

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 base-

line 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. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1484–1492, 2004

Key words: thermogravimetric analysis (TGA); polyolefins; thermoplastic; wood; composites

INTRODUCTION

The thermoplastic wood composites industry is currently undergoing rapid growth, with more combinations and more structural lumber profiles being introduced into the marketplace.¹ 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,^{2–4} interfacial compatibility,^{5–8} and method of compounding,⁹ 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 that 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 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 Blazey¹⁰ 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.^{11–14} One conclusion (from Sharypov et al.¹²) shows a nonlinear dependence of the degradation products on the ratio of wood to polyolefin fraction. 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

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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.,¹² 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 nonadditive 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 corefining 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 1,400 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 5 min. The steam-exploded fiber was washed, dried, and stored in a desiccator until further experimentation. For costeam-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.

TGA of PO and wood components

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

TGA method A: constant heating rate

Binary mixtures of dried steam-exploded red oak fiber and polyethylene, with a total mass of 10 mg were weighed on a balance with a resolution of 0.05 mg. Weight fraction of PE content was varied from 1 to 10 mg in 1-mg 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.

Data analysis

The TG curves were transformed into their first derivative (Δ weight loss/ Δ 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 costeam-exploded red oak fiber and polyethylene materials.

RESULTS AND DISCUSSION

TGA of components

The thermal degradation profiles of wood, pure cellulose fibers (lyocell), PE, and iPP by TGA reveal that

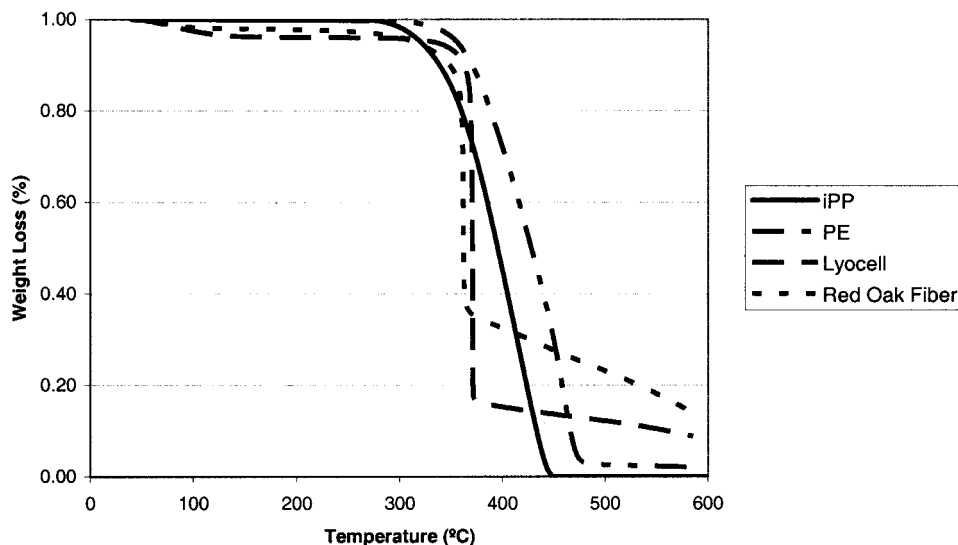


Figure 1 Overlapping degradation profiles for wood-filled thermoplastic components.

most of the degradation events occur between 300 and 500°C (Fig. 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% (Fig. 1). This is in general agreement with reports on the thermal degradation of wood and cellulose.^{15,16}

Moreover, Negro et al.,¹⁷ 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.^{18,19} The low value of the molecular weight of the polyethylene may contribute to onset and peak degradation at lower temperatures.²⁰

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 (Fig. 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

