

Processing Thermal Stability and Degradation Kinetics of Poly(vinyl Chloride)/Montmorillonite Composites

Chaoying Wan, Guohua Tian, Ning Cui, Yinxi Zhang, Yong Zhang

Research Institute of Polymer Materials, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

Received 12 May 2003; accepted 10 September 2003

ABSTRACT: Thermal stability of polyvinyl chloride (PVC) based montmorillonite composites with either sodium montmorillonite (MMT) or alkyl ammonium ion modified montmorillonite (OMMT) were investigated by thermogravimetric analysis. The apparent activation energies associated with the first thermal degradation stage were calculated by the methods of Flynn–Wall–Ozawa and Kissinger in nitrogen atmosphere at several different heating rates. The processing thermal stability of PVC and PVC/MMT(OMMT) composites was also discussed. Increase of mixing torque did not result in a larger intercalation extent of PVC on MMT; instead, it unexpectedly induced discoloration of PVC and then deteriorated the processing stability,

especially in the presence of OMMT. The apparent activation energies in the first thermal degradation stage exhibited little difference among PVC, PVC/MMT, and PVC/OMMT composites, and the kinetic compensation effect of S_p^* kept a constant value, indicating that the thermal stability and thermal degradation mechanism of PVC were not affected by the presence of either MMT or OMMT, although the processing discoloration of PVC is observed for PVC/OMMT composite. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1521–1526, 2004

Key words: poly (vinyl chloride) (PVC); montmorillonite; thermal stability; kinetic analysis

INTRODUCTION

As a commodity thermoplastic, polyvinyl chloride (PVC) is of great technical and economic importance. PVC based layered silicate nanocomposites have also attracted increasing interest in recent years.^{1–6} Previous studies showed that PVC clay nanocomposites have intercalated or exfoliated structures depending on the type of organic modifier of the clay.^{1,2,5,6} The flame retardancy,³ dimensional stability, gas permeability barrier properties⁴, and mechanical properties^{1,5,6} of PVC/clay nanocomposites could be highly enhanced with a low extent of clay addition.

Despite the favorable improvements in properties, the processing stability of PVC was found to deteriorate in the presence of clay.^{4,7} Under the processing temperature of 170°C, PVC was quickly turned purple and then black after being blended with clay. Solomon⁸ and Jerzy⁹ also reported that silicate layers could promote a dehydrochlorination reaction of PVC and particular stabilizers were needed to protect against PVC discoloration. However, a study on the thermal stability of PVC/clay nanocomposites by X-ray photoelectron spectra reported that clay could enhance the thermal stability by delayed loss of allylic species.³

To explore the effect of montmorillonite (MMT) on the processing discoloration and thermal degradation of PVC, we investigated the dynamic thermal degradation of PVC using thermogravimetric analysis and calculated the kinetic parameters according to the Flynn–Wall–Ozawa¹⁰ and Kissinger methods.¹¹ In addition, the effects of sodium montmorillonite (Na⁺-MMT) and alkyl ammonium ion modified montmorillonite (OMMT) on the processing stability and thermal degradation of PVC were also compared.

EXPERIMENTAL

Materials and sample preparation

A suspension PVC (WS 800S) with degree of polymerization of 800 was obtained from Shanghai Chlor-Alkali Chemical Co., Ltd. (China). The sodium-montmorillonite clay (MMT) and dimethyl bis(hydrogenated tallow) ammonium exchanged montmorillonite clay (OMMT) were provided by Zhejiang Huate Group Co. (China). The mean particle size of montmorillonite clay was 18–23 μm . The processing additives used in this study, including dimethyltin *S,S'*-bis(isooctyl mercaptoacetate)(TM-181, Rohm and Haas Co.), dioctyl phthalate (DOP), and stearic acid were commercial products.

PVC resin, processing additives (containing 5 parts per hundred parts of resin (abbreviated as 5 phr) TM-181, 5 phr DOP, and 0.3 phr stearic acid) and 5 phr MMT or OMMT were melt blended using a Haake

Correspondence to: Y. Zhang (yong_zhang@sjtu.edu.cn).

