



# Interactions between coking coals and plastics during co-pyrolysis<sup>☆</sup>

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## Abstract

Blends of three Australian coking coals and polypropylene, polystyrene, polyacrylonitrile and polyphenylene sulfide were prepared and the extent to which the blends fused on heating was monitored using proton magnetic resonance thermal analysis in order to identify interactions between them that could affect their fluidity. Different plastics had different effects. Polystyrene strongly reduced the fluidity of all of the coals, confirming previous findings. Polypropylene did not affect the fluidity of the two coking coals of lower rank. Polyphenylene sulfide reduced the fluidity of the coals at temperatures near the solidification temperature of the coals, and polyacrylonitrile appeared to increase the fluidity of the coals at temperatures near the softening temperature of the coals. The very different effects different plastics have on coal fluidity show that the interaction between plastics and coals must be carefully examined before plastics are added to coking coal blends.

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## 1. Introduction

Non-coal materials are often introduced to blends of coals used for coke manufacture. Sometimes they are added to modify the properties of the product coke (such as adding petroleum coke to reduce the ash yield of coke) but increasingly they are being added because they are waste materials that would be more expensive to dispose of in other ways. Waste materials that have been trialled include tyres [1,2], plastics [3], by-product materials generated during coking [4,5] and brown coal liquefaction products [6].

Many plastics form reactive intermediates during pyrolysis and these may interact with the coal and thus affect the quality of the product material. This interaction has been noted in the coprocessing or coliquefaction of coals and plastics [7]. For example, coals and polyethylene wastes interact to produce different light oil and gas products during pyrolysis [8–11]. However, interest in using waste plastics in coking coal blends and studies of the effect of adding plastics to coking blends on the properties of the product coke is relatively recent. Brzozowska et al. [12] monitored interactions between coal tar pitches and

plastics by examining optical texture and product yield. Many plastics were found to increase carbonisation yield but most had little effect on the optical anisotropy of the semi-coke. Polyvinylchloride was observed to increase anisotropy development, suggesting that some plastics may enhance coking properties. Zhou et al. [13] also reported that polyvinylchloride enhances anisotropy development. However, polyvinylchloride would not be suitable in industrial coke ovens because of its high organic chlorine content.

Uzumkesici et al. [14] performed Gray-King tests on a perhydrous, high-volatile bituminous coal, and its blends with polyethylene and polystyrene. They inferred from their results that polyethylene acted as a hydrogen donor towards the coal, because the tars from polyethylene were enriched in unsaturated aliphatic compounds in the presence of coal. Polystyrene was suggested to act as a strong hydrogen acceptor because it produces ethylbenzene as a major pyrolysis product when blended with coal and pitch [15]. They found that up to 10% polyethylene could be added to this coal without seriously affecting coke properties, but only 2% polystyrene could be added before the Gray-King coke type was seriously compromised. Interestingly, they also found that the oil yield using the Gray-King assay was additive. This finding is consistent with results for

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biomass/coal blends whose total gas and tar yields were additive [16,17] even though charcoals that are produced by biomass pyrolysis strongly reduce the fluidity of coking coal blends [18].

Nomura et al. [19] investigated the effects of five different plastics on the coking properties of four coals. Polyethylene, polypropylene and polyvinylchloride had little effect on fluidity (even at the 5% level) or coke strength—in some cases the addition of polyethylene improved coke strength—but polystyrene and polyethylene terephthalate inhibited fluidity and decreased coke strength, in one case reducing the Gieseler fluidity from 1000 to 1 ddpm at 5% addition. The magnitude of this fluidity loss varied strongly between coals.

In this paper the interactions that occurred between three coking coals and four plastics when their blends were heated were measured using proton magnetic resonance thermal analysis (PMRTA). PMRTA measures the extent to which coals and plastics and their blends become fused. Because the extent of fusion as determined by PMRTA is an additive parameter, interactions between coals and plastics that affect the extent to which the blend fuses can be quantified [18]. This is unlike Giesler plastometry or dilatometry, which require complex—and assumption-rich—modelling to predict the behaviour of blends even in the absence of interactions [20,21]. We confirmed that polypropylene has little effect on the fluidity of coking coals and that polystyrene strongly reduced the fluidity of coking coals.

