Compounds and Materials with Specific Properties

B. A. Howell
N. Lekishvili
G. E. Zaikov
Editors

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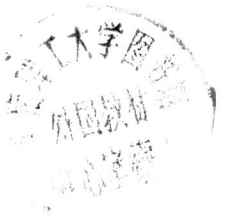
COMPOUNDS AND MATERIALS WITH SPECIFIC PROPERTIES

B. A. HOWELL, N. LEKISHVILI
AND G.E. ZAIKOV
EDITORS



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COMPOUNDS AND MATERIALS WITH SPECIFIC PROPERTIES

PREFACE

This book discusses pure and applied chemistry studying polymers, materials and compounds with specific properties as well as physical and chemical processes involved in this analysis.

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I. POLYMERS AND MATERIALS WITH SPECIFIC PROPERTIES

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Chapter 1

THERMAL AND THERMAL-OXIDATIVE DEGRADATION OF POLYETHYLENE NANOCOMPOSITE PREPARED BY INTERCALATION POLYMERIZATION

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ABSTRACT

A comparative study of thermal and thermal-oxidative degradation processes for polyethylene/organically modified montmorillonite (PE-MMT) nanocomposites, prepared by the ethylene intercalative polymerization in situ with or without subsequent addition of an antioxidant, is reported. The results of TGA and time/temperature dependent FTIR spectroscopy experiments have provided evidence for an accelerated formation and decomposition of hydroperoxides during the thermal oxidative degradation tests of PE-MMT nanocomposites in the range of 170-200oC as compared to the unfilled PE, thus indicating to a catalytic action of MMT. It has been shown that effective formation of intermolecular chemical cross-links in the PE-MMT nanocomposite has ensued above 200oC as the result of recombination reactions involving the radical products of hydroperoxides decomposition. Apparently, this process is induced by the oxygen deficiency in PE-MMT nanocomposite due to its lowered oxygen permeability. It is shown that the intermolecular cross-linking and dehydrogenation reactions followed by the shear carbonization lead to appreciable increase of thermal-oxidative stability of PE nanocomposite as compared to that of pristine PE. Notably, the TGA traces for the antioxidant-stabilized PE-MMT nanocomposites recorded in air were quite similar to those obtainable for the non-stabilized PE-MMT nanocomposites in argon. The results of treatment of the experimentally acquired TGA data in frames of an advanced model kinetic analysis are reported and discussed.

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Keywords: Catalysis; intercalation polymerization; kinetics; layered clay; nanocomposite; oxidation; polyethylene; thermal degradation.

INTRODUCTION

Polyethylene (PE), being the most commercially important thermoplastic commodity, is heavily used for consumer products in many applications, but in a number of cases general applicability of PE turns out to be undermined by its relatively low thermal stability and flame resistance. The concept of compounding polymer matrices with nanoscale fillers (in particular, clays or layered silicates) has already been proved to be an effective method of preparing nanocomposites with excellent physicochemical properties [1 – 11]. It is believed that, in the course of high temperature pyrolysis and/or combustion, clay nanoparticles are capable of promoting formation of protective clay-reinforced carbonaceous char which is responsible for the reduced mass loss rates, and hence the lower flammability. Accordingly, considerable attention has been paid also to polyolefin/layered silicate nanocomposites. Reportedly, the latter have exhibited improved mechanical properties, gas impermeability, thermal stability, and flame retardancy as compared with corresponding pristine polymers [4, 5, 9, 10].

This study deals with polyethylene/layered silicate nanocomposites that can be prepared by intercalative polymerization route. In accordance with the latter [12], the polymer chains growing within the interlayer spacing of montmorillonite (MMT) should be able to exfoliate the original MMT particles down to the nanoscale inorganic monolayers. Here, an experimental study of the universal intercalative approach, involving in the particular case (1) intercalation of a metallorganic catalyst system into the interlayer spacing of organically modified MMT and (2) subsequent polymerization of ethylene on thus intercalated catalyst, will be reported as well as the properties of the correspondingly produced PE/MMT nanocomposites will be discussed.

