

Thermal stability of PP with acetylated sisal fiber: Romero García kinetic method

C. Albano^{1,2(✉)}, J. González³, M. Ichazo³, N. Velasco², J. Guevara², F. La Mantia⁴

¹Laboratorio de Polímeros, Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apdo. 21827, Caracas 1020-A, Venezuela.

²Universidad Central de Venezuela, Facultad de Ingeniería, Escuela de Ingeniería Química, Los Chaguaramos, PO Box: 48146, Caracas 1041A, Venezuela.

³Universidad Simón Bolívar, Departamento de Mecánica, Caracas 1080A, Venezuela.

⁴Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Palermo, Italia.

E-mail: calbano@ivic.ve/ albanoc@camelot.rect.ucv.ve

Received: 14 May 2003/Revised version: 22 October 2003/Accepted: 22 October 2003

Summary

This work deals the effect of acetylated and non-acetylated sisal fiber on thermal degradation of polypropylene. Applying the R-G method at constant conversion levels of 0.1, 0.3, 0.5, 0.7 and 0.9 to thermograms of the “PP/untreated sisal fiber” blend, E_a values of 99, 213, 224, 187, and 145 kJ/mol were obtained, whereas they were 99, 299, 255, 205, 154 kJ/mol for the “PP/treated sisal fiber” blend. On the other hand, with the R-G method at constant temperature, activation energies within the range of 156–417 kJ/mol were obtained for the “PP/treated sisal fiber” blend and within the range of 126–344 kJ/mol for the “PP/untreated sisal fiber” blend. Additionally, the method establishes as dominant the following decomposition mechanisms: three-dimension limiting surface reaction between both phases, diffusion in two and three dimensions and first-order random nucleation and nuclei growth.

Introduction

Lignocellulosic fibers such as jute, sisal, coir, pineapple, bamboo, hemp, cotton, banana and straw have been used as reinforcement in different polymers. However, the lack of good interfacial adhesion and poor resistance to moisture absorption rendered the use of natural-fiber-reinforced composite less attractive.

Almost all polymers undergo decomposition reactions at any stage of their life cycle, i.e. during manufacturing, storing, processing, or final usage of the product. Factors related to polymers, production and manufacturing processes, and the environment are among the possible causes of decomposition (1).

The degradation of polymers is a complex phenomenon, involving many simple reactions that are difficult to analyze separately. The quantitative contributions of these reactions to the degradation process are impossible to evaluate. For this reason, though the global mechanism does not agree with the real mechanism, it is useful as an indicator to quantify the global velocity of the reaction, to acquire further knowledge of the structure of polymers, and to analyze the behavior of the finished product.

Therefore, this work deals the effect of acetylated and non-acetylated sisal fiber on thermal degradation of polypropylene (PP). With the purpose of determining the activation energy (E_a) as well as the decomposition mechanism of the blends. Thermograms were used for a kinetic analysis following the Romero-García method (2,3).

The classical models used in the kinetic analysis of this kind of reactions study the simultaneous influence of temperature and conversion. However, the effect of temperature can mask that of conversion or vice versa. The Romero-García method (2,3) tries to separate both effects; therefore experimental data at different heating rates is needed.

The Romero-García equations are:

-At constant temperature:

$$G(\alpha) = \frac{RT_1^2 A}{(T_1 - T_0)} * \left(1 - \frac{2RT_1}{E}\right) * \exp\left(-\frac{E_a}{RT_1}\right) * t \quad (1)$$

-At constant conversion:

$$\ln \frac{\beta}{RT^2} = \ln \frac{A}{E_a G(\alpha)} - \frac{E_a}{RT} \quad (2)$$

where α is the reacted fraction at the time t , E is the activation energy (J/mol), A is the pre-exponential factor, R is the gas constant and T is the temperature (K), T_0 is the initial temperature of the reaction (K), β is the heating rate and T_1 : temperature at which the study is carried out at constant temperature (K). The reaction mechanism is represented by different equations (4) expressed as a function of conversion, depending upon the controlling mechanism; therefore, there is a $G(\alpha)$ function for each one of these mechanism (Table 1).

