Thermogravimetric Analysis Studies of Thermally-treated Glycerol Impregnated Poplar Wood

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The effects of glycerol pretreatment and thermal modification on poplar wood was examined using thermogravimetric analysis (TGA). The total mass losses of thermally-treated samples before and after glycerol impregnation were studied. The thermal degradation process was divided into three stages based on natural breaks in the slope of the TGA curves. The set-on and set-off temperatures, mass loss, and activation energy (E_a) of each stage were compared. Pretreatment with 60% glycerol followed by thermal modification at 160 °C produced pronounced differences in the three decomposition stages. Fewer wood components were decomposed in the first stage in glycerol-pretreated wood, which suggested that the pretreatment had modified the wood components into more thermally stable substances. However, the mass losses were higher in the next stage, suggesting that the effect on thermal stability was limited. The E_a values of wood decomposition during the first stage were decreased, while those during the second and third stages were increased. These results illustrate the potential for using a glycerol pretreatment to alter the thermal stability of wood.

Keywords: Thermogravimetric analysis (TGA); Glycerol impregnation; Thermal treatment; Kinetic analysis

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INTRODUCTION

Thermal modification is an environmentally attractive wood treatment method that is performed in a protected atmosphere or in a liquid medium under high temperature conditions. The process has been reported to improve wood color (Ayadi *et al*. 2003; Shi and Jiang 2011), dimensional stability (Stamm and Hanson 1937; Burmester 1973), and decay resistance (Kamdem *et al*. 2002; Schwarze and Spycher 2005).

Thermogravimetric analysis (TGA) has been used widely to study the pyrolysis process and thermal stabilities of thermoplastic wood (Scott *et al*. 2004), liquefied wood polymer composites (Doh *et al*. 2005), thermally-modified wood (Chen *et al*. 2011), and ionic liquid-modified wood (Patachia *et al*. 2013).

Analysis of the thermogravimetric (TG) curve can be used to determine the pyrolysis parameters, such as residual mass, pyrolysis stage division, set-on temperature, and set-off temperature, of the pyrolysis stages (Kercher and Nagle 2001; Grønli *et al*. 2002; Doh *et al*. 2005). The differential thermogravimetric (DTG) curve is derived from the first derivative of the TG curve and reveals the pyrolysis rate of the sample. Safi *et al*. (2004) studied the thermal degradation of pine needles and reported that the entire degradation range could be divided into four stages based upon the natural breaks in the slope of the TG curves. The activation energy of each stage was calculated and compared.

Shen *et al.* (2009) studied the thermal properties of four species of wood and separated the DTG curves into a first stage with a range of 200 °C to 370 °C characterized by hemicellulose and cellulose degradation, and a second stage with a temperature range of 370 °C to 490 °C where lignin was decomposed. Several studies report three main stages of thermal decompositions, including dehydration (26.85 °C to 106.85 °C), active pyrolysis (176.85 °C to 386.85 °C), and passive pyrolysis (> 386.85 °C). Two peaks observed in active pyrolysis are related to hemicellulose and cellulose decompositions, while lignin is decomposed during both the active and passive pyrolysis stages without any characteristic peaks in the thermogram (Strezov *et al*. 2003; Gašparovič *et al*. 2010; Slopiecka *et al*. 2012).

Kinetic analysis can also be applied to thermal analysis. According to the Arrhenius formula, the kinetic parameters, such as activation energy (E_a) and pre-exponential factor (A), are obtained after a series of calculations (Safi *et al*. 2004; Fang *et al*. 2006; Gašparovič *et al*. 2010). Gašparovič *et al.* (2010) calculated that the activation energy of wood chips (residual processing wood) during the main decomposition stage ranged from 190 kJ/mol to 217 kJ/mol. Studies from the pyrolysis of several hardwoods and softwoods have revealed that wood devolatilizes at temperatures above 280 °C in three parallel reactions (Grønli *et al.* (2002). The activation energies for hemicellulose, cellulose, and lignin were determined as 100 kJ/mol, 236 kJ/mol, and 46 kJ/mol, respectively. Bartocci *et al.* (2017) studied pyrolysis of biomass pellets (10% glycerol and 90% sawdust) and described glycerol pyrolysis as a first order reaction. They also calculated activation energies and pre-exponential factors for hemicellulose, cellulose, lignin, and glycerol.