TABLE I
Data of TGA and XRD for MMT (OMMT) and PVC/MMT (OMMT) Composites

Sample	TGA		XRD	
	T_1 (°C) ^a	Δm_1 (%) ^b	2θ (°) ^c	d (nm) ^d
MMT	—	—	7.30	1.20
OMMT	337.8	27.6	3.39	2.60
PVC/MMT	273.6	62.4	2.76	3.20
PVC/OMMT	272.3	61.0	2.20	4.00

^a The onset temperature in the first stage of degradation measured by TGA at a heating rate of 10°C/min.

^b The maximum weight loss in the first degradation stage measured by TGA at a heating rate of 10°C/min.

^c The diffusion angle of d (001) of MMT(OMMT) measured by XRD.

^d The interlayer distance between MMT(OMMT) layers calculated according to Bragg's equation, $\lambda = 2d\sin\theta$.

Rheocord 90 at 170°C for 6 min, with a rotor speed of 50 rpm. To investigate the effect of different mixing torque on microstructure and physical properties the rotor speeds of 30, 70, 90, and 120 rpm were also applied.

The above composites were compression-molded at 175°C and 20 MPa for 6 min, followed by cooling to room temperature under 10 MPa pressure to give 1- and 3-mm-thick plates. The samples for morphology characterization and physical properties measurements were cut from these plates.

Characterization and measurements

X-ray diffraction (XRD) measurements were performed using a Dmax-rC X-ray diffractometer, with a $\text{CuK}\alpha$ radiation ($\lambda = 0.154$ nm) and a scanning rate of 4°/min at 40 kV and 100 mA. The basal spacing of the silicate layers, d , was calculated according to Bragg's equation, $\lambda = 2d\sin\theta$.

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA7 thermal analysis system under a flowing nitrogen atmosphere (60 mL/min). The heating rates were set as 5, 10, 20, and 40°C/min and the scanning temperature was in the range from room temperature to 800°C.

Optical properties were measured on a spherical Hazemeter M57 at room temperature, using 3-mm-thick plates. Yellowness index (YI) was measured in accordance with ASTM D1925 on a Macbeth Color Eye 7000A spectrophotometer, using 3-mm-thick plates.

RESULTS AND DISCUSSION

Processing thermal stability

The characterization results of MMT(OMMT) and PVC/MMT(OMMT) composites by TGA and XRD are shown in Table I. It is shown that after organic mod-

ification by alkyl ammonium, the interlayer distance of MMT increases from 1.2 to 2.6 nm, and the organic content is about 27.6%. After melt blending with PVC, the interlayer distance of MMT is further increased to 3.2 nm, indicating that PVC molecular chains have intercalated into MMT layers through dipolar interactions.⁵ The interlayer distance of OMMT in the PVC/OMMT composite increases to 4.0 nm, which is larger than that of MMT in the PVC/MMT composite. This means the organic modification can not only increase the interlayer distance of MMT, but also enhance its affinity to PVC.

The effects of processing conditions on melt-intercalation of the PVC/MMT(OMMT) composites are shown in Table II. Increasing rotor speed aims to increase the shear stress and facilitate PVC intercalation. The XRD results show that the interlayer distance of MMT or OMMT in the PVC/MMT(OMMT) composites has little dependence on the shear stress, varying in the range of 3.0~3.2 and 3.8~4.2 nm with increasing shear stress (Table II). So the increase in shear stress is not necessary to enhance PVC intercalation. Furthermore, the PVC/OMMT composite changed its color from light yellow to pink with increasing shear stress, and the YI and haze values of the composite were increased consequently (Table II). In contrast, the resultant PVC/MMT composite showed less discoloration than the PVC/OMMT composite. During melt processing, the PVC is exposed to a high temperature and, in addition, the presence of oxygen could lead to thermooxidative degradation and the mechanical stress may cause chain scission. PVC is sensitive to dehydrochlorination and the conjugated polyene sequence could result in discoloration of PVC materials. The decomposing of the alkyl ammonium modifier under the processing temperature could cause the discoloration mechanisms to be more complex. Table I shows that the onset temperature of OMMT in the first degradation stage is about 337.8°C, which results from the decomposition of the alkyl ammonium modifier. But some free alkyl ammonium molecules between the silicate layers are not as stable

