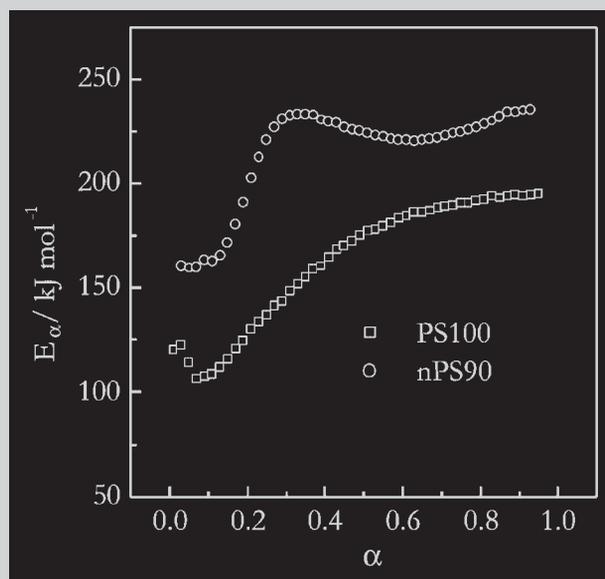


Summary: Thermogravimetry and differential scanning calorimetry have been used to study the thermal and thermo-oxidative degradation of polystyrene (PS) and a PS–clay nanocomposite. An advanced isoconversional method has been applied for kinetic analysis. Introduction of the clay phase increases the activation energy and affects the total heat of degradation, which suggests a change in the reaction mechanism. The obtained kinetic data permit a comparative assessment of the fire resistance of the studied materials.

The change in activation energy for the degradation of PS and the PS–clay nanocomposite with the extent of polymer conversion.



Kinetics of the Thermal and Thermo-Oxidative Degradation of a Polystyrene–Clay Nanocomposite

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Introduction

Implanting layered silicates into polymers is known^[1] to dramatically modify various physical properties including thermal stability and fire resistance.^[2] A great deal of attention has been focused on the thermal behavior of polystyrene (PS)–clay nanocomposites^[3–9] as studied by using cone calorimetry as well as standard thermal analysis methods, such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). It has been found that, compared with virgin PS, the clay nanocomposites have somewhat higher glass transition temperatures,^[4,6] decompose at significantly greater temperatures,^[4,7–9] and demonstrate a substantial decrease in the maximum heat release rate on combustion.^[5,7–9] It should be stressed that even when the

clay content is as little as 0.1% the initial decomposition temperature is increased by 40 °C and the peak heat release rate is decreased by about 40% relative to virgin PS.^[7] The mechanism of such a remarkable effect is not yet well understood. The effect is most commonly rationalized in terms of the barrier model, which suggests that the enhanced fire resistant properties arise because of a carbonaceous-silicate char that builds up on the surface of the polymer melt and provides the mass and heat transfer barrier.^[5,9–11] It has also been suggested that the effect may be associated with radical trapping^[8] by the structural iron in clays.

Although the thermal behavior of polymer–clay nanocomposites has been studied extensively, the kinetic aspects of the thermal and thermo-oxidative degradation remain practically unknown. The importance of reliable kinetic

analysis cannot be overestimated as it may provide information on the energy barriers of the process as well as offer mechanistic clues. Finding a reliable approach to kinetic analysis presents a certain challenge as the thermal analysis literature describes a great number of kinetic methods that make use of either single or multiple heating rate data. The shortcomings of the single heating rate methods have been repeatedly stressed.^[12,13] The recent publication^[14] summarizing the results of the ICTAC Kinetics Project has recommended the use of multiple heating rate methods such as isoconversional methods.^[12]

In this paper, we employ an advanced isoconversional method^[15,16] in order to obtain reliable kinetic information on the thermal and thermo-oxidative degradation of a PS–clay nanocomposite. We demonstrate that the obtained kinetic information provides important mechanistic conclusions about the effect of the clay phase on degradation of the polymer composites. Also, for the first time, we present the application of the advanced isoconversional method for assessing the fire resistance of polymeric materials. This paper is intended to initiate systematic kinetic studies of polymer nanocomposites and, therefore, to fill the presently existing void in the understanding of the thermal behavior of these exciting materials.