Glycerin is a major by-product of biodiesel production. Increased biodiesel production should provide abundant supplies of low cost glycerol. Manara and Zabaniotou (2016) suggested that co-valorization of crude glycerol with waste biomass could help decrease biodiesel production costs, while providing an application for waste glycerol. Fantozzi *et al.* (2016) studied the pyrolysis kinetics of glycerol and developed a skeletal kinetic model of glycerol pyrolysis. They found that non-condensable gas yields of 70% (wt basis) could be achieved at 750 to 800 °C with hydrogen concentrations up to 44 ~ 48% (volume basis). Yields increased the increasing temperature.

Previous studies have suggested that glycerol impregnation prior to thermal modification improved the physical properties of wood. For example, the dimensional stability of compressed wood was improved when wood was pretreated with 40% glycerol solution prior to compression (Inoue *et al*. 2000). Yan *et al.* (2010) reported that the compression deformation was more permanent when the wood was impregnated with 50% glycerol followed by thermal modification at 160 °C for 60 min. Douglas-fir (*Pseudotsuga menziesii*), when impregnated with 20% glycerol solution prior to thermal modification at 200 °C for 6 h, showed a higher anti-swelling efficiency (48%) than normal thermally-modified wood (26%) (Yan and Morrell 2014). However, the effects of glycerol on thermal degradation reactions are unknown.

The objective of this study was to assess the effects of a glycerol treatment followed by thermal modification on the thermal properties of wood using thermogravimetric analysis (TGA). Activation energy (E_a) was also used to study the effects of the glycerol pretreatment on the thermal degradation reactions.

EXPERIMENTAL

Materials

Poplar wood (*Populus tomentosa*), from Xian Yang City, Shaanxi Province, China, that was free of defects or biological attack was ground to pass through 40- to 60-mesh screens.

Methods

Glycerol treatment

Wood powder ground to pass a 20 mesh screen was first mixed with an excess of glycerol solution (99 % concentrate) diluted with water to 20%, 60%, or 100% (wt/wt) and a screen was placed over the wood material to limit the particles from floating. The material was then subjected to vacuum (0.09 MPa) for 30 min. The vacuum was released and the glycerol was drained. The treated ground wood was then oven-dried at 60 °C for 3 d.

Thermal modification

The glycerol-impregnated and non-impregnated wood powders were thermally-treated by placing them in an oven at 120 °C, 140 °C, 160 °C, 180 °C, or 200 °C for 4 h. The resulting powders were washed with anhydrous ethanol in an ultrasonic cleaner for 30 min, then the ethanol was removed, and the wood was oven-dried to a constant weight at 60 °C. This step removed residual, non-reacted glycerol that might interfere with subsequent thermogravimetric analyses.

TGA measurement

The TGA (thermogravimetric analysis) measurements were performed using a Mettler TGA/DSC 3+ synchronous thermal analyzer (Mettler-Toledo, Zurich, Switzerland). High purity nitrogen was used at a flow rate of 50 mL/min as the carrier gas to maintain pyrolysis conditions. Five milligrams (± 1.0 mg) of wood powder was added to the holder and the temperature was raised from room temperature to 600 °C at a rate of 10 °C/min. The decomposition stages were divided using the TG curves as described earlier, the set-on and set-off temperatures were found, and reaction enthalpy was calculated using Mettler STARe Software (V15.00, Mettler-Toledo, Zurich, Switzerland).

Kinetic theory

The pyrolysis process in biomass is a series of complex reactions. The effect of reaction temperature on active energy was usually neglected, assuming that the reaction met the simple kinetic equation. The kinetic reaction equation (Eq. 1) of a sample pyrolysis reaction was expressed as follows:
Pyrolysis reaction rate.

$$V = \frac{\mathrm{d}a}{\mathrm{d}t} = k(1-a)^n \tag{1}$$

where

$$a(\%) = \frac{w_0 - w}{w_0 - w_\infty} \times 100$$

and where W_0 denotes the initial mass of the sample (mg), *a* represents the mass loss rate (%), *W* is the mass of sample at temperature *T* (mg), and W_∞ denotes the final quantity of the sample (mg).

