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Investigating the role of transreactions on degradation behavior of phenoxy/poly(trimethylene terephthalate)/clay nanocomposites using thermal analysis techniques

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ABSTRACT

The properties of reactive polymer blends are strongly influenced by the interchange/exchange reactions. The effect of nanofillers on these reactions, in particular transreactions, has not yet fully understood. This work is devoted to investigate transesterification and its consequent effect on degradation behavior of phenoxy/poly(trimethylene terephthalate) (PTT) nanocomposites using thermal analysis techniques. ^{1}H NMR results showed that the maximum extent of transreactions occurred in the blends loaded with just 1 wt.% nanoclay. A mechanism based on nanoconfinement was proposed to show how nanoclay particles affect transreactions of the blend constituents. Thermal degradation kinetic studies, using KAS isoconversion method, revealed that addition of only 1 wt.% clay improves thermal stability of the pristine blend whereas higher amount of clay accelerates degradation process. An attempt was made to establish correlations among these changes in thermal degradation behavior, the extent of transreactions and dynamic mechanical properties.

1. Introduction

Reactions in polymer blends are extensively used both to improve the blend properties such as compatibility, and to synthesize new polymeric materials with desired properties [1]. Interchange/exchange reactions significantly affect the primary structure of polymer chains and, consequently, change the final properties. Exchange reactions, in particular transesterification reactions in polymer blends have been extensively researched [2–7]. Recently, melt blends of phenoxy resin, which is a poly(hydroxyl ether) of bisphenol A, with poly(trimethylene terephthalate) (PTT) have gained special attention [6–9]. It has been demonstrated that the properties of phenoxy/PTT blends are strongly determined by transesterification reactions [7]. The influence of transreactions on rheological response [7], phase behavior and thermal degradation [6], as well as mechanical properties [8] of phenoxy/PTT blends has been investigated.

Polymer nanocomposites have been progressively growing field of research for developing new materials with enhanced physical, mechanical and thermal properties. Among these, clay-containing nanocomposites based on polymer blends are of considerable importance and many studies have been devoted to study their morphology, mechanical and thermal properties [10–13]. Based on the literature, the presence of nanofillers in polymeric systems can affect interchain interactions. Chen et al. [14,15] showed that nanoconfinement effect of clay particles on polystyrene chains intensified the intermolecular interaction. There has been little literature addressing the influence of nanoparticles on transesterification reactions in polymer blends [16–18]. Recently, Wang et al. [17] investigated the influence of SiO_2 nanoparticles on transesterification of PET/PBT blends and reported that the incorporation of SiO_2 inhibited transreactions in the blends.

Thermal degradation of polymers is a very important phenomenon, which affects the performance of all polymeric materials in daily life. Recently, thermal stability of polymer nanocomposites improved by montmorillonite clay has been reviewed [19,20]. Depending on the nanoclays chemical nature and their interactions with polymers, they have often increased the thermal stability of polymers, although a reduction in a few cases has also been reported [21,22]. Barrier model has been commonly used to explain the improved thermal stability of polymer nanocomposites. However, according to Chen et al. [15], nanoconfinement appears to be a more specific description of the phenomenon. They concluded that nanoconfinement is responsible for the enhancement of thermal stability of PS/clay nanocomposites in the early stages of degradation. Clay-induced nanoconfinement of polymer chains could affect

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interchange/exchange reactions between reactive polymer blend components which could be responsible for variation in degradation behavior of nanocomposites. In order to deeper investigate the effects of transreactions on thermal degradation behavior of nanocomposites, a kinetic analysis could be very useful because it provides information on energy barriers of the degradation process by calculating kinetic parameters such as activation energy which can be extracted from dynamic experiments by means of different methods.

To the best of our knowledge, this is the first time that transesterification reactions in polymer blends and their influence on thermal properties in presence of nanoclay particles are investigated. An attempt is made to establish correlations among the extent of transreactions, DMA properties and thermal degradation behavior. The thermal degradation kinetic studies, using KAS isoconversion method, were also performed for a better interpretation of the degradation process of phenoxy/PTT blend and nanocomposites.

2. Experimental

2.1. Materials

The materials used in this work were commercial grades. Phenoxy resin (PAPHEN® PKFE®) with a weight average molecular weight of 58 kg/mol was obtained from InChem Company, USA. PTT (RTP 4700 natural grade) with a melting temperature of 228 °C was supplied by RTP Company, USA. The nanoclay used in this study was Cloisite®30B, purchased from Southern Clay Products which is a bis(hydroxyl) methyl tallow ammonium exchanged montmorillonite.

2.2. Nanocomposite preparation

Prior to melt mixing, all samples were dried in a vacuum oven at 100 °C for 4 h. The melt blending of the samples was conducted in a microcompounder (DACA) with a screw speed of 100 rpm, at a temperature of 230 °C and a mixing time of 10 min. Weight ratio of phenoxy/PTT blend was kept constant at 80/20. A range of phenoxy/PTT nanocomposites containing 0, 1, 3, 5 and 7 wt.% nanoclay was also prepared (PhPTT, PhPTT1, PhPTT3, PhPTT5 and PhPTT7).

