

Thermal degradation behavior of polystyrene blended with propyl ester phosphazene

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The thermal degradation behavior of polystyrene (PS) blended with propyl ester phosphazene (FR) was studied by thermogravimetric analysis (TGA) coupled with Fourier transform infrared spectroscopy (FTIR). The results showed that during thermal degradation the evolved gas product of polystyrene blends was similar to the gas product of pure PS, and that the thermal stability of polystyrene blends was slightly improved by the addition of FR. The major thermal degradation temperature and residual char yield of PS blends increased with increasing FR content. © 1997 Elsevier Science Limited

1 INTRODUCTION

Polystyrene (PS) is a commonly used polymer and has many excellent properties, such as high electrical resistance, good mechanical properties and high workability under various processing conditions. However, since PS degrades easily at high temperatures, the use of additives to improve thermal stabilization and flame retardant properties is an area of great interest. Among the work in this area, interest in avoiding the generation of toxic and corrosive gases during thermal degradation of PS has led to the development of non-halogen additives as replacements for halogen flame retardants. Reghunan Nair *et al.*¹ reported that thermal stabilization of PS could be improved by phosphorylation only in the chain ends and chain middle. In addition, the thermal degradation behavior of polystyrene, including the mechanism and kinetics, was investigated by Guaita² and McNeill *et al.*³ They concluded that the thermal degradation of polystyrene was a single step process. The main volatile product was styrene monomer together with certain amounts of benzene and toluene, and a small cold-ring fraction that consisted of oligomer parts such as

dimer, trimer, tetramer and pentamer. Audisio *et al.*⁴ showed that some inorganic substances such as silica, alumina and zeolites could be regarded as additives and catalyzed degradation of polystyrene.

Phosphazenes, as flame retardants with high phosphorus and nitrogen content, have been incorporated into polymers by blending or through chemical modification. A large improvement in the thermal stability of rayon blended with phosphazene has been reported.⁵ In order to investigate further the use of phosphazenes as inorganic retardants for thermal degradation in this article, the thermal degradation behavior of polystyrene blended with propyl ester phosphazene is examined. The gas products and residual char yield are examined by thermogravimetric analysis (TGA) coupled with Fourier transform infrared spectrometry (FTIR), and kinetic analysis during thermal degradation of PS blends is also discussed.

2 EXPERIMENTAL

2.1 Preparation of polystyrene blended with propyl ester phosphazene

Samples were prepared from mixtures of polystyrene (supplied by Chi Mei Industrial Co. Ltd.)

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and propyl ester phosphazene (supplied by the Chung Shan Institute of Science and Technology). Samples were blended in THF and prepared at room temperature by a solvent casting technique. The cast films were dried slowly in an oven at 106°C until the weight of the specimens remained unchanged. The physical properties of PS and propyl ester phosphazene are listed in Table 1 and the symbolic meanings of the formulation used in this study are shown in Table 2.

2.2 Measurement of phosphorus content

The phosphorus content of the PS blends was determined using a colorimeter⁶ and the results are also listed in Table 2.

2.3 Thermal degradation behavior of PS blends

The thermal degradation behavior of the PS blends was investigated using a Perkin-Elmer TGA7 thermogravimetric analysis (TGA) at various heating rates under nitrogen atmosphere.

2.3.1 Analysis of evolved gas product and residual char yield from thermal degradation of PS blends

The gas products of PS blends at various temperatures were studied using a SEIKO SSC 5000 TGA coupled with BIO-RAD FTIR FTS-40 at a heating rate of 10°C/min under nitrogen atmosphere. The resulting spectra were identified by visual analysis and by searching the spectral data bases. The residues at various temperatures in TGA were also investigated using BIO-RAD FTIR FTS-40.

