

## Thermal degradation kinetics of Arylamine-based Polybenzoxazines

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### ABSTRACT

In this research, the thermal degradation kinetics of arylamine-based polybenzoxazines (i.e. PBA-a, PBA-mt, and PBA-35x) were determined. The thermogravimetric analysis (TGA) was carried out in nitrogen atmosphere, at several heating rates: 5, 10, 20, and 40° C/min. In order to determine kinetics of thermal decomposition of three arylamine-based polybenzoxazines, the derivative of TGA (DTG) was deconvoluted via peak-fit program. The DTG thermograms of the blends exhibited three sub-stages of degradation reaction. In this study, Kissinger method and Flynn-Wall-Ozawa method were employed to determine the apparent activation energy ( $E_a$ ) of each sub-stage.

*Keywords:* Polybenzoxazine, Thermal Degradation Kinetics, Activation Energy.

### INTRODUCTION

Polybenzoxazine is a newly developed class of thermosetting resins derived from ring-opening polymerization of their precursors. The polymer possesses various good properties such as high thermal stability, easy processability, low water absorption, near zero shrinkage after processing with excellent mechanical properties. The polymer can be synthesized using the patented solventless technology to yield a clean precursor without the need for solvent elimination or monomer purification (Ishida, 1996). The degradation temperature and char yield of three arylamine-based polybenzoxazines has been reported in somewhere else. However, the apparent activation energy of the degradation of each sub-stage of these polymers has not been reported before.

### Kinetic Theory

Generally for polymer degradation, it is assumed that the rates of conversion are proportional to the concentration of reacted material. The rate of conversion can be expressed by the following basic rate equation

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

$$\alpha = \frac{(M_o - M_t)}{(M_o - M_f)} \tag{2}$$

where  $\alpha$  is the fraction of decomposition  
 $M_t$  is the weight of the sample at time  $t$   
 $M_o$  is the initial weight of the sample and  
 $M_f$  is the final weight of the completely decomposed sample

In the Arrhenius equation

$$k = Ae^{-E_a/RT} \tag{3}$$

Substituting “ $k$ ” from Eq. (1) into Eq. (3)

$$\frac{d\alpha}{dt} = Af(\alpha)e^{\frac{-E_a}{RT}} \tag{4}$$

According to non-isothermal kinetic theory, thermal degradation of a polymer can be expressed by the following function.

$$\beta = dT / dt \tag{5}$$

$$g(\alpha) = \frac{d\alpha}{dT} = \frac{1}{\beta} Ae^{\frac{-E_a}{RT}} f(\alpha) \tag{6}$$

where  $f(\alpha)$  is the differential expression of a kinetic model function,  $\alpha$  is the conversion,  $\beta$  is the heating rate (K/min),  $E_a$  and  $A$  are the so-called activation energies (kJ/mol) and pre-exponential factor ( $\text{min}^{-1}$ ) for the decomposition reaction, respectively.  $R$  is the gas constant ( $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ ) and  $g(\alpha)$  is the integral function of conversion which is able to predict the decomposition mechanism.

Kissinger method, the most well-known differential method (Barrel *et al.*, 1998; Ozawa, 1965; Kissinger, 1957; Liaw and Shen, 1994) was applied to determine the activation energy of each sub-stage of decomposition. The activation energy can be determined by Kissinger method without a precise knowledge of the reaction mechanism, using the following equation.

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) + \ln[n(1 - \alpha_p)^{n-1}] - \frac{E_a}{RT_p} \tag{7}$$

where  $T_p$  and  $\alpha_p$  are the absolute temperature and weight loss at maximum weight-loss rate  $(d\alpha/dt)_p$ , respectively, and  $n$  is the reaction order. From a plot of  $\ln(\beta/T_p^2)$  versus  $1/T_p$ , the activation energy can be obtained from the slope.

Flynn-Wall-Ozawa method is another well-known method that can be employed to quantify kinetic parameters without any knowledge of the reaction

mechanisms. The main advantage of this method is that it is not based on any assumption concerning the temperature integral, giving, thus, a higher degree of precision to the results.

