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Kinetic Study of Thermal Degradation of Varieties of Plywood by Using Thermogravimetry under Nitrogen Atmosphere

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Abstract
The thermal degradation of widely used different varieties of plywood viz. Simple (veneer) plywood (SP), Water proof plywood (WP) and Fire retardant treated plywood (FRP) was investigated by thermogravimetric analysis (TGA). The TGA experiments were conducted from ambient temperature to 700 ^{0}C at the heating rate of 10 ^{0}C/min. The experiments are conducted under an inert atmosphere of nitrogen in order to study the thermal degradation, pyrolysis and oxidative processes of these different plywoods. The different stages of the degradation mechanism are signified by the modified Arhenius Law containing some unidentified kinetic parameters such as activation energy (E_a) and pre-exponential factor (Z). These unknown parameters are analysed by using non isothermal single heating rate method i.e. Broido Method. The maximum value of activation energy in 2nd degradation stage is obtained for FRT plywood (80.64 kJ/mol) confirms the fact that FRT plywood is highly thermally stable over other two plywoods.

Keywords: *Thermogravimetric analysis, kinetic parameters, activation energy, plywood.*

1. Introduction

Plywood is one of the most significant building and furniture resources. Several kinds of plywood such as simple (veneer) plywood (SP), water proof plywood (WP), fire retardant treated plywood (FRP), oriented based board and laminated boards etc. are the main structural panel both in housing and marketable timber construction (APA, 1982 and AWPA, 1987). Walls, Kitchens and other panels are usually framed with all the types of plywood. Now days, many types of wood and plywood are used in most of the fields. The use of plywood for diverse functions may cause the problem of fire hazards due to their flammability (Antal et al., 1995; Antal et al.,1998; Cozzani et al., 1997; Koufopanos et al., 1985 and Shafizadeh et al., 1982). Therefore, there is need to study the thermal stability and flammability of plywood. Untreated (Veneer) plywood has a long history in service of roof sheathings. SP, WP and FRT plywood are rarely used as structural sheathings. Thus, they represent an increasing share of plywood creations in the market. SP, WP and FRT plywood has taken a major market share from last three decades and still is driven by strong demand (Sinha et al., 2011 and APA 2005). The introduction of FRT plywood for roof sheathings permitted the building codes to recognize this Plywood roof sheathings as a substitute for non-combustible decking in some multifamily structures. With the increased use of SP, WP and FRT plywood, it becomes important to assess their fire and water proof quality and reliability after disclosure to elevated temperatures because they are less colossal and they are less likely to oppose a rapid temperature rise (Cramer et al., 1997). Hence, the effect of enhanced temperature on the thermal degradation of varieties of plywood is the focal point. Thermal degradation analysis involves the understanding and forecasting the behavior of plywood after exposure to the high temperatures.

Thus, the main purpose of this study was to investigate the kinetic parameters of thermochemical conversion of varieties of plywood (SP, WP and FRT). These samples of plywood were analysed by TGA. Their activation energy (E_a), frequency factor (Z), and char yield up to 700 ^{0}C at the heating rate of 10 ^{0}C/ min were determined.

2. Experimental Techniques, Materials and Methods

2.1 Materials

Three kinds of plywood Simple (veneer) plywood (SP), Water proof plywood (WP) and Fire retardant treated plywood (FRP) were chosen for the experiment. These samples of different kinds of plywood were obtained from Green plywood Industries Limited, Karnal (Haryana).

2.2 Apparatus and Conditions

Thermogravimetric analyses were performed on the Perkin Elmer Diamond TG analyzer. Various thermograms were obtained at the heating rate of 10 ^{0}C/min in inert atmosphere of nitrogen from ambient temperature to 700 ^{0}C. Dried alumina powder as the reference compound and sample holders of ceramics were used for TGA analysis. In order to make sure the regularity of temperature of the sample and superior reproducibility, small size of the samples were taken.