2.3. Characterization

Wide angle X-ray scattering (WAXS) analysis was performed using an X-ray diffractometer (Xpert, Philips) operating at 40 kV and 30 mA for Cu Kα radiation (λ = 0.154 nm). The scanning rate was 1°/min with a step size of 0.04° under the diffraction angle, 2θ, in the range of 1–10°. ^{1}H NMR spectra were recorded on a high resolution Bruker spectrometer operating at 400.13 MHz for ^{1}H. A 70/30 (v/v) mixture of deuterated chloroform (CDCl3) and deuterated trifluoroacetic acid (TFA-*d*) was used as solvent. The thermal stability of phenoxy/PTT blend and nanocomposites was investigated by nonisothermal thermogravimetric analysis (TGA) using a PerkinElmer-Pyris1 TGA instrument. The measurements were conducted from 50 to 700 °C at heating rates of 5, 10 and 20 K/min in a dynamic nitrogen atmosphere (flow rate of 50 ml/min). Aluminum pans with sample weights of about 8 mg were used. Dynamic mechanical analysis was performed using a Tritec 2000 DMA instrument (Triton Technology Co.) in a bending mode on extruded rod-like samples with a frequency of 10 Hz, a temperature range of 20–150 °C and a heating rate of 5 K/min. The dispersion of silicate layers in the blend was analyzed by means of a JEM 2100 F transmission electron microscope (TEM) operating at 200 kV.

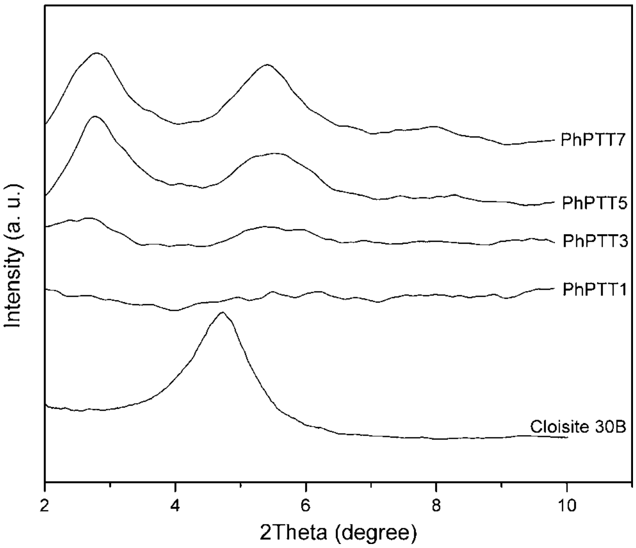


Fig. 1. XRD patterns of Cloisite 30B and phenoxy/PTT nanocomposites with various nanoclay loadings.

3. Results and discussion

3.1. Structure and morphology

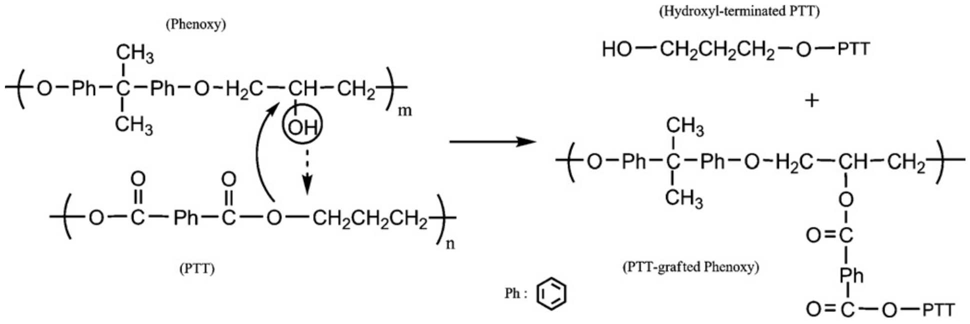
In order to gain some insight into the morphology of the phenoxy/PTT nanocomposites, the samples were analyzed by means of WAXS and TEM. The X-ray diffraction (XRD) patterns of nanocomposites and neat nanoclay are shown in Fig. 1. The (0 0 1) plane peaks of nanocomposites shift to the lower angles as compared to the neat nanoclay, which indicates an increase in the gallery height of the silicate layers. This increased interlayer spacing suggests that phenoxy and PTT chains intercalated into the galleries of nanoclay layers. Table 1 lists the parameters calculated from the XRD patterns. The largest d-spacing was found in PhPTT3 with 34.2 Å.

According to the XRD results, PhPTT1 showed no obvious clay peak in the low angle region whereas basal peaks shift to the lower angles as the nanoclay loading increases, implying the intercalation of polymer chains into the nanoclay galleries. It is well established that a necessary prerequisite for polymer chains to penetrate into a narrow gallery of silicate layers and forming a thermodynamically stable intercalation is strong interaction between polymer chains and surfactants of nanoclay layers. In case of our system, these strong interactions are mostly hydrogen bonds between the functional groups of polymer chains and hydroxyl groups of Cloisite 30B, which were verified using Fourier transform infrared analysis [23]. It should be noted that at very low clay contents it is not unusual to not see the peak related to clay layers therefore TEM investigation is needed to confirm the XRD results. The TEM results will be discussed subsequently.

The broad peak of PhPTT3 suggests that clay layers are largely exfoliated, although there exist some unexfoliated clay tactoids.