From Eq. (6), it can be integrated using the Doyle approximation (Flynn, 1997; Doyle, 1961). The result of the integration after taking logarithms is

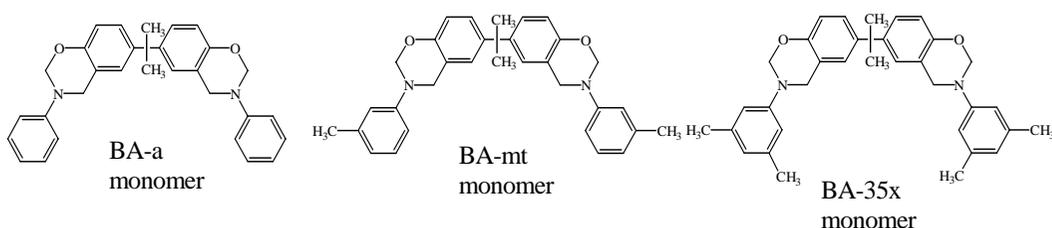
$$\log \beta = \log \frac{AE_a}{g(\alpha)R} - 2.315 - \frac{0.457E_a}{RT} \quad (8)$$

The apparent activation energy of the thermal degradation process of the blending system was determined from a plot of  $\log \beta$  versus  $1/T$ . This value can be obtained from the slope of the straight line.

## EXPERIMENTAL

### Raw Materials

Three different aromatic amines (i.e. aniline, m-toluidine, and 3,5-xylidine) were used to synthesize 6,6'-bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane (BA-a), 6,6'-bis(3-(3-methyl)phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane (BA-mt), and 6,6'-bis(3-(3,5-dimethyl)phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane (BA-35x), (Figure1). Bisphenol-A and paraformaldehyde were received from Thai Polycarbonate Co. Ltd. and Merck Company, respectively. A series of aromatic amines, i.e. aniline (99%) and 3,5-xylidine (98%), purchased from Fluka Chemika were used as received. A series of benzoxazine resin based upon alkyl-substituted arylamines were investigated. Bisphenol-A (Commercial grade) provided by Thai Polycarbonate Co., Ltd. (TPCC) was used as received. Para-formaldehyde (AR grade) and aniline (AR grade) were purchased from Merck and APS Finechem Companies.



**Figure 1** Benzoxazine monomers of three different aromatic amines

### Resin Preparation

BA-a resin was synthesized from bisphenol A, aniline and formaldehyde at the molar ratio of 1:2:4. The arylamines of m-toluidine, and 3,5-xylidine were applied to synthesize BA-mt resin and BA-35x resin, respectively with the same molar ratio. The mixture was constantly stirred at 110°C using the patented

solventless technology (Ishida H., 1996). The benzoxazine monomer is solid powder at room temperature with yellow color.

**Thermal gravimetric analysis (TGA)**

The decomposition temperature ( $T_d$ ) and char yield of the blends were studied using TGA Instruments (model TGA/SDTA 851<sup>o</sup>). The experiments were performed using various heating rates 5, 10, 20, and 40<sup>o</sup>C/min from 40 to 1000<sup>o</sup>C under nitrogen atmosphere. The flow of purging nitrogen was kept at 80 ml/min. The sample of approximately 20 mg was placed in 70  $\mu$ m alumina crucible during analysis.

**RESULTS AND DISCUSSION**

The TGA thermograms of benzoxazines with three different arylamines are shown in Figure 2. The degradation temperature and char yield of the polymers are summarized in Table 1.

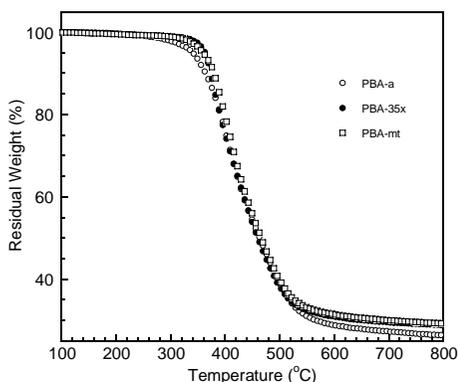


Figure 2 TGA thermograms of PBA-a, PBA-35x, and PBA-mt at 20<sup>o</sup>C/min in nitrogen atmosphere.