Weight measurement was done by microbalance working on the principle of Horizontal differential balance method, which has precision of ± 0.2micrograms. The furnace temperature was controlled in such a way that the sample temperature followed by the preferred outline. For this principle, the manufacturer provided the temperature equilibration function between the furnace and the sample. The precision of the temperature measurement for TGA/DTA analyzer was ± 0.01 ^{0}C. The continuous record of weight, % weight, TGA and DTA signals against temperature/time were obtained and analyzed by using pyrex thermal analysis software. Different kinetic parameters such as E_a, Z and Char yield of these plywoods were also determined.

2.3 Kinetic Methods of analysis

Differential and integral techniques are usually used to compute the kinetic parameters. Differentiation makes available the kinetic parameters by using a sequence of given points using local data while integration refers to the overall data within which the kinetic parameters are supplied by the integral value.

The pyrolysis kinetics (Ge et al., 2016 and Poletto et al., 2012) generally assumes that under adiabatic condition

$$\frac{d\alpha}{dT} = kf(\alpha) \quad (1)$$

Here conversion rate is defined as $\alpha = \frac{m_0 - m_t}{m_0 - m_\infty}$ and heating rate as $\beta = \frac{dT}{dt}$.

Thus, Eq. (1) changes to the following form:

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = \beta k f(\alpha) \quad (2)$$

According to the Arrhenius equation:

$$K = A\exp\left(-E_a/RT\right) \quad (3)$$

Combining Eq. (2) and Eq. (3) gives the following relationship:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) f(\alpha)\exp\left(-E_a/RT\right) \quad (4)$$

The non-isothermal single heating rate method i.e. Broido method was used to study the degradation kinetics of these plywoods.

The Broido (Broido et al., 1969) equation is listed as follows:

$$\ln(\ln(1/y)) = -\frac{E_a}{RT} + \ln\left(\frac{RZT_m^2}{E_a\,\beta}\right) \quad (5)$$

where, T_m is the temperature at which maximum weight loss rate obtained.

When plotting ln(ln(1/y)) vs. 1/T, straight line is obtained whose slope and intercepts corresponds, respectively to E_a and Z.

3. Results and Discussion

3.1 Degradation process of three kinds of plywood

The shapes of TG and DTG curves are shown in Fig.1 and 2 respectively. The shapes of DTA curves are shown in Fig. 3 for all three types of plywood. The temperatures at which samples began to pyrolyze and the degradation temperature ranges of all the plywoods were different. In DTG curves, there are three noticeable weight loss peaks which represent the maximum weight loss rates of the samples in three stages of decomposition. So the process of degradation of varieties of plywood can be divided in to three stages, which are dehydration drying stage (the first peak between 150-211.3 ^{0}C), rapid decomposition stage (the second peak between 200 -345 ^{0}C) and slow decomposition stage (the third peak between 450 -550 ^{0}C). The second stage was the major phase of the process in which the most of the weight loss percentage was obtained. The characteristic parameters of curves are exposed in Table 1. The calculation of activation energy (E_a) and frequency factor (Z) was done for the 2nd and 3rd thermal degradation stage of plywood.

The TGA of varieties of plywood revealed an initial slight weight loss of 1.13% between ambient temperature to 175 ^{0}C. This could be due to the elimination of physically absorbed water in the plywood. Loss of light volatiles could also be the contributing factor. The initial decomposition of plywood samples (second degradation stage) began at the temperature range of 290.9 to 323.2 ^{0}C , whereas the final temperature for the second stage of thermal degradation were 341.5, 345.2 and 310.0 ^{0}C for SP, WP and FRP respectively. This zone referred as the active pyrolysis zone, during which different plywood samples SP, WP and FRP were undergone through weight loss of 58.96%, 51.85% and 43.15% respectively. Weight loss in this zone can be attributed to the evolution of volatile compounds during decomposition of cellulose and hemicelluloses. This stage corresponds to the first sharp exotherm in the DTA curve of plywood samples. A major change in the slope of all TGA curves was observed at around 430 ^{0}C in 2nd reaction zone (3rd degradation stage). This zone is referred to the passive pyrolysis zone as the rate of thermal decomposition was lower as compared to the first pyrolysis zone i.e. active pyrolysis zone. This zone was ended at around 478 ^{0}C. They show the Weight loss of 39.06%, 36.18% and 34.98% for SP, WP and FRP respectively. The weight loss in this zone is attributed to the Lignin decomposition.