When the activation energy varies with the level of conversion, Budrugaec et al.(5)

propose the following equation: $E = E_0 + E_1 \ln(1 - \alpha)$, where, E_0 and E_1 are constants.

Experimental

-*Materials*: The materials used in this work were PP (MFI: 7.0g/10min) supplied by Propylven and sisal fiber supplied by Sisaltex. Sisal fiber is made up of 66-72% of cellulose, 10-14% of lignin, approximately 12% of hemicellulose, 0.9% of pectin and 10% of water (6). The sisal fiber was chopped to a length of 10mm (7) and was acetylated according to the methods reported by Varghese et al. (8). Treated and non-treated fibers were dried for 1 h at 80°C before mixing with the polymers.

- *Preparation of blends*: The blends were prepared in one stage in a W & P intermeshing co-rotating twin screw extruder. The temperature profile was 130, 170, 190, 180 and 165 °C and the screw speed was 110 rpm. In this one-stage process, the sisal fiber was incorporated through an additional feed port, located in a part of the extruder where complete fusion of the PP was guaranteed. Acetylated and non-acetylated sisal fiber was used at 20wt.% (9).

- *Thermogravimetric Analysis*: The samples were analyzed in a thermogravimetric analyzer (Mettler Toledo, 851) to produce the decomposition process. Thermograms were obtained under the following conditions: the samples were heated up to a temperature of 800 K at different rates 5, 10, 15 and 20 degree/minute, in nitrogen atmosphere. Subsequently, the composites were kinetically examined in order to determine the global activation energy and the reaction mechanism.

Results and discussion

The variation of the conversion as a function of temperature, α versus T, is shown in Figure 1 for the PP with untreated sisal fiber.

Figure 1 shows that two decomposition stages can be observed for heating rates of 5 and 10°C/min, corresponding to the sisal fiber and the polymer; whereas at faster heating rates (15 and 20°C/min) this behavior is not detected. Wendlant (10) reports that the different decomposition mechanisms are more easily observed at slow heating rates. The first stage in composites (PP/untreated sisal fiber) corresponds to two phenomena: thermal depolymerization of hemicellulose (12%wt. loss) and prenucleation of PP, which is a period when the nucleus formation velocity is low. This process of prenucleation corresponds to the formation of the first radicals. In the second stage, these nuclei accelerate the decomposition process, being this behavior similar to that of a catalytic process. Similar behavior present the PP with treated sisal fiber.

Table 1. Kinetic-equations used for the construction of the simulated decomposition reactions (4)

Mechanism	Symbol	G(α)
Random nucleation and nuclei growth (Ec. Avrami-Erofev)		
Bidimensional nuclei growth	A2	$(-\ln(1-\alpha))^{1/2}$
Three-dimensional nuclei growth	A3	$(-\ln(1-\alpha))^{1/3}$
Random nucleation and nuclei growth		
First order random nucleation	F1	$(-\ln(1-\alpha))$
Second order	F2	$(1-\alpha)^{-1}$
Third order	F3	$(1-\alpha)^{-2}$
Diffusion		
One-way transport	D1	α^2
Two-way transport	D2	$\alpha+(1-\alpha)\ln(1-\alpha)$
Three-way transport	D3	$(\alpha+(1-\alpha)^{1/3})^2$
Limiting surface reaction between both phases		
One dimension	R1	α
Two dimensions	R2	$(1-\ln(1-\alpha))^{1/2}$
Three dimensions	R3	$(1-\ln(1-\alpha))^{1/3}$

Tables 2 and 3, let us infer that once the decomposition process is complete, almost all of the material is transformed into volatile material and the remaining residues, less than 3%, correspond to cross-linking material and/or additives incorporated into the polymer during its synthesis or for its preservation against environmental agents. On the contrary, these values for treated and untreated fiber are higher (Tables 3 and 4), ranging within 10-23 wt.%; this means that the cellulose degradative process can be accompanied by chain scission or cross-linking reactions due to the presence of water in the sisal fiber interstices.

