

Investigation of the thermostability of poly(ethylene terephthalate)-hemp fiber composites: Extending natural fiber reinforcements to high-melting thermoplastics

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ABSTRACT: The thermal stability of poly(ethylene terephthalate) reinforced with 1, 5, 10, 15, and 20% hemp fibers was investigated with the aim of extending the applications of biocomposites to high-melting thermoplastics. The material was injection-molded following compounding with a torque-based Rheomix at 240, 250, and 260°C. A combination of thermogravimetric methods at 5, 10, and 20°C/min, Liu and Yu's collecting temperature method, and Friedman's kinetic method were used for testing and analysis. A significant thermostability for all formulations was observed below 300°C; this demonstrated their potential for successful melt processing. Moreover, two degradation steps were observed in the temperature ranges 313–390 and 390–490°C. The associated apparent activation energies within the temperature ranges were determined as 150–262 and 182–242 kJ/mol, respectively. We found that the thermostability was significantly affected by the heating rates; however, the effect of the temperature of the mixing chamber was negligible. These findings suggest that the successful melt processing of high-melting thermoplastics reinforced with natural fibers is possible with limited fiber thermodegradation. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42500.

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INTRODUCTION

The composites of high-melting thermoplastics reinforced with natural fibers are potential materials for numerous engineering applications. They are, however, still underexploited because of the possibility of thermodegradation during the processing of the melt.^{1,2} In fact, the melt onset of high-melting thermoplastics is by definition higher than 200°C, whereas the onset of thermal degradation of natural fibers has been reported^{3–5} to be as low as 160–190°C. Such disparity coupled with the variation of natural fibers properties with fiber type, harvesting season, and even postharvest treatments are detrimental to the processing of the molten composites and their optimal applications. The thermodegradation of the nontreated natural fibers during production of their composites with high-melting thermoplastics is thus an immediate consequence of such a temperature difference.

The thermodegradation of natural fibers has a strong effect on both composites' processing and their optimal applications

because of the crystallization process. In fact, it has been reported^{6,7} that both the presence of natural fibers and the application of heat-treatment operations enhanced the crystallization of biocomposite materials. This yielded a significant increase in their elastic moduli and a drastic reduction in their elongation at break. Although the former is necessary for many high-end composite applications, the latter is an additional challenge for multistage processing and large deformation-related processes such as thermoforming. Moreover, the thermodegradation of natural fibers negatively affects every optimal application of high-melting thermoplastics reinforced with natural fibers because randomly degraded fibers represent biocomposite structural flaws, which cannot easily be traced out. Thus, the determination of the biomaterial's life cycle is challenging.⁸

Our study has shown that strategically processed poly(ethylene terephthalate) (PET)-hemp fiber composites are thermally stable below 300°C and can thus undergo multiple-stage processing. Moreover, two main thermodegradation steps were found

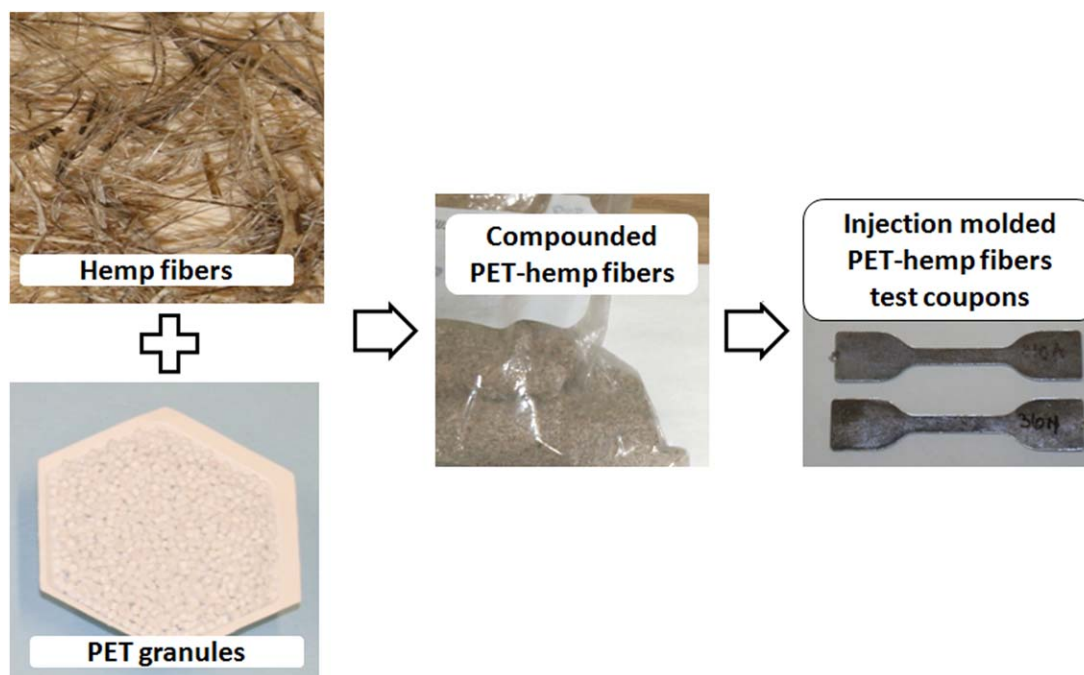


Figure 1. Overview of the major products and semiproducts involved in PET-hemp fiber composite processing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

below 600°C. On the basis of the case study of PET-hemp fiber composites, this study was an assessment of the thermostability of high-melting thermoplastics reinforced with natural fibers with respect to their compounding parameters and fiber concentration. Our aim was to achieve the optimal use of natural fibers as a reinforcement for biocomposite materials while limiting their thermodegradation in the presence of high-melting thermoplastics. Consequently, this study provided a basis for the optimal formulation of biocomposite materials with high-melting thermoplastics and safe processing conditions for natural fibers. Furthermore, the results are directly applicable to thermoforming applications as the thermoplastics did not require further melting.

