

Thermal decomposition of polyolefin/carbon black composites

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Abstract

The thermal decomposition of carbon black composites with polyethylene (PE), polypropylene (PP) and polyisobutylene (PIB) has been studied in order to clarify the influence of carbon black on the thermal behavior of polymers in inert atmosphere. The thermal stability of the composites and mixtures has been monitored by thermogravimetry, whereas the decomposition product distribution of the composites has been determined by pyrolysis–gas chromatography/mass spectrometry. Using various types of carbon blacks, it has been established that the effect depends on the volatile content of the carbon blacks. Carbon black of high volatile content is able to initiate the decomposition of PP and PIB, whereas carbon blacks of low volatile content increase the thermal stability of the polymers. Carbon blacks affect the product distribution of polymers, the magnitude of the changes increases with increasing volatile content of the carbon black. Lower amount of α,ω -alkadienes and more *n*-alkanes are released from PE/carbon black composite indicating the occurrence of a hydrogenation process. The intensity of the 1-alkene oligomers of PP is reduced, while several other products are formed during thermal decomposition of PP/carbon black composites. The product distribution indicates that carbon black participates in the hydrogen transfer reactions. Enhanced monomer evolution and hindered oligomer formation are observed in PIB that can be explained by a chain end initiation reaction in the presence of carbon black.

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1. Introduction

Carbon additives are used in polymer composites as fillers, reinforcing agents and pigments [1]. The rubber industry is the biggest consumer of carbon black, where it is applied as a reinforcing agent and a filler to increase the bulk of the rubber. Butyl rubber is composed of 95–98% isobutylene and a few percent of butadiene or isoprene. Butyl rubber has low gas permeability and, therefore, it is used in the production of tires and other rubber goods. The use of carbon black in thermoplastic polymers is becoming increasingly important in civil and construction industry. In these applications, carbon black is used for various purposes, e.g., to enhance the UV stability, electrical conductivity or weather resistance of plastics and to modify the mechanical

properties. Large amount of carbon black is used in polyethylene (PE) pipelines to enhance the weathering performance and thermooxidative stability of PE. Polypropylene geotextiles containing carbon black fillers are applied for soil reinforcement, filtration and other construction purposes.

Carbon black is produced by partial combustion of liquid or gaseous hydrocarbons. It has a polyaromatic structure containing various oxygen-functional groups, thus it possesses radical scavenger capabilities [2]. The antioxidant effect is probably due to the catalytic decomposition of peroxides and free radical scavenging by carbon black [3]. The resistance to UV degradation is usually related to the type and particle size of the carbon black as well as to the concentration and dispersion of the carbon black in a polymer matrix [3,4]. The impact of carbon black on the thermal and oxidative stability of natural and synthetic rubbers has been widely studied [5,6]. However, the effect of

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carbon black on the thermal stability of polyolefins in inert atmosphere is poorly understood.

The pyrolysis mechanisms of polyolefins are well known [7–10]. Pyrolysis can be applied for recycling of polymeric waste producing chemical feedstock [11,12] and carbonaceous materials [13]. Recently, the recycling of waste plastics brought up several research topics concerning the interactions between the constituents of waste, such as the pyrolysis of mixed plastics [14,15], co-pyrolysis of plastics with coal [16–18] and biomass [19–22] as well as the effect of additives [23–25] and catalysts [26–28]. The stability of electrical and mechanical properties of composites PE/carbon black, and modified carbon black with conductive polymers containing 30% of fillers, during cyclic thermal treatment was investigated recently [29,30]. Previously, we have studied the thermal decomposition of carbon black mixtures with thermoplastic polymers [31]. It was established that carbon black had different effects on the thermal stability of polymers depending on the structure of the polymers. The char yield of char-forming polymers (PAN and PVC) increased significantly in the presence of carbon black. The pyrolysis product distribution of polystyrene changed markedly in carbon black mixtures.

