

## **CHAPTER 3**

### **Compositional Analysis of Thermoplastic Wood Composites by TGA**

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#### **Abstract**

A method has been developed for the quantitative determination of the composition of thermoplastic wood composites. The method involves area measurements of the two peaks in the derivative curve of a tracing produced by the thermogravimetric analysis (TGA) of a thermoplastic composites sample in an inert atmosphere. This may involve the standard, constant heating rate-method, or the high resolution (Hi-Res™) TGA method; both produce virtual baseline separation between wood and polyolefin peaks over a wide compositional range. Because this baseline separation suffers from a mutual effect on the thermal degradation of wood and polyolefins, best results are obtained if the parameters relating peak area with polyolefin content are different below and above 40% polyolefin content.

Keywords: thermogravimetric analysis (TGA), polyolefins, thermoplastic, wood, composites

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## Introduction

The thermoplastic wood composites industry is currently undergoing rapid growth, with more combinations and more structural lumber profiles being introduced into the marketplace.<sup>1</sup> Although a vast array of thermoplastic polymers have been evaluated for their utility with wood flour and wood fibers, the commodity polyolefins, polyethylene (PE) and isotactic polypropylene (iPP) represent by far the vast majority of plastics employed.

While much work in the published literature has focused on mechanical properties,<sup>2-4</sup> interfacial compatibility,<sup>5-8</sup> and method of compounding,<sup>9</sup> relatively little work has dealt with the methodology for determining the overall composition of the composites in terms of their components. However, the composition of thermoplastic wood composites is indeed expected to be an important performance parameter that needs to enter into the standards by which thermoplastic wood composites are described. Options for the determination of the overall composition of thermoplastic wood composites include solvent separation (extraction); chemical (wet) analysis using a “tag” component, such as glucose or methoxyl; solid state NMR or FTIR spectroscopy; or thermogravimetric analysis (TGA).

TGA is a method that is based on the measurement of weight change in relation to temperature. The standard TGA method employs a constant heating rate and usually an inert environment of nitrogen or argon; or this may employ a “high resolution” heating method which is based on adjusting the heating rate in accordance with the rate of weight loss. This method, which results in a very slow heating rate at the temperature at which the conversion of solid mass into gaseous degradation products reaches a maximum, has significantly increased sensitivity as compared to the standard (constant heating rate) methodology. In addition to gaining resolution by adjusting the heating method, the sample’s surrounding atmosphere may be changed to cause degradation of a particular component. Phillips and Blazey<sup>10</sup> used TGA in the composition analysis of starch filled thermoplastics. By switching to an oxidizing atmosphere such as air at 550°C, the starch char component was fully degraded. This technique of using two purge gases of varying reactivity allowed for the total quantification of the natural and synthetic components.

Moreover, there is a body of work investigating decomposition products of wood and polyolefin waste.<sup>11-14</sup> One conclusion (from Sharypov et al.<sup>12</sup>) shows a nonlinear dependence of the degradation products on the ratio of wood to polyolefin fraction. In order to use a step analysis procedure where the quantity of one component is determined from the Y-axis by

measuring the percentage at the plateau values before and after the decomposition temperature range, it is assumed that the decomposition is not influenced by the ratio of components. In other words, the degradation of a mixture is the same as the combination of individual components. The isothermal TGA work by Sharypov et al.,<sup>12</sup> however, indicates that the decomposition products are influenced by the component ratio of wood and polyolefin. Therefore, the shape of the thermogravimetric curve will deviate from the linear combination of the individual components.

This study was motivated by the desire to quantitatively determine the composition of thermoplastic wood composites consisting of wood and/or wood components (cellulose fibers) with common polyolefins, polyethylene and polypropylene, by thermogravimetric analysis. However, poor resolution of the components in the TG curve, combined with non-additive degradation effects based on polyolefin and wood quantity prevented determination of components from the TG curve. An alternative calibration method was developed in this study to quantify the composition of wood thermoplastic composites from analysis of the derivative thermogravimetric (DTG) curve. This calibration method was then applied to determine the polyolefin content in material derived from the co-refining of wood fiber and polyolefin by steam-explosion processing.

## **Experimental**

### **Materials:**

Polyethylene and polypropylene powder were obtained from Scientific Polymer Products and were used as received. The polyethylene had a reported number average molecular weight of 1400 and the polypropylene had an intrinsic viscosity value of 2.2 to 2.5. Chopped lyocell fiber was donated by Tencel. *Quercus rubra* chips of a length less than 5/8" and greater than 3/8" were steam-exploded in a batch reactor after exposure to steam with a temperature of 230°C and a residence time of five minutes. The steam-exploded fiber was washed, dried and stored in a dessicator until further experimentation. For co-steam-explosion experiments the wood chips and polyethylene were combined at levels of 20%, 33% and 50% polyethylene loading. Prior to the introduction of steam, the atmosphere in the pressure vessel was evacuated and replaced with argon, air, or a 50:50 mixture of argon-oxygen gas.

### **Methods:**

TGA was performed with a TA Instruments 9222 Hi-Res instrument with a platinum sample pan for the sample holder. All tests were performed in a nitrogen atmosphere.

#### 1. TGA of PO and wood components:

Analysis of individual components of thermoplastic composites were performed with both a constant heating rate of 20°C/minute and variable Hi-Res™ rate. Samples of 10 milligrams (mg) were heated to 600°C. TA Instruments Thermal Solutions Software was used to transform the TG curve to the derivative thermogravimetric (DTG) curve.

