Thermal Properties Of Chitin Whiskers Reinforced Poly(Acrylic Acid)

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ABSTRACT: Thermal analysis(TGA) of samples of Chitin, PAA and Chitin-PAA complexes, containing different weight fractions of chitin whiskers were investigated. The activation energies (Ea) and other kinematic parameters; ΔS, ΔH, and ΔG for the filler, matrix and blend were calculated using the Coats and Redfern, Broido and Horowitz and Metzger methods at the second and third stages of decomposition. The study showed that the kinetic parameters for the composites lie between the matrix and the filler. .At each filler loading level, the activation energies, changes in enthalpies, entropies and Gibbs functions obtained using all three methods are comparable for the second region of decomposition. The pattern is such that the value of these energy parameters gradually decreased as filler loading decreases. The gradual increase in activation energy as filler increases is attributed to even dispersion of the whiskers and interfacial adhesion between the matrix and the chitin whiskers.

Keywords: Activation energy, Chitin, filler loading, poly(acrylic), whiskers

1.0 Introduction

Thermogravimetric analysis (TGA) is one of the analytical experimental techniques used to investigate the behaviour of materials as a function of temperature, which has a bearing on the actual behaviour of the composite. The ability of thermogravimetric analysis to characterize, quantitatively and qualitatively, engineering materials over a wide range of temperature gave it a general acceptability as an analytical technique. The thermogravimetric analysis has proved to be useful in evaluating kinetic parameters such as the activation energy (Ea), pre-exponential factor (A) and the analytical expression describing the kinetic model f(α). Other parameters that can be determined are change in enthalpies ΔH, change in entropies ΔS and the Gibbs functions ΔG. Various methods (Freeman and Carroll, (1958); Coats and Redfern, (1964); Cao and Wunderlich, (1985); Li *et. al.,(*1998); Chang, (1994); Broido, (1969); Sharp and Wentworth, (1969) and Horowitz and Metzger, (1963)) have been proposed to estimate these kinetic parameters for thermal degradation of materials at any stage of the decomposition. In all the methods, two basic assumptions are made; these are: the validity of the Arrhenius relation over the entire temperature range and the difference between the thermal and diffusion processes remains insignificant. Various authors Shehap, (2008) and Moharram and Khafagi (2006), have used these methods to characterise polymers. For instance, thermogravimetry was used to investigate films of polyvinyl alcohol (PVA), sodium carboxy methyl cellulose (NaCMC) homopolymer at different blend loadings using the Coats–Redfern method to determine the kinetic parameters Shehap, (2008). The result indicates that the values of the kinetic parameters; that is E ΔS, ΔH, and ΔG in both the 1st and 2nd decomposition steps for NaCMC are less than those of PVA and the blend samples. In the same vain the values of E, ΔS, ΔH, and ΔG in the first decomposition step were less than those of the second decomposition step in the filler, the matrix and the blend. Using the modified Dharwadhar and Kharkhanawala's equation to determine the thermodynamic parameters of PAA, PVP, PAA-PVP complexes, at different weight fractions of PAA, Moharram and Khafagi, (2006) report shows that the activation energies for decarboxylation reaction, anhydride formation and thermal degradation of polyacrylic anhydride were 0.70, 1.06 and 3.97 kcal/mol respectively. In this work the Coats and Redfern, Broido and Horowitz and Metzger methods are employed to evaluate the kinetic parameters for chitin, PAA and chitin whiskers reinforced PAA at the second and third stages of thermal degradation.