According to the Arrhenius formula, the reaction rate constant is given by:

$$k = A\exp(-\frac{E}{RT}) \tag{2}$$

The heating rate $\phi = (\mathrm{d}T / \mathrm{d}t)$ in the experiment was constant.

A combination of Eqs. 1 and 2 gives the fundamental expression Eq. 3,

$$\frac{\mathrm{d}a}{\mathrm{d}T} = \frac{A}{\Phi}\exp\,(-\frac{E}{RT})(1-a)^n \tag{3}$$

which was integrated to obtain the following Eq. 4:

$$\int_b^a \frac{\mathrm{d}a}{(1-a)^n} = \int_{T_0}^{T} \frac{A}{\Phi}\exp(-\frac{E}{RT})\mathrm{d}T \tag{4}$$

Allow $\frac{E}{RT} = \frac{1}{x}$, then $T = \frac{E}{R}x$, $\mathrm{d}T = \frac{E}{R}\mathrm{d}x$, an then

$$\int_b^a \frac{\mathrm{d}a}{(1-a)^n} = \frac{AE}{\Phi R}\int_{X_0}^{X} \exp(-\frac{1}{x})\mathrm{d}x \tag{5}$$

With Doyle's approximation (Flynn and Wall 1966; Tripathi and Srivastava 2011), which allows for E/RT ≥ 20, Eq. 5 now can be simplified as:

$$\frac{AE}{\Phi R}\int_{X_0}^{X} \exp(-\frac{1}{x})\mathrm{d}x = -2.135-0.4567\frac{E}{RT} \tag{6}$$

Thus, a linearized pyrolysis kinetic equation can be obtained.

When n = 1 , then

$$\ln(-\ln(1-a)) = \ln\frac{AE}{\Phi R} - 2.315 - 0.4567\frac{E}{RT} \tag{7}$$

When n ≠ 1 , then

$$\ln(\frac{(1-a)^{n-1}}{n-1}) = \ln\frac{AE}{\Phi R} - 2.315 - 0.4567\frac{E}{RT}\ , \tag{8}$$

where φ is the rate of heating (K/min), *A* is the pre-exponential factor (1/min), *R* is the gas constant [8.314 J/(K·mol)], *T* is the heating temperature (K), and *E* represents the activation energy (kJ/mol).

To facilitate the analysis and comparison of the results, the wood pyrolysis process was assumed as a primary reaction (n = 1).

Allow $Y = \ln(-\ln(1-a))$, $X = \frac{1}{T}$, $a_1 = -0.4567\frac{E}{R}$, $b_1 = \ln\frac{AE}{\Phi R} - 2.315$, then a linear function was obtained as follows:

$$Y = a_1 X + b_1 \tag{9}$$

The linear function (Eq. 9) was obtained by linear regression of the temperature (*T*) and mass loss rate (*a*) of the TG curve in each wood pyrolysis process. The slope *a1* and the intercept *b1* of the linear function were obtained. These values were used to determine the activation energy (E_a) and the pre-exponential factor *A*.

RESULTS AND DISCUSSION

TGA Analysis

The TG (thermogravimetric) curves for the thermally modified (at 120 °C to 200 °C), non-impregnated, and glycerol-impregnated poplar wood are shown in Fig. 1. The TG curves for the control, thermally modified, and glycerol pretreated/thermally-modified wood samples showed similar trends. The mass loss processes of all samples could be divided into three stages, such as the water evaporation phase, thermal degradation phase, and carbonization phase, according to the rate of mass loss. Free and bound water evaporated during the water evaporation phase (35 °C to 100 °C) (Gašparovi *et al.* 2010; Slopiecka *et al.* 2012). Wood components degraded rapidly during the thermal degradation phase (220 °C to 390 °C), and the corresponding mass losses rapidly increased reflecting the decompositions of hemicelluloses, cellulose, and partial lignin. Thermal degradation slowed during the carbonization phase (> 390 °C) and the mass losses reflected decomposition of the remaining lignin and combustion of char residues (Orfao *et al.* 1999; Safi 2004; Shen *et al.* 2009).