According to Broido (11) and Bradbury et al. (12) the decomposition process of the cellulose-based organic materials (sisal fiber, etc.), involve series and competitive reactions. In addition, in all of them the existence of a residue is noticed, which results from the time the volatile products remain in the cellulose, since such products give origin to a cross-linked material.

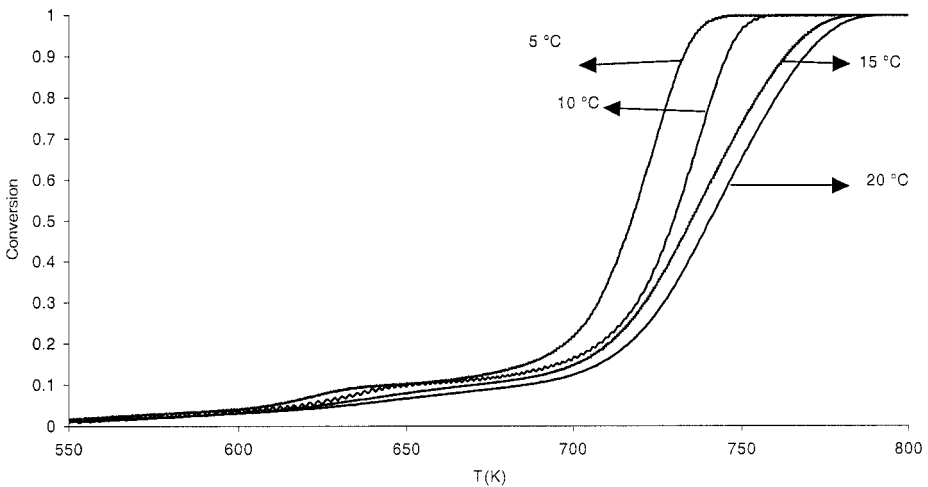


Figure 1. The TG curves of PP/untreated sisal fiber

Table 2. Results obtained based on the termograms of the PP with untreated sisal fiber

Heating rate degree/min	T_{initial} (K)	T_{final} (K)	Mass final (%)
5	590	749	1.99
10	610	750	1.66
15	610	770	1.10
20	610	792	1.20

Table 3. Results obtained based on the termograms of the PP with treated sisal fiber

Heating rate degree/min	T _{initial} (K)	T _{final} (K)	Mass final (%)
5	602	748	1.75
10	614	760	3.2
15	640	786	2.18
20	648	796	1.57

Table 4. Results obtained based on the termograms of untreated sisal fiber

Heating rate degree/min	T _{initial} (K)	T _{final} (K)	Mass final (%)
5	540	650	22.97
10	550	670	18.45
15	555	688	19.33
20	555	692	17.74

Table 5. Results obtained based on the termograms of the treated sisal fiber

Heating rate degree/min	T _{initial} (K)	T _{final} (K)	Mass final(%)
5	550	672	16.09
10	580	682	10.57
15	625	691	15.08
20	630	692	16.23

The temperature at the beginning of the decomposition process (Tables 2 and 3) ranges within 590 and 650 K for both composites, and is slightly higher in the composites with treated fiber due to the presence of functional groups in the sisal fiber that might slightly delay the degradative process.