1. Experimental Section

2.1 Preparation of chitin whiskers (CHW), chitin film and chitin whiskers reinforced Poly (acrylic acid) (PAA) films. Shrimp Chitin, Poly (acrylic acid) and all chemicals were purchased from Sigma Aldrich UK. Purification and acid hydrolysis of chitin were carried out as previously published Junkasem, *et.al.* (2010); Junkasem, Rujiravanit, and Supaphol, (2006); Morin, and Dufresne, (2002). The solid content of the chitin whiskers suspensions was approximately 0.3 wt%. Chitin film was fabricated according to a modified method Ifuku, *et.al.* (2010); Ifuku, *et.al.* (2011). Chitin was roughly crushed with domestic blender and then vacuum sieve. Sieved chitin was dispersed in water to make 0.5wt% nanofibre content. Acetic acid was added to raise the pH to 3 and then magnetically stirred over night at room temperature. The suspension was vacuum filtered. The obtained chitin nanofibre was hot pressed for about 60min maintaining the temperature at between 80 and 90^0 C to obtain chitin nanofibre film. Chitin whiskers suspension and 1 wt % PAA solution were gently mixed in beaker and magnetically stirred at room temperature for about 3-5 min maintaining the pH at 2. The solution was cast in a plastic Petri dish and allowed to dry at the fume hood for 72 hours and later oven dried at 30°C to remove residual water for 10 hours or until the film detached itself from the dish. The films were prepared at different filler loading of whiskers.

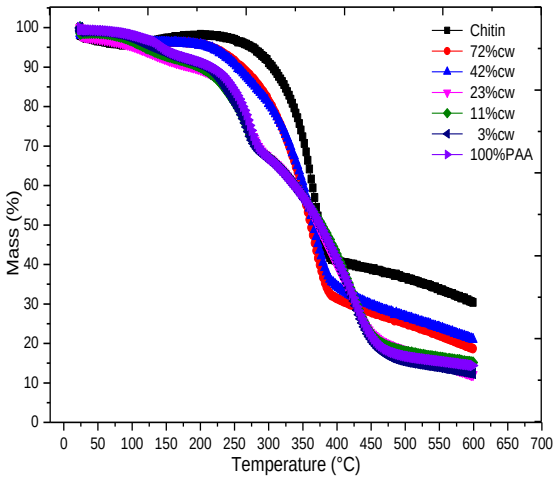
2.2 Characterisation

A NETZSCH Simultaneous Thermogravimetric Analysis (STA) 449C instrument was used to characterise the degradation pattern and weight loss as a function of temperature for PAA, chitin film and CHW-PAA composites. Samples of mass 8.0 ± 1.5 mg were placed in an aluminium crucible, and then heated in the range of 23 - 600 °C at 10 °C min^{-1} under 50 ml min^{-1} nitrogen serving as the purge gas. Three samples runs were taken for each and averages values calculated.

3.0 ResultS and Discussion

3.1 Thermogravimetric Analysis (TGA/DTG)

Figure 1 shows the TGA curves of chitin, PAA (Mw=25,000). Chitin shows two decomposition stages, the 1st occurs between 51-120°C with a maximum decomposition rate at 82.9°C with a weight loss of 3.9 wt%. This decomposition is ascribed to loss of water. The next degradation occurs between 257-391°C at a maximum decomposition rate occurring at 362.3°C and a weight loss of 28.2wt%. Typically, this stage relates to the degradation of saccharide rings and the depolymerisation and decomposition of both acetylated and deacetylated units of chitin (Peniche,, *et.al*., (1999); Kim, *et.al.,* (1994)). The final weight loss at the end of the degradation was 50.8 wt %.



Figures 1 *TGA curves of chitin, PAA and its composites*

For pure PAA a three-stage degradation process was observed. The first weight loss of about 7.3 % due to loss of water and the formation of intra- and inter-molecular anhydride bonds occurs at 50-162°C. The second stage degradation due to the decarboxylation process of the anhydride bonds occurs at 217-294 °C with a further weight loss of about 25.6%. A full degradation of the macromolecule occurs within the range 362-464°C (Lin, Lee and Chiu (2005); Tanodekaewa, *et.al.*,(2004)). The final weight loss at the end of degradation was 84%. For the composites, the decomposition falls between the matrix and the filler. The weight loss for the first decomposition stage decreases as the filler increases and is between 3.6% and 6.8%. At the end of the second stage degradation, the weight loss falls between 30 and 67.3% with 73% filler loding having the least. The decrease in loss in weight as chitin whiskers increases is an indication of thermal stability. The final percentage loss in weight decreases from 86.1% at 3% chitin whiskers to 78% at 73 % chitin whisker content.

