Rheological Behaviour of Coal Modified by Waste Plastics and Lubricating-Oils

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Abstract

The aim of this work is to study the interactions between a coking coal and two types of wastes: plastics from municipal wastes (single and mixed) and lubricating-oils coming from the iron and steel sector. For this purpose, Gieseler plastometry, rheometry and *in situ* high-temperature ^{1}H NMR spectroscopy can be combined to discern the most suitable wastes for using as secondary raw materials in metallurgical coke production. It was found that there is a relationship between the Gieseler fluidity, the complex viscosity and the percentage of the mobile hydrogen of the blends coal+additive. Three groups directly related to the structure of the polymers and the nature of the lubricating oils could be established. Polyolefins and hydrocarbon oil are the weaker modifiers of coal rheological properties, increasing the viscosity of the coal (decreasing fluidity) slightly. PET is the stronger modifier and it has a negative effect on the development of the plastic phase and inhibits its formation when 5 wt% is added to the coal. Finally, PS and the synthetic oil show an intermediate behaviour.

Keywords

Coal, Plastics, Rheology

INTRODUCTION

The recycling process of organic wastes, plastics and oils, using coke ovens for metallurgical coke production is a possible alternative by adding these wastes to typical coal blends as secondary raw materials. Recent investigations have established that the incorporation of plastic wastes to bituminous coals reduces the coal fluidity during the thermal treatment and the extent of the reduction is dependent of the structure of the polymer (Diez, 2000, 2005; Domínguez, 2001; Nomura, 2003; Sakurovs, 2003; Vivero, 2005). This paper describes the effects of blending a series of plastic wastes (single and mixed) and oil wastes with a bituminous coal on the rheological properties of the coal by means of different techniques, Gieseler plastometry, rheometry and *in situ* high-temperature ^{1}H NMR. The former technique is widely used by the steel industry in the classification and control of coking coals as well as in the mathematical models developed to optimize the coking blends to be carbonized.

EXPERIMENTAL

Materials

A bituminous coal (O) was selected for its volatile matter content (21.2 wt% db) and for its medium Gieseler fluidity (423 ddpm). The wastes used include: five of the six major thermoplastics in municipal wastes (LDPE, HDPE, PP, PS, and PET), two mixed plastics (M1 and M2), and two residual oils (an aliphatic oil -OIL1- and the other containing organic esters –OIL2-). M1 has polyolefins as major components (73 wt% HDPE, 20 wt% PP and 5 wt% PET), while M2 contains the six thermoplastics contained in municipal wastes (PP, 39.2 %; PET, 18.8 %; PS, 16.6 %; HDPE, 0.7 %; LDPE, 5.4 %; PVC, 1.2 % and non-identified plastics, 6.9 %). The wastes were added to the coal O in proportions of 2 and 5 wt%.

Gieseler plastometry

The fluidity was determined in a constant-torque Gieseler plastometer, R.B. Automazione PL2000, which is a viscometer specially designed and standardized for the measurement of the fluidity of coals. The equipment and the procedure are described in detail in the ASTM D2639-04 standard procedure. Briefly, a packed coal sample (5 g, particle size 0.425 mm) is heated from 330 to 550 °C at a heating rate of 3.0 ºC/min, while a constant torque is applied. The characteristic parameters derived from this test are: (i) softening temperature (Ts), the temperature at which the coal starts to be fluid; (ii) temperature of maximum fluidity (Tm); (iii) resolification temperature (Tr), the temperature at which the fluid mass resolidifies into a semicoke; (iv) plastic or fluid range (Tr-Ts) which is defined as the difference between the resolidification and softening temperatures; (v) the maximum fluidity (MF) expressed as dial divisions per minute (ddpm).

Rheometry

The rheology experiments were carried out using a Rheometrics RDA-III high-torque strain-controlled rheometer. The experimental conditions were described elsewhere (Steel, 2004). Briefly, coal and its blends with the selected wastes (1.5 g, particle size 53-212 µm) were pressed at 5 tons to form disks of 25 mm in diameter and 2.6 mm in thickness. The disk was heated up to 330 °C at 60 ºC/min and from this temperature to 500 ºC at a slow heating rate, 3 ºC/min. A constant nitrogen flow rate to transfer heat to the sample and to remove volatiles was used. From the measurements, different parameters can be deduced: minimum complex viscosity (η^*), storage and loss modulus (G' and G", respectively) and characteristic temperatures in the viscosity development (the softening temperature, Trs, defined as the crossed point of G´ and G"; temperature of minimum complex viscosity, Tmf, and the resolidification temperature, Tgp).