## 2. Experimental

All three coal samples were washed commercial products of Australian coals. Samples of the coals were stored in a freezer until required in order to minimise potential effects of sample oxidation. Table 1 lists their properties. Subsamples for PMRTA were crushed to  $-212\ \mu\text{m}$  by hand in order to minimise the loss of fluidity of the sample. The polystyrene was a commercial sample with a MW of  $5.2 \times 10^4$ ; the polypropylene was from Aldrich and used as received. Polyacrylonitrile (PACN) and polyphenylenesulfide (PPS) were samples of commercial power station filter bags that had been crushed in a vertical reciprocating ball

Table 1  
Properties of coals

Coal	Ash yield (%, db)	VM (%, daf)	Rv,max (%)	Vitrinite (%, mmf)	Liptinite (%, mmf)	Tmf (°C)	Fmax (%)
1	9.4	35.8	0.74	48	8	431	42
2	6.1	37.0	0.96	79	5	430	51
3	9.7	22.1	1.40	82	0	468	26

Notes: Tmf is temperature of maximum extent of fusion as measured by PMRTA (heating at  $4^\circ/\text{min}$ ); Fmax is the  $F$  value at this temperature. VM is volatile matter yield.

mill for 1 h (disposal of old filter bags can be an environmental problem for the power industry). The PMRTA of the coals, plastics and 80:20 blend were measured.

In a standard PMRTA experiment, 0.4 g of  $-212\ \mu\text{m}$  sample is heated under flowing nitrogen from room temperature to  $550\ ^\circ\text{C}$  at a rate of four degrees per minute. The ‘solid-echo’ nmr signals [22] are recorded every 30 s, giving a two degree temperature resolution of the data. In this study the repetition rate was fixed at 2 s, so that the signal intensity per gram of plastic would be the same whether it was pure or in a blend with the coal if the materials did not interact. (Each recorded signal was therefore the average of 15 measurements). All PMRTA measurements were conducted in duplicate. The shapes of the nmr signals obtained from PMRTA were used to provide the  $F$  value, a measure of the extent to which the material was fused, at each temperature [18]. The  $F$  value ranges from 0 for a fully rigid material, such as dry anthracite at room temperature to 100 for a fully mobile material, such as molten plastic or water [18].

Since the  $F$  value—the extent to which a material is fused—is additive, it is easy to calculate the  $F$  value for the blend in the absence of interactions from the  $F$  values of the component materials. This calculated value is termed here the ‘asynergic’ [8]  $F$  value. The magnitude of the interaction between the materials at any temperature was given by the difference between the measured and asynergic  $F$  value of the blend. Differences of less than 2% are not considered significant.

## 3. Results

Fig. 1 shows the variation of  $F$  value with temperature for coal 1 and polypropylene. This sample of polypropylene melted completely below  $200\ ^\circ\text{C}$  and had largely volatilised by  $425\ ^\circ\text{C}$ . The results expected for the 80:20 coal-polypropylene blend if interactions did not occur (‘asynergic’ results) match the measured results at all temperatures: these two components behaved independently in the blend. There was no evidence that coal 1 and polypropylene interacted in any way that affected fluidity.

In contrast, the  $F$  values measured for the 80:20 blend of coal 1 and polystyrene (Fig. 2) were very different to the asynergic values above  $400\ ^\circ\text{C}$ : the measured fluidity of the blend was substantially less than that expected in the absence of interactions. This reduction in fluidity occurred after the polystyrene had completely volatilised. This means that the polystyrene had reacted with the coal prior to its evaporation. This finding is consistent with earlier work [14,15,19].

Fig. 3 compares the difference between measured and asynergic  $F$  values for blends of the three coals with polystyrene. It shows that polystyrene drastically reduced the fluidity of all three coals at temperatures between 420