3.2 Kinematic Parameters from Thermal Degradetion

In a TGA analysis the weight loss at any given temperature, the percentage of un-combusted residue at the end of reaction and the temperature at various degradation steps can be evaluated. Thermo gravimetric data have been used to evaluate kinetic parameters. These parameters are indicators to the thermal stability of polymers. Three kinetic components are described by the mathematical decomposition process of materials in the solid state. These are the activation energy (Ea), pre-exponential factor (A) and the analytical expression describing the kinetic model f(α). Among the three Kinetic parameters (activation energies (*E*a), the reaction order (*n*), and the pre-exponential factors (A)), the activation energy (Ea) is the most widely used to discuss the thermal properties of materials. These three parameters depends on several factors among which are flow rate and the nature of the purge gas , the heating rate, the sample mass, and the mathematical methods used in evaluating the data (Sreedhar, *et.al.,* (2005)). In a dynamic TGA experiment the rate of conversion at a constant heating is expressed as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad (1)$$

Where t is the time, α is the conversion degree,(T) is the temperature, $k(T)$ the temperature dependent rate constant and $f(\alpha)$ the temperature independent function. From Arrhenius equation the rate constant $k(T)$ is given, and is written below

$$K(T) = Aexp\left(-\frac{Ea}{RT}\right) \qquad (2)$$

Where A is the pre-exponential factor, $\mathbf{Ea}$ the activation energy, R is the universal constant.
Substituting equation 2 into 1

$$\frac{d\alpha}{dt} = Aexp\left(-\frac{Ea}{RT}\right) f(\alpha) \qquad (3)$$

if the heating rate is $\beta = \frac{dT}{dt}$ then equation 3 is expressed as

$$\frac{d\alpha}{dT} = \frac{1d\alpha}{\beta dT} = \frac{A}{\beta}Aexp\left(-\frac{Ea}{RT}\right)(1-\alpha)^n \qquad (4)$$

by variable separation we have equation 5

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}Aexp\left(-\frac{Ea}{RT}\right)dT \qquad (5)$$

Equations 4 or 5 serve the bases for the calculation of the kinetic parameters (Ea, A and n) of the thermal degradation processes of polymers. Different authors methods (Freeman and Carroll (1958); Coats and Redfern (1964); Cao and Wunderlich (1985); Li *et. al*.,(1998); Chang, (1994); Broido, (1969); Sharp and Wentworth (1969); Horowitz and Metzger, (1963)) developed different methods for calculating the activation energy. Three of these methods Coats and Redfern, Broido and Horowitz and Metzger will be used in determining the kinetic parameters at the second and third stages of the thermal degradation of chitin film, PAA and chitin whiskers reinforced PAA composites. The first stage of decomposition was omitted most water evaporation takes place here. The graphical figures for the chitin and PAA are presented here while the values for chitin, PAA and the composites are presented in a tabula form.

3.2.1 Coats - Redfern Method

The simplified form of Coats and Redfern (1964), equation is;

$$ln\left\{\frac{f(\alpha)}{T^2}\right\} = \left\{\frac{AR}{\beta Ea}\{1-\frac{2RT}{Ea}\}\right\} - \frac{Ea}{RT} \quad (6)$$

T = Temperature
A = Pre-exponential factor
R = Gas constant
Ea = Activation energy
β = Heating rate
where α is given by

$$\alpha = \frac{W_o - W_t}{W_o - W_f} \quad (7)$$

W_o = Initial weight of the sample
W_t = Residual weight of the sample at the temperature
W_f = Final weight of the sample
n = reaction order

$$ln\left\{\frac{-ln(1-\alpha)}{T^2}\right\} \; vs \; \frac{1}{T} \; is \; plotted \; for \; n = 1 \quad (8)$$

$$ln\left\{\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right\} \; vs \; \frac{1}{T} \; is \; plotted \; for \; n \neq 1 \quad (9)$$

$$where \; the \; slope = -\frac{Ea}{RT} \; and \; intercept = ln\frac{AR}{\beta Ea}$$

3.2.2 Broido Method

Broido, (1969), developed a model where the activation energy at each stage of decomposition can be evaluated. The equation used is as follows.

$$lnln\left\{\frac{1}{Y}\right\} = \left\{\frac{-Ea}{R}\right\}\frac{1}{T} + constant \quad (10)$$

$$Y = \frac{W_t - W_\infty}{W_o - W_\infty} \quad (11)$$

Where,
Y = the fraction of the number of initial molecules not yet decomposed;
W_t = the weight at any time t;
W_∞ = the weight at infinite time (= zero) and
W_o = the initial weight.

