

Properties and Thermal Degradation Study of Blend Films with Poly(4-Vinylpyridine) and Lignin

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ABSTRACT: A series of blend films with different ratio of poly(4-vinylpyridine) (PVP) to lignin were subjected to dynamic DSC and TGA measurement under nitrogen atmosphere at various heating rates. DSC curves showed that the glass transition temperatures of these blends decreased with the increase of lignin content. TGA studies indicated that the lignin content produced obvious effect on the thermal stability of these blends. The kinetic model function of the

thermal decomposition of these blends obeyed the Avrami-Erofeev model equation, $g(\alpha) = [-\ln(1-\alpha)]^{1/m}$. The degradation kinetic parameters were also obtained. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1875–1879, 2005

Key words: poly(4-vinylpyridine) (PVP); lignin; blend; glass transition; thermal stability

INTRODUCTION

There has been a great deal of interest in using organic materials in light-emitting diodes because of their low cost, ease of fabrication, low operating voltages, and good quantum efficiencies. Since poly(phenyl-vinylene) (PPV) was reported, a number of different polymers have been synthesized, and extended efforts have been made to get a better device from polymeric materials.^{1–3} Recently, the new photoluminescence (PL) of organic polymer poly(4-vinylpyridine) (PVP) has played a more important role⁴ and opened the route to polymer analogous reactions, which can introduce other electro-optically active components to be assembled via the electrostatic self-assembly (ESA) in various nano-devices.⁵ As a functional polymer, it should also be noted that PVP is very brittle and strongly adheres to the most solid surfaces, from which it is not possible to remove the membrane easily, to form a free-standing membrane. Lignin is a nontoxic, commercially available, and low-cost natural resource that has the potential to be utilized as a basic raw material in the chemical industry.⁶ Lignin, especially, with its many reactive hydroxyl groups, can form strong hydrogen bonding with many polymers, which has improved and modified the physical properties of the pure polymers.^{7–11} Therefore, a blend film prepared from PVP with lignin could overcome the strong adhesion with the most solid surfaces as well as the brittleness of PVP.

Based on the information mentioned above, we attempted to use the differential scanning calorimetry technology to measure the blend films at a heating rate 10°C/min. The degradation process and kinetic analysis using the dynamic TG method of these samples have also been described in detail.

EXPERIMENTAL

Material

By changing the weight ratio of PVP to lignin to 100 : 0, 96 : 4, 92 : 8, 90 : 10, 85 : 15, and 80 : 20, a series of blend films, coded as PVP-0, PVP-1, PVP-2, PVP-3, PVP-4, and PVP-5, were prepared at Wuhan University. These six samples have been characterized by MS, ¹H-NMR, ¹³C-NMR, and FT-IR.

Measurement by differential scanning calorimetry (DSC)

Glass transition temperatures of the PVP/lignin blend films were measured by DSC. The DSC analysis was performed on a METTLER-TOLEDO DSC822^e (Co., Switzerland). The temperature was recorded from room temperature to 250°C with heating rates of 10°C min⁻¹ under nitrogen flow of about 50 mL min⁻¹. The reference pan was pure aluminum pan.

Thermogravimetry (TG) and derivative thermogravimetry (DTG)

Dynamic TG of the PVP/lignin blend films was conducted on a TGS-2 thermal-balance (Perkin-Elmer Co., USA). The nominal heating rates of 8, 10, 15, 20,

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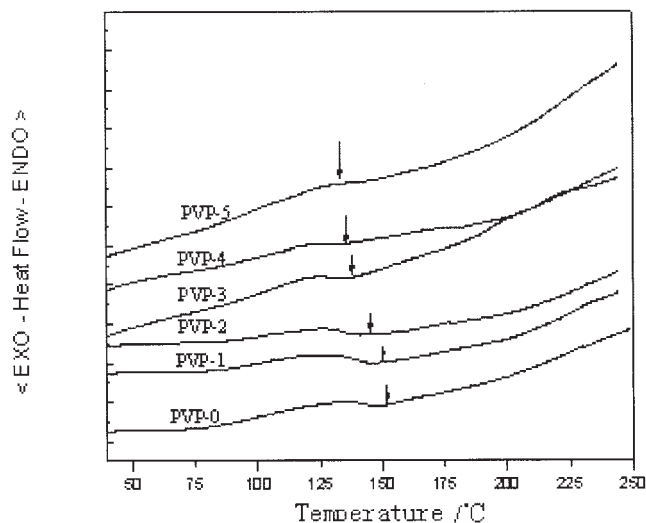


Figure 1 DSC curves of all samples with heating rate of $10^{\circ}\text{C min}^{-1}$ under nitrogen flow.

and $25^{\circ}\text{C min}^{-1}$ were employed from room temperature to 950°C . A pure nitrogen flow of 80 mL min^{-1} was used with sample size about 10.0 mg . All samples were preheated with a scan rate of 10°C/min over a temperature range $25\text{--}120^{\circ}\text{C}$ and maintained at 120°C for 10 min to ensure complete removal of residual solvent. The T_g was taken as the setout point of the heat capacity transition.