The residual mass of thermally modified wood ranged from 14.38% to 18.76%, which were higher than those for the control sample (14.31%) (Table 1). The residual mass of glycerol-pretreated wood ranged from 8.55% to 14.68%. However, the residual masses of glycerol-pretreated wood exposed to the same thermal modification temperature were lower than those for the material that was only thermally modified. These results suggested that the thermal degradation of wood decreased after thermal treatment, while glycerol impregnation before thermal treatment accelerated the degradation.

Table 1. Effect of Glycerol Pretreatment and Thermal Modification on Residual Masses of Polar Wood Following Thermogravimetric Analysis

	Residual Mass Loss (%)			
Thermal Modification Temperature (°C)	No Glycerol Pre-treatment	20% Glycerol Pre-treatment	60% Glycerol Pre-treatment	100% Glycerol Pre-treatment
-	14.13	-	-	-
120	15.10	13.95	13.13	8.55
140	14.39	10.97	13.66	13.25
160	14.38	12.80	8.90	13.49
180	14.80	14.08	13.50	14.02
200	18.76	13.67	14.40	14.68

The variations seen in the decomposition rates of wood components were well recognized in the second peak in Fig. 2. Glycerol impregnation followed by thermal modification appeared to affect the decompositions of wood components. These effects were further explored by dividing the second peak into three stages according to the three steps found from the DTG (differential thermogravimetric) curves. An example of this approach is shown for samples that were impregnated with 20% glycerol prior to thermal modification at 120 ℃ (Fig. 3).

