Macromol. Symp. **2003**, *202*, 297—305

Kinetics of Reactions of Coal with Polystyrene: TGA-DSC Approach

P. Straka, J. Náhunková, Z. Brožová*

Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic, V Holešovičkách 41, Prague 8, CZ-182 09, Czech Republic

Summary: Kinetics of thermal reactions of coal with polystyrene by TGA and DSC methods was studied. In the range of about 350-550 °C a thermal degradation of coal proceeds, and gas, tar and coke are evolved. Simultaneously, decomposition of polystyrene occurs (360-470 °C). Unsaturated products of polystyrene decomposition are hydrogenated by coal, because coal is a strong H-donor. Moreover, some aromatic products react with coal tar structures and new aromates are formed. The yield of tar from copyrolysis is then higher in comparison with pyrolysis of coal alone. Kinetic parameters of the process were evaluated and discussed.

Keywords: aromates; coal; copyrolysis; kinetics; polystyrene

Introduction

From the results obtained from copyrolysis of coal with waste polymers in a laboratory and macrolaboratory scale[1-3] it follows that copyrolysis is a good way of recycling. It was found that yields of tar or gas from copyrolysis are significantly higher in comparison with those obtained from pyrolysis of coal. E.g. yield of tar from copyrolysis of waste ABS polymer with coal was very high in comparison with coal alone[4] (Table 1). As tar can be a main product of copyrolysis, attention was paid to thermal decomposition of polymers in the presence of coal and kinetics of reactions was investigated. In this case, kinetics of thermal reactions of coal structures with polystyrene (PS) was studied. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were applied.

Table 1. Mass balance of copyrolysis (wt.-%).

Feedstock	Coke	Tar	Water	Gas	Losses
coal	71	10	5	10	4
coal + 60 % ABS polymer	34	52	2	9	3

DOI: 10.1002/masy.200351226

Experimental

Materials

Coal from mine Dukla (Ostrava-Karviná District) was used. Proximate, elemental and petrographic analyses of the coal used are summarized in Table 2. Further, powdered polystyrene (Polymer Laboratories Ltd., U.K.) was used.

Table 2. Proximate (wt-%), elemental (wt.-%) and petrographic (vol.-%) analyses of the coal used. VM – volatile matters, SI – swelling index, V, E, I – content in vitrinite, exinite and inertinite, resp.

Water	Ash (db)[a]	VM (daf)[b]	SI	C	H	N (daf)[b]	S	O	V	E	I
1.6	10.4	33.1	1	81.6	5.5	1.3	0.7	10.9	63	15	22

[a]dry sample; [b]dry ash free basis

Thermogravimetry and Differential Scanning Calorimetry

TGA and DSC measurements with powdered PS and coal with grain size under 0.2 mm were carried out on Perkin-Elmer Pyris TGA 6 and Pyris DSC 7 analyzers. TGA analyses were performed in a nitrogen atmosphere in the temperature range of 25–700 °C with heating rates of 5, 10 and 20 °C.min^{-1}. DSC analyses were carried out in the temperature range of 25–550 °C with heating rates of 10, 15 and 20 °C.min^{-1}. Kinetic data were evaluated with a Perkin-Elmer software as follows. For reaction order and parameters of the Arrhenius plot calculations a Pyris Series DSC Scanning Kinetics and Pyris Series TGA Decomposition Kinetics were used. For conversion time calculations from both DSC and TGA data a Pyris Series Model Free Kinetics based on generalized descriptions of solid-phase reactions[5] was applied.

NMR Spectrometry

Representative structures of coal used were 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 MHz and 200.14 MHz (^{13}C and ^{1}H, resp.). 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. The number of scans for the accumulation of ^{13}C CP/MAS NMR spectra was 3600–7200, repetition delay 3 s and spin lock pulse 1 ms. During the detection a high power dipolar-decoupling was used to eliminate strong heteronuclear dipolar coupling. ^{13}C scale was calibrated by external standard glycine (δ = 176.03 – low field carbonyl signal). For ^{1}H-^{13}C dipolar-dephasing experiments standard pulse sequence was used where cross-polarization period was followed after τ delay by two simultaneous π pulses on both (^{13}C and ^{1}H) channels. Data acquisition starts after second τ delay. 2τ delay was incremented from 2 to 200 µs. 24 increments were performed to obtain dipolar-dephasing dependence. The number of scans amounted to 400. From ^{13}C CP/MAS NMR parameters, coal structures were constructed according to work.[6]

Results and Discussion

First, an influence of the coal presence on PS decomposition was investigated by the DSC method. From the data obtained, the conversion time at conversion degree of 95 %, reaction order, and parameters of the Arrhenius plot were calculated. Results are shown in Table 3.