#### 2. TGA Method A: Constant heating rate:

Binary mixtures of dried steam-exploded red oak fiber and polyethylene, with a total mass of ten mg were weighed on a balance with resolution of 0.05 mg. Weight fraction of PE content was varied from 1 to 10 mg in 1mg increments. The samples were scanned with a constant heating rate of 20°C/min from room temperature to 600°C.

#### TGA Method B: High resolution:

Binary mixtures were prepared in a similar manner to the samples with the constant heating rate, except sample size was 11 mg. In addition, PE content increased in increments between 0.1 and 1 mg. The heating method was programmed for 50°C/min with a Hi-Res™ factor of “3” up to 600°C.

#### 3. Data analysis:

The TG curves were transformed into their first derivative ( $\Delta$  weight loss/ $\Delta$  time) and analyzed with TA Instruments Thermal Solutions Software package. Peak areas in the DTG curve related to the decomposition of steam-exploded fiber and polyethylene were calculated with the linear area function. The decomposition of steam-exploded fiber was constant above 385°C resulting in a flat baseline in the DTG curve. The peak above this temperature was attributed to the bulk of the polyethylene decomposition. The range for the computed area of the polyethylene peak was measured from the temperature (or time) at the minimum value after the decomposition peak of steam-exploded fiber to the extrapolated temperature (or time) value at the end of the polyethylene decomposition peak. Peak area was plotted as a function of polyethylene weight fraction and a linear regression equation was obtained. This calibration curve was then used in the quantitative determination of polyethylene content for co-steam-exploded red oak fiber and polyethylene materials.

## Results and Discussion:

### 1. TGA of components:

The thermal degradation profiles of wood, pure cellulose fibers (lyocell), PE and iPP by TGA reveal that most of the degradation events occur between 300 and 500°C (Figure 3.1). Whereas the polyolefins degrade over a 150 to 200°C temperature range, PP at a slightly lower temperature level than PE, wood and cellulose degrade over a much narrower temperature range (less than 50°C) with wood having a slightly more gradual onset than cellulose. Typically wood has a larger shoulder region before the degradation of cellulose due to degradation of hemicelluloses, however most of the hemicelluloses are removed after steam-explosion and water extraction. In addition, wood does not lose more than 60% of its original weight by off gassing before leveling off at 350°C, whereas cellulose has a sharp decline at 360°C with an overall weight loss of 80% (Figure 3.1). This is in general agreement with reports on the thermal degradation of wood and cellulose.<sup>15-16</sup> Moreover, Negro et al.<sup>17</sup> testing steam-exploded wood fiber in an air atmosphere, noted a second peak in the DTG curve due to the degradation of the lignin fraction. The polyolefin degradation temperature range is broader and occurs at lower than reported values with similar heating rates and atmospheres.<sup>18-19</sup> The low value of the molecular weight of the polyethylene may contribute to on-set and peak degradation at lower temperatures.<sup>20</sup>

A comparison of the constant heating rate technique with the “high resolution” method, which employs heating rates adjustable in accordance with the rate of weight loss (Figure 3.2), reveals several significant differences in the decomposition of polyethylene. Whereas the constant heating rate-method produces a single peak with a maximum at 495°C (at a heating rate of 20°C min<sup>-1</sup>) with a shoulder between 250 and 450°C in the first derivative curve for PE, the “high resolution” method indicates three different and clearly distinguishable degradation processes. The latter manifest themselves in stepwise plateaus at 385, 415, and 460°C. These differences are consistent with the expectation that the slower heating rate as the degradation process begins results in a better differentiation of the decomposition events, and in the completion of the degradation at lower temperature (Figure 3.2). A reduced thermal lag, in part, is the mechanism responsible for the better differentiation.

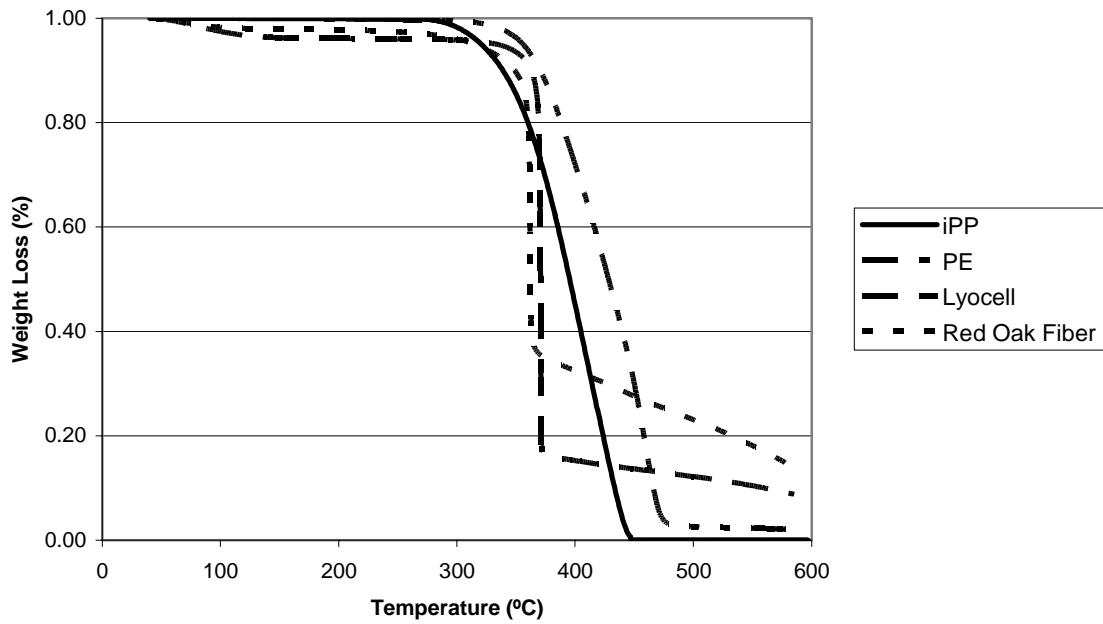


Fig. 3.1 Overlapping degradation profiles for wood-filled thermoplastic components

