Study of thermal degradation behavior and kinetics of ABS/PC blend

Saira Bano[1*], Naveed Ramzan[2], Tanveer Iqbal[3], Hamayoun Mahmood[3], Farhan Saeed[4]

[1]*Department of Chemical & Polymer Engineering, University of Engineering & Technology, Lahore, FSD Campus, 38000, Pakistan*
[2]*Department of Chemical Engineering, University of Engineering & Technology, Lahore, 54890, Pakistan*
[3]*Department of Chemical, Polymer & Composite Materials Engineering, University of Engineering & Technology, Lahore, KSK Campus, 54890, Pakistan*
[4]*Department of Polymer and Process Engineering, University of Engineering & Technology, Lahore, 54890, Pakistan*
Corresponding author: saira.bano@uet.edu.pk

This work investigated kinetics and thermal degradation of acrylonitrile butadiene styrene and polycarbonate (ABS/PC) blend using thermogravimetric analysis in the range of 25 to 520ºC. For thermal degradation of blend, activation energy (E_a) and pre-exponential factor (A) were calculated under various heating rates as 5, 10, 15 and 20ºC/min using iso-conversional model-free methods (Kissinger, Flynn-Wall- Ozawa and Friedman). Mass loss of the blend as a function of temperature was plotted as thermogravimetric curve (TG) while derivative values of mass loss were drawn as derivative thermogravimetric (DTG) curve. Using Kissinger method, E_a was 51.4 kJ/mol, while values calculated from FWO and Friedman method were 86–161 and 30–251 kJ/mol respectively. Results showed increasing trend of E_a with higher conversion values indicating different degradation mechanisms at the initial and final stages of the experiment. Thermodynamic parameters such as enthalpy change (ΔH), Gibbs free energy (ΔG) and entropy change (ΔS) were also calculated.

Keywords: ABS/PC blend, thermal degradation, iso-conversional analysis, activation energy, thermodynamic parameters.

INTRODUCTION

Polymer blending is an efficient way of developing new materials with a desirable balance of properties. Started about six decades ago, polymer blending now occupies a considerable share of the commercial market. It is an economical technique for producing new materials using already existing polymers in a cost-effective way. The physical properties of the blends can be adjusted according to end application requirements. Careful selection of ingredients, processing method and control of processing conditions are important to ensure better performance of blend[1].

Blends of polycarbonate (PC) with acrylonitrile buta-diene styrene (ABS) have been available commercially from the past few decades. As blending improves the characteristics of a neat polymer, one can expect fair boost in the performance of ABS with the addition of polycarbonate. Not only PC processing is improved by the addition of ABS, enhancement in toughness, heat resistance and environmental stress cracking in a cost-effective way have also been reported[2, 3]. ABS is a heterogeneous terpolymer that consists of a dispersed rubbery phase made up of polybutadiene rubber grafted with styrene-acrylonitrile and it is then dispersed in continuous phase of more styrene-acrylonitrile. PC is a single-phase, homogeneous polymer. Blending of PC and ABS changes the ratio of plastic and rubber phase components. The structural morphology of the system is altered by blending and it yields different rheological and mechanical properties[3]. PC finds extensive applications in areas such as electronics, 3D printing construction material, medical equipment and automobile. It is a polymer that possesses good mechanical characteristics i.e. high impact strength and modulus, thermal stability at high temperatures and high electrical resistance but difficult processability[4]. Amongst commercial polymers, ABS is a thermoplastic characterized by poor flame and chemical resistance. It is commercially available since the early 1950s. As it is made up of three monomers, all three impart their characteristics in the final polymer form. Acrylonitrile contributes chemical and heat resistance, and high strength; butadiene contributes with improved toughness, impact strength; styrene contributes rigidity and processability. ABS is considered to be hard, tough and rigid and its major uses include pipes, fittings, tele-phones, automotive parts and appliances[5, 6].