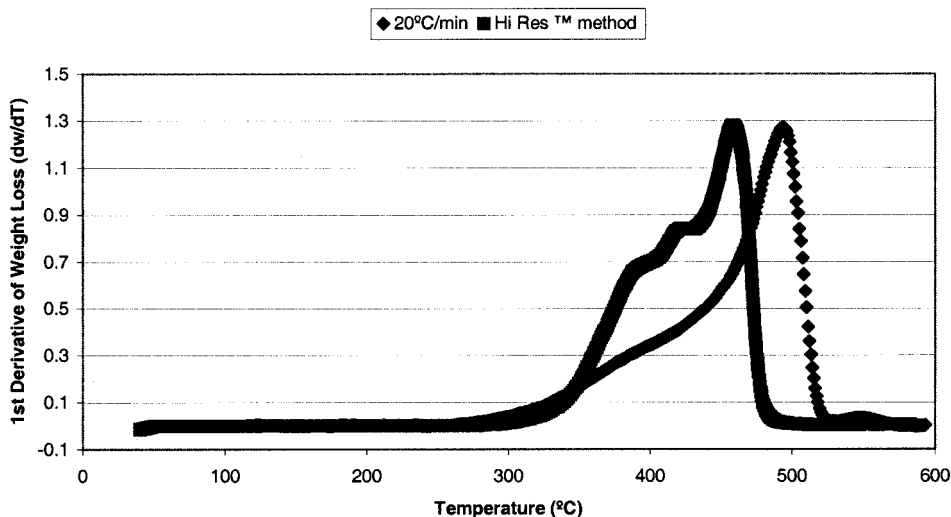


Figure 2 Comparison of the constant ramp heating method to the Hi-Res™ variable heating method for polyethylene.

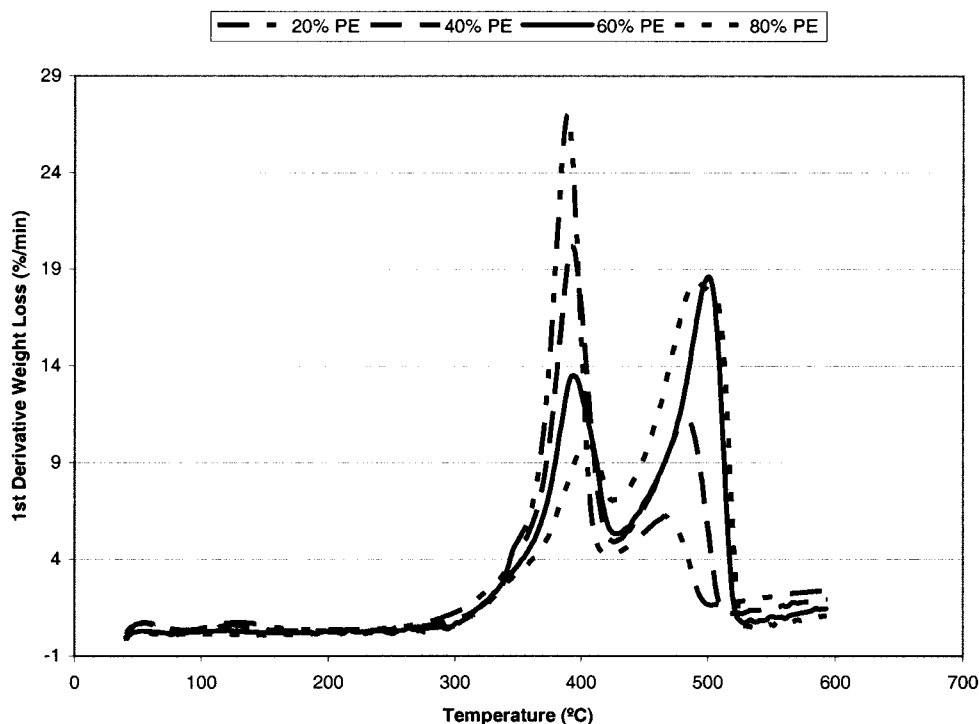


Figure 3 DTG curves of binary mixtures of steam-exploded fiber and polyethylene. Constant heating ramp of 20°C/min.

20°C min⁻¹) 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 (Fig. 2). A reduced thermal lag, in part, is the mechanism responsible for the better differentiation.

TGA of composite

A combination of wood and polyolefins (Fig. 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-ResTM data for 81 and 91% polyethylene contents are not included in the calibration curves and data for

the curves in this range are only from the constant heating ramp experiments.

The temperature migration of the PO peak (Fig. 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.¹⁹ that investigated the thermal stability of modified wood fibers with polypropylene.

The mutual effect of wood and polyolefins on the thermal degradation of the individual components is most dramatically revealed by the high resolution method (Fig. 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°C peak completely when the wood content reaches 36% (Fig. 5). In addition, the new peak begins to migrate to lower temperatures, from 485 to 475°C, as wood content rises.