TABLE II
Effects of Different Mixing Torque on the Microstructure and Physical Properties of PVC/MMT (OMMT) Composites^a

Rotor speed (rpm)	PVC/MMT			PVC/OMMT		
	d (nm)	YI (%)	Haze (%)	d (nm)	YI (%)	Haze (%)
30	1.2	28.8	12.0	3.8	28.8	12.0
50	3.2	29.2	12.1	4.0	55.9	12.9
70	3.2	38.2	18.4	4.2	75.7	14.1
90	3.2	42.1	30.3	4.0	118.4	31.6
120	3.0	62.5	58.2	3.8	153.6	52.9

^a Processing conditions: temperature, 170°C; time, 6 min.

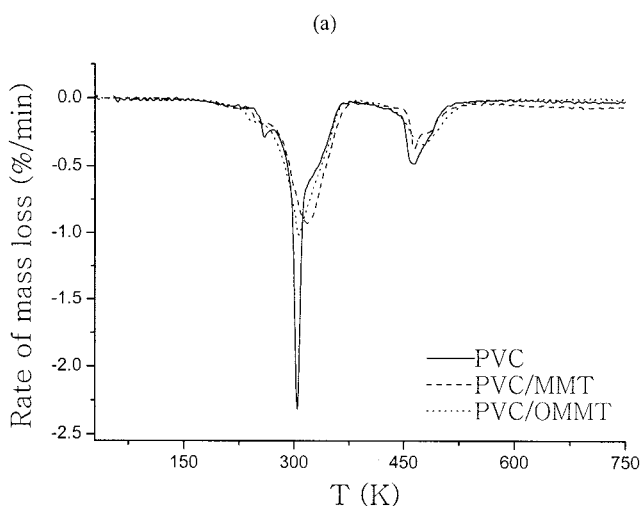
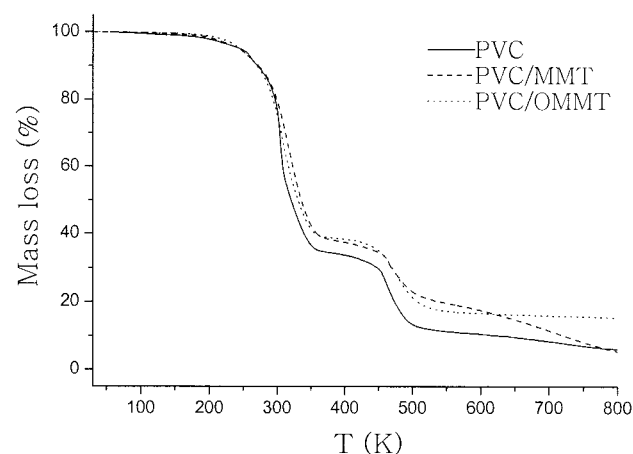


Figure 1 TG (a) and DTG (b) thermograms for the thermal degradation of PVC and its composites at a heating rate of 10°C/min.

as the ion-bonded ones, and the free alkyl ammonium molecules begin to decompose at about 155°C independent of their molecular structures.¹² The decomposition of free alkyl ammonium molecules leaves numerous acidic sites, which act as catalysts for PVC dehydrochlorination. An increase in rotor speed could result in high shear stress and local overheating, which may accelerate the decomposition of the alkyl ammonium modifiers and induce PVC dehydrochlorination. Therefore, processing conditions should be carefully selected to facilitate PVC chain intercalation and to prevent PVC systems from discoloring. In this case, the proper processing condition is suggested to be 170°C, 50 rpm, and 6 min.

