

Investigation of the Thermal Decomposition Behavior and Kinetic Analysis of PTT/Phenoxy Blends

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ABSTRACT: Thermal decomposition of binary blends composed of poly(trimethylene terephthalate) (PTT) and a phenoxy resin, namely poly(hydroxy ether) of bisphenol A, and prepared by melt blending was studied using thermogravimetric analysis. The thermal decomposition behavior of the blends could be explained in terms of formation and loss of hydrogen bonds and appearance of both low and high molecular weight species due to transesterification reaction between hydroxyl groups of phenoxy with ester bonds of PTT. The kinetics of decomposition reaction was analyzed by Freeman–Carroll, Friedman, Chang, and Vachuska–Voboril methods. It was found that all of the methods well described the decomposition reaction of the blends. The correlation between the

calculated values and the chemical nature of the blends was acceptable. Among all the investigated methods the Chang method showed the best correlation with the experimental data. FTIR spectroscopy was employed to study the chemical structure of the blends. The results revealed strong interaction between the blend components in the form of hydrogen bonding. Progress of these interactions was followed with time and temperature. The effects of blending and loss of hydrogen bonding on degradation behavior in this kind of reactive blends were emphasized. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2924–2931, 2008

Key words: thermal decomposition; kinetics; blends; poly(trimethylene terephthalate); phenoxy; PTT/phenoxy

INTRODUCTION

Degradation of polymers has received much scientific and industrial interest because of its importance in polymer processing^{1–5} and research purposes.^{6–8} Although many studies have been conducted to investigate the degradation of individual polymers^{9–18} and also the modeling of degradation processes,^{15–17} only few research activities have been done to analyze the thermal decomposition of polymer blends.^{19–22} Degradation processes in polymer blends are more complex than those of single-component systems. The complexity results from the coreaction phenomena at the interfaces and in the bulk, and the involvement of macromolecular and low-molecular-weight degradation products. These reactions are strongly influenced by the heterogeneous blend morphology.

One difficulty in modeling of the degradation of polymer blends originates from their immiscibility and phase separation behavior. These phenomena change the blend to a biphasic system in which each phase decomposes separately with its own

degradation mechanism. Simultaneity of two reactions may cause two separate degradation peaks or a single peak depending on the degree of overlapping of the individual peaks of the components. To interpret the degradation behavior of polymer blends, a profound knowledge of the blend morphology and the chemical structure of the blend constituents is essential.

Several techniques have been developed to analyze the thermal decomposition kinetics of polymers.^{23–26} Among these techniques, those proposed by Friedman,²³ Freeman–Carroll,²⁴ Chang,²⁵ and Vachuska–Voboril²⁶ have been widely used. Wang et al.¹⁷ studied the thermal decomposition kinetics of pure poly(trimethylene terephthalate) (PTT) with different molecular weights under different atmospheres using the Friedman, the Freeman–Carroll, and the Chang techniques and found that the kinetic parameters for the different models are in a satisfactory conformity. Liang et al.²⁰ employed the Vachuska–Voboril method for the evaluation of the thermal oxidative degradation of UV-cured epoxy acrylate blended with phosphate triacrylate and compared the resulting activation energy with that obtained by the multiple heating rate method.

Since being commercialized by Shell Chemicals (Houston, TX), PTT has received much scientific

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attention both in its pure form^{9,17,27–35} and its blends.^{36–44} Several blends of PTT were studied with regard to their morphology,^{9,17} rheological properties,^{36,37} miscibility,³⁸ chemical structure, and reactions occurring during blending.^{38,42} In this study, the thermal decomposition behavior of PTT and its blends with phenoxy is discussed on the basis of different kinetic models.

THEORETICAL SECTION

The data obtained from thermogravimetric analysis (TGA) experiments can be analyzed using the general equation of degradation as follows:

$$d\alpha/dt = Z(1 - \alpha)^n e^{-E/(RT)} \quad (1)$$

where α , t , $d\alpha/dt$, Z , n , E , R , and T are the weight loss of the polymer undergoing degradation, the time at which α is measured, the weight-loss rate, the frequency factor, the decomposition reaction order, the activation energy, the gas constant (8.3136 J mol⁻¹ K⁻¹), and absolute temperature (K), respectively.