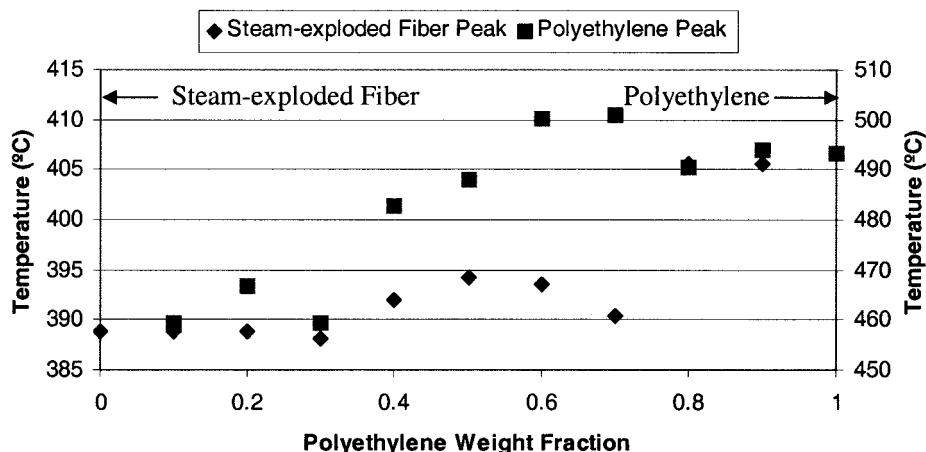


Figure 4 Migration of the DTG curve peak temperature as a function of polyethylene content for both steam-exploded fiber and polyethylene components. Constant heating ramp of 20°C/min.

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 ~ 40% that results in a loss of baseline separation of the polyolefin and the wood peak.

Jakab et al.¹¹ noted that the thermal stability of polypropylene in the presence of wood was reduced without influencing the decomposition of wood. 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 ana-

lyzing the evolved gases Jakab et al.¹¹ found that copyrolysis hindered intermolecular H-transfer with a reduction of stepwise radical transfer reactions. 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 (Fig. 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 prod-

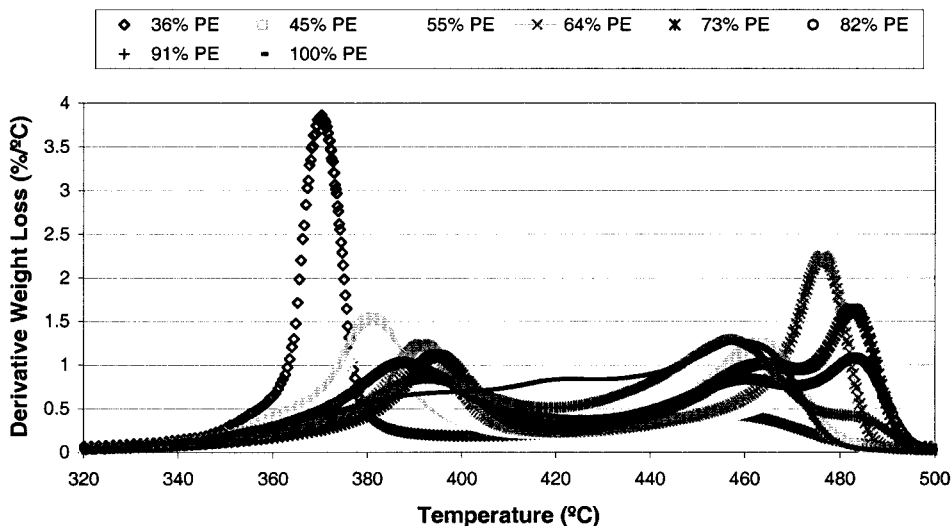


Figure 5 Nonadditive effect on the degradation of thermoplastic composite components in a binary mixture using Hi-Res™ heating method.

