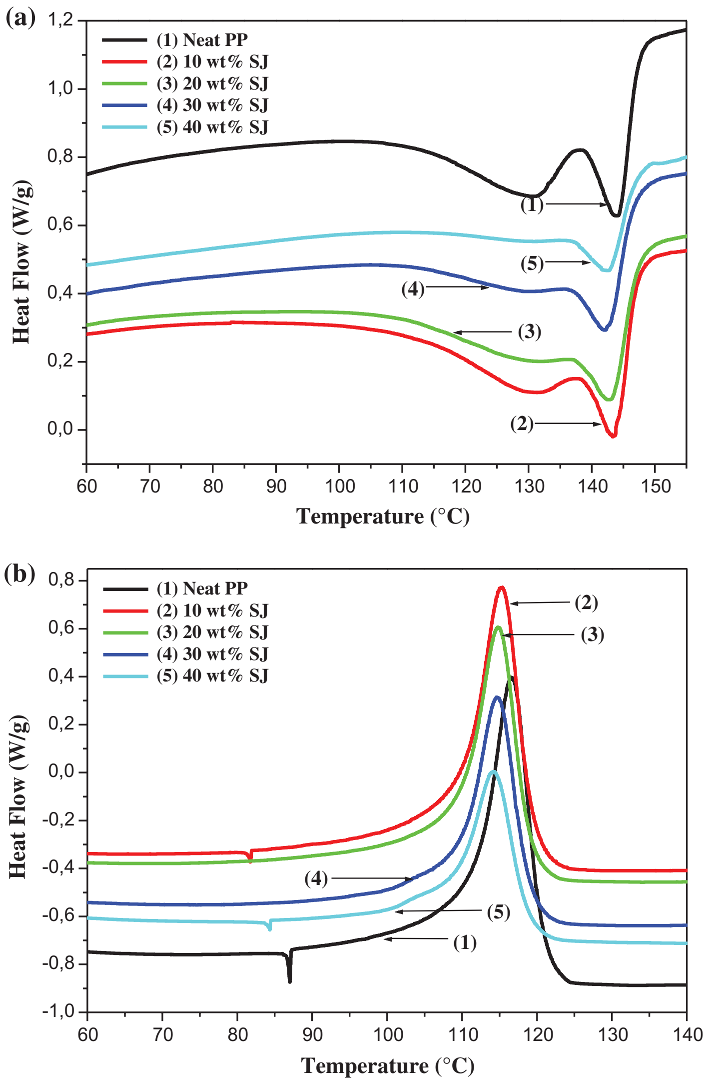

Figure 9. DSC thermograms of neat PP and PP/48 h-Alkali treated SJ flour composites: heating; (b) cooling.

apparent increase in the crystallinity. Also Joseph et al. [36] reported that the addition of sisal fibers into PP increases the crystallinity of composites.

3.2.2. Effects of chemical treatments

The comparison between the thermograms obtained from neat PP and the composites filled with 20 wt% of untreated SJ flour and treated by NaOH at different time and treated by VTMS are presented in Figure 11. It was observed that the treatment by NaOH or by VTMS had no significant effect on the melting and crystallization temperature.