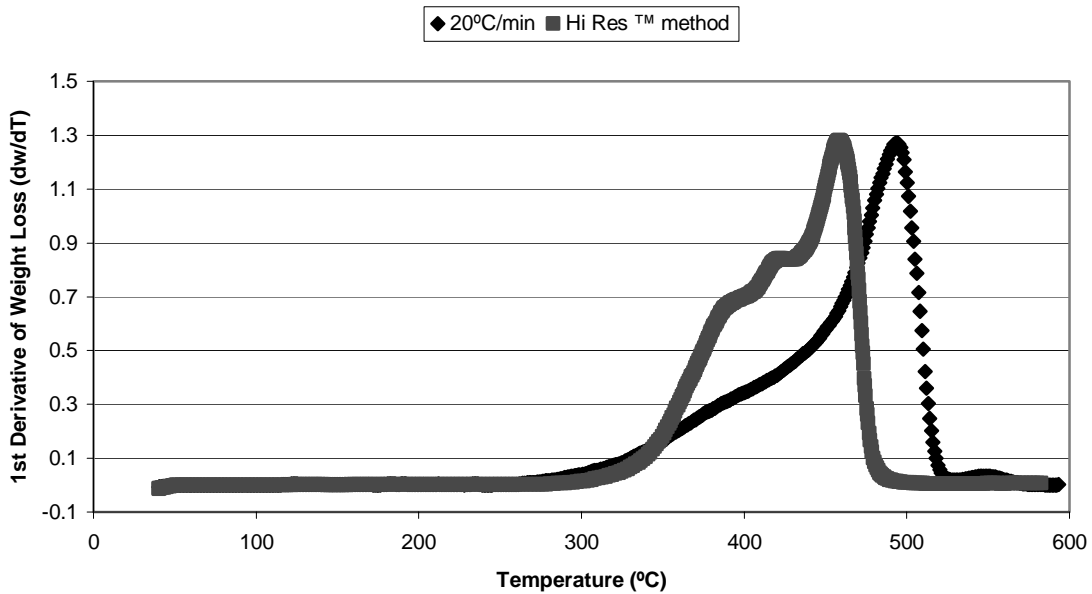


Fig.3.2 Comparison of the constant ramp heating method to the Hi-Res™ variable heating method for polyethylene

## 2. TGA of Composite:

A combination of wood and polyolefins (Figure 3.3) reveals two very distinct degradation events in the derivative curve of the constant heating-rate method, and these represent wood and plastic. These events are virtually baseline separated, and this justifies the adoption of the method for analytical purposes. The data also indicate that the main wood peak migrates to higher temperatures as the PO-content rises; and the PO-peak also migrates to higher temperature with rising PO-content, and it grows progressively broader. Due to the broadening, the baseline separation suffers markedly as the PE content reaches 80%. Therefore the Hi-Res<sup>TM</sup> data for 81% and 91% polyethylene contents are not included in the calibration curves and data for the curves in this range is only from the constant heating ramp experiments.