RESULTS AND DISCUSSION

Determination of the glass transition temperature by DSC

DSC is a convenient method to determine the miscibility of polymer blends. The special intermolecular interaction between PVP and lignin would be confirmed from the distinct changes in glass transition temperature T_g of

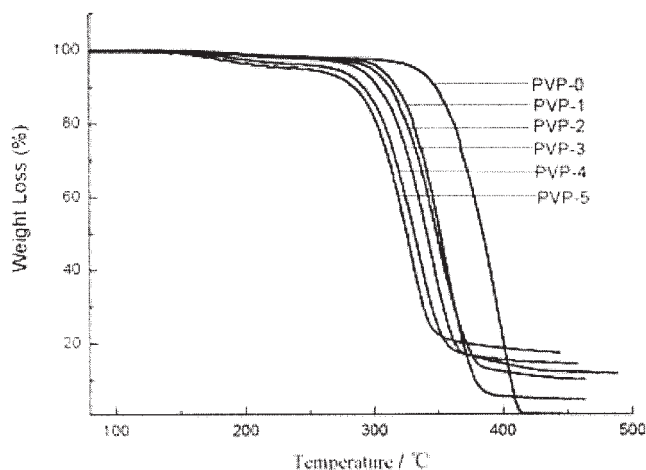


Figure 2 TG curves of all samples.

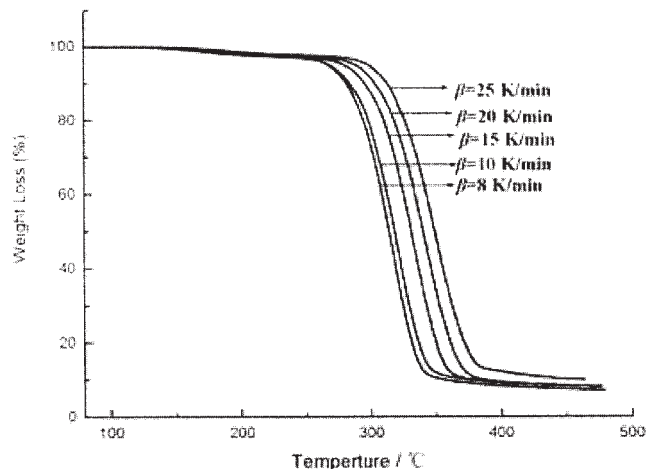


Figure 3 TG curves of the thermal degradation for sample PVP-2 at various heating rates.

the PVP component. In this study, to detect the parameter, all samples were preheated with a scan rate of 10°C/min over a temperature range of $25\text{--}120^{\circ}\text{C}$ and maintained at 120°C for 10 min to ensure complete removal of residual solvent. The DSC curves are shown in Figure 1. It can be seen that the T_g of each blend shifts to lower temperature with varying the blend composition by comparing with that of pure PVP. The glass transition temperatures of PVP-0, PVP-1, PVP-2, PVP-3, PVP-4, and PVP-5 lie on 151°C , 149°C , 144°C , 141°C , 139°C , and 136°C , respectively. Therefore, it is judged that PVP/lignin blends are completely miscible over the entire composition range. It may be the hydrogen bond interaction between the hydroxyl groups of lignin and the pyridine group of poly(4-vinylpyridine). Namely, the lignin contains a high density of hydroxyl groups that can interact with poly(4-vinylpyridine) through hydrogen bonding and weaken the interaction within the PVP. The stronger hydrogen bond decreased more the T_g of PVP.

Thermal degradation process of blend films with poly(4-vinylpyridine) and lignin

Figures 2 and 3 show the dynamic TG plots in nitrogen atmosphere of the six samples at the heating rate

TABLE I
Phenomenological Data for the Thermal Degradation of All Samples ($\beta = 25^{\circ}\text{C}\cdot\text{min}^{-1}$)

Samples	TG plateaux ($^{\circ}\text{C}$)	DTG peak ($^{\circ}\text{C}$)	T_d ($^{\circ}\text{C}/10\%$)	Mass loss (%)
PVP-0	305–415	398	350	99.2 (0.8)
PVP-1	273–395	356	319	95.4 (4.6)
PVP-2	266–398	350	313	89.7 (10.3)
PVP-3	263–399	346	302	88.2 (11.8)
PVP-4	244–390	334	293	85.2 (14.8)
PVP-5	239–377	328	283	80.7 (19.3)