The activation energy (E) is the energy required for the onset of degradation, and the higher the activation energy, the higher the thermal stability of a polymer. On the other hand, the higher the activation energy the higher would be the temperature dependency of the degradation process. The decomposition reaction order, n , indicates the exponent of the reactants, $(1 - \alpha)$, in the decomposition equation, and because the value of $(1 - \alpha)$ is less than 1, higher values of n indicates lower rates of decomposition reaction. Therefore, a thermostable system is characterized by higher values of E and n and vice versa. The dependence of the weight-loss rate on frequency factor (Z) is such that by increasing Z the weight-loss rate increases, but Z has no effect on the temperature dependency of the degradation process.

The parameters of eq. (1) have been calculated by several researchers using different techniques. One of these techniques is the Freeman–Carroll technique,²⁴ which is a single heating rate treatment technique. The equation is as follows:

$$\Delta \ln(d\alpha/dt) / \Delta \ln(1 - \alpha) = n - (E/R) \Delta(1/T) / \Delta \ln(1 - \alpha) \quad (2)$$

By plotting $\Delta \ln(d\alpha/dt) / \Delta \ln(1 - \alpha)$ against $\Delta(1/T) / \Delta \ln(1 - \alpha)$ a straight line is obtained. The slope of the line is $-E/R$ and the interception is n . The value of Z can be calculated using eq. (1) along with the values of n and E obtained from eq. (2).

Another technique for the calculation of thermal decomposition parameters is the Friedman method.²³ The equation is the logarithmic form of eq. (1) and can be written as follows:

$$\ln(Z) = \ln(d\alpha/dt) - n \ln(1 - \alpha) + E/(RT) \quad (3)$$

The value of activation energy can be obtained by plotting $\ln(d\alpha/dt)$ or $\ln(1 - \alpha)$ against $1/T$. The value of Z can be calculated from eq. (1).

The Chang technique²⁵ is another method for the calculation of thermal decomposition parameters using TGA and DTGA curves. This technique is based on the following equation:

$$\ln[(d\alpha/dt)/(1 - \alpha)^n] = \ln(Z) - E/(RT) \quad (4)$$

A straight line is obtained by plotting $\ln[(d\alpha/dt)/(1 - \alpha)^n]$ against $1/T$. The values of $\ln(Z)$ and $-E/R$ can be obtained from the intercept and the slope, respectively.

Another technique of calculation, based on the second order differentiation of the weight loss is the Vachuska–Voboril method.²⁶ The equation used in this technique is as follows:

$$\frac{d^2\alpha/dT^2}{d\alpha/dT} T^2 = E/R - n/(1 - \alpha)(d\alpha/dT)T^2 \quad (5)$$

In this method, the values of activation energy and reaction order can be calculated using the straight line obtained by plotting $\frac{d^2\alpha/dT^2}{d\alpha/dT} T^2$ against $1/(1 - \alpha)(d\alpha/dT)T^2$.

EXPERIMENTAL

Materials

The materials used in this study were commercial grades. The phenoxy resin grade (PAPHEN[®] PKFE[®]) was obtained from the InChem Company (Rock Hill, SC). PTT (grade: RTP 4700), with a melting temperature of 228°C and an intrinsic viscosity of 0.901 mL g⁻¹ measured at 25°C in a 60/40 mixture of phenol and tetrachloroethane, was obtained from the RTP Company (Winona, MN). All the materials were dried prior to blending.