Tables 6 and 7 show the values of activation energy for PP/ untreated and treated sisal fiber, at different conversions using the R-G method at constant conversion. It can be seen, that E_a values increase and then decrease as a function of conversion, and that at 0.1% conversion a low value of E_a (99 kJ/mol) is detected, which is in agreement with the E_a value corresponding to the sisal fiber, obtained by Albano et al. (13). In addition, this variation in conversion as a function of temperature clearly implies a change in the decomposition mechanism as a function of conversion. The change in the reaction

mechanism is a reflection of the existence of multiple competing steps in polymer degradation. Moreover, E_a values are higher for the composite with treated sisal fiber. Activation energy of the treated and untreated sisal alone (Tables 8 and 9) show very low values at low conversion levels and then start to increase suddenly, which might be due to cross-linking processes originated in the cellulose with OH. Prince et al. (14) studied the degradation of cellulose and found that this process was accompanied by chain branching, which indicates that the process may be a much more complicated one. On the other hand, Leavitt (15,16) reported that the degradation of cellulose in the presence of a controlled amount of water leads to cross-linking; this effect presumably results from an indirect action involving the polymer free radicals formed by interaction of the primary H^* and OH^* radical with the cellulose backbone.

In addition, E_a values of the blend of PP with untreated sisal fiber and of untreated fiber alone are lower than that of the blend with treated fiber and of treated fiber alone, at the different conversion levels. This behavior is due to the fact that in the sisal fiber treatment, OH groups are replaced with more voluminous groups, which brings about restrictions in the segmental mobility, thereby increasing the stiffness of the cellulose backbone. This is also partially due to the fact that some components of the fiber, such as lignocellulose, wax etc., which degrade at lower temperature, may be extracted during alkali treatment.

Table 6. Activation energy (E_a) and pre-exponential factor (A) values at constant conversion, using Romero-García method for the PP with untreated sisal fiber

Conversion	E_a (kJ/mol)	A (min^{-1})
0.1	99	5.2×10^4
0.3	213	6.6×10^{14}
0.5	224	4.1×10^{15}
0.7	187	9.6×10^{12}
0.9	145	1.1×10^{10}

Table 7. Activation energy (E_a) and pre-exponential factor (A) values at constant conversion, using Romero-García method for the PP with treated sisal fiber

Conversion	E_a (kJ/mol)	A (min^{-1})
0.1	99	7.2×10^5
0.3	299	4.9×10^{20}
0.5	255	2.5×10^{17}
0.7	205	5.6×10^{13}
0.9	154	1.1×10^{10}

Table 8. Activation energy (Ea) and pre-exponential factor (A) values at constant conversion, using Romero-García method for the treated sisal fiber

Conversion	Ea (kJ/mol)	A (min ⁻¹)
0.1	72	2.8x10 ⁸
0.3	177	9.8x10 ¹⁴
0.5	251	6.1x10 ²⁰
0.7	261	1.2x10 ²¹
0.9	287	2.1x10 ²²

Table 9. Activation energy (Ea) and pre-exponential factor (A) values at constant conversion, using Romero-García method for the untreated sisal fiber

Conversion	Ea (kJ/mol)	A (min ⁻¹)
0.1	74	2.1x10 ³
0.3	133	1.3x10 ¹¹
0.5	154	3.9x10 ¹²
0.7	176	1.3x10 ¹⁴
0.9	179	6.2x10 ¹³