Experimental Part

The PS–clay nanocomposite was prepared by intercalating a monocationic free radical initiator into the montmorillonite clay and the subsequent solution surface-initiated polymerization (SIP), where the chain growth was initiated in situ from the clay surface. The initiator we synthesized was an 2,2'-azoisobutyronitrile (AIBN)-analogue molecule with a quaternized amine group at one end. The intercalation process was realized by a cation exchange reaction in which the cationic end of the initiator was ionically attached to the negatively charged clay surfaces. The structure of the initiator and details regarding the preparation and characterization of the intercalated clay can be found in our previous paper.^[17] The subsequent SIP with the clay that had been intercalated by the initiator was performed in tetrahydrofuran (THF) solvent with styrene as the monomer, resulting in a PS–clay nanocomposite by in situ polymerization. The molecular weight ($\sim 90\,000$) and polydispersity (~ 2.3) of the product were measured by size exclusion chromatography (SEC) using PS standards. Details of the initiator synthesis and similar procedures of the SIP process and product analysis can be found in another publication,^[18] in which the results have shown that this free radical SIP strategy can achieve exfoliated PS–clay nanocomposites with even higher clay loading by using the same monocationic initiator. The obtained material will be referred to as nPS90. For comparison purposes, we have used virgin PS that was purchased from Alfa Aesar and used as received. Its \bar{M}_w value is 100 000 and it will be referred to as PS100.

The degradation kinetics have been measured as the temperature dependent mass loss by using a Mettler–Toledo TGA/SDTA851^c module. Polymer samples of ~ 5 mg have

been placed in 40 μL Al pans and heated from 30 to 600 $^{\circ}\text{C}$ at the heating rates 2.5, 5.0, 7.5, 10.0, and 12.5 $^{\circ}\text{C} \cdot \text{min}^{-1}$. Thermal and thermo-oxidative degradations have been performed in the flowing atmosphere of N_2 and air at a flow rate of 70 $\text{mL} \cdot \text{min}^{-1}$, respectively. The buoyancy effect in TGA has been accounted for by performing empty pan runs and subtracting the resulting data from the subsequent sample mass loss data. DSC measurements have been conducted by using a Mettler–Toledo DSC 822^c module. The conditions for the DSC runs were similar to those of TGA except that the DSC runs were performed at a single heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$. Both instruments have been calibrated by using an indium standard. In order to determine the clay content, three repetitive TGA runs under N_2 have been performed on ~ 25 mg samples of nPS90 that have been heated in alumina pans to 1 000 $^{\circ}\text{C}$. The amount of residue was $\sim 1\%$.

Kinetic Method

The overall rate of polymer degradation is commonly described by Equation (1).^[12]

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (1)$$

α is the extent of polymer conversion, t is the time, T is the temperature, R is the gas constant, A is the pre-exponential factor, E is the activation energy, and $f(\alpha)$ is the reaction model. The latter is frequently taken in the form of the reaction order model $(1 - \alpha)^n$. The deficiencies of such a model-based approach are well known.^[12] In addition to the difficulty of determining a unique reaction model, the degradation of polymers tends to demonstrate complex kinetics^[19] that cannot be described by the single Equation (1) throughout the whole temperature region.^[20,21]

In order to adequately represent the temperature dependence of degradation, one may use a model that involves several steps, such as recombination, random scission, and end-chain scission, each of which is represented by a respective Equation (1).^[22] However, simultaneously solving three kinetic equations presents a considerable computational problem. A simpler alternative is to use a model-free isoconversional method. The method is based on the isoconversional principle that states that at a constant extent of conversion the reaction rate is only a function of the temperature [Equation (2)].

$$\left[\frac{d \ln(d\alpha/dt)}{dT^{-1}} \right]_{\alpha} = -\frac{E_{\alpha}}{R} \quad (2)$$