Table 3. DSC of the decomposition of polystyrene in the presence of coal at the temperature of maximum decomposition (T_{max}). Degree of conversion 95 %, conversion time calculated for heating rates of 10, 15 and 20 °C.min^{-1}. n – reaction order; E_A, ln Z – parameters of the Arrhenius plot calculated for heating rate of 15 °C.min^{-1}.

Mixture (wt.-% PS /wt.-% coal)	T_{max} (°C)	Conversion time (min)	n	E_A (kJ.mole^{-1})	ln Z
100/0	425	121.4	1.25	442.8	72.7
60/40	440	87.6	1.25	459.1	74.0
50/50	440	73.7	1.2	525.5	85.0
40/60	440	32.9	1.2	457.7	73.6
30/70	440	34.7	1.1	314.0	48.8

As the data in Table 3 prove, the conversion time of the PS decomposition was significantly lower in the presence of coal in comparison with that for PS alone. With an increasing share of coal in the mixture the conversion time decreased. It can be deduced that coal improves an endothermic decomposition of PS by an exothermic effect of coal decomposition in the range of 400–500 °C (ΔH -273.8 J.g^{-1}). The DSC maximum of PS shifted to higher temperature in the presence of coal (Fig. 1).

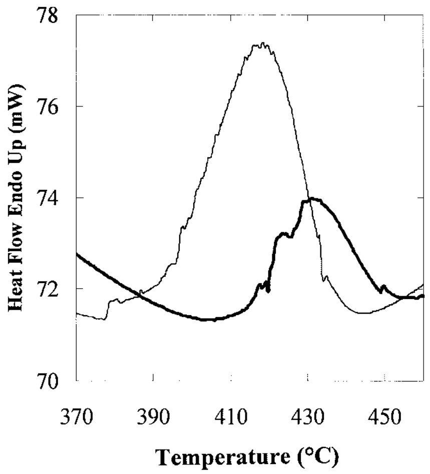

Fig. 1. DSC curves of polystyrene (thin line) and polystyrene with 50 wt.-% of coal (thick line).

It means that conditions of PS decomposition and distribution of products was changed. For this reason, thermal decomposition of PS-coal mixtures were further studied by the TGA method. The temperature of maximum decomposition (T'_{max}), the maximum rate of decomposition (w_{max}), and the percentage of the reacted mixture were measured. Results are summarized in Table 4. Typical courses of decomposition are pictured in Fig. 2.

Table 4. TGA of polystyrene-coal mixtures: thermal decomposition parameters at the heating rate of 10 °C.min^{-1}. T'_{max} – temperature of maximum decomposition, w_{max} – the rate of decomposition at T'_{max}.

Mixture	T'_{max}	w_{max}	Reacted mixture
(wt.-% PS/wt.-% coal)	(°C)	(mg.min^{-1})	(wt.-%)
100/0	426.3	0.99	99.9
60/40	441.0	0.45	75.9
50/50	484.8	0.53	65.5
40/60	442.7	0.45	57.5
30/70	447.3	0.21	52.3
0/100	463.5	0.26	35.0

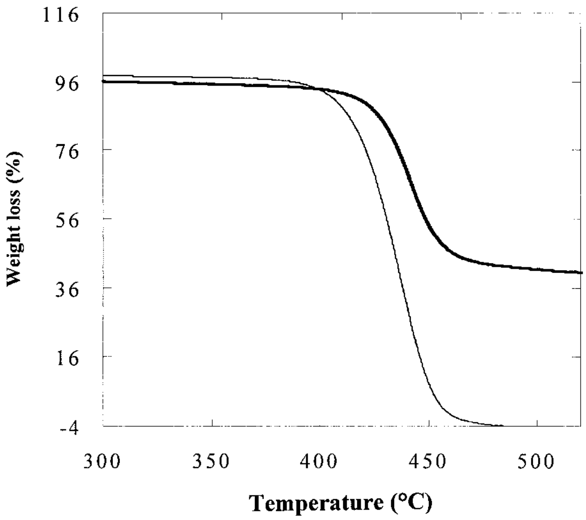

Fig. 2. TGA curves of polystyrene (thin line) and polystyrene with 50 wt.-% of coal (thick line).

