ISSN 1068-364X, Coke and Chemistry, 2009, Vol. 52, No. 1, pp. 35–37. © Allerton Press, Inc., 2009.
Original Russian Text © S.G. Gagarin, 2009, published in Koks i Khimiya, 2009, No. 1, pp. 38–41.

INFORMATION. CHRONICLES

Rheological Behavior of Coal Modified by Waste Plastics and Lubricant Oils[1]

DOI: 10.3103/S1068364X09010116

In order to use plastic wastes in coking batch, the influence of such materials and their polymer components on carbonization processes must be investigated. In the study considered, the example examined is O coking coal with a yield of volatiles $V^d = 21.2\%$; the Giesler fluidity of the plastic of 423 ddpm.

The coal is modified by 2–5% of individual polymers that are typical components of domestic thermoplastic wastes: low- and high density polyethylene (LDPE and HDPE, respectively), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET), as well as two waste samples: M1, containing 73% HDPE, 20% PP, and 5% PET; and M2, containing 39.2% PP, 18.8% PET, 16.6% PS, 0.7% HDPE, 5.4% LDPE, 1.2% polyvinylchloride (PVC), and 6.9% unidentified plastic components. In addition, two types of lubricant oils are considered: aliphatic oil (OIL1); and oil based on organic esters (OIL2).

The plastic characteristics of the coal and the mixtures are measured using a PL2000 Giesler plastometer (produced by R. B. Automazione), in accordance with ASTM D2639-04. To this end, 5 g of the crushed coal (≤0.425 mm) is heated from 330 to 550°C at a rate of 3°C/min, with the determination of the softening temperature T_s (transition to the fluid state), the attainment of complete fluidity T_m, the solidification temperature T_r with the formation of semicoke, the temperature interval of plasticity T_r–T_s, and the maximum fluidity *MF*.

The rheological properties of coal and its mixtures with plastics are studied using a Rheometrics RDA-III rheometer, with a high torque and a controlled mechanical load. To this end, the coal samples, crushed to a particle size of 53–212 μm (mass 1.5 g), are shaped under a pressure of 5 t into disks (diameter 25 mm; thickness $L \sim 2.6$ mm), which are placed between the two parallel plates of the rheometer. A sinusoidal mechanical stress (frequency 1 Hz, amplitude 0.1%) is applied to one of the plates. The disks are heated to 330°C at 60°C/min in a nitrogen current and then to 500°C at 3°C/min. In the experiments, the viscosity η^*, elastic modulus G', and viscosity modulus G'' are determined, as well as the softening temperature T_{rs} (at the intersection of the G' and G'' curves), the temperature T_{mf} of minimum viscosity η^*, and the solidification temperature T_{gp} of the plastic.

To evaluate the hydrogen distribution in the samples on heating, we use the high-temperature version of the ^{1}H NMR method (200-MHz Doty cell, with a Bruker MSL200 spectrometer). To this end, 120 mg of the mixtures (particle size 53–212 μm) are placed in a boron-nitride container heated in nitrogen from room temperature to 525°C at 3°C/min. The proton signals are split into Lorentzian and Gaussian components, reflecting the proportions of mobile and bound hydrogen, respectively. The mobility of hydrogen is characterized by the T_{2L} value for the Lorentzian component of the NMR signal (the spin–spin relaxation time, μs). The basic characteristics of the plastic state are expressed as combined thermograms. (An example for the initial coal is shown in Fig. 1).

At 420°C, the coal may be regarded as a thermoplastic material characterized by a fluid state. At T_m (or T_{mf}), its fluidity is greatest according to Giesler measurements (minimum η^* in rheometer measurements). With further heating, the Giesler mobility declines, and the viscosity η^* increases. At 500°C, the plastic mass

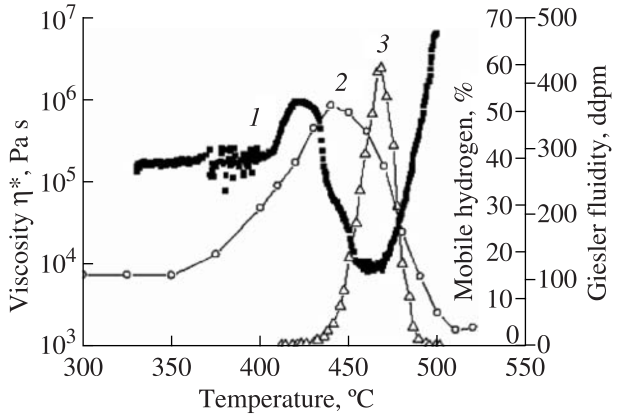

Fig. 1. Temperature dependence of the viscosity η^* (*1*), the content of mobile hydrogen (*2*), and the Giesler fluidity of the plastic mass (*3*) on heating coal samples.