To clarify the mechanisms of the clay-reinforced carbonaceous char formation, which may be responsible for the reduced mass loss rates, and hence the lower flammability of the polymer matrices, a number of thermo-physical characteristics of the PE/MMT nanocomposites have been measured in comparison with those of the pristine PE (which, by itself is not a char former) in both inert and oxidizing atmospheres. The evolution of the thermal and thermal-oxidative degradation processes in these systems was followed dynamically with the aid of TGA and FTIR methods. Proper attention was paid also to the effect of oxygen on the thermal-oxidative stability of PE nanocomposites in their solid state, in both the absence as well as in the presence of an antioxidant. Several sets of experimentally acquired TGA data have provided a basis for accomplishing thorough model-based kinetic analyses of thermal and thermal-oxidative degradation of both pristine PE and PE/MMT nanocomposites prepared in this work.

EXPERIMENTAL

Materials

A Cloisite 20A (purchased from Southern Clay Products, Inc.) has been used as the organically modified montmorillonite (MMT) to prepare PE/MMT nanocomposites throughout this study. The content of an organic cation-exchange modifier, N^+2CH_32HT (HT=hydrogenated tallow, C18≈65%; C16≈30%; C14≈5%; anion: Cl^-), in the MMT was of 38 % by weight. VCl_4 (vacuum distilled at 40°C before use, TU 48-05-50-71) and $Al(i\text{-}Bu)_3$ (Aldrich) have been used for catalytic activation of MMT. Ethylene monomer was of a standard polymerization grade.

Procedure of Polyethylene Nanocomposite Synthesis

Intercalation of the catalyst has been accomplished by treating the freshly dehydrated MMT with $Al(i\text{-}Bu)_3$ and then with VCl_4. The polymerization reaction was started by admitting ethylene into the reactor and then was carried out until desired amount of PE nanocomposite (PE-n-MMT) was obtained. The polymerization reaction was stopped by adding ethanolic HCl solution (5 wt % HCl) to the reactor. The polymer composite product was filtered off, washed with ethanol and dried under vacuum at 60°C. The weight loads of MMT in the resulting composites were calculated by neglecting the contribution of the organic modifier in MMT.

The sample of unfilled polyethylene (PE) was prepared by ethylene polymerization on VCl_3 activated with $Al(i\text{-}Bu)_3$ at the same conditions as applied to the nanocomposite synthesis.

Stabilized samples of both the nanocomposites (st-PE-n-MMT) and pristine PE (st-PE) were prepared by treating them with synergetic composition of Topanol CA and di-lauryl-3,3'-thiodipropionate (DLTDP) solutions in heptane [Voigt J., Die Stabilisierung der Kunstoffe Gegen Licht und Wärme, Springer-Verlag, Berlin-Heidelberg-New York, 1966, p.542] at 70°C, followed by drying in vacuum. The concentrations of Topanol and DLTDP in (st-PE-n-MMT) and (st-PE) comprised 0.3 and 0.5 wt.%, respectively.

For further testing, the prepared materials were hot-pressed into films at applied pressure of 20 MPa and 160°C.

Characterization of Materials

Small-angle X-ray scattering (SAXS). The structure of the composites was studied by SAXS using a KRM-1 camera (Cu Kα radiation, $\lambda = 0.154$ nm, Ni filter). The test samples were powders or films. The data collected were normalized with due regard to the concentration of MMT and the coefficients of attenuation.

Transmission electron microscopy (TEM). Micrograph of PE nanocomposite sample was obtained on a JEM-100B transmission electron microscope at an accelerating voltage of 80

kV. The sample of 70 nm thickness was cut with the aid of LKV-III ultramicrotome from the composite plate prepared by hot pressing.

Thermogravimetric analysis (TGA). A Perkin-Elmer TGA-7 instrument calibrated by Curie points of several metal standards has been employed for non-isothermal thermogravimetric analysis. The measurements were carried out at a desired heating rate (in the range of 3 – 40 K/min) in both inert (argon) and oxidizing (oxygen) atmospheres, as appropriate.

Fourier transform infrared (FTIR) spectroscopy. Infrared spectra of the investigated materials in their nascent form were acquired with the aid of a Perkin-Elmer 1725X FTIR instrument by using a Spectra-Tech "Collector" DRIFT accessory furnished with a heated sample post, embedded thermo couple and the corresponding external heater/controller providing temperature reading precision of ±1.0C. The series of FTIR spectra for the polymer samples have been recorded at systematically varied temperatures or over predetermined time intervals (in isothermal regimes) by employing a modified diffuse reflectance-absorbance Fourier Transform (DRAFT) spectroscopy technique published elsewhere [13]. All measurements were performed using the instrument DTGS detector and a $4cm^{-1}$ resolution.