**Table 1** Degradation temperatures and char yield of three different aromatic amines

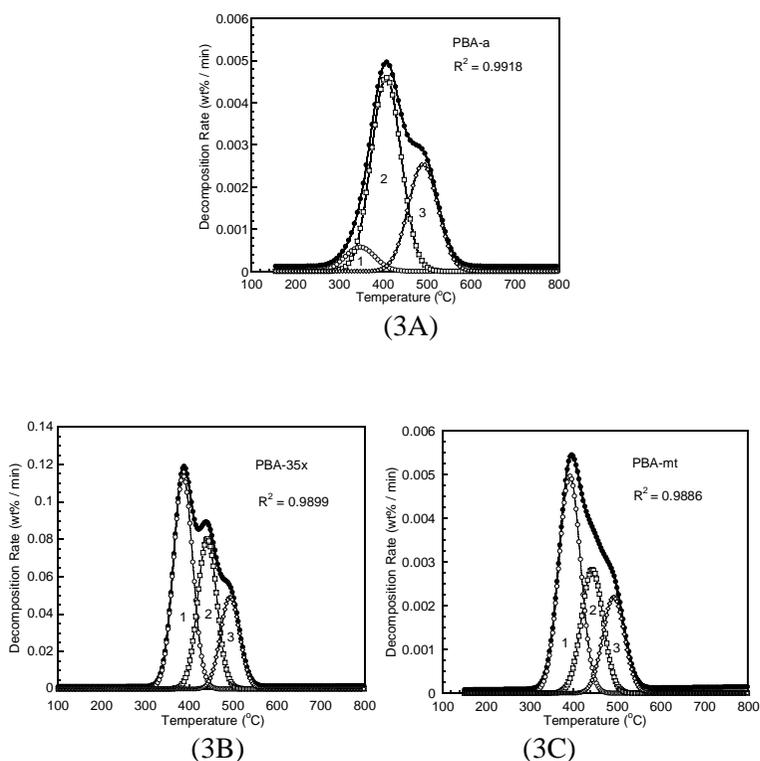
	$T_{10}$ ( <sup>o</sup> C) *	Char Yield at 800 <sup>o</sup> C (wt%)
PBA-a	364	26
PBA-35x	374	28
PBA-mt	377	31

\* Degradation temperature at 10% weight loss

From Figure 2 and Table 1, it could be noticed that PBA-a rendered the lowest thermal stability among three polybenzoxazine. Normally, the char yield indicates to the crosslink density and the amount of benzene ring (Takeichi *et al.*, 2005). Therefore, the values of char yield of three polymers had no significant difference.

When changing the heating rate from 20°C/min to 40°C/min, it could be noticed that the TG curves were shifted to the higher temperature with increasing heating rate. That was attributed to the short time required for a sample to reach a given temperature at high heating rate. (Saikrasun and Saengsuwan, 2009)

Table 1 also shows that the degradation temperature of PBA-35x is close to that of PBA-mt. The degradation temperatures and char yield of both polymers are higher than those of PBA-a. When the derivative curves of the TGA thermograms (DTG) of each polymer were deconvoluted via Peak-fit program. It can be seen that three sub-stages of each polymer were observed in Figure 3. That means the decompositions of each polymer are composed of three main sub-stages.



**Figure 3** DTG curve and individual contributions of three polybenzoxazines at 20°C/min: (3A) PBA-a; (3B) PBA-35x; (3C) PBA-mt.

The initial degradation temperature ( $T_i$ ), final degradation temperature ( $T_f$ ), peak temperature ( $T_{peak}$ ), and area under the curve of each sub-stage at 20°C/min are shown in Table 2.

**Table 2** Initial temperature ( $T_i$ ), final temperature ( $T_f$ ), and peak temperature ( $T_{peak}$ ) of each sub-stage for polybenzoxazines at 20°C/min in  $N_2$  atmosphere.

sub-stage		PBA-a		PBA-35x		PBA-mt	
		peak	% area	peak	% area	peak	% area
1	$T_i$	280		304		323	
	$T_{peak}$	353	14	386	47	392	50
	$T_f$	426		467		459	
2	$T_i$	316		361		379	
	$T_{peak}$	408	58	441	33	444	28
	$T_f$	499		519		506	
3	$T_i$	413		416		430	
	$T_{peak}$	496	28	493	20	493	22
	$T_f$	577		569		552	
		$R^2 = 0.9918$		$R^2 = 0.9899$		$R^2 = 0.9886$	

From Table 2, it can be noticed that the initial degradation temperature for sub-stage 1 of PBA-a was lower than those of PBA-35x and PBA-mt. Area under the peak of sub-stage 1 of PBA-35x and that of PBA-mt were close to each other. That possibly related to the activation energy shown in the next part.

