

Thermal Degradation Kinetics of Polyethylene and Silane-Crosslinked Polyethylene

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ABSTRACT: The thermal degradation of linear low-density polyethylene (LLDPE) and linear low-density silane-crosslinked polyethylene (SXLPE) was studied. Kinetic evaluations were performed by model-free kinetic analysis and multivariate nonlinear regression. Apparent kinetic parameters for the overall degradation were determined. The results show that the thermal stability of SXLPE was higher

than that of LLDPE. Their decomposition reaction model was a single-step process of an n th-order reaction. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1172–1179, 2005

Key words: activation energy; crosslinking; kinetics; polyethylene (PE)

INTRODUCTION

Crosslinking is an important way to improve the thermal and chemical resistance of polyethylene (PE). Crosslinked low-density PE is one of the polymeric materials used extensively as an insulating compound for electrical cables, ranging from underground cables to aerial bundle cable networks.¹ Silane-crosslinked linear low-density polyethylene (SXLPE) has been the subject of considerable research in recent decades. In the production of SXLPE, peroxide, silane (e.g., vinyl trialkoxy silane), a hydrolysis catalyst, and PE are mixed by a melt process. During the process, the silane is grafted onto the backbone of PE via free radicals. The silane-grafted PE is then hydrolyzed and crosslinked by the formation of Si—O—Si linkages.

Thermogravimetric analysis (TGA) is a common method for studying the kinetics of polymer degradations. Kinetic analysis may effectively assist in the probing of degradation mechanisms and in the prediction of the thermal stability of polymers. These goals are accomplished only when proper methods for kinetic evaluations are used. There have been a number of studies that have reported the activation energies (E 's) of the thermal degradation of PE.^{2–6} In a

previous study,⁷ we investigated the flame retardancy of SXLPE. In this study, the thermal degradation kinetics of linear low-density polyethylene (LLDPE) and SXLPE were studied.

EXPERIMENTAL

Materials

LLDPE with a melt flow index of 2.0 g/10 min and a number-average molecular weight of 32,000 was supplied by Zhongyuan Petrochemical Co. (Zhenzhou, China). Vinyl trimethoxysilane (VTMS; purity = 99%) and dibutyltin dilaurate (DBDL) were standard laboratory reagents and were used as received. Dicumyl peroxide (DCP) was recrystallized with anhydrous ethanol.

Preparation of the samples

The VTMS grafting of LLDPE was carried out in a Brabender-like apparatus (XK-160, made by JinTan Apparatus, Ltd., Jiangsu, China). After LLDPE melted at about 120°C, the mixtures of VTMS, DCP, and DBDL were added into the apparatus and blended for about 3 min. The temperature was raised to 160°C in a transient period of about 3 min. Then, the mixtures were blended at 32 rpm at 160°C for 15 min. The grafted samples were first compression-molded at approximately 130°C into 1 mm thick sheets under a pressure of 9 MPa for 10 min and were then immersed into water at $90 \pm 2^\circ\text{C}$ for 10 h. The formulations containing different initiator levels are shown in Table I.

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TABLE I
Formulations Containing Different Initiator Levels

Sample code	LLDPE	VTMS (phr)	DCP (phr)	DBDL (phr)
A	100	—	—	—
B	100	3.0	0.05	0.2
C	100	3.0	0.1	0.2
D	100	3.0	0.2	0.2
E	100	3.0	0.4	0.2

Determination of the gel content

About 0.2–0.3 g of weighed samples of small pieces in a copper net were put into boiling xylene for 24 h. The extracted samples were washed with acetone and then dried to a constant weight. The gel content is expressed in terms of the percentage of weight remaining:

$$\text{Gel (\%)} = \left(1 - \frac{W - W_1}{G} \right) \times 100\%$$

where G is the weight of the sample, W is the total weight of the sample and copper net before extraction, and W_1 is the total weight of the sample and copper net after extraction.

