

Thermal Degradation of a Phenolic Resin, Vegetable Fibers, and Derived Composites

C. N. Zárate, M. I. Aranguren, M. M. Reboredo

Facultad de Ingeniería-INTEMA, Universidad Nacional de Mar del Plata, Juan B. Justo 4302, (7600) Mar del Plata

Received 4 May 2007; accepted 3 September 2007

DOI 10.1002/app.27455

Published online 26 November 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The thermal degradation behavior of resol, several vegetable fibers (two types of cotton fibers, sisal and sugar cane bagasse) and derived polymer composites have been investigated using thermogravimetric analysis (TGA). The initial thermal degradation temperature T_{ONSET} , the temperature at the maximum degradation rate T_{D_M} , and the char left at 500°C corresponding to the crosslinked resol were higher than the values measured for the fibers and their composites. Thus, the addition of the fibers reduced the thermal resistance of the phenolic thermoset. The polymer and the fiber-composites showed a complex degradation involving different thermal decomposition processes. For that reason,

the DTG curves were deconvoluted and a phenomenological kinetic expression was found for each individual peak. The overall thermal decomposition curve was recalculated adding each degradation process weighted according to its contribution to the total weight loss. An increase in the activation energy corresponding to the cellulose degradation was observed in the composites, highlighting the protective action of the resin encapsulating the fibers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2977–2985, 2008

Key words: resol; vegetable fibers; composites; thermal degradation

INTRODUCTION

Phenolics resins are among the most common synthetic thermosets, used in a wide variety of applications. These resins have high rigidity and dimensional stability, but they are brittle and several types of 2nd phase materials such as glass fiber,¹ elastomeric nanoparticles,² and silica hybrid ceramers³ are added to obtain tougher materials or simply, to control volume shrinkage during curing.

Natural fibers are low cost materials of large availability around the world; they present good mechanical properties combined with low specific mass. In particular, their use in composites with phenolic matrices has been known in the market for years, mainly the incorporation of wool flour to produce moulding powders, or in the fabrication of particle boards, in which the resin is actually just a binder.

Different studies on phenolic based composites have been presented in the literature, which include the use of banana fibers,¹ sugar cane bagasse,⁴ non-woven mat of jute,⁵ or oil palm fibers.⁶ In general, the researchers have focused their study on the mechanical properties of the composites and found that they improved by addition of the natural fibers compared with the nonfilled thermoset. However, there

are few studies on the complex thermal degradation of these same composites.

The analysis of the thermal degradation of polymers and their composite is of high interest in the development of heat resistant polymers, in determining polymer stability, and in identifying high temperature reactions mechanisms in long-term utilizations. Generally, thermal degradation of polymers follows different mechanisms and it is characterized by the weight loss. Thermogravimetric Analysis is the most intensively used technique to study the thermal degradation of polymers⁷ because it is possible to relate the mass loss of a sample with the temperature and/or time in which this occurs.

Kinetic characterization of thermoset resins is fundamental in understanding the structure-property-processing relationship for high performance composite processing and application. Different models have been presented in the literature to describe the degradation kinetic of polymer materials,^{7–10} although not all of them are equally flexible to treat complex processes with more than one chemical reaction taking place simultaneously at some temperature/time interval.

Phenolic resins are excellent flame retardant and heat resistant thermosets. Compared with other polymeric materials, they are more difficult to burn, release less smoke and toxic gases, and generate the highest amount of carbon residues, which retard further burning. Chiu et al.¹¹ used phenolic resin to improve the poor properties on burning of unsaturated polyester.

Correspondence to: C. N. Zárate (cnzarate@fi.mdp.edu.ar).

In a previous work,¹² different vegetable fibers were incorporated to a resol matrix and the effect of this addition on the mechanical properties of the resulting composites was discussed. Nevertheless, the presence of fillers in a polymer matrix can also modify the overall thermal properties of the material.¹³

In this work, the thermal decomposition of these phenolic-vegetable fiber composites was investigated, using thermogravimetric analysis. The characteristic values of decomposition were determined or calculated, such as the initial and maximum temperature degradation, maximum degradation rate, and char left as well as the kinetics parameters: activation energy, preexponential factor, and reaction order. These parameters allow to achieve a better understanding of the thermal stability and the prediction of the degradation behavior.

EXPERIMENTAL

Materials

A resol type phenol-formaldehyde resin was used as the matrix for the composites, RESOL 472, supplied by Atanor, Argentina.

Different fibers were selected to prepare the composites. Three textile fibers and one fibrous residue were used:

1. Loose raw cotton (RC) as obtained from the crop, without any treatment (Algodonera San Nicolás, Buenos Aires, Argentina);
2. Loose clean cotton (CC), which consists of mechanically cleaned fibers, used generally for making nonwoven products, like blankets (Matexsud SA, Mar del Plata, Argentina);
3. Sisal (S) provided as a nonwoven mat (Incomar Industria e Comercio Marques LTDA, Sao Paulo, Brasil);
4. Sugar Cane Bagasse (SCB), residue supplied by Papelera del Tucumán (Tucumán, Argentina).