Table 1
d-Spacing (d_{001}) and diffraction angles (2θ) for Cloisite 30B and nanocomposites with different nanoclay loadings.

Samples	2θ (°)	d_{001} (Å)
Cloisite 30B	4.8	18.5
PhPTT1	–	–
PhPTT3	2.57	34.2
PhPTT5	2.77	31.8
PhPTT7	2.82	31.3



Scheme 1. Schematic representation of grafting reaction of phenoxy with PTT.

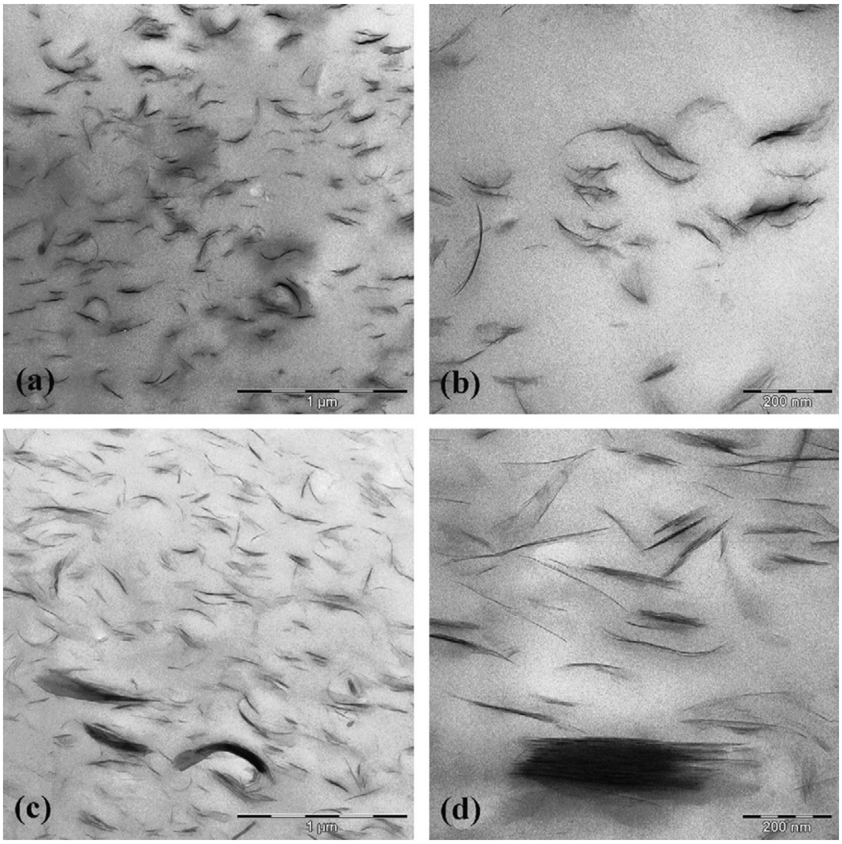


Fig. 2. TEM micrographs of (a and b) PhPTT3 and (c and d) PhPTT5.

Thus it is reasonable to presume that a mixture of intercalated and exfoliated morphologies has been formed in this sample. According to Scherrer formula, the width of the basal peaks (β) could be related to the thickness of silicate layers ($D_c \sim \beta^{-1}$). The broader width of diffraction peak for PhPTT3 as compared to other samples indicates the smaller thickness of stacks of silicate layers, which is indicative of more delaminated silicate layers.

In case of PhPTT5 and PhPTT7, only a shift of (0 0 1) peak to the lower angles was observed which is a hint for formation of intercalated structures. Exfoliation of the clay layers for both aforementioned samples is hindered due to the geometrical constraints in the matrix, particularly rigid phenoxy chains. The calculated widths for the pristine clay, PhPTT5 and PhPTT7 samples are 0.8°, 0.9° and 1.05°, respectively. It is quite interesting to note that the width of diffraction peak for PhPTT7 is broader than that of PhPTT5 which reveals a better dispersion state of nanoclays in PhPTT7.

Fig. 2 shows TEM micrographs of PhPTT3 and PhPTT5 with different magnifications. The images with the low magnification could give us a good overview about the clay dispersion throughout the samples whereas; the images with higher resolutions were used to analyze the individual clay layers. It is evident from the low magnification micrographs that nanocomposites show relatively good dispersion and ordered intercalated structures. It can be seen that both nanocomposites exhibit quite the same dispersion except the fact that some agglomerated clay networks can be observed in PhPTT5. At higher magnification, one can better see the differences of structure and state of nanoclay dispersion in the blend matrix. As was predicted from the XRD results, in case of PhPTT3 silicate layers are delaminated to some extent, although some unexfoliated layers can be found in the form of tactoids. TEM micrograph of PhPTT5, at high magnification, clearly indicates the formation of a mixture of intercalated and exfoliated morphologies which verifies the XRD results.