The increasing use of polymer blends requires the need to evaluate the thermal stability of these materials. Thermal degradation of polymers usually follows more than one mechanism. Kinetics determination becomes complicated due to the presence of concurrent chemi-cal reactions along with evaporation. The kinetic study is important to determine as it provides information on useful treatments to avoid thermal degradation and to estimate the service life of materials[7]. A large number of publications have been presented to understand the thermal degradation phenomena and its kinetics[8–11]. Py-rolysis of polymers involves complex reactions. To identify and understand the pyrolysis process, TGA is useful in evaluating decomposition and its reaction kinetics. Research has been carried out worldwide to use TGA for thermal decomposition behavior analysis of various polymer blends. Sanjiv Arora et al.[12] did a comparative kinetic study of some biopolymers using TGA/DTA at multiple heating rates and proposed reaction mechanism using model-free methods (FWO, Kissinger, Friedman and modified Coats-Redfern) to calculate activation energy. These methods are being used increasingly for the kinetic parameters determination of polymers. Esin Apaydin-Varol et al.[4] used TGA-FTIR study to determine pyrolysis kinetics and thermal decomposition behavior of polycarbonates. Katarzyna Slopiecka et al.[13] described kinetic studies of poplar wood using model-free methods. Yuezhan Feng et al.[14] applied iso-conversional methods

on TGA data to understand the thermal decomposition mechanism and kinetics of polycarbonate/silica nanocomposites. Thermal degradation of bisphenol A polycarbonate was evaluated by Xin-Gui Li et al.[15] using high-resolution thermogravimetry. They used Freeman-Carroll, Friedman and Chang methods to determine kinetic parameters. Hamou Moussout et al.[16] investigated the kinetics and degradation mechanisms of biocomposites using FTIR and TGA. The activation energy (E_a) was calculated using Flynn-Wall-Ozawa (FWO), Friedman and Kissinger-Akahira-Sunose (KAS) methods. These model-free methods were also applied on chitosan by M. A. Gamiz-Gonzale et al. to understand kinetic and degradation mechanisms under various heating rates[17].

As blending improves the characteristics of ABS by the addition of PC, the study of their thermal behavior and kinetics determination is very important. Rafael Balart et al.[18] used non-isothermal thermogravimetric analysis for the kinetic study of recycled ABS using model-free methods while Shuying Yang et al.[19] used an isothermal approach to find activation energy values for ABS. Esin Apaydin-Varol et al.[4] determined pyrolysis kinetics and decomposition behavior of polycarbonate using FWO and Friedman methods. Kinetics of ABS and PC have been determined individually using model-free methods in the past. To better understand the characteristics of blends, their thermal and kinetic analysis is very important so this work focused to determine the activation energy values and thermodynamic parameters of the blend of ABS and PC, present in equal amounts, using thermogravimetric analysis.

This work aimed to investigate the kinetics of thermal decomposition of ABS/PC polymer blend at four different heating rates. Thermogravimetric analysis was used to record the changes in mass with respect to time and temperature. It is a common technique used for the kinetic analysis of the heating process. Kinetic data from TGA can be analyzed using model-fitting or model-free methods. In the model-fitting method, a statistically best-fit model is obtained and kinetic parameters are calculated. Model-free methods make no assumption about the reaction order or reaction function. Kinetic curves were plotted and analysis performed. This work utilized model-free methods to investigate kinetic parameters. Various computational methods are available, amongst which iso-conversional and multi-heating methods (Kissinger, Flynn-Wall-Ozawa, and Friedman) are quite simple and widely used to estimate the kinetics of polymer blends[19, 20]. In the present work, above mentioned three model-free non-isothermal methods were used to estimate the activation energy. Thermodynamic parameters such as enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS) have been calculated using FWO method.

