

# Pyrolysis Studies of Polyethylene Terephthalate/Silica Nanocomposites

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**ABSTRACT:** The decomposition of pure polyethylene terephthalate (PET) and PET/silica nanocomposites was investigated by thermal gravimetry (TG) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The influence of the nanosized silica on the pyrolysis properties of the composites was found from the results that the activation energies of decomposition and the residual carbon content increase with

silica nanoparticles. It is deduced that the increase of the activation energies and the residual carbon content result from the adsorption of the decomposed products on the surface of silica. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 9–14, 2007

**Key words:** polyethylene terephthalate; silicas; composites; pyrolysis; residual carbon content

## INTRODUCTION

Polyethylene terephthalate (PET), a familiar polymer, is extensively used as packing material, fabric, engineering plastic, and so on. The decomposition of PET is very important for its application. For example, when PET is applied to the packing of a beverage, the decomposition of PET has effect on the taste and purity of the beverage. Villain et al.<sup>1</sup> studied the effect of temperature and drying conditions on degradation of PET (leading to volatile products being formed) used to bottle mineral water, using different technological processes. Moreover, the decomposition of PET also plays an important role in its combustion behavior. The formation of char in and of itself has a significant effect on the degradation because char formation must occur at the expense of other reactions that may form volatiles; thus, char formation may limit the amount of fuel available.<sup>2</sup> It was believed that there are connections between the magnitude of the residual carbon in the TG analysis and the oxygen indices.<sup>3–8</sup> It has been reported that the higher residual carbon content and oxygen index values mean better flame-retardant properties.<sup>7</sup>

The PET/silica nanocomposites have been synthesized in our laboratory.<sup>9</sup> This paper reports the results of TG and Py-GC/MS investigations of PET/silica degradation. The decomposition of the pure PET was also studied. The results from PET/silica nanocompo-

sites were compared with those from pure PET to examine the effect of nanosilica on the processes and the volatile products of the thermal degradation of PET. Apart from the identification of the volatile products formed, the mechanism of formation of the products is elucidated according to the general mechanism of polyester degradation.<sup>10–14</sup> The apparent activation energies of these composites were also studied.

## EXPERIMENTAL

### Materials

Pure PET labeled as PET0 and PET/silica nanocomposites with silica content of 1, 3, 5 wt %, labeled as PET1, PET3, PET5, respectively, were used in the present study. The sample preparation has been reported in the previous work.<sup>9</sup>