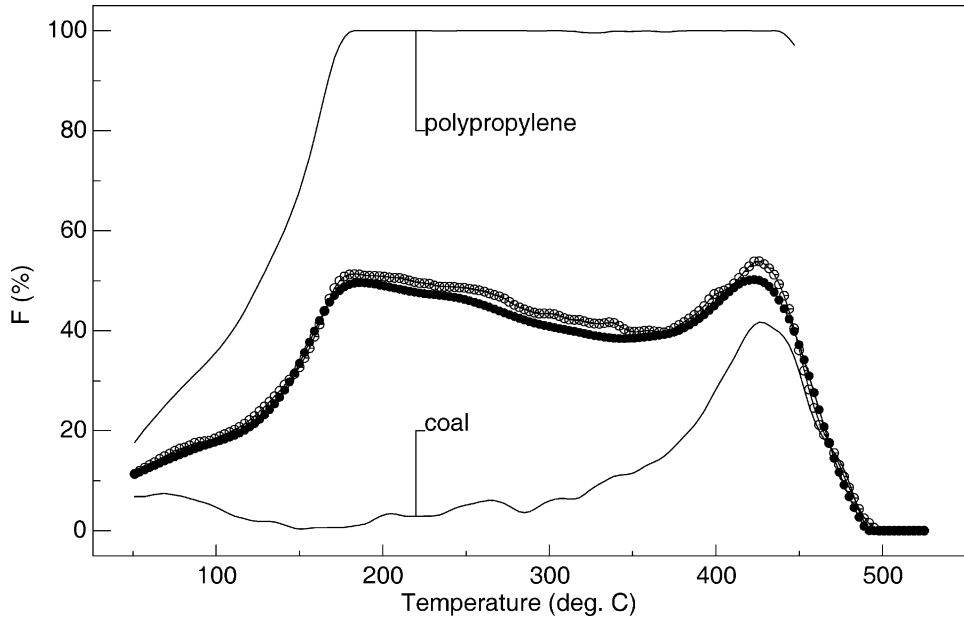


Fig. 1.  $F$  values predicted for a 80:20 blend of coal 1 and polypropylene blend (o) in the absence of interactions and the values measured for the blend (filled circles).

and 470 °C and the temperature at which the interaction was most negative was greatest for the highest rank coal. In the case of coal 2, the difference reaches  $-23\%$  at 440 °C. Since the asynergic  $F$  value was 44% at this temperature for this blend, it means that half of the blend that would have been liquid at this temperature had there been no interaction is in a solid form.

The measured  $F$  values in the temperature range 370–420 °C were greater than the asynergic values for coal 3. This could be due to a positive interaction at these

temperatures, but was more probably due to the retention of fluid polystyrene degradation products by the coal (this polystyrene sample started devolatilising at these temperatures). The effect of polystyrene on fluidity has been attributed to its ability to abstract hydrogen from hydrogen-containing materials during its decomposition [14,15,19].

Fig. 4 shows that there is no significant interaction between coals 1 and 2 and polypropylene. The blend with coal 3 showed a negative interaction above 450 °C: polypropylene did appear to interact with coal 3 at high

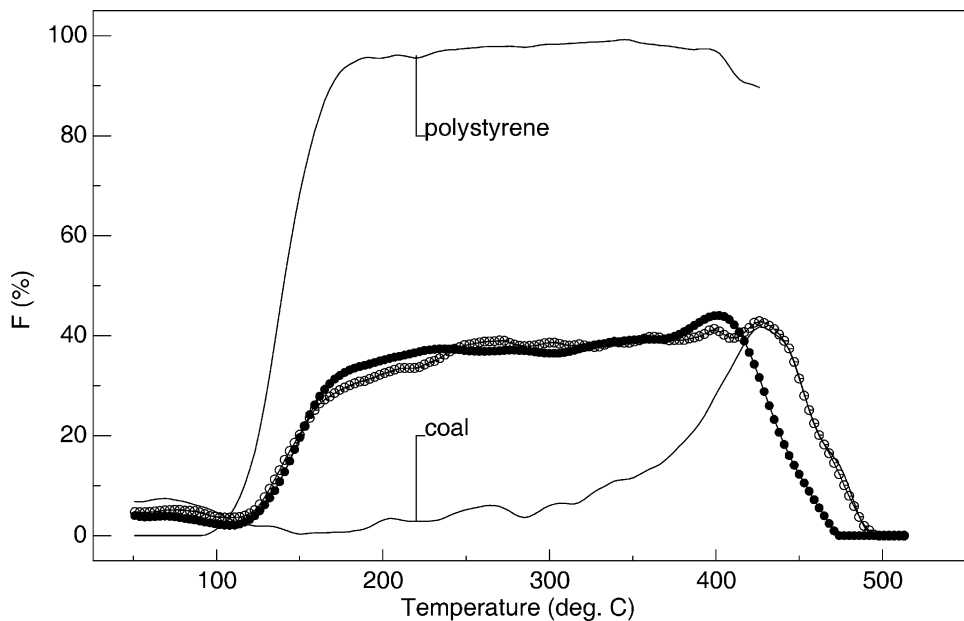


Fig. 2.  $F$  values predicted for a 80:20 blend of coal 1 and polystyrene (o) in the absence of interactions and the values measured for the blend (filled circles).

