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THERMAL REACTIONS OF POLYETHYLENE WITH COAL (TG/DSC APPROACH)

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Abstract

Thermal reactions of polyethylene with coal were studied. Coal used exhibited an endothermal effect in the temperature range of 425–495°C with a flat maximum (about 460°C). In contrast, polyethylene alone was decomposed in the temperature range of 420–540°C (mainly of 485–540°C) with the significant DSC maximum at 510°C. In the presence of coal this maximum shifted to lower temperature (483°C), therefore, coal promoted the decomposition of polyethylene. As decomposition of polyethylene yields alkenes and alkadienes, the thermal reaction of polyethylene with coal under low temperature conditions can be described as two-stage process in which the first stage includes the decomposition of polyethylene giving unsaturated hydrocarbons and the second stage adsorption and hydrogenation of these products (mainly by coal hydrogen) on the inner surfaces of semicoke and coal.

Keywords: coal, DSC, polyethylene, TG

Introduction

In the municipal and industrial wastes, various plastics cannot be separated economically. As methods of treatment the chemical recycling and incineration can be taken into account. Chemical recycling is preferable to incineration with respect to the greenhouse effect, hazardous emissions, energy consumption, maintenance of equipments and investment costs. Several papers have been devoted to the effect of coal on the thermal decomposition of polymers in order to investigate yields and properties of products obtained during copyrolysis of these materials [1–3]. As polyethylene frequently occurs in both municipal and industrial wastes, its thermal decomposition in the presence of coal was studied in this case. For this purpose, thermogravimetric analysis (TG), differential scanning calorimetry (DSC) and Gieseler constant-torque plastometry were applied.

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Experimental

Materials

For experiments, the coal fraction with an apparent density under 1.24 g cm^{-3} separated from the initial coal (mine Dukla, Ostrava-Karviná District) was chosen. This fraction was obtained from powdered coal by sink float method. The coal fraction obtained had low ash content (4.7 mass%, dry basis), the micropore surface of 140 m^2 g^{-1} and well defined average structure (see later). Further, medium density polyethylene with density of 0.940 g cm^{-3} and melting point of 109–111°C (Sigma-Aldrich Ltd.) was used as a model compound.

TG, DSC and Gieseler constant-torque plastometry

Thermal measurements were carried out with TG and DSC Perkin Elmer analyzers (Pyris TGA 6 and Pyris DSC 7). TG analyses were performed in a nitrogen atmosphere in the temperature range of 25–900°C with the heating rate of 10°C min^{-1}. DSC analyses were carried out in the temperature range of 25–550°C with the heating rate of 5°C min^{-1}. DSC kinetic data were evaluated with Perkin Elmer DSC Scanning Kinetics software. Plastic properties of the coal used (initial softening, maximum devolatilisation and resolidification temperatures) were determined on Gieseler constant-torque plastometer PL 2000 (RB Automazione, Genova) according to standard test method (ASTM D 2639) at the heating rate of 3°C min^{-1}.

NMR spectrometry

Representative structure of the coal used was expressed from ^{13}C CP/MAS NMR parameters. ^{13}C CP/MAS NMR spectra were measured with the spectrometer Bruker DSX 200 in 7 mm ZrO_2 rotor at the frequencies of 50.33 and 200.14 MHz (^{13}C and ^{1}H, respectively). Number of data points was 0.5 K, magic angle spinning frequency 5.0 kHz, 'strength' of B_1 field (^{1}H and ^{13}C) was 50.0 kHz. For ^{1}H–^{13}C dipolar–dephasing experiments standard pulse sequence was used where cross-polarization period was followed after delay by two simultaneous pulses on both (^{13}C and ^{1}H) channels. From ^{13}C CP/MAS NMR parameters, the representative structure was constructed [4].

Results and discussion

At first, decomposition of medium density polyethylene (MDPE) in the presence of coal was investigated by the DSC method. DSC curves of coal alone, MDPE-coal mixture (1:1) and MDPE alone were carried out (Fig. 1). As Fig. 1 shows, coal used exhibits an endothermal effect in the temperature range of 425–495°C with a flat maximum (about 460°C). In contrast, MDPE alone is decomposed in the temperature range of 420–540°C (mainly of 485–540°C) and attains the significant DSC maximum at 510°C. In the presence of coal this maximum shifts to lower temperature (483°C),

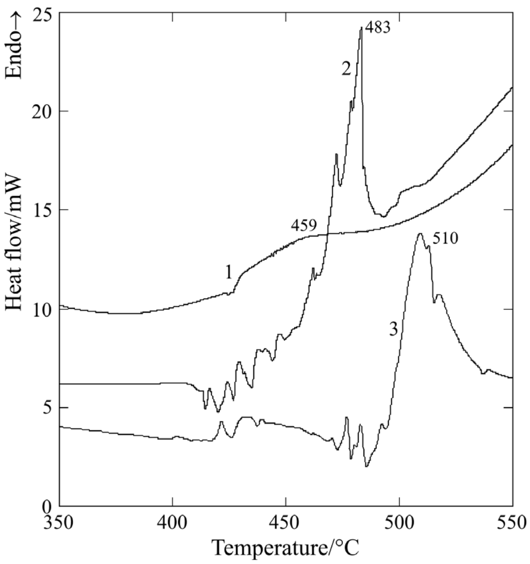

Fig. 1 DSC curves of coal alone (line 1), MDPE with 50 mass% of coal (line 2) and MDPE alone (line 3)

