

COMPARATIVE KINETICS STUDY OF THE THERMAL AND THERMO-OXIDATIVE DEGRADATION OF A POLYSTYRENE-CLAY NANOCOMPOSITE BY TGA AND DSC

Ion Dranca*, Nicon Ungur, Tudor Lupascu, Oleg Petuhov

*Institute of Chemistry, ASM, Center of Physical Chemistry and Nanocomposites
3 Academiei Str., Chisinau MD2028, Moldova
Tel. +37322 739 781 Fax. 37322 725 490
drancai@yahoo.com*

Abstract: The methods of thermogravimetry (TGA) and differential scanning calorimetry (DSC) 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 fire resistance of the studied materials.

Keywords: degradation; fire resistance; nanocomposites; thermogravimetric analysis (TGA); differential scanning calorimetry (DSC);

Introduction

Alexandre and Dubois found that implanting layered silicates into polymers is known [1] to modify dramatically 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 to virgin PS the clay nanocomposites have somewhat higher glass transition temperature, [4,6], decompose at significantly greater temperatures, [4-9] and demonstrate a substantial decrease in the maximum heat release rate on combustion. [5-9] It should be stressed that even when 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 remarkable effect is not yet well understood. The effect is most commonly rationalized in terms of the barrier model that suggests the enhanced fire resistant properties to arise due to a carbonaceous-silicate char that builds up on the surface of the polymer melt and provides the mass and heat transfer barrier. [5-11]. 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 Vyazovkin, 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.

Experimental part

The PS clay nanocomposite was prepared by intercalating a monocationic free radical initiator into montmorillonite clay and the subsequent solution surface-initiated polymerization (SIP), where the chain growth was initiated in situ from clay surfaces. The initiator we synthesized was an azobisisobutyronitrile (AIBN)-analogue molecule with a quaternized amine group at one end. The intercalation process was realized by 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 the paper [17]. The subsequent SIP with the clay that had been intercalated by the initiator was performed in THF solvent with styrene as the monomer, resulting in a PS-clay nanocomposite by the in situ polymerization. The molecular weight (~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 Mw 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^e module. Polymer samples of ~5mg have been placed in 40μL Al pans and heated from 30 to 600°C at the heating rates 2.5, 5.0, 7.5, 10.0, and 12.5 °C min⁻¹. Thermal and thermo-oxidative degradations have been respectively performed in the flowing atmosphere of N₂ and air at a flow rate of 70 mL min⁻¹. 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^e module. The conditions of DSC runs have been similar to those of TGA except that DSC runs have been carried at a single heating rate 10 °C min⁻¹. Both instruments have been calibrated by using an Indium standard. The amount of residue has been ~1%.

Kinetic method

The overall rate of polymer degradation is commonly described by the following equation [12]

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

where 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 model-based approach are well known. [12] In addition to the difficulty of determining a unique reaction model, degradation of polymers tends to demonstrate complex kinetics [19] that cannot be described by single eq. 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 the respective eq. 1. [22] However, simultaneously solving of 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:

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

Henceforth the subscript α indicates the values related to a given conversion). While based on eq. 1, the method assumes that E_{α} is constant only at a given extent of conversion and the narrow temperature region related to this conversion at different heating rates. In other words, the isoconversional methods describe the degradation kinetics by using multiple eq. 1 each of which is associated with a certain extent of conversion and has its own value of E_{α} . 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, $T(t)$, the activation energy is determined at any particular value of α by finding E_{α} , which minimizes the function [Equation (3)].

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

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 .

Results and discussion

Figure 1 provides a comparison of the mass loss curves for degradation of virgin polymer and nanocomposite under nitrogen and air. PS100 degrades without forming any residue. Degradation of nPS90 leaves some residue in amount of ~1% that remains practically constant up to 1000°C. Assuming 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 30-40°C that 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.