Blend preparation

The PTT/phenoxy blend samples with compositions of 90/10, 75/25, 50/50, and 25/75 (wt/wt) were melt blended in a DACA Micro Compounder (DACA Instruments, Goleta, CA) at a temperature of 250°C and a screw speed of 100 rpm for 10 min. Subsequently, the strands produced by the compounder were cooled to ambient temperature. The

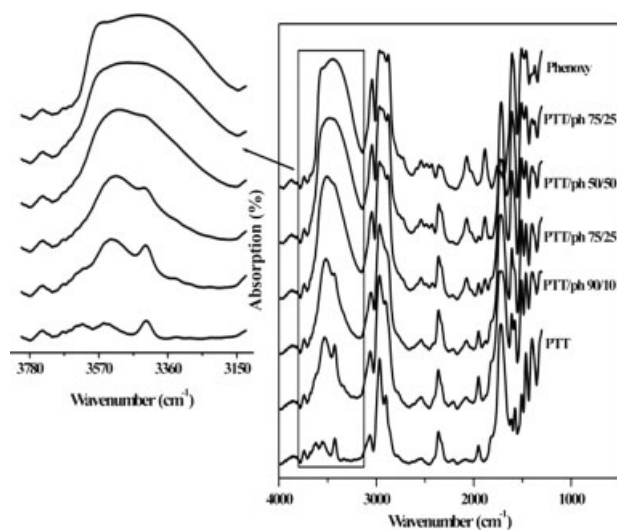


Figure 1 FTIR spectra of PTT/phenoxy blends recorded in the region of 1000–4000 cm^{-1} .

neat polymers namely PTT and phenoxy were also processed under the similar processing conditions.

Characterization

The TGA tests were carried out on a Perkin–Elmer TGA instrument (USA) using samples of about 10 mg. The tests were done in the range of ambient temperature to 700°C at a rate of 10 K min^{-1} under the flow of either N_2 or O_2 , with a flow rate of 50 mL min^{-1} . The data obtained from the TGA instrument were in the form of weight percentage versus temperature.

Reactions in the blends were studied by FTIR examinations on a NEC242 FTIR instrument using thin films of the samples. The resolution of the spectra was 4 cm^{-1} .

RESULTS AND DISCUSSION

Analysis of the chemical structure

Figure 1 exhibits the FTIR spectra of phenoxy and its blends with PTT in the region of 1000–4000 cm^{-1} . In this region, several spectroscopic stretching bands are discernible. For PTT, the band at 1720 cm^{-1} is attributed to the carbonyl group, the band at 1265 cm^{-1} is ascribed to the ester group, and the band at 3000 cm^{-1} is attributed to the aromatic CH groups. On the other hand, for phenoxy, the band at 1601 cm^{-1} is ascribed to the ether group, the band at 2947 cm^{-1} is attributed to the CH groups connected to hydroxyl groups, and the broad band in the region of 3300–3600 cm^{-1} with a small shoulder at the high frequency side is related to the hydroxyl groups. The small shoulder belongs to free or less associated hydroxyl groups, while the broad band is attributed

to the associated ones. In other words, the spectrum of phenoxy clearly shows that a high degree of intramolecular hydrogen bonds is predominant in the polymer. It is well known from the literature that this part of the spectrum reacts very sensitive to alterations of interactions.^{45–47} This can also be demonstrated for the blends under investigation.

As shown in Figure 2, in the range of 3300–3600 cm^{-1} , the blend spectra differ distinctly from that of the neat phenoxy. The maximum of the hydroxy group band was shifted to a frequency in between the associated and nonassociated hydroxy group maxima. Furthermore, the band width became distinctly narrower. This clearly indicates a new type of interaction which can be assigned to hydrogen bonds between the hydroxy groups of phenoxy and the ester carbonyl groups of PTT. As there are no indications for free or self-associated hydrogen groups, one can conclude that hydrogen bonding with the carbonyl groups proceeds more or less quantitatively. Obviously, the intermolecular hydrogen bonding strength in phenoxy/PTT blends is stronger than that of the self-association of pure phenoxy. It has also to be taken into account that the PTT is in strong excess. This may also favor the intermolecular interactions over the intramolecular ones.