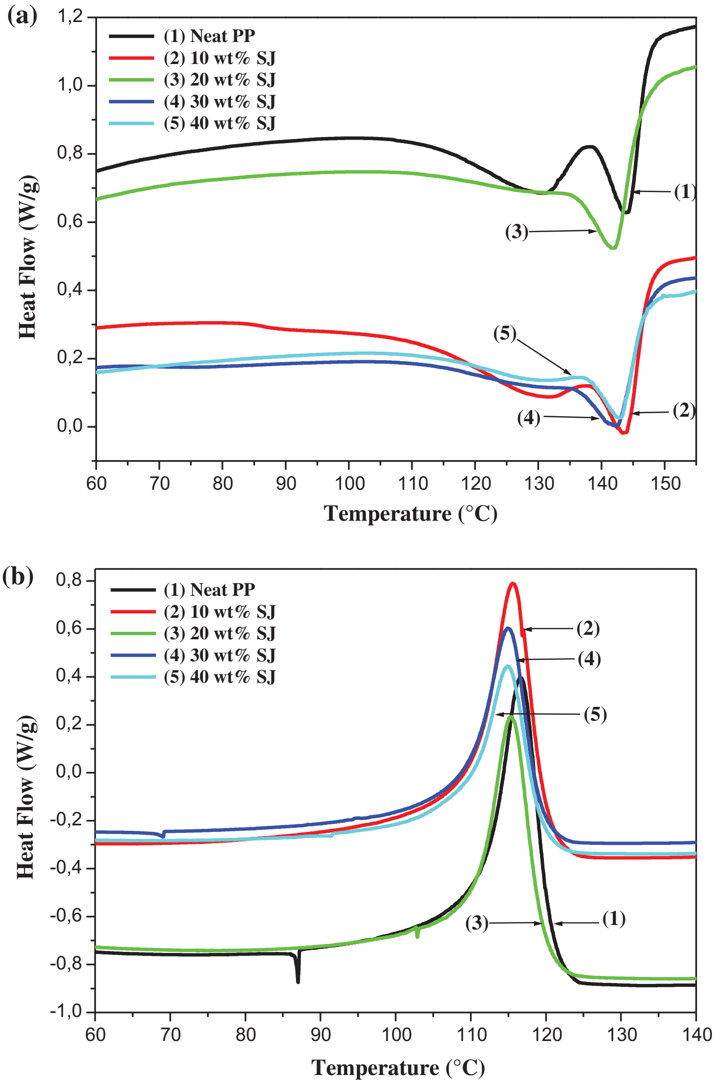

Figure 10. DSC thermograms of neat PP and PP/VTMS-Treated SJ flour composites: (a) heating; (b) cooling.

On the other hand, the melting heat (ΔH_m) and the crystallization heat (ΔH_c) are lower in the composites containing VTMS-SJ flour compared to that containing alkali treated ones. This behavior is due to the crosslinking of SJ flour on the PP chains which forms a network structure. The network structure makes the macromolecules chain less flexible. Bengtsson et al. [39] found that the melting temperature and the melting heat were lower in the crosslinked composites than in the non-crosslinked ones, which indicates a lower degree of crystallinity in the crosslinked samples. The researchers reported that the crystallinity also decreases with increased amount of added silane to the samples during processing. A lower crystallinity in silane crosslinked specimens has also been reported by other authors [40,41]. Quan et al. [35] mentioned that the untreated and treated cellulose fibers all had a

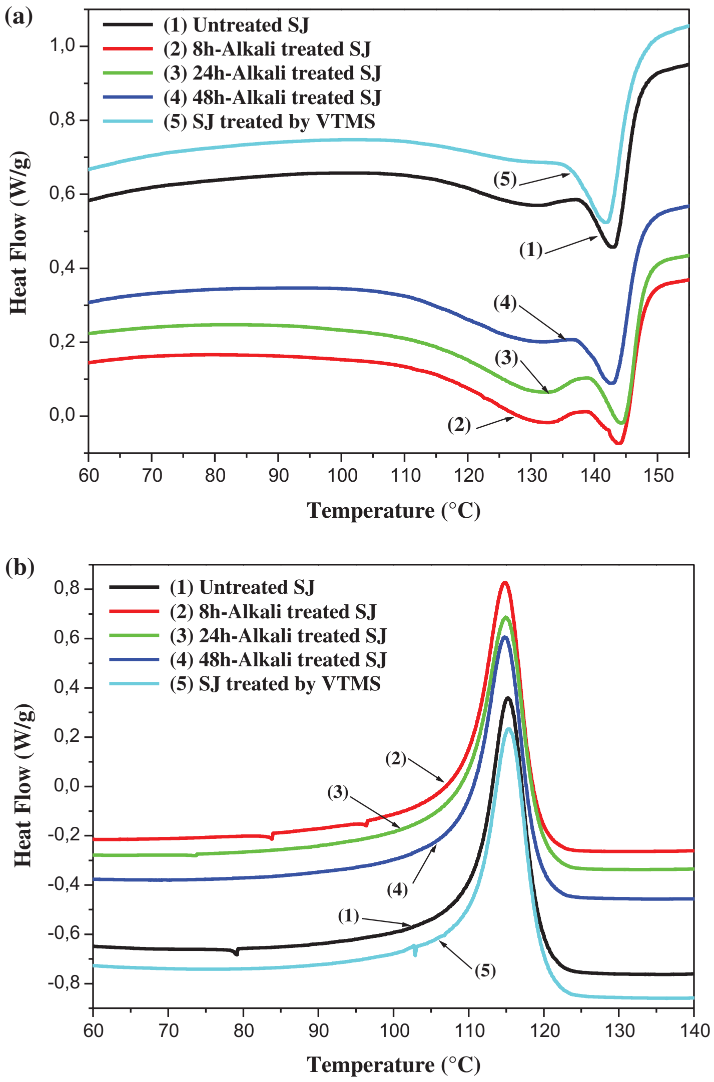

Figure 11. DSC thermograms of PP/20 wt% SJ flour composites: (a) heating; (b) cooling.