In situ high-temperature ^{1}H NMR

A Doty 200 MHz ^{1}H NMR probe was used with a Bruker MSL200 instrument for the NMR fluidity development. For NMR experiments, approximately 120 mg of sample with a particle size 53-212 µm, packed lightly into a boron-nitride container, was heated from room temperature to 525 ºC at a heating rate of approximately 3 ºC/min. A nitrogen flow was used to transfer heat to the sample and to sweep the volatile products. The ^{1}H NMR spectra were deconvoluted into Lorentzian and Gaussian components. These components make possible to know the percentage of mobile/fluid (Lorentzian) and rigid (Gaussian) hydrogen together with the spin-spin relaxation time of the Lorentzian function (T_{2L}), which indicates the mobility of the mobile hydrogen (Steel, 2004).

RESULTS AND DISCUSSION

Figure 1 displays, as an example, the fluidity development, the viscoelastic behaviour and the amount of the mobile/fluid hydrogen of the bituminous coal as a function of the temperature. At around 420 °C coal and its blends with the additives behave like a thermoplastic material, developing a fluidity/complex viscosity with progressive heating, reaching a minimum value of complex viscosity (maximum Gieseler fluidity) and, afterwards, become thermosetting around 500 °C with the formation of the semicoke.

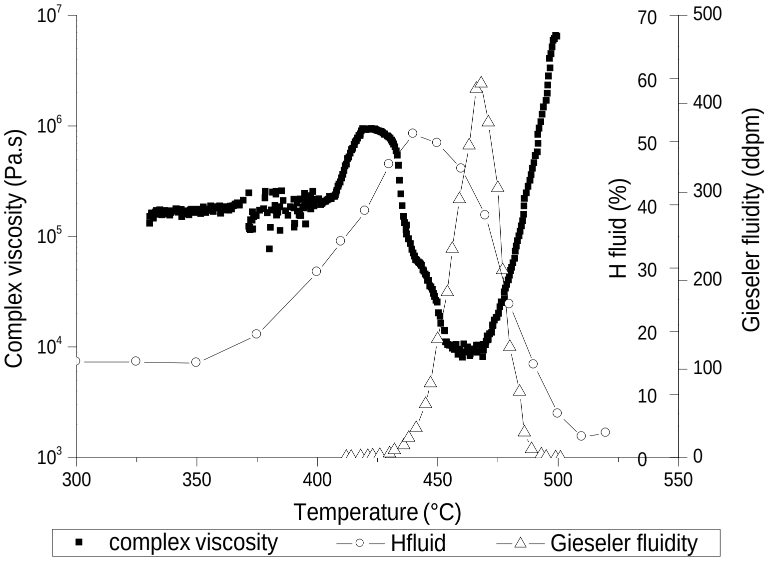

FIGURE 1: Variation of Gieseler fluidity, complex viscosity and the amount of mobile H of the coal with the temperature.

The complex viscosity, as a function of temperature, shows three temperature regions. As an example, Figure 2 shows that in the first region coal begins gradually to soften with the temperature and the viscosity begins to decay considerably. The storage (G’) and loss (G”) modulus cross at around 430 ºC and afterwards, G” values are higher than G´. This fact marks the beginning of the second region in which the complex viscosity diminishes until a minimum value, marking the end of the second region and the beginning of the third one. These temperatures are comparable to the temperatures of softening (T_s), maximum fluidity (T_m) and resolidification (T_r) obtained by Gieseler plastometer test.

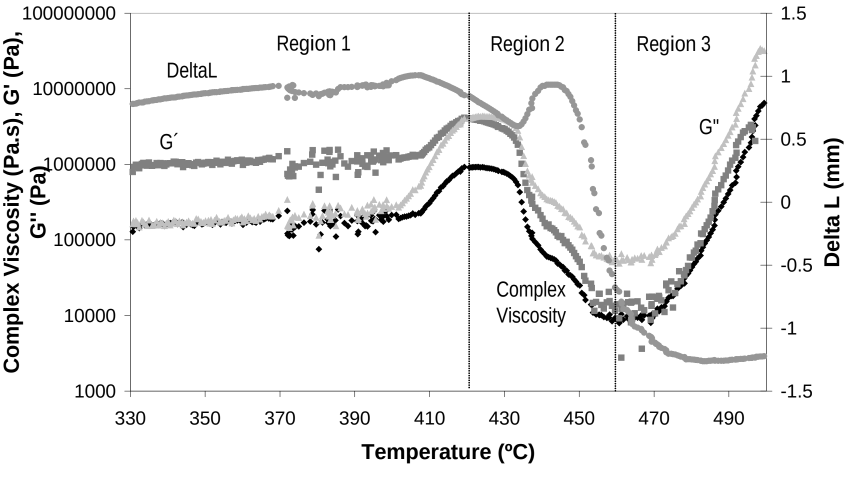

FIGURE 2: Viscoelastic behaviour of the bituminous coal.