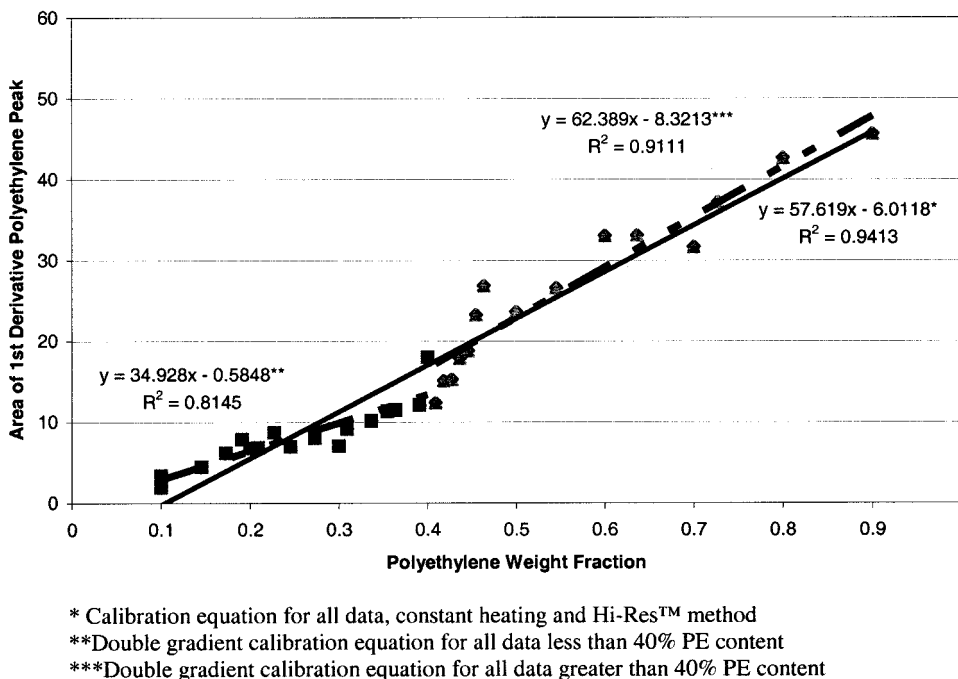


Figure 6 Calibration curves derived from the linear regression of DTG polyethylene peak area versus polyethylene content.

ucts 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.

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 (Fig. 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 (Fig. 5). The parameters for the calibration of equation 1 are listed in Table I, 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.

$$Y = (mX) + n \tag{1}$$

The parameters for eq. 1 differ for the “single-gradient” versus the “double gradient” method (Table I). For the double gradient method the slope parameter

increases approximately twofold above 40% PE content, indicating a quantitative value for the above-mentioned observation of peak broadening above 40% PE content.

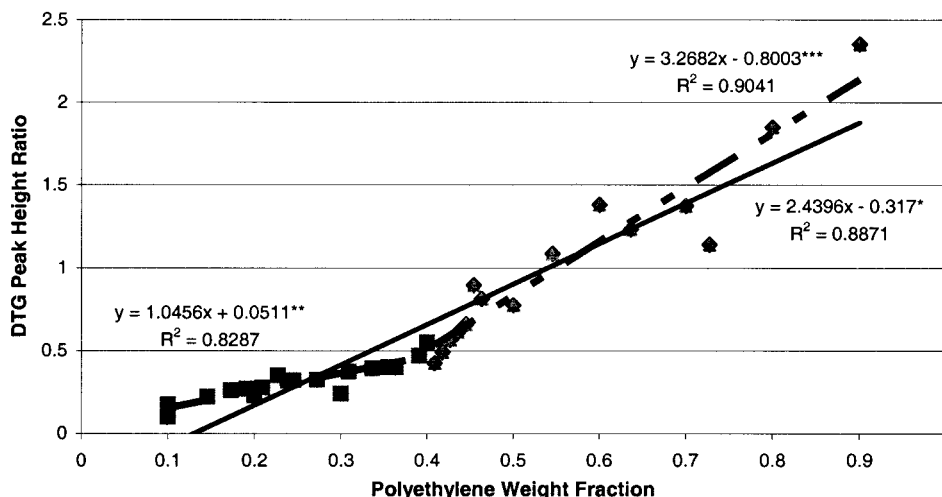
An alternative method of calibration, using peak height ratio instead of peak area (Fig. 7), also reveals two different gradients, for composites with PE contents below and above 40%. An additional differentiation is recorded between the constant heating rate and the high resolution method at PE contents 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%).

Comparing the three calibration methods, single and double gradient and step function method, an

TABLE I
 Calibration Parameters Used in Regression Models for Polyolefin Determination

Method	Parameters for equation $Y = mX + n^a$		
	M	N	Predicted 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	3.96
Ratio < 40% PE	1.05	0.05	4.43
Ratio > 40% PE	3.3	-0.8	4.43
Step-function	X	X	7.44

^a Where Y = area of 1 g derivative curve representing the PE peak, and X = PE – content (in %).



* 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%

Figure 7 Calibration curve derived from the linear regression of DTG ratio of polyethylene peak height to steam-exploded wood peak height versus polyethylene content.

error evaluation can be performed by noting the difference between the true PE content value and the predicted PE content (Fig. 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 (Fig. 9) reveals general agreement, with an error range reduced to ± 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^2 , is reduced for the equations of PE content from 10 to 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.

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 (Fig. 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 that 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 is minimum for 50% PE loading, with an error value of 4%; this assumes the initial loading value is the true polyethylene content value.

In addition, most TGA equipment requires sample sizes 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 (Fig. 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.