Table 5. The thermal properties of PP/20 wt% SJ flour composites.

	Cycle 1 (heating)		Cycle 2 (cooling)		
Materials	ΔH_m (J/g)	T_m (°C)	ΔH_c (J/g)	T_c (°C)	X_c (%)
Untreated SJ	39	131/143	−50	115	35
8 h-Alkali treated SJ	49	132/144	−55	115	44
24 h-Alkali treated SJ	47	131/144	−53	115	43
48 h-Alkali treated SJ	46	131/143	−52	115	42
SJ treated by VTMS	40	142	−50	115	36

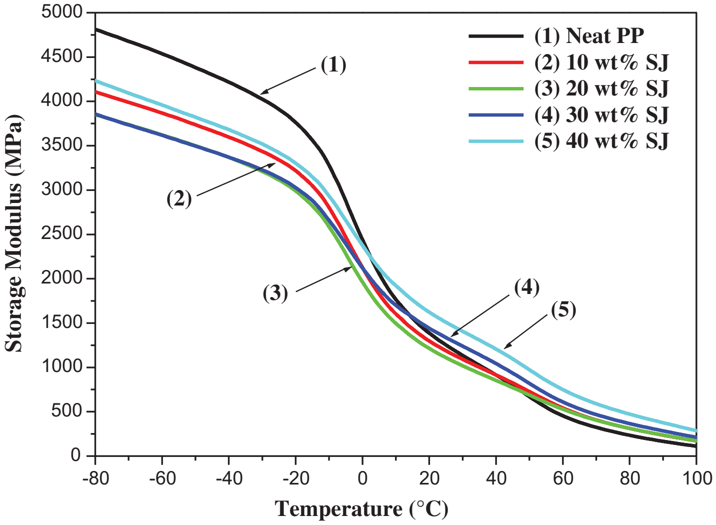

Figure 12. The storage modulus of the neat PP and PP/Untreated SJ flour composites as a function of temperature.

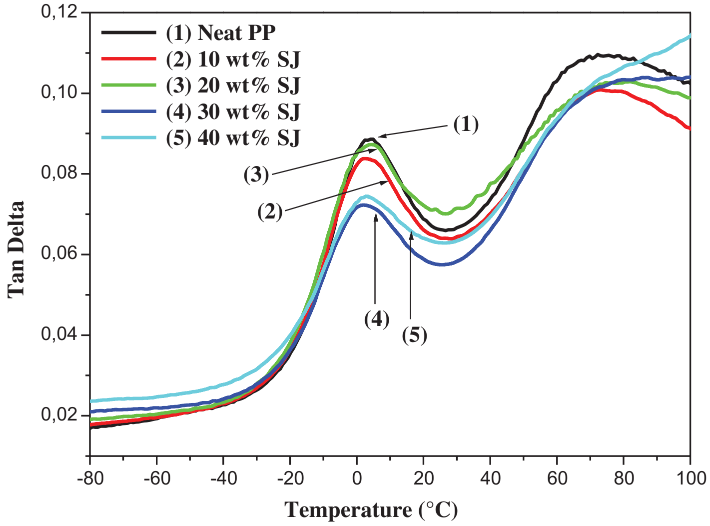

Figure 13. Tan Delta of the neat PP and PP/Untreated SJ flour composites as a function of temperature.

nucleating ability to transcrystallize at PP matrix, especially for the cellulose fibers treated with sodium hydroxide.

The degree of crystallinity, melting heat (ΔH_m), the melting temperatures, crystallization heat (ΔH_c), and the crystallization temperatures values from the DSC analysis are reported in the Table 5 near here.