### Characterization

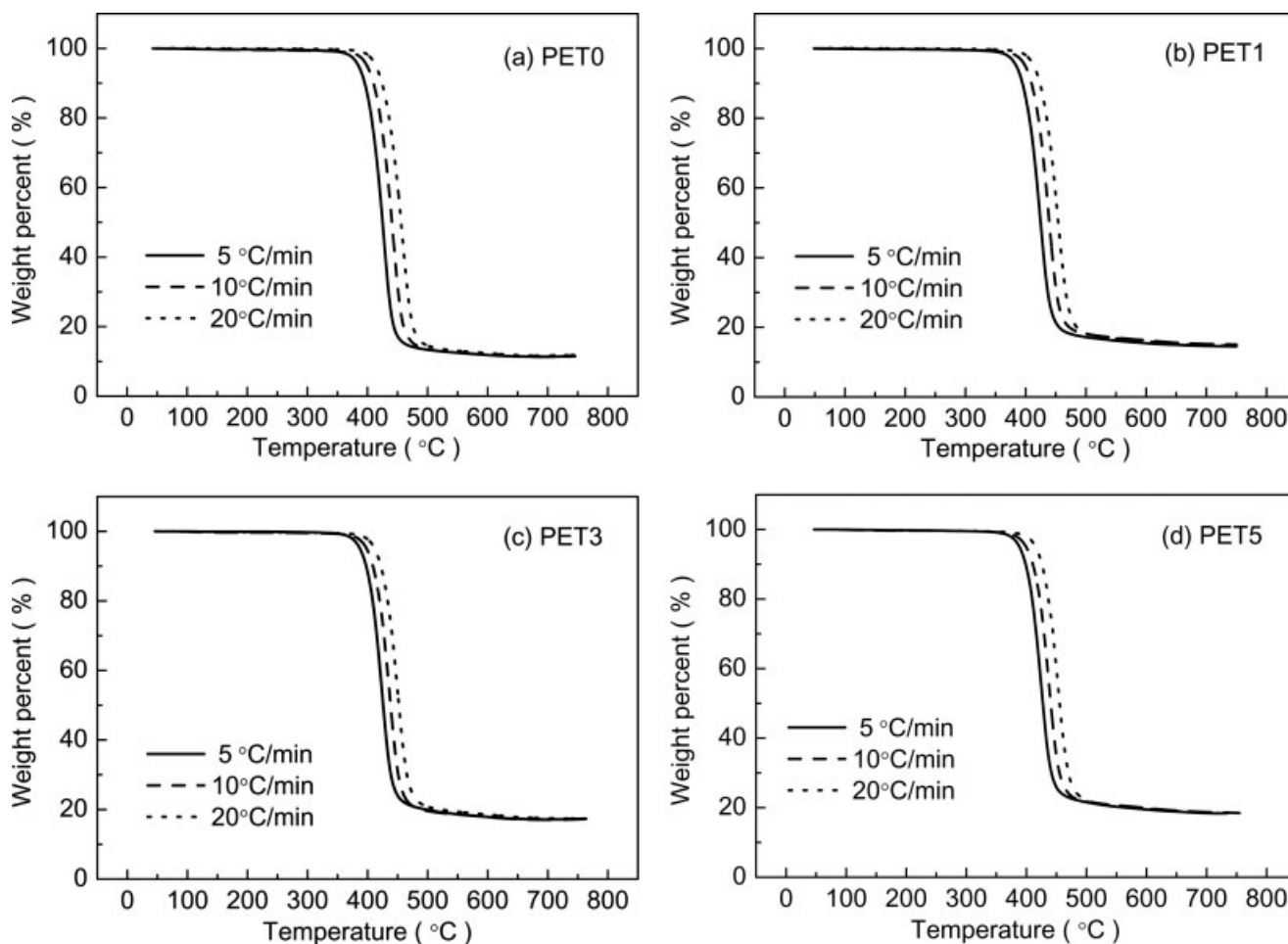
#### TGA studies

A Perkin–Elmer Pyris1 TG analyzer was used to obtain weight loss data for the pyrolysis of PET and PET/silica nanocomposites. TG measurements were carried out in nitrogen gas at a flow rate of 80 cm<sup>3</sup>/min. Three heating rates of 5, 10, and 20°C/min were operated for all four samples in the present experiment. The initial sample weight was ~ 5 mg in all cases.

#### Pyrolysis gas chromatography studies

Py-GC/MS was used to study the degradation mechanism and the degradation products. PET and

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**Figure 1** The curves of the thermal degradation of PET and PET/silica nanocomposites.

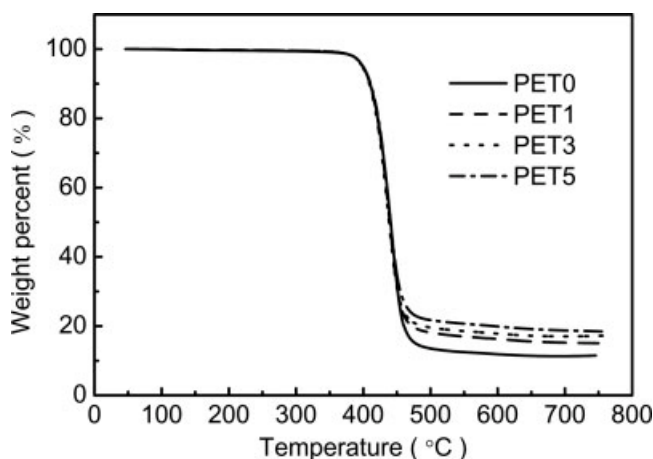
PET/Silica composites were decomposed in the Py-2020iS single-shot pyrolyzer (Frontier Laboratories, Japan) at 420°C, at which the thermal decomposition rate of PET is the highest according to the TG analysis. The separation and identification of products in the degradation were carried out using QP-2010 GC-MS (Shimadzu Corp., Japan); inert helium was used as a carrier gas with a total flow of 49.7 cm<sup>3</sup>/min and split ratio of 60 : 1. Rtx-1701 chromatograph column was used and heating process was as follows: initial temperature was kept at 50°C for 2 min, then heated to 200°C at 7°C/min, later to 260°C at 15°C/min and held at 260°C for 10 min. Mass spectrometry was used with an ion source of 70 eV, and the detection range of mass-to-charge ratio was 19 : 600.