Different parameters for all the three degradation stages of plywood, water proof plywood and fire retardant plywood in nitrogen atmosphere are given in table 1.

The effect of degradation of different type of plywood at the temperature range up to 700 ^{0}C was also deliberated by DTA analysis. DTA curves of varieties of plywood showed first exotherm in the temperature zone 195.1 to 345.2 ^{0}C with peak value obtained at 323.7, 321.1 and 290.4 ^{0}C respectively for SP, WP and FRP. This exotherm may be due to the decomposition of plywood components i.e. cellulose and hemicellulose. It is well documented in the literature also that in the nitrogen atmosphere the DTA curve of cellulose shows endotherm around 330 ^{0}C and hemicelluloses shows exotherm around 275 ^{0}C owing to pyrolysis reactions occurring in them. Thus, it is concluded that the first exotherm occurring in the plywood is the consequence of overlapping of decomposition curves of cellulose and hemicellulose component of wood. This also demonstrated that hemicelluloses decomposition process yields more amount of heat than the amount which should be given to the cellulose for decomposition. Similar to the shape of first exotherm, second exotherm was obtained in the temperature zone 415.0-513.0 ^{0}C with peak value obtained at 471.3, 435.7 and 476.4 ^{0}C respectively for SP, WP and FRP. This exotherm may be alloted to the oxidation of volatile and charred products.

Table 1. Characteristic parameters of TG and DTA

Sr. no.	Sample	Degradtion stage	Initial temp. °C	Peak temp. °C	Termination temp. °C	Nature of peaks
1	plywood	First Second Third	150 211.3 341.5	175 323.7 471.3	211.3 341.5 545.4	Endo Exo Exo
2	Water proof	First Second Third	150 204.7 345.2	172 321.18 435.7	204.7 345.2 540	Endo Exo Exo
3	Fire retardant	First Second Third	150 195.1 310	170.3 290.4 476.4	195.1 310 547.6	Endo Exo Exo

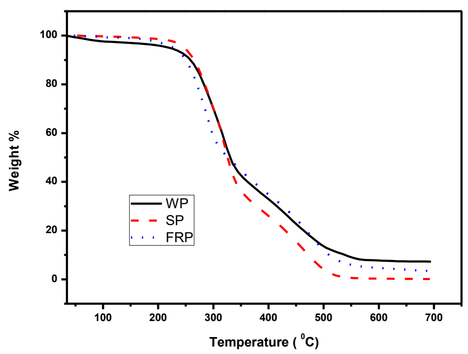

Fig. 1 TG Curve of (a) Water Proof Plywood (b) Simple Plywood (c) Fire Retardant Plywood

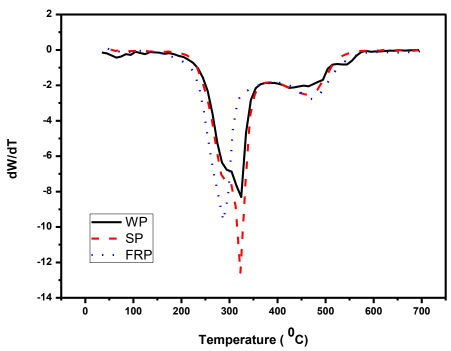

Fig. 2 DTG Curve of (a) Water Proof Plywood (b) Simple Plywood (c) Fire Retardant Plywood

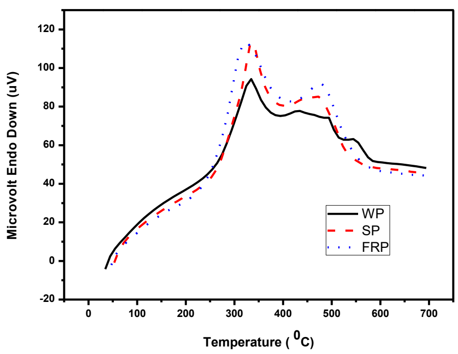

Fig. 3 DTA Curve of (a) Water Proof Plywood (b) Simple Plywood (c) Fire Retardant Plywood