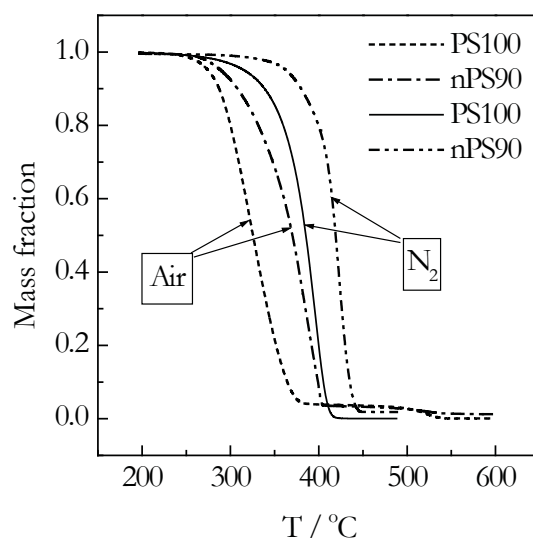


Figure 1. TGA curves for degradation of PS100 and nPS90 at heating rate 5°C min⁻¹ in air and nitrogen.

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 ~200 kJ mol⁻¹ throughout degradation. The variation suggests a change in a limiting step of the process. It has been suggested [25, 26] that PS degradation is initiated at weak link sites inherent to the polymer itself. Similar increases from smaller values of E_{α} have been observed for degradation of other polymers (PE, PP, and PMMA). [20, 21] The values of E_{α} for nPS90 also show an increase with the extent of degradation that suggests a change in the rate limiting step. That latter occurs at the early stages of degradation ($\alpha < 0.25$) after which the effective activation energy practically levels off at 220 – 230 kJ mol⁻¹. The whole process of

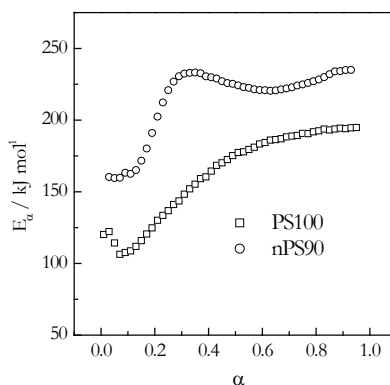


Figure 2. Dependence of the effective activation energy on the extent of conversion for the thermal degradation of PS100 and nPS90 in nitrogen.

nPS90 degradation demonstrates markedly larger effective activation energy as compared to 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 J g $^{-1}$.

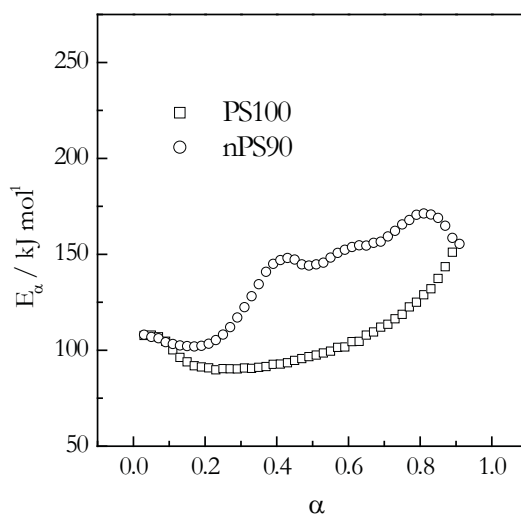


Figure 3. Dependence of the effective activation energy on the extent of conversion for the thermo-oxidative degradation of PS100 and nPS90 in air.

Figure 3 presents variations in E_α for thermo-oxidative degradation of PS100 and nPS90. For PS100 the initial stages of degradation occur with lower activation energy of $\sim 90 - 100$ kJ mol $^{-1}$ that later ($\alpha > 0.6$) rises to ~ 150 kJ mol $^{-1}$. This behavior is consistent with the mechanism of thermo-oxidative degradation of PS that assumes [19,27] the initial formation of hydroperoxide radicals whose decomposition determines the degradation at early stages. At later stages and 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. 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 nanocomposites is likely to be associated with this increase.

It does not seem that this result can be easily rationalized in terms of the barrier model that suggests that the degradation rate of a polymer clay nanocomposite should be limited by 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 $40 - 50$ kJ mol $^{-1}$. [28] Also 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 a more than 30% smaller endothermic effect 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 endothermic effect is almost twice larger than the respective effects observed for PS100. These facts suggest that introduction of the clay phase in PS is likely to change the concentration distribution of degradation products and/or maybe cause the formation of some new products of degradation. This suggestion appears to correlate with the results of cone calorimetry experiments [5-9] which indicate that the clay enhanced PS composites tend to burn with releasing a significantly smaller amount of the total heat. This may be because for the clay enhanced PS the concentration distribution of the polymer degradation products changes toward the formation of less combustible products.