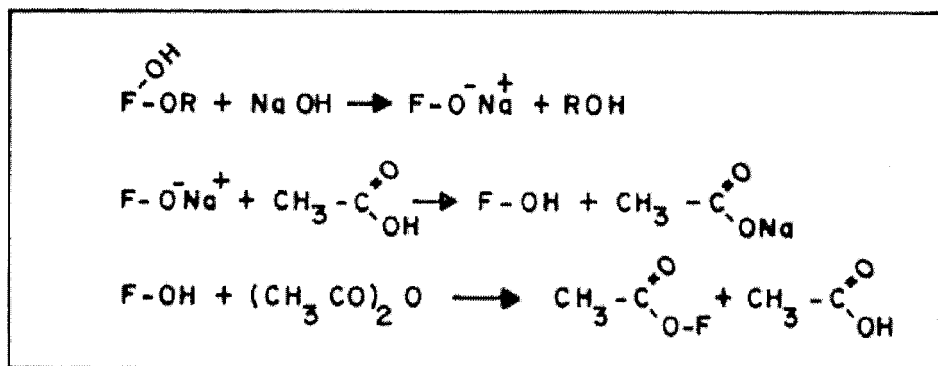
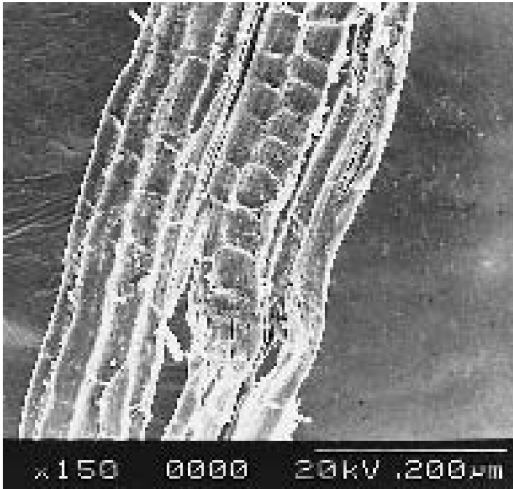


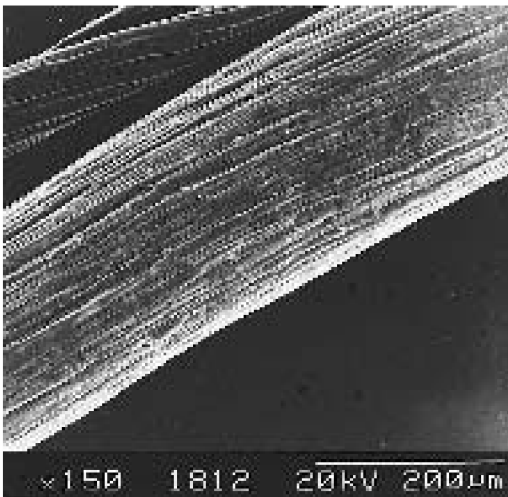
Figure 2. Chemical modification sisal fiber due to acetylation

Table 10. Maximum and minimal activation energy at constant temperature, using Romero García method for the sample

Samples	Ea (minimum) (kJ/mol)	Ea (maximum) (kJ/mol)
PP/ treated sisal fiber	156	417
PP/ untreated sisal fiber	126	344
Treated sisal fiber	33	53
Untreated sisal fiber	132	192



a)



b)

Figure 3. SEM micrographs of a) untreated and b) treated sisal fiber

The reaction mechanism of the acetylation process of sisal fiber is shown in Figure 2. As can be observed, sodium hydroxide abandons the center occupied by organic groups (R). It is also used to eliminate lignin from sisal fiber. Moreover, the reaction with glacial acetic acid transforms oxygenated centers into hydroxyls. The addition of acetic anhydride introduces more voluminous groups into the filler main chain. This renders it more rigid and allows interactions in the polymer-filler interface. Additionally, the treatment produces a number of small voids on the surface of the fiber that promote

mechanical interlocking between fiber and matrix. This leads to an increase in E_a of the blend with treated sisal fiber.

Based on the values presented in Tables 6-9, thermal stability of the PP and the fiber alone is affected by the characteristics of the sisal fiber surface.

Figure 3 is SEM photomicrographs of the surface of untreated and treated sisal fiber, respectively. The surface elevation (Fig. 3a) was considerably diminished with acetylation fiber (Fig. 3b), in which the microfibrils forming the sisal fibers can be seen clearly. This treatment produced an improvement in the wettability property. In addition, the treatment led to fiber fibrillation, that is breaking down of the composite fiber bundles into smaller fibers. This increases the effective surface area available for contact with the matrix and increases the aspect ratio. Therefore, an improvement in the wettability properties and enhancement in aspect ratio offer better fiber-matrix interface adhesion and an increase in thermal stability.