TGA

TGA was carried out with a STA 409C from Netzsch GmbH (Selb, Bayern, Germany). The STA 409C was equipped with a computer to analyze all of the kinetic parameters. The samples of PE and SXLPE, about 10 mg each, were investigated at heating rates (β 's) of 5, 10, 15, and 20°C/min in a temperature range of 20–800°C. Nitrogen was used as a purge gas at a flow rate of 50 mL/min. The temperature and weight scales were calibrated with all of the high-purity standard samples (indium, nickel, zinc, aluminum, and gold) over a specific range of β 's with calibration parameters of their respective melting points.

Fourier transform infrared (FTIR) spectroscopy

The hot-pressed films of SXLPE were extracted in boiling acetone to remove the unreacted silane. IR spectra of the films were obtained with an FTIR spectrophotometer (Nicolet MAGNA-IR 750; Madison, WI).

Method

Model-free methods

Several measurements were run on each sample at different β 's. Model-free approximations of E were

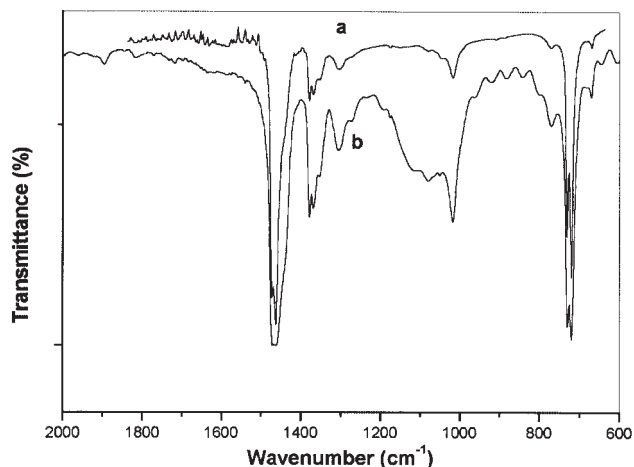


Figure 1 FTIR spectra of (a) the virgin LLDPE and (b) SXLPE.

made with the Friedman analysis and the Kissinger method. They were used to gain the first insights into the reaction process.

In the model-free analyses, for a set of measurements with different β 's, the points of the reaction rate ($d\alpha/dt$) at the same degree of reaction ($\alpha = \alpha_i$, where α is defined as the reaction degree and α_i is defined as the reaction degree at some point) were connected and are displayed versus the inverse temperature. Friedman proposed the application of the logarithm of the conversion rate ($d\alpha/dt$) as a function of the reciprocal temperature.⁸ The Friedman lines exhibited a slope that was proportional to E .

Analysis according to the Kissinger method is based on the assumption that the maximum [e.g., maximum of the DSC or derivative thermogravimetry (DTG) curve] of a single step reaction is reached at the same conversion degree independent of β . Although this assumption was only partly right, the resulting errors

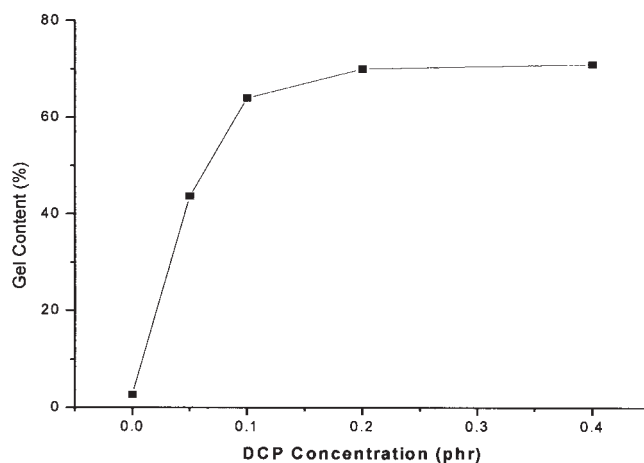


Figure 2 Effect of DCP concentration on the gel content of SXLPE.