3 RESULTS AND DISCUSSION

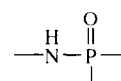
3.1 Thermal degradation of PS blends

Figure 1 and Table 3 represent weight loss versus temperature and the characteristics of various PS

blends at a heating rate of 10°C/min under nitrogen atmosphere. Figure 1 shows that the thermal degradation of FR occurs in three stages, 140–268°C, 270–340°C and above 340°C. Gas discharge during the thermal degradation of FR and the FTIR spectrum at various times (or temperatures) during that gas discharge are shown in Figs 2(a) and 3(a), respectively. The FTIR spectra in Fig. 3(a) were very similar all the way through the thermal degradation process by visual analysis and a search of the spectral data bases led to the conclusion that the major gas product was propylene. The FTIR spectrum of the condensed phase of FR at various degradation temperatures is shown in Fig. 4(a). Both the stretching and bending in the methyl and methylene groups at 2940, 2900, 2850 and 1478 cm⁻¹ decreased with increasing temperature, as did the P=N bond at 1250 cm⁻¹, but the intensity at 1400 cm⁻¹ due to the



bond⁷ increased with increasing temperature. This implies that the methyl and methylene groups of FR gradually disappear due to the formation of propylene gas. The P=N bond undergoes an isomerization reaction during the thermal degradation of FR as it seeks a more thermally stable structure. The thermal degradation and isomerization mechanism of FR are proposed by Papkov *et al.*⁸ and Maynard *et al.*⁹ as follows:



The amount of propylene produced during the thermal degradation of FR in eqns (1) and (2) are calculated to be 23 and 23 wt%, respectively, but in fact from Fig. 1 the amount of propylene

Table 1. Physical properties of materials

Material	Formula	T _g (°C) ^a	Melt flow index (gm/10 min)	Remark
Polystyrene		96	8.0 ^b	PG-33
Propyl ester phosphazene		-100		Cyclic/linear structure = 65:35 Cl < 0.1%wt

^a By ASTM Code D-1238. ^b Determined by DSC. ^c Viscosity > 10⁶ Poise (25°C).

evolved during the thermal degradation of FR is 29 and 17 wt%. Therefore, the thermal degradation of FR in stage 1 can be inferred to include eqn (1) and to partially include eqn (2). The reaction occurring in stage 2 can be inferred to mainly follow eqn (2).

As shown in Fig. 1, the thermal degradation of PS, unlike FR, is a one stage reaction; the temperature range of the thermal degradation is between 285 and 450°C. This agrees with data

published by Grassie *et al.*¹⁰ where the proposed degradation mechanism included depolymerization and intramolecular transfer. TGA/FTIR results which detail the gas discharge with time and identify the gas evolved during the thermal degradation of PS at various times are shown in Figs 2(b) and 3(b). FTIR spectra show that the major gas products at 40-04 min were styrene, α -methyl styrene or benzene mixtures. This was determined by visual analysis and by searching spectral data bases. This determination agreed with the results of Guaita.² The FTIR spectrum of the condensed phase is similar to PS without additives as shown in Fig. 4(b). From the FTIR spectra of evolved gas and residual yield, the mechanism of thermal degradation of PS can be deduced to be the result of competition between a random chain scission which induces monomer volatilization and an intramolecular transfer reaction that produces oligomeric fragments and low molecular substances. From Fig. 1 the

Table 2. Symbolic meaning and phosphorus content of blended samples

Code	Description ^a	P(wt%) ^b	P(wt%) ^c
PS0F	PS/FR = 10:0	0	< 0.01
PS1F	PS/FR = 10:1	2.01	1.92
PS2F	PS/FR = 10:2	3.68	3.99
FR	PS/FR = 0:10	22.1	22.1

^a By weight ratio. ^b Phosphorus content calculated from composition. ^c Phosphorus content by the colorimeter.