EXPERIMENTAL

Materials

PET grade AA-48 (Eastman, QC, Canada), with an intrinsic viscosity of 0.80 ± 0.02 dL/g and containing less than 60% crystallinity; Polycaprolactone (PCL) (Sigma Aldrich, Oakville, Canada) with a number-average molecular weight of 70,000–80,000 units; and hemp fibers of composite grade had an average length of 6 cm (Lanaupôle, Berthierville, Canada) were used in this study. They were modified through selected applications to allow melt processing with limited thermodegradation and to create an improved fiber-matrix interface.

An overview of the major products, semiproducts, and steps involved in the PET-hemp fiber composites processing is given on Figure 1. Because esterification is an alternative synthesis route for PET with water as a side product, it is degradable through reverse esterification,^{9–11} especially in the presence of water at high temperature. In the same manner, natural fibers are hydrophilic in nature and vulnerable to humidity.¹² There-

fore, to prevent such degradation in the presence of humidity, PET and its various biocomposite formulations were predried at 150°C for 4 h before each processing stage.

Methodology

During PET-hemp fiber composite processing, the thermal stability of hemp fibers and the melt depression of PET were assured as follows.

The thermal stability of the hemp fibers was achieved by treatment with an alkaline solution in view of melt processing above 200°C. The treatment method was a modification of the method presented by Bledzki *et al.*⁶ The fibers were soaked in an alkaline solution and heated at 80°C for 4 h; this was followed by neutralization with acetic acid and drying for 4 h at 125°C. On the basis of some preliminary work, 5N was chosen as an optimal concentration for processing.

The melting-point depression of PET was achieved by blending with 5% PCL with the same torque-based Rheomix also used for the PET-PCL-hemp fiber composite processing. Such a concentration was appropriate for an efficient blending process and the blend's melting-point depression on the basis of preliminary work summarized in Figure 3. In fact, PET-PCL blends have been largely studied by many authors, who reported the impact of the blend composition on both its thermal and rheological properties.^{13–15} The blends investigated by these authors showed macromolecular behavior with the existence of different crystal populations. However, a greater impact was shown on the melting point of the blends containing less than 20% PCL.

The composites of PET reinforced with 1, 5, 10, 15, and 20% w/w alkaline-treated hemp fibers were produced by compounding with 5% PCL in a torque-based internal batch mixer (Haake

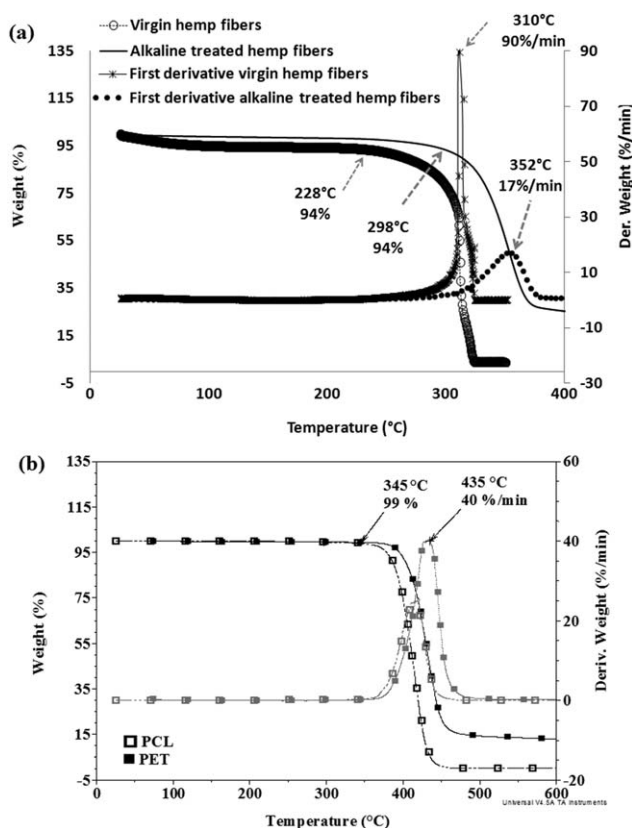
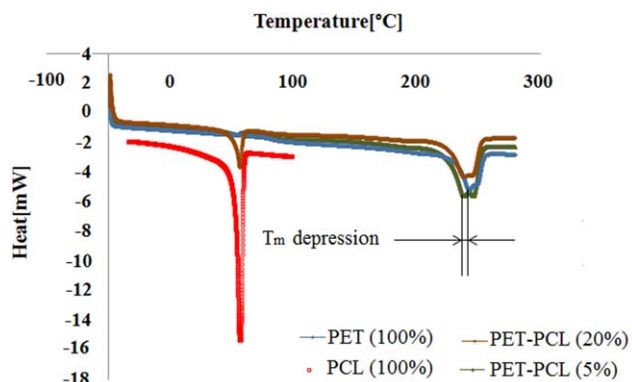


Figure 2. TGA and DTG thermograms of the raw materials tested at 20°C/min: (a) virgin and alkaline-treated hemp fibers and (b) PCL and PET. The secondary axis shows the variation of the weight loss derivative with time (Der. for (a) and Deriv. for (a)).

Rheomix, PolyLab OS System) at temperatures of 240, 250, and 260°C; this was followed by injection molding with a Haake Minijet at 250°C.