Thermal analysis

Since the decomposition of the alkyl ammonium modifier in OMMT is adverse to the processing stability of PVC, it is necessary to study its effect on the thermal degradation of PVC. TG thermograms and the corresponding differential thermogravimetric (DTG) thermograms of the PVC and PVC/MMT(OMMT) composites obtained at a heating rate of 10°C/min under nitrogen are given in Figure 1. Similar thermograms were obtained for other heating rates, and the onset temperatures shifted to high temperatures with increasing the heating rate. The thermal degradation of PVC and PVC/MMT(OMMT) composites in nitrogen generally exhibits three-stage patterns. The first degradation stage was observed in the temperature range of 270~360°C and should be assigned to the progressive dehydrochlorination of PVC and the formation of conjugated polyene structure. The second degradation stage of 400~500°C should be accounted from the pyrolysis of the polyenes. The third stage was observed in the high-temperature region and should be assigned to some structure changes, crystallization, isomerization, crosslinking, and aromatization.¹³ The temperatures at the maximal rate of degradation in the

TABLE III
Characteristics of Thermal Degradation of PVC and PVC/MMT (OMMT) Composites

Sample	β (°C/min)	T_1 (°C)	T_m (°C)	α_m (%)	Δm_1 (%)	Δm_{total} (%)
PVC	5	264.4	302.6	36.6	63.5	86.8
	10	285.5	304.3	34.0	64.6	87.4
	20	292.1	320.6	30.9	63.0	100
	40	303.6	346.0	33.8	64.0	99.0
PVC/MMT	5	266.6	304.5	41.6	61.4	86.9
	10	273.6	318.3	37.8	62.4	94.7
	20	285.4	326.8	34.9	61.6	90.7
	40	301.3	351.6	35.4	64.3	98.1
PVC/OMMT	5	262.0	293.5	40.4	61.4	85.7
	10	272.3	306.8	36.7	61.0	84.6
	20	276.4	316.4	35.9	64.1	94.7
	40	291.1	339.6	38.4	61.3	85.6

first step of degradation (T_m) for PVC, PVC/MMT, and PVC/OMMT composites are 304, 318, and 307°C, respectively. The corresponding mass losses at the end of the first degradation stage (Δm_1) are 64, 62, and 61%, respectively. Judging from the first degradation stage, the PVC/MMT composite is more thermally stable than the PVC and PVC/OMMT composite, indicating that the partially intercalated MMT layers can act as a barrier to hinder the diffusion of heat and migration of degraded volatile, and then retard the decomposition rate. The PVC/OMMT composite does not exhibit high thermal stability as expected. The decomposition of the alkyl ammonium modifier of OMMT could speed up the thermal degradation process of the PVC/OMMT composite.

Kinetic analysis

Thermal stability is associated with both the initial temperature and the rate of degradation of polymers, so it is useful to determine the kinetic parameters by kinetic analysis for the degradation process. Since the Flynn–Wall–Ozawa¹⁰ and Kissinger¹¹ methods were derived from the basic kinetic equations for heterogeneous chemical reactions and were not necessary to determine the reaction order or the conversional function,^{14–16} we used the two methods to calculate the kinetic parameters of PVC systems in this paper.

The Flynn–Wall–Ozawa method is expressed by the equation¹⁰

$$\log g(\alpha) = \log(AE_a/R) - \log \beta - 2.315 - 0.4567E_a/RT, \quad (1)$$

where $g(\alpha)$ is the conversion functional relationship, A is the preexponential factor (min^{-1}),^{17,18} E_a is the apparent activation energy (kJ/mol), R is the gas constant, β is the heating rate ($^{\circ}\text{C}/\text{min}$), and T is the absolute temperature (K). E_a can be calculated from the slope of the most probable straight line obtained by drawing the dependence $\log \beta$ versus $1/T$ at different conversion degrees.

The Kissinger method is expressed by the equation¹¹

$$\ln\left(\frac{\beta}{T_m^2}\right) = -\frac{E_a}{RT_m} + \ln\frac{AR}{E_a} + \ln[n(1 - \alpha_m)^{n-1}], \quad (2)$$

where T_m is the most rapidly decomposing temperature (K) and is measured using DTG curves at various heating rates. α_m is the degree of conversion at the maximum rate. E_a can be determined from the plot of $\ln(\beta/T_m^2)$ against $1/T_m$ according to Eq. (2).