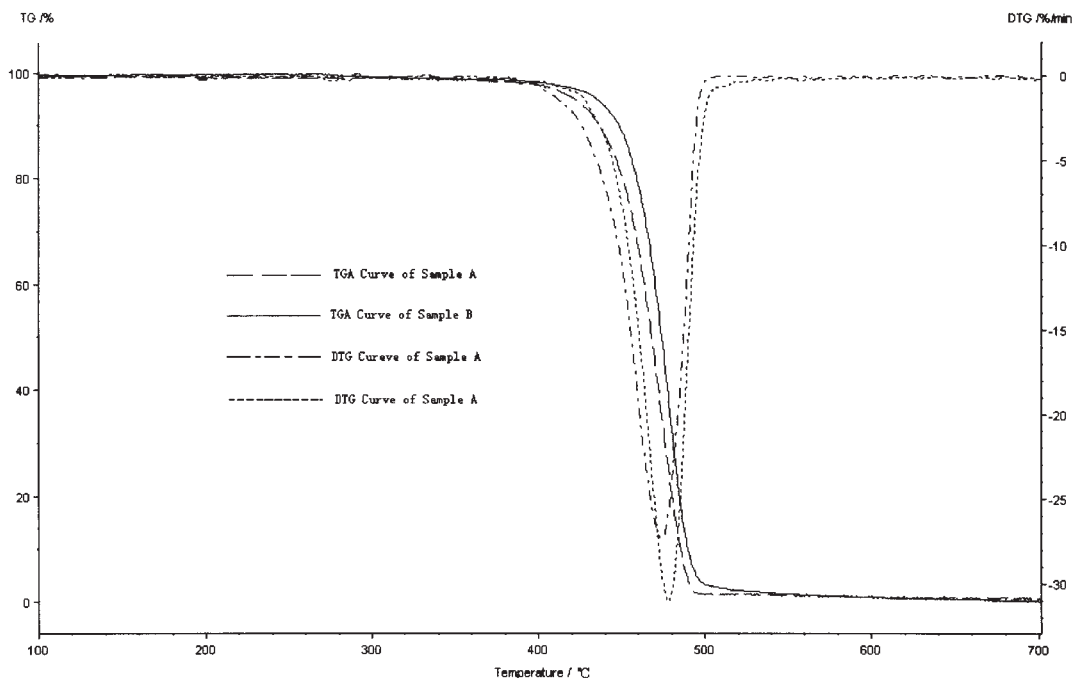


Figure 3 TGA and DTG results for samples A and B under N_2 ($\beta = 10^\circ\text{C}/\text{min}$).

were low.⁹ In this method, E can be calculated from the slope of the plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ with fitting to a straight line,¹⁰ where β is the heating rate and T_p is the peak temperature, or the temperature corresponding to the inflection point of the thermal degradation curves, which corresponds to the maximum reaction rate.

Computation procedure¹¹

Different models were evaluated to describe the total mass loss of the experiments at various β 's. There was a set of ordinary differential equations (ODEs) for each model. The simultaneous numerical solution of the ODE system and the estimation of the kinetic parameters by the least squares (LSQ) method were calculated. We fitted the kinetic parameters were by running the optimization routine and the ODE solver simultaneously, according to the technique of multivariate regression. The task of nonlinear regression is the iterative calculation of the minimum sum of LSQ. When the multivariate regression technique is applied, the total LSQ yields a sum of LSQ calculated with data from the different experimental runs:

$$LSQ = \sum_{k=1}^m \sum_{i=1}^n (y_{\text{exp } k,i} - y_{\text{mod } k,i})^2 \quad (1)$$

The experimental values ($y_{\text{exp } k,i}$) are the normalized mass values, $y = m(T)/m_0(t = 0)$, where $m(T)$ is defined as the mass of sample at some time, and m_0 is

defined as the mass of sample at the initial time, from TGA. Data for all β 's were used simultaneously. The model values ($y_{\text{mod } k,i}$) resulted from the numerical solutions of the respective ODEs. The multivariate analysis was based on the assumption that the kinetic parameters had to be identical for all of the experimental conditions in the modeled parameter range. This constraint facilitated the choice of an appropriate model considerably and improved the model validity. Fundamentally, multistep processes can only be analyzed with nonlinear regression. However, nonlinear regression is advantageous for one-step processes as well because it provides a considerably better quality of fit compared to multiple linear regressions.

