

A STUDY OF THERMAL REACTIONS OF COAL WITH POLYAMIDES

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*Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic, V Holešovičkách 41, Prague 8, CZ-182 09***Corresponding author's e-mail: straka@irms.cas.cz**(Received April 2003, accepted August 2003)***ABSTRACT**

Kinetics of thermal reactions of coal with polyamide 6 by TGA and DSC methods was studied. In the range of about 350 – 500 °C the thermal degradation of coal proceeds, and gas and tar are evolved. Simultaneously, the thermal decomposition of polyamide 6 occurs and mainly ϵ -caprolactam is formed. The ϵ -caprolactam formation is promoted by reaction water from the coal degradation and coal hydrogen, because coal is a strong H-donor. Under high-temperature conditions carbon oxides, ammonia, aliphatic hydrocarbons, simple aromatics, and stable oil are formed during copyrolysis of coal with polyamide 6. The yields of gas and tar from copyrolysis with waste polyamides are then higher in comparison with those from pyrolysis of coal alone.

KEYWORDS: coal, kinetics, polyamides**INTRODUCTION**

From the results obtained from copyrolysis of coal with waste polymers in a laboratory and macrolaboratory scale (Straka et al., 1998; Buchtele, 1998; Kříž et al., 2001) it follows that copyrolysis is a good way of recycling. It was found that yields of gas or tar/oils from copyrolysis are significantly higher in comparison with those obtained from pyrolysis of coal. As gas and stable oils are main products 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 with polyamide 6 was studied. Regarding works (Bockhorn et al., 1999) thermogravimetric analysis and differential scanning calorimetry were applied.

EXPERIMENTAL

Coal from mine Dukla (Ostrava-Karviná District) with grain size under 0.2 mm was used. Proximate, elemental and petrographic analyses of the

coal used are summarized in Table 1. Further, powdered polyamide 6 (Katchem Praha Ltd., melting point of 205 – 210 °C, density 1.16 g cm⁻³) and waste polyamides were used.

TGA and DSC measurements with powdered polyamide 6 and coal 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, 15 and 20 °C min⁻¹. DSC analyses were carried out in the temperature range of 25 – 550 °C with heating rate of 10 °C min⁻¹. Kinetic data were evaluated with a Perkin-Elmer software as follows. For the apparent reaction order and parameters of the Arrhenius plot calculations a Pyris Series DSC Scanning Kinetics and a Pyris Series TGA Decomposition Kinetics were used. For conversion time calculations from TGA data a Pyris Series Model Free Kinetics based on generalized descriptions of solid-phase reactions (Vyazovkin and Lesnikowich, 1990) was applied. As background for application of mentioned

Table 1 Proximate (wt-%), elemental (wt-%) and petrographic (vol.-%) analyses of the coal used. VM – volatile matters, SI – swelling index, V, E, I – content in vitrinite, liptinite and inertinite, resp.

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

^adry sample; ^bdry ash free basis

software the works (Bockhorn et. al., 1999) were used.

In addition, copyrolyses of coal with waste polyamides were carried out on a laboratory unit. A steel reactor in a vertical tube oven was used. 50 g of coal or coal-polyamide mixture with 60 wt.-% of polyamide were heated at heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ to the final temperature of $900\text{ }^{\circ}\text{C}$; the soaking time was 30 min. Samples with grain size up to 3 mm contained 0.7–1.6 wt.-% of water and 4–10 wt.-% of ash (dry basis). After cooling of raw gas and tar separation (Buchtele and Šrogl, 1994), gas and liquid products were analyzed by GC.

GC determinations of gas products were carried out on a Chrom 5 chromatograph (LP Praha) with integrators Hewlett Packard 3390A and CI-105 (LP Praha). Gas products were separated on Porapak QS and molecular sieve 5A packed columns at the temperature of 110°C and detected by TCD and FID detectors. Liquid products were identified on a Chrom 61 chromatograph (LP Praha) with an integrator PE Nelson 1022 GC (Perkin-Elmer). These products were separated on a OV-101 (Lachema Brno) capillary column (28.3 m x 0.23 mm i.d.) and detected by FID

detector. The GC oven was programmed to hold at $50\text{ }^{\circ}\text{C}$ for 5 min and then increase to $300\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Ammonia was trapped in 1700 ml of H_2SO_4 solution (pH = 2) and analyzed electrochemically by ion selective NH_3 electrode (IS 570- NH_3 , Philips).