3.2 Kinetics Analysis

Using the Broido equation, plots of ln(ln(1/y)) against 1/T for second and third degradation stages of thermal degradation of plywood, water proof plywood and fire retardant plywood samples were analysed and shown in figure 4 and 5 for all three plywoods. The calculation of Broido method for water proof plywood is shown in Table 2. The computation of activation energies of decomposition for the second degradation stage is also shown in Table 2. The activation energy and frequency factor (pre-exponential factor) for 2nd and 3rd degradation

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zone is shown in Table 3 and 4 respectively. In the active pyrolysis zone i.e. 2nd degradation stage of different plywoods higher value of activation energy was obtained for fire retardant plywood (80.64 kJ/mol) as compared to those of simple veneer plywood (71.74 kJ/mol) and waterproof plywood (67.65 kJ/mol). The experimental conditions in which thermal degradation takes place have significant effects on the thermal degradation rates and activation energies. The pre-exponential factors or frequency factors were find out in active pyrolysis zone ranged as high as 3.4 x 10^6 s^{-1} for FRP. The activation energies calculated for the third stage of degradation were in the range of 26.85-49.61 kJ/mol and frequency factors were in the range of 2.41 x 10^2- 4.0 x 10^2 s^{-1}.

Here, W_0 = 5.21 mg and W_∞ = 0.379 mg

Slope of straight line = -8.137
Therefore, activation energy, E_a = 67.65 kJ/mol
Intercept of straight line =13.235
Intercept of straight line = ln(z R Tm /ß E_a) Where, ß = 10 K /min
R= 8.314 JK^{-1} mol^{-1}
Thus, frequeny factor (Z) = 1.3 xl0^5 $s^{-1.}$ Similarly the activation energy and frequency factor for remaining two samples of plywood were determined.
On the basis of activation energy data it can be said that the fire retardant treated plywood having higher value of E_a will not catch fire even at high temperature than the other two types of plywood.

Table 2 Calculation of energy of activation, E_a, and frequency factor (Z) by Broido method for the second (decomposition) stage of thermal degradation of water proof plywood

T(k)	10^3 /T	Wt(mg)	y	Ln(l/y)	Ln(ln(l/y))
553.75	1.805869	4.238	0.798799	0.224645	-1.49323
559.75	1.786512	4.065	0.762989	0.270512	-1.30744
565.75	1.767565	3.881	0.724002	0.321719	-1.13408
571.75	1.749016	3.692	0.685779	0.377199	-0.97498
577.75	1.730852	3.507	0.647485	0.43466	-0.83319
583.75	1.713062	3.315	0.607742	0.498005	-0.69714
589.75	1.695634	3.106	0.564479	0.571851	-0.55888
595.75	1.678556	2.875	0.516663	0.660364	-0.41496
601.75	1.66182	2.655	0.471124	0.7522634	-0.28418
607.75	1.645413	2.487	0.436349	0.829314	-0.18716

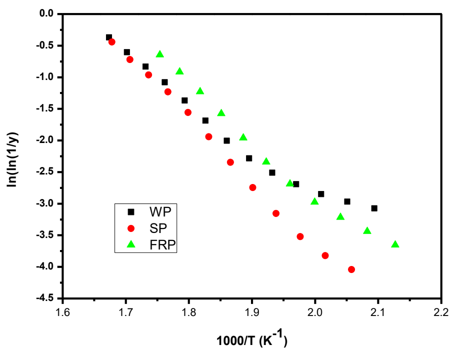

Fig. 4 Plot of activation energy of second degaradation stage

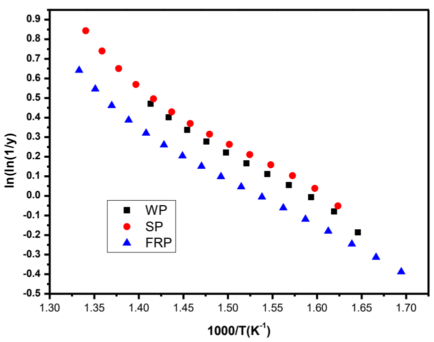

Fig. 5 Plot of activation energy of third degaradation stage

Table 3 Activation energy and frequency factor for the second stage of thermal degradation of varieties of plywood