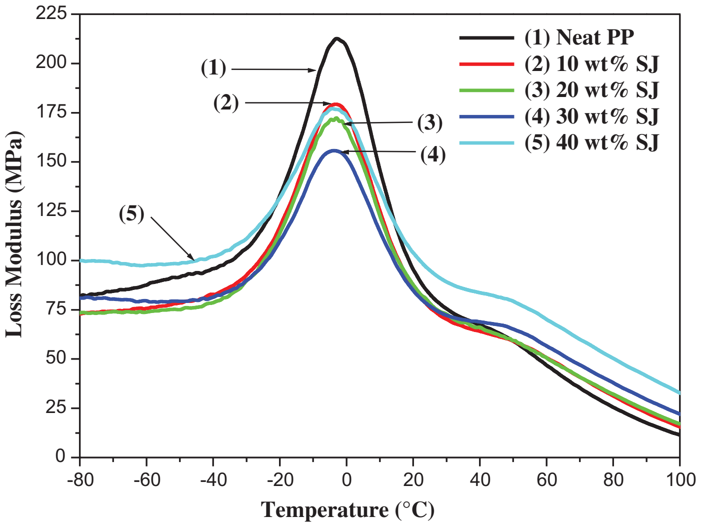

Figure 14. The loss modulus of the neat PP and PP/Untreated SJ flour composites as a function of temperature.

3.3. Dynamical mechanical analysis (DMA)

The dynamic mechanical properties such as storage modulus (E′), loss modulus (E″) and the damping coefficient (Tanδ) of neat polypropylene and polypropylene/ Spartium junceum flour composites were evaluated in a temperature range between −80 and 100 °C.

3.3.1. Effect of flour content

Figure 12 shows the curves of E′ as a function of temperature for neat PP and the composites filled with 10, 20, 30, and 40 wt% of untreated spartium junceum flour. Notice that E′ decreases with temperature due to an increased segmental mobility. In semicrystalline materials like PP, during transition, only the amorphous part undergoes segmental motion, whereas the crystalline region remains solid until its melting temperature. The comparison of neat PP and PP/SJ flour composites shows that the addition of untreated flour results in a decrease of storage modulus. This can be explained by two reasons: the combination of the hydrodynamic effects of the flour embedded in a viscoelastic medium and the mechanical restraint produced by the flour, which reduce the mobility and deformability of the PP matrix [42]. The E′ values lower than those of PP may be attributed to the ball-bearing or pseudo lubricating effect offered by the SJ flour. The Spartium junceum flour facilitate the slippage of methylene groups of the PP chains, which facilitates the molecular conformational changes, thus, introducing flexibility and mobility of short segments of PP (i.e., crank-shaft motion of methylene segments) in the PP/SJ flour composite systems [43].

Figure 13 shows the variations of Tanδ as a function of temperature. Two relaxations are observed over the temperature range studied; a lower temperature relaxation between −20 and 20 °C, which is attributed to the glass transition of the amorphous phase. Another one appears near 75 °C and is due to the transition related to the formation of crystallites.