The thermal properties of the composites and those of their constituents were determined with thermogravimetric analysis (TGA)/differential thermogravimetry (DTG); (model Q50, TA Instruments, New Castle, DE) at a constant nitrogen flow rate of 70 mL/min and a pressure of 60 Pa. During the first stage, the composite samples weighing about 12 mg were heated from room temperature to 600°C at constant heating rates of 5, 10, and 20°C/min. Then, we analyzed the TGA data, taking into account the temperature of the compounding chamber and the fiber concentration. The temperature interval used was selected on the basis of the main thermodegradation steps and the temperature range used for classical melt processing of the plastic and composite materials. Finally, the study was carried out within the range of Liu and Yu's¹⁶ collecting temperature, which was within the temperature intervals previously determined, and where the Friedman's kinetic model was applicable.

The collecting temperature (T_C), defined in eq. (1) by Liu and Yu,¹⁶ was the first investigation and analysis method used to study the composite formulation during the identified thermodegradation steps. T_b , T_p , and $T_{1/2}$ are the onset and maximum peak temperatures and the temperature at which the half-conversion of the thermodegradation is achieved, respectively.



Blends	Peak, PCL [°C]	Peak, PET [°C]
PET (100%)	nil	247
PET-PCL (20%)	56	237
PET-PCL (10%)	55	237
PET-PCL (5%)	nil	237

Figure 3. Differential scanning calorimetry thermograms showing the depression of the melting point (T_m) of PET with 5% PCL. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

C_i is the weight coefficient of i , and it is also known as a factor that influences the effect of each typical thermodegradation temperature. In this study, the triplet (C_1, C_2, C_3) set suggested by Liu and Yu¹⁶ as (7,2,1) was adopted:

$$T_C = \frac{C_1 T_i + C_2 T_p + C_3 T_{1/2}}{\sum C_i} \quad (1)$$

The investigated PET–hemp fiber formulations were compared for the determined degradation steps. Their kinetic parameters, such as the apparent activation energies (E_a) and apparent reaction orders (n), were determined with Friedman's kinetic model, as shown in eq. (2).^{16–19} α is the species conversion calculated at a given time from eq. (3), dx/dt is the rate of species conversion, and T , R , and A are the absolute temperature, universal gas constant (8.3145 J mol⁻¹ K⁻¹), and pre-exponential factor, respectively. w_0 is the initial weight of the sample, w_i is the weight of the sample at time t , and w_r is the residual weight of the sample at the end of the degradation step:

$$\frac{dx}{dt} = A \cdot e^{-E_a/RT} (1-\alpha)^n \quad (2)$$

$$\alpha_i = \frac{w_0 - w_i}{w_0 - w_r} \quad (3)$$

The formulations were assumed to follow two consecutive thermodegradation steps to 500°C. With the natural logarithm of both sides of eq. (2), eq. (4) was obtained:

$$\ln\left(\frac{dx}{dt}\right) = \ln(z) + n \ln(1-\alpha) - \frac{E_a}{R \cdot T} \quad (4)$$

The formulation of eq. (4) showed that the linear regressions of $\ln(dx/dt)$ versus $1/T$ and $\ln(1-\alpha)$ versus $1/T$ at a constant heating rate yield, E_a , and n , from the respective slopes $-E_a/R$ and E_a/nR . The E_a s were determined and compared for the various formulations and heating rates. Finally, the onset temperature and duration of the composite's thermodegradation were

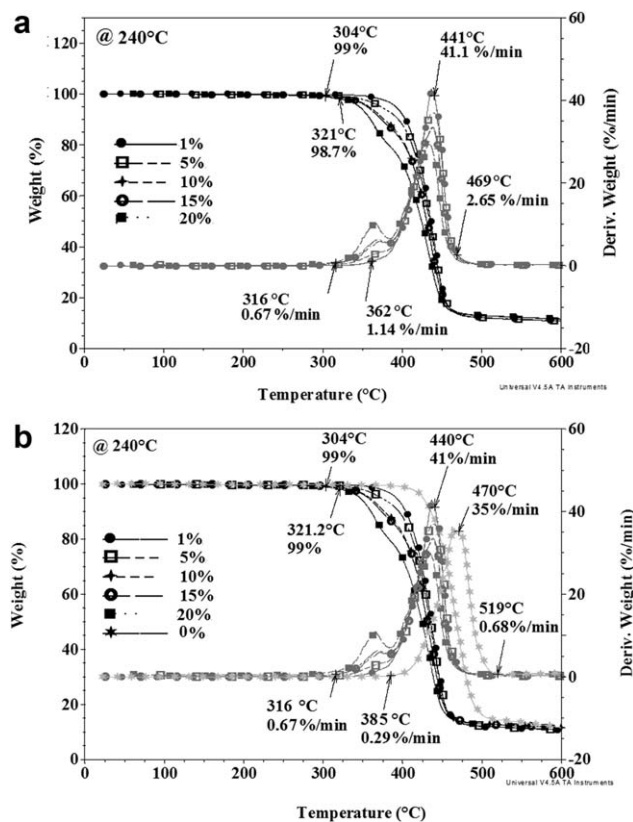


Figure 4. TGA and DTG thermograms for the PET–PCL blend and PET–hemp fiber composites reinforced with 1, 5, 10, 15, and 20% fibers, compounded with the mixing chamber heated to 240°C, and tested at 20°C/min. The variation of the weight loss derivative (Deriv.) with time is shown on the secondary axis.

compared with those of the classical melt-processing cycle of the thermoplastic matrices.