Composite preparation

Composites were prepared by randomly placing the fibers into an aluminum mold. After that, the liquid resin was carefully poured onto them and the mold was closed. The curing process was always performed under pressure (2.1 MPa), following the same thermal schedule: 60 min at 90°C, 90 min at 140°C and 30 min at 175°C. Then the composites were cooled, still under pressure. For each type of vegetable fibers, a different series of composites was prepared by varying the weight fraction of fibers, W_f .

Along the text, the following abbreviations are used: R-RC (Resol-Raw Cotton Composite); R-CC, (Resol-Clean Cotton Composite); R-SCB (Resol-

Sugar Cane Bagasse Composite); and R-S (Resol-Sisal Composite). The numbers between brackets that appears next to the abbreviations correspond to the weight fraction of fibers in the composite.

Test methods

Thermogravimetric analysis (TGA) were performed using a TGA/DTA Exstar-6000 Seiko Instruments. The thermograms were obtained under nitrogen atmosphere, at a constant heating rate of 10°C/min, from 30 to 500°C for all the materials. In the case of pure resol, additional thermogram was also obtained from 30 to 1000°C at a constant heating rate of 20°C/min.

Theoretical background

Simple methods have been implemented over the years to treat the thermal degradation of materials corresponding to a single degradation process. When the decomposition occurs through different processes the analysis is not so simple, especially when these processes may appear in overlapping temperature ranges. In those cases, it is essential to separate each contribution, so that it can be analyzed individually. As an example, Yang et al.⁹ have analyzed the DTG curves of a rubber, separating the oil contribution from that of the elastomer components. Then, the kinetics parameters for each component decomposition were calculated and finally, the thermal degradation of mixed elastomers of known composition could be predicted (simulated).

An overall degree of thermal decomposition, α , is usually defined as:

$$\alpha = (M_0 - M)/(M_0 - M_f) \quad (1)$$

with M , M_0 , and M_f being the actual, initial, and final weights of the sample, respectively. In the present study, M_0 was taken as the weight of the samples at 105°C. At this temperature, the evaporation of the humidity contained in the sample is completed, and thus this process is not considered in the analysis of the thermal degradation.

In the case of complex TG curves, a different degree of thermal decomposition, α_i , can be defined for each individual process, each one ranging from 0 to 1, and in such a way that the overall degree of decomposition and decomposition rate can be calculated as:

$$\alpha = \sum_i w_i \alpha_i \quad \text{and} \quad \frac{d\alpha}{dt} = \sum_i w_i \frac{d\alpha_i}{dt} \quad (2)$$

where w_i is the weight contribution of the i process to the total weight loss. It can be calculated as the ratio:

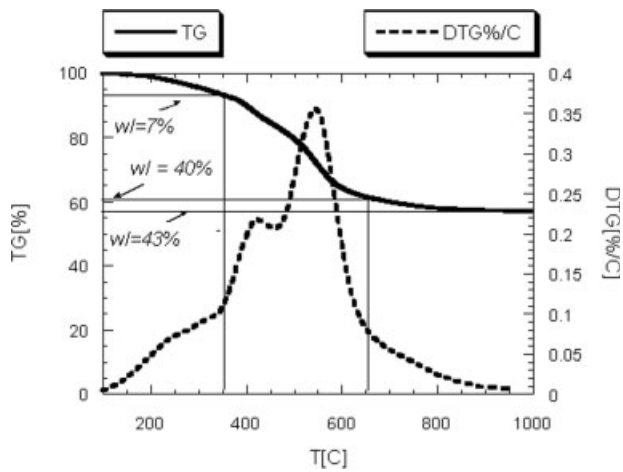


Figure 1 Thermal degradation of resol, at $q = 20^\circ\text{C}$ ($wl =$ weight loss).

$$w_i = \frac{A_{\text{peak},i}}{\sum_i A_{\text{peak},i}} \quad (3)$$

where $A_{\text{peak},i}$ is the area under the i deconvoluted peak. The summation in the denominator equal the total weight loss.

Additionally, each process can be mathematically represented using a phenomenological kinetic model as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha_i) \quad (4)$$

where $k(T)$ is represented by an Arrhenius type expression:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (5)$$

with A being the preexponential factor, E the activation energy, R the gas constant and T the absolute temperature. Besides, temperature and time are not independent in dynamic runs and are related through the heating rate, q , as follows:

$$\frac{dT}{dt} = q \quad (6)$$

The phenomenological function selected for $f(\alpha_i)$, is taken as a simple n th order function, $(1 - \alpha_i)^n$. According to Chang,¹⁰ the best fitting parameters can be obtained after rearranging the kinetic expression as:

$$\ln[(d\alpha/dt)/(1 - \alpha)^n] = \ln A - E/RT \quad (7a)$$

$$\ln[(d\alpha/dT)/(1 - \alpha)^n] = \ln A/q - E/RT \quad (7b)$$

A plot of $\ln[(d\alpha/dt)/(1 - \alpha)^n]$ against $1/T$ will yield a straight line fit of the data if the correct decomposition order n has been selected. From the slope of this line, the activation energy is calculated and the intercept provides the preexponential factor.