Henceforth the subscript α indicates the values related to a given conversion. While based on Equation (1), the method assumes that E_{α} is constant only at a given extent of conversion and a narrow temperature region related to this conversion at different heating rates. In other words, the isoconversional methods describe the degradation kinetics by using multiple Equations (1) each of which is associated with a certain extent of conversion and has its own value of E_{α} . The resulting experimental dependence of E_{α} on α reflects changes of a limiting step^[12,20,21,23,24] and adequately represents the temperature dependence of complex processes as proven by successful kinetics predictions^[25,26] (vide infra, Equation (5)).

By using the integral form of Equation (2), Vyazovkin^[15,16] has developed an advanced isoconversional method. The method offers two major advantages over the frequently used methods of Flynn and Wall^[27] and Ozawa.^[28] The first advantage is that the method has been designed to treat the kinetics that occur under an arbitrary variation in temperature, $T(t)$, which allows one to account for self-heating/cooling detectable by the thermal sensor of the instrument. For a series of n experiments carried out under different temperature programs, $T_i(t)$, the activation energy is determined at any particular value of α by finding E_α , which minimizes the function [Equation (3)].

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (3)$$

where [Equation (4)]:

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_\alpha - \Delta\alpha}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \quad (4)$$

The second advantage is associated with performing the integration over small time segments (Equation (4)), which allows the elimination of a systematic error^[16] occurring in the Flynn and Wall and Ozawa methods when E_α varies significantly with α . In Equation (4), α is varied from $\Delta\alpha$ to $1 - \Delta\alpha$ with a step $\Delta\alpha = m^{-1}$, where m is the number of intervals chosen for analysis. The integral, J in Equation (4) is evaluated numerically by using the trapezoid rule. The minimization procedure is repeated for each value of α to find the dependence of E_α on α .

Vyazovkin^[25] proposed a model-free method that allows one to use nonisothermal data to predict the isothermal kinetics outside the experimental temperature region. By using kinetic data obtained at arbitrary temperature programs, one can estimate the time, t_α , to reach a given conversion at an arbitrary isothermal temperature, T_0 , by Equation (5):

$$t_\alpha = \frac{J[E_\alpha, T(t_\alpha)]}{\exp\left(\frac{-E_\alpha}{RT_0}\right)} \quad (5)$$

The t_α value is determined by substituting the experimentally determined values of E_α and T_α in Equation (5). Repeating the procedure for different values of α results in an isothermal kinetic curve, α versus t_α . Predictions made by Equation (5) are called "model-free predictions" because they do not require knowledge of the reaction model, $f(\alpha)$. The reliability of such predictions has been demonstrated elsewhere.^[25,26] The following section discusses the results of the application of the model-free kinetic analysis to degradation of the PS materials.

Results and Discussion

Figure 1 provides a comparison of the mass loss curves for the degradation of virgin polymer and the nanocomposite under nitrogen and air. PS100 degrades without forming any residue. Degradation of nPS90 leaves some residue in

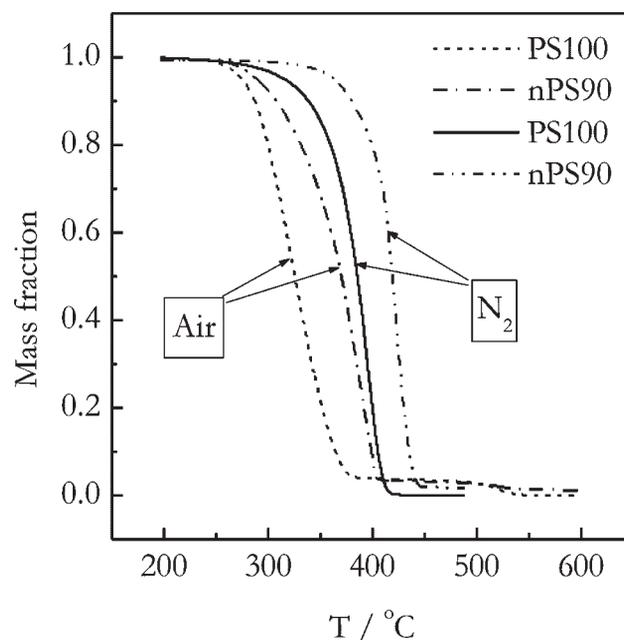


Figure 1. TGA curves for the degradation of PS100 and nPS90 at a heating rate $5^\circ\text{C} \cdot \text{min}^{-1}$ in air and nitrogen.