3.2. Transesterification of phenoxy/PTT/clay nanocomposites

It was previously shown that phenoxy/PTT blends undergo transesterification reactions during melt mixing process [7]. The

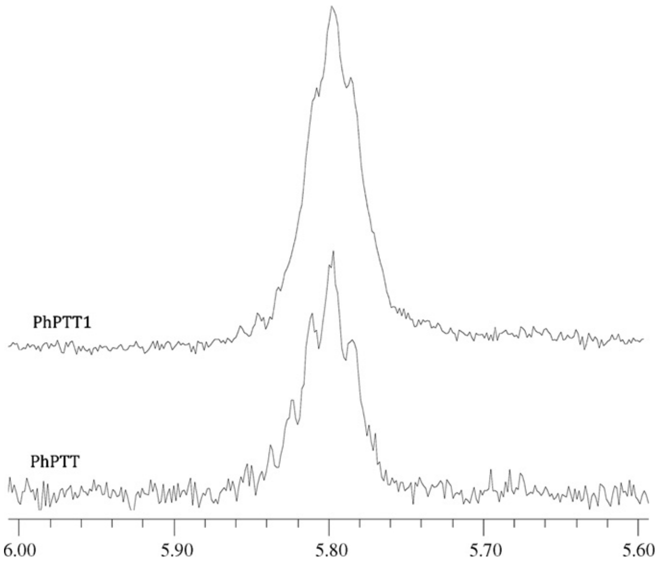


Fig. 3. Section of ^{1}H NMR spectra of PhPTT and PhPTT1.

reaction of the aliphatic hydroxyl group of phenoxy with the ester bond of PTT changes the blend to a homogeneous system through formation of a PTT-grafted phenoxy and a hydroxyl-terminated PTT, as illustrated in Scheme 1.

In order to have a deeper scrutiny on the structural changes arising from transreactions of phenoxy/PTT blends and the impact of transreactions on thermal properties of these systems, ^{1}H NMR spectroscopy was employed. The new structures formed by transesterification in polymer blends could be studied using ^{1}H NMR spectra. In phenoxy/PTT blends, signal at about 5.8 ppm which is ascribed to the CH–O–CO–Ph moiety is of particular interest to estimate the extent of transreactions [7]. In Fig. 3, a magnified view of the signal at 5.8 ppm for PhPTT and PhPTT1 is presented. In order to approximate the degree of conversion of the hydroxyl groups (i.e., extent of transreactions), the intensity of the above mentioned signal has to be related to the intensity of any signal of the ungrafted moiety that is $-CH_2-CH(OH)-CH_2-$ which appears at 4.3 ppm. The results of quantitative analysis for the extent of transreactions are reported in Table 2. It should be mentioned that the experimental uncertainty for the reported values for extent of transreactions is about ±0.25%. It is obvious that the introduction of only 1 wt.% nanoclay into the blend enhances the extent of transreactions by more than three folds.

It is reasonable to assume that presence of specific interactions between the nanoclay and the blend components could cause both phenoxy and PTT chains to be located in a confined environment around the nanoclays. The very high specific surface area generated by the large amount of delaminated silicate layers in PhPTT1 could lead to more adjacent phenoxy and PTT chains around the nanoclays which should increase the probability of exchange reactions. For this reason, the highest extent of transreactions occurs in this sample. A schematic representation of this proposed mechanism is illustrated in Scheme 2a.

Table 2
Extent of transreactions for phenoxy/PTT blend and nanocomposites.

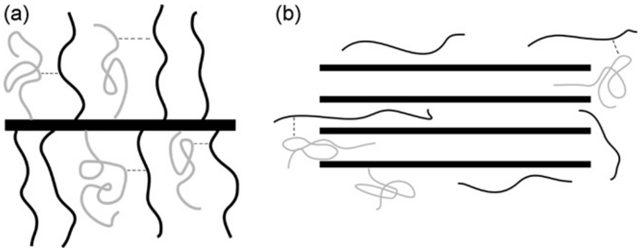
Samples	Extent of transreactions (%)
PhPTT	5.0
PhPTT1	17.2
PhPTT3	12.5
PhPTT5	4.5
PhPTT7	9.3

By taking a glance at Table 2, it can be seen that as the nanoclay content is increased to 3 wt.%, the extent of transreactions becomes smaller than that of PhPTT1 but still larger than that of the pristine blend. As can be seen in Scheme 2b, for nanocomposites with intercalated structure (ones with higher than 1 wt.% nanoclay), the nanoconfinement of polymer chains is localized mainly in the narrow interfacial region within the galleries of silicate layers. This could cause a decrease in number of phenoxy and PTT chains in the vicinity of each other as compared to PhPTT1, which might be a reason for reduction of transreactions in these samples.

As the nanoclay content increases from 5 to 7 wt.%, an increment in the extent of transreactions is observed. According to XRD results, PhPTT7 shows a better dispersion of nanoclay layers relative to PhPTT5. The better dispersion of layered silicates, the larger the interfacial area, and more polymer chains experience nanoconfinement which leads to higher extent of transreactions between the blend components.

3.3. *Thermal degradation behavior*

TGA curves of the samples are presented in Fig. 4. The onset temperature for degradation (T_{onset}), which is the temperature corresponding to 5% weight loss and the T_{max} i.e. the temperature of the maximum rate of degradation are reported in Table 3. As compared to the pristine blend, an increased T_{onset} was observed only in case of adding 1 wt.% nanoclay. Very interestingly, T_{onset} of



Scheme 2. Schematic representation of the effect of nanoclay-induced nanoconfinement on transreactions for (a) exfoliated structures and (b) intercalated structures. (▬) represents PTT chains, (-) represents phenoxy chain and (- - -) represents probable location of transreactions.

