

Effect of Adding Low-Density Polyethylene to Coal on Semicoke Structure and Morphology

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Abstract

The objectives of this study are to determine the influence of low-density polyethylene (LDPE) on the structure and morphology of the resulting semicoke as an intermediate carbon material in metallurgical coke manufacture; and, to explain the differences in the fluidity and the coking pressure generated during the carbonization process. The semicokes were obtained in a Gray King oven from blends of a bituminous coal and LDPE at different temperatures (450, 500 and 600 °C). The characterization of the semicokes was carried out by elemental analysis, Fourier transform infrared spectroscopy using the diffuse reflectance mode (DRIFT) and scanning electron microscopy (SEM). LDPE incorporated into the carbon matrix of the semicokes causes a modification in the pyrolysis process and also influences the swelling process of the plastic stage.

Keywords

Cokemaking, Semicoke, Plastic waste

INTRODUCTION

The use of plastics in metallurgical coke production is a new and environmentally friendly alternative for recycling municipal plastic wastes. These wastes could be added as minor components to the coal that is used as feedstock in this industrial process (Diez, 2000; Kato, 2002; NSC-NKK, 2000). Depending on the composition of the plastic wastes, a different effect can be expected on the fluidity of the coal or the coal blends, the semicoke structure and the structure and properties of the high-temperature cokes (Diez, 2000; 2005; Domínguez, 2001; Nomura, 2003; Sakurovs, 2003; Vivero, 2005). To investigate the relevance of the amount of low-density polyethylene (LDPE) on coal fluidity development and coking pressure generation, Gray-King pyrolysis at three different temperatures was carried out using a coking coal and its blends with up to 10 wt% additions of LDPE. The structure and morphology of the semicokes could be a useful way to elucidate the mechanism of the interactions between coal and polyethylene. LDPE was chosen as being representative of the polyolefins contained in municipal, agricultural or other different sectors.

EXPERIMENTAL

A bituminous coal (O) with 21.2 wt% volatile matter on a dry basis and with a medium Gieseler fluidity of 423 ddpm was used as the basic component of the blends with plastic waste. LDPE comes from agricultural greenhouses films and can be taken as being representative of polyolefins from other different post-consumer sectors. The thermoplastic properties of the coal and its blends with up to 10 wt% LDPE were tested in a Gieseler plastometer, R.B. Automazione model PL2000, following the ASTM D 2639 standard procedure. The specific parameters for this test are: (i) the softening temperature at which the coal starts to be fluid; (ii) the temperature of maximum fluidity reached during the thermal heating; (iii) the resolidification temperature at which the fluid mass resolidifies into a

semicoke; (iv) the plastic or fluid range, which is defined as the difference between the resolidification and softening temperatures; (v) the maximum fluidity, expressed as dial divisions per minute (ddpm).

The pyrolysis of the coal and its blends with LDPE (8 g, <0.212 mm) was also carried out in a Gray-King oven at three temperatures, 450, 500 and 600 °C under the atmosphere of evolved gases, applying a heating rate of 5 °C/min and a soaking time of 5 min. The design of the Gray-King reactor is described in the standard procedure ISO502. After leaving the reactor the volatile products were condensed in a trap cooled by an ice-salt bath (primary tar). The non-condensable fraction was removed from the reactor by means of an outlet tube. The solid carbon material (semicoke) was removed from the oven after cooling at room temperature. The semicokes were characterized by elemental analysis, Fourier transform infrared spectroscopy using the diffuse reflectance mode (DRIFT) and scanning electron microscopy (SEM).

The coking coal and its mixtures with LDPE were also carbonised in a semi-pilot moveable-wall oven of 15 kg of capacity (MWO15) with electrical heating and of the following dimensions: 150 mm length, 750 mm height and 250 mm width. During the carbonisation tests, the temperature of the wall was maintained constant at 1010 °C. The coking time was nearly 3 hours and the temperature in the centre of the charge rising to 950 °C. After the coke was pushed from the oven, it was quenched with water. During the co-carbonization tests, the temperature evolution at the centre of the charge and the coking pressure exerted on the wall as a function of the carbonization time were monitored. The LDPE waste was added in amounts ranging from 1 to 30 wt%. The bulk density in the carbonization test was $690 \pm 30 \text{ kg/m}^3$ on a dry basis.