RESULTS AND DISCUSSION

Thermostability of Various Components and Composite Formulations

The thermostability of the composites and their constituents are given in Figures 2 and 4–6. All of the data were analyzed with TA's built-in universal analysis software. Figure 2 shows the thermostabilities of the various composite constituents. They indicated good thermostability in the matrix blend (PCL and PET) below 400°C and appreciable stability in the alkaline-treated hemp fibers below 300°C. The residual weight of PET was attributed to its pyrolysis; this was studied by authors such as Brems *et al.*²⁰ and produced benzoic acid and solid carbonaceous residues depending on the applied heating rate. These observations were in good agreement with previous literature^{12,21,22} and suggested a possible thermostability in the composite materials derived from their combination. Moreover, no clear difference was observed between the thermal degradation of individual polymers in the PET–PCL blend; this further suggested its macromolecular structure. These results also show the effects of the applied treatment on the hydrophilic nature of the constituents and the thermodegradation of hemicelluloses and α cellulose. In fact, the hemp fibers showed about 30% weight

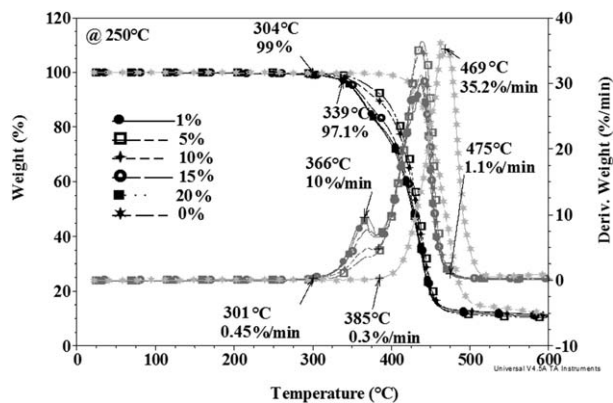


Figure 5. TGA and DTG thermograms for the PET–PCL blend and PET–hemp fiber composites reinforced with 1, 5, 10, 15, and 20% fibers, compounded with the mixing chamber heated to 250°C, and tested at 20°C/min. The variation of the weight loss derivative (Deriv.) with time is shown on the secondary axis.

loss after the alkaline treatment; this indicated a composition that was consistent with hemp fiber's cellulose content and reported by authors such as Bledzki *et al.*⁶ and Ouajai and Shanks⁴ and the cellulose and hemicellulose contents reported by White and Diertenberger.⁵ The degradation peak displayed by the weight derivative of alkaline-treated hemp fibers around 350°C was previously identified by D'Almeida *et al.*¹² as the degradation point for α cellulose. An onset of the thermodegradation of alkaline-treated hemp fibers heated at 20°C/min was found around 275°C, which was a higher temperature than that of virgin hemp fibers. This suggested some early hemicellulose–pectin degradation and confirmed the effect of the alkaline treatment on the fibers' thermostability. These results were also in agreement with earlier observations made by previous authors, such as Ouajai and Shanks⁴ and White and Diertenberger.⁵ A 10% loss by depolymerization of hemicelluloses and pectin between 250–320°C was reported in the former study, whereas a possibility for the pyrolysis of hemicelluloses and lignin between 225 and 450°C was mentioned by the latter. Among all of the constituents, only virgin hemp fibers showed

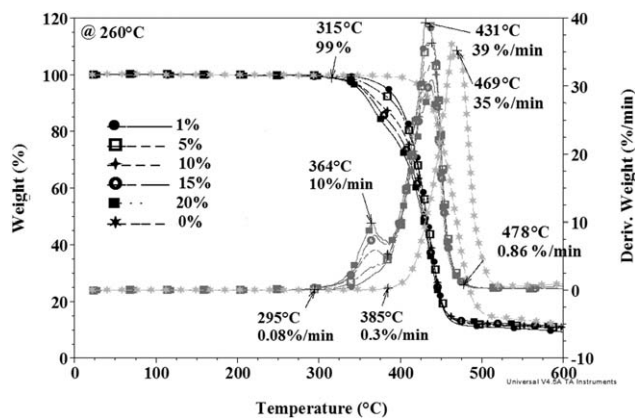


Figure 6. TGA and DTG thermograms for the PET–PCL blend and PET–hemp fiber composites reinforced with 1, 5, 10, 15, and 20% fibers, compounded with the mixing chamber heated to 260°C, and tested at 20°C/min. The variation of the weight loss derivative (Deriv.) with time is shown on the secondary axis.

a marked weight loss at 75°C; this was in contrast to previous works reported by D'Almeida *et al.*¹² This suggested that the virgin hemp fibers had a higher vulnerability to moisture when compared to alkaline-treated fibers. However, the untreated hemp fibers were only tested up to 300°C. The thermostability of alkaline-treated hemp fibers and those of unmodified composites' constituents were previously reported by Saheb and Jog,¹ McNeill *et al.*,²³ and Bacaloglu *et al.*²⁴ These further highlighted their critical effects on the processing of high-melting thermoplastics with natural fibers and their potential engineering applications.

The thermostabilities of PET–hemp fiber composites compounded with the mixing chamber heated at 240, 250, and 260°C are given in Figures 4–6. Many observations are similar to those reported in the previous section for the matrices and alkaline-treated hemp fibers. For temperatures below 300°C, all of the composite formulations showed comparable thermostabilities to those of the isolated constituents, shown in Figure 2, regardless of the compounding chamber temperature. This observation indicated a significantly low impact of the mixing chamber's temperature on the thermostability of the composites studied, especially below 300°C. A similar impact^{10,25} was thus expected within the PET's melt-processing temperature range (250–280°C). These observations were in agreement with those previously reported by Samperi *et al.*²² and suggested the importance of the processing time and additives used at the processing temperature of the fiber-reinforced composites. Furthermore, the data suggested a lower moisture absorption by the composite formulations; this was either due to the hemp fibers' alkaline treatment or possible hydrogen bonding between the hydroxyl groups of the fibers and the carbonyl groups of PET. The latter hypothesis, which was verified earlier with the mechanical properties of the investigated composites,⁷ was also the motivation for the processing without the use of coupling agents.