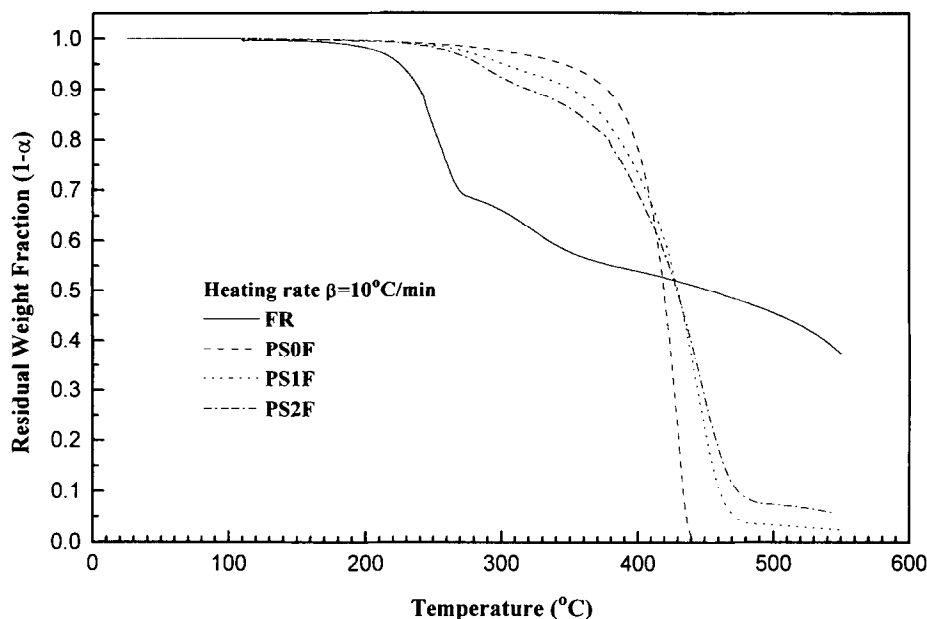


Fig. 1. TGA thermogram of PS blends at a heating rate of 10°C/min under nitrogen atmosphere.

Table 3. Weight loss characteristics of various blends at a heating rate of 10°C/min under nitrogen atmosphere

Blends	T_{onset} (°C) at 5% wt loss	%wt at 550°C	Temperature range for thermal degradation (°C)		
			Stage 1	Stage 2	Stage 3
FR	224-98	37.47	140 ~ 268	271 ~ 340	340 ~
PS0F	345-03	0.00	—	289 ~ 445 ^a	—
PS1F	301-38	2.42	269 ~ 336	337 ~ 482 ^a	—
PS2F	283-42	5.78	254 ~ 325	326 ~ 491 ^a	—

^a Major degradation in polymer or polymer blends.

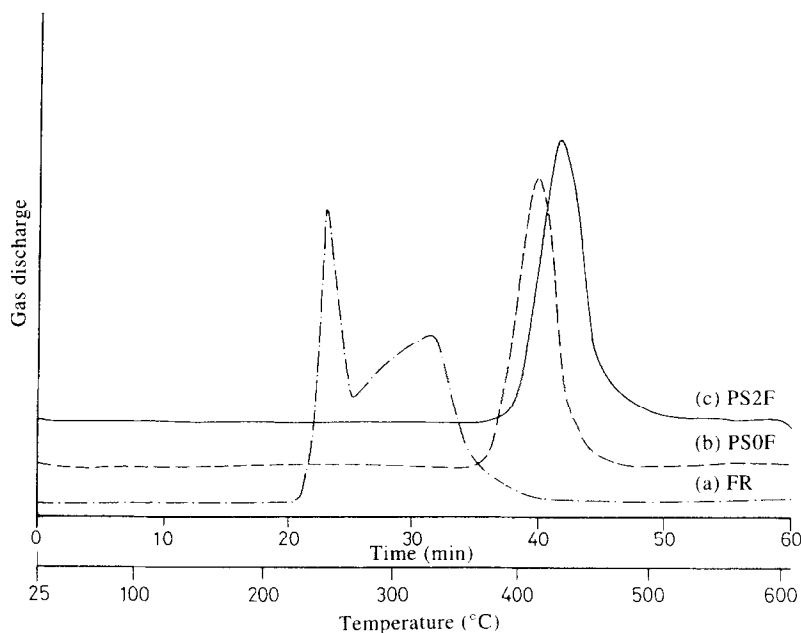
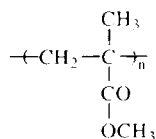


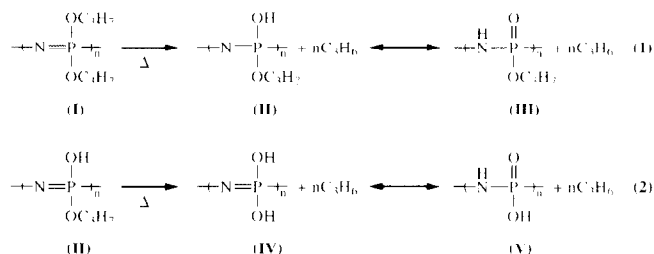
Fig. 2. The gas discharge with time (temperature) for (a)FR, (b)PS0F and (c)PS2F in TGA/FTIR.