To investigate the influence of the processing conditions on the formation of intermolecular hydrogen bonds, the IR spectra of PTT/phenoxy 90/10 samples processed at 250°C for 5, 10, and 15 min and at 270°C for 10 min are presented in Figure 2. The influence on the OH vibration band is not very strong. A slight shift of the maximum from 3555 to

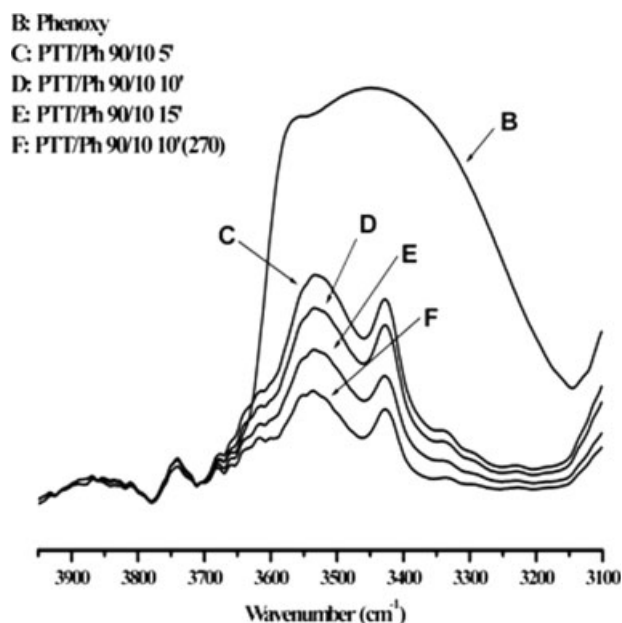


Figure 2 FTIR spectra of PTT/phenoxy 90/10 blends processed at different mixing times and temperatures.

3535 cm^{-1} is observed which might be caused by an improvement of the homogeneity of the blends resulting in an improved hydrogen bonding. As known from ^1H NMR investigations,⁴² transesterification reactions may also occur under the processing conditions mentioned earlier. However, the extent of these reactions is not high enough to be detected by IR spectroscopy unambiguously.

The band at $\sim 3440 \text{ cm}^{-1}$, which is an overtone of the carbonyl vibration band of PTT at 1720 cm^{-1} , is not much influenced by the interactions and can be excluded from further discussions.

Thermal decomposition of the PTT/phenoxy blends

Figure 3 shows the TGA and DTGA curves corresponding to the thermal degradation of PTT/phenoxy with different compositions under nitrogen atmosphere. All the samples show a large drop in the TGA curves and a single peak in the DTGA curves. The TGA curves show that the onset of decomposition temperature of each blend sample is lower than that of pure phenoxy and higher than that of pure PTT. In addition, the temperatures of completion of degradation are higher for the blends than those of the individual components. These findings suggest that some reactions of the blend components lead to the formation of structures with both lower and higher thermal stability compared with the individual components. The occurrence of these reactions was confirmed by NMR investigations presented elsewhere.⁴² It was shown that at high temperatures transesterification reactions resulting from the reaction of the aliphatic hydroxyl group of phenoxy with the ester bonds of PTT occur in the course of which a PTT grafted phenoxy and a hydroxyl-terminated PTT with reduced molar mass are formed. Additionally, crosslinking is possible if two phenoxy chains react with the same PTT chain. Therefore, the transesterification reactions lead to formation of both low- and high-molecular-weight species with different thermal stabilities. Hence, a broader decomposition temperature range is observed for the blends when compared with the neat components (see Fig. 3). It might be that the hydrogen bonding also influences the decomposition process at lower temperature, but, obviously, these bonds disappear at high temperatures used for the TGA investigations.