From the data in Table 4 it follows that the presence of coal influenced the T'_{max} and w_{max}. It was found that the T'_{max} of PS was significantly lower than those obtained for PS with coal, on the contrary, the w_{max} of PS alone was much higher in comparison with values obtained for PS-coal mixtures. The highest value of T'_{max} at 50 wt.-% of coal in the mixture was observed. The DTG maximum increased by 58–59 °C in this case. Further, the amount of reacted mass decreased linearly with the increasing amount of coal in the mixture. As this decrease was due to a semicoke/coke formation, the increase of the w_{max} with the PS content in the mixture occurred in consequence of tar formation. Practically all PS is decomposed to tar components, but only a part of coal degrades to tar. The yield of tar obtained during copyrolysis and w_{max} then increase with the increasing amount of PS in the mixture. Composition of coal tar changes in the presence of PS, because products of PS decomposition (mainly styrene) are hydrogenated by coal hydrogen and/or, probably, they react with coal degradation structures.

Reactions of PS with coal were further evaluated by the Model Free Kinetics and TGA Decomposition Kinetics. The conversion time (for 95 % of conversion) and the parameters of Arrhenius plot were calculated. Results are showed in Table 5.

Table 5. TGA of decomposition of PS in the presence of coal at temperature of 445 °C. Degree of completion 95 %, coversion time calculated for heating rates of 5, 10, and 20 $°C.min^{-1}$ in the temperature range of 350–500 °C. n – reaction order; E_A, ln Z – parameters of the Arrhenius plot.

Mixture (wt.-% PS/wt.-% coal)	Conversion time (min)	n	E_A ($kJ.mole^{-1}$)	ln Z
100/0	23.9	0.8	199.2	29.7
60/40	29.5	1.1	204.4	30.0
50/50	101.9	1.5	225.0	33.5
40/60	154.9	1.5	272.3	40.9
30/70	85.2	1.9	173.3	24.5

As it is proved by the data in Table 5, the conversion time was much higher with 50–70 wt.-% of coal in the mixture. Reaction order increased from about 1 (PS alone) up to 1.9 (70 wt.-% of coal in the mixture). It means that reactions between PS decomposition products and coal degradation products occur. Two possibilities can be taken into account – hydrogenation and aromates–aromates reactions. As styrene monomer is a main product of polystyrene decomposition (72 %, beside dimer – 11 %, and trimer – 14 %), and also 1,3-diphenyl propene and other unsaturated compounds are formed,[7] hydrogenation of these products takes place, because coal is a strong hydrogen donor (content of hydrogen 5.5 %, Table 2). Moreover, α-methyl styrene is formed7. Therefore, styrene, ethyl benzene, toluene, isopropyl benzene, 1,3-diphenyl propane and α-methyl styrene enrich coal tar (beside rests of dimer and trimer). Further, a formation of new aromatics by reactions of aromates from PS with coal tar aromatic structures can be considered, as coal tar structures are derived from coal structure. Because composition of coal (as well as charcoal[8]) is very complicated, its chemical structure was expressed by four representative aromatic/cyclanic clusters (Fig. 3) constructed from ^{13}C CP/MAS NMR parameters.

Cyclanic parts of clusters are cleaved during copyrolysis and aromatic rests (essential constituents of tar[9,10] react with products of PS decomposition by free radical mechanism. New aromates like diphenyl, phenyl naphtalene, benzo fluorenes and benzo fluoranthenes are created,[11] therefore, amount and composition of tar are changed. Probably, that is why the conversion time was much higher in the presence of coal.

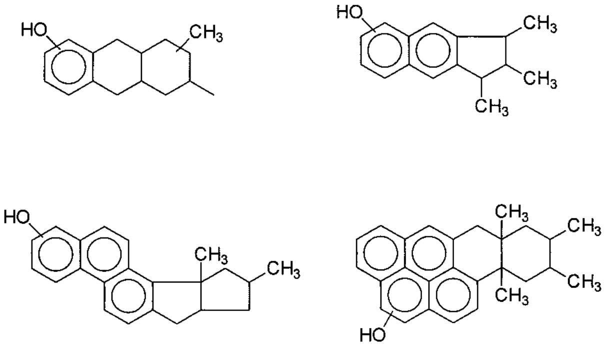

Fig. 3. Representative structures of coal used.

For comparison, decomposition of polypropylene was followed. Results are shown in Table 6.