Kinetic analysis of PE compositions thermal degradation was carried out using Thermokinetics software by NETZSCH-Gerätebau GmbH.

RESULTS AND DISCUSSION

Morphology (Structure Evaluation)

Small-angle X-ray scattering (SAXS) has been used to evaluate the degree of exfoliation of the organoclay particles in the polymer matrix [12]. SAXS diffractograms of pristine C20A MMT and those of PE nanocomposites prepared by the intercalation polymerization route for MMT contents of 2.0 vol. % (*2*) and 6.5 vol. % (*3*) are shown in Figure1. The SAXS curve for C20A MMT shows a reflection at around of 3.6^{o} corresponding to the interlayer mean distance of 2.46 nm (Figure 1, *1*). As can be seen from the same Figure 1 (*2, 3*), for the PE/clay nanocomposites having different MMT contents, the 3.6^{o} reflection is absent. This result infers that PE chains, while growing in the course of polymerization in the interlayer spacing of the layered filler particles, are able to commit full exfoliation of the MMT particles down to the monolayers.

Figure 2 shows TEM image of the PE nanocomposite containing 1 vol. % of MMT. The dark features in the micrograph correspond to the exfoliated monolayers and nanostacks of MMT distributed throughout the PE matrix. It can be seen that the nanoscale MMT layers lack any sort of orientation in the matrix of the pressed composite. Moreover, the exfoliated MMT particles exhibit a very high aspect ratio (longitudinal size: thickness).

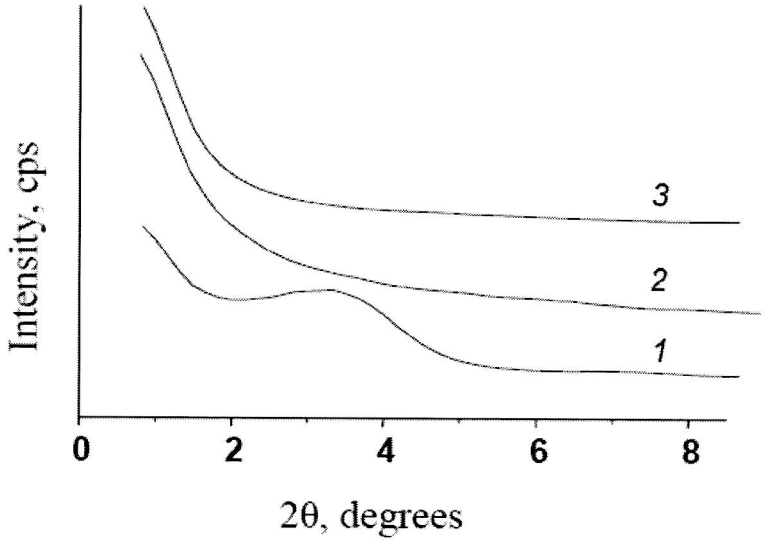


Figure 1. SAXS patterns for the original C20A MMT (*1*) and PE nanocomposites with MMT content of 2.0 vol. % (*2*) and 6.5 vol. % (*3*).

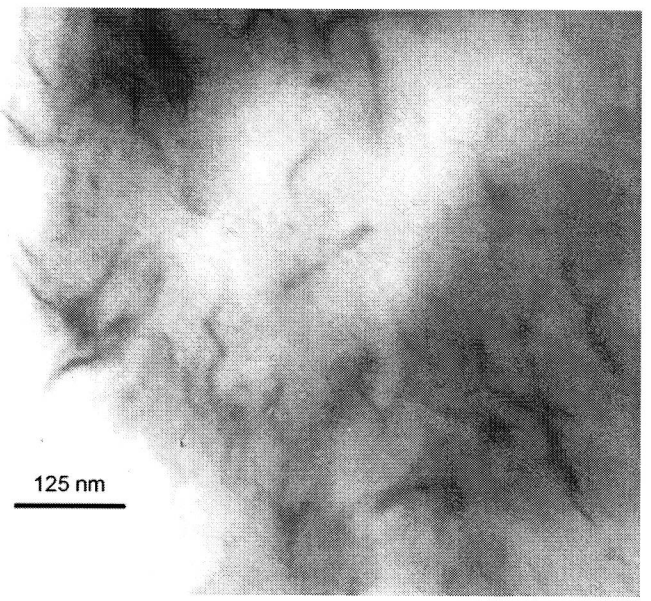


Figure 2. TEM micrograph of the PE nanocomposite containing 1% by volume of MMT.