RESULTS AND DISCUSSION

FTIR characterization of SXLPE

Figure 1 shows the IR spectra of the LLDPE resin and SXLPE. As shown by the IR spectrum of the crosslinked LLDPE, the absorption band of

TABLE II
TGA Results for LLDPE and SXLPE at a β of $10^\circ\text{C}/\text{min}$

Sample code	T_{onset} ($^\circ\text{C}$)	T_{max} ($^\circ\text{C}$)
A	422.4	474.3
B	435.6	477.8
C	442.0	479.2
D	446.1	480.2
E	443.8	481.4

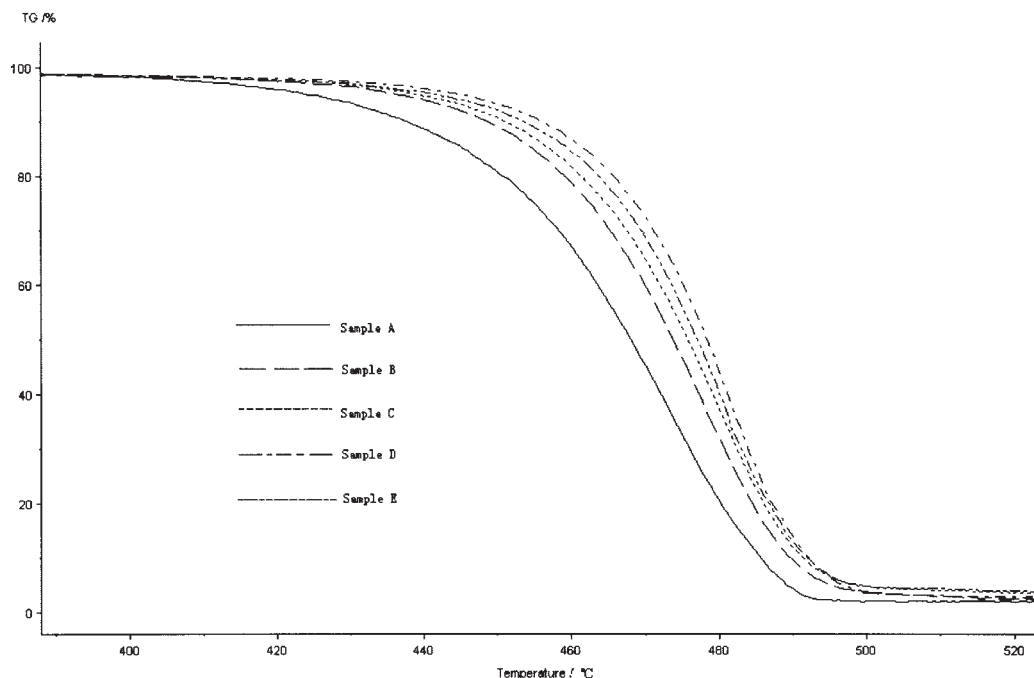


Figure 4 Comparison of TGA results for all samples ($\beta = 10^\circ\text{C}/\text{min}$).

$\text{—Si—O—C}_2\text{H}_5$ appeared at about 1080 cm^{-1} , and the peak at 1020 cm^{-1} was assigned to the absorption of Si—O—Si .¹²

Effect of the initiator concentration on the gel content of SXLPE

The effect of the initiator concentration on the gel content of SXLPE is shown in Figure 2. Clearly, the gel content increased rapidly at first and then increased slightly with increasing DCP concentration beyond 0.1 phr. This result indicates that when the DCP concentration reached a limit (0.1 phr), it had no obvious effect on silane grafting.

TGA

TGA of PE and SXLPE was performed on the STA system. The TGA and DTG results for samples A (LLDPE) and B (SXLPE) are shown on Figure 3. Figure 3 indicates that it was possible to model the thermal decomposition by a one-step reaction. Under a nitrogen atmosphere, both sample A (LLDPE) and sample B (SXLPE) degraded in a single, smooth step and reached near zero mass at the last. Table II shows the TGA parameters of all of the samples [the onset point of 5 wt % weight loss (T_{onset}) and the maximum mass loss from the DTG curves (T_{max})]. From the TGA curves, the onset temperature of thermal degradation and the maximum weight loss temperature were obtained, which indicated the thermal stability of the samples. Figure 4 also shows that the curves of SXLPE

moved to a higher temperature compared to that of LLDPE, meaning that the SXLPE samples were more stable than the LLDPE samples. Moreover, the thermal stability of the crosslinked PE was enhanced with increasing gel content, and this enhancement reached its limit when the gel content did not increase anymore.