an amount of $\sim 1\%$ which remains practically constant up to 1000°C . Assuming the PS has been completely volatilized, this number represents the amount of the clay phase in the nanocomposite. As seen in Figure 1, in both nitrogen and air the mass-loss curves for nPS90 are found at markedly greater temperatures than the curves for PS100. The decomposition temperature increases by as much as $30\text{--}40^\circ\text{C}$, which is consistent with the results of other workers.^[7-9] Given the small amount of the clay phase, this obviously represents a dramatic increase in thermal stability.

Figure 2 displays the results of the isoconversional kinetic analysis for the thermal degradation of PS100 and nPS90 in the atmosphere of nitrogen. For PS100, the effective activation energy increases from ~ 100 to $\sim 200 \text{ kJ} \cdot \text{mol}^{-1}$ throughout degradation. The variation suggests a change in a limiting step of the process. It has been suggested^[29,30] that PS degradation is initiated at weak-link sites inherent to the polymer itself. These sites arise during polymerization that is carried out in the presence of oxygen, which gives rise to hydroperoxy^[29] and peroxy^[30] structures. Once all of the weak-link sites have given way to initiation, the mass loss of PS is controlled by the random scission process. In view of this mechanism, the increase in E_α most likely represents a shift of the limiting step from initiation at the weak links to random scission. Similar increases from smaller values of E_α have been observed for degradation of other polymers (polyethylene (PE), PP, and poly(methyl methacrylate) (PMMA)).^[20,21] The values of E_α for nPS90 also show an increase with the extent of degradation, which suggests a change in the rate limiting step. The latter occurs at the early stages of degradation ($\alpha < 0.25$) after which the

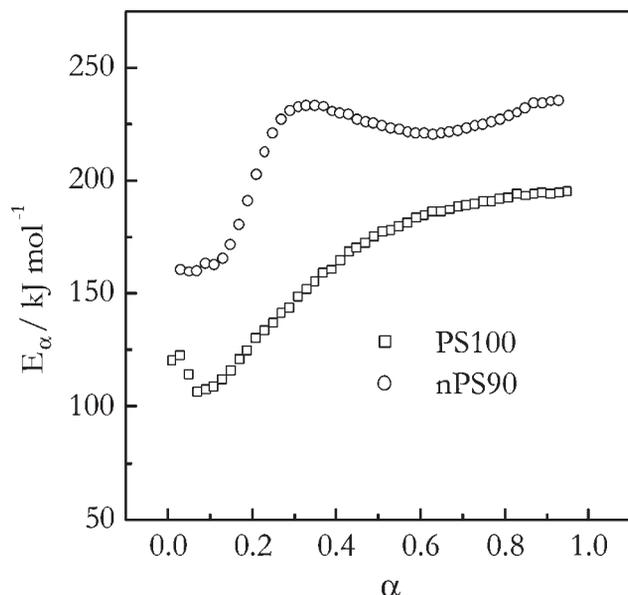


Figure 2. Dependence of the effective activation energy on the extent of conversion for the thermal degradation of PS100 and nPS90 in nitrogen.