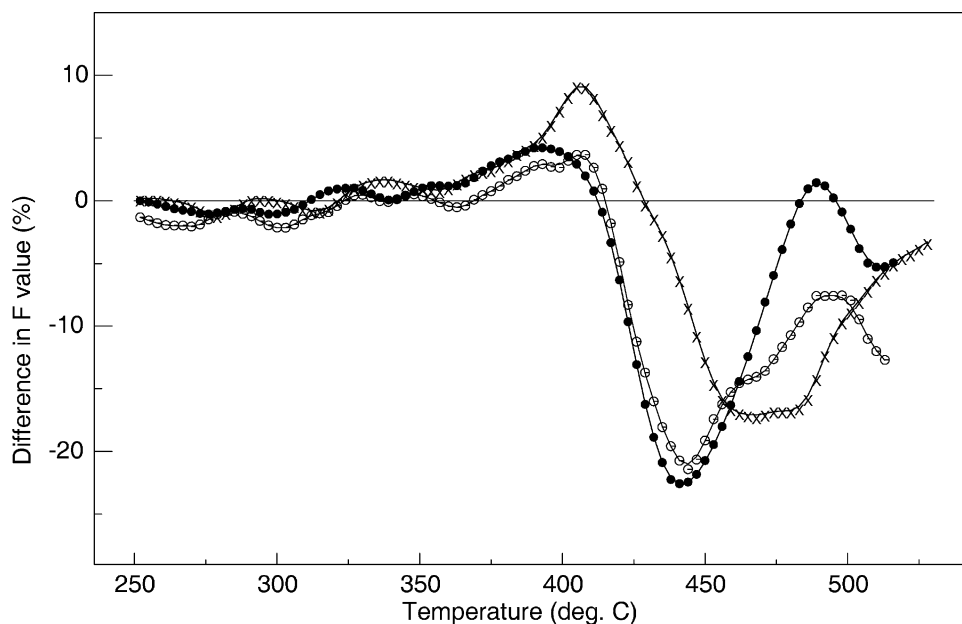


Fig. 3. Difference between measured and asynergic  $F$  values for 80:20 blends of coals 1 (o), 2 (filled circles) and 3 (x) with polystyrene.

temperatures, but to a much lesser extent than was observed for polystyrene.

Poly-phenylene sulfide (PPS) interacted with all coals, reducing their fluidity at high temperatures (Fig. 5), though not to the same extent as polystyrene. Polyacrylonitrile (PAN) appeared to enhance the fluidity of all of the coals at lower temperatures (Fig. 6). This increase was not due to retention of the PAN by the coal because there was little reduction in signal intensity due to polyacrylonitrile devolatilisation at these temperatures. It was possible that PAN enhanced the fluidity of the blend

by releasing materials during its decomposition that plasticised the coals. PAN releases some aromatic materials such as pyridine and benzene carbonitriles during its decomposition [23,24], which may plasticise coal.

#### 4. Discussion

The thermoplasticity—fluidity—of coking coals can be readily altered. The interactions responsible for this