The dynamic degradation results of the first degradation stage of PVC and its composites are shown in Table III. Both the onset temperatures (T_1) and decom-

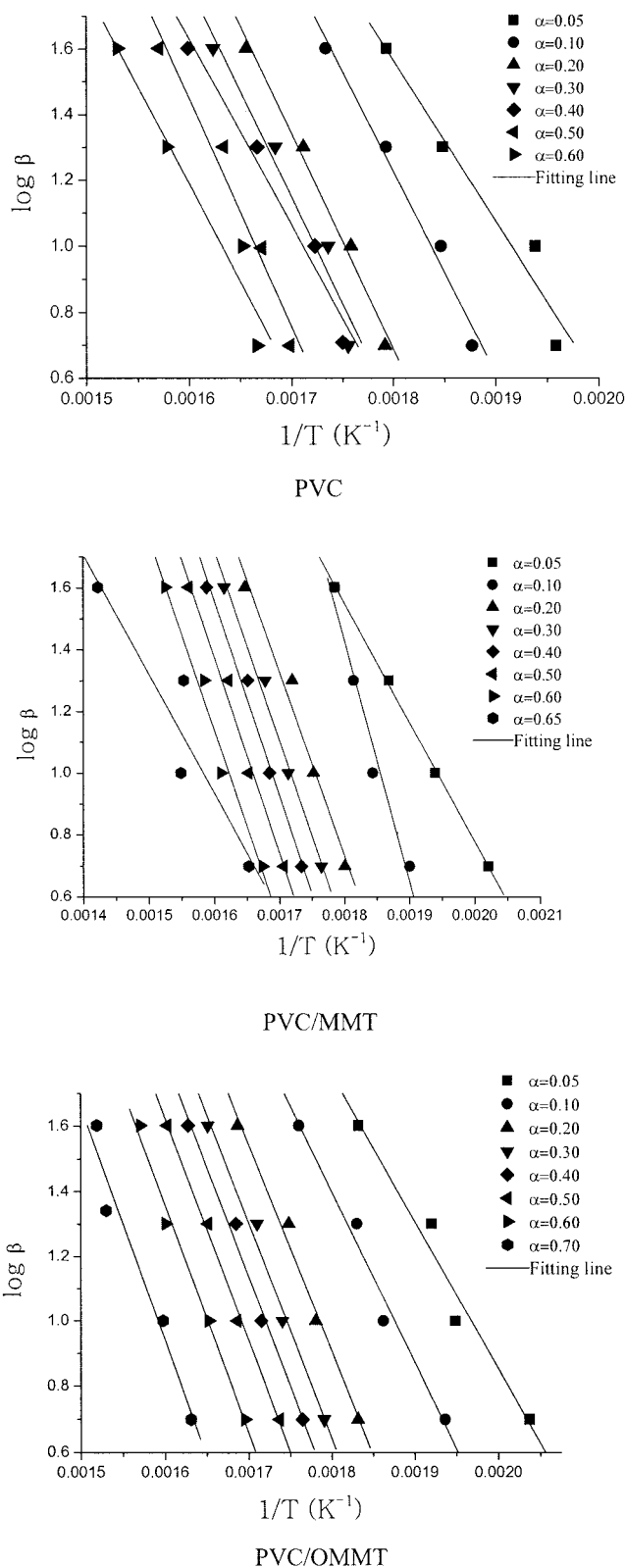


Figure 2 Plots of $\ln \beta$ versus $1/T$ for PVC and its composites at various conversion degrees according to the Flynn–Wall–Ozawa method.

posing temperature (T_m) at the maximal decomposition rate of the PVC and PVC/MMT(OMMT) composites shifted to high temperatures as the heating rate

TABLE IV
Calculated Apparent Activation Energies of Thermal Degradation by the Flynn–Wall–Ozawa Method