A plot of ln ln (1/Y) vs. 1/T gives a straight line. The slope is related to the activation energy.

3.2.3 APPROXIMATION METHOD OF HOROWITZ AND METZGER

The integral equation of Horowitz and Metzger (1963). could equally be used to calculate the activation energy. The equation used for the calculation of energy of activation (Ea) is:

$$lnln\left\{\frac{W_o}{W_t}\right\} = \left\{\frac{\theta Ea}{R\,T^2}\right\} \quad (12)$$

Where,
θ = (T – T_s); the difference between the peak temperature and the temperature at particular weight loss
W_o = the initial weight;
W_t = the weight at any time t;
T_s is the peak temperature; and
T is the temperature at particular weight loss.
A plot of lnln (W_o)/ (W_t) vs. θ gives a straight line where the activation energy is related to the slope. The activation entropy ΔS, enthalpy ΔH and free energy of activation ΔG were calculated using the following equations (Yakuphanoglua, Gorgulub and Cukurovali (2004)).

$$\Delta S = 2.303\left\{log\,\frac{Ah}{kT}\right\}R \quad (13)$$

$$\Delta H = Ea - RT \quad (14)$$

$$\Delta G = \Delta H - \Delta ST \quad (15)$$

where
k = Boltzmann constants (1.38 x 10^{-23} J/K)
h = Planck constants (6.63 X 10^{-33} Js)
R = Universal constant (8.314 J/K)
T is the temperature involved in the calculations selected as the temperature at the maximum decomposition rate. The calculated thermodynamic parameters for chitin at the 2nd stage are shown in table 1, while the parameters for the 2nd and 3rd stages for PAA are presented in tables 2 and 3 respectively and figures 2 and 3 are the graphical representation of the three methods for chitin and PAA respectively. For the composite only values where the order of reaction n=0.5 are presented for Coats - Redfern method. R^2 stands for the regression analysis which the more it approaches unity, indicates the quality of the estimation

Table 1 : *R^2, n, Ea, ΔS, ΔH and ΔG values for 2nd decomposition regions of chitin*

Sample	Method	n	R^2	Ea KJ/mol	ΔS J/mol	ΔH KJ/mol	ΔG KJ/mol
Chitin	B		0.995	73.19	-135.45	67.91	153.92
	H-M		0.996	87.16	-159.81	81.88	183.36
	C-R	0	0.988	49.40	-76.41	43.87	94.69
		0.5	0.967	59.81	-56.11	54.28	91.59
		1	0.922	73.25	-30.35	67.72	87.90
		2	0.784	111.40	41.13	105.87	78.52

Table 2 : *R^2, n, Ea, ΔS, ΔH and ΔG values for 2nd decomposition regions of PAA*

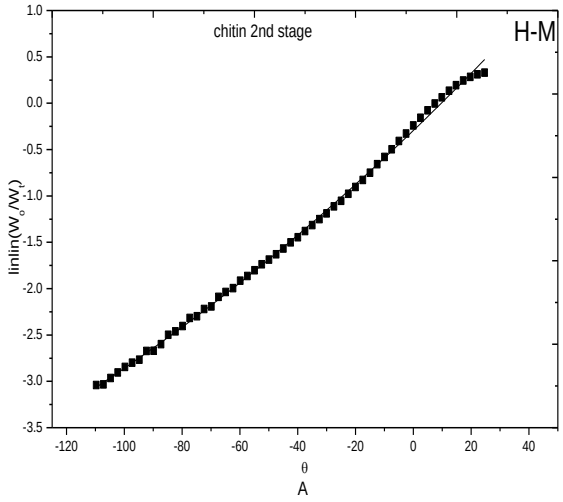
Sample	Method	n	R^2	Ea KJ/mol	ΔS J/mol	ΔH KJ/mol	ΔG KJ/mol