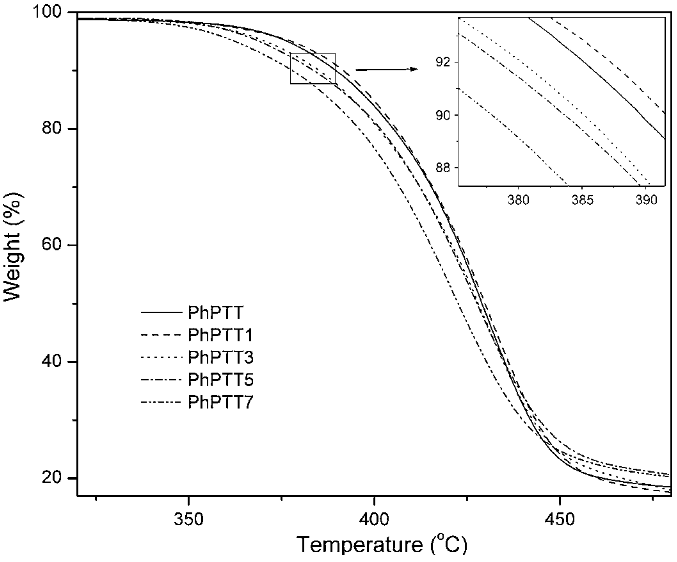


Fig. 4. TGA curves of phenoxy/PTT blend and nanocomposites in nitrogen at 10 °C/min^{-1}.

the other nanocomposites shifted to lower temperatures. The shift was most pronounced in PhPTT7. This unexpected behavior suggests that thermal stability of polymer-clay nanocomposites cannot be explicitly explained by the dispersion state of the clay. Thus, a kinetic analysis is performed in order to better elucidate the role of nanoclay on degradation behavior of phenoxy/PTT nanocomposites.

3.4. Kinetic analysis

Among all mathematical models suggested for measurement of the overall kinetics of degradation, isoconversional methods are able to detect and treat multi-step processes [24]. These methods need a series of experiments at various heating rates. The isoconversional methods are based on the single-step kinetic equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A\exp\left(\frac{-E_\alpha}{RT}\right)f(\alpha) \qquad (1)$$

where α is the extent of conversion, t is the time, $k(T)$ is the Arrhenius rate constant, A and E_α are the Arrhenius parameters (pre-exponential factor and activation energy, respectively), T is the temperature, R is the gas constant, and $f(\alpha)$ is the reaction model. It is now well-recognized that polymer degradation process is too complex to be elucidated in terms of a single pair of Arrhenius parameters and the traditional set of reaction models [25]. The shortcomings in single-heating-rate methods also could be overcome by the isoconversional methods which allow the effective activation energy of a process to be unequivocally estimated as a function of the extent of conversion. In this work, degradation process is followed at three different heating rates (β). By dividing Eq. (1) by the heating rate ($\beta = dT/dt$), rearranging and integration, Eq. (2) can be obtained:

$$g(\alpha) \equiv \int_0^\alpha \frac{1}{f(\alpha)}d\alpha = \frac{A}{\beta}\int_{T_0}^{T} \exp\left(\frac{-E_\alpha}{RT}\right)dT = \frac{A}{\beta}I(E_\alpha, T_\alpha) \qquad (2)$$

where $g(\alpha)$ is the integral form of the reaction model. Using a particular approximation, rearranging and taking logarithms yields:

$$\ln\frac{\beta}{T_\alpha^2} = \ln\left(\frac{RA}{E_\alpha g(\alpha)}\right) - \frac{E_\alpha}{RT_\alpha} \qquad (3)$$

This equation was derived by Kissinger [26] and Akahira and Sunose (KAS) [27]. By plotting $\ln\beta/T_\alpha^2$ versus $1/T_\alpha$ for each conversion, the activation energy as a function of conversion can be calculated from the slope of the straight line in Eq. (3). The obtained activation energies as a function of conversion are shown in Fig. 5 for all the samples studied. It is observed that PhPTT1 shows higher activation energy values compared to the other samples. Quite unexpectedly, the presence of 3, 5 and 7 wt.% nanoclay in the system causes a reduction in the activation energy of degradation compared to the pristine blend, which is indicative of a loss in thermal stability of the pristine blend upon introduction of more than 1 wt.% nanoclay. Barrier model which is the commonly invoked mechanism cannot be used here to explain this behavior because according to this model, with increasing the clay content more silicate-enriched char layer builds up on the remaining mass surface which could cause an increased thermal stability. As mentioned before, a large number of polymer chains experience the nanoconfinement in PhPTT1. Chen et al. [15] suggested that in the nanoconfined environment, diffusion of degrading radicals slows to the point that they can recombine which makes the degradation process partially reversible. This might be the main reason for increasing Ea values in PhPTT1. The descending trend of Ea values could be attributed to the fact that as the degradation progresses toward higher conversions, nanoconfinement disintegrates and probability of recombination of the degrading radicals decreases [15].