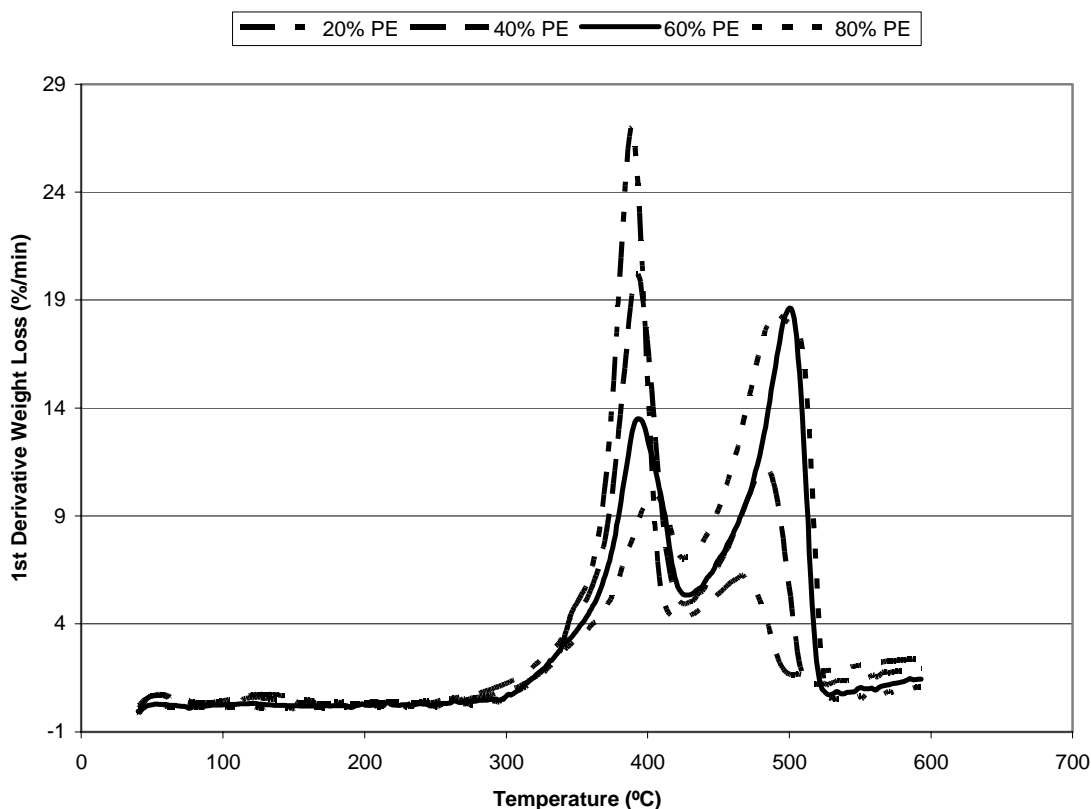


Fig. 3.3 DTG curves of binary mixtures of steam-exploded fiber and polyethylene. Constant heating ramp of 20°C/minute.

The temperature-migration of the PO-peak (Figure 3.4) shows a rising tendency up to 60% PE content after which it remains constant, probably due to overall peak broadening. It is apparent from the data presented that the presence of wood influences the thermal degradation of polyolefins and *vice versa*. This result agrees with a study by Coutinho et al.<sup>19</sup> that investigated the thermal stability of modified wood fibers with polypropylene.

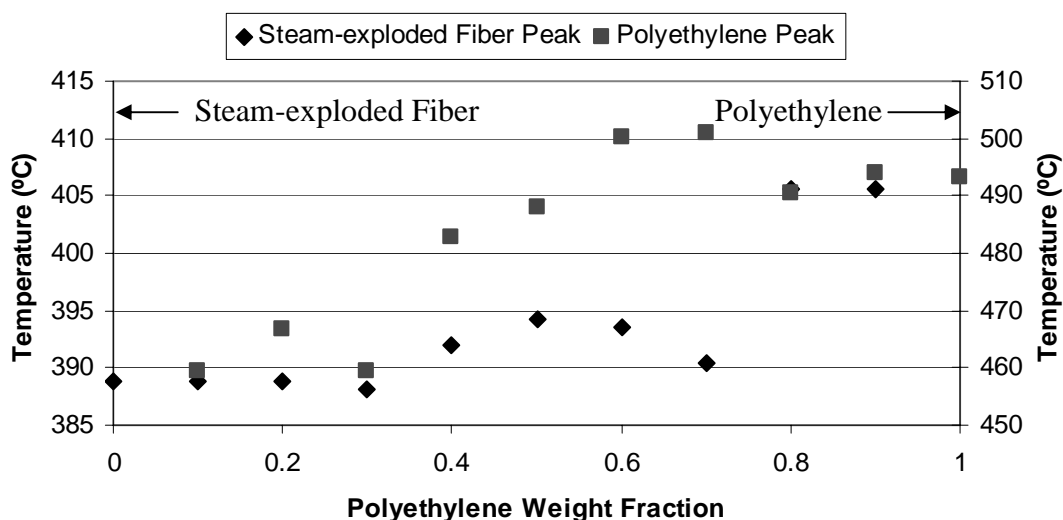


Fig. 3.4 Migration of the DTG curve peak temperature as a function of polyethylene content for both steam-exploded fiber and polyethylene components. Constant heating ramp of 20°C/minute.

The mutual effect of wood and polyolefins on the thermal degradation of the individual components is most dramatically revealed by the high resolution-method (Figure 3.5). Whereas the wood-peak gradually migrates from about 370 to 390°C as the PE-content rises from 36 to 91%, the PE-peak reveals an unexpected behavior: under wood-free conditions, three separate thermal degradation events are identified at 385, 415, and 460°C, as pointed out earlier. In the presence of less than 10% wood, the two lower temperature events are suppressed, and a new shoulder begins to form at high temperature, above the 460°C peak. This latter shoulder grows



to a prominent peak at less than 20% wood content, and it replaces the 460°-peak completely when the wood content reaches 36% (Figure 3.5). In addition, the new peak begins to migrate to lower temperatures, from 485 to 475°, as wood content rises.