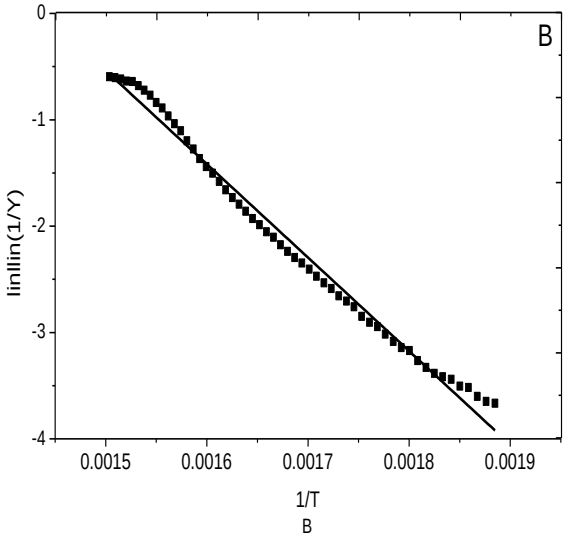
	B		0.993	40.61	-143.24	36.07	114.22
100% PAA	H-M		0.992	42.57	-158.20	38.03	124.34
	C-R	0	0.975	18.09	-124.14	13.44	82.95
		0.5	0.956	32.87	-89.02	28.22	78.07
		1	0.903	52.41	-60.51	47.76	81.64
		2	0.804	112.21	80.59	107.56	62.43

Table 3 : *R^2, n, Ea, ΔS, ΔH and ΔG values for 3rd decomposition region of PAA*

Sample	Method	n	R^2	Ea KJ/mol	ΔS J/mol	ΔH KJ/mol	ΔG KJ/mol
	B		0.997	37.84	-146.61	32.02	134.65
100% PAA	H-M		0.997	41.96	-179.77	36.14	161.98
	C-R	0	0.855	4.13	-168.11	-1.93	120.62
		0.5	0.971	21.06	-126.97	15.00	107.56
		1	0.913	49.57	-74.54	43.51	97.85
		2	0.804	139.42	75.02	133.36	78.67

The calculated activation energies for the three methods Broido (B), Horowitz and Metzger (HM) and Coats - Redfern (C-R) are 40.61, 42.57 and 52.41 for n=1 and 32. 87 KJ/mol for n=0.5 respectively for decarboxylation reaction while the activation energies for the thermal degradation of poly(acrylic) anhydride for the three methods are respectively 37.84, 41.96 and 49.57 for n=1 and 21.06 KJ/mol for n=0.5. The result obtained here are lower than Kabanov, Dubnitskaya and Khar'kov (1975), for a decarboxylation reaction, but compare favourably with that of Çaykara and Güven (1998). The results are equally higher than those obtained by Moharram and Khafagi (2006). The difference could mainly be attributed to the drying temperature and the processing methods. The results for Broido and Horowitz and Metzger are comparable. Both authors: Broido (1969) and Horowitz and Metzger (1963) assumed that the reaction order n was unity. Equally the values obtained using the Coats-Redfern method with $0.5 \leq n \leq 1$ are comparable to Broido and Horowitz and Metzger. This is because the standard errors (SE) obtained were ≈ 3.0 and 3.6 respectively for the decarboxylation reaction. For the thermal degradation of poly (acrylic) anhydride, SE of 6.4 was obtained when n=0.5 and 3.4 when n=1 which indicates better estimation with the rise in order of the reaction. The calculated activation energies for the three methods Broido, Horowitz and Metzger and Coats - Redfern for degradation of saccharide rings of chitin are respectively 73.19, 87.16 and 73.25 for n=1 and 59.81 KJ/mol for n=0.5 with a SE of 4.6 and 7.9 for n=1 and n=0.5 respectively. Earlier published report Jang, *et.al,* (2004) gave as 60.56, 58.16 and 59.26 KJ/mol for α-chitin, β-chitin and ϒ-chitin respectively. For a good decomposition step a correlation factor (R^2) of between 0.900 and 0.999 is accepted. Tables 1-3 also show other kinematic parameters. These are the change in enthalpy ΔH, change in entropy ΔS, the change in free energy (Gibbs function ΔG) and the regression values for chitin and the matrix.





