



Curing behaviors and thermal degradation kinetics of polybenzoxazine-polycaprolactone blends

Sukantika Manatsittipan¹⁾, Sarawut Rimdusit²⁾ and Sunan Tiptipakorn^{*1)}

¹⁾Research Unit to develop polymeric materials for industrial purpose, Department of Chemistry, Faculty of Liberal Arts and Science, Kasetsart University, 73140, Thailand.

²⁾Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, 10330, Thailand.

Received April 2016
Accepted June 2016

Abstract

In this study, the blends of polybenzoxazine (PBA-a)/polycaprolactone (PCL) was prepared at the weight ratio of 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100. The curing behaviors of the blends were studied. The results reveal that the curing temperature of the blends was increased with the increase of PCL content. The decomposition temperature at maximum decomposition rate were increased and the char yield were decreased with the PCL content. In addition, the kinetics of thermal degradation were determined using Kissinger Model.

Keywords: Polybenzoxazine, Polycaprolactone, Curing, Kinetics, Thermal degradation

1. Introduction

Benzoxazine resins which is a novel kind of high-performance thermosets can be synthesized from the formation of aldehyde, phenol and amine groups. The advantage of this resin is that there is no need to apply any catalyst, curing agent, or solvent upon synthesis. Moreover, no any by-product occurs when curing therefore no void was found in the final products. Great attention has been attracted because of many outstanding mechanical, thermal and physical properties with low water absorption and near zero shrinkage or expansion. [1-7]. However, the shortcoming of this polymer is its brittleness. One method to decrease this drawback is alloying the thermoset with other flexible component. Some blending systems are given as examples such as polybenzoxazine /dianhydride copolymer [8], benzoxazine/epoxy copolymer [7, 9], and polybenzoxazine/polycaprolactone blends [6, 10].

Huang and Yang studied the system of bisphenol-A/methylamine-based benzoxazine resin (BA-m) and poly(ϵ -caprolactone) (PCL). They reported that two glass transition temperatures (T_g s) of the blends exhibited partial miscibility of the two polymeric materials. [6] One interesting point of this system is that synergistic behavior in glass transition temperatures of the blends was previously revealed. Tiptipakorn et al. reported the effect of molecular weight of PCL on the blends and presented that the higher molecular weight of PCL led to the higher glass transition temperature of the blend because of the greater hindrance effects on the chain mobility. [10] Despite of many

interesting aspects, there was no report about its curing behavior including the thermal degradation kinetics of this blends. In this study, curing temperature and some parameters about thermal degradation such as activation energy and pre-exponential factor were determined.

In general, the rate of conversion for thermal degradation is proportional to the concentration of the polymers. Based on Arrhenius equation, the constant k can be calculated as the following equation

$$k = A \exp \left(-\frac{E_a}{RT} \right) \quad (1)$$

, where the gas constant of R is equal to $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, the activation energy (E_a) in the unit of $\text{kJ} \cdot \text{mol}^{-1}$, and A is the pre-exponential factor. In general, the E_a could be calculated by using Kissinger method [11]

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

, where β is heating rate upon analysis, R is gas constant, α_p is weight loss at maximum rate of decomposition, and T_p is absolute temperature at highest rate of thermal decomposition. From the slope of the straight line plotted between $\ln \left(\frac{\beta}{T_p^2} \right)$ and $1/T_p$, the activation energy of each step of thermal decomposition could be calculated. The benefit of this model is that there is no need to know the thermal decomposition mechanism in advance.

2. Methodology

2.1 Materials

Benzoxazine monomer (BA-a) could be synthesized via solventless technique using aniline, paraformaldehyde, and bisphenol A [12]. Polycaprolactone (PCL) was applied with the molecular weight of 10000 Da. All chemicals were purchased from Sigma-Aldrich. The BA-a monomer and PCL were mixed at the mass ratio of 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100. All mixtures were heated at 200°C for 4 hours before characterization of thermal degradation kinetics.

2.2 Curing temperature and thermal kinetics determination

The curing temperatures of unheated mixture were analyzed using differential scanning calorimeter (DSC) at the heating rate of 10°C/min with the nitrogen flow of 60 mL/min. The thermal degradation kinetics was investigated applying thermogravimetric analyzer (TGA). The heating rate was kept at 10, 15, 20, and 25°C/min at the heating rate of 10°C/min with the nitrogen flow of 80 mL/min. The weight of sample for both DSC and TGA analysis were kept at ca. 5-10 mg. All the derivative curves of the TGA thermogram were convoluted via Peak Fit Programs. The Kissinger model was used to calculate the kinetics parameters of each step of thermal decomposition.