Once that the kinetic parameters are obtained, the overall degree of reaction can be recalculated [Eq. (4)] by any available integration method, obtaining the simulated curve.

In this study, a 4th order Runge Kutta routine was utilized. This last step was implemented to verify the validity of the calculated parameters, and its efficiency to reproduce complex experimental data.

RESULTS AND DISCUSSION

Thermal behavior of the raw materials

The TG curve corresponding to the neat resol thermoset is shown in Figure 1. The thermal decomposition is clearly the result of different overlapping processes, that according to Knopp and Pilato¹⁴ can be grouped into three different stages. In a first step, below 350°C , a relatively low percentage of the weight is lost, mainly due to the release of excess phenol, aldehyde, short oligomers, and water. The second step of the thermal decomposition within the range of $350\text{--}650^\circ\text{C}$ is clearly the result of two different degradation processes, where most of the weight loss is the result of the formation of products such as CO , CO_2 , benzaldehyde, phenol, and its polymers, with random chain scission and the initial formation of char. In this temperature range most of the polymer decomposition takes place. For temperatures above 650°C , dehydration occurs and a carbon-like structure (char) is gradually formed, generating carbon monoxide as byproduct. Beyond this temperature, the curve becomes flat.

The thermal degradation curves for the vegetable fibers were also registered and are shown in Figure 2.

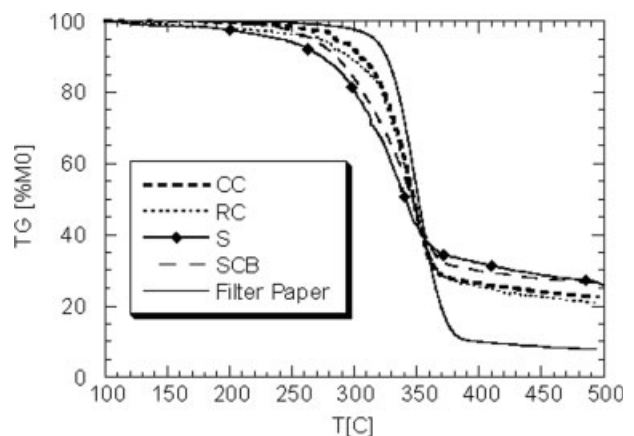


Figure 2 TG for natural fibers and filter paper.

TABLE I
Chemical Composition of Fibers

Fiber	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Others (%)
Cotton ¹⁵	94.0	2.0	0.0	4.0
Sisal ¹⁵	73.2	13.3	11.0	2.5
Sugar cane bagasse ¹⁶	41–44	25–27	20–22	≈ 10

The curve corresponding to filter paper is also included for comparison.

The TG values (%) are reported as the weight of the sample referred to its initial weight (M_0) and expressed as a percentage. The TG% left at 500°C is named "char" and varies as follows: Cellulose < Raw cotton < Clean cotton < Sisal < Sugar cane bagasse.

The differences in char between the fibers can be attributed to the different chemical compositions (Table I). Sisal and sugar cane bagasse contain measurable quantities of hemicellulose and lignin in their structure, while cotton fibers are ~ 95% cellulose. As observed in Figure 2, the cellulose decomposes almost fully into volatile products, leaving only a very small percentage of char at the end of the run. Then, the presence of hemicellulose and lignin produces an increase in the char left.

Figure 3 shows the first derivative TG curves, DTG curves, for the fibers. It can be noticed that a main peak appears around 330–350°C. The range of temperatures involved indicates that this peak is a consequence of the cellulose degradation process, considering the curve of neat cellulose (filter paper).

A second peak between 290–310°C appears as a small contribution in the dTG/dt curves of CC and RC, but it represents a significant signal in the degradation of sisal and sugar cane bagasse. It would correspond to the degradation of hemicellulose, in accordance with the results of Mitra et al.¹⁷ and Albano et al.¹⁸ The weight loss due to the thermal degradation of hemicellulose is 15% for sisal and 23% for sugar cane bagasse. In the case of the cottons, in particular RC, it is just the result of the presence of the hemicellulose and lignin contained in the inevitable small vegetable impurities present into the entangled fibers.

Characteristic values obtained from the TG and DTG curves of the raw materials are reported in Table II. T_{ONSET} is the temperature at which decomposition initiates. Because samples can contain different amounts of absorbed water and the rate of weight loss is different from sample to sample, T_{ONSET} was taken as the temperature at which the sample has suffered a 7% loss of its initial weight, M_0 . This initial weight was taken as the weight measured at 105°C considering that at this temperature the humidity contained in the sample has already been

evaporated. Thus, only degradative processes are considered in the analysis.

TD_M is the temperature at which the maximum rate of degradation occurs, and $(dTG/dt)_M$ is defined as the maximum rate of decomposition of the sample (%mg/min).