RESULTS AND DISCUSSION

Figure 1 shows the variation of Gieseler fluidity with the amount of LDPE added to the coal. At all levels of LDPE addition, there is a reduction in Gieseler maximum fluidity. However, the rate of the fluidity loss is totally dependent on the LDPE added to the blend.

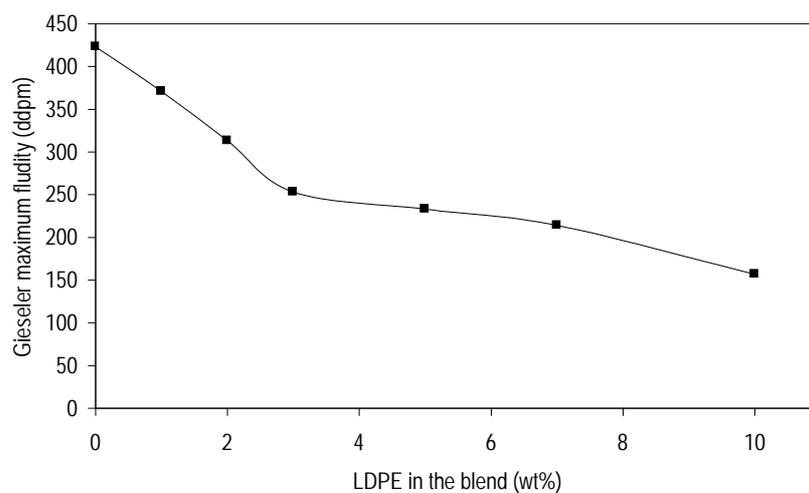


FIGURE 1: Variation of Gieseler fluidity of the blends coal-LDPE with the amount of LDPE in the blend.

At low amounts of LDPE (1-3 wt%) a progressive reduction in plasticity occurs from 423 to 253 ddpm, which accounts from 12 to nearly 40 % of the initial fluidity of the coal. An increase of LDPE up to 7 wt% causes a less pronounced decrease in fluidity from 253 to 214 ddpm, which represents a loss of fluidity of 40 and nearly 50 %. It should be noted that coal O has initially a Gieseler MF which falls within the established optimum window defined from the MOF diagram (Miyazu-Okuyama-Fukuyama model) as coals given a coke with acceptable quality for the blast furnace. With an addition of up to 10 wt% LDPE, this coal still keeps its fluidity inside or very close to the optimum range (200-1000 ddpm) defined for conventional charges (Miyazu, 1974).

During the thermal treatment of the coal under an inert atmosphere, the coal particles start to soften at 412 °C. They develop fluidity with increasing temperature, reaching a maximum value at 468 °C and, then, fuse together into a semicoke at nearly 500 °C. These characteristic temperatures derived in a Gieseler plastometer define the physical changes during the plastic stage of a given coal or a coal blend. The presence of LDPE does not affect these temperatures at any level and, consequently, the plastic temperature range is quite constant.

It is also well known that the release of volatile matter from coal during the plastic stage plays a significant role in the generation of coking pressure and therefore in determining danger posed by a coal. A moderate pressure inside the oven is necessary for the development of the structure and properties of the resultant cokes. However, when the coking pressure is excessive, the coke oven walls may be damaged and operational difficulties during coke pushing can arise, resulting in substantial economic costs for the steel industry. Among the factors thought to affect coking pressure generation are the oven design, the coking conditions applied and the properties of the coal.

In order to establish the effect of plastic wastes on the development of coking pressure, carbonizations at a semi-pilot scale were carried out using from 1 to 30 wt% amounts of LDPE. It should be pointed out that due to a great loss in coke productivity a high amount of plastic wastes added to coal or coal blends is not industrially viable. However, in this work, LDPE was added up to 30 wt% in order to emphasize the effects of polyethylene on coking pressure development. Figure 2 shows the variation in coking pressure as a function of the LDPE added to the coking coal. It can be observed that coking pressure increases for low level of additions from about 8 kPa to 11-13 kPa. As the amount of LDPE increases up to 30 wt%, there is an exponential decrease and the coking pressure reaches safe values, which are, even, lower than that of the base coal.