Figure 3 shows the relationship between the Gieseler maximum fluidity and the minimum complex viscosity, expressed as logarithm on a basis 10, for the coal and its blends with the different wastes. There is a good correlation between the two kinds of measurements of the thermoplastic behaviour of the blends. In general, the data obtained from the rheometry measurements confirm those obtained in a Gieseler plastometer. The amount and the type of the waste influence the complex viscosity of the coal (7940 Pa.s) and the Gieseler fluidity (423 ddpm), giving a wide spectrum of blends with complex viscosity from nearly 9000 Pa.s to 137000 Pa.s and Gieseler fluidity from 424 ddpm (similar to the coal) to 2 ddpm.

Comparing the effects of single plastics on coal rheological properties, two different groups can be established:

- the first group contains the three polyolefins (HDPE, LDPE and PP) with complex viscosity of the blends between 9000 and 13500 Pa.s at 2 and 5 wt% addition.
- the second group includes the stronger modifiers of the rheological properties of the coal (PS and PET). A common feature of these two polymers is that they contain an aromatic ring in the structure. At 2wt% addition the complex viscosity is 23000-57000 Pa.s and Gieseler fluidty around 100 ddpm. An increase in the amount added to coal (5 wt%) prevents the blend coal+plastic to be fluid during carbonization, the complex viscosity increases up to 120000-137000 Pa.s and the Gieseler fluidity decreases up to 2-5 ddpm.

At low concentrations of PS and PET (2 wt%), the second group can be split into two groups, because PS has an intermediate behaviour between the polyolefins and PET.

The above classification of the plastics is in agreement with that previously reported which is based on the variation of the Gieseler fluidity of coals with different rank and fluid behaviour (Diez, 2000, 2005).

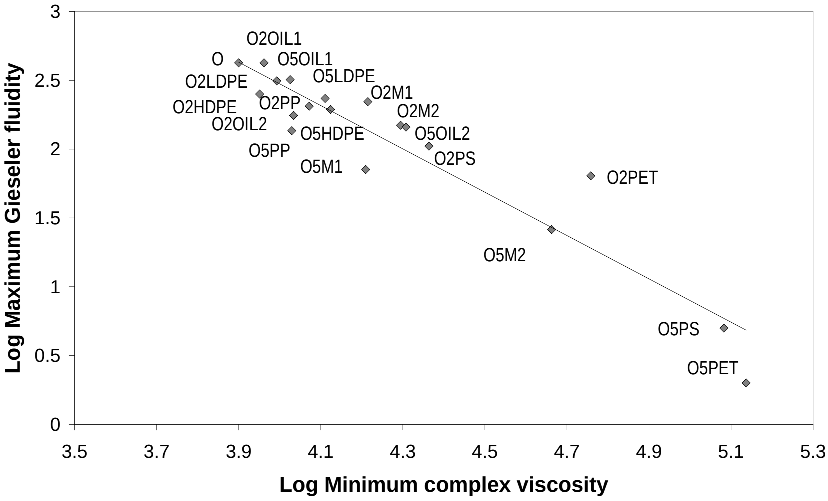

FIGURE 3: Relationship between minimum complex viscosity and maximum Gieseler fluidity.

As regards the mixed plastic wastes, the relative proportions of plastics classified as type 1 (polyolefins) and type 2 (PS and PET) have a great influence on the fluidity/viscosity development. For example, when mixed polyolefins are the major components (M1 waste), the minimum viscosity/maximum fluidity is quite comparable to the single plastics of type 1. On the other hand, wastes with a high proportion of PET and PS like M2 (35 wt% PET+PS) cause a greater change in thermoplastic behaviour.

In the case of the lubricating oils, the composition is also a critical factor. The oil containing long-chain aliphatic esters reduces fluidity (increase in complex viscosity) in a greater extent than the oil containing long-chain alkanes (OIL1). This effect is comparable to that observed for the two types of polymers, polyolefins and PET. Indeed, lubricating oil (OIL1) and polyolefins are very similar materials from a chemical point of view. Both additives are of organic origin composed of C and H arranged as methylene groups.