---

[1] Based on an article by S. Melendi, M.A. Diez, R. Alvarez, M. Castro, K. Steel, and C.E. Snape, presented at the 2007 Conference on Coal Science and Technology, Nottingham Fuel and Resource Center (NFRC), Nottingham, England, 2007 (NFRC CD-ROM, paper 2P45).

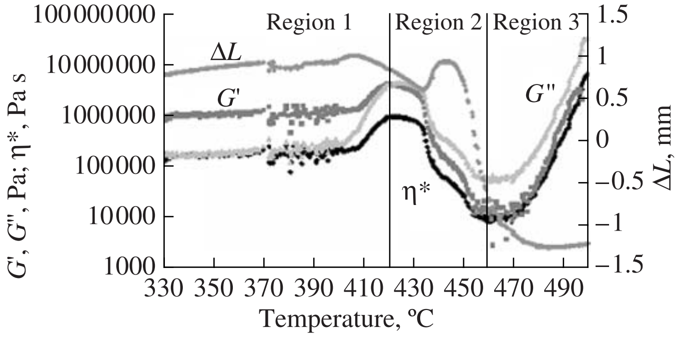

Fig. 2. Temperature variation of the rheometric characteristics: viscosity η^*, elastic modulus G', viscosity modulus G'', and the change in sample thickness ΔL (the change in the distance between the rheometer plates).

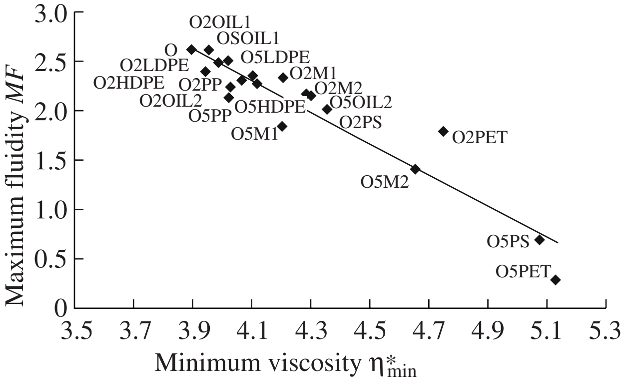

Fig. 3. Maximum Giesler fluidity *MF* of plastic mass as a function of the minimum viscosity $\eta^*_{\min}$ (in logarithmic coordinates) for samples of O coal and its mixtures with plastic: O2, O5, mixtures with 2 and 5% plastic, respectively.

solidifies, with the formation of semicoke. Thus, in considering the temperature dependence of η^*, we may distinguish three regions (Fig. 2).

Region *1* is characterized by gradual softening of the coal, with increase in the elastic modulus G' and viscosity modulus G''. In region *2*, G' and G'' equalize at 430°C, with sharp drop in the viscosity and in G' and G''. In region *3*, which begins with minimum values of η^*, G', and G'', these characteristics increase as the plastic mass solidifies; $G'' > G'$.

The change in sample thickness ΔL (the distance between the plates of the rheometer in which the coal disk is placed) is also different in the three regions. In region *1*, there is little variation in ΔL. In region *2*, there is a surge in ΔL at ~440°C. Subsequently, ΔL declines sharply on transition to region *3*, characterized by sample compression ($\Delta L < 0$) on solidification. The maximum of ΔL in region *2* is evidently associated with the formation of microbubbles as volatiles are released within the coal grains.

In Fig. 3, the maximum Giesler fluidity of the plastic mass is shown (in logarithmic coordinates) as a function of the minimum viscosity $\eta^*_{\min}$ determined by the rheometric method for samples of coal and coal–plastic mixtures.

For the given samples, the maximum fluidity is 2–424 ddpm (for the initial coal, $MF = 423$ ddpm), while the minimum viscosity is 9000–137000 Pa s (for the initial coal, $\eta^*_{\min} = 7940$ Pa s). As is evident from Fig. 3, there is a stable correlation between *MF* and $\eta^*_{\min}$ within these intervals.