EXPERIMENTAL

Materials and sample preparation

ABS/PC sample used for TGA studies was commercial grade blend (50/50 wt. %) obtained from Lucky Plastics, Pakistan. Blend preparation was done using an internal mixer and then the desired sheet was molded, using equal weights of ABS and PC at about 280°C.

Thermogravimetric analysis

No pretreatments were done and the sample was used directly for the analysis. Thermogravimetric analysis was performed using simultaneous TGA/DSC (model, TA instruments, USA). The results were analyzed by a Qtech SDT Q600 analyzer. For each test, about 10 mg sample was taken and heated from 25°C to 520°C at different heating rates of 5, 10, 15 and 20°C/min. Experiments were performed in nitrogen environment where its flow was maintained at 10 ml/min. For each heating rate, experiments were repeated twice, to verify the reproducibility of kinetic curves.

Kinetic analysis: Theoretical approach

Iso-conversional methods do not need reaction mechanism information to determine kinetic parameters. In these methods, reaction rate depends on temperature and time, at constant value of α, degree of conversion. Kinetics of polymer thermal degradation is described by a single step equation as[22, 23]

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = k(T)f(\alpha) \tag{1}$$

where t is time, T is temperature, and α is degree of conversion, determined from TGA, calculated as α = $(m_o - m_t)/(m_o - m_f)$, with m_o, m_t and m_f representing initial, instantaneous and final mass of sample, β is heating rate dT/dt and $k(T)$ is the rate constant, which is expressed using Arrhenius equation

$$k = Ae^{-E_a/RT} \tag{2}$$

In this equation, A is pre-exponent factor, E_a is the activation energy, R is the universal gas constant and T is absolute temperature

Substituting the value of $k(T)$, equation (1) will be

$$\frac{d\alpha}{dt} = Ae^{-\frac{E_a}{RT}}f(\alpha) \tag{3}$$

Three iso-conversional model-free methods, Kissinger, Flynn-Wall-Ozawa and Friedman have been used to find the kinetics of the degradation process. Expressions and plots of each method have been summarized in Table 1[24, 25]. Model-free methods allow the determination of activation energy without using any reaction mechanism assumptions.

Table 1. Iso-conversional model-free methods used to determine activation energy

Methods	Expressions		Plots
Kissinger	$ln\frac{\beta}{T^2} = ln\frac{AR}{E} - \frac{E_a}{RT}$	(4)	$ln(\beta/T_p^2)$ vs $1/T_p$
Flynn-Wall-Ozawa	$ln\beta = log\left(\frac{AE_a}{Rg(x)}\right) - 5.331 - 1.052\frac{E_a}{RT}$	(5)	$ln\beta$ vs $1/T$
Friedman	$ln\frac{d\alpha}{dt} = lnA.f(\alpha) - \frac{E_a}{RT}$	(6)	$ln\frac{d\alpha}{dt}$ vs $1/T$

Kissinger method uses maximum decomposition temperature (T_p) at which reaction rate is maximum and the highest conversion is obtained. The slope of the curve $ln(\beta/T_p)^2$ vs $1/T_p$ gives the value of activation energy. FWO method is the most commonly used technique for kinetics calculation. In this model, $ln\beta$ vs $1/T$ curves are plotted at different heating rates for conversion degree

values of α = 0.1 – 0.9. The slope of the curves gives −0.453E_a/R value[4]. Friedman method also used plot of *ln* (*dα/dt*) vs 1/*T* at progressing conversion degrees α = 0.1 to 0.9 for β values of 5, 10, 15 and 20ºC/min. From the slopes of curves, activation energies were calculated. This work used heating rate of 10ºC/min to calculate pre-exponential factor (*A*) and thermodynamic parameters (such as enthalpy *ΔH*, Gibbs free energy *ΔG* and entropy *ΔS*) using FWO method. All these can be expressed as following equations[26, 27]

$$A = \beta \cdot E_a \cdot \exp(\frac{E_a}{R \cdot T_p})/(R \cdot T_p^2) \qquad (7)$$

$$\Delta H = E_a - RT \qquad (8)$$

$$\Delta G = R \cdot T_p \cdot \ln(\frac{K_B \cdot T_p}{h \cdot A}) \qquad (9)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_p} \qquad (10)$$

where K_B is Boltzmann constant with value of 1.381 × 10^{-23} (J/K) and h is Plank constant 6.626 × 10^{-34} (Js).