thermal degradation of PS blended with FR shows a two stage pyrolysis. The weight loss of the first stage occurs from 250 to 330°C and is attributed to FR. The second stage is mainly attributed to PS. Following the above analytical method, the results of thermal degradation of PS blends are shown in Figs 2(c) and 3(c). The major evolved gases at 41.69 min are still benzene, styrene and α -methyl styrene mixture, similar to pure PS, but the relative content of each constituent is different. Propylene is not observed in the FTIR spectrum. The residual content of PS blends at 550°C increases with increasing content of FR. It is interesting that the degradation temperature at maximum weight loss rate for PS blends is delayed and that the maximum degradation rate is smaller, as shown in Fig. 5. A comparison of the FTIR spectra of residual yield of PS2F and PS0F, shown in Figs 4(c) and 4(b), shows that the intensity of the



bands at 1600, 1500 and 1468 cm^{-1} becomes less defined in the presence of FR. The total evidence indicates a difference in the thermal degradation mechanism of PS and PS blends. One explanation for the result is that FR could act as an acid catalyst which reacts with the benzene rings of PS

and releases benzene from the PS chains. The mechanism proposed is as follows:^{2,4,11-14}



This explains the relative contents of benzene, styrene or α -methyl styrene in the evolved gas for PS and PS blends.

In order to examine the degree of interaction between PS and FR during the thermal degradation of PS blends, a mixing rule, eqn (9) which assumed no interaction effect, was employed.

$$W_{\text{blend}}(T) = W_{\text{FR}}(T) \cdot X_{\text{FR}} + W_{\text{PS}}(T) \cdot X_{\text{PS}} \quad (9)$$

where

$W_{\text{blend}}(T)$: residual weight fraction of PS blend at any temperature

$W_{\text{FR}}(T)$: residual weight fraction of FR at any temperature

$W_{\text{PS}}(T)$: residual weight fraction of PS at any temperature

X_{FR} : weight fraction of FR in blends

X_{PS} : weight fraction of PS in blends.

A comparison of the experimental results and the result calculated from the mixing rule is shown in Fig. 5. The thermal degradation rate