A comparison in the position of the maximum in the dTG curves, TD_M in Table II, shows that there are essentially no differences between SCB and CC and just a slightly lower value is reported for the RC. However, sisal (S) shows a significantly lower decomposition temperature. Because the neat cellulose degradation shows a TD_M at 352°C, the small downward shift that occurs in the rest of the fibers is considered to be the consequence of the interaction with other components of the fibers.

Similar reasoning can be used to explain the differences in the maximum value of the $(dTG/dt)_M$ peak. The highest value of the maximum degradation rate is seen in the curve of the neat cellulose, followed by clean cotton. Sisal shows a more progressive degradation and consequently, the maximum in the peak is the lowest of the series. The values for TD_M and $(dTG/dt)_M$ for cotton and cellulose are similar to the values found by Huan and Li.¹⁹

The char left at 500°C correlates inversely with the cellulose content. The highest the cellulose concentration, the lowest the residual char. This is expected, since lignin produces carbonaceous porous

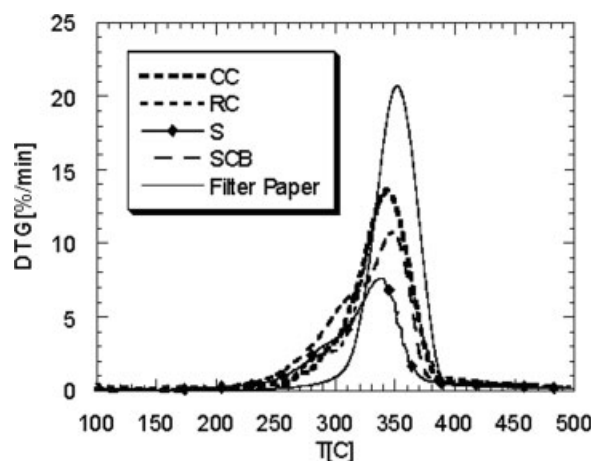


Figure 3 DTG for natural fibers.

TABLE II
Thermal Degradation Results of Raw Materials

Material	T_{ONSET} (°C)	TD_M (°C)	$(dTG/dt)_M$ [%M ₀ /min]	Char left _{500°C} (%M ₀)
Neat resol	358.2	526.6	4.28	79.66 (56.94 at 1000°C)
Sisal	257.8	337.0	7.62	25.90
Bagasse	275.3	347.3	10.76	26.47
Clean cotton	296.5	347.5	13.62	22.57
Raw cotton	281.8	342.4	13.39	21.17
Cellulose	321.0	352.4	20.70	7.83

products of low thermal conductivity, that further reduce the rate of degradation.

To summarize, the presence of lignin and hemicellulose reduces the resistance of the fibers to begin the thermal decomposition, but leads to a wider more progressive decomposition and so to a lower rate of degradation.

Thermal behavior of the composites

The thermogram curves, TG% and $dTG(\%)/dt$, obtained for the raw cotton composites (R-RC) are shown in Figure 4 (a,b), together with those corresponding to the individual components, raw cotton and resol, for the sake of comparison. As the percentage of fiber increases, the char left at 500°C and the T_{ONSET} decrease, while the maximum rate of degradation increases. Similar behavior was found in all composites analyzed. Table III summarizes the resulting characteristic values for the thermal degradation of all the composites analyzed.

These results were expected because of the nature of the raw materials (see Table II). The beginning of degradation is shifted to lower temperatures and the maximum rate of degradation is increased, when the % fiber increases. This indicates that the thermal stability decreases when vegetable fibers are added into a resol matrix. Moreover, the char left at 500°C decreases as the percentage of fibers increases. Then, the TG analysis can be used to estimate the weight fraction of fibers, W_f , in composites of known behavior.

When no specific interactions arise between the components of the composite (matrix and reinforcement), it should be possible to simply reconstruct the TG (%) data from those of the neat components, according to:

$$\begin{aligned} TG(\text{composite})_C &= TG(\text{fiber})_{EX} \times W_f \\ &+ TG(\text{resol})_{EX} \times (1 - W_f) \end{aligned} \quad (8)$$

$$\begin{aligned} DTG(\text{compuesto})_C &= DTG(\text{fiber})_{EX} \times W_f \\ &+ DTG(\text{resol})_{EX} \times (1 - W_f) \end{aligned} \quad (9)$$

where W_f is the weight fraction of fibers as measured experimentally during the composite prepara-

tion and the subindices *c* and *ex* mean calculated and experimental, respectively.

Figure 5 shows the DTG experimental curve for R-CC (52%) and the "calculated curves," DTG_C , resulting from applying Eq. (9). Although the shapes are similar, it is clear that the experimental curve is shifted to higher temperatures, showing a higher TD_M than the calculated curve. Similar results were found in R-RC and R-S composites, which would indicate that the resol matrix interacts with the fiber leading to the observed increase in TD_M . Marcovich et al.¹³ have reported similar results in composites prepared from wood flour and an unsaturated polyester resin and suggested that the matrix protects the fiber, delaying its thermal degradation.