RESULTS AND DISCUSSION

Thermogravimetric analysis of ABS/PC

TG and DTG curves of the blend at four different heating rates have been shown in Figures 1 & 2. From room temperature to 230ºC, there is no significant change in the original sample mass. Upon heating above 230ºC, thermal degradation starts and it occurs in two ranges, from 230 to 370ºC, and from 380 to 490ºC. From 5ºC/min to 20ºC/min heating rate, mass loss has been measured to be approximately 12%, 10%, 4% and 3% respectively at temperature 370ºC. This loss represents moisture removal from the sample. In general, the sample shows a major mass loss from approximately 370 to 490ºC. As shown in the figure, the blend experiences approximately total weight loss in the given temperature range at all heating rates. For β = 20ºC/min, major mass loss starts at around 390ºC while it is 370ºC for β = 5ºC/min. At 5ºC/min, sufficient time is available for the moisture removal, so mass loss is higher (12%) while at 20ºC/min, moisture loss is only 3% until major degradation starts at 390ºC. So thermal stability is more at higher heating rates as the onset temperature of degradation is higher in case of 20ºC/min heating rate.

From Fig. 2, it can be seen that for β = 5ºC/min, highest weight loss (7.5%) occurs at 393ºC while for 20ºC/min, weight loss is 40.8% at 481ºC. There is no significant
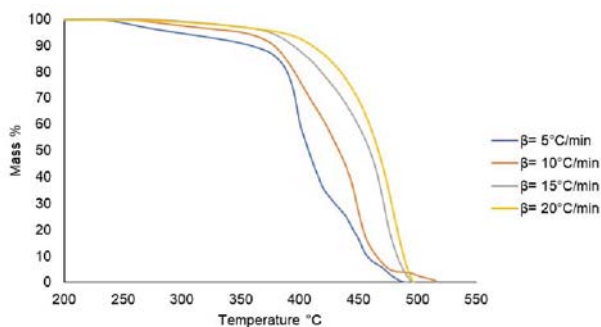
Figure 1. Thermogravimetric curves of ABS/PC at four different heating rates

change in thermal decomposition pattern by increasing β (except at 5ºC/min), but TG and DTG curves have been shifted towards higher temperatures. The maximum peak temperature is moved from 393 to 481ºC, when β increases from 5 to 20ºC/min. Therefore, it can be said that higher heating rate caused change in maximum peak temperature. As shown in Figure 2, curves show shifting to higher temperatures as β increases from 5 to 20ºC/min. So there is delay in the thermal degradation of the sample, due to heat transfer lag since the sample attains decomposition temperature in a shorter time when heating rate is increased[23, 28]. At 20ºC/min, there is a broader temperature range between onset and offset temperature while this range narrows down as heating rate is reduced to 5ºC/min. This variation exists due to shorter time to attain decomposition temperature at higher heating rates.
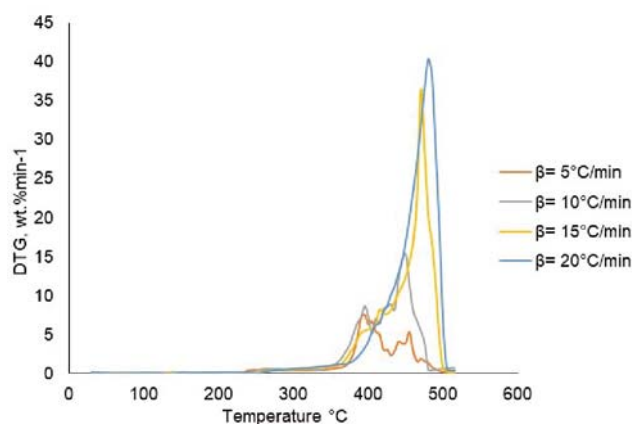
Figure 2. DTG curves of ABS/PC at four different heating rates