As regards the temperatures at which the different physical changes occur (softening, maximum fluidity/minimum viscosity and resolidification), some considerations can be drawn. The differences between the resolidification of the fluid mass to semicoke in the plastometer and the rheometer (< 6 °C) are comparable to experimental errors obtained by the two techniques. The same observation can be also drawn for the differences between the temperature at which the maximum fluidity and the minimum complex viscosity (< 9 °C). However, a shift in the softening temperatures between 3 and 20 °C is observed. With some few exceptions, the softening temperature in the rheometer is always higher than that determined by a Gieseler plastometer. In general, a good relationship between the two temperatures exists and the same trend can be observed. From the two techniques, the temperature at which softening begins varies little with the addition of polyolefins, but the differences become significant for blends with PET. In Gieseler plastometry, an increase of 14 and 39 °C is observed for blends with PET at 2 and 5 wt% additions. Consequently, the plastic range is considerably reduced. The same effect on softening temperature is caused by a 5 wt% PS addition. These differences are also confirmed from the rheometer measurements.

The opposite effect can be observed in the blends with oil addition. In such blends, the petroleum-derived oil acts as a diluting agent, lowering the softening temperature by nearly 10-15 °C.

Blends with polyolefins have a similar amount of fluid H to that of the coal (51 %). It appears that an increase in the concentration of the polyolefins from 2 to 5 wt% does not affect the concentration of fluid H and mobility (Figure 4). However, the blend with PET contains less fluid material (41 %) than the coal alone or the blends with polyolefins, which is in agreement with the lower Gieseler fluidity. The same occurs for the blend containing 5 wt% PS (fluid H, 46 %).

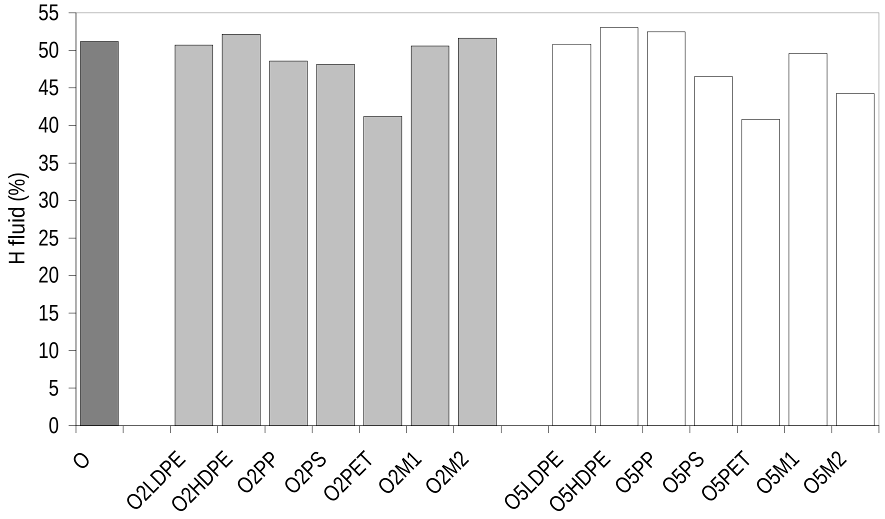

FIGURE 4: Variation of the maximum fluid phase concentration for the coal O and its blends with plastic wastes.

Finally, if PET and PS are in a significant amount in the wastes, the amount of fluid H is inhibited greatly. This is the case of the M2 plastic waste which contains nearly 35 wt% PET+PS. At 5 wt% addition, the amount of fluid H drops up to 44 %.

CONCLUSIONS

The Gieseler plastometry, the rheometry and *in situ* high-temperature ^{1}H NMR provide useful information on the modifications of the thermoplastic behaviour of coal caused by single and mixed plastic wastes and lubricating oils. By the three techniques, a moderate negative effect on the fluidity development of coal is caused by the polyolefins, mixed plastic wastes with a high proportion of them and petroleum-derived oil oils of an aliphatic nature. Plastics such as PET and PS cause more significant changes in the thermoplastic behaviour of coal, and even at high amounts they prevent the coal to be fluid during carbonization. The relative proportion of the five major thermoplastics from municipal wastes strongly affects the extent of the reduction of fluidity of the coal and, consequently, the structure and properties of metallurgical cokes.

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