CONCLUSION

Thermogravimetric analysis is a useful technique for the quantitative determination of the composition of

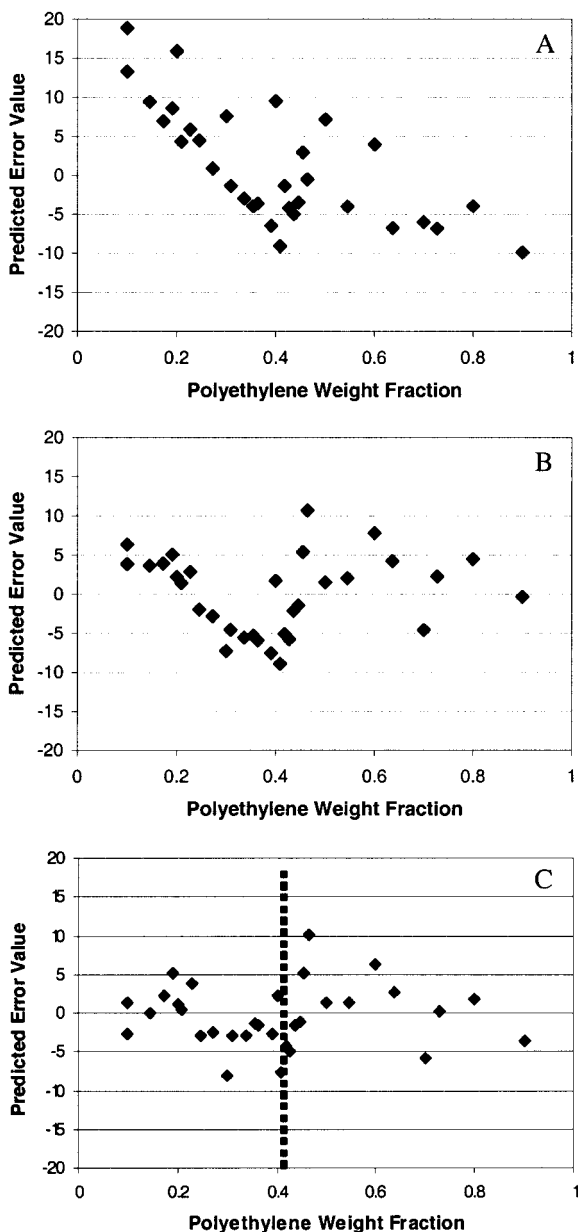


Figure 8 Error of prediction of actual polyethylene content when using step and calibration methods for polyethylene determination. (A) Step method, (B) single gradient, (C) double gradient.

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 compared with the standard step analysis procedure. In the latter procedure only the temperature for the onset 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 in which there is no overlap of degradation for any of the components. Contrary to the step analysis procedure, the calibration

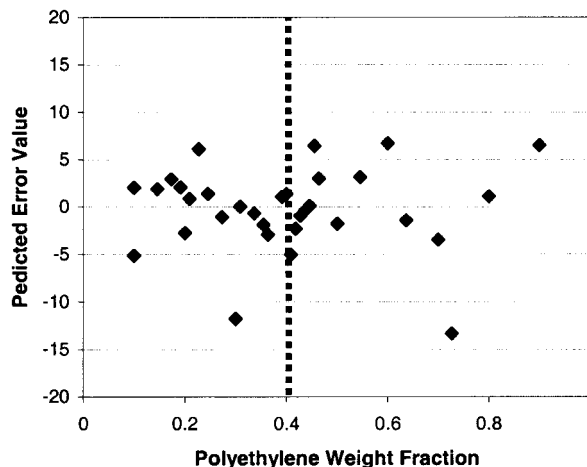


Figure 9 Error of prediction of actual polyethylene content when using peak height ratio calibration method for polyethylene determination.

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 ± 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.

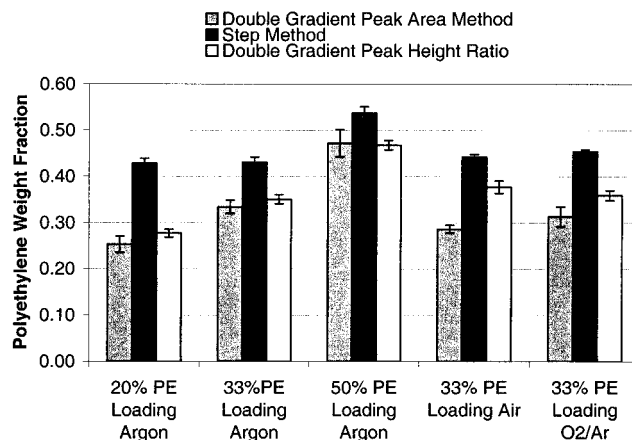


Figure 10 Double gradient calibration method used to determine polyethylene content in costeam-exploded wood.

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 < 0.0001 . The error range of predicted values rises as high as 12% if a single set of calibration parameters is applied.

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