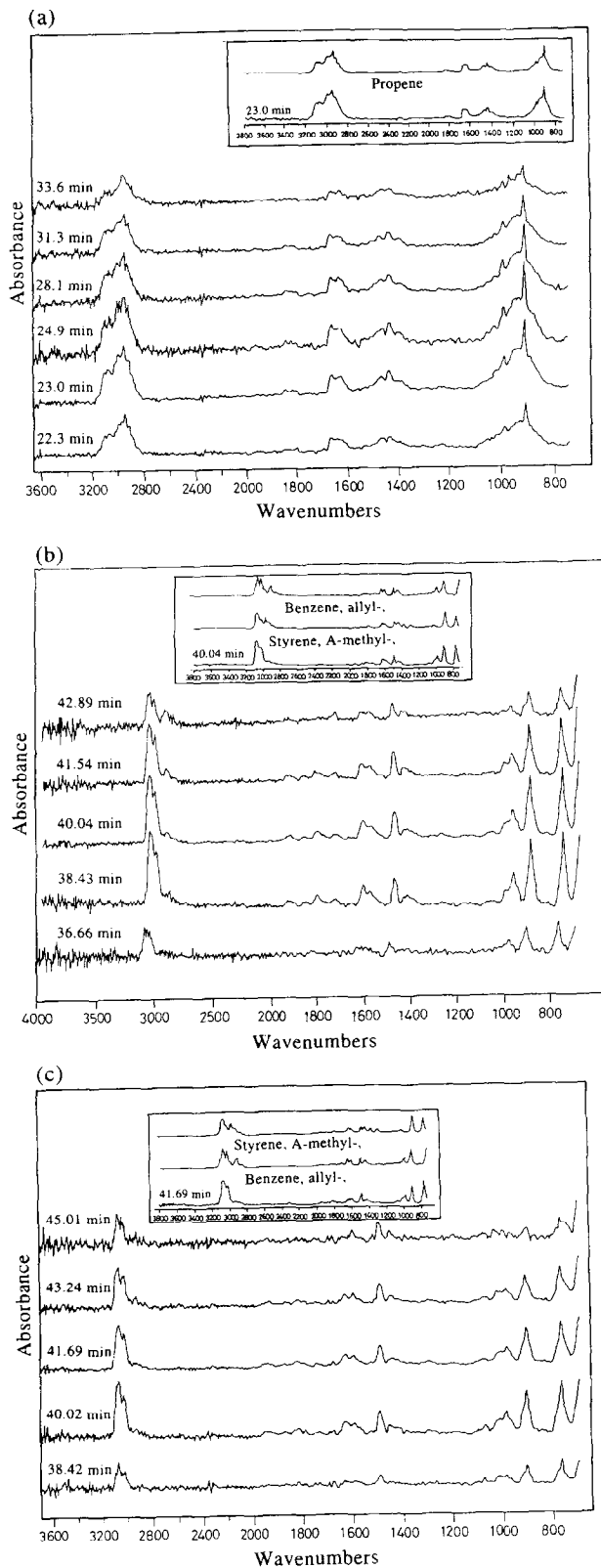


Fig. 3. FTIR spectrum of gas phase during thermal degradation at various times for (a) FR, (b) PS0F and (c) PS2F.

calculated from the mixing rule was slower than the experimental results before $(DTG)_{max}$, and faster than experimental results after $(DTG)_{max}$, as shown in Fig. 6. Incorporation of FR in the PS polymer chains accelerated the breakage of polymeric chains in the early stage of thermal degradation as mentioned above, probably forming some stable structures and hence retarding the following degradation reaction. The residual content above 500°C calculated from the mixing rule was close to the experimental results. This suggests that while FR may change the degradation reaction route, it does not form extra stable char with PS segments through the interaction.

3.2 Kinetic analysis

The relationship between apparent activation energy and weight loss fraction (α) of PS blends was determined using Ozawa's method.¹⁵ The results are shown in Fig. 7. The range of activation energy of PS is from 140 to 277 kJ/mol. Based on previous reports^{3,16} degradation in this range is a competitive reaction between random-chain scission and end-chain scission. In our experiment, the activation energy of PS was constant at 130 kJ/mol ($\alpha = 0.2 \sim 0.9$). Since FR thermally degrades in three stages, the activation energy of thermal degradation also has three parts. The first part is from 100 to 120 kJ/mol ($\alpha = 0.04 \sim 0.29$) with an average value of 110 kJ/mol. Different competing reactions cause the range of activation energy for the second and third stages to become less well defined and so their physical meaning is less clear. The activation energy of thermal degradation of PS blends increases with increasing weight loss fraction, and the average activation energy is 175 and 150 kJ/mol for PS1F and PS2F, respectively. This shows that the activation energy is increased and the maximum thermal degradation temperature of PS blends is delayed relative to pure PS.

4 CONCLUSIONS

1. The thermal degradation of FR occurs in three stages up to 550°C . Propylene is the major evolved gas.
2. The thermal degradation of PS shows a one stage reaction and the major gas products are styrene, α -methyl styrene and benzene.
3. Two stage reactions are observed in the thermal degradation of PS blended with FR.