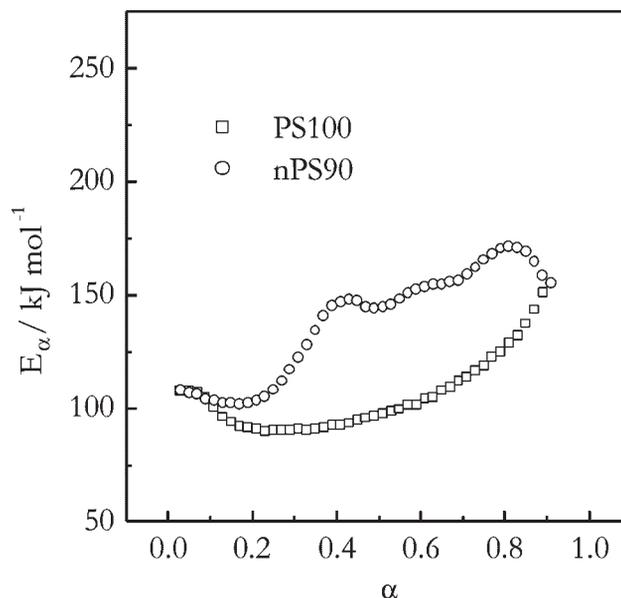


Figure 3. Dependence of the effective activation energy on the extent of conversion for the thermo-oxidative degradation of PS100 and nPS90 in air.

effective activation energy practically levels off at 220–230 $\text{kJ} \cdot \text{mol}^{-1}$. The whole process of nPS90 degradation demonstrates a markedly larger effective activation energy as compared with that of PS100 degradation. According to our DSC data the degradation of PS100 and nPS90 demonstrates single endothermic peaks whose respective heats are -990 and $-670 \text{ J} \cdot \text{g}^{-1}$.

Figure 3 presents variations in E_α for the thermo-oxidative degradation of PS100 and nPS90. For PS100 the initial stages of degradation occur with a lower activation energy of $\sim 90\text{--}100 \text{ kJ} \cdot \text{mol}^{-1}$ that later ($\alpha > 0.6$) rises to $\sim 150 \text{ kJ} \cdot \text{mol}^{-1}$. This behavior is consistent with the mechanism of thermo-oxidative degradation of PS that assumes^[19,31] the initial formation of hydroperoxide radicals whose decomposition determines the degradation at the early stages. At later stages and at higher temperatures these radicals are no longer stable so that the degradation rate becomes controlled by unzipping. This mechanism is consistent with our DSC data that show that initial stages of thermo-oxidative degradation are exothermic, whereas the later ones are endothermic. For nPS90, the initial degradation ($\alpha < 0.2$) demonstrates an activation energy similar to that for the degradation of PS100, which appears to suggest that the rate of the early degradation stages of both materials is limited by the decomposition of hydroperoxide radicals. At $\alpha > 0.2$, the effective activation energy quickly rises to $150\text{--}170 \text{ kJ} \cdot \text{mol}^{-1}$, which is markedly larger than the activation energy for the degradation of PS100 at similar extents of conversion. Note that in DSC runs the degradation of nPS90 demonstrates a small exothermic peak followed by a larger endotherm.

Putting the above results together we may conclude that the introduction of the clay phase into PS causes a considerable increase in the effective energy of degradation. The enhanced thermal stability of the PS–clay nanocomposite is likely to be associated with this increase. It does not seem as though this result can be easily rationalized in terms of the barrier model, which suggests that the degradation rate of a polymer–clay nanocomposite should be limited by the diffusion of gaseous decomposition products through the surface barrier of the silicate char. However, diffusion of gases in liquids and solids, including polymers, tends to have a low activation energy of about $40\text{--}50 \text{ kJ} \cdot \text{mol}^{-1}$.^[32] In addition, the presence of the surface barrier cannot affect the total value of the heat of degradation. Nevertheless, the degradation of the nanocomposite in nitrogen demonstrates an endothermic effect more than 30% smaller than that for virgin PS. In air, the degradation of nPS90 shows an exothermic effect followed by an endotherm, as is observed for PS100. However, the exothermic effect appears somewhat smaller and the endothermic effect is \sim three times larger than the respective effects observed for PS100. These facts suggest that the introduction of the clay phase in PS is likely to change the concentration distribution of degradation products and/or may cause the formation of some new products of degradation. This suggestion appears to correlate with the results of cone calorimetry experiments^[5,7,9] which indicate that the clay-enhanced PS composites tend to burn with the release of a significantly smaller amount of total heat. This may be because the concentration distribution of the polymer degradation products for the clay-enhanced PS changes toward the formation of less combustible products.