## RESULTS AND DISCUSSION

### The activation energies of decomposition and the residual carbon percentages

Figure 1(a–d) show the curves of the thermal degradation of PET and PET/silica composites. It can be

seen that the shape of the pyrolysis curves of PET/silica composites is similar to those of the pure PET, which means the degradation process of the nanocomposites is same as that of pure PET. The main



**Figure 2** The TG curves of pure PET and the nanocomposites at the heating rate of 10°C/min.

**TABLE I**  
**Comparison of the Residual Percentages**  
**of Pure PET and PET/Silica Nanocomposites**  
**at Different Temperatures<sup>a</sup>**

T (°C)	Residue (%)			
	PET0	PET1	PET3	PET5
500	13.5352	18.1329	19.5817	21.7399
525	12.869	17.4511	18.9696	21.1363
550	12.4887	16.9967	18.5632	20.6997
575	12.1979	16.6026	18.1998	20.3083
600	11.8745	16.2869	17.8238	19.8947
625	11.617	15.8968	17.4642	19.4896
650	11.4173	15.558	17.2215	19.1547
675	11.3216	15.3469	17.0773	18.9125
700	11.3156	15.212	17.0383	18.749

<sup>a</sup> The heating rate were 10°C/min.

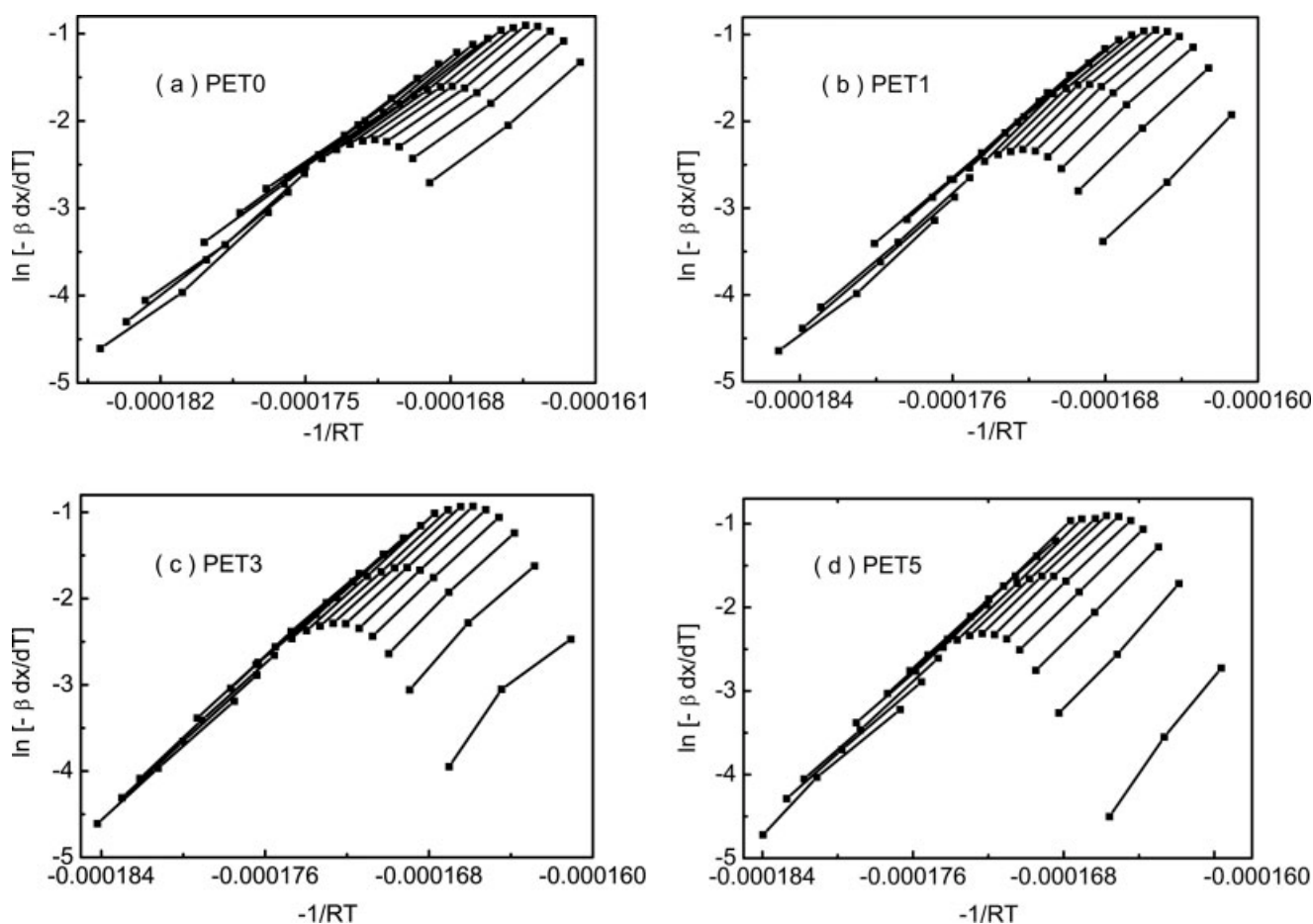
difference between them is the different residue content above 500°C, where the residue content of composites is always larger than that of pure PET. In Figure 2, four TG curves of pure PET and the nanocomposites at the heating rate of 10°C/min are shown. The residue content of PET and PET/silica nanocomposites at different temperatures is given in