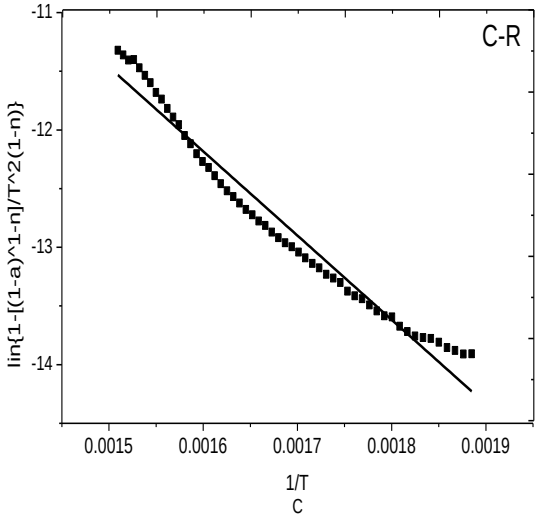


Figure 2: *Horowitz and Metzger(A), Broido (B) and Coats-Redfern (C) plots for chitin*

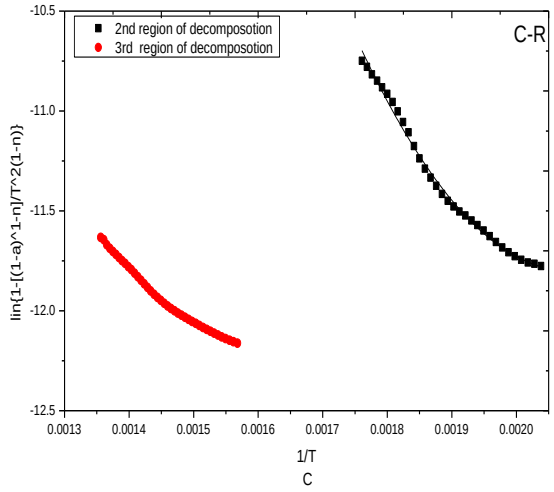
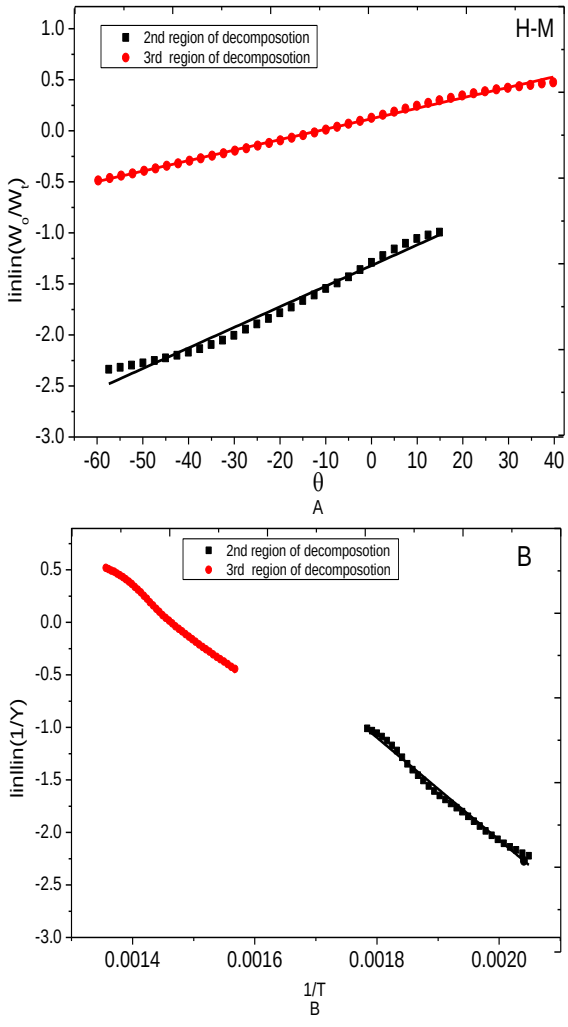


Figure 3: *Horowitz and Metzger (A), Broido (B) and Coats-Redfern (C) plots for 2nd and 3rd regions of decomposition for PAA.*