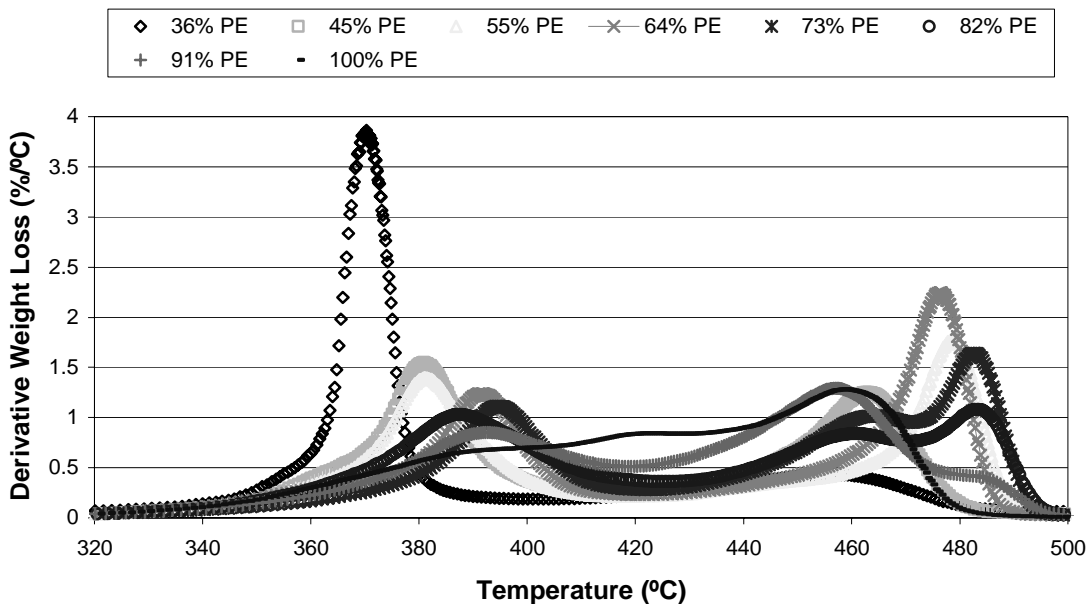


Fig. 3.5 Non-additive effect on the degradation of thermoplastic composite components in a binary mixture using Hi-Res™ heating method.

The data confirm, consistent with the constant heating rate-method, that the presence of wood influences the thermal degradation of polyolefins, and *vice versa*. Both degradation events are delayed and shifted to higher temperatures. This can be attributed to the temperature-dependent formation of char at the expense of gaseous decomposition products. It is the broadening of the PE-peak at PE-contents between < 10 and ca. 40% that results in a loss of baseline separation of the polyolefin and the wood peak.

Jakab et al. noted that the thermal stability of polypropylene in the presence of wood was reduced without influencing the decomposition of wood.<sup>11</sup> The authors linked the amount of wood char to the reduction of both the initial decomposition temperature and maximum rate of

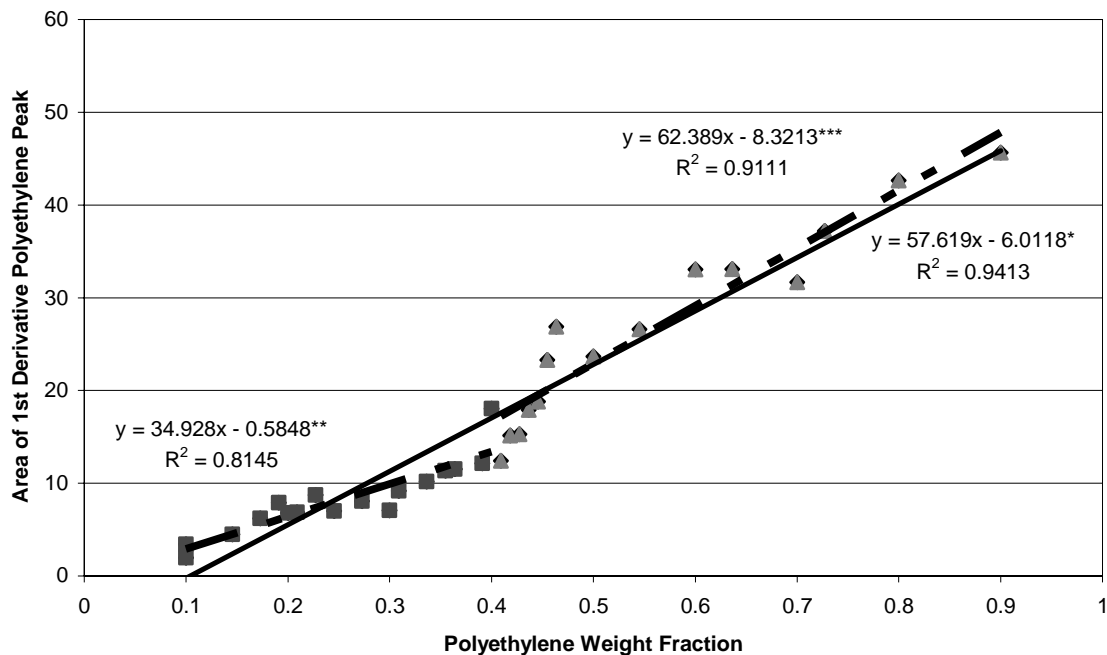
decomposition for polypropylene. Drawing from data using activated charcoal and analyzing the evolved gases Jakab et al. found that co-pyrolysis hindered intermolecular H-transfer with a reduction of step-wise radical transfer reactions.<sup>11</sup> Also, the presence of charcoal enhanced the homolytic scission of polypropylene, explaining the lower decomposition temperature of the polypropylene. The mutual enhancement of stability between wood fiber and polyethylene (Figure 3.3) seems to be in contradiction to the above-mentioned work. The enhancement of thermal stability for polyethylene in the presence of wood may possibly arise from wood reducing the intermolecular H-transfer without an enhanced homolytic scission. Polypropylene is inherently less stable than polyethylene due to the tertiary hydrogen located on the alpha carbon of the polypropylene repeat unit. In other words homolytic cleavage of the polyethylene may not be initiated by the wood decomposition products as seen with polypropylene. Additionally, thermal stability enhancement of the wood fraction may be connected with the scavenging of free radicals by polyethylene during the degradation of wood.