Moreover, occurrence of radical reactions, which might eventually result in the formation of additional crosslinked structures, cannot be ruled out. The radical reactions may become predominant at elevated temperatures and especially in the presence of oxygen atmosphere. It is known that oxygen with its biradical nature is able to abstract protons. With respect to the concerned system all the CH_2 groups,

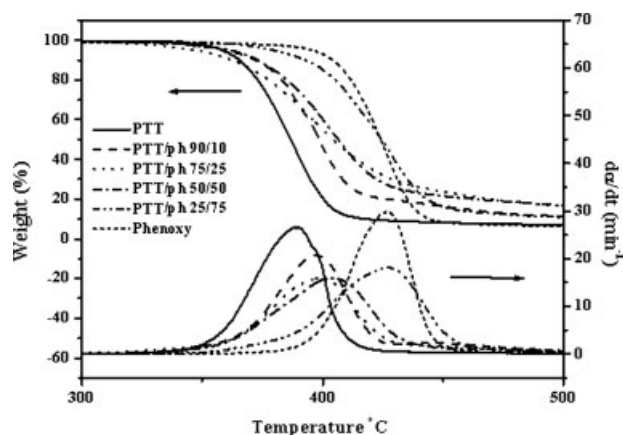


Figure 3 TGA and DTGA curves of PTT/phenoxy blends at a heating rate of 10 K min^{-1} under nitrogen atmosphere.

and especially the CH group of phenoxy, are susceptible for proton abstraction leading to formation of highly reactive radicals. When two such radicals are recombined it results in crosslinking. This type of crosslinked structures would be different from those formed because of the transesterification reactions. Formation of these crosslinked structures can broaden the decomposition range of the blends when compared with the pure components.

Kinetic analysis of degradation

As discussed earlier, the PTT/Phenoxy blend is a highly reactive and complicated system in which the reactions change the overall structure of the system with increasing time. Therefore, it is very likely that the kinetic of decomposition changes during heating. However, it is possible to use some simplified kinetic models to have an estimation of the kinetic parameters for the degradation process.

Table I exhibits the kinetic parameters of the thermal decomposition of the PTT/phenoxy blends of different compositions obtained using the techniques developed by Freeman–Carroll, Friedman, Chang, and Vachuska–Voboril. The parameters of degradation modeling are E and n , which are the activation energy and the degradation reaction order, respectively.

The average values of E and n are summarized in Table I. It can be seen from the average values of E that phenoxy has higher activation energy than PTT. This means that phenoxy is thermally more stable than PTT. The activation energies of the blends are lower than those of the pure components. This negative synergy results from the reactions of the blend constituents. The transesterification reactions results in the formation of small PTT chains as well as the large grafted phenoxy chains. The small PTT chains have hydroxyl terminal groups which can be split

TABLE I
Kinetic Parameters of Thermal Degradation for PTT/Phenoxy Blends Under Nitrogen

| Sample | Freeman-Carroll method | | | Friedman method | | | Chang method | | | Vachuska-Voboril method | | | Average | | |
|---------|------------------------|-----|-------|-----------------|-------|----------------|--------------|-----|-------|-------------------------|-----|-------|---------|-----|-----|
| | E | n | ln(z) | r ₁ | ln(z) | r ₁ | E | n | ln(z) | E | n | ln(z) | r | E | n |
| PTT | 369 | 2.2 | 48.8 | 0.9989 | 47.2 | 0.999 | 352 | 2 | 61.8 | 355 | 2 | 50.03 | 0.9957 | 351 | 1.9 |
| 90/10 | 276 | 1.6 | 52.65 | 0.9971 | 54.28 | 0.9984 | 315 | 1.8 | 53.9 | 332 | 2.2 | 54.13 | 0.9955 | 289 | 1.7 |
| 75/25 | 204 | 2.5 | 39.31 | 0.9962 | 34.93 | 0.9995 | 187 | 1.7 | 30.31 | 202 | 2.4 | 35.42 | 0.9944 | 188 | 2.2 |
| 50/50 | 260 | 2.6 | 38.93 | 0.9949 | 36.52 | 0.999 | 257 | 2.6 | 42.93 | 252 | 2.3 | 40.5 | 0.9918 | 251 | 2.4 |
| 25/75 | 253 | 1.6 | 58.6 | 0.9986 | 44.92 | 0.9854 | 298 | 2.1 | 48.76 | 263 | 1.9 | 47.92 | 0.997 | 254 | 1.9 |
| Phenoxy | 460 | 2.1 | 61.8 | 0.9969 | 49.4 | 0.9993 | 453 | 2 | 75.92 | 441 | 1.8 | 57.98 | 0.9999 | 443 | 1.8 |