On the other hand, a different behavior was found for the R-SCB composites, as it is shown in Figure 6. In this case, the "experimental" and "calculated" curves are in a relatively better agreement with respect to the position of the degradation peaks. This result would indicate a reduced interaction between fiber and matrix. The observation can be

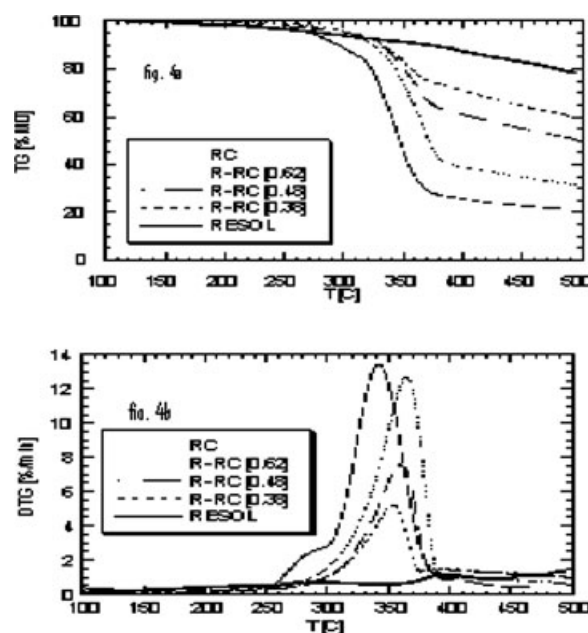


Figure 4 (a) TG Curves for raw cotton, resol, and their composites. (b) DTG curves for raw cotton, resol, and their composites.

TABLE III
Characteristics Values of the Thermal Degradation of the Formulated Composites

Material	T_{ONSET} (°C)	T_{D_M} (°C)	$(dT_G/dt)_M$ [%M ₀ /min]	Char left _{500°C} (%M ₀)
R-RC[0.38]	319.76	354.79	5.19	59.57
R-RC[0.48]	317.54	360.42	7.53	50.28
R-RC[0.62]	313.85	364.89	12.68	31.36
R-CC[0.39]	330.59	368.94	7.88	46.95
R-CC[0.52]	327.34	369.65	7.98	45.54
R-CC[0.68]	312.2	362.01	11.95	34.11
R-SCB[0.39]	281.68	341.51	3.89	60.3
R-SCB[0.53]	277.33	346.33	6.01	50.48
R-SCB[0.77]	274.67	343.92	7.98	43.04
R-S[0.35]	280	351.28	5.12	58.11
R-S[0.55]	278.22	346.23	7.1	50.44
R-S[0.72]	272.19	343.64	7.65	42.04

easily understood because of the coarse fibers used to prepared these composites, in contrast with the finer fibers of sisal and in particular of the cotton fibers. In the last case, cotton fibers offer a large surface area to interact with the resol matrix, while bagasse fibers are not in perfect contact with the matrix because of the bigger particle size and the high irregularity of the distribution in the mold (agglomeration takes place, reducing the wetting of the fibers by the resin). This distribution problem has also effect on the final mechanical properties as it was already reported in a previous publication.¹²

Kinetics of the thermal degradation

Because the degradation of clean cotton is essentially that of cellulose, a single degradation process can be assumed. Thus, only one set of kinetics parameters are needed that would correspond to the cellulose thermal degradation in an inert atmosphere.

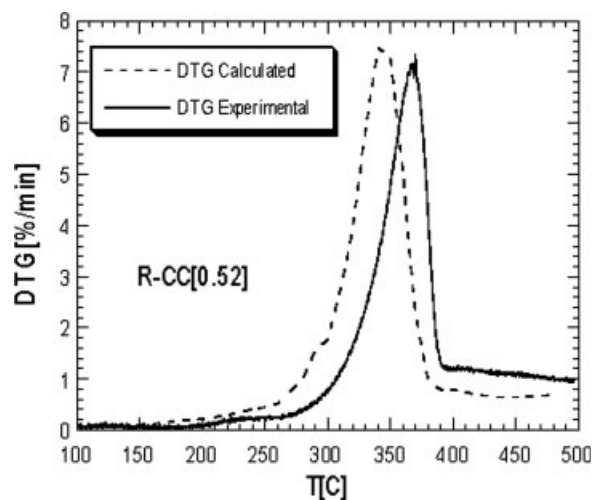


Figure 5 Experimental and calculated curve for R-CC composite.

From the plot of $\ln[d\alpha/dt/(1-\alpha)^n]$ vs. $1/T[K]$, the best set of fitting kinetics parameters were determined:

$$E_a = 151.95 \text{ kJ/mol}$$

$$A = 2.95 \times 10^{12} \text{ (min}^{-1}\text{) and}$$

$$n = 1$$

These values were introduced in Eq. (4) and the α values calculated, obtaining the simulated curves. Figure 7 shows the curves α and $d\alpha/dt$ as a function of temperature for clean cotton (experimental and simulated curves). It can be observed that the simulated and experimental degradation curves match closely. Besides, the values of the parameters obtained for cotton fibers (Table IV) are in good agreement with results published in the literature by other authors (Table V).