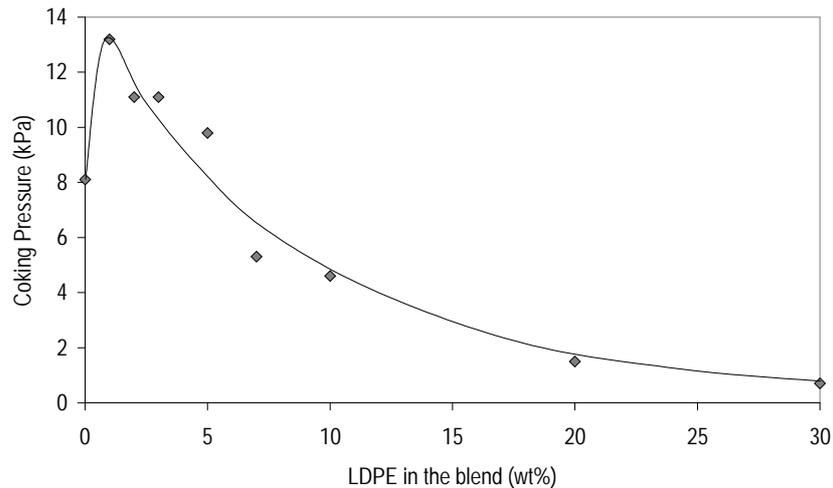


FIGURE 2: Effect of LDPE addition on the coking pressure measured in a movable wall oven of 15 kg capacity.

In summary, the addition of LDPE to a bituminous coal gradually reduces Gieseler maximum fluidity, does not affect the fluid temperature region and increases the coking pressure generated during the coking process when low concentrations of LDPE are added to coal.

In an attempt to elucidate how LDPE affects the formation of semicoke, pyrolysis experiments in a Gray-King oven were carried out at three different temperatures (450, 500 and 600 °C). These temperatures were selected on the basis of the different phenomena occurring in coal carbonization: 450 °C, is the approximate at which maximum fluidity and maximum wall pressure in the coking process is achieved; 500 °C is the temperature at which fluid coal solidifies to form the semicoke; and 600 °C is the initial step of the post-plastic stage of the coking process. The quantities of LDPE (2, 5 and 10 wt%) were chosen on the basis of the effect of LDPE on fluidity reduction and coking pressure generation. The percentage of 2 wt% addition influences the coking pressure to a greater degree while, at the same time, the reduction in fluidity is moderate in the order of 100 ddpm (nearly 25 % of the initial fluidity); an amount of 5 wt% LDPE, because it produces a coking pressure slightly lower than that of the base coal and a fluidity reduction close to 50 %; and, finally, an amount of 10 wt% LDPE, because the coking pressure generated in the semi-pilot oven is negligible and the reduction of the fluidity nearly 63 %, the Gieseler fluidity of the coal+plastic blend remaining at nearly 150 ddpm.

The mass balance at the three different temperatures and at a relatively slow heating rate (5 °C/min) is presented in Table 1. At 450 °C, a low decomposition degree takes place and all the blends show an almost identical products distribution. At a higher temperature (500 and 600 °C), however, thermal cracking seems to promote the release of condensable products as primary tars at the expense of semicoke formation. Although a slow heating rate is applied, the removal of pyrolysis products from the hot zone in the reactor is favoured, reducing the residence time and the extent of secondary reactions. As a consequence, the amount of tar increases because the pyrolysis products condense before further reaction breaks down the high-molecular weight compounds into gaseous products. Linear relationships were also found between the amount of LDPE added and the semicoke and tar yields, when the pyrolysis was carried out up to 500 and 600 °C.

TABLE 1: Yields of products obtained in the pyrolysis in a Gray-King oven.