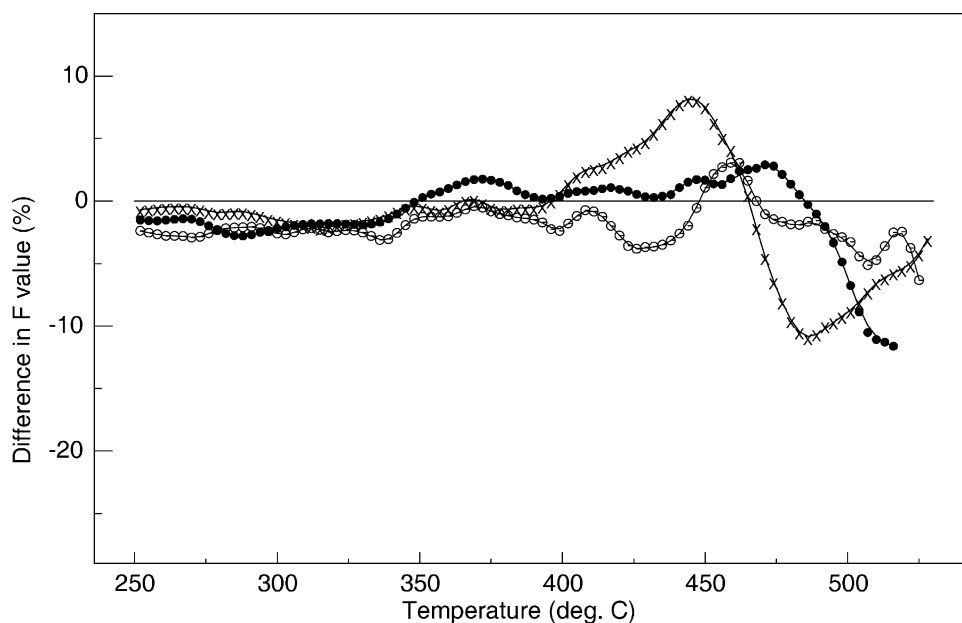


Fig. 4. Difference between measured and asynergic  $F$  values for 80:20 blends of coals 1 (o), 2 (filled circles) and 3 (x) with polypropylene.

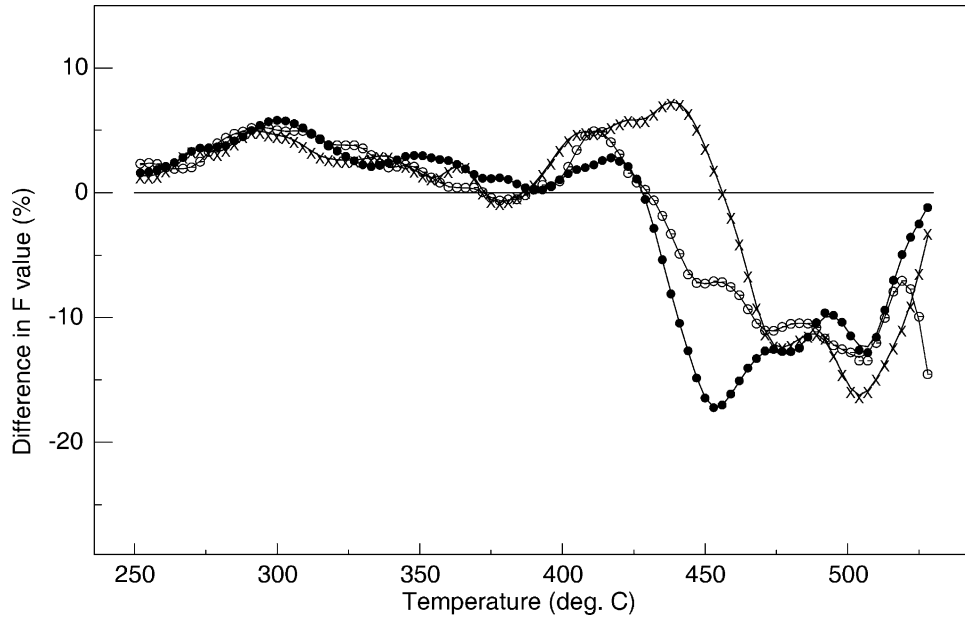


Fig. 5. Difference between measured and asynergic  $F$  values for 80:20 blends of coals 1 (o), 2 (filled circles) and 3 (x) with poly phenylene sulfide.

alteration can be broadly divided into two types, physical and chemical.

Physical interactions can result in a decrease in fluidity by removing the internal plasticising component of coal, for example by evacuation or the addition of charcoal [25,26], or they can result in an increase in fluidity by addition of an appropriate solvent, or applying pressure, which retains the plasticising component of coal. For example, the fluidity of coals can be substantially increased by the addition of an aromatic solvent such as *p*-quaterphenyl, which is liquid

at the temperatures coal is plastic. The coal is plasticised to extents far greater than the asynergic value for the mixture, even though at these temperatures *p*-quaterphenyl is chemically inert [27].

Chemical interactions involve transfer of hydrogen, either to the coal (resulting in an increase in fluidity) or from the coal (resulting in a decrease in fluidity) [9,28].