off relatively easy by further transesterification reactions. The formation of small PTT chains can increase the rate of degradation reaction and hence decrease the degradation temperature. For the blends, the values of the activation energy are decreased with increasing of PTT content. As PTT is less stable than phenoxy, the thermal stability reduces with increasing amounts of the less stable component. An exception is the PTT/phenoxy 90/10 blend, which reveals higher activation energy despite having a high PTT content. This can be explained by the relatively small amount of hydroxy groups in the blend which reduces the degree of exchange reactions between the hydroxy groups and the ester bonds of PTT. Because of this, the formation of small volatile molecules is retarded.

The values of *n* are an indication of the decomposition reaction rate. Higher values of *n* represent a slow reaction and vice versa. Lower onset temperatures and higher temperatures of completion of degradation result in a broader drop of decomposition curve corresponding to a lower reaction rate. This can be observed clearly in the PTT/phenoxy 50/50 system, which shows higher *n* than those of other systems. The higher temperature of completion of degradation in PTT/phenoxy 50/50 is due to the formation of thermostable products resulting from the crosslinking reactions of PTT with phenoxy chains.

The results of degradation modeling of PTT/phenoxy blends of different compositions by the Freeman technique along with the experimental data are shown in Figure 4. As the axes representing $\Delta[\ln(d\alpha/dt)]/\Delta[\ln(1-\alpha)]$ and $10^4 \Delta(1/T)/\Delta[\ln(1-\alpha)]$ are the same for all the samples, a 3D view was

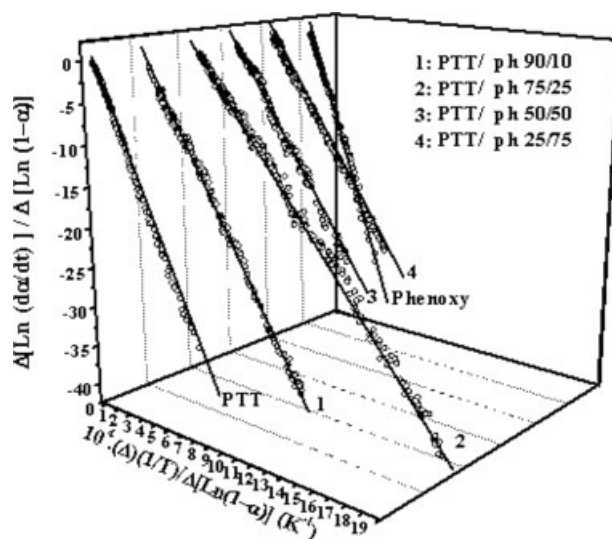


Figure 4 Freeman-Carroll plots for the thermal degradation of PTT/phenoxy blends (heating rate: 10 K min⁻¹, under nitrogen atmosphere).

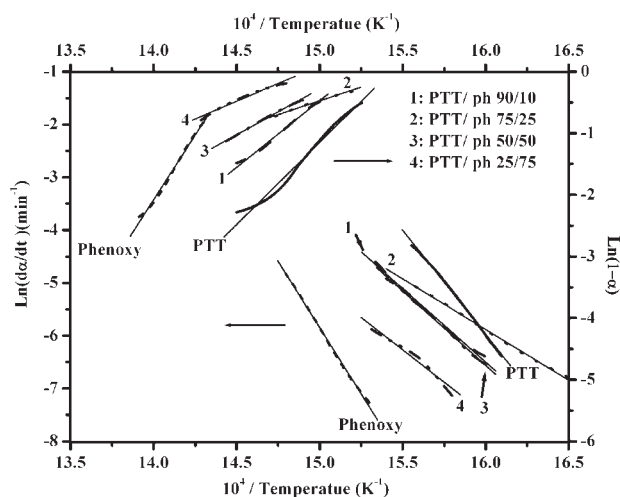


Figure 5 Friedman plots for the thermal degradation of PTT/phenoxy blends (heating rate: 10 K min^{-1} , under nitrogen atmosphere).

chosen for a better presentation of the data. The characteristic degradation parameters as well as the correlation coefficients (r values) are listed in Table I. It is evident from the correlation coefficients that the correlation is very good in a broad temperature range. All the correlation coefficients are higher than 0.99, which proves a good correlation of the analysis in the temperature range studied.