Sample	Coal O	O2LDPE	O5LDPE	O10LDPE
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LDPE in the blend (wt%)	0	2	5	10
<i>Pyrolysis temperature 450 °C</i>				
Semicoke (wt% db)	97.9	97.3	97.0	97.1
Tar (wt% db)	2.0	2.1	2.4	2.6
Gas (wt% db)	0.1	0.6	0.6	0.2
<i>Pyrolysis temperature 500 °C</i>				
Semicoke (wt% db)	91.6	89.5	87.1	84.3
Tar (wt% db)	5.7	7.6	9.8	12.8
Gas (wt% db)	2.7	3.0	3.1	2.9
<i>Pyrolysis temperature 600 °C</i>				
Semicoke (wt% db)	87.1	85.1	82.7	78.5
Tar (wt% db)	6.7	7.9	10.8	15.1
Gas (wt% db)	6.3	6.9	6.5	6.3

A comparison of the DRIFT spectra of the semicokes obtained at 450 °C reveals that there is some melted LDPE, although it can not be clearly distinguished in an examination of the semicokes by SEM. The DRIFT spectra of the semicokes containing LDPE show a high relative intensity for the characteristic absorption bands at 2960, 2920 and 2850 cm^{-1} , attributed to C-H in aliphatic groups. This is in agreement with a decrease in the atomic C/H ratio of such semicokes (1.53-1.33) compared to that obtained from the base coal (1.56).

In the semicokes obtained at 500 °C the C/H ratio decreases with the amount of LDPE added to coal, due to a higher H content. In addition, the relative proportion of aliphatic groups also increases. These findings may be associated to the presence of melted LDPE incorporated into the semicokes which is in agreement with the presence of two carbon phases of different densities as was observed by SEM. One of them corresponds to LDPE randomly distributed within the surface of the semicoke obtained at 500 °C (bright areas on the SEM micrographs, Position A, Figure 3).

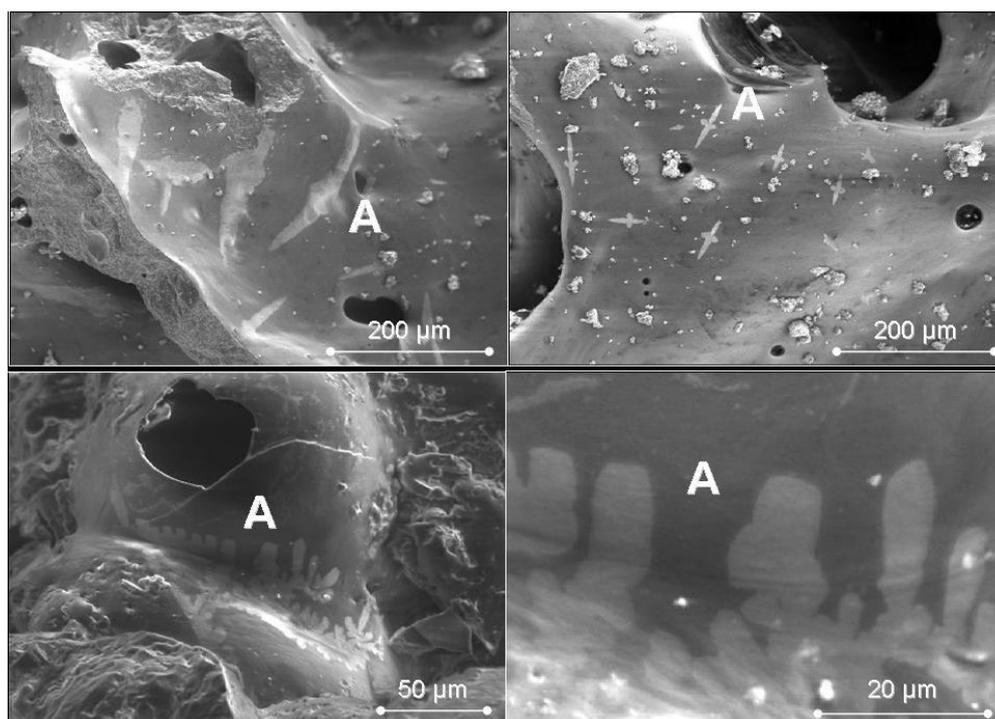


FIGURE 3: SEM micrographs of the semicokes obtained with LDPE addition at 500 °C (top: 2 wt%, bottom: 10 wt%).