RESULTS AND DISCUSSION

First, an influence of the coal presence on polyamide 6 decomposition was investigated by the DSC method. From the data obtained the reaction enthalpy, apparent reaction order, and parameters of the Arrhenius plot were calculated. Results are shown in Table 2.

As the data in Table 2 prove, the reaction enthalpy of the polyamide 6 decomposition was significantly lower in the presence of coal in comparison with that for polyamide 6 alone. With an increasing share of coal in the mixture the reaction enthalpy decreased from 297.9 (polyamide 6 alone) up -273.8 J g^{-1} (coal alone). The DSC maximum of polyamide 6 shifted to lower temperature in the presence of coal (Fig. 1).

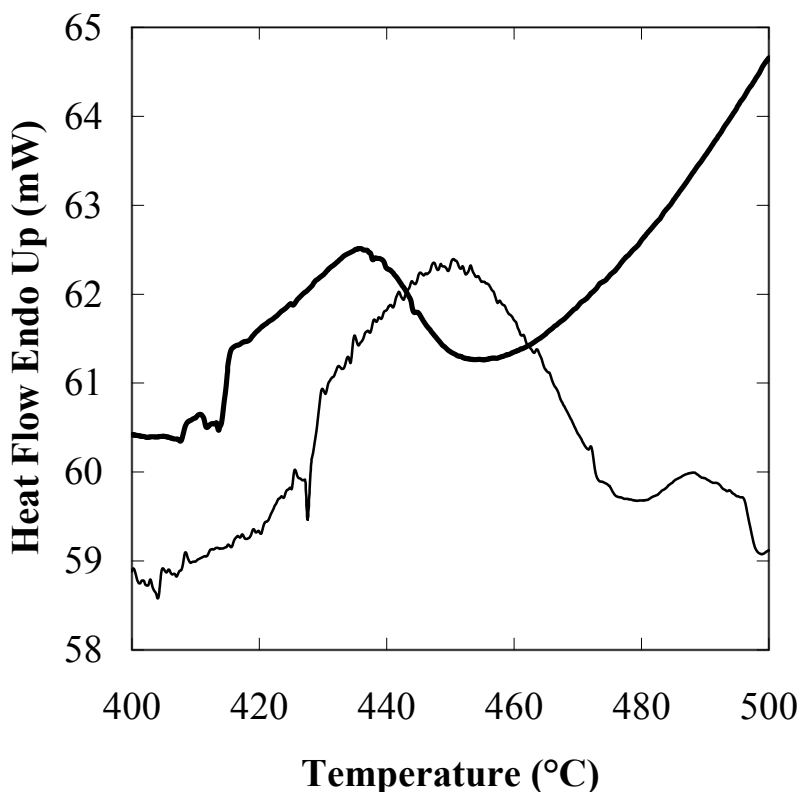


Fig. 1 DSC curves of polyamide 6 (thin line) and polyamide 6 with 50 wt.-% of coal (thick line)

Table 2 DSC of the decomposition of polyamide 6 in the presence of coal. n – apparent reaction order; E_A , $\ln Z$ – parameters of the Arrhenius plot (calculated for heating rate of $10\text{ }^\circ\text{C min}^{-1}$, temperature range of 370 – $500\text{ }^\circ\text{C}$, DSC Scanning Kinetics)

Mixture (wt.-% PA-6 / wt.-% coal)	n	E_A (kJ mole^{-1})	$\ln Z$	ΔH (J g^{-1})
100/0	1.5	372.2	57.7	297.9
60/40	0.8	278.0	42.9	182.7
50/50	0.7	289.2	44.7	153.4
40/60	0.6	240.1	36.6	128.5
30/70	0.9	362.9	57.9	86.0
0/100	1.3	220.2	31.9	-273.8

Table 3 TGA of polyamide 6-coal mixtures: temperature of maximum decomposition (T_{\max}), the rate of decomposition at T_{\max} (w_{\max}), and the percentage of the mixture reacted at the heating rate of $10\text{ }^\circ\text{C min}^{-1}$ up to $700\text{ }^\circ\text{C}$

Mixture (wt.-% PA-6 / wt.-% coal)	T_{\max} ($^\circ\text{C}$)	w_{\max} (mg min^{-1})	Reacted mixture (wt.-%)
100/0	435.7	0.91	86.5
60/40	450.5	0.47	64.1
50/50	452.6	0.35	53.9
40/60	445.5	0.26	44.5
30/70	454.7	0.22	40.8
0/100	463.5	0.26	35.0