Table I. It can be found from Figure 2 and Table I that the increment of residue content is larger than the content of silica in the composites and that the residue content increases with the addition of silica in the composites, indicating that the addition of nanosized silica decreases formation of volatile products during the degradation because char formation must occur at the expense of other reactions that may form volatiles.

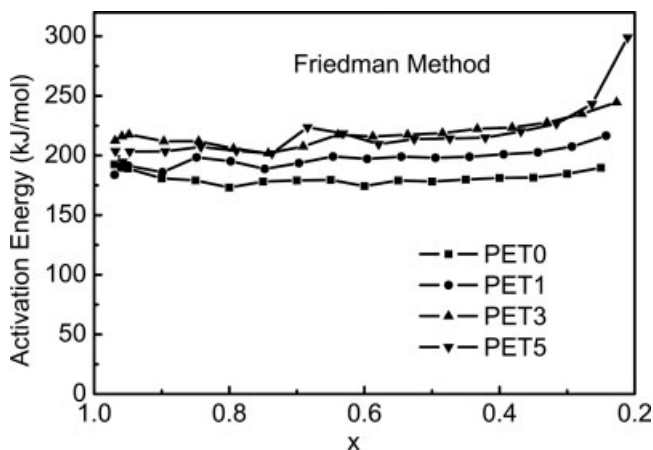
There are many methods for the kinetic analysis of TG data.<sup>15–18</sup> A modified Friedman method was used in the present work to investigate the activation energy of composites during thermal decomposition. The Friedman equation<sup>17</sup> is expressed as follows:

$$\ln \left[ \beta \frac{d\alpha}{dT} \right] = \ln[Af(\alpha)] - E/RT \quad (1)$$

where  $\beta$  is the heating rate,  $\alpha$  the reaction degree,  $A$  the pre-exponential factor,  $E$  the activation energy,  $T$  the temperature, and  $R$  the gas constant. In our experiment, three different heating rates were used. Choosing a constant reaction degree, a plot of  $\ln[\beta \frac{d\alpha}{dT}]$  versus  $-1/RT$  should be a straight line and