### 3. Calibration:

By preparing various physical mixtures of PE and either lyocell fibers or steam exploded wood fibers, and by determining the area of the derivative-peak for PE, a calibration curve for the composition of a wood plastic-mixture can be established (Figure 3.6). In a crude approximation, a straight-line relationship can be produced from the data points ranging from 10 to 90% PE-content. With greater precision, however, the data points can be represented by two different gradients (i.e., “single” and “double” gradient-method), which are distinct for the PE-content-range between 10 and 40% and another for the range between 40 and 90%. This reflects the change in baseline separation at about 40% PE (Figure 3.5). The parameters for the calibration equation (equation 1) are listed in Table 3.1, where Y is the area of the first derivative curve representing the PE-peak area, X is the PE-content (in %), and m and n are curve-fitting constants.

$$Y = (mX) + n \quad \text{[Eqn. 1]}$$

The parameters for equation 1 differ for the “single-gradient” versus the “double gradient”-method (Table 3.1). For the double gradient method the slope parameter increases approximately two-fold above 40% PE content, indicating a quantitative value for the above-mentioned observation of peak broadening above 40% PE content.



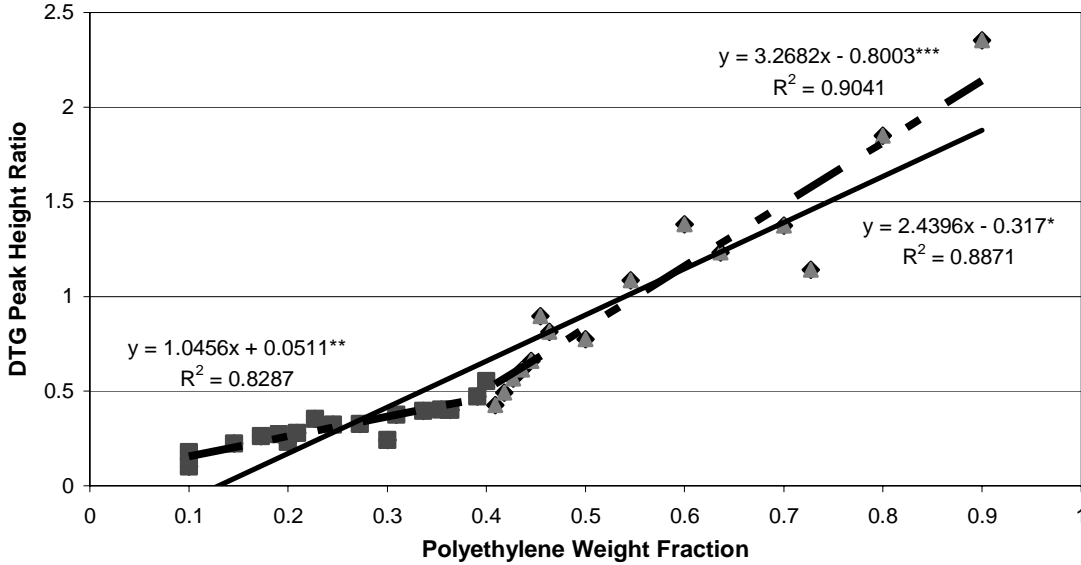
\* Calibration equation for all data, constant heating and Hi-Res™ method

\*\*Double gradient calibration equation for all data less than 40% PE content

\*\*\*Double gradient calibration equation for all data greater than 40% PE content

Figure-3.6 Calibration curves derived from the linear regression of DTG polyethylene peak area v. polyethylene content.

An alternative method of calibration, using peak height ratio instead of peak area (Figure 3.7), also reveals two different gradients, for composites with PE contents below and above 40%. An additional differentiation is recorded between the constant heating rate and the “high resolution” method at PE contents greater than 60%. The high resolution-method produces peaks that fail to differ in height (but not in area if PE content rises above 60%).



\* Calibration equation for all data

\*\*Double gradient calibration equation for PE content less than 40%

\*\*\*Double gradient calibration equation for PE content greater than 40%

Fig-3.7 Calibration curve derived from the linear regression of DTG ratio of polyethylene peak height to steam-exploded wood peak height v. polyethylene content.

Table 3.1. Calibration Parameters Used in Regression Models for Polyolefin Determination

Method	Parameters for Equation $Y = m X + n^1)$		
	M	N	Pred. Error RMS
Single Gradient	57.6	-6.0	4.95
Double Gradient <40% PE	34.9	-0.58	3.96
Double Gradient >40% PE	62.4	-8.32	
Ratio <40% PE	1.05	.05	4.43
Ratio >40% PE	3.3	-0.8	
Step-Function	X	X	7.44

<sup>1)</sup>where Y = area of 1 g. derivative curve representing the PE-peak, and X = PE – content (in %).

Comparing the three calibration methods, single and double-gradient, and step function-method, an error evaluation can be performed by noting the difference between the true PE content value and the predicted PE content (Figure 3.8). This evaluation reveals that using the standard step-function method over the entire PE-range, the error range is  $\pm 20\%$  with the greatest error occurring at low PE-contents (less than 20%). If the single gradient method is applied, the error range is reduced to  $\pm 12\%$ , with the greatest error occurring at the 40 to 50% PE-content transition. The double gradient method produces the smallest error range,  $\pm 10\%$ , with the best performance at PE-contents of less than 40%, and the greatest error being detected at approximately 50% PE-content. The root mean square (RMS) value, which is a measure of the magnitude of error from zero, is greatest for the step method, 7.44 and reduces to 4.95 and 3.96 for the single and double gradient calibration methods, respectively. A comparison of peak area and peak height method (Figure 3.9) reveals general agreement, with an error range reduced to  $\pm 15\%$  with the double gradient method. The RMS value for the predicted error using this calibration method is 4.42.