As shown in Figures 2 and 4–6, the height of the thermodegradation peaks of the alkaline-treated hemp fibers observed around 340°C decreased in the composite formulations without being shifted. This indicated that the functional groups responsible for those peaks decreased as they formed coupling bonds with PET. Moreover, the peaks intensities increased with increasing fiber concentration for all of the compounding temperatures. Finally, the onset of thermodegradation of hemp fibers was found to increase in all of the composite formulations with decreasing alkaline-treated fiber percentages and compounding temperatures. In fact, the alkaline-treated fibers' onset of thermodegradation (~250°C) was significantly increased to 316, 300, and 298°C, for the composites compounded at 240, 250, and 260°C, respectively. This highlighted the importance of the compounding temperature on the thermostability of the PET–hemp fiber composites and suggested their minimum effect in the reduction of the fiber stability. Overall, a better thermal stability of the PET–hemp fiber composites could be achieved through a careful tradeoff between the fiber load, compounding temperature, and process cycle. In all cases, two consecutive steps of thermodegradation were observed. The first one was in the range 313–390°C, and the

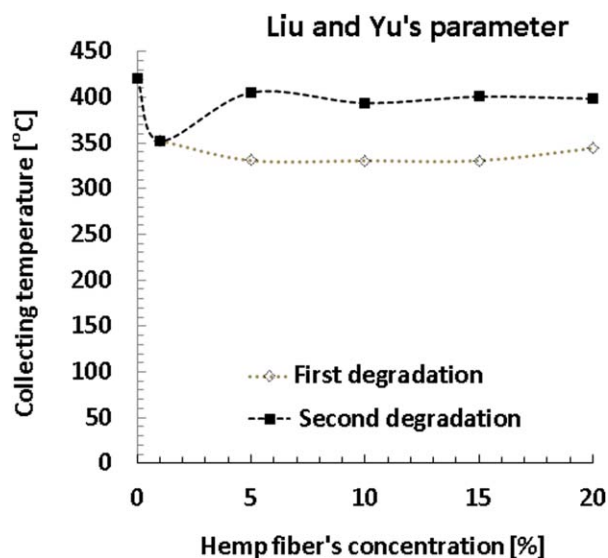


Figure 7. Comparative collecting temperatures between the thermodegradations of the PET–PCL blend and the two thermodegradations of PET reinforced with 1, 5, 10, 15, and 20% hemp fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

second one was in the range 390–490°C; this corresponded to an overall conversion between 15 and 85% or 2 and 15%, depending on the fiber concentration.

Comparison of the Thermodegradation Steps on the Basis of the Collecting Temperature

The variation of the collecting temperature with the fiber concentration is given in Figure 7. By definition, high values of the collecting temperature index are an indication of the thermostability of the investigated materials. The average values of the first and second collecting temperatures (T_{C1} and T_{C2}) observed were $T_{C1} = 334 \pm 3^\circ\text{C}$ and $T_{C2} = 400 \pm 2^\circ\text{C}$, respectively. These values showed little variation with the fiber's concentration and were significantly higher than the classical melt-processing temperature of PET. In this regard, both values confirmed the thermostability of all of the composite formulations investigated in this study regardless of their fiber concentration. A similar behavior was observed for the formulations compounded at all three temperatures of the mixing chamber. The composite properties obtained at different mixing temperatures were repeatable; this was a confirmation of the consistency of the formulated material with the developed processing method. Although the collecting temperature was a good indication of the thermostability of natural fiber-reinforced composites as explained previously, it could not be adequately applied to differentiate or choose between different formulations of these composites; this was in contrast to the thermostability of manmade high-performance fibers reported by Liu and Yu.¹⁶ This behavior could have been related to the thermoinsulation properties of natural fibers and natural fiber-reinforced composites, as reported earlier by Valorvita and Vinha,²⁶ this indicated that the thermodegradation observed could only have significantly negative effects on very long processes. This drawback of the collecting temperature could be solved by the consideration of the intensities of various thermodegradation peaks.

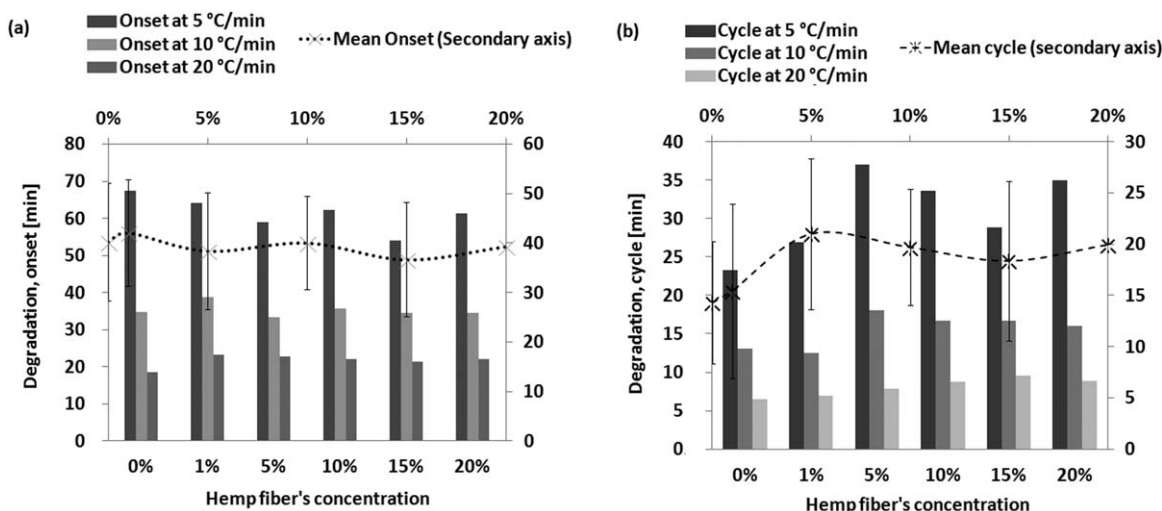


Figure 8. (a) Onset and (b) cycle of the thermodegradation of the PET–PCL blend and PET–hemp fiber composites at 5°C/min.