Model-free kinetic analysis

The models described the total mass loss of the samples and were calculated with the thermogravimetric results. The advantages of using the mass signal for kinetic modeling instead of the heat flow rate signal lie in its higher validity and resolution and its accessibility over a broad range of experimental conditions. Furthermore, the mass signal is directly proportional to the extent of the reaction, even if the process contains endothermic and exothermic steps simultaneously.¹¹

TABLE III
E Values of LLDPE and SXLPE Found with the Kissinger Method

Parameter	Sample A	Sample B	Sample C	Sample D	Sample E
E (kJ/mol)	250	260	268	337	303
Correlation coefficient	0.9990	0.9967	0.9929	0.9970	0.9913

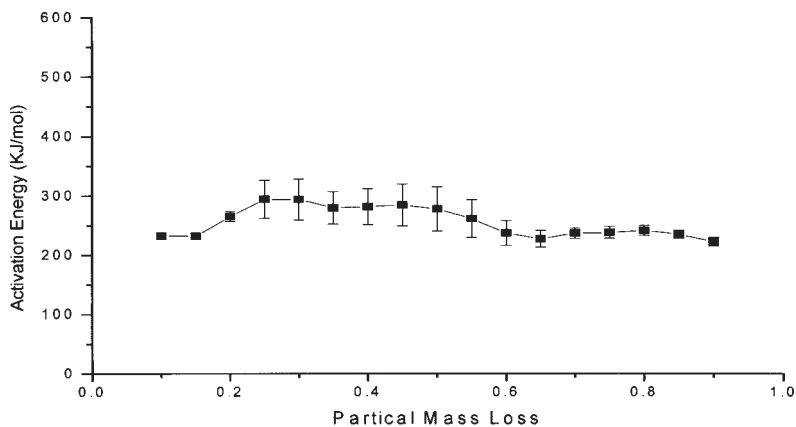


Figure 5 Friedman analysis–energy plot of sample A (β 's = 5, 10, 15, and 20°C/min).

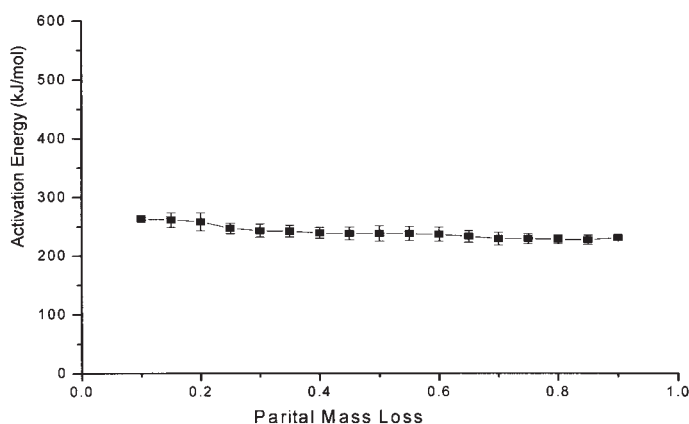


Figure 6 Friedman analysis–energy plot of sample B (β 's = 5, 10, 15, and 20°C/min).