Temperatures for maximum reaction rate are 393, 446, 470 and 481ºC for 5, 10, 15 and 20ºC/min respectively. Figure 3 represents the relationship between heating rate and maximum thermal degradation temperature. It is evident from figure that linear relationship exists between degradation temperature and heating rate.
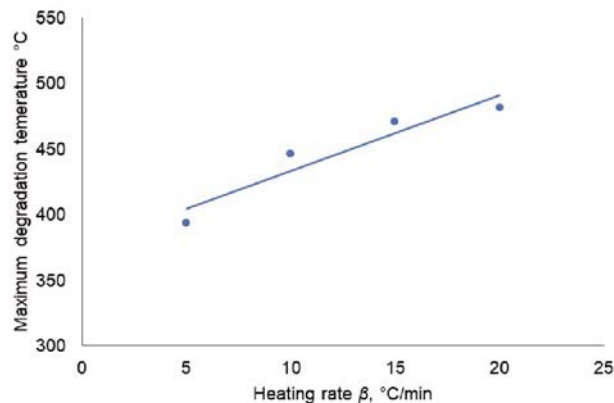
Figure 3. Relationship between *β* and maximum peak temperature T_p

Activation energy

Kinetic studies have been done on heating rates (5, 10, 15 and 20ºC/min) according to three methods (Kissinger, FWO and Friedman), for thermal degradation process ranging from room temperature to 520ºC.

Figure 4 represents the plot of Kissinger method. To estimate the activation energy through Kissinger method, peak temperatures are determined from DTG curves (Fig. 2). Decomposition activation energy has been found from slope of the straight line plot of $ln(\beta/T_p^2)$ against $1/T_p$, as evident from Figure 4. Activation energy is calculated to be 51.44 kJ/mol with R^2 value of 0.97 from slope of the line.
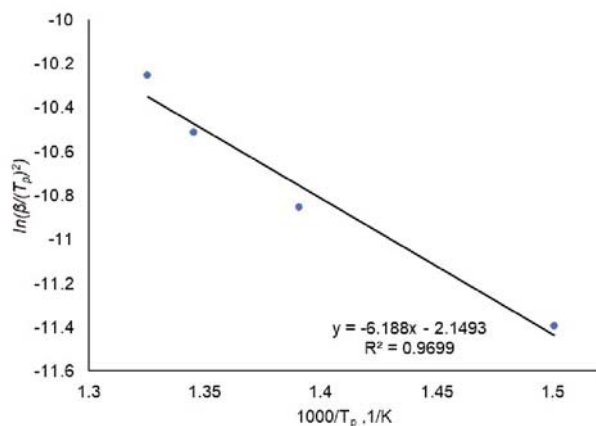

Figure 4. $ln(\beta/T_p^2)$ vs $1000/T_p$ plot for ABS/PC at four different heating rates

The conversion values (α) from 0.1 to 0.9 have been used to determine the activation energy by using FWO method. In this method, the temperature corresponding to specific α value has been measured from TG, at different heating rates and E_a values have been calculated from the curves of $ln\beta$ vs $1000/T$ (Fig. 5). For each value of α, slope corresponds to E_a/R. Since fitted lines appeared to be almost parallel to each other, there is possibility of single reaction mechanism. Activation energy values at different conversion (α) values have been presented in Table 2. For conversions, less than 50%, activation energy value lied between 80 to 90 kJ/mol. Highest E_a value 161.5 kJ/mol, occurred at 90% conversion of the blend. E_a values are believed to play a key part in the degradation kinetics of the blend at the initial and final stages of thermal decomposition. Low activation energy values are for the initial stages where weak bonds exist. Later its value rises when complex chemical bonding involves[8, 29].