It is worth noting here that the organic ammonium cations present in pristine C20A MMT are susceptible to washing out from the interlayer spacing of MMT under acidic treatment of the latter with ethanolic HCl (5% by wt.). The ammonium cations are substituted for protons, and this leads to a prominent decrease of the interlayer distances in the MMT structure (Figure3). If the intercalative polymerization of ethylene would not accomplish exfoliation of the MMT particles in the composite to the full extent, the diffractogram should contain a wide reflection positioned somewhere at greater angles than in the pristine C20A MMT. It is

obvious also that the acidic after-treatment of the synthesized exfoliated nanocomposites should lead to removal of the major part of the original organic MMT modifier.

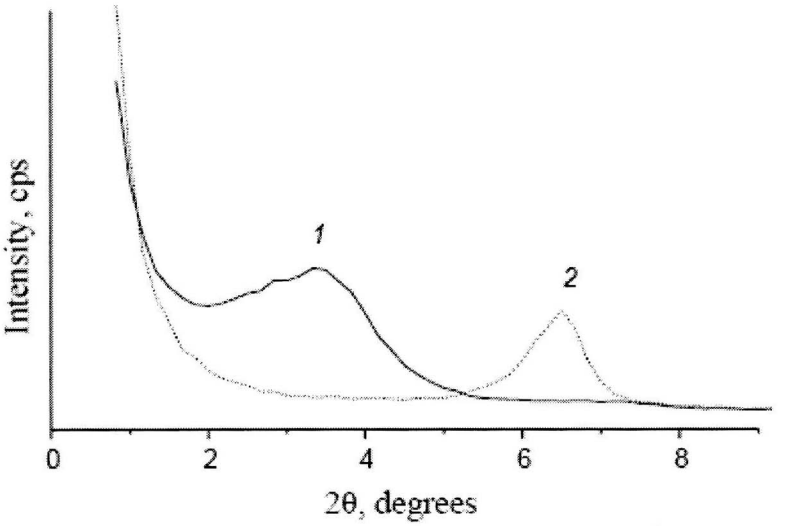


Figure 3. SAXS patterns for the original C20A MMT (*1*) and C20A MMT treated with HCl solution in ethanol (5 wt % HCl) (*2*).