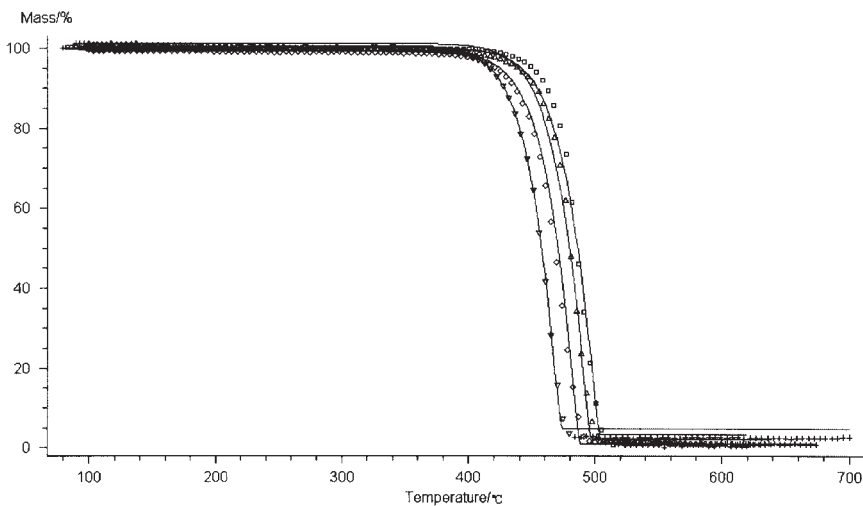


Figure 7 Global model for the thermal decomposition of sample A (β 's = 5, 10, 15, and 20°C/min, increasing from left to right).

TABLE IV
Kinetic Data for the Decomposition of LLDPE and SXLPE

Parameter	Sample A	Sample B	Sample C	Sample D	Sample E
Log (A)	13.6	16.4	18.3	18.3	16.8
E (kJ/mol)	226	266	294	293	272
Reaction order	0.24	0.59	0.52	0.49	0.41
Correlation coefficient	0.9992	0.9998	0.9997	0.9996	0.9997

Log(A): logarithm of the pre-exponential of reaction step.

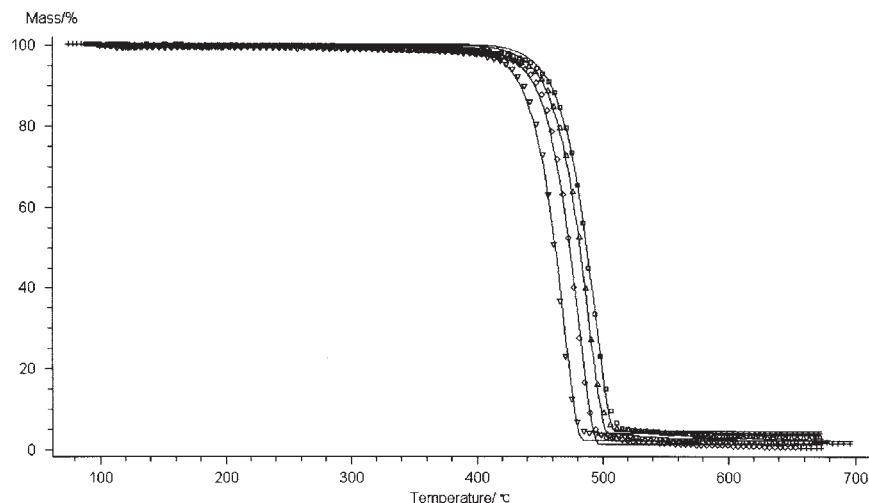


Figure 8 Global model for the thermal decomposition of sample B (β 's = 5, 10, 15, and 20°C/min, increasing from left to right).

From the DTG curves of all of the samples, T_p was determined. E was determined by the Kissinger method. The results are shown in Table III.

The Friedman analysis for the thermal decomposition reactions yielded the apparent E with the extent of reaction. Figure 5 shows the Friedman analysis result of sample A (LLDPE), whereas Figure 6 shows the Friedman analysis result of sample B (SXLPE). Other Friedman analysis results of SXLPE were similar. The Friedman plot with multiple peaks or inconstant E values seriously indicated the presence of a multistep process. The Friedman plots of LLDPE and SXLPE inferred that the data sets could be almost described by a single-step reaction.

Kinetic models

Single step reaction models were developed with the qualitative facts described previously. The n th-order

(Fn) reaction model was analyzed with multivariate nonlinear regression. The results for the best fit of various samples are shown in Figures 7–11; for the kinetic parameters, see Table IV.

The decomposition reaction of SXLPE and LLDPE could best be modeled via reactions A→B of the Fn type [$f(\alpha) = (1 - \alpha)^n$].