α	E_a (kJ/mol)		
	PVC	PVC/MMT	PVC/OMMT
0.05	89.3	70.5	82.6
0.10	111.4	142.3	95.9
0.20	119.1	108.4	116.0
0.30	117.0	112.4	120.5
0.40	111.8	115.3	122.5
0.50	109.8	115.5	124.3
0.60	107.68	113.21	127.39

increased, while the degree of conversion at the maximal rate (α_m) decreased. This means that degradation of the PVC and PVC/MMT(OMMT) composites is not only temperature-dependent but also time-dependent. In general, the thermograms obtained at low heating rates represent a reliable pattern of thermal stability.

According to the Flynn–Wall–Ozawa method, the activation energies were calculated from a linear fitting of $\ln \beta$ versus $1/T$ plot at different conversion degree (α). Figure 2 shows that for the PVC and PVC/MMT(OMMT) composites, the fitting lines are almost kept parallel to each other, indicating the unique degradation mechanism. That is, MMT or OMMT does not affect the degradation mechanism of PVC. The obtained E_a is shown in Table IV. Figure 3 shows that the E_a values and α of the three materials kept linear relationship in the range of $\alpha = 0.2\sim 0.6$, which belongs to the first degradation stage and is in agreement with the fitting lines in Figure 2.

The fitting lines of $\ln(\beta/T_m^2)$ versus $1/T_m$ for the PVC and PVC/MMT(OMMT) composites at various heating rates and the corresponding kinetic parameters calculated by the Kissinger method are shown in Fig-

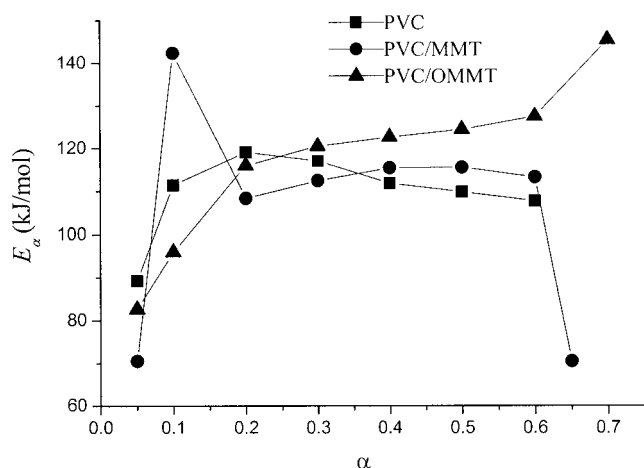


Figure 3 Plot of E_a versus α for the dynamic degradation of PVC and its composites.

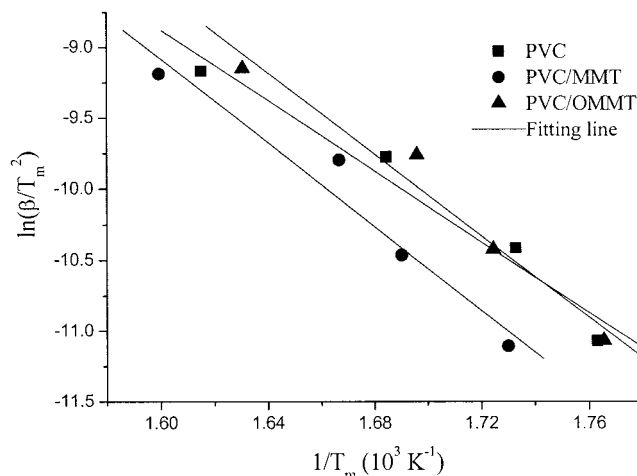


Figure 4 Plot of $\ln(\beta/T_m^2)$ versus $1/T_m$ for PVC and its composites according to the Kissinger method.

ure 4 and Table V. Figure 4 shows single linear regressions for the PVC and PVC/MMT(OMMT) composites. The E_a values of the PVC, PVC/MMT, and PVC/OMMT composites are about 103, 123, and 119 kJ/mol, respectively. The preexponential factors, A , were about 0.80×10^{10} , 3.15×10^{10} , and $2.53 \times 10^{10} \text{ min}^{-1}$. To estimate the thermal stability of the three materials, the compensation parameters, S_p^* , were calculated according to $S_p^* = E/\log A$.¹⁹ As shown in Table V, the PVC, PVC/MMT, and PVC/OMMT composites have the constant S_p^* , indicating that all the materials show the kinetic compensation effect and have similar thermal stability. That is, MMT or OMMT does not change the degradation mechanism of PVC, and the intercalated structure has little influence on the improvement of the thermal stability of PVC as analyzed by the above kinetic methods.