The neat crosslinked resol, sisal, and sugar cane bagasse and its derived composites, including the cotton composites, present two or more peaks in the $d\alpha/dt$ curves. The data were kinetically analyzed after deconvoluting overlapping peaks to improve the quality of data input.

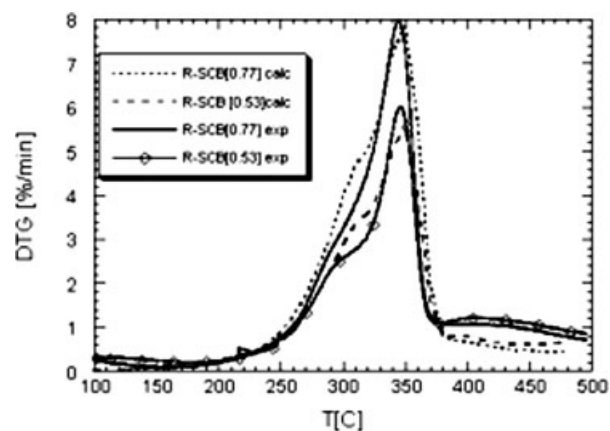


Figure 6 Experimental and calculated curves for R-SCB composites.

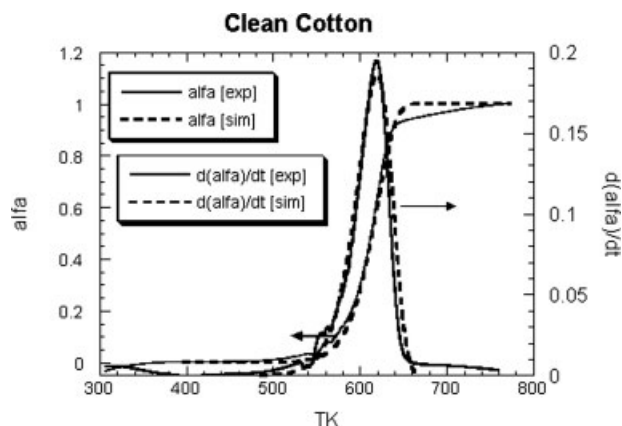


Figure 7 Experimental and simulated curves for clean cotton.

In these cases, the first step of the calculations was to deconvolute the $d\alpha/dt$ curves to obtain the separated contributions of the different degradation processes to the overall thermogram. The contribution of each one to the overall degradation was calculated as the area under each peak divided by the total area. The kinetics parameters for each process were determined considering a degree of degradation α_i varying from 0 to 1 and from the best fit of each deconvoluted peak. Then, each peak was modeled (simulated) using the same method as mentioned above.

The final curves was obtained as the integration of each peak, considering the % of the contribution of each one to the total percentage of weight loss.

Figure 8 shows the $d\alpha/dt$ curves for Bagasse, experimental and simulated. It can be seen that the two peaks deconvoluted and their sum that results in a good agreement with the experimental curve.

TABLE IV
Kinetics Parameters for Natural Fibers, Resol, and Their Derived Composites

Material	Wg % fiber	E (kJ/Mol K)	n	$\text{Ln}A$ (min^{-1})
CC	–	152	1	28.7
R-CC[0.39]	39	210	1.5	39
R-CC[0.52]	52	197	1.5	37
R-CC[0.58]	68	173	1.5	32
RC	–	169	1	32
R-RC[0.38]	38	270	1.5	52
R-RC[0.48]	48	256.4	1.5	48
R-RC[0.62]	62	223	1.5	42
SCB	–	197	1	37.4
R-SCB[0.39]	39	178	1	37.6
R-SCB[0.53]	53	183	1	35
R-SCB[0.77]	77	196	1	37.3
R-S[0.35]	35	206	1	39
R-S[0.55]	55	196	1	37.6
R-S[0.72]	72	177	1	35
RESOLPI1	–	26.3	1	4
RESOLPI2	–	143	2	24.7
RESOLPI3	–	199.2	2	29.5
RESOLPI4	–	42.4	1.2	3.8

TABLE V
Activation Energy (kJ/Mol) for Several Cellulosic Fibers

Fiber	E (kJ/Mol)	Ref
Filter cotton	121–160	19
Cotton	142	19
Cellulose	214	19
Cellulose	140	20
Cellulose	182.4	21
Sisal peak 1	137–154	18
Sisal peak 2	237–278	18

Moreover, Table IV shows the kinetics parameters obtained for resol, bagasse, and all composites analyzed.

The order of the reaction was taken to be equal to 1 in all fibers degradation cases and the resulting activation energy was in the 152–197 kJ/Mol range.