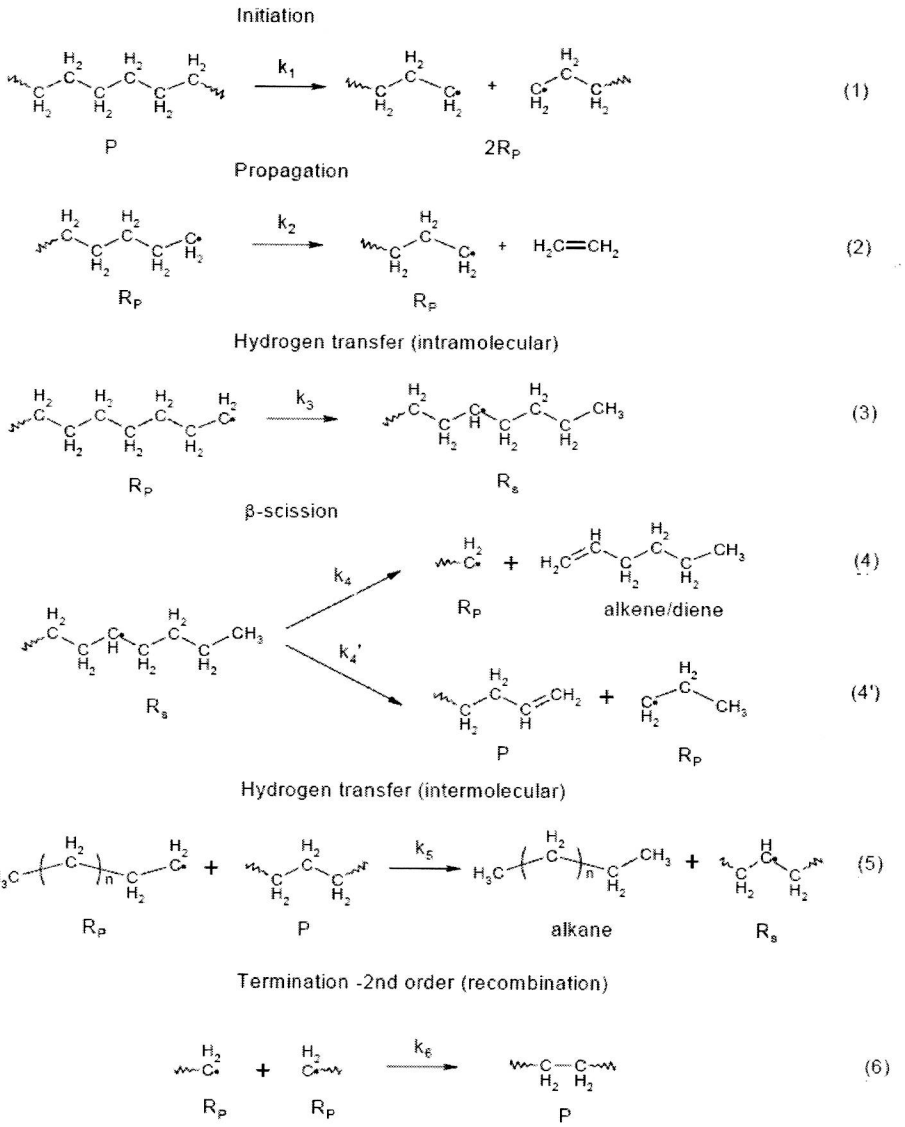
Thermal Degradation of PE Nanocomposite

It is generally accepted that thermal stability of polymer nanocomposites is higher than that of pristine polymers, and that this gain is explained by the presence of anisotropic clay layers hindering diffusion of volatile products through the nanocomposite material. It is important to note that the exfoliated nanocomposites, prepared and investigated in this work, had much lower gas permeability in comparison with that of pristine unfilled PE [12]. Thus, the study of purely thermal degradation process of PE nanocomposite seemed to be of interest in terms of estimation of the nanoclay barrier effects on thermal stability of polyolefin/clay nanocomposites.

The radical mechanism of thermal degradation of pristine PE has been widely discussed in a framework of random scission type reactions [14-22]. It is known that PE decomposition products comprise a wide range of alkanes, alkenes and dienes. Branching of PE chains causes enhanced intermolecular hydrogen transfer and results in lowering thermal stability. The polymer matrix transformations, usually observed at lower temperatures and involving molecular weight alteration without formation of volatile products, are principally due to the scission of weak links, e. g. oxygen bridges, incorporated into the main chain as impurities. The kinetics of thermal degradation of PE is frequently described by a first-order model of mass conversion of the sample [21]. A broad variation in Arrhenius parameters can be found in literature, i. e., activation energy (E) ranging from 160 to 320 kJ/mol and pre-exponential factor (A) variations in the range of 10^{11} and 10^{21} s^{-1} [20-22] are not unusual. It is believed that the broad range of E values reported may be explained by the polymers molecular mass

variations, by use of various additives, and by different experimental conditions [22] employed by different authors.

Previously Bockhorn et al. have reported that thermal degradation of PE leads to a large number of paraffins, dienes and olefins without a residue formation [20]. Analysis of the pyrolysis products with GC-MS revealed high yields of linear *n*-alkanes and *n*-alkenes. Neither branched aliphatics, alicyclics or aromatic compounds nor Diels-Alder derivatives of butadiene have been detected [20]. In order to formulate a simple kinetic model adequately explaining the isothermic global kinetic data of the authors, a mechanism embracing only the main reactions has been proposed [20]. The latter is based on a radical chain mechanism (Scheme 1) initiated by random scission of the polymer chains into primary radicals R_p (1). β-Scission of these radicals leads to ethylene (2).



Scheme 1. Mechanism of PE thermal degradation [20].

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