CONCLUSION

Processing thermal stability and dynamic thermal degradation of PVC and PVC/MMT(OMMT) composites were investigated. Increase of mixing torque does not significantly affect the intercalation extent of PVC but induces the processing discoloration of PVC, especially in the presence of OMMT. The dynamic thermal degradation of the PVC and PVC/MMT(OMMT) composites analyzed by the Flynn–Wall–Ozawa and

TABLE V
Calculated Kinetic Parameters of Thermal Degradation by the Kissinger Method

Sample	E_a (kJ/mol)	A ($10^{-10} \text{ min}^{-1}$)	S_p^*
PVC	103.6	0.80	11.6
PVC/MMT	122.9	3.15	11.7
PVC/OMMT	119.4	2.53	11.5

Kissinger methods shows that the calculated apparent activation energies are similar to each other and the compensation parameters, S_p^* , are constant, indicating that both MMT and OMMT only affect the degradation rate of PVC and do not change its degradation mechanism.

REFERENCES

1. Wang, D. Y.; Parlow, D.; Yao, Q.; Wilkie, C. A. *J Vinyl Add Tech* 2001, 7, 203.
2. Wang, D. Y.; Parlow, D.; Yao, Q.; Wilkie, C. A. *J Vinyl Add Tech* 2002, 8, 139.
3. Du, J. X.; Wang, D. Y.; Wilkie, C. A.; Wang, J. Q. *Polym Degrad Stab* 2003, 79, 319.
4. Trilica, J.; Kalendova, A.; Malac, Z.; Simonik, J. *Proc SPE AN-TEC Dallas Texas* 2001, May 6–10, 2162.
5. Wan, C. Y.; Qiao, X. Y.; Zhang, Y.; Zhang, Y. X. *Polym Test* 2003, 22, 453.
6. Wan, C. Y.; Qiao, X. Y.; Zhang, Y.; Zhang, Y. X. *J Appl Polym Sci* 2003, 89, 2184.
7. Ishida, H. U.S. Patent No. 6, 271, 297, 2001, August 7.
8. Solomon, D. H. *Physical Chemistry of Pigments in Paper Coating*; Tappi Press: Atlanta, 1977.
9. Jerzy, W. *Polyvinyl Chloride Stabilization*; Elsevier: New York, 1986.
10. Ozawa, T. *Bull Chem Soc Jpn* 1965, 38, 1881.
11. Kissinger, H. H. E. *Anal Chem* 1957, 29, 1702.
12. Xie, W.; Gao, Z. M.; Pan, W. P.; Hunter, D.; Singh, A.; Vaia, R. A. *Chem Mater* 2001, 13, 2979.
13. Owen, E. D. *Degradation and Stabilization of PVC*; Elsevier: London, 1984.
14. Schneider, H. A. *Thermochim Acta* 1985, 83, 59.
15. Kovacic, T.; Baric, B.; Klaric, I. *Polym Degrad Stab* 1995, 49, 365.
16. Nam, J.; Seferis, J. C. *J Polym Sci Polym Phys* 1991, 29, 601.
17. Lee, J. Y.; Shim, M. J.; Kim, S. W. *Mater Chem Phys* 1996, 44, 74.
18. Kim, Y. J.; Sim, I. C.; Lee, C. G.; Sung, Y. K. *J Korean Ind Eng Chem* 1995, 6, 15.
19. Maciejewski, M. *J Thermal Anal* 1988, 33, 1269.