It should be noted that although error is reduced with the double gradient method the goodness of fit parameter, "R<sup>2</sup>" is reduced for the equations of PE content from 10-40%. This is in part due to the reduction in the range of values for the PE content. However, the linear regression model still is an excellent predictor with a P-value<0.0001 for all calibration equations within the double gradient regression model.

#### **4. Application of method to wood fibers produced by joint steam explosion with polyethylene:**

Applying the analytical methodology using the double gradient methodology to wood fibers produced by steam explosion in the presence of polyethylene (Figure 3.10) a remarkable agreement between formulation parameters and polyethylene content is produced. This provides the method with a high level of confidence. Applying the step-function procedure by attributing the weight loss below 400°C to wood and above 400°C to polyethylene the error analysis follows a similar trend to the one found with the prediction data. The error is maximum for the 20% PE loading with an error value of 23% and minimum for 50% PE loading with an error value of 4%; this assumes the initial loading value is the true polyethylene content value.

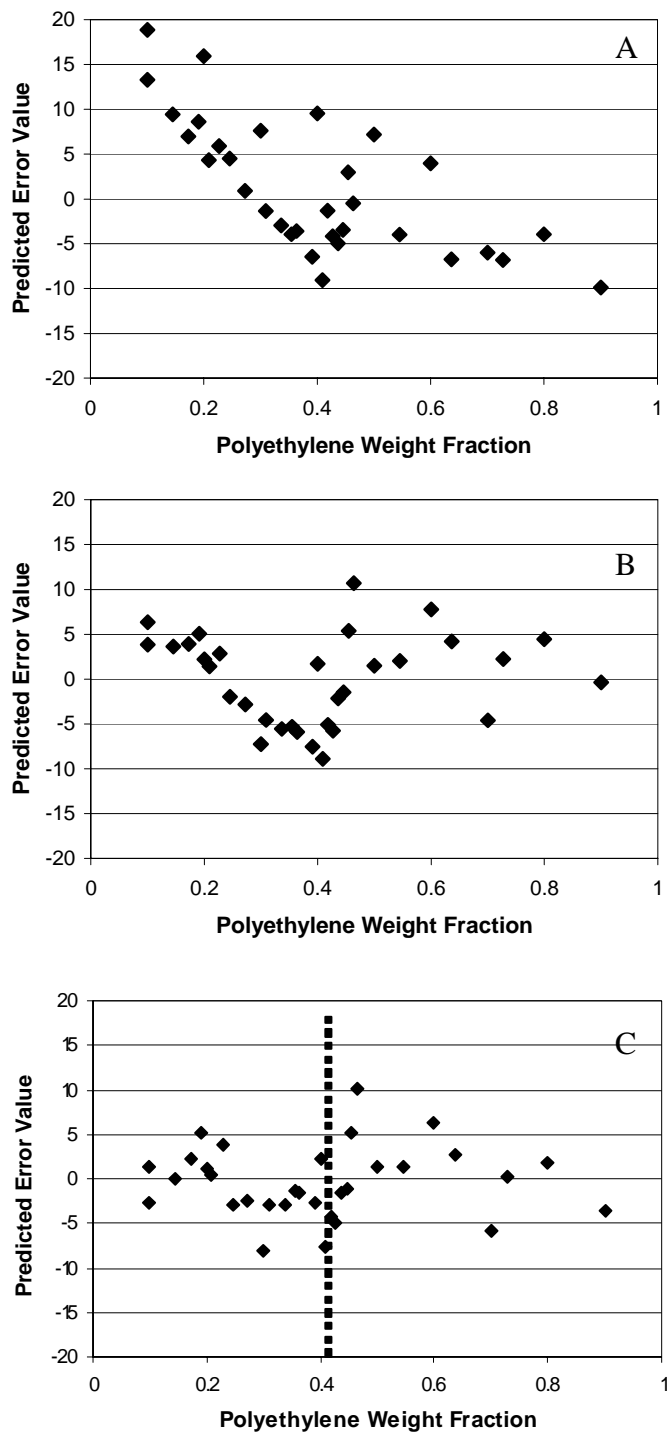


Fig. 3.8 Error of prediction of actual polyethylene content when using step and calibration methods for polyethylene determination. A) Step method, B) Single Gradient, C) Double Gradient

In addition, most TGA equipment requires sample size to be in the milligram range. By measuring random samples of 10 mg, as performed in this experiment, the method provides a test of homogeneity for the processing method. With relatively little scatter in the data (Figure 3.10), for the 33% polyethylene loading treatment, the method shows approximately that for every 7 mg of wood fiber there is 3 mg of polyethylene. This provides evidence that the polyethylene is distributed with the wood fiber in the milligram range.