It can be observed that some variations in reaction order are registered for cotton composites ($n = 1–1.5$), which are due to the more complex material investigated and the fact that the model chosen is phenomenological and not mechanistic. On the other hand, the values of the activation energy show an interesting trend that is a direct result of the shift observed in TD_M when the fibers are included in the polymeric matrix [Fig. 4(b)]. Accepting the explanation that the fibers are better protected when they are included in the polymer (which also have low thermal conductivity), the activation energy of the degradation of the cellulosic material should increase as more polymer is added to the formulation. This is actually the observed trend with E_a ranging from 270 to 223 kJ/mol (38 and the 62 wt % raw cotton composites, respectively) and from 210 kJ/mol to 173 kJ/mol (39 and 68 wt % clean cotton composites, respectively). This increases of E_a result in the experimentally observed shift of the degradation peak

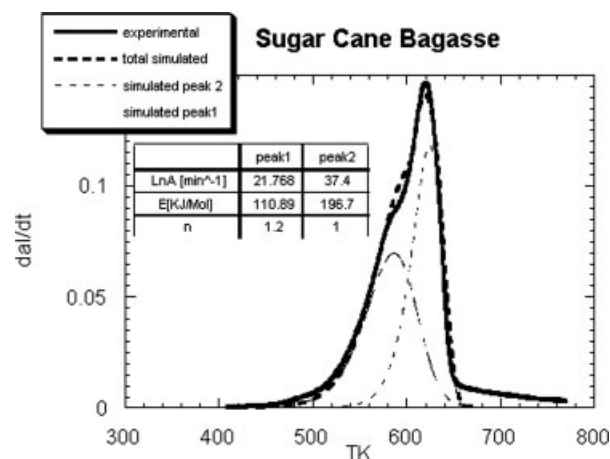


Figure 8 Experimental and simulated curves for sugar cane bagasse.

toward higher temperatures, which was discussed in a previous section. Similar trend shows the kinetics parameters for sisal composites.

In the case of bagasse composites, little interaction between fiber and matrix was anticipated as it has been previously discussed. Actually the first order kinetic model can represent the degradation of fibers and composites with little variation of E_a . Then the kinetic parameters from bagasse when it is embedded in resol, are not affected for the presence of matrix.

Kinetic parameters varying the heating rate

The thermal degradation of resol is complex and the result of different overlapping processes.

Figure 9 shows the experimental curve obtained at heating rate of 20°C/min and the simulated curve obtained from the kinetic parameters of each peak (See Table IV), considering their proportional contribution.

To test the validity of the equation, these kinetic parameters were also utilized to calculate the $d\alpha/dt$ curves corresponding to a 10°C/min run only doing $q = 10$ in eq. (7b).

The new curve obtained was compared with the curves obtained experimentally for 10°C/min up to 500°C, resulting in a good agreement (Fig. 10).

Apparently, no changes of degradation mechanism occur by simply changing the rate of heating and the model proposed is complete and versatile enough to predict the degradation under different heating conditioning. Similar conclusions have been reached by Yang⁹ working with neat elastomers and changing the heating rate from 1 to 10°C/min. When the heating rate was 40°C/min only some differences appeared in the values of kinetic parameters. Then, it can be concluded that the kinetic parameters are similar for a wide range of heating rates.

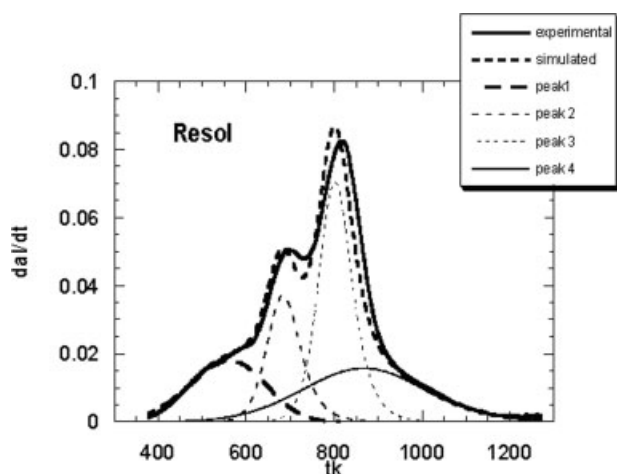


Figure 9 Experimental and simulated curves for resol at heating rate of 20°C/min.

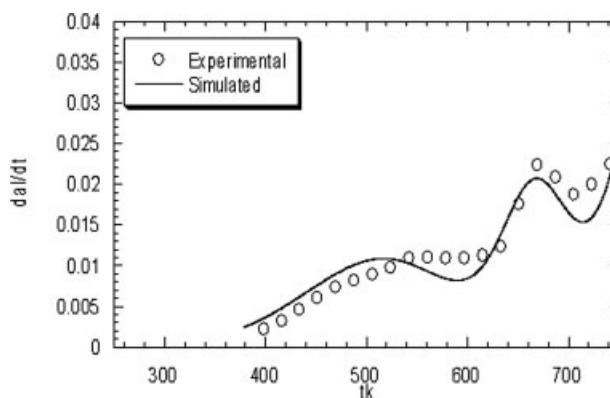


Figure 10 Experimental and simulated DTG curves for resol at a heating rate of 10°C/min.