3. Results and discussion

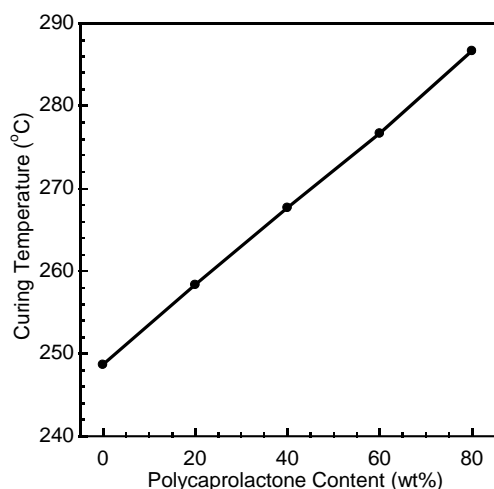


Figure 1 curing temperature of the PBA-a/PCL blends at various PCL contents

The curing temperatures of the PBA-a/PCL blends at various PCL contents are exhibited in Figure 1. It could be noticed that the curing temperature of the blends was systematically increased with PCL contents. This could be due to the hydrogen bonds between carbonyl group of polycaprolactone and hydroxyl group of benzoxazine monomer [13]. When the fully-cured blends were analyzed using TGA, the thermal decomposition temperature at maximum decomposition rate and char yield at 800°C were shown in Figure 2, respectively. It could be found that the temperatures at maximum decomposition rate were increased while the char yields were increased with PCL contents. The results were corresponded to those of

Tiptipakorn *et al.* studying PBA-a and PCL blends at 0-40wt% of PCL content [10].

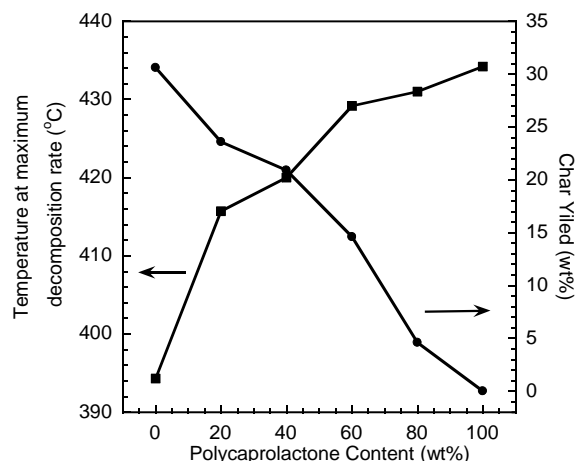


Figure 2 Temperature at maximum decomposition rate and char yield of the blends

As an example, the de-convoluted curves of pure PBA-a at heating rate of 20°C/min were presented in Figure 3. The derivative of TGA thermogram (DTG) of all compositions could be de-convoluted into three sub-stages of thermal decomposition. The peak of de-convoluted DTG thermogram and the area under the curve could be presented in Table 1.

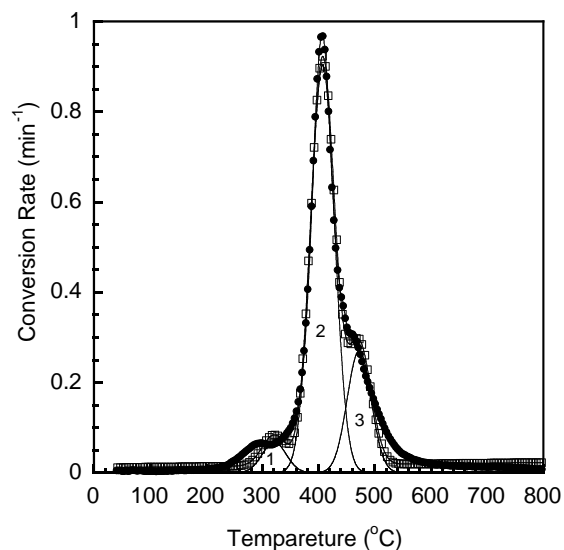


Figure 3 De-convoluted curves of pure PBA-a at 20°C/min

In this study, the composition of PCL at 40wt% was selected to determine the activation energy of thermal decomposition because the blends at this PCL content provided the optimum value of decomposition temperature and char yield (Figure 1). Furthermore, the blends at this composition provided greater glass transition temperature.

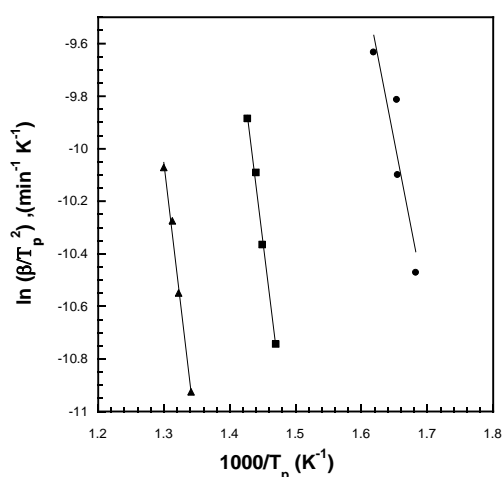
[10] The plot between $\ln\left(\frac{\beta}{T_p^2}\right)$ and $1/T_p$ were presented in Figure 4. The activation energy of each decomposition stage were presented in Table 2.