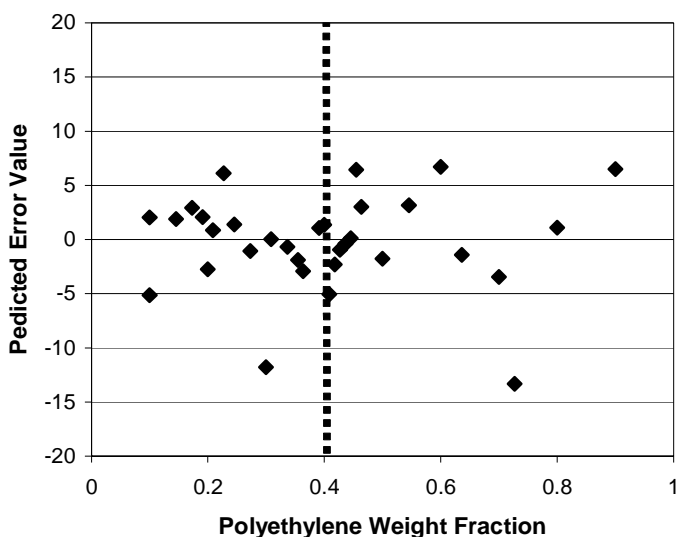


Fig. 3.9 Error of prediction of actual polyethylene content when using peak height ratio calibration method for polyethylene determination

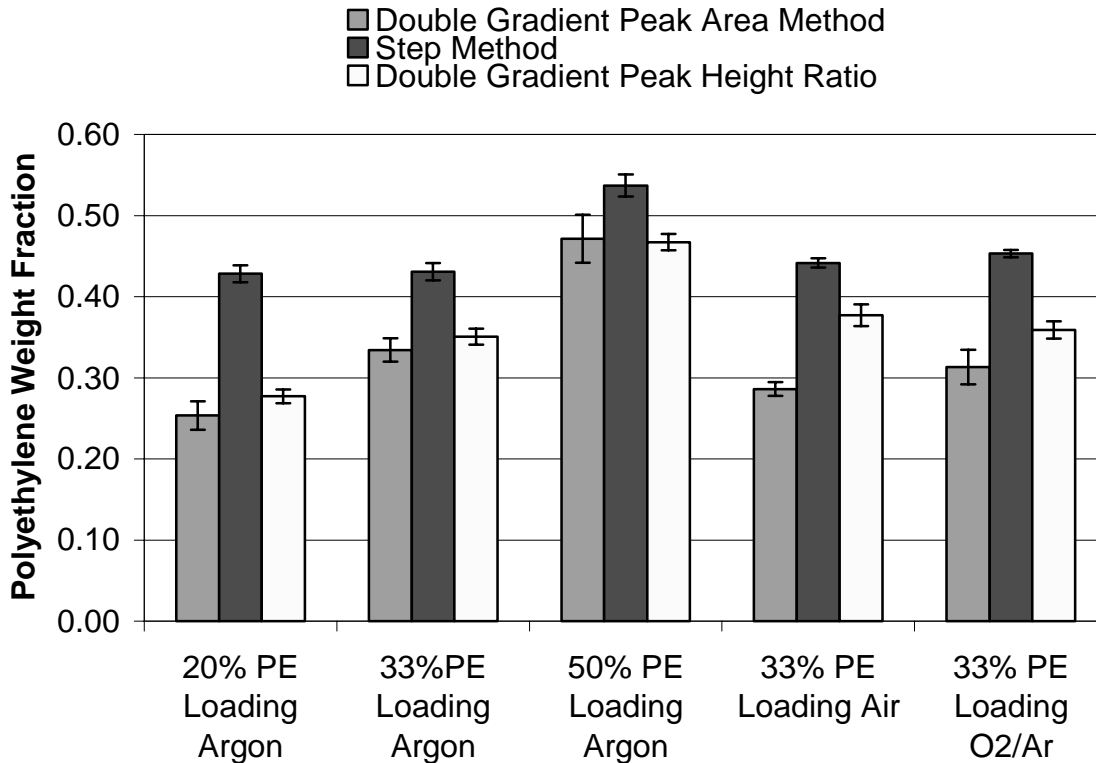


Fig. 3.10 Double gradient calibration method used to determine polyethylene content in co-steam- exploded wood.

### Conclusions:

Thermogravimetric analysis (TGA) is a useful technique for the quantitative determination of the composition of thermoplastic wood composites with polyolefins, PE and iPP. By using the area of peaks found in the DTG curve, more data points are included in the component analysis making the procedure more robust as compared with the standard step analysis procedure. In the latter procedure only the temperature for the on-set of weight loss and corresponding weight loss point is used to calculate the composition of components while all other points are neglected. This limits the step procedure to mixtures where there is no overlap of degradation for any of the components. Contrary to the step analysis procedure, the calibration method offers a reduced error for component analysis when there is partial baseline separation of degradation peaks of *the first derivative* curve. In addition, by utilizing a



regression model to predict the component quantity, concerns of a mutual degradation influence are addressed by the model.

Although wood and polyolefins mutually influence each other in the composite mixture, and a shift in peak location on the temperature scale is observed, the calibration method holds with the range in prediction error between  $\pm 10$  and 12% and a RMS value of 3.96 to 4.95. The TGA-method may involve the standard, constant heating-rate-technique, or a “high resolution” method that adjusts heating rate in accordance with rate of weight loss. Peak broadening in the high resolution-method at PE-contents of greater than 40% makes this method slightly less desirable.

The relationship between area of the PE-peak in the derivative curve and PE-content has two different sets of parameters, reflecting two different gradients, for composites with PE-contents below and above 40%. This is the result of the mutual effect wood and polyolefins have on each other. If the more sensitive double gradient calibration method is applied, the precision of the method is significantly increased with a reduction in the “RMS” to 3.95, and the linear model equations having a P-value < .0001. The error range of predicted values rises as high as 12% if a single set of calibration parameters is applied.

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