In this work, we extended our study to three carbon black samples and examined the thermal behavior of PE, polypropylene (PP) and polyisobutylene (PIB). Furthermore, we employed polymer/carbon black composites to ensure good physical contact between the constituents. We prepared composites with 3% and 30% carbon black to model the two main applications: low concentration of carbon black is used as a pigment in plastics and higher concentrations are applied as filler. The objective of this study was to clarify the effect of the type and amount of carbon black and the physical contact within the composites on the decomposition of polymers. Moreover, we chose three polymers decomposing by different mechanisms in order to compare the impact of carbon blacks on the product distribution and thermal stability of the various polymers.

2. Experimental

2.1. Materials

Low-density polyethylene (Bralen RA 2-19, MFR = 1.7 g/10 min, melting point $T_m = 109.3$ °C) containing a common antioxidizing system (BHT based) was received from Slovnaft, Slovakia. Isotactic polypropylene (Tatren FF 500, MFR = 10 g/10 min, $T_m = 167.3$ °C Slovnaft, Slovakia) was used without additives and with 0.05 wt.% Irganox 10 and 0.1 wt.% Irgafos 168 stabilizers. Polyisobutylene ($M_w = 1,200,000$) stabilized with 500 ppm 2,6-di-*tert*-butyl-4-methylphenol was obtained from Aldrich. Carbon blacks FW 200 and Printex V were generously provided by Degussa Hüls AG, and carbon black VULCAN[®] XC-72 by Cabot Corp., USA. In a few

experiments, heat-treated carbon black FW 200 was used. The heat treatment was carried out in a tube furnace flushed with nitrogen using a heating rate of 10 °C min^{-1} . The samples were kept at 800 °C for 30 min.

2.2. Composite preparation

PE/carbon black and PP/carbon black composites were prepared by melt mixing of the compounds in a 30 ml mixing chamber of a Plastograph Brabender PLE 330 (Brabender, Germany) for 10 min at 160 °C or 180 °C, respectively. PIB/carbon black composites were prepared by melt mixing in a conical twin-screw extruder (DACA micro-compounder, USA) for 10 min at 200 °C.

Test samples were prepared in the form of disks by compression moulding at composite processing temperatures for 2 min, followed by cooling at ambient conditions. The compositions of prepared composite samples are given as weight fractions.

The same processing, mixing or extruding, followed by compression moulding of pure PE, PP and PIB matrices, were carried out for comparison of the results of composite samples. Polymer samples without any additional treatment were used in the corresponding experiments of simple mixtures of polymers and carbon black. Nevertheless, no perceptible differences in the thermal behaviors were observed between the heat-treated polymers and the original samples.

2.3. Thermogravimetry/mass spectrometry (TG/MS)

The TG/MS system is built of a Perkin-Elmer TGS-2 thermobalance and a HIDEN HAL 2/301 PIC quadrupole mass spectrometer. Typically 0.4–0.5 mg polymer samples were placed into the platinum sample pan and heated at a 10 °C min^{-1} up to 600 °C in argon atmosphere. The baseline of the thermobalance is shifted due to the change of Bouyancy effect during temperature programming. Therefore, the baseline of a blank experiment was subtracted from all experiments. Portions of the volatile products were introduced into the mass spectrometer through a glass lined metal capillary transfer line heated to 300 °C. The quadrupole mass spectrometer operated at 70 eV electron energy. The polymers studied decompose with the formation of aliphatic products, and are strongly fragmented in the mass spectrometer producing similar aliphatic fragments. Therefore, the thermogravimetric curves of polymers and composites were only used in this study. However, TG/MS experiments were very informative for the carbon black samples.

2.4. Pyrolysis–gas chromatography/mass spectrometry

Pyroprobe 2000 pyrolyzer (Chemical Data System) was used interfaced to an Agilent 6890A/5973 gas chromatograph/mass spectrometer. Approximately, 100–200 μg

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