Comparison of the Thermodegradation Steps Based on Friedman's Parameters

Different thermostability parameters were considered, including the onset and cycle of the various thermodegradation processes, the variation of E_a and n with respect to time, temperature, and composition. Taking advantage of the comparable effects of the mixing chamber's temperature on the thermostability of PET–hemp fiber composites reported in the previous section, we only report the values of the investigated E_a and n for the composite formulations compounded at 250°C.

The onset of thermodegradation of the PET–hemp fiber formulations and the degradation cycle as a function of the hemp

fiber concentration at different heating rates are reported in Figure 8(a,b), respectively.

In general, the onset time of thermodegradation measured from the beginning of the heating process was found between 22 and 60 min [Figure 8(a)]. Moreover, the onset varied inversely with the heating rate. The thermodegradation cycle was found to vary between 5 and 32 min. The results show that it was somewhat dependent on the heating rate. In fact, the thermodegradation cycle was found to be almost constant at high and medium heating rates (20 and 10°C/min) for all of the fiber concentrations. However, it varied significantly with the fiber concentration at 5°C/min [Figure 8(b)]. The observed onset of

Table I. E_a s and Reaction Constants for the Two Steps of the PET–PCL Blend and PET–Hemp Fiber Composite Degradation

Formulation (%)	Degradation step I				Formulation (%)	Degradation step I			
	E_a					n			
	Heating rate (°C/min)					Heating rate (°C/min)			
	5	10	20	Mean		5	10	20	Mean
0	213.35	181.04	218.28	204.23 ± 11.7	0	5.73	3.20	6.08	5.0 ± 0.91
1	247.03	231.30	252.30	243.54 ± 6.31	1	13.41	12.01	11.23	12.22 ± 0.64
5	151.61	172	167	163.47 ± 6.11	5	13.18	12.28	10.55	12.01 ± 0.77
10	200.30	199.38	190.57	196.75 ± 3.10	10	13.55	10.04	12.73	12.11 ± 1.06
15	180.00	154.03	135.26	156.43 ± 13	15	13.88	9.21	13.57	12.22 ± 1.51
20	168.11	172.82	167.7	169.53 ± 1.65	20	10.32	7.18	13.71	10.40 ± 1.89
	Degradation step II					Degradation step II			
1	188.00	167	246.07	200.31 ± 23.68	1	3.08	1.95	2.05	2.36 ± 0.36
5	194.17	238.67	294.55	242.46 ± 29.04	5	5.00	3.57	4.04	4.20 ± 0.42
10	214	222.64	214	216.77 ± 2.93	10	2.18	1.92	3.24	2.44 ± 0.40
15	182	235.08	160.54	193 ± 22.09	15	4.03	2.44	2.56	3.01 ± 0.51
20	126.49	223.18	198.47	182.71 ± 29.00	20	1.56	2.95	2.15	2.22 ± 0.40

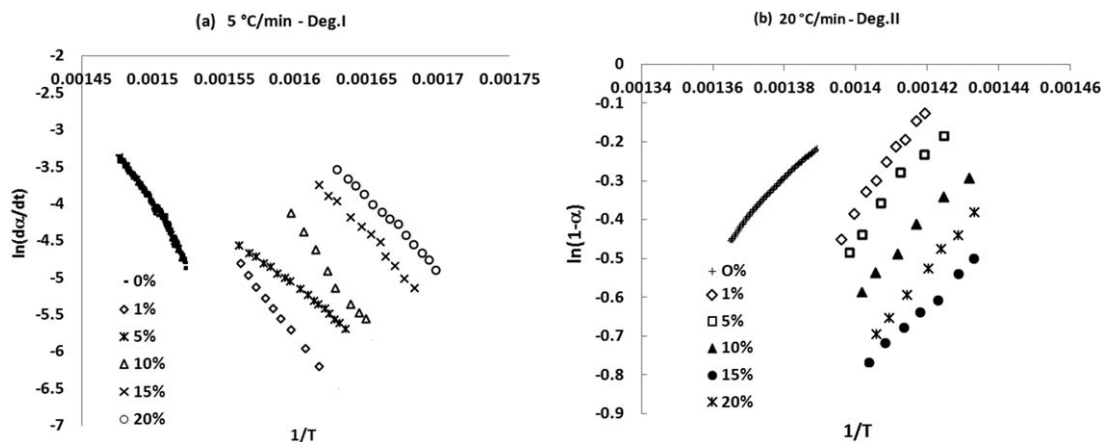


Figure 9. Example of Friedman's model application for the PET–PCL blend as well as the PET–hemp fiber composites at (a) 5°C/min for the E_a values of the first degradation step (Deg. I) and (b) 20°C/min for the n values of the second degradation step (Deg. II).

thermodegradation of the composite materials studied, and their cycle was significantly higher compared to the classical melt-processing cycle (30–240 s) for composite materials.^{27,28} This was another indication of the thermostability of the PET–hemp fiber composites in this range.

A summary of the E_a and n values for the two degradation steps of all of the PET–hemp fiber formulations investigated is given in Table I. All of the data were derived from the Friedman's kinetic method; they were based on the various applicable linear regressions. These were also found to properly match with the two degradation steps indicated earlier by the DTG results below 500°C. Examples of such regression for the E_a and n values are shown in Figure 9(a,b), respectively. Almost all of the slopes that we observed were found to be related to the fiber concentration with linear regression coefficients greater than 0.9. However, a few deviations were found for the first thermodegradation of the formulations reinforced with 1% hemp fibers. This either indicated the minimal magnitude of the matrix–reinforcement interface in comparison to the thermodegradation process of this formulation or simply the kind of random variations often found with composite materials processed with natural fibers.