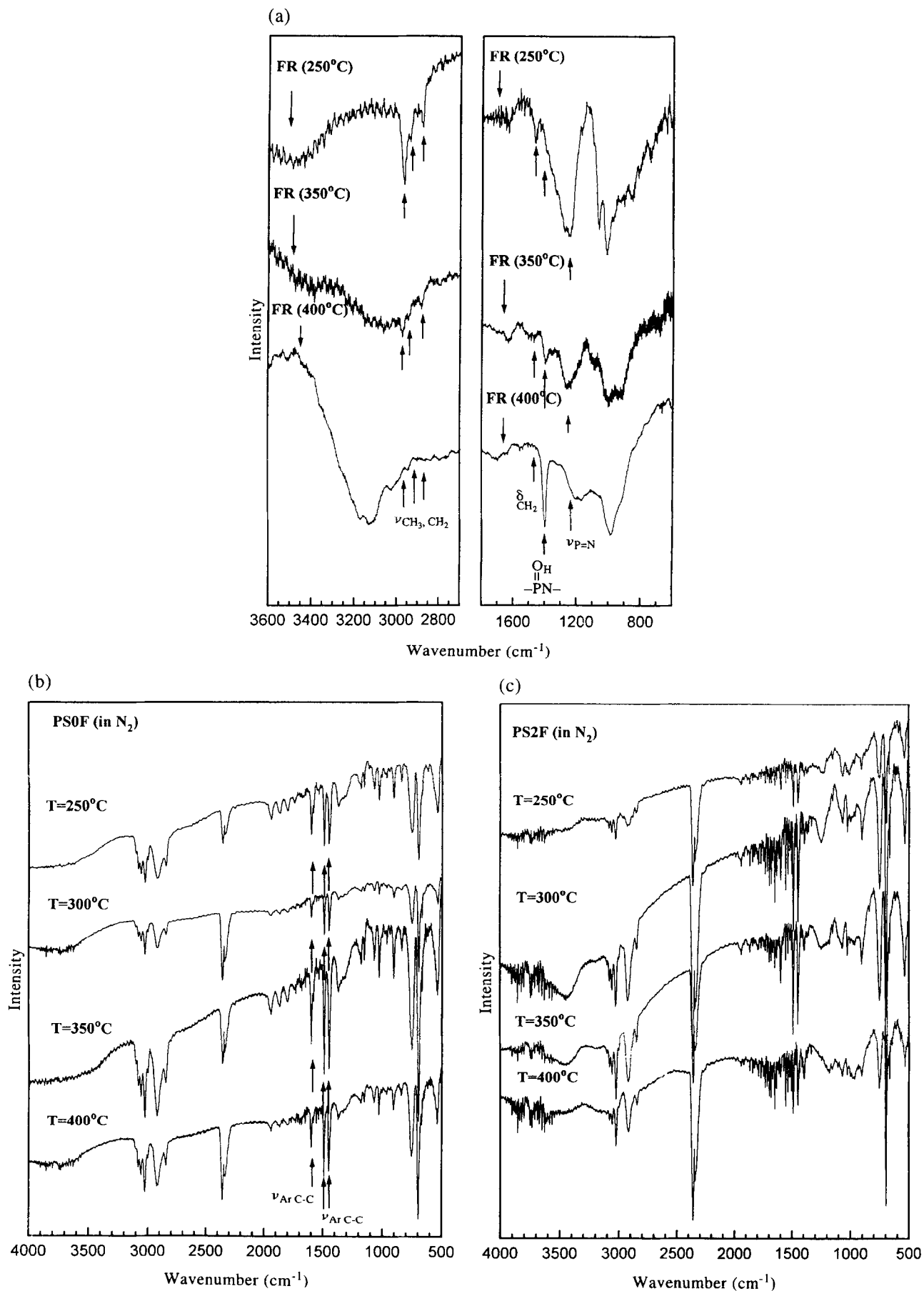


Fig. 4. FTIR spectrum of condensed phase during thermal degradation at various temperatures for (a) FR. (b) PS0F and (c) PS2F.

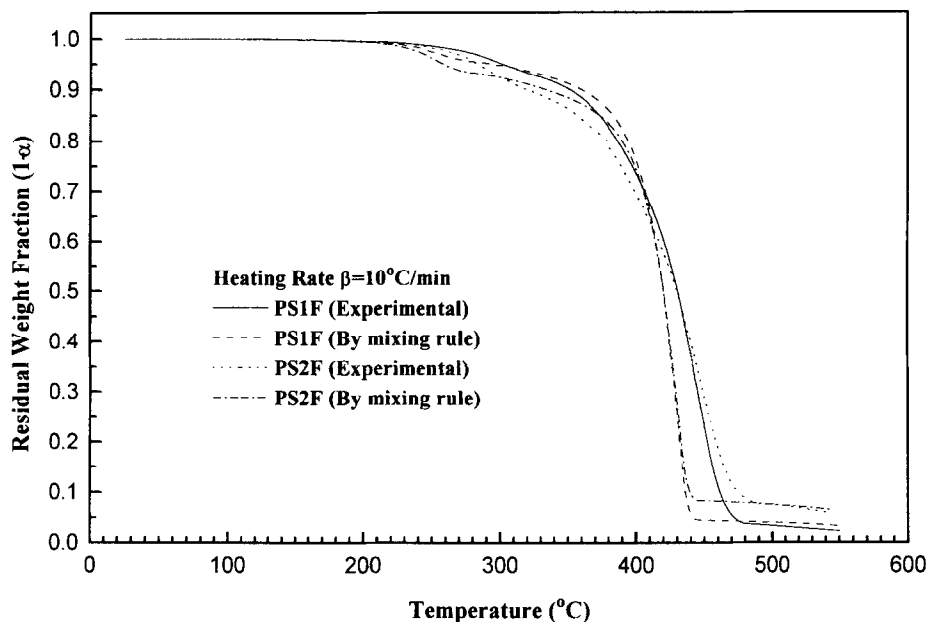


Fig. 5. Comparison of TGA thermogram between experimental results and mixing rule for PS1F and PS2F.