Table 1 Temperature at the highest decomposition (T_{peak}) and area under each sub-stage curve

PCL(%)		0	20	40	60	80	100
stage 1	T_{peak}	357	332	333	304	388	391
	% Area	21	5	4	3	8	12
stage 2	T_{peak}	415	415	421	428	430	433
	% Area	53	70	77	49	83	87
stage 3	T_{peak}	498	487	488	443	485	-
	% Area	26	25	17	46	8	-
R^2		0.9941	0.9958	0.9939	0.9999	0.9984	0.9977

Table 2 Activation energies calculated using Kissinger method for the blend (PCL = 40wt%)

Peak1		Peak2		Peak3	
E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2
107	0.9246	168	0.9965	175	0.9958

**Figure 4** Plots of $\ln\beta/T_p^2$ versus $1000/T_p$ at different heating rate according to Kissinger method for the blend at PBZ/PCL=60/40 (●) Peak 1, (■) Peak 2, and (▲) Peak 3.

From the E_a values of Table 2, the 1st stages could be expected to the decomposition of benzoxazine to the products such as benzene derivatives, phenolic compounds, and Mannich base compounds [14]. The 2nd stage could be proposed to be the de-polymerization step of PCL [15]. The 3rd stage could be related to the last step of PBA-a decomposition [14].

4. Conclusions

The curing temperature of the PBA-a/PCL blends were increased with PCL content. The decomposition temperature at maximum decomposition rate were increased and the char yield at 800°C were decreased with PCL content. The activation energy values of thermal decomposition for PBA-a/PCL at 40wt% were presented.

5. Acknowledgements

Financial support for this research was granted through a scholarship of the Graduate School, Kasetsart University, Year 2015, to Sukantika Manatsittipan.

6. References

- [1] Ishida H, Allen DJ. Physical and mechanical characterization of near-zero shrinkage polybenzoxazines. *J Polym Sci Polym Phys Ed* 1996; 34:1019-1030.
- [2] Ishida H, Allen DJ. Mechanical characterization of copolymers based on benzoxazine and epoxy. *Polymer* 1996;37:4487-4495.
- [3] Low HY, Ishida H. Structural effects of phenols on the thermal and thermo-oxidative degradation of polybenzoxazines. *Polymer* 1999;40(15):4365-4376.
- [4] Rimdusit S, Tiptipakorn S, Jubsilp C, Takeichi T. Polybenzoxazine alloys and blends: some unique properties and applications. *React Funct Polym* 2013; 73(2):369-380.
- [5] Rimdusit S, Jubsilp C, Tiptipakorn S. *Alloys and Composites of Polybenzoxazine: Properties and Applications*. Singapore: Springer; 2013.
- [6] Huang JH, Yang SJ. Studying the miscibility and thermal behavior of polybenzoxazine/poly(ϵ -caprolactone) blends using DSC, DMA, and solid state ^{13}C NMR spectroscopy. *Polymer* 2005;46:8068-8078.
- [7] Rimdusit S, Mongkhonsi T, Kamonchaivanich P, Sujirote K, Tiptipakorn S. Effects of polyol molecular weight on properties of benzoxazine-urethane polymer alloys. *Polym Eng Sci* 2008;48:2238-2246.
- [8] Jubsilp C, Takeichi T, Rimdusit S. Property enhancement of polybenzoxazine modified with dianhydride. *Polym Degrad Stabli* 2010;96(6):1047-1053.
- [9] Xu M, Yang X, Zhao R, Liu X. Copolymerizing behavior and processability of benzoxazine/epoxy systems and their applications for glass fiber composite laminates. *J Appl Polym Sci* 2013;128:1176-1184.
- [10] Tiptipakorn S, Keungputpong N, Phothiphiphit S, Rimdusit S. Effects of polycaprolactone molecular weights on thermal and mechanical properties of polybenzoxazine. *J Appl Polym Sci* 2015;132(18):1-11.
- [11] Kissinger HE. Reaction kinetics in differential thermal analysis. *Anal Chem* 1975;29:1702-1706.
- [12] Ishida H. Process for Preparation of Benzoxazine Compounds in Solventless Systems. US Patent 5,543,516. 1996 Aug 6.
- [13] Ishida H, Lee YH. Study of hydrogen bonding and thermal properties of polybenzoxazine and poly(ϵ -caprolactone) blends. *J Polym Sci Polym Phys Ed* 2001;39: 736-749.
- [14] Tiptipakorn S, Damrongsakkul S, Ando S, Hemvichian K, Rimdusit S. Thermal degradation behaviors of polybenzoxazine and silicon-containing polyimide blends. *Polym Degrad Stabli* 2007;92:1265-1278.
- [15] Persenaire O, Alexandre M, Degee P, Dubois P. Mechanisms and Kinetics of Thermal Degradation of Poly(ϵ -caprolactone) Biomacromolecules 2001;2:288-294.