the decomposition starts also at 420°C, but ends at 495°C. The main decomposition preceeds at 455–495°C. It means that coal promotes the decomposition of MDPE. The second small DSC maximum between 490–515°C can be attributed to releasing of alkanes formed during co-pyrolysis and adsorbed on the inner surface of coal and semicoke (see later). Over all reaction order and parameters of the Arrhenuis plot (Table 1) evaluated by one curve kinetics [5, 6] prove this conclusion, because the activation energy of the decomposition of MDPE in the presence of coal is significantly lower in comparison with that for MDPE alone. Because one curve kinetics was used, the data in Table 1 have only illustrative character.

Table 1 DSC of the decomposition of coal, MDPE and coal–MDPE mixture. H – reaction enthalpy, n – reaction order; E_A, $\ln Z$ – parameters of the Arrhenius plot

Sample	H/J g^{-1}	n	E_A/kJ mol^{-1}	ln$Z$	Temperature range/°C
Coal alone	242.7	0.9	184.6	24.7	425–500
Coal–MDPE(1:1)	775.1	0.9	290.8	40.9	455–515
MDPE alone	218.8	1.2	634.6	93.7	485–540

In this connection, the thermal decomposition of the coal used was investigated. As DTG curve (Fig. 2) proves, coal decomposition commences at 410°C, it attains its maximum at 460°C and ends at 500°C. After this temperature the semicoke formation proceeds. These measurements were in good agreement with parameters determined by Gieseler plastometer as initial softening temperature was of 405°C, maximum devolatilisation temperature of 440–460°C and resolidification temperature of 490°C. As the maximum devolatilisation temperature corresponds with maximum of tar production and resolidification temperature with a significant formation of semicoke, material with a higher inner surface was formed during thermal decomposition.

It is widely accepted that polyethylene decomposes by a free radical mechanism and the major products are 1-alkenes, -alkadienes and *n*-alkanes [7, 8]. In this case, formed unsaturated products were adsorbed on the inner surfaces of coal and semicoke. In this way, unsaturated products were removed from reaction equilibria and the decomposition of MDPE proceeded at lower temperatures. These products were further hydrogenated (by hydrogen from coal and MDPE) on the coal and semicoke surfaces and then released as alkanes at higher temperature. It means that maximum of mass losses of the coal-MDPE mixture must occur at higher temperature in comparison with that from the decomposition of MDPE alone. As Fig. 2 prove, the DTG maximum of MDPE alone occurs at 475°C, but in the case of coal-MDPE mixture it comes at 490°C. The temperature of the DTG maximum then increased by 15°C in the presence of coal. Analogical conclusion was presented by Jakab, Blazsó and Faix for the polyethylenes decomposition in the presence of charcoal [7].

On the basis of ^{13}C CP/MAS NMR measurements the average chemical structure of coal used was expressed as an aromatic-cyclanic cluster which includes the phenanthrene structure with OH group and two five-membered cyclanic rings with two methyl substituents (Fig. 3). During decomposition the cyclanic part of the cluster yields mainly hydrogen, further methane and lower aliphatic hydrocarbons. As decomposition of MDPE yields alkenes and alkadienes, the thermal reaction of MDPE with coal under low temperature conditions (up to 550°C) can be then described as two-stage process in which the first stage includes the decomposition of MDPE giving

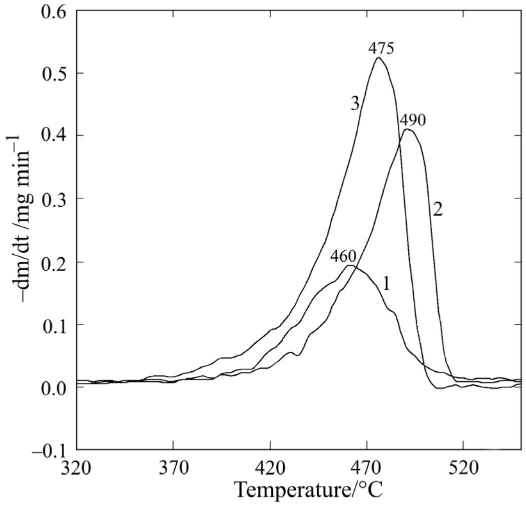

Fig. 2 DTG curves of coal alone (line 1), MDPE with 50 mass% of coal (line 2) and MDPE alone (line 3)

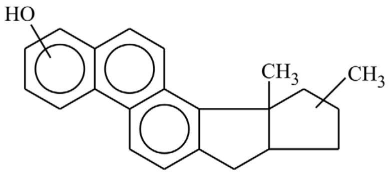

Fig. 3 Average chemical structure of coal used

unsaturated hydrocarbons and the second stage adsorption and hydrogenation of these products (mainly by coal hydrogen) on the inner surfaces of semicoke and coal.

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