Sample	Temp. range (^{0}C)	E_a (kJ $mole^{-1}$)	Z (s^{-1})
Plywood	211.3-341.5	71.74	$2.9x10^5$
Water proof plywood	204.7-345.2	67.65	$1.3x10^5$
Fire retardant plywood	195.1-310	80.64	$3.4x10^6$

Table 4 Activation energy and frequency factor for the third stage of thermal degradation of varieties of plywood

Sample	Temp. range (^{0}C)	E_a (kJ $mole^{-1}$)	Z (s^{-1})
Plywood	341.5-495	49.61	788.4
Water proof plywood	345.2-485	26.85	409.1
Fire retardant plywood	310-498	44.48	230

Table 5 Char yield of varieties of plywood at 700 ^{0}C Temperature

Sample	Plywood	Water proof	Fire Retardant
Char Yield % at 700 ^{0}C	0.2	7.4	3.5

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4. Conclusion

The thermal degradation of different varieties of plywood viz. Simple (veneer) plywood (SP), Water proof plywood (WP) and Fire retardant treated plywood (FRP) was investigated by thermogravimetric analysis (TGA). These plywoods found to show a three stage degradation process. The non-isothermal single heating rate method of Broido was used for the computation of kinetic parameters such as activation energy (E_a) and pre-exponential factor (Z) for 2nd and 3rd degradation stage of these plywoods. During the 2nd degradation stage maximum weight loss was observed for all these plywoods. The maximum value of activation energy in 2nd degradation stage was obtained for FRT plywood (80.64 kJ/mol) confirms the fact that FRT plywood will not catch fire at high temperature.

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References

[1] APA (2005) APA Economics Report E171. American Plywood Association, Tacoma

[2] APA 1982 Standard PSI Tacoma, WA, American Plywood Association.

[3] Antal M J, Varhegyi G. Cellulose pyrolysis kinetics: the current state of knowledge. Industrial & Engineering Chemistry Research. 1995 Mar;34(3):703-17.

[4] Antal M J, Varhegyi G, Jakab E. Cellulose pyrolysis kinetics: revisited. Industrial & Engineering Chemistry Research. 1998 Apr 6;37(4):1267-75.

[5] AWPA 1987 Washington, DC: American wood preservers Association. Standards C20 and C27.

[6] Broido A. A simple, sensitive graphical method of treating thermogravimetric analysis data. Journal of Polymer Science Part A‐2: Polymer Physics. 1969 Oct; 7(10):1761-73.

[7] Cozzani V, Lucchesi A, Stoppato G, Maschio G. A new method to determine the composition of biomass by thermogravimetric analysis. The Canadian Journal of Chemical Engineering. 1997 Feb; 75(1):127-33.

[8] Cramer, S.M. and White, R.H., 1997. Fire performance issues. In Wood engineering in the 21st century: research needs and goals: proceedings of the workshop offered in conjunction with the SEI/ASCE Structures Congress XV, Portland, Oregon, April 16, 1997. Reston, VA: Structural Engineering Institute; American Society of Civil Engineers, c1998: p. 75-86.

[9] Ge J, Wang RQ, Liu L. Study on the thermal degradation kinetics of the common wooden boards. Procedia Engineering. 2016 Jan 1;135:72-82.

[10] Koufopanos C, Maschio G, Paci M, Lucchesi A. Some kinetic aspects on the pyrolysis of biomass and biomass components. InEnergy from biomass: 3rd EC conference, held Venice 25-29 March, 1985 (pp. 837-841). Elsevier Applied Science Publishers.

[11] Poletto M, Zattera AJ, Santana RM. Thermal decomposition of wood: kinetics and degradation mechanisms. Bioresource Technology. 2012 Dec 1; 126:7-12

[12] Shafizadeh F. Introduction to pyrolysis of biomass. Journal of Analytical and Applied Pyrolysis. 1982 Apr 1; 3(4):283-305.

[13] Sinha A, Nairn JA, Gupta R. Thermal degradation of bending strength of plywood and oriented strand board: a kinetics approach. Wood science and technology. 2011 May 1; 45(2):315-30.