Although the barrier model makes sense from both an experimental^[9,10] and theoretical standpoint,^[11] the barrier formation does not seem to be the only factor that contributes to the enhanced thermal and fire stability of polymer–clay nanocomposites. Indeed, there is still a lot to learn about the mechanism of enhancing these important properties. In particular, an experimental comparison of the concentration distribution of degradation products in virgin polymer and in polymer–clay composite should be of fundamental importance.

Is the obtained kinetic information for the thermo-oxidative degradation of PS100 and nPS90 relevant to combustion? According to the cone calorimetry measurements^[6] performed at a heat flux of $35 \text{ kW} \cdot \text{m}^{-2}$, virgin PS loses 86% of its mass by 190 s. By iteratively using Equation (5) we find that for PS100, $\alpha = 0.86$ is reached after 190 s at $T_0 = 380^\circ\text{C}$ (Figure 4). At this temperature the predicted mass loss for nPS90 at 190 s is $\sim 46\%$, which compares well with the values 53 and 54% measured experimentally^[6] for some of the nanocomposites. This indicates that the obtained kinetic data are relevant to the combustion conditions. It should also be noted that the value $T_0 = 380^\circ\text{C}$ is close to the so-called flash ignition temperature that, according to ASTM D1929, is defined as the lowest initial temperature of air passing around the specimen, at which a sufficient amount of combustible gas is evolved to be ignited. For instance, for Huntsman PS the flash ignition temperature is reported to be 370°C . Therefore, by using the model-free Equation (5) for predicting the degradation kinetics at the flash ignition temperature, one can obtain comparative estimates for the potential fire resistance of polymeric materials.

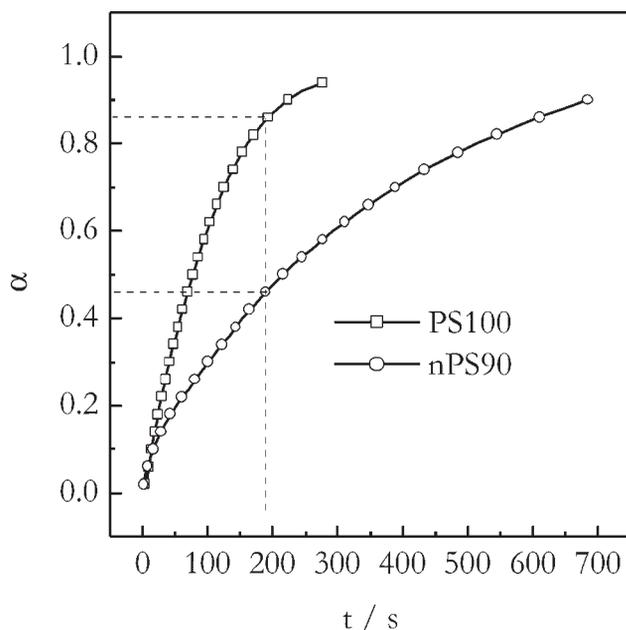


Figure 4. Predicted kinetic curves for the thermo-oxidative degradation of PS100 and nPS90 at a temperature of 380°C .

Conclusion

The application of the advanced isoconversional method allows one to obtain meaningful information on the kinetics of the thermal and thermo-oxidative degradation of PS–clay nanocomposites that, in particular, can be used for the comparative assessment of fire resistance. The kinetic analysis suggests that an enhanced thermal stability of nanocomposites is associated with the increase of the effective activation energy of their degradation. Introduction of the clay phase in PS markedly affects the total heat of degradation, which is indicative of a change in the concentration distribution of degradation products, the measurement of which will be a subject of further investigation.

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