The values of the average E_a s derived from the variations of the type shown in Figure 9(a) were 150–262 and 182–242 kJ/mol for the first and second degradation steps, respectively. The magnitudes of E_a of the first and second degradation steps were comparable; this suggested that the difference between the two thermodegradation steps were due to the chemical species involved. Moreover, for the second thermodegradation step, E_a variation with the fiber concentration was highly influenced by the heating rates, whereas the first thermodegradation step showed no special variation pattern. In this regard, for all of the applied heating rates, the E_a of the second thermodegradation step increased with the fiber concentration until a maximum value was reached; this was followed by a gradual decrease. Such behavior was similar to the variation of the elastic modulus of the same formulations, which were reported⁷ in a previous work.

Two major observations were also drawn from the comparison of these data with those of previously reported works in the literature. First, we observed that the first thermodegradation step had an average E_a value higher than those of pure PET; this was thermally stable between 280 and 320°C, as reported successively by Kelsey *et al.*²⁹ and Coudane *et al.*³⁰ Second, the combined first and second thermodegradations had E_a values that were higher than the pure E_a values of PET (~227 kJ/mol) found in the literature.³¹

These observations were an indication of the thermostability of the investigated PET–hemp fibers. In fact, the high E_a values were associated with difficulties in initiating the thermodegradation reactions, as suggested earlier by Ruseckaite and Jiménez²¹ with regard to the thermal stability of PET reinforced with cellulose derivatives and Girija *et al.*³¹ with regard to the thermal stability of PET–cyanocell and PET–cyanowood. Moreover, specific implications could also be drawn from their variations with the fiber concentration and from the magnitude of n .

Furthermore, a comparison of the variations of E_a with the fiber concentration at different heating rates (Table I) showed the slightest variation at 10°C/min. This heating rate could then be considered as an optimal processing parameter to limit PET–hemp fiber thermodegradation. This information is not available in the literature^{1,32} nor is the relationship between the low heating rates and longer thermodegradation.

Still in Table I, the values of n derived from Figure 9(b) were between 10 and 12 and 2 and 4 for the first and second thermodegradation steps, respectively. This implied significantly higher values for the first step of each formulation. One can only speculate that the difference was due to the high number of species involved in the first step, which at times also took part in the second thermodegradation step. White and Dietenberger⁵ listed cellulose, lignin, and aromatic chain scission examples of such species. An implication of all of those species could result in an increase in the overall n .

The variation of n affected the composite kinetics of the thermal stability in two ways. These included the complexity and

slow nature of these reactions; this further confirmed their thermostability. In fact, although there was no specific meaning for high n , they were associated with complex reactions.³³ Similar reactions included the thermodegradation reactions of PET, initiated by the instability of the vinyl end groups, which acted as a competing reaction; this was investigated by Kelsey *et al.*²⁹ Such complexity has been associated with the fractional nature of n in the example of the pyrolysis of coal blends with corn and sugarcane residues.³⁴ Moreover, the first degradation steps of all of the formulations showed higher n values, and this indicated complex reactions. Given the high error associated with the values, they were comparable to those previously published by Jandura *et al.*³⁵ for the thermodegradation of cellulose fibers partially esterified by organic acids and Tang *et al.*¹⁸ for the thermal decomposition kinetics of thermotropic copolyesters made from *trans-p*-hydroxycinnamic acid and *p*-hydroxybenzoic acid. Jandura *et al.*³⁵ attributed such observations to physical rather than chemical means and suggested the implication of various parameters in the thermodegradation of the material investigated. Because of the importance of the kinetic study on the reaction mechanism, further investigation of the kinetics of PET–hemp fiber thermodegradation is ongoing.

In general, the reinforcement of PET with hemp fibers induced the thermostability of PET–hemp fiber composites, as indicated by the disappearance of all their thermodegradation steps before 316°C, especially with respect to virgin PET, the shift in the onset of the composites' thermal degradation, the stability of the collecting temperature, and an increase in E_a . Moreover, a significantly high value of the first thermodegradation's n indicated empirical values related to the complexity of the reactions. Similar observations were made for low-melting thermoplastics reinforced with natural fibers.³⁶ However, high-melting thermoplastics' melt reinforcements with natural fibers have not been reported by any other author to the best of our knowledge. These observations also showed the minimal effects of the mixing chamber's temperature on the thermodegradation of the investigated PET–hemp fiber composites.

Apart from the PET–PCL blend, which showed an approximate single thermal degradation step in the range of our studies, all of the other results were based on an assumption of the consecutive two step thermodegradation up to 500°C. Such a choice was justifiable by the work of Lautenberger *et al.*,³⁷ which showed an insignificant difference in the kinetic parameters resulting from the application of either a single-step or three-step degradation of polyester composites.

The considered thermostability of alkaline-treated hemp fibers during melt processing with the PET and PET–hemp fiber composites was further supported by Figure 10, where Figure 10(a–d) shows the scanning electron micrographs of the virgin hemp fibers and PET–5% alkaline-treated hemp fibers used in the tensile tests, the structural pattern around a fiber of heat-treated PET–5% hemp fiber composite, and the variation of virgin hemp fiber's elastic modulus with its linear density (Denier), respectively. Hemp fibers could clearly be seen in the composite structure; this signified their limited thermal degradation during melt processing at high temperature. Moreover, the alkaline-