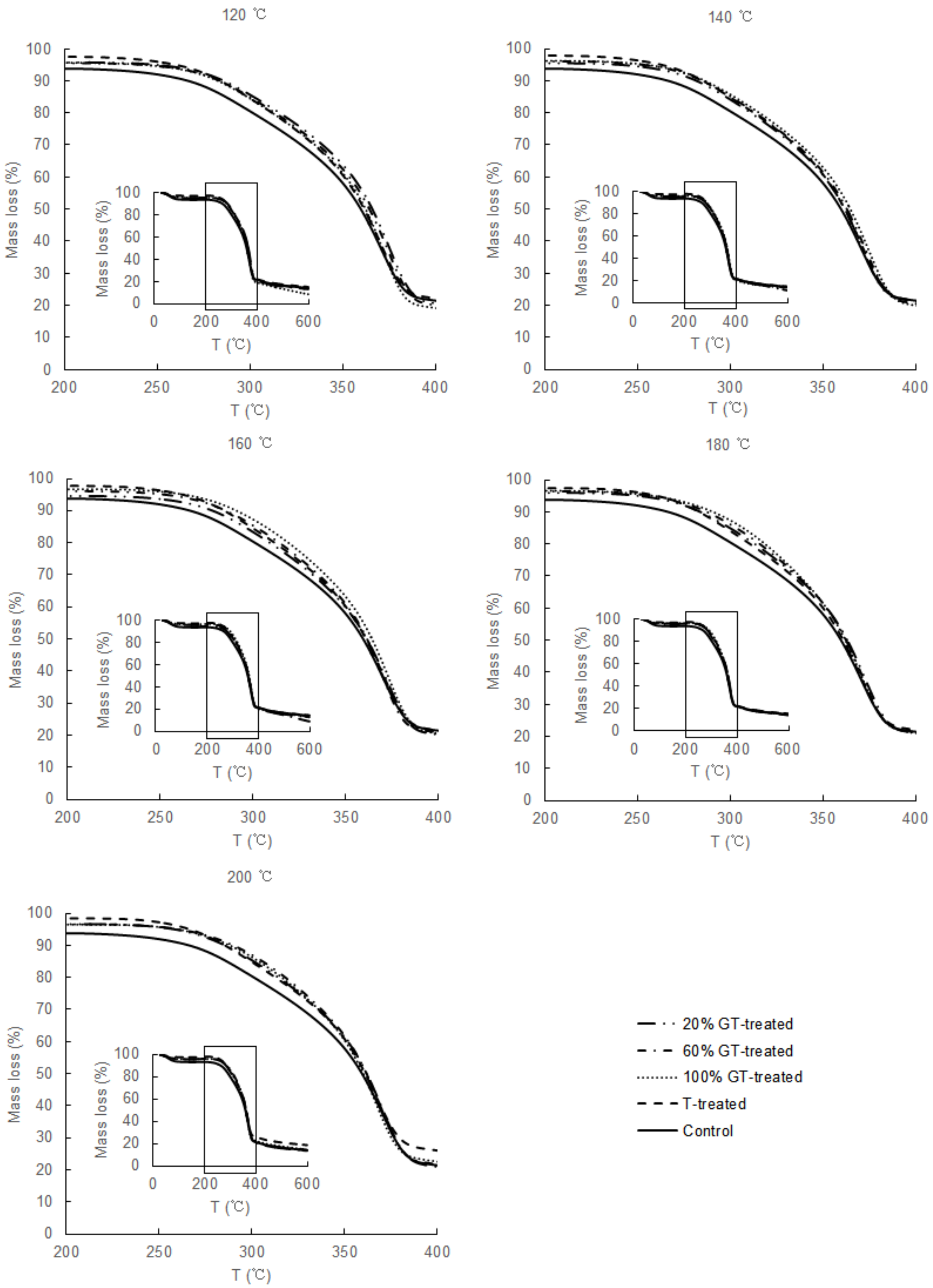

Fig. 1. Effects of glycerol pretreatment and thermal modification on TG curves of poplar (*Populus tomentosa*)

The set-on and set-off temperatures were found at each treatment level in the DTG curve, and then the TG (thermogravimetric) curves were divided into three stages using the corresponding temperatures. The R^2 for the regression lines for these curves were above 0.88, although the slopes of the lines indicated that reaction rates differed for each stage (Fig. 4). The set-on and set-off temperatures and calculated mass losses for the three stages are shown in Table 2. The temperature ranges of the three stages for the controls were 226.7 °C to 287.4 °C, 287.4 °C to 338.7 °C, and 338.7 °C to 389.2 °C, respectively.