Figure 5 illustrates the results of modeling the experimental data using the Friedman technique. Two sets of curves are presented in the figure, in which one of them is the plot of $\ln(d\alpha/dt)$ against $1/T$, which gives the E values, and the other set is $\ln(1 - \alpha)$ against $1/T$, which gives the n values. The parameters of the model are presented in Table I. The values of activation energy and reaction order obtained from the Friedman plot are lower than those obtained using the Freeman method. The plots of the Chang method for calculation of the thermal decomposition parameters of the blends are illustrated in Figure 6. As can be observed from the Figure 6 and the data presented in Table I, the results of this method fit to the experimental data better than those of the other methods. The correlation coefficients for this method are higher than 0.998, showing a better correlation than the other methods.

The Vachuska–Voboril method was also used to calculate the decomposition activation energies and the reaction orders of all samples. The results of modeling by this method are plotted in Figure 7. The values of the respective parameters are listed in Table I. The values of the activation energy and the reaction order calculated by this method are close to the ones determined by the other methods and the calculated curves also fit to the experimental data. However, the fit is not as good as that of the Chang method. As it is seen from Table I, the values of acti-

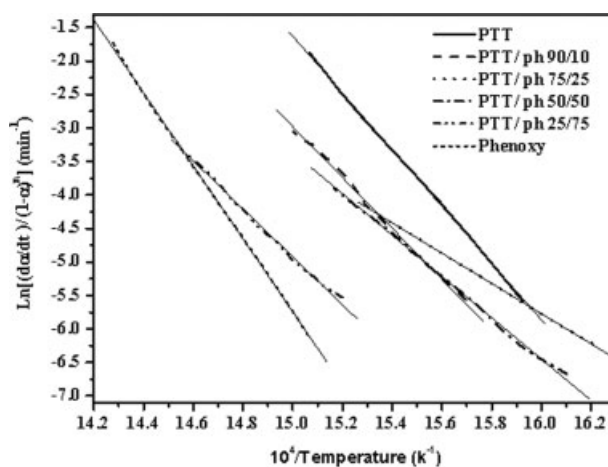


Figure 6 Chang plots for the thermal degradation of PTT/phenoxy blends (heating rate: 10 K min^{-1} , under nitrogen atmosphere).

vation energies obtained from the different kinetic models are not the same.

For the PTT/phenoxy 50/50 blend, the effect of atmosphere on the degradation was investigated. The results are summarized in Table II. The higher values of activation energy and the higher reaction order determined under oxygen suggest that decomposition in presence of oxygen is retarded. Obviously, decomposition in presence of oxygen is different from that under nitrogen. It is assumed that in presence of oxygen radical reaction become more significant. Under certain conditions, the formation and recombination of radicals may result in the formation of network structures stabilizing the system temporarily. These processes may compensate the formation of small volatile particles by