Table 6. TGA of decomposition of polypropylene in the presence of coal at the temperature of 476 °C. Degree of conversion 95 %, time of conversion was calculated for heating rates of 5, 10, 15 and 20 $°C.min^{-1}$ in the temperature range of 400 – 520 °C. n – reaction order; E_A, ln Z – parameters of the Arrhenius plot.

Mixture (wt.-% PP / wt.-% coal)	Conversion time (min)	n	E_A ($kJ.mole^{-1}$)	ln Z
100/0	36.2	0.6	208.3	29.0
60/40	30.6	0.7	225.5	31.4
50/50	30.4	0.8	245.2	34.6
40/60	29.2	1.1	231.3	32.5
30/70	29.6	1.3	227.2	31.9

From the data in Table 6 it follows that the conversion time of decomposition of the PP was rather shorter in the presence of coal in the temperature range of 400–520 °C. As the reaction order was always about 1, it seems that reactions in the question are more simple in this case. PP decomposes above 400 °C, and propylene trimer is main decomposition product.[8] The presence of coal promotes the formation of monomer and dimer and unsaturated products with low MW (unsaturated hydrocarbons C_2–C_7).[8] These product are hydrogenated by coal. With an increasing content of coal in the mixture the reaction time is then a litle shorter. No such phenomenon was observed in the case of PS. It means that longer conversion times at PS-coal mixtures can be attributed to aromates-aromates reactions.

From above-mentioned findings it follows that coal tars differs from tars obtained from copyrolysis. Due to higher concentration of simple aromates with low substitution a lower aromaticity, substitution degree and density can be expected with copyrolysis tars. We compared these parametrs for tars obtained under high-teperature conditions on a laboratory unit. Coal tars[9] and tars from copyrolysis of coal with polymers of PS type[1,4,12] were taken into account. As Table 7 proves, these parameters were lower in the case of copyrolysis.

Table 7. Parameters of tars.

Tar	Aromaticity	Substitution degree	Density ($g.cm^{-1}$)
dry coal tar	0.69–0.76	0.26–0.61	1.02–1.03
dry copyrolysis tar	0.60–0.71	0.17–0.37	0.96–1.02

Conclusion

Kinetic parameters of thermal reactions of coal with polystyrene by DSC and TGA were determined. On this basis, reactions in question were described. In the range of 350–550 °C a thermal degradation of coal proceeds, simultaneously, decomposition of polystyrene occurs. Because coal is a strong H-donor, unsaturated products of polystyrene decomposition are hydrogenated by coal. Some aromatic products of PS decomposition react with coal tar structures and new aromates are formed. That is why the conversion time of PS decomposition is much higher in the presence of coal. The yield of tar from copyrolysis is then higher in comparison with pyrolysis of coal alone. Also tar composition is changed.

Acknowledgement

Academy of Sciences of the Czech Republic supported this work as the grant project No. S3046004.

[1] Straka P., Buchtele J. and Kovářová J.: Macromolecular Symposia 135, 19 (1998)
[2] Buchtele J. et al.: Research Report, Institute of Rock Structure and Mechanics ASCR, Prague, 1998
[3] Kříž V., Chovancová P. and Buchtele J.: Proc. 2nd Int. Conf. on Metallurgy and Environmental Technologies, 11-12 September, Herlany/Slovakia, 2001, pp.59-66
[4] Bičáková O.: PhD. Thesis, The Institute of Chemical Technology of Prague, Prague, 2002
[5] Vyazovkin S.V. and Lesnikovich A.I.: Journal of Thermal Analysis 36, 599 (1990)
[6] Solumn M.S., Pugmire R.J. and Grant D.M.: Energy and Fuels 3, 187 (1989)
[7] Jakab E., Blazsó M. and Faix O.: Journal of Analytical and Applied Pyrolysis 58-59, 49 (2001)
[8] Jakab E., Várhegyi and Faix O.: Journal of Analytical and Applied Pyrolysis 56, 273 (2000)
[9] Černý J.: Energy and Fuels 5, 781 (1991)
[10] Černý J.: Petroleum and Coal 34, 339 (1992)
[11] Straka P., Náhunková J. and Brožová Z.: Proc. 15th Int. Symp. on Analytical and Applied Pyrolysis, 17-20 September, Leoben/Austria, 2002, p.48
[12] Kozubek E., Buchtele J. and Roubíček V.: Petroleum and Coal 39, 43 (1997)