The values of the pre-exponential factor "A" obtained using the proposed method (R-G) are shown in Tables 6-9. It can be seen that this factor "A" considerably varied depending on the conversion level. Similar results were reported by Chan & Blake (17). It can be noticed that the values of conversion presented in Tables 6 and 7 for the blends of PP with treated and untreated sisal fiber approximately fall within the range determined by R-G of maximum and minimum conversion at constant temperature (Table 10) except for the 0.1% conversion, which corresponds to the thermal depolymerization of hemicellulose and the glycosidic linkages of cellulose. These values lead us to infer that, it is possible to use the Romero-García method to determine with a good degree of certainty the thermal stability and the mechanism of degradation of these composites.

Regarding treated fiber alone (Table 8), E_a values at constant conversion are not within the E_{max} and E_{min} interval (Table 10), therefore the R-G method cannot be applied to determine the possible reaction mechanisms.

When the R-G method was applied to these samples, we observed that the dominant decomposition mechanisms are:

-PP/treated sisal fiber: F1, D3 and R3, which implies that the decomposition process starts with a nucleation in the active sites (F1) and then continues with reaction processes in three dimensions on the limiting surface (R3) and diffusion of the smaller molecules (D3), which would correspond to the gases formed in the interface decomposition process.

- PP/untreated sisal fiber: F1, D2 and R3.

- Untreated sisal fiber: F2, D2 y D3.

- Treated sisal fiber: none of the models matches.

Conclusions

Based on the results and according to the pattern of R-G, we can infer that the degradation of the blends occurs under the control of more than one stage of decomposition, where one or several decomposition mechanisms can be present, so that the values of global activation energy for these blends depend on each individual stage and on the relative effect of these on the different conversion and temperature levels. As

it can be seen, values obtained using conversion method fall within the range for the constant temperature method, except for the 0.1% conversion, corresponding to sisal fiber degradation.

Additionally, according to the Romero-García method the dominant decomposition mechanisms are for PP/treated sisal fiber: F1, D3 and R3, for PP/untreated sisal fiber: F1, D2 and R3, for untreated sisal fiber: F2, D2 y D3 and for treated sisal fiber: none of the models matches.

The thermal stability of PP and the fiber alone is affected by the characteristics of the sisal fiber surface. The E_a values obtained for the PP/treated sisal fiber composite are higher than those of the composite with untreated sisal fiber, there might exist a polymer-filler interaction in the first composite, giving origin to higher stability of this composite.

References

1. Rabello MS, White JR (1997) *Polym Deg Stab* 56:55
2. Romero S, García E (1984) *Thermochemica Acta* 73:101
3. Romero S, García E (1988) *Anales de Química* 58:464
4. Criado JM, Dollimore D, Heal GR (1982) *Thermochemica Acta* 59:159
5. Brudugeac P, Segal E (1995) *Thermochemica Acta* 260:75
6. Al-Qureshi HA, Silva JLH (1998) Wetting analysis of natural fiber with polymeric matrix, ICCST/2. Durban, South Africa 69
7. Perera R, González J, Ichazo M, Rosales C, Albano C. (1999) Antec'99. New York, USA 3:3908
8. Varghese S, Kuriakose B, Thomas S (1994) *J Appl Polym Sci* 53:1051
9. Kuruvilla J, Thomas S, Pavithran C (1996) *Polymer* 37(23):5139
10. Wendlant W (1956) *Thermal Methods of Analysis*. Wiley & Son, New York
11. Broido A, Nelson MA (1975) *Combust Flame* 24:263
12. Bradbury AGW, Sakai Y, Shafizadeh F (1979) *J Appl Polym Sci* 23:3271
13. Albano C, González J, Ichazo M, Kaiser D (1999) *Polym Deg Stab* 66:179
14. Prince FP, Bellamy WD, Lawton EJ (1954) *J Phys Chem* 58:821
15. Leavitt J (1960) *J Polym Sci* 45:536
16. Leavitt J (1961) *J Polym Sci* 51:349
17. Chan JH, Balke ST (1997) *Polym Deg Stab* 57:135