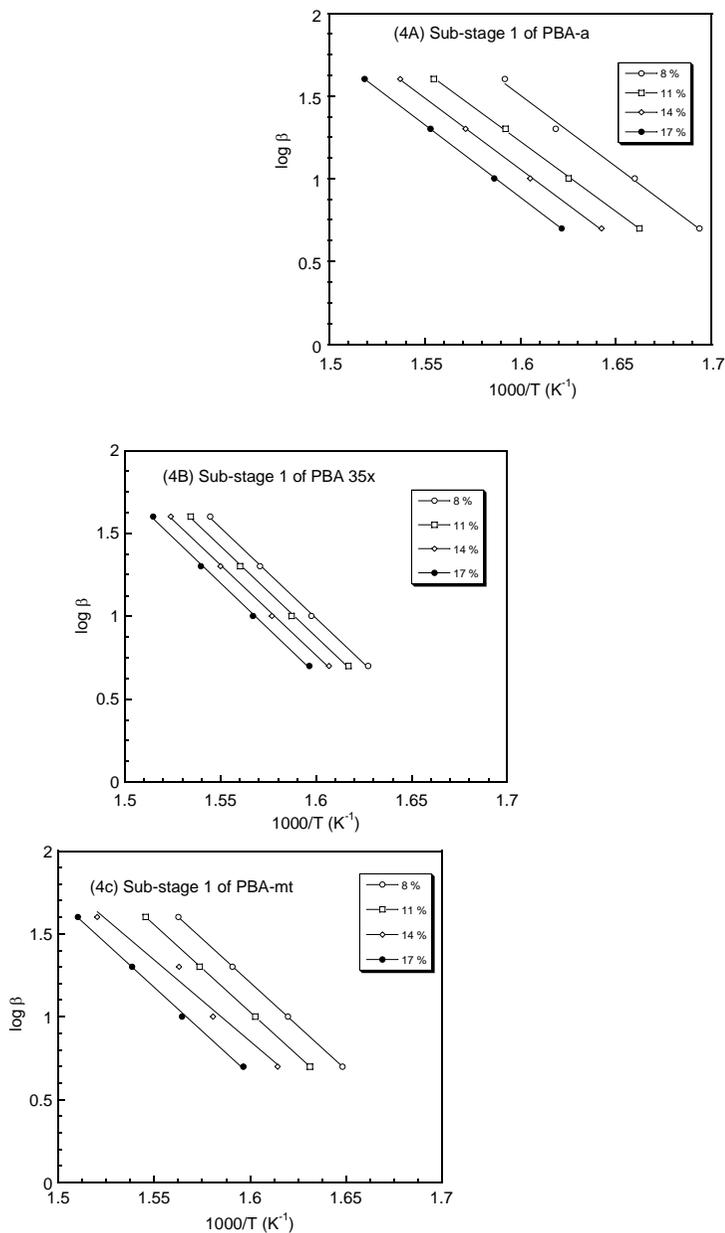
After the samples were characterized at different heating rates (i.e. 5, 10, 20, 40 °C/min), the activation energy of each sub-stage could be obtained from the slope of the curve between  $\ln(\beta/T_p^2)$  and  $1/T_p$ . The calculated values of  $E_a$  from Kissinger method are exhibited in Table 3.

**Table 3** Calculated activation energy of the sub-stage decomposition from Kissinger method

	$E_a$ of sub-stage 1 (kJ/mol)	$E_a$ of sub-stage 2 (kJ/mol)	$E_a$ of sub-stage 3 (kJ/mol)
PBA-a	115	178	235
PBA-35x	201	228	238
PBA-mt	202	215	246

From Table 3, it could be noticed that the activation energies of sub-stages of PBA-35x and PBA-mt were higher than those of PBA-a. That could be related to the initial degradation temperature and area under the peaks shown in Table 2.

To confirm the activation energies calculated from Kissinger method, Flynn-Wall-Ozawa method was employed. Figures 4(a) to (c) were examples of plots between  $\log \beta$  and  $1000/T$  for sub-stage 1.



**Figure 4** Plots of  $\log \beta$  versus  $1000/T$  according to Flynn-Wall-Ozawa method for sub-stage 1 of PBA-a, PBA-35x and PBA-mt with weight loss from 8% to 17% conversion. The plots for the other sub-stages of three polybenzoxazines were not shown in this report.

The calculated activation energies from Flynn-Wall-Ozawa method were shown in Table 4.

**Table 4** Calculated activation energy of the sub-stage decomposition from Flynn-Wall-Ozawa Method

	$E_a$ of sub-stage 1 (kJ/mol)	$E_a$ of sub-stage 2 (kJ/mol)	$E_a$ of sub-stage 3 (kJ/mol)
PBA-a	157	194	240
PBA-35x	190	217	230
PBA-mt	199	212	243

The activation energies obtained from Flynn-Wall-Ozawa method were in agreement with those obtained from Kissinger method. It could be noticed that the activation energies of sub-stage 3 for three polybenzoxazine were close to each other, while this phenomenon could not be observed in sub-stage 1.

## CONCLUSION

The degradation temperature and char yield of PBA-a were lower than those of PBA-35x and PBA-mt. The DTG thermograms of three polybenzoxazines with different aromatic amines reveal three sub-stage of thermal decomposition. The apparent activation energy of each sub-stage was reported using Kissinger model. The values for each decomposition stage of PBA-35x and PBA-mt were higher than those of PBA-a.

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