DISCUSSION

Under a nitrogen atmosphere, the degradation of PE may be assumed to a single-step reaction. It is generally believed the thermal degradation of PE occurs by random chain scission, which produces small amounts of monomer, and that the degradation proceeds by a free-radical mechanism.¹³ Although random scission is a primary degradation pathway of PE, it can also result in polymer chain branching. Both scission and branching occurred simultaneously and gave rise to a

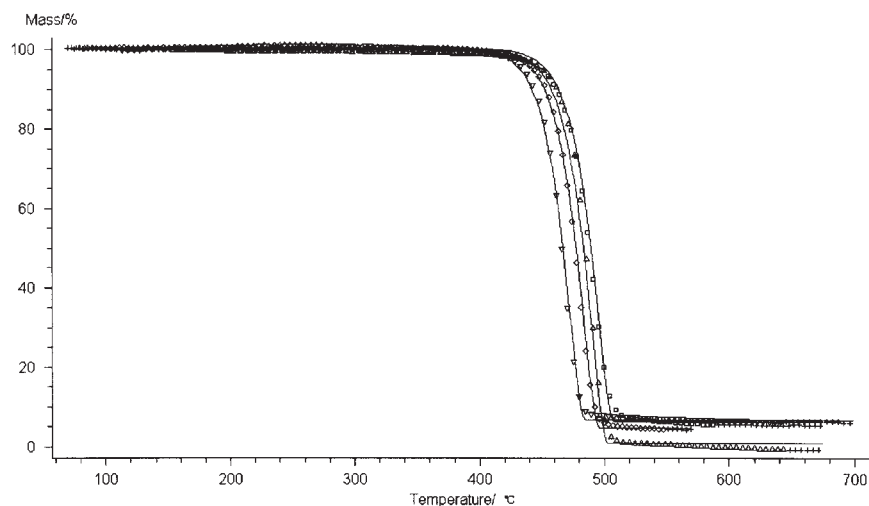


Figure 9 Global model for the thermal decomposition of sample C (β 's = 5, 10, 15, and 20°C/min, increasing from left to right).

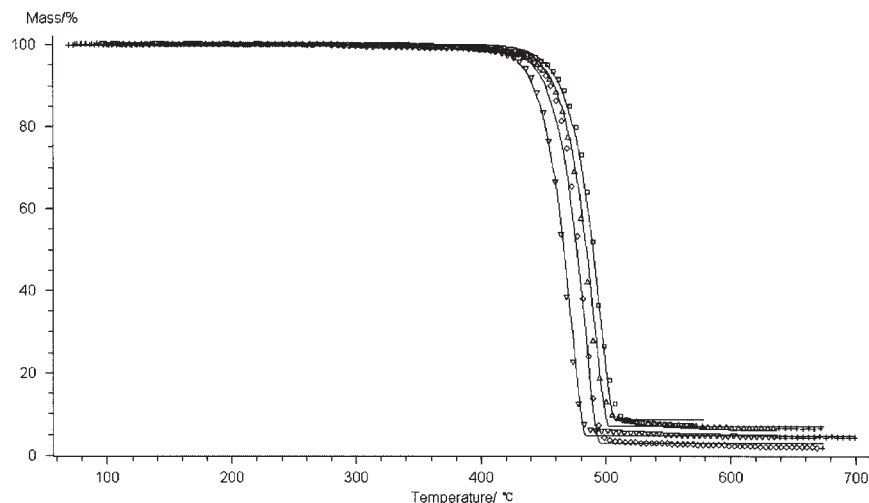


Figure 10 Global model for the thermal decomposition of sample D (β 's = 5, 10, 15, and 20°C/min, increasing from left to right).

single mass loss step (Fig. 3). The observed variation in E (Fig. 5) suggests that the degradation kinetics was governed by different processes at the initial and final stages. However, from the calculation from nonlinear regression, a single-step reaction model was obtained that forced E to be constant. The resulting values could only be treated as the values averaged over the corresponding regions of temperature and extent of reaction.¹⁴

Figure 12 shows that the average E values of SXLPE (samples B, C, D, and E) were bigger than those of LLDPE (sample A). This suggests that SXLPE needed more E in degradation and, therefore, was more thermally stable. The kinetic analysis suggested that its reaction scheme was a single overall reaction model, indicating the random scission type occurs. Although the E values varied with the calculation methods, they

showed a similar trend. E increased with increasing gel content, but this increase reached its limit when the gel content did not increase anymore. This trend coincided with the thermal analysis results, and it was also in agreement with the gel test.