Table 3
T_{onset} and T_{max} of degradation of phenoxy/PTT blend and nanocomposites at 5 K/min.

Samples	T_{onset} (°C)	T_{max} (°C)
PhPTT	360	411
PhPTT1	365	414
PhPTT3	357	411
PhPTT5	352	410
PhPTT7	330	404

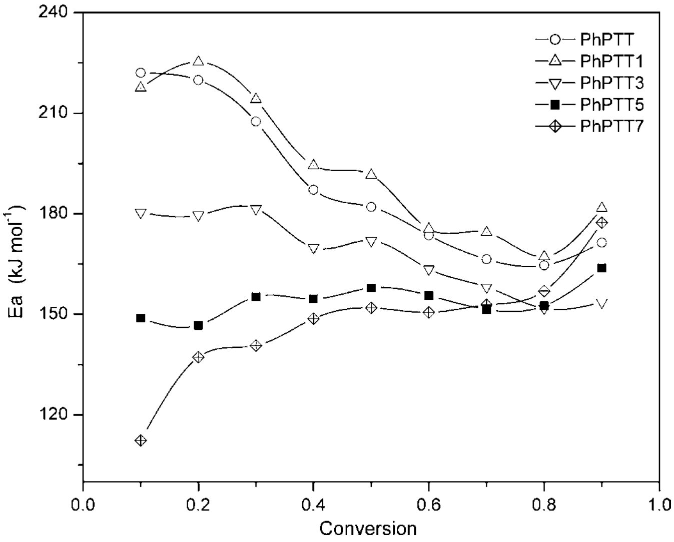


Fig. 5. Dependence of activation energy on conversion for the pristine blend and different nanocomposites.

The obvious reduction of activation energies for nanocomposites containing higher than 1 wt.% nanoclay could be due to several factors. It is clear that the above hypothesis cannot be used for these samples. One possible explanation for this unexpected behavior could be the degradation of organic molecules within the Cloisite 30B layers, which has been reported to occur in temperature range of 250–500 °C [28]. It was shown that the degradation of organic modifiers used in clays results in creation of active catalytic sites in the polymer matrix [29], which could accelerate the decomposition of the nanocomposites. Another possible reason for this phenomenon will be discussed later.

In contrast with other samples, an ascending trend for activation energies of PhPTT7 as a function of conversion is seen in Fig. 5. In order to explain this behavior one could use barrier model which suggests that as the degradation progresses toward larger extent of conversions, a silicate-enriched char layer builds up on the remaining mass surface and acts as thermal insulator and mass transport barrier which could increase the activation energy of degradation.

3.5. Nonisothermal data simulation

A reconstruction or simulation program, using calculated kinetic parameters, is usually used to visually check how the fitted result match the original [30]. In Eq. (1), the function $f(\alpha)$ is generally complex and in order to solve the differential equation, one has to use some simplifications for determination of the kinetic parameters. The most simple expression for $f(\alpha)$ is the nth order model represented in Eq. (4) [31]:

$$f(\alpha) = (1-\alpha)^n \qquad (4)$$

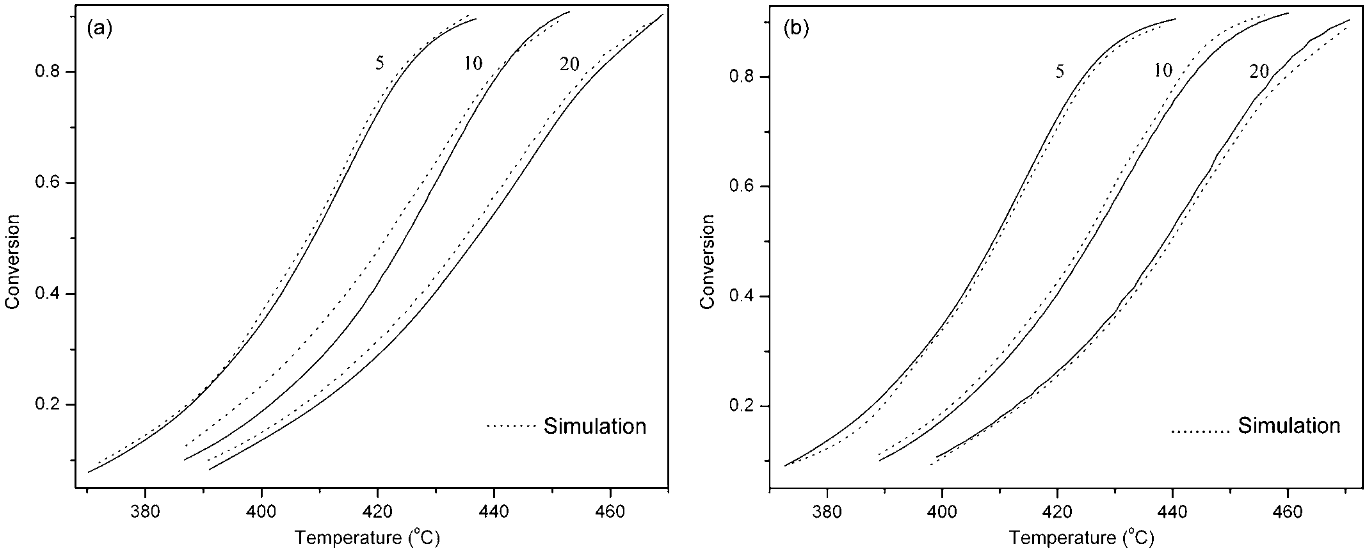


Fig. 6. Simulations (dots) and experimental (lines) data for nonisothermal decomposition of (a) PhPTT and (b) PhPTT1 at three heating rates of 5, 10 and 20 °C/min.