Domínguez et al. [9] have reported a slight but significant reduction in Gieseler fluidity when polyethylene is added to coking coal, which they attribute to a chemical

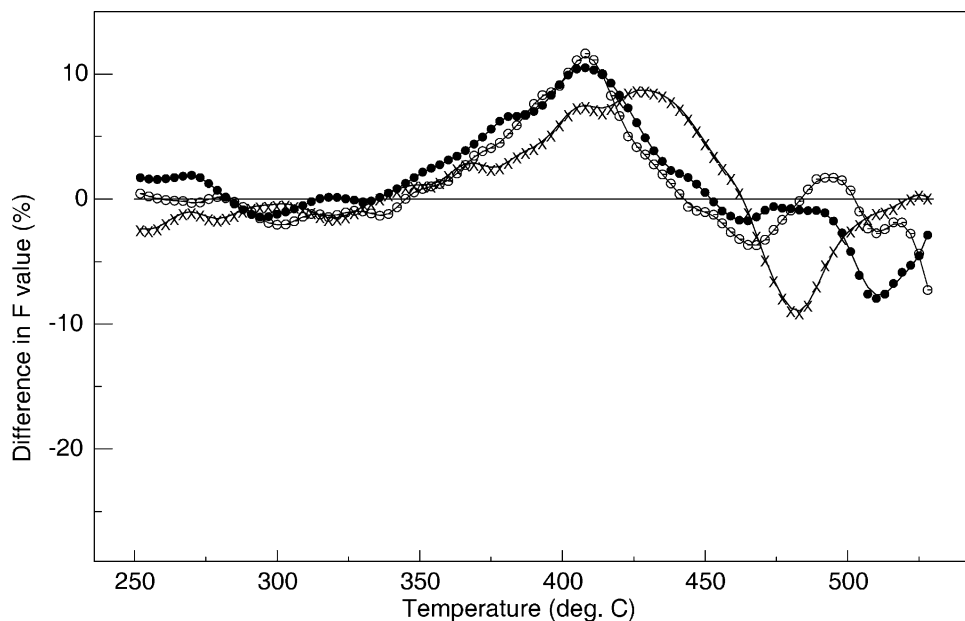


Fig. 6. Difference between measured and asynergic  $F$  values for 80:20 blends of coals 1 (o), 2 (filled circles) and 3 (x) with polyacrylonitrile.

interaction, where polyethylene degradation products act as hydrogen acceptors.

Polystyrene was observed to have very strong, negative effects on the fluidity of coal, consistent with previous findings [14,15,19]. This effect is too strong to be explained by a physical process and a chemical effect is necessary to explain this result. Polystyrene is known to abstract hydrogen from hydrogen-containing materials during its decomposition, and abstracting hydrogen from coal leads to a loss in fluidity. The results here confirm that the amount of polystyrene that could be added to coking coals without severely compromising their ability to form a good coke is severely limited. These results also indicate that the composition of plastic waste must be determined before its addition to coking coal blends.

Polyphenylene sulfide reduced the fluidity of the blends, but only at high temperature. Whether the reduction fluidity is due to charring of the polymer or active hydrogen abstraction by the polymer remains to be determined.

Polyacrylonitrile was the only polymer investigated that significantly increased the fluidity of the coking coal. This increase is attributed to the tar formed by polyacrylonitrile during its decomposition plasticising the coal.

The results here indicate that polystyrene has very strong effects on fluidity and the coking properties of coal blends will be severely compromised by its addition. The results of Nomura [19] suggest that PET-type plastics will also have deleterious effects. It is likely that other types of plastics will affect coking properties strongly and these should be identified. Users of plastics in coking blends will have to determine the composition of the plastic they add so as to optimise its addition into coking blends. It is possible that some plastics may enhance some coking properties under some conditions and these should be identified as well. For example, the strong fluidity reduction by polystyrene and PET may reduce coking pressure as well as coke strength; their addition to swelling coals may be an advantage if their effect on coking pressure is greater than that on coke properties.

The different responses to plastic addition by the high and low volatile coal suggest that rank has a strong effect on how a coal will interact with plastics. The similar effects seen when coals 1 and 2, which have different maceral compositions, are blended with plastics suggest that changing maceral composition will have a smaller effect than changing rank on the interactions between plastics and coking coals.

## 5. Conclusions

- Different plastics have very different effects on the fluidity of coking coals.
- Polystyrene substantially reduced the fluidity of all coking coals above 420 °C. It may act as

a dehydrogenation agent.

- The resolidification temperature of the low volatile coal was reduced by all of the plastics tested.
- Polypropylene had no effect on the fluidity of high-volatile coals.
- Polyacrylonitrile appeared to increase the fluidity of coking coals at temperatures at which the coals first softened.

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