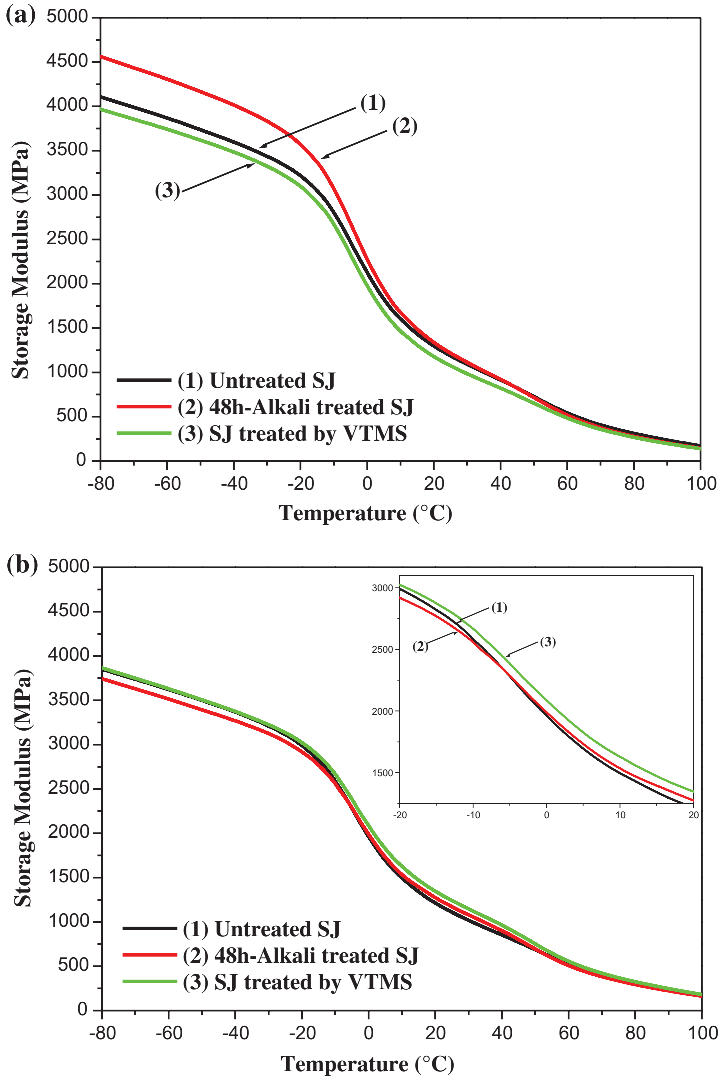

Figure 15. The storage modulus of the PP/ SJ flour composites as a function of temperature: (a) 10 wt%; (b) 20 wt%; (c) 30 wt%; (d) 40 wt%.

These results are in agreement with those presented by Joseph et al. [44]. The variations of loss modulus (E″) with temperature presented in Figure 14 also show the same behavior as that described for Tanδ.

3.3.2. *Effects of chemical treatments*

Figure 15 depicts the dynamic mechanical spectra E′ as a function of temperature for composites filled with 10, 20, 30, and 40 wt% of SJ flour, respectively. The results indicated that chemical treatments significantly affect the storage modulus of a composite. Storage modulus increases in composites with the treated flour in comparison to the untreated ones.

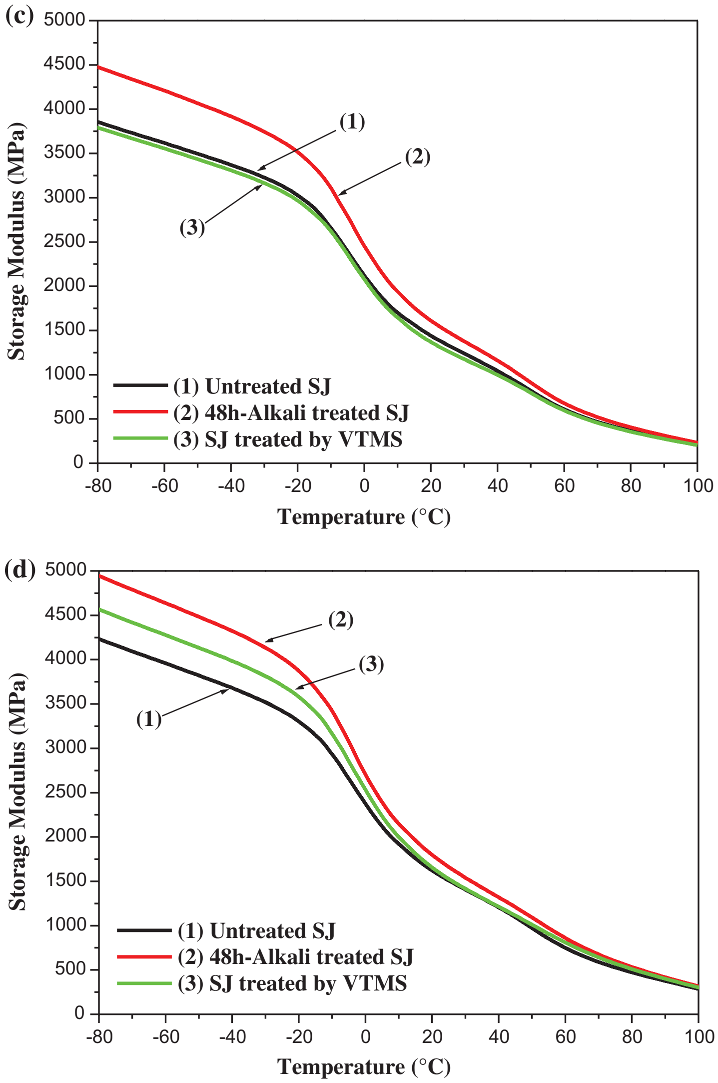

Figure 15. (*Continued*).