**Figure 3** The plots of  $\ln[\beta d\alpha/dT]$  versus  $-1/RT$ . Application of Friedmann method.



**Figure 4** The activation energies of PET and the composites versus the normalized residual carbon contents. The Friedman method was used;  $x$  is the normalized residual content,  $x = (x_0 - b)/(1 - b)$ , where  $b$  is the silica content in the composites,  $x_0$  is the original residual content in TG analysis.

the activation energy can be obtained from the slope. As we know,

$$\alpha = \frac{1 - x}{1 - x_\infty}, \quad \frac{d\alpha}{dT} = -\left[\frac{1}{1 - x_\infty}\right] \frac{dx}{dT} \quad (2)$$

where  $x$  is the residual fraction of the test,  $x_\infty$  the ultimate residual fraction. In this work, the residual fraction is preferred. Through simple calculations, we get

$$\ln\left[-\beta \frac{dx}{dT}\right] = \ln[Af(x)] - E/RT + B \quad (3)$$

in which  $B = 1/(1 - x_\infty)$  is a constant. If we plot  $\ln[-\beta \frac{dx}{dT}]$  versus  $-1/RT$ , the activation energy of the composites can be obtained from the slope of the derived lines [shown in Fig. 3(a-d)].

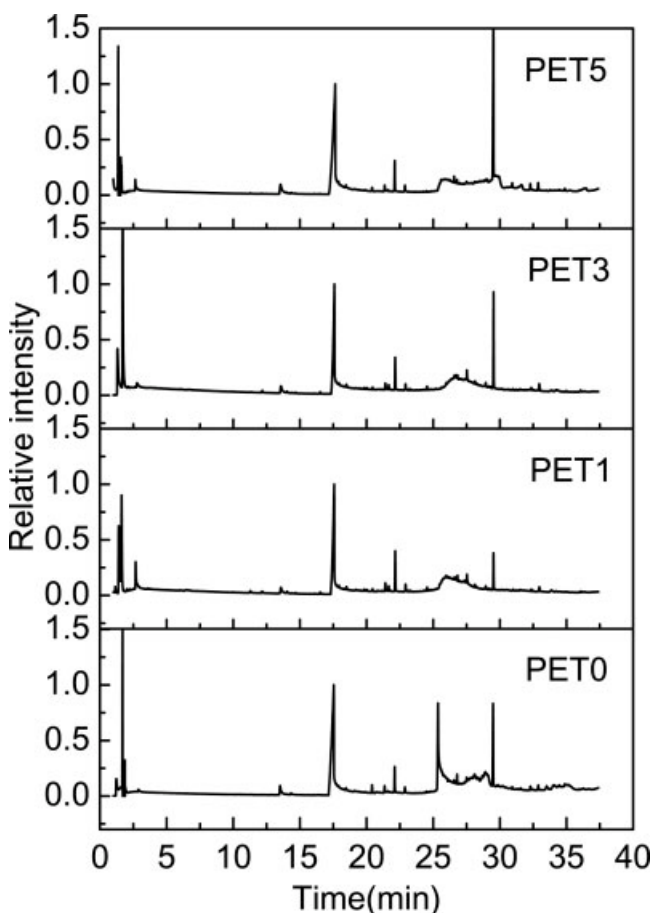
The decomposition activation energies of composites and pure PET in the different reaction degree are shown in Figure 4. It is clear that the values of  $E$  for nanocomposites are higher than those for pure PET. The average of activation energies at different residual content (from  $x = 0.85$  to  $x = 0.35$ ) for PET0, PET1, PET3, and PET5 is 178, 198, 215, and 214 kJ/mol, respectively. The activation energy of nanocomposites increases with addition of silica from 0 to 3 wt %. The value of activation energy has no significant variation when increasing silica content from 3 to 5 wt %. It seems that decomposition in nanocomposites is more difficult than that in pure PET under same experimental conditions. It is evident that the addition of silica leads to the increment of the activation energy of decomposition and there exists a maximum value of  $E$ . It was concluded from Figures 1–4 that the addition of nanosized silica in the composites could efficiently improve the thermal stability of PET/silica nanocomposites by increasing

the activation energy and char formation of the composites during thermal decomposition.