Although the barrier model makes sense from both experimental [9, 10] and theoretical standpoint, [11] the barrier formation does not seem to be the only reason 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, experimental comparison of the concentration distribution of degradation products in virgin polymer and in polymer clay composite should be of fundamental importance.

Conclusions

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 comparative assessment of fire resistance. The kinetic analysis suggests that enhanced thermal stability of nanocomposites is associated with the increase of the effective activation energy of their degradation.

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REFERENCES

- [1]. M. Alexandre, P. Dubois, *Mater. Sci. Eng., R*, **2000**, 28, 1.
- [2]. D. Porter, E. Metcalfe, M. J. K. Thomas, *Fire Mater.* **2000**, 24, 45
- [3]. R. A. Vaia, H. Ishii, E. P. Giannelis, *Chem. Mater.* **1993**, 5, 1694
- [4]. M. W. Noh, D. C. Lee, *Polym. Bull.* **1999**, 42, 619.
- [5]. J. W. Gilman, C. L. Jackson, A. B. Morgan, R. Harris, E. Manias, E. P. Giannelis, M.
- [6]. M. Okamoto, S. Morita, H. Taguchi, Y. H. Kim, T. Kotaka, H. Tateyama, *Polymer* **2000**
- [7]. J. Zhu, C. A. Wilkie, *Polym. Int.* **2000**, 49, 1158.
- [8]. J. Zhu, F. M. Uhl, A. B. Morgan, C. A. Wilkie, *Chem. Mater.* **2001**, 13, 4649
- [9]. A. B. Morgan, R. H. Harris, T. Kashiwagi, L. J. Chyall, J. W. Gilman, *Fire Mater.* **2002**, 26, 247.
- [10]. J. Wang, J. Du, J. Zhu, C. A. Wilkie, *Polym. Degrad. Stab.* **2002**, 77, 249.
- [11]. M. Lewin, *Fire Mater.* **2003**, 27, 1.
- [12]. J.H. Flynn, In *Encyclopedia of Polymer Science and Engineering*; H.F. Mark, N.M. Bikales, C.V.Overberger, J.I. Kroschwitz, Eds.; J. Wiley & Sons, New York, 1989, Suppl. Vol., p. 690.
- [13]. S. Vyazovkin, N. Sbirrazzuoli, *Macromol. Chem. Phys.* **1999**, 200, 2294.
- [14]. M.E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H.L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H.O. Desseyn, C-R. Li, T.B.Tang, B. Roduit, J. Malek, T. Mitsuhashi, *Thermochim. Acta* **2000**, 355, 125.
- [15]. Vyazovkin, S. *J. Comput. Chem.* **1997**, 18, 393.
- [16]. Vyazovkin, S. *J. Comput. Chem.* **2001**, 22, 178.
- [17]. Fan, C. Xia, R. C. Advincula, *Collids and Surfaces: A* **2003**, 219, 75
- [18]. X. Fan, C. Xia, R. C. Advincula, *Langmuir* **2003**, 19, 4381
- [19]. J. H. Flynn "Polymer Degradation" in "*Handbook of Thermal Analysis and Calorimetry*", Vol.3, S. Z. D. Cheng, ed., Elsevier, 2002, p. 587.
- [20]. J. D. Peterson, S. Vyazovkin, C. A. Wight, *J. Phys. Chem. B*, **1999**, 103, 8087.
- [21]. J.D. Peterson, S. Vyazovkin, C. A. Wight, *Macromol. Chem. Phys.* **2001**, 202, 775.
- [22]. Y. Kodera, B. J. McCoy, *Energy & Fuels* **2002**, 16, 119.
- [23]. H. Flynn, L. A. Wall, *J. Res. Nat. Bur. Standards: A* **1966**, 70, 487.
- [24]. T. Ozawa, *Bull. Chem. Soc. Japan* **1965**, 38, 1881.
- [25]. S. L. Madorsky, "*Thermal Degradation of Organic Polymers*", Interscience Publishers, New York 1964.
- [26]. N. Grassie, G. Scott, "*Polymer Degradation and Stabilisation*", Cambridge University Press, Cambridge 1985.
- [27]. M. Celina, D. K. Ottesen, K. T. Gillen, R. L. Clough, *Polym. Degrad. Stab.* **1997**, 58, 15.
- [28]. W. Jost, "*Diffusion in Solids, Liquids, Gases*", Academic Press, New York, 1960.