CONCLUSIONS

1. Kinetic analysis helped us to probe the degradation mechanisms and to predict the thermal stability of polymers. The nonlinear multivariate regression is an indispensable method to derive kinetic models. This technique is a good method for deciding between different reaction models and for getting a global model that gives reliable results for the whole parameter range.

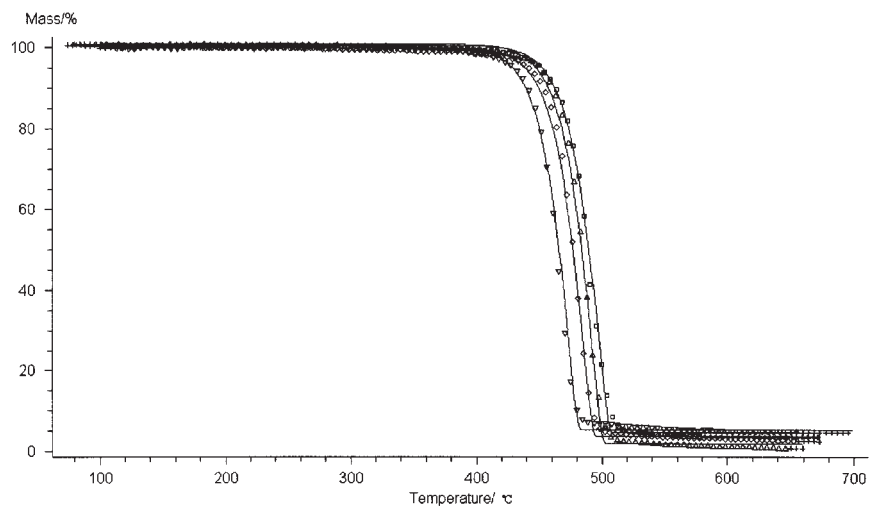


Figure 11 Global model for the thermal decomposition of sample E (β 's = 5, 10, 15, and 20°C/min, increasing from left to right).

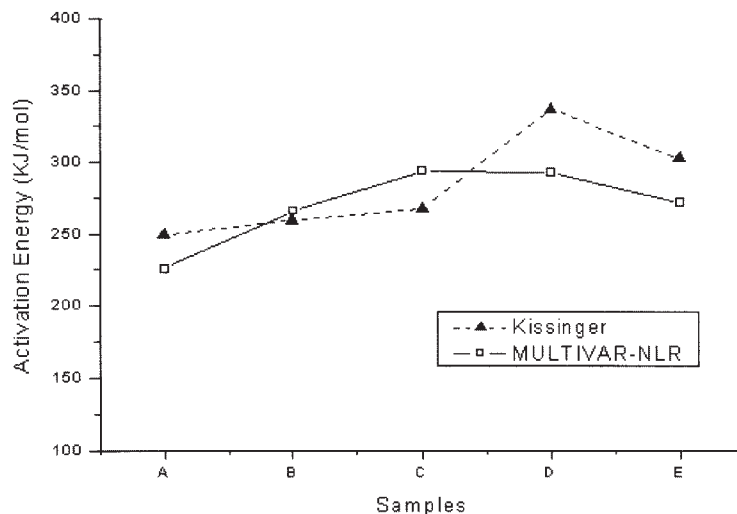


Figure 12 Comparison of the E values of all of the samples with different calculation methods.

2. From the thermal analysis and the kinetic analysis of LLDPE and SXLPE, we deciphered the main idea of the thermal stability and thermal degradation reaction model. SXLPE and LLDPE had a similar reaction type, a one-step reaction. However, E of SXLPE was larger than that of LLDPE, indicating that SXLPE was more stable.

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