### The decomposition mechanism of the nanocomposites

To study further the thermal decomposition of the PET/silica nanocomposites, Py-GC/MS measurements were carried out. The GC (gas chromatography) graphs of the pure PET and the composites are shown in Figure 5, in which each of the GC graphs was normalized to the peak of No.2, benzoic acid. In the initial stage of GC measurement, the signal is sometimes interfered with due to the instability of instrument, and so the initial data in GC (before 2 min; Fig. 3) were not used in the present study to obtain reliable result. The products formed by pyrolysis were determined by mass spectra and data from literature<sup>10,19,20</sup> and results are shown in Table II. In the following sections of the paper, the number shown in Table II represents the decomposed product for simplicity.

It can be seen from the GC graphs and Table II that the decomposition products of the composites are basically same as those of the pure PET, which means that



**Figure 5** The gas chromatographs of PET and the composites.



ucts of No.2, No.3, No.4, and No.8 can be formed in this way. Ritchie<sup>14</sup> found that the vinyl benzoate was decomposed by the reaction shown as in Scheme 1(d), where acetophenone (No.1) was formed. This reaction [Scheme 1(d)] can also account for the formation of the product of No.7 [Scheme 1(e)]. Although the mechanisms and the products of decomposition are greatly similar between the composites and the pure PET, there are still some differences.

The product of No.3 can be obtained by the decarboxylation of the diethylene glycol (DEG) produced during the preparation of the samples. It is shown in Figure 3 that the peaks of the product of No.3 for composites are smaller than that of pure PET. This result is consistent with the content of DEG in PET and the composites. The content of DEG in PET0, PET1, PET3, and PET5 is 3.6, 1.4, 0.9, and 1.2, respectively, which was determined according to Chinese standard GB/T 14,190-1993: Analysis methods for fiber grade polyester chip.

In the GC graphs, the peak of No.7 (25.36 min) for the pure PET is different from that for the composites. Compared with the composites, the peak of No.7 for the pure PET in the GC graph is sharper and has a larger area, indicating the decrease of the product of No.7 in the composites, which is corresponding to the TG analysis that the residual carbon content increases with the addition of silica. The forming process of No.7 is considered to be related to the formation of the transition state, [HOOPh-COCH<sub>2</sub>CHO], and the addition of silica probably plays a role in the formation of the transition state.

There are many hydroxyls or silanol groups at the surfaces of the silica nanoparticles, and they interact not only with the carbonyl through hydrogen bond but also with phenyl through  $\pi$  electrons to adsorb the organic molecules.<sup>21</sup> The OH groups act as the centers of molecular adsorption during their specific interaction with adsorbates capable of forming a hydrogen bond with the OH groups, or more generally, of undergoing donor-acceptor interaction.<sup>22</sup> The adsorption of organic molecules on the surface of silica has been established experimentally by most of techniques including infra-red adsorption, nuclear magnetic resonance, dielectric measurement, and gas-solid chromatography.<sup>21,23</sup> Thus, we think that the adsorption of these organic molecules on the surface of silica and the action of thermal energy promote the formation of the residual carbon, thus preventing the volatilization of products,<sup>24</sup> which is the reason why the activation energy of decomposition increases in the TG measurements.

The No.8 peak of PET1 is much lower than that of PET0, which is probably caused by the reason mentioned above. However, it is still unclear why the product of No.8 increases with the addition of silica in PET3 and PET5.

## CONCLUSIONS

TG and Py-GC/MS investigations on the thermal degradation of PET and PET/silica nanocomposites were carried out. The main conclusions are summarized as follows:

1. The thermal decomposition process and mechanism of PET/silica nanocomposites are basically consistent with those of pure PET, but the addition of silica has an effect to some extent on the decomposition process and products.
2. The PET/silica nanocomposites exhibited better thermal stability, higher residual carbon content, and larger activation energy in comparison with the pure PET.
3. The result that activation energy and residual carbon content increase with the addition of silica is attributed to the adsorption of organic molecules on the silica surface, because this adsorption leads to the decrease of volatile products.

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