TABLE II
The Activation Energies for the Six Samples at the Rate of 10 °C min⁻¹

Conversion α	E_a (kJ mol ⁻¹)					
	PVP-0	PVP-1	PVP-2	PVP-3	PVP-4	PVP-5
0.1	98.48	97.50	96.26	90.34	89.17	88.98
0.2	99.34	101.18	96.35	92.75	91.35	91.00
0.3	102.81	100.21	96.49	94.91	91.97	89.77
0.4	105.13	99.24	95.39	95.42	93.64	90.11
0.5	106.09	99.78	93.93	95.00	94.63	88.92
0.6	106.57	98.10	97.19	95.07	92.86	88.11
0.7	107.7	98.34	94.89	95.23	93.20	87.64
0.8	106.93	96.49	93.70	97.86	91.89	86.06
0.9	108.34	96.07	95.20	97.57	93.15	83.54
avg.	104.6	98.55	95.49	94.91	92.42	88.24

of 25 K min⁻¹ and the typical TG curves of the thermal degradation at different heating rates for the sample PVP-2. The phenomenological aspects of the porphyrin polymers are presented in Table I.

From Table I, we can see that all the films show one step of active weight loss at 50–420°C. The weight loss rates reduce with increasing content of lignin. The degradation is assigned to the degradation of PVP.¹² Because over 390°C the PVP has degraded almost completely, the residue was thought to be almost entirely lignin. The thermal degradation temperature of blend films clearly decreases, indicating that lignin had a destabilizing effect on PVP. The existence of lignin in the blends might aggravate the degradation of PVP at high temperature. It may be that the lignin caused the fall of the degree of crystallization of PVP, which decreased the thermal stability of the blends. The closest analog of the phenomenon was the poly(L-lactic acid)/lignin system.¹³

Thermal degradation kinetics of blend films with (4-vinylpyridine) and lignin

Kinetic parameters

We use the comparative method¹⁴ to evaluate reliable kinetic triplets (the activation energy E_a and the pre-exponential factor A) for the thermal degradation of the six polymer blends. The typical values of E_a cor-

responding to different values of α at the rate of 10°C min⁻¹ are shown in Table II.

Kinetic mechanism function

Through comparing the activation energies obtained from the KAS method with those obtained from the Achar equation and the Coats–Redfern equation with better correlation coefficients, the mechanism would be determined. All the decomposition courses of the six polymer blends are following the same mechanism function $g(\alpha) = [-\ln(1-a)]^{1/m}$ with different values of m . Hence the mechanism is “random nucleation and growth,” representing the Avrami–Erofeev equation. The possible kinetic models and respective kinetic parameters from differential and integral equations at various heating rates for these samples are shown in Tables III–VIII.

The various kinetic parameters calculated are given in Table IX. The activation energies E_a in the different stages are in the range of 88.24 ~ 104.6 kJ mol⁻¹. The respective values of the pre-exponential factor A vary from 1.27×10^5 (s⁻¹) to 1.03×10^8 (s⁻¹).

Thermal stability

From the decomposition temperatures and the values of activation energies in Tables I and IX, the informa-

TABLE III
The Kinetic Parameters from Differential Method and Integral Method at the Five Heating Rates for PVP-0

β (K · min ⁻¹)	Function no.	Coats–Redfern method			Achar method		
		E_a (kJ/mol)	$\ln A$ (s ⁻¹)	R	E_a (kJ/mol)	$\ln A$ (s ⁻¹)	R
8	9	92.34	12.18	0.9994	107.22	15.19	0.9948
10	9	92.82	12.27	0.9998	101.54	14.06	0.9962
15	9	87.80	11.45	0.9998	90.76	12.13	0.9985
20	9	88.66	11.68	0.9992	104.13	14.72	0.9913
25	9	87.17	11.16	0.9988	100.50	13.76	0.9514

TABLE IV
The Kinetic Parameters from Differential Method and Integral Method at the Five Heating Rates for PVP-1

β (K · min ⁻¹)	Function no.	Coats-Redfern method			Achar method		
		E_a (kJ/mol)	lnA(s ⁻¹)	R	E_a (kJ/mol)	lnA(s ⁻¹)	R
8	8	107.68	18.46	1.0001	108.45	18.69	0.9995
10	8	104.67	17.84	0.9997	99.10	16.79	0.9990
15	8	95.26	17.92	0.9999	99.65	16.87	0.9987
20	8	96.94	18.28	0.9997	101.10	17.20	0.9981
25	8	103.36	19.83	1.0000	107.66	20.73	0.9982