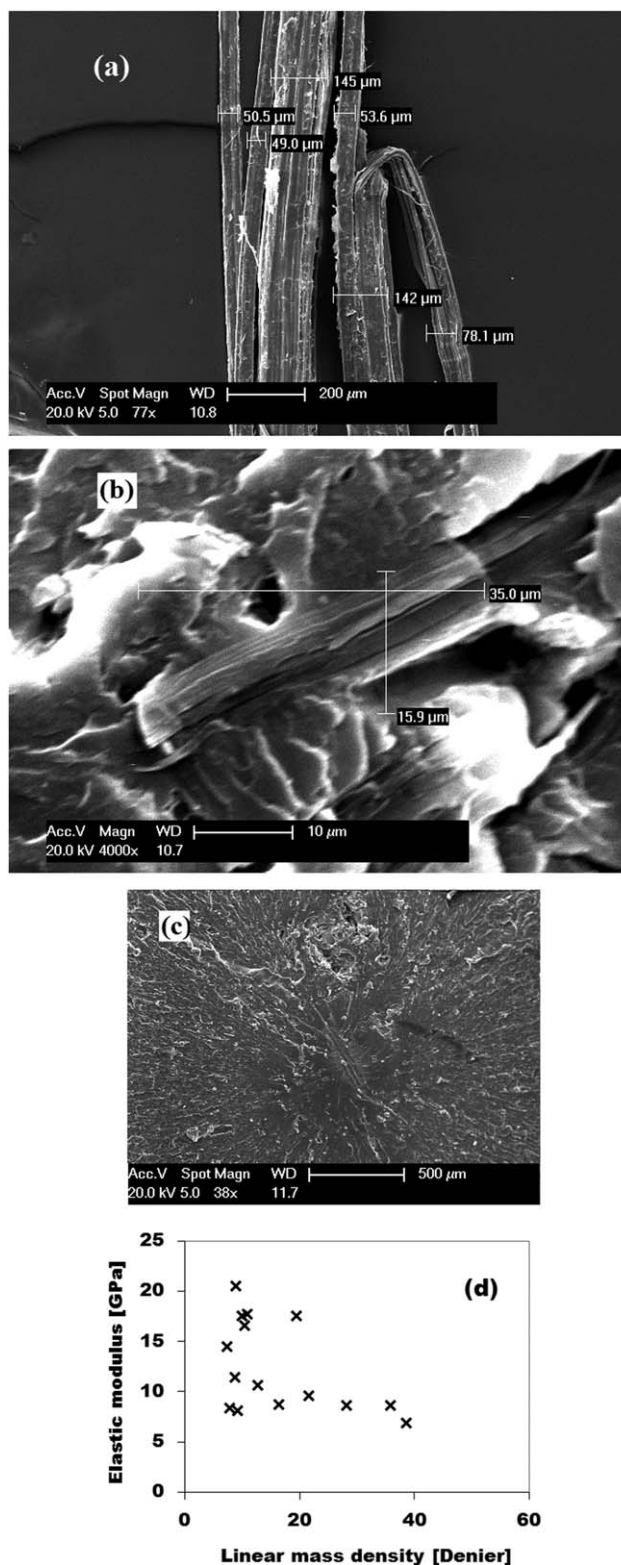


Figure 10. Scanning electron micrographs of the (a) virgin hemp fibers, (b) PET–5% hemp fibers, and (c) the pattern of crystal growth around the hemp fibers and (d) the variation of the hemp fiber modulus with the linear density.

treated and virgin hemp fibers had significantly different sizes, with the former being much smaller. This indicated the structural transformation which occurs during the alkaline treatment. In fact, Figure 10(d) indicates that microfibrils and microfibrils have better reinforcing abilities as higher moduli correspond to lower deniers. Furthermore, a closer look at the hemp fibers in [Figure 10(c)] indicated possible crystallization after reinforcement and heat treatment. These structural observations were consistent with the same phenomenon previously reported with lower melting thermoplastics by authors such as Ho *et al.*³ and Aigbodion *et al.*³⁶

CONCLUSIONS

The thermostability of melt-processed composites of PET reinforced with hemp fibers were investigated as an important melt and multistage processing parameter. All of the formulations were processed by the compounding of alkaline-treated hemp fibers of different concentrations (1, 5, 10, 15, and 20%) and modified PET at three different mixing chamber temperatures (240, 250, and 260°C).

The constituents showed a single peak of maximum degradation for variations below 600°C, whereas the composites showed closely related double peaks in the same temperature range. Two consecutive thermodegradation steps were considered. A combination of the TGA results analysis, Liu and Yu¹⁶ collecting temperatures, and Friedman's kinetic method attested to their thermostability with respect to the fiber concentration, individual constituents, heating rates, and mixing chamber temperatures.

The onset of the thermal degradation of the alkaline fibers was 275°C, and that of the matrix was around 400°C. However, those of the composites were above 300°C; this indicated the thermostability in the presence of hemp fibers. Such thermostability was further shown by the variation of Liu and Yu's collecting temperature (330–400°C).

Two consecutive composite thermodegradation steps were observed at 316–500°C, with $E_{a,s}$ between 150 and 262 kJ/mol and between 182 and 242 kJ/mol for the first and second degradation steps, respectively. High values of n were also observed; this indicated the complexity of the reaction mechanism. The results suggest an appreciably good thermostability of the PET–hemp fiber composites both within the classical processing cycle and the melt temperature range of natural fiber-reinforced composites.

The thermostability of the composite materials made of thermoplastics reinforced with natural fibers was significantly important with applications in industry and academia. Its impact extended to the processing and recycling of biocomposite materials, as it increased the melt-processing range of thermoplastics reinforced with natural fibers. Therefore, this study provided proof for the thermostability of PET–hemp fiber composites and indicated nondegrading processing conditions. These results show the potential of reinforcing high-melting thermoplastics such as PET with natural fibers and the multistage processing for engineering applications with limited thermodegradation.

They also reveal the complexity of the thermodegradation reactions involved. Further work on the kinetics of PET–hemp fiber composite thermodegradation is ongoing based on the standards provided by the International Confederation for Thermal Analysis and Calorimetry (ICTAC).

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