In analyzing the effect of the plastic additives on the rheological properties of the coal, we may distinguish two groups. The first group consists of three types of polyolefins (HDPE, LDPE, and PP), which, when added to coal in amounts of 2 or 5% result in a minimum viscosity of 9000–13500 Pa s. The second group of plastics, including polystyrene PS and polyethylene terephthalate PET with aromatic rings in the structure, has a more pronounced influence on the rheological properties of the mixture. With 2% PS or PET, $\eta^*_{\min}$ and *MF* are, respectively, 23000–57000 Pa s and ~100 ddpm. Increasing the PS or PET content in the mixture to 5% sharply retards the formation of plastic mass on carbonization, increasing $\eta^*_{\min}$ to 120000–137000 Pa s and reducing the maximum Giesler fluidity to 2–5 ddpm.

When mixed plastic wastes are added to coal, the rheological properties of the mixture will depend on which group of plastics predominates in the mixture. Thus, for wastes of type M1, consisting basically of polyolefins, the $\eta^*_{\min}$ and *MF* values will be close to those of group 1; when using wastes of type M2, with 35% PET + PS, the values will correspond to those of group 2.

In the case of lubricant oils, their composition is again a critical factor in determining the rheological properties of their mixture with coal. Thus, the reduction in fluidity of the coal's plastic mass (the increase in η) is greater for OIL2, containing mainly long-chain complex aliphatic esters, than for OIL1, consisting mainly of long-chain alkanes. In fact, in terms of chemical structure (predominantly methylene groups CH_2), OIL1 may be assigned to the polyolefine group (polyethylene and polypropylene).

The authors compare the temperature characteristics of the plastic state according to plastometric and rheometric data. The difference is greatest (<6°C) for the solidification temperature of the plastic mass with semicoke formation: T_r according to the Giesler method and T_{gp} according to rheometric measurement. Somewhat greater discrepancies (up to 9°C) are observed for the temperatures of maximum fluidity (T_m) and minimum η^* (T_{mf}).

The difference in the estimates of the softening temperatures T_s and T_{rs} is 3–20°C; greater values correspond to mixtures with plastics from the second group. In most cases, $T_{rs} > T_s$. In other words, the transition temperature to the plastic state is higher in rheological measurements than in the Giesler method, as a rule. In particular, when PET is added to the coal, T_{rs} exceeds T_s by 14 and 39°C in mixtures with 2 and 5% PET, respectively. Analogous behavior is observed with PS, on account of the lower content of mobile hydrogen in coal mixtures with plastics of the second group (Fig. 4).

Thus, if the mobile hydrogen content is 51% for the initial coal, it falls to 46 or 41%, respectively, on adding 5% PS or PET. For plastic wastes of type M2, containing up to 35% PS + PET, the mobile-hydrogen content falls to 44% on adding 5% M2 to the coal.

The authors have studied the change in the rheological properties of coking coal under the influence of additions of individual polymers from two distinctive groups or plastic wastes with different compositions. Their results indicate that the fluidity of the coal may be reduced on carbonization in the presence of 2–5% plastic wastes, which may affect the quality of the metallurgical coke produced.

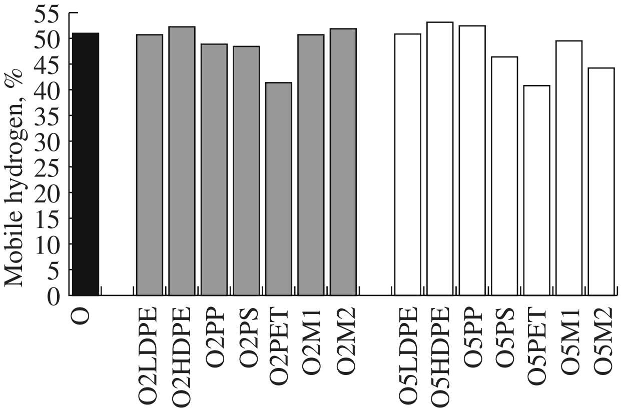

Fig. 4. Histograms of the maximum mobile-hydrogen content for samples of coal O and its mixture with 2% (gray columns) and 5% (white columns) LDPE, GDPE, PP, PET, M1, and M2.

Reviewer S.G. Gagarin