where n is the reaction order of the degradation process which can be determined by the Kissinger method [26]:

$$n = 1.26\sqrt{s} \tag{5}$$

where s is the shape index of the DTG curve which is defined as the ratio of slopes of tangents to the DTG curve at the inflation point. In order to further corroborate the accuracy of the calculated kinetic parameters by KAS method, the nth order equation can be solved after transforming Eq. (2) to:

$$\alpha = 1 - \left[\left(\frac{AI(E_\alpha, T_\alpha)}{\beta}\right)(n-1)+1\right]^{1/1-n} \quad (\text{for } n \neq 1) \tag{6}$$

$$\alpha = 1 - \exp\left(\frac{-AI(E_\alpha, T_\alpha)}{\beta}\right) \quad (\text{for } n = 1) \tag{7}$$

The kinetic parameters obtained from the KAS method were used to reconstruct nonisothermal decomposition data based on Eq. (6). In Fig. 6, both the simulated and experimental data for PhPTT and PhPTT1 at different heating rates are illustrated. It is evident that the calculated kinetic parameters at 5 K/min, better predict the experimental data. The simulation of nonisothermal data was performed for all the samples and the results showed the potential of KAS method in the prediction of experiments.

3.6. *Isothermal degradation behavior*

Thermal stability of polymers can also be described as the time to reach a certain extent of conversion at a given temperature. The isothermal test was carried out under nitrogen atmosphere for PhPTT and PhPTT1 at two different temperatures. As it was expected, PhPTT1 showed higher thermal stability than that of PhPTT. It was observed, for instance, that for the pristine blend to lose 70% of its weight, it is necessary for it to be exposed at 375 °C for a period of 80 min; whereas for the nanocomposites with 1 wt.% nanoclay, to lose the same weight at the same temperature the exposure time of 100 min is needed.

Using Eq. (8), which has been introduced by Vyazovkin [32], isothermal behavior can be estimated for all the samples:

$$t_\alpha = \frac{I(E_\alpha, T_\alpha)}{\beta \exp(-E_\alpha/RT_0)} \tag{8}$$

where t_α is the time to reach the extent of conversion (α) at a given temperature (T_0) under isothermal conditions. Fig. 7 presents a comparison between the simulated data and the experimental results at 375 °C. It can be observed that up to about 60% conversion, the trend observed in both simulated and experimental results are almost the same for both samples. After 60% conversion, an obvious difference between these datasets is observed, however, the slope of plots remains nearly the same. Since isoconversional methods can predict the isothermal degradation up to 60% conversion fairly well, the predicted graphs for all the samples were also calculated (not shown here). These graphs further confirm the reduced thermal stability of nanocomposites with higher than 1 wt.% nanoclay.

3.7. *Correlation between thermal stability and DMA properties*

In contrast with our expectation from polymer-clay nanocomposites, incorporation of nanoclay into phenoxy/PTT blend decreases its thermal stability with the exception of adding 1 wt.% nanoclay for which the thermal stability is slightly increased. As mentioned before, reduced thermal stability of nanocomposites could be due to several factors.

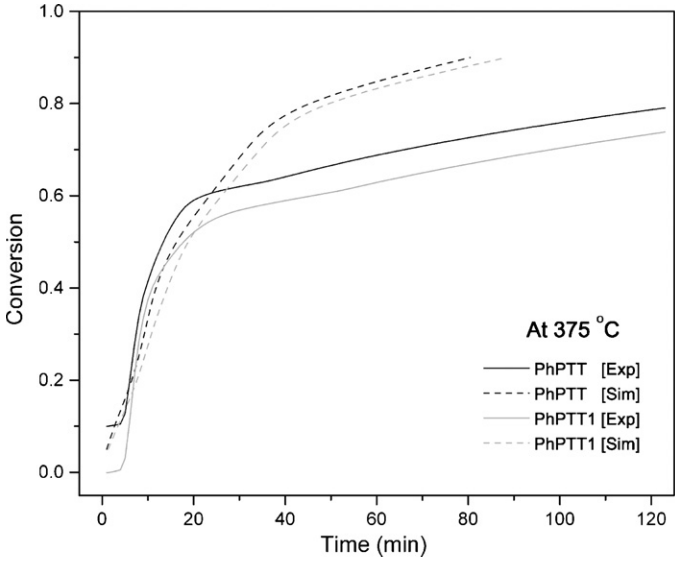


Fig. 7. Comparison of isothermal data obtained from simulation with that of experimental.