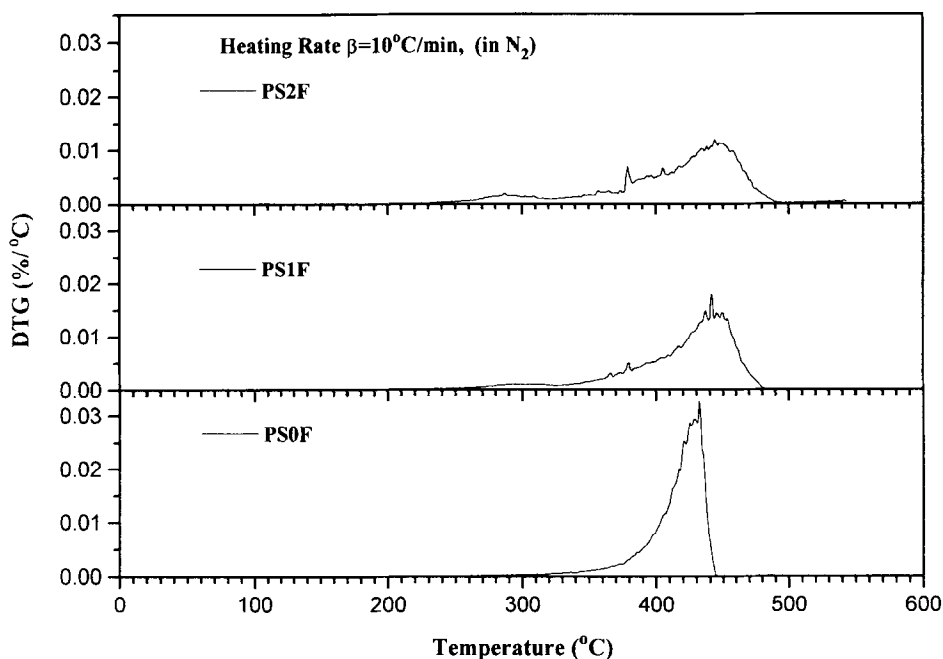


Fig. 6. DTG thermogram for thermal degradation of PS blends at a heating rate of 10°C/min under nitrogen atmosphere.

The residual char yield increases with increasing FR content.

- The evolved gas products and the residual char yield of PS are not significantly affected by blending with FR, but the major degradation temperature is delayed.

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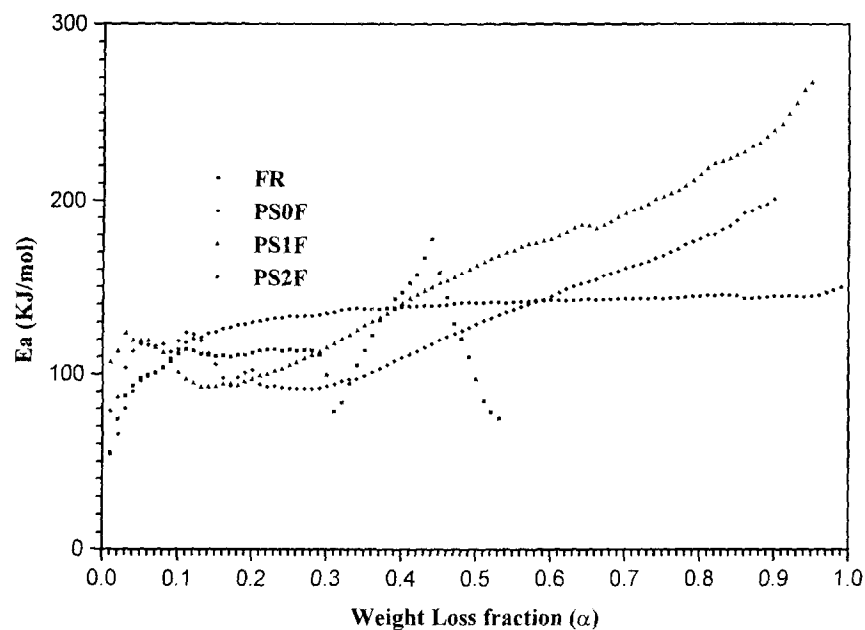


Fig. 7. The relationship of activation energy versus weight loss fraction for PS blends.

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