The appearance of the semicokes obtained in the Gray-King pyrolysis at different temperatures is quite different. At 500 °C, coal forms a hard, well fused and highly swollen semicoke (the same volume as the cylindrical tube-reactor). The semicoke obtained from the blend containing 10 wt% LDPE is also hard, very compact and moderately swollen, but slightly shrunken in length (Figure 4). At 2 and 5 wt%, the blends produce a hard and less-porous semicoke which has increased its length and width near the exit zone of the reactor, especially in the case of the 2 wt% addition.

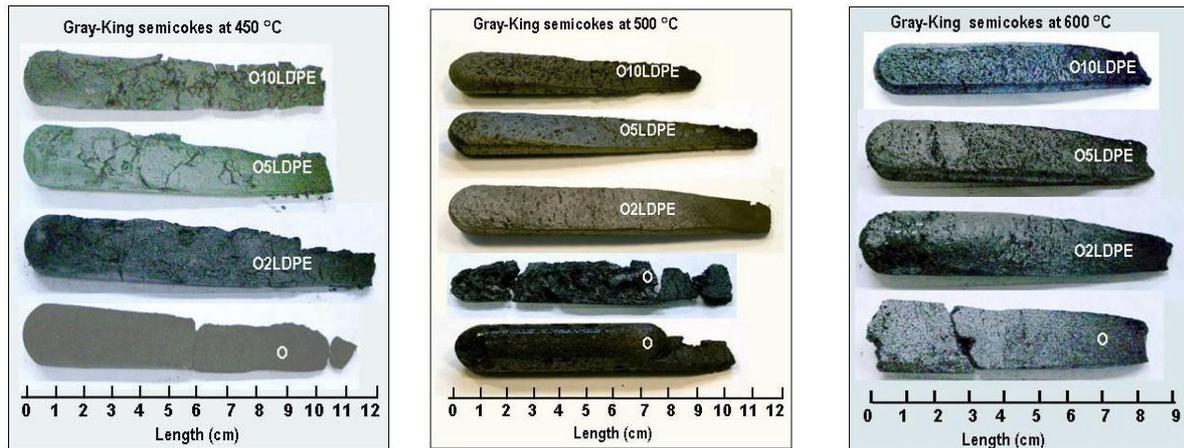


FIGURE 4: Profiles of the semicokes obtained by Gray-King pyrolysis at 450, 500 and 600 °C. The profile of the semicoke from coal O at 500 °C is showed as a whole and a longitudinal section.

CONCLUSIONS

LDPE modifies the different phenomena that take place at the key stages of coal fluidity development, loss of volatile matter and swelling of the fused mass. Depending on the amount of LDPE added to a coal, a different effect on coking pressure can be observed. On the one hand, with a low concentration of LDPE in the blend (1-3 wt%), a coking pressure higher than that of the base coal was observed. On the other hand, the coking pressure decreased considerably when high amounts of LDPE (5-10 wt%) were incorporated. Although explanation for this is not easy to find, it is obvious that, as in conventional charges, various combined effects may be taking place. The high viscosity of the melted LDPE and its decomposition products, especially waxes (long hydrocarbons chains), make it more difficult for the primary pyrolysis products to be transported through the coal bed. Thus, a certain proportion of these may be captured by the fluid mass of coal, thereby decreasing fluidity. In addition, the plastic layer will be less homogeneous with some local areas containing LDPE randomly distributed in the matrix which progresses at a different rate during carbonization. The evolution of gas from the mass of the coal and LDPE results in further dilatation, giving rise to an increase in coking pressure. However, higher amounts of LDPE reduce coking pressure. This result is somewhat surprising, because the effects of polyethylene should be more pronounced (i.e. more condensable and non-condensable gases, a great number of local areas containing melted LDPE). The reason that this is not so may be due to a reduction in the bulk density of the charge and the better permeability to the migration of oil components, which suggest a lower interaction between the coal and LDPE.

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