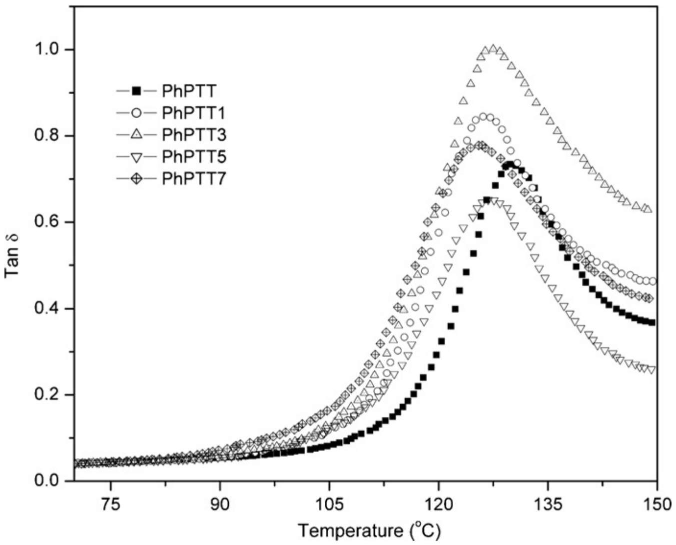


Fig. 8. Plots of tan δ versus temperature for the blend and nanocomposites containing various loadings of nanoclay.

It is mostly anticipated that with the addition of clay into a polymer, the segmental motion of polymer chains would be restricted [33,34]. But in our work, as shown in Fig. 8, DMA results show that the area under the tan δ peak of all samples except PhPTT5 is larger than that of PhPTT, which indicates that the mobility of polymer chains in the glass transition region increases with the addition of nanoclay. The enhancement in mobility of polymer chains can most probably be attributed to the formation of less crosslinked networks [35], which in phenoxy/PTT systems are formed through the transesterification reactions. As demonstrated before [7], during the melt mixing process of phenoxy/PTT blends, if two phenoxy chains react with the same PTT chain, crosslinked networks can be formed. For nanocomposites with intercalated structure, the probability of these reactions is diminished due to both high rigidity of phenoxy chains and the steric hindrance effect of nanoclays. The lower content of crosslinks in these samples could be one of the factors that cause a reduction in their thermal stability [36]. It is also noteworthy to mention that as a result of the lower extent of transreactions in PhPTT3 compared with PhPTT1, lower amounts of crosslinked networks are formed which could be another reason for the reduction in thermal stability.

Another interesting observation is that a reduction in tan δ intensity is seen for the sample with 5 wt.% nanoclay content. This indicates that PhPTT5 has more restricted chains and lower mobility as compared to the pristine blend. As mentioned before, the extent of transreactions was also less in this sample, thus less network structures are formed which leads to the reduction of thermal stability. It should be noted that crystallization of PTT might also affect the relaxation behavior of this system and consequently diminish the mobility of polymer chains. But, according to our differential scanning calorimetry results (not reported here), the crystallization of PTT is inhibited due to its low content in the system together with the suppressing effect of transreactions on the crystallization process.

Another unusual observation was made when the nanoclay content was increased from 5 to 7 wt.%. In this case, opposing effects of nanoclay on mobility of polymer chains were observed. On one hand, formation of network structures are inhibited due to the steric hindrance effect of nanoclay layers on progress of transesterification reactions, leading to the improvement in mobility of polymer chains. On the other hand, nanoclay layers are able to affect the segmental motions of polymer chains. This could be explained by penetration of polymer chains into the galleries of silicate layers and formation of hydrogen bonds with surfactants on the surface of nanoclay layers which results in the reduction of mobility of polymer chains. DMA results revealed that with increasing the nanoclay content from 5 to 7 wt.%, the tan δ intensity is increased. This means that the steric hindrance effect of nanoclays on the progress of transreactions is more dominated, leading to an overall enhancement of mobility or increased tan δ intensity.

4. Conclusion

In this study, the effects of nanoclay loading on transreactions and their consequent impact on thermal degradation behavior of phenoxy/PTT blends were investigated. The results showed that with addition of only 1 wt.% nanoclay, the extent of transreactions reaches its maximum. This promotion of transreactions was a hint for formation of locally confined environments. Based on the proposed mechanism, this so-called nanoconfinement of polymer chains around silicate layers could be responsible for enhancement in the extent of transreactions between the blend components. It was also observed that the extent of transreactions becomes smaller at higher amounts of nanoclay content which was attributed to the intercalated structure of nanocomposites.

Upon addition of higher amounts of nanoclay (>1 wt.%) into the blend, thermal stability of the system was decreased. Barrier model which has been commonly used in the literature failed to explain the observed trend in thermal stability of the samples. Combining the evidence from DMA, ^{1}H NMR and TGA, it was proposed that silicate layers promoted transreactions but inhibited their progress, thus formation of less crosslinked structures, due to a steric hindrance effect, resulted in a reduction of thermal stability in the nanocomposites.

The degradation kinetic of the samples was characterized by calculating the activation energies using the KAS method. The results verified the reduced thermal stability of the pristine blend upon incorporation of higher than 1 wt.% nanoclay. The isothermal decomposition results also confirmed the increased thermal stability of the blend upon addition of 1 wt.% nanoclay. In order to verify the accuracy of the calculated kinetic parameters, the *n*th order equation was solved to reconstruct the experimental data. Simulation results demonstrated the potential of KAS method to predict the experiment.

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