The alkali treatment caused the cellulosic flour to swell and removed the hemicellulose and other impurities from the flour surface. The removal of the impurities led to better dynamic mechanical properties, flour wetting characteristics and flour–matrix adhesiveness in composite applications [18]. The treatment permits to separate the lignin of the SJ flour, decreasing the number of agglomerates and thus contributing to a better scattering of the particles in the polymeric matrix. The treatment with silane induces reinforcement effect, due to the fact that silane coupling agent modifies the interface flour–matrix with the formation of chemical bridge bonds between the two components. That's why an increase is noticed in modulus values when the treated flours with silane are used, indicating better interfacial bonding between polymer and the flour. Many studies showed that silane coupling agent

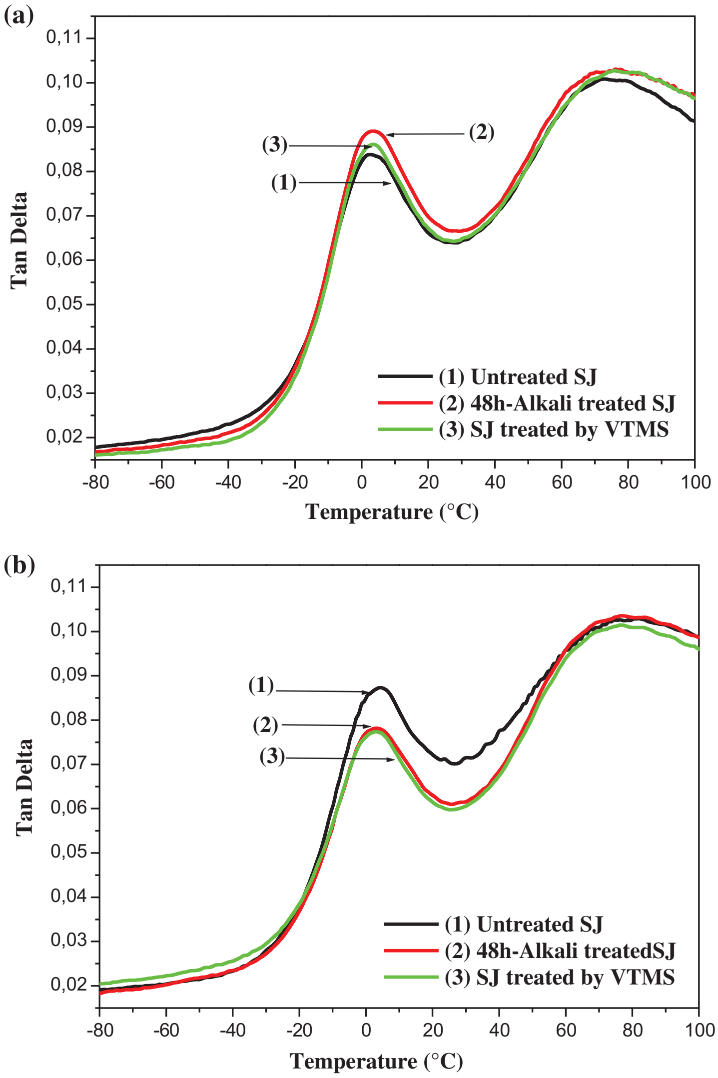

Figure 16. Tan Delta of the PP/ SJ flour composites as a function of temperature: (a) 10 wt%; (b) 20 wt%; (c) 30 wt%; (d) 40 wt%.

displays a good affinity toward cellulosic substrates. It is known that the methoxy groups (-OCH_3) in the silane can be hydrolyzed to produce silanol (-$Si(OH)_3$), during the flour pretreatment process [45,46]. These silanol groups can either develop covalent siloxane bond, or form hydrogen bonds with -OH groups of cellulosic flour.

Figure 16 shows the variation of Tanδ as a function of temperature for composites filled with 10, 20, 30, and 40 wt% of SJ flour respectively. Two relaxations can be observed: (β) and (α). The dominant (β) peak represents the transition of the amorphous portions in PP, and the temperature of the loss peak maximum is assigned to the glass transition temperature (Tg) at 3 °C. This transition corresponds to a significant decrease of the E′ modulus.