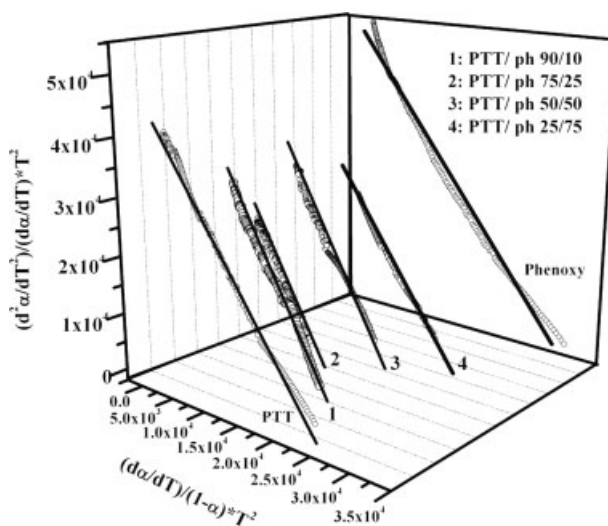


Figure 7 Vachuska–Voboril plots for the thermal degradation of PTT/phenoxy blends (heating rate: 10 K min^{-1} , under nitrogen atmosphere).

TABLE II
Kinetic Parameters of the First and Second Thermal Degradation Stages for PTT/Phenoxy 50/50 Under Nitrogen and Oxygen

| Sample | Freeman–Carroll method | | Friedman method | | Chang method | | Vachuska–Voboril method | | Average | |
|--------------------|------------------------|----------|-----------------|----------|--------------|----------|-------------------------|----------|----------|----------|
| | <i>E</i> | <i>n</i> | <i>E</i> | <i>n</i> | <i>E</i> | <i>n</i> | <i>E</i> | <i>n</i> | <i>E</i> | <i>n</i> |
| 50/50 ^a | 260 | 2.6 | 257 | 2.6 | 252 | 2.3 | 251 | 2.4 | 234 | 1.9 |
| 50/50 ^b | 270 | 3.5 | 243 | 3.3 | 267 | 3.7 | 257 | 3.4 | 243 | 3.2 |
| 50/50 ^c | 321 | 3.4 | 324 | 3.4 | 496 | 6.4 | 360 | 3.9 | 299 | 2.3 |

^a Under N₂.

^b Under O₂, first stage of decomposition.

^c Under O₂, second stage of decomposition.

transesterification reactions as observed under nitrogen.

CONCLUSIONS

The thermal decomposition behavior of PTT and its blends with phenoxy was discussed on the basis of different kinetic models. The thermal decomposition behavior of the blends could be explained in terms of the formation and loss of hydrogen bonds and the appearance of both low- and high-molecular-weight species due to transesterification reaction between hydroxyl groups of phenoxy with ester bonds of PTT. The formation of hydrogen bonds, which proceed more or less quantitatively, was confirmed by FTIR spectroscopy and the slight thermal stability observed at low temperature was assigned to these bonds. However, at higher temperatures, because of the loss of hydrogen bonds, the transesterification reactions leading to the formation of both crosslinked and low-molecular-weight species were found to be responsible for changes in the thermal stability behavior. The extent of these transesterification reactions was not high enough to be detected by IR spectroscopy unambiguously. Phenoxy showed a higher thermal stability when compared with PTT because of its self-association. The TGA curves showed that the onset of decomposition temperature of each blend sample was lower than that of the neat phenoxy and higher than that of pure PTT. In addition, the temperatures of completion of degradation are higher for the blends than those of the individual components. Therefore, a broadening in the TGA decomposition curve over full composition range was attributed to formation of both the low- and high-molecular-weight species. Although the kinetic of decomposition of PTT/phenoxy blend might change during the heating, however, it was possible to use some simplified kinetic models to have an estimation of the kinetic parameters for the degradation process.

The kinetic parameters (*E* and *n*) of the thermal decomposition of the PTT/phenoxy blends of different compositions were obtained using the techniques developed by Freeman–Carroll, Friedman, Chang, and Vachuska–Voboril. It was found that the activation energies of the blends were lower than those of the pure components. This negative synergy resulted from the reactions of the blend constituents. Moreover, for the blends, the values of the activation energy were decreased with increasing content of PTT. From the values of correlation coefficients it was evident that all the models showed a good correlation with experimental data and well described the decomposition of the blends. Among all the investigated models the Chang model showed the best fit. The higher values of activation energy and the higher reaction order determined under oxygen suggested that the decomposition in the presence of oxygen was retarded when compared with nitrogen.

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