Since calculated activation energy is different at all α values, there must be complex multistep mechanism involved in thermal degradation, with E_a dependent upon α. Activation energies of ABS/PC sample have also been calculated using Friedman method over a range of α values (0.3 to 0.8). Figure 6 represents the plot of $ln(d\alpha/dt)$ against $1000/T$, where slopes of the fitted lines give activation energy values.
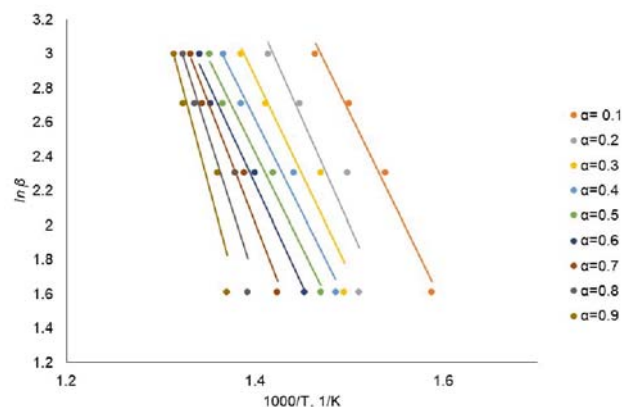

Figure 5. Plot of $ln\beta$ vs $1000/T$ for ABS/PC blend at various conversion α values
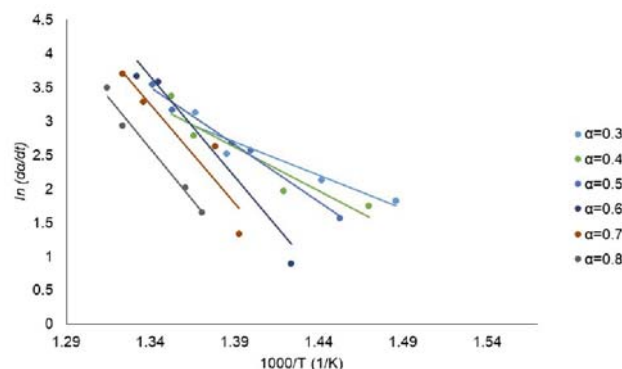

Figure 6. Linear plots of $ln(d\alpha/dt)$ against $1000/T$ in Friedman method

Most of the lines in the plot are parallel to each other except some lines (such as $\alpha = 0.3$ and 0.4) which are not parallel. It indicates the complexity of the decomposition mechanism. Values at low conversion ($E_a = 55.7$ kJ/mol at $\alpha = 0.3$) have been different than values at high conversion ($E_a = 241.7$ kJ/mol at $\alpha = 0.8$), indicating the different degradation mechanisms at initial and final stages of the process. Values calculated by Friedman method have been mostly higher than by FWO method and the same trend is followed in the case of ABS/PC blend[8]. Variation of E_a (calculated by FWO and Friedman methods) with α is shown in Figure 7.

E_a values of different ABS samples have been reported to be above 200 kJ/mol by H. Polli et al. while the ABS/PC blend gives average values to be 105 and 145 kJ/mol by FWO and Friedman method respectively[30].