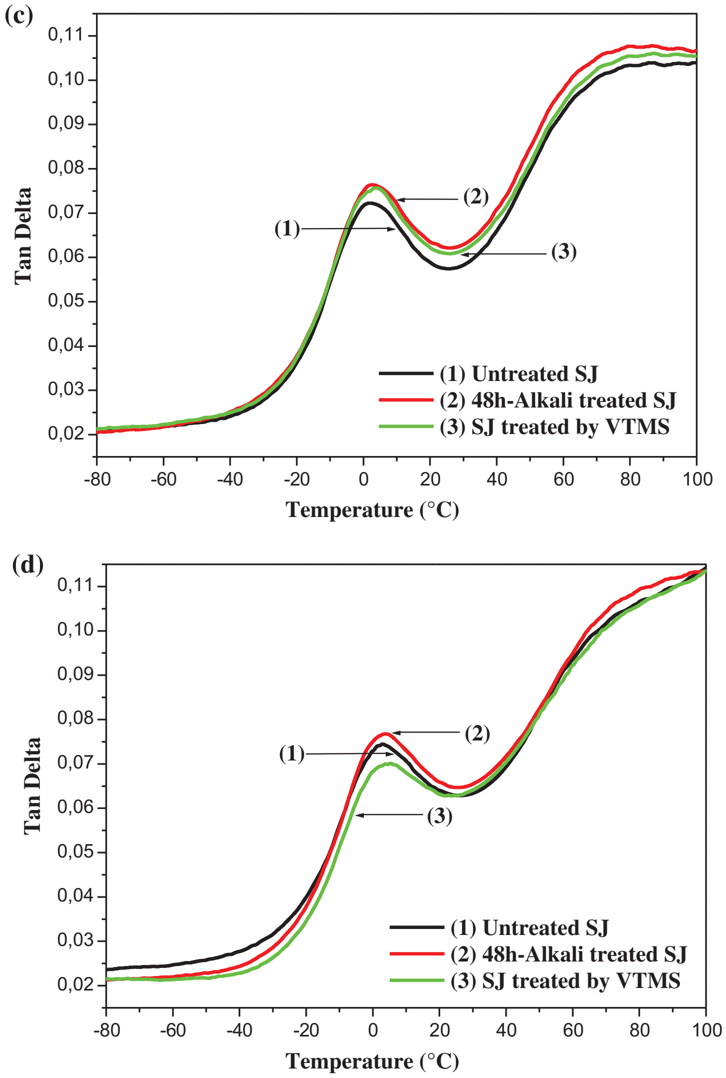

Figure 16. (*Continued*).

4. Conclusions

The effects of the *Spartium junceum* (SJ) flour content and surface treatment of PP/SJ composites were investigated. The study was detailed by the investigation of the thermal and thermomechanical properties.

TGA measurements showed an increase of decomposition temperature of treated flour. The use of the silane coupling agent (VTMS) improves the thermal stability of SJ flour much as the alkali treated SJ flour which is more stable than the untreated SJ flour and the raw ones. Also, the results from the TGA indicate that the addition of flour decreases the thermal stability of the composite. Further, the treatment with VTMS is more effective than mercerization in reducing the thermal decomposition of composites.

Calorimetric investigations showed that the incorporation of spartium junceum flour in the polymeric matrix has no significant impact on the value nor on the shape of the melting or crystallization peaks. The results revealed also a considerable shifting in the melting heat (ΔH_m) and the crystallization heat (ΔH_c) to lower values for composites containing VTMS-SJ flour compared to that containing alkali treated ones. This behavior is due to the crosslinking of SJ flour on the PP chains which forms a network structure. Furthermore, the degree of crystallinity (X_c) increases with addition of SJ flour, indicated that the SJ flour plays a significant role in heterogeneous nucleating of PP, due to the nucleating ability of the cellulosic filler, which alter the kinetics of crystallization of the PP matrix.

DMA studies showed that the addition of untreated flour reduce the storage modulus (E′) of composites compared to that of neat PP. On other hand, the chemical treatments significantly affect the storage modulus of a composite, where E′ increases for composites containing treated flour in comparison to the untreated ones. The treatment with silane induces reinforcement effect, due to the fact that silane coupling agent modifies the interface flour–matrix with the formation of chemical bridge bonds between the two components.

Disclosure statement

No potential conflict of interest was reported by the authors.

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