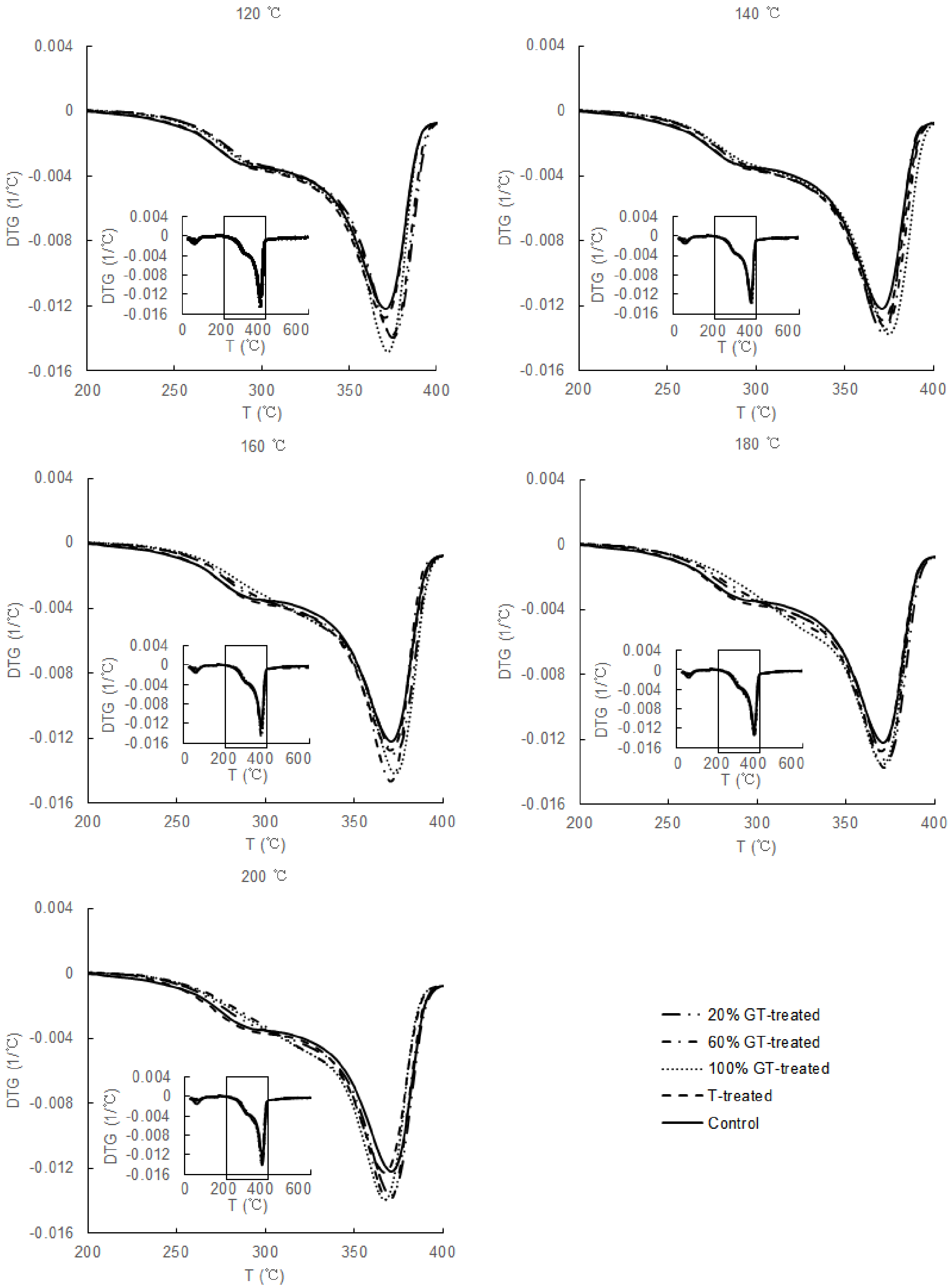

Fig. 2. Effects of glycerol pretreatment and thermal modification on DTG curves of poplar (*Populus tomentosa*)

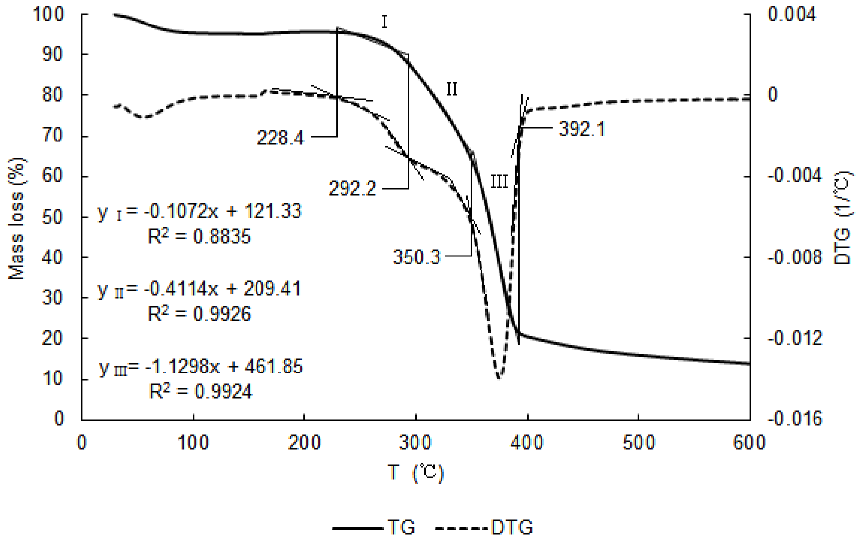

Fig. 3. Effect of glycerol pretreatment and thermal modification of poplar wood at 120 °C on mass loss (%) and DTG curve

Table 2. Effect of Glycerol Pretreatment and Thermal Modification on Set-on and Set-off Temperatures and Mass Losses During the Three Stages of Thermogravimetric Analysis