Table 2. Kinetic and thermodynamic parameters of ABS/PC blend at the maximum differential conversion under the heating rate of 10°C/min

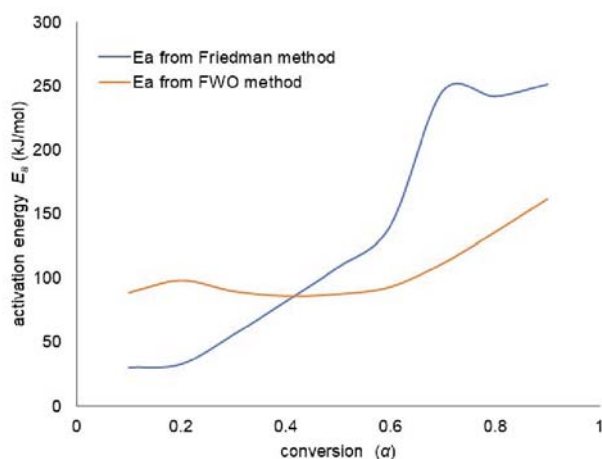| α	E_a (kJ/mol)	A (s^{-1})	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol)
0.1	88.75	2.09×10^{-04}	82.77	320.77	−331.01
0.2	98.16	2.31×10^{-04}	92.18	329.57	−330.16
0.3	89.70	2.11×10^{-04}	83.72	321.65	−330.92
0.4	86.14	2.02×10^{-04}	80.16	318.34	−331.26
0.5	87.50	2.06×10^{-04}	81.52	319.60	−331.13
0.6	93.10	2.19×10^{-04}	87.12	324.83	−330.61
0.7	111.43	2.63×10^{-04}	105.45	342.06	−329.09
0.8	135.54	3.21×10^{-04}	129.56	364.98	−327.42
0.9	161.46	3.84×10^{-04}	155.48	389.83	−325.93

Figure 7. Effect of activation energy obtained from FWO and Friedman methods vs conversion

Similar E_a value (134 kJ/mol) for ABS has been determined by Shuying Yang et al.[19], using Freeman and Carroll isothermal approach. Pure polycarbonate average E_a values have been determined to be 216 and 230 kJ/mol using FWO and Friedman methods respectively[4]. Table 2 shows kinetic parameters at the point of maximum conversion. Activation energies have been calculated using FWO equations using peak temperature. Pre-exponent factor (A) is calculated using equation (7) and its values lie in the range of 2×10^{-4} to 3.8×10^{-4}. These values are related to material structure while activation energies give information about sample reactivity. Low values of A and E_a depicts how fast degradation of the blend occurs. Table 2 also shows the values of ΔH, ΔG and ΔS for the main degradation steps. The enthalpy variation of the blend exists between 82 and 156 kJ/mol. Enthalpy is a state function and represents reactions from the heat absorbed or released. Its value increases with an increase in conversion and temperature. So more thermal energy is supplied to break the stronger bonds at higher temperature[26]. Gibbs free energy shows the favorability of the reaction according to thermodynamics laws. Its value is in between 318 to 390 kJ/mol. From Table 2, it can be seen that ΔS values are negative. It indicates that the degree of disorder of products made by pyrolysis is lower than that of reactants. Low values also mean that material is closed to its thermodynamic equilibrium state, indicating less reactivity and more time required to form activated complex[31].

CONCLUSION

TG analysis was performed to evaluate the thermal degradation kinetics of ABS/PC blend in nitrogen atmosphere. The present study showed that ABS/PC showed thermal stability up to 230°C. The major mass loss occurred above 230°C and continued until 500°C. The apparent activation energy was determined using Kissinger, Flynn-Wall-Ozawa and Friedman methods. The activation energy of ABS/PC blend was 51.4 kJ/mol when calculated by Kissinger method. The average value from FWO and Friedman methods was 105.75 and 145.65 kJ/mol respectively. Results obtained from FWO and Friedman were in good agreement. These kinetic analysis results showed that activation energy is dependent upon conversion, implying the complex nature of thermal degradation of ABS/PC blend. Thermodynamic parameters were also calculated. Enthalpy values increased with an increase in temperature and conversion, which showed more thermal energy requirement at higher temperature to break bonds. ΔS values varied from –331.26 to 325.93 J/mol indicated decreased disorder of products. Work is in progress to study nano surface mechanical characteristics of ABS/PC blends having different compositions of ABS and PC.

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