TABLE V
The Kinetic Parameters from Differential Method and Integral Method at the Five Heating Rates for PVP-2

β (K · min ⁻¹)	Function no.	Coats-Redfern method			Achar method		
		E_a (kJ/mol)	lnA(s ⁻¹)	R	E_a (kJ/mol)	lnA(s ⁻¹)	R
8	8	107.14	16.48	1.0000	104.90	16.09	0.9997
10	8	107.12	16.52	0.9998	103.30	15.81	0.9979
15	8	106.46	16.28	0.9999	103.30	15.72	0.9993
20	8	101.90	15.27	0.9993	90.43	13.09	0.9984
25	8	104.08	15.67	0.9991	91.93	13.39	0.9981

TABLE VI
The Kinetic Parameters from Differential Method and Integral Method at the Five Heating Rates for PVP-3

β (K · min ⁻¹)	Function no.	Coats-Redfern method			Achar method		
		E_a (kJ/mol)	lnA(s ⁻¹)	R	E_a (kJ/mol)	lnA(s ⁻¹)	R
8	8	96.78	14.24	0.9998	93.34	13.61	0.9990
10	8	101.90	15.54	0.9998	101.22	15.48	0.9987
15	8	105.14	16.18	0.9998	102.84	15.80	0.9997
20	8	98.29	14.57	1.0000	93.67	13.75	0.9992
25	8	107.34	16.53	0.9995	103.03	15.76	0.9972

TABLE VII
The Kinetic Parameters from Differential Method and Integral Method at the Five Heating Rates for PVP-4

β (K · min ⁻¹)	Function no.	Coats-Redfern method			Achar method		
		E_a (kJ/mol)	lnA(s ⁻¹)	R	E_a (kJ/mol)	lnA(s ⁻¹)	R
8	8	98.15	15.02	0.9996	103.43	16.24	0.9961
10	8	97.68	14.91	0.9999	101.24	15.75	0.9975
15	8	98.09	14.99	0.9995	105.34	16.58	0.9960
20	8	96.58	16.84	0.9996	104.11	18.47	0.9958
25	8	101.79	15.86	0.9998	97.27	15.03	0.9990

TABLE VIII
The Kinetic Parameters from Differential Method and Integral Method at the Five Heating Rates for PVP-5

β (K · min ⁻¹)	Function no.	Coats-Redfern method			Achar method		
		E_a (kJ/mol)	lnA(s ⁻¹)	R	E_a (kJ/mol)	lnA(s ⁻¹)	R
8	8	91.82	16.17	0.9999	91.00	16.07	0.9972
10	8	90.96	16.03	0.9998	90.99	16.12	0.9934
15	8	97.71	17.41	0.9997	98.79	17.71	0.9978
20	8	97.60	17.36	0.9998	91.38	18.21	0.9983
25	8	97.51	17.34	0.9998	93.09	18.56	0.9984

tion of thermal stability of the polymer films can be obtained such that the existence of lignin in the blends might aggravate the degradation of PVP at high tem-

perature. It may be that the lignin caused the fall of the degree of crystallization of PVP, which decreased the thermal stability of the blends. The order of thermal

TABLE IX
Kinetic parameters for the Thermal Decompositions of the Polymer Films

Samples	E_a (kJ mol ⁻¹)	A (s ⁻¹)	Function no.	Mechanism
PVP-0	104.6	1.27×10^5	9	Avrami-Erofeev equation (m = 2)
PVP-1	98.55	1.03×10^8	8	Avrami-Erofeev equation (m = 3/2)
PVP-2	95.49	9.25×10^6	8	Avrami-Erofeev equation (m = 3/2)
PVP-3	94.91	4.64×10^6	8	Avrami-Erofeev equation (m = 3/2)
PVP-4	92.42	5.50×10^6	8	Avrami-Erofeev equation (m = 3/2)
PVP-5	88.24	2.10×10^7	8	Avrami-Erofeev equation (m = 3/2)

stability is therefore: PVP-0 > PVP-1 > PVP-2 > PVP-3 > PVP-4 > PVP-5.

CONCLUSIONS

The glass transition temperatures of these blends, which were measured by DSC to decrease with the increase of lignin content, indicated that these blends are able to form a miscible phase mainly due to the formation of intermolecular hydrogen bonding between the hydroxyl of lignin and the pyridine ring of poly(4-vinylpyridine).

The thermal stability of this series of polymer blends was studied using TG. The thermostability of these blends decreased with the increase of lignin content, which is in agreement with the values of activation energies. It may be that the lignin caused the fall of the degree of crystallization of PVP.

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