Treatment		Set-on Temperature (°C)			Mass Loss (%)			Set-off Temp (°C)
Glycerol (%)	Temp (°C)	Stage I	Stage II	Stage III	Stage I	Stage II	Stage III	
-	-	226.7	287.4	338.7	8.54	20.00	42.18	389.2
-	120	225.5	288.7	343.5	8.73	23.48	41.33	387.8
20		228.4	292.2	350.3	7.48	24.55	41.92	392.1
60		228.4	293.1	349.9	8.14	24.75	41.29	391.2
100		227.3	292.4	349.9	8.37	25.75	40.63	387.5
-	140	228.4	288.3	342.6	8.54	23.27	42.94	389.0
20		231.0	290.3	348.4	7.78	25.84	39.09	388.0
60		230.0	290.6	347.7	7.63	25.21	41.40	390.3
100		228.2	292.6	348.2	7.94	23.97	43.27	392.4
-	160	226.2	288.6	343.7	8.81	24.08	41.75	388.6
20		225.6	291.4	346.9	8.07	24.41	40.56	389.7
60		228.7	266.4	348.1	2.17	31.31	39.81	385.7
100		221.4	264.3	350.0	1.74	31.64	41.56	390.4
-	180	227.8	288.0	342.4	8.83	23.28	41.69	388.0
20		227.6	291.4	348.1	8.06	25.03	40.61	390.6
60		227.5	266.4	348.5	2.25	31.55	40.05	388.5
100		226.2	269.7	348.4	2.58	31.20	40.22	388.7
-	200	226.8	284.3	339.2	7.88	22.27	40.29	384.7
20		227.5	289.4	345.2	7.56	24.04	42.56	389.0
60		222.5	266.3	348.2	2.06	31.11	39.74	386.3
100		226.4	262.0	344.7	1.64	30.14	40.27	384.6

Hemicelluloses, cellulose, and lignin in wood decompose rapidly at 180 °C to 300 °C, 240 °C to 400 °C, and 280 °C to 550 °C, respectively (Kuriyama 1967), suggesting that the hemicelluloses and a small amount of cellulose decompose in the first stage of heating. The remaining hemicelluloses' decomposition and continuous cellulose decomposition occur in the second stage, while the reaction rate slowly increases. In the third stage, the remaining cellulose decomposes and the reaction rate further accelerates. Lignin decomposition also occurs more slowly over these three decomposition stages.

The set-on temperatures at stage I and stages III of the control, thermally modified, and glycerol pretreated/thermally modified materials were very similar. Set-on temperatures at stage II of the control and thermally modified samples were also similar, but the set-on temperatures at stage II were much lower of wood that was treated with 60% glycerol prior to thermal modification. The reasons for this temperature shift were unclear. The samples were washed to remove excess glycerol so that any effect on temperature, due to reaction between the glycerol and wood that was mediated by the original thermal modification, was eliminated.

Mass losses at stage I tended to be lower in the poplar samples that were pretreated with 60% glycerol/thermally modified at 160 °C than those of samples only thermally modified or those that received no treatment. The mass losses of glycerol-pretreated wood were higher than those for the control and thermally modified wood during stage II of thermal degradation. These results suggested that the initial glycerol pretreatment reduced the susceptibility of wood components to thermal decomposition. It is unclear how glycerol reacted with the wood prior to thermal modification, but one possibility is that it accelerated the thermal decomposition of the carbohydrate components as these polymers were less abundant at the initial stage of TGA analysis. The mass losses of samples from all three treatments were similar at stage III, which suggested that neither glycerol pretreatment nor thermal modification affected the thermal sensitivity of the residual lignin.

Kinetic Analysis

The thermal degradation phases of the TG curve were divided into three decomposition stages, and the activation energy of each decomposition stage was calculated for each treatment. The activation energies (E_a), pre-exponential factor (A), and the correlation coefficient (R^2) are presented in Table 3.

The E_a values of thermally modified wood at the three decomposition stages were higher than the E_a values for the controls, indicating that the thermal modification increased the thermal stability of wood components.

The E_a values of wood pretreated with 60% glycerol prior to thermal modification at 160 °C were much lower than those for the control and just thermally modified wood.