CONCLUSIONS

The fibers with high content of cellulose (cotton) present a higher rate of degradation and a higher temperature at which decomposition initiates, T_{ONSET} , than the fibers containing hemicellulose and lignin (sugar cane bagasse and sisal). This indicates that the presence of noncellulosic materials in the fibers produces an acceleration in the beginning of decomposition, but a lower rate of degradation producing a more progressive degradation of fibers.

The char left at 500°C in lignocellulosic fibers is always higher than cellulosic fibers.

The parameters describing the thermal degradation of resol, TD_M , T_{ONSET} , maximum rate of decomposition and char left_{500°C}, indicate that the resol has a higher thermal stability than any of the fibers.

It was found that the char left is nearly proportional to the fiber content in the composite. Then, it can be concluded that the TG tests can be used as semiquantitative method to estimate the percentage of fiber in each composite.

As the fiber content increases in the composites, T_{ONSET} decreases and $(dTG/dt)_M$ increases. Thus, the incorporation of fibers in the resol matrix reduces the thermal stability of resol.

The decomposition peak of the cotton composites is shifted to higher temperatures with respect to that of the neat cotton fiber. Because of this, the calculated curves (obtained from data of neat raw materials) predict lower temperatures of thermal degradation. The upward temperature shift was attributed to the existence of an interaction between matrix and fiber, with the matrix enclosing the fibers and protecting them against thermal degradation. For R-SCB composites, negligible interaction was found, which could be attributed to large particle size, extensive agglomeration, leading to incomplete contact fiber-resin. Thus, the overall thermal degradation is essentially the sum of the individual processes of fibers and resin.

The kinetic parameters were calculated utilizing the Chang method, and the model was used to recalculate the overall degree of reaction. A good agreement was found between the experimental and simulated curves.

For resol, the kinetic parameters calculated can be applied to predict degradation at different heating rate. It is mean that when the rate of degradation is varied, no change of degradation mechanism occurs.

The knowledge of the polymer and fibers degradation kinetics could be used, in principle, to predict the behavior of different composites. However, this will be only true if there are no specific interactions between filler and matrix. It is also clear, from this study that this simple approach cannot be extended to systems, such as cotton-resol, where the interaction between the two components affects the stability of the individual components.

References

1. Joseph, S.; Sreekala M. S. Oommen, Z.; Koshy, P.; Tomas, S. *Compos Sci Technol* 2002, 62, 1857.
2. Ma, H.; Wei, G.; Liu, Y.; Zhang, X.; Gao, J.; Huang, F.; Tan, B.; Song, Z.; Qiao, J. *Polymer* 2005, 46, 10568.
3. Lin, J.; Ma, Ch. *Polym Degrad Stabil* 2000, 69, 229.
4. Paiva, J.; Frollini, E. *J Appl Polym Sci* 2002, 83, 880.
5. Sarkar, S.; Adhikari, B. *Polym Compos* 2001, 22, 518.
6. Sreekala, M.; Kumaran, M.; Thomas, S. *Compos A* 2002, 33, 763.
7. Nam, J.; Seferis, J. *J Appl Polym Sci* 1993, 50, 1555.
8. Jimenez, A.; Iannoni, A.; Torre, L.; Kenny, J. *J Therm Anal Cal* 2000, 61, 483.
9. Yang, J.; Kaliaguine, S.; Roy, C. *Rubber Chem Technol* 1992, 66, 213.
10. Chang, W. *J Appl Polym Sci* 1994, 53, 1759.
11. Chiu, H.; Chiu, S.; Jeng, R.; Chung, J. *Polym Degrad Stabil* 2000, 70, 505.
12. Zárate, C.; Aranguren, M.; Reboredo, M. *J Appl Polym Sci* 2000, 77, 1832.
13. Marcovich, N.; Reboredo, M.; Aranguren, M. *Thermochim Acta* 2001, 372, 45.
14. Knop, A.; Pilato, L.; *Phenolic Resins*, Springer-Verlag: New York, 1985, Chapter 8.
15. Mark, H.; Bikales, N.; Overberger, C.; Menges, G. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1985; Chapter 6.
16. Editorial Científico Técnica. *La industria de los derivados de la caña de azúcar*. 1985; Chapter 4.
17. Mitra, B.; Basak, R.; Sarkar, M. *J Appl Polym Sci* 1998, 67, 1093.
18. Albano, C.; González, J.; Ichazo, M.; Kaiser, D. *Polym Deg Stabil* 1999, 66, 179.
19. Huan, M.; Li, X. *J Appl Polym Sci* 1998, 68, 293.
20. Jandura, P.; Riedl, B.; Kokta, B.; *Polym Deg Stabil* 2000, 70, 387.
21. Nada, A.; Hassan, M. *Polym Deg Stabil* 2000, 67, 111.