Based on the standard error between the three methods for the filler and the matrix and a better regression value obtained assuming reaction order of n = 0.5, the kinematic parameters of the composites are presented using the Coats – Redfern. The activation energies, change in enthalpies ΔH, change in entropies ΔS, Gibbs functions ΔG and the regression values of the thermal decomposition of chitin whiskers reinforced Poly(acrylic acid) composites are shown in tables 4 and 5 for the second and third stages respectively. From the tables, at each filler loading all values obtained for the three methods are comparable within the second region of decomposition and all gradually decrease as the filler decreases. The gradual increase in activation energy as filler increases could be attributed to even dispersion of the whisker and interfacial adhesion between the matrix and the whiskers. From the table 4 and 5, it can be observed that the kinetic parameters Ea, ΔS, ΔH, and ΔG for both second and third regions of decomposition lie between those of the matrix and the filler. The values of Ea, ΔS, ΔH, and ΔG in the third decomposition step are less than those of the second decomposition step. Lower values of activation energies at the final stages are most likely associated with process that occurs at weak linkage of PAA and chitin. Lower values of Ea as chitin decreases confirms the amorphous nature of PAA compared to chitin a semi crystalline polymer. Negative values of ΔS, indicates that the decomposition is slow while positive values of ΔH indicate endothermic decomposition and positive values of ΔG indicate slow reaction (Singh and Chhatpar, (2011); Ozawa,(1975)).

Table 4 : *R^2, Ea, ΔS, ΔH and ΔG values for 2nd region of PAA composites*

Sample	Method	R^2	Ea	ΔS	ΔH	ΔG

			KJ/mol	J/mol	KJ/mol	KJ/mol
73%CW	B	0.996	52.58	-140.62	47.26	137.28
	H-M	0.992	55.54	-169.69	50.22	158.85
	C-R	0.953	34.65	-148.73	29.16	127.32
42%CW	B	0.993	47.44	-142.37	42.16	132.60
	H-M	0.991	53.68	-165.49	48.40	153.52
	C-R	0.938	34.00	-148.03	28.67	123.56
23%CW	B	0.992	43.39	-142.12	38.84	116.72
	H-M	0.994	45.69	-157.37	41.13	127.37
	C-R	0.942	33.18	-150.82	28.53	112.99
11%CW	B	0.991	38.41	-144.17	33.88	112.45
	H-M	0.992	41.73	-158.16	37.20	123.40
	C-R	0.953	32.36	-150.83	27.70	112.17
3%CW	B	0.995	39.91	-143.49	35.38	113.58
	H-M	0.993	43.22	-158.05	38.68	124.82
	C-R	0.972	33.77	-151.53	29.12	113.95

Table 5 : *R^2, Ea, ΔS, ΔH and ΔG values for 3rd decomposition regions of PAA composites*

Sample	Method	R^2	Ea KJ/mol	ΔS J/mol	ΔH KJ/mol	ΔG KJ/mol
42%CW	B	0.997	40.48	-145.87	34.66	136.77
	H-M	0.996	42.28	-170.72	36.46	155.96
	C-R	0.966	24.29	-149.93	18.34	125.54
23%CW	B	0.999	39.47	-146.48	33.66	136.05
	H-M	0.999	41.84	-175.91	36.03	159.00
	C-R	0.961	19.82	-150.38	13.77	123.10
11%CW	B	0.956	38.56	-146.96	32.68	136.65
	H-M	0.993	41.73	-178.20	36.35	162.42
	C-R	0.909	19.21	-150.99	13.16	122.93
3%CW	B	0.992	38.06	-146.45	32.30	133.79
	H-M	0.996	41.53	-178.23	35.76	159.28
	C-R	0.944	20.81	-150.58	14.75	124.52

Conclusion

The thermal stability and some kinetic parameters, such as activation energy, change in enthalpies, change in entropies, Gibbs functions and the order of decomposition reaction of chitin, Poly(acrylic) and chitin whiskers reinforced composites at different filler weight of chitin whiskers were determined using three different thermogravimetric analytical techniques namely Coats and Redfern, Broido and Horowitz and Metzger methods. Four reaction orders (n) were obtained from the thermograms and it was observed that the reaction order n=0 for Coats and Redfern method gave the best regression value for the second stage of decomposition for both the matrix and the filler while the reaction order n=0.5 gave the best regression value for the third stage of decomposition for the matrix. As expected all values for chitin were higher than those of matrix and the blend. At the second stage of decomposition all values for the three methods were comparable but gradually decreases as the filler decreases.

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