The E_a values of glycerol-pretreated wood at stage II were higher than those were for the control and thermally modified wood samples. The E_a values for all glycerol-pretreated wood samples at stage III were also higher. These results indicated that the glycerol pretreatment coupled with thermal modification altered the stability of wood components. The treatment initially accelerated decomposition at stage I, but improved stability at the second and third stages of thermogravimetric analysis. These results suggest that glycerol pretreatment altered the thermal modification process. These effects may be exploited to alter the process to improve specific wood properties, such as heat resistance, water repellency, or other desirable properties.

Table 3. Effect of Glycerol Pretreatment and Thermal Modification on Thermodynamic Parameters During the Three Stages of Thermogravimetric Analysis

Treatment		Stage I			Stage II			Stage III		
Glycerol (%)	Temp. (°C)	E_a (kJ/mol)	A (1/min)	R^2	E_a (kJ/mol)	A (1/min)	R^2	E_a (kJ/mol)	A (1/min)	R^2
-	-	71.97	5.46×10	0.9510	115.31	2.72×10^3	0.9995	201.28	3.15×10^6	0.9923
-	120	118.82	2.26×10^3	0.9697	140.91	1.99×10^4	0.9987	222.58	1.67×10^7	0.9954
20%		83.27	9.68×10	0.9304	137.18	1.33×10^4	0.9995	244.04	8.45×10^7	0.9946
60%		82.88	9.98×10	0.9289	136.03	1.26×10^4	0.9996	242.56	7.88×10^7	0.9949
100%		85.30	1.25×10^2	0.9934	136.98	1.42×10^4	0.9995	258.39	3.10×10^8	0.9946
-	140	133.68	8.45×10^3	0.9785	143.90	2.53×10^4	0.9985	223.27	1.77×10^7	0.9950
20%		88.23	1.65×10^2	0.9942	137.43	1.51×10^4	0.9995	236.66	5.27×10^7	0.9941
60%		92.73	2.22×10^2	0.9409	142.55	2.22×10^4	0.9994	234.32	4.20×10^7	0.9953
100%		91.70	1.97×10^2	0.9386	141.59	1.95×10^4	0.9996	238.74	5.71×10^7	0.9944
-	160	130.71	6.47×10^3	0.9740	143.86	2.56×10^4	0.9985	222.38	1.66×10^7	0.9952
20%		72.43	4.56×10	0.9200	133.36	1.10×10^4	0.9997	226.12	2.23×10^7	0.9950
60%		55.86	7.55	0.9588	150.86	4.45×10^4	0.9996	253.30	2.07×10^8	0.9946
100%		46.43	2.80	0.9299	158.83	7.88×10^4	0.9996	250.47	1.49×10^8	0.9952
-	180	127.49	5.05×10^3	0.9688	136.43	1.89×10^4	0.9983	220.33	1.42×10^7	0.9949
20%		90.88	1.96×10^2	0.9383	140.51	1.88×10^4	0.9997	231.67	3.36×10^7	0.9946
60%		60.13	1.02×10	0.9579	153.84	5.59×10^4	0.9998	240.84	7.24×10^7	0.9951
100%		62.74	1.26×10	0.9643	159.41	8.55×10^4	0.9987	239.55	6.57×10^7	0.9944
-	200	163.18	1.19×10^5	0.9789	146.83	3.22×10^4	0.9962	206.85	4.58×10^6	0.9915
20%		100.26	4.12×10^2	0.9455	145.47	2.79×10^4	0.9995	236.53	5.13×10^7	0.9945
60%		56.09	6.75	0.9459	158.17	7.69×10^4	0.9996	248.66	1.38×10^8	0.9951
100%		51.64	4.61	0.9423	156.54	6.98×10^4	0.9994	227.86	2.70×10^7	0.9924

CONCLUSIONS

1. Thermal modification decreased the subsequent rate of degradation of wood components during thermogravimetric analysis while glycerol pretreatment appeared to accelerate the process.
2. The combination of pretreatment with 60% glycerol followed by thermal modification at 160 °C appeared to be the optimum condition for initiating this effect. This effect was also demonstrated with the calculated E_a (activation energy) values.
3. The results suggest that pretreatments may be a potential tool for altering the thermal modification process to produce products with differing resistances to thermal degradation or to create other attractive properties such as improved water resistance or stability.

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