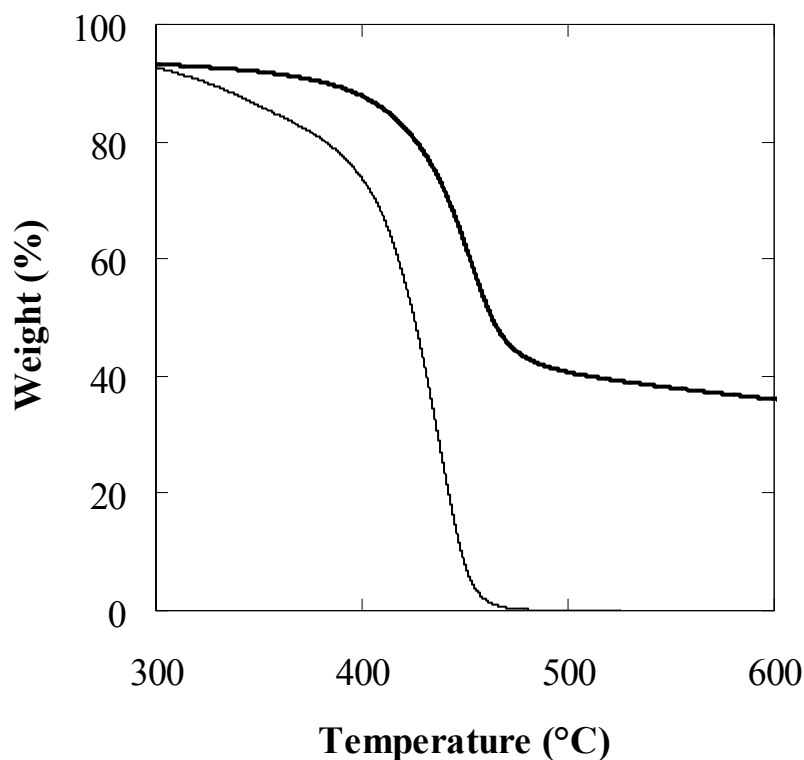


Fig. 2 TGA curves of polyamide 6 (thin line) and polyamide 6 with 50 wt.-% of coal (thick line)

It is evident that the decomposition of polyamide 6 starts at lower temperature in the presence of coal. The reason is that the main reaction is ϵ -caprolactam formation through a cyclic rearrangement reaction (Bockhorn et al., 1999), which is promoted by reaction water and hydrogen from the thermal degradation of coal. Due to this the decomposition temperature was lowered by about 15 °C.

The thermal decomposition of polyamide 6 and polyamide 6-coal mixtures were further studied by TGA. The temperature of maximum decomposition (T_{\max}), the maximum rate of decomposition (w_{\max}), and the percentage of the reacted mixture were measured. Typical courses of decomposition are pictured in Fig. 2. Results are summarized in Table 3.

From the data in Table 3 it follows that the presence of coal influenced the T_{\max} and w_{\max} . It was found that the T_{\max} of polyamide 6 alone was significantly lower than that obtained for polyamide 6 with coal, on the contrary, the w_{\max} of polyamide 6 alone was much higher in comparison with values obtained for polyamide 6-coal mixtures. Further, the amount of reacted mass decreased linearly with an increasing amount of coal in the mixture. All these changes were due to semicoke formation, because in the range of about 350 – 500 °C the thermal degradation of coal proceeds, and gas (mainly hydrogen, methane and carbon oxides), reaction water and tar are evolved. Simultaneously polycondensation reactions of aromatic structures of tar occurs and semicoke structures are developed. Semicoke is then formed in the range of about 500 – 750 °C. Practically all polyamide 6 is decomposed to ϵ -caprolactam. Because water plays an important role in hydrolyzing of amide linkages (Katorzhnov and Strepikheev, 1958), kinetics of decomposition was investigated.

Kinetics of reactions of polyamide 6 with coal were evaluated by the Model Free Kinetics and TGA Decomposition Kinetics. The conversion time (for 90 % of conversion) and the parameters of Arrhenius plot

were calculated. Results are showed in Table 4. From the data in Table 4 it follows that the conversion time was much more lower with 40–50 wt.-% of coal in the mixture in comparison with that for polyamide 6 alone. Apparent reaction order increased from 0.7 (polyamide 6 alone) up to 1.7 (50 wt.-% of coal in the mixture). It means that reactions between polyamide 6 coal degradation products occur. It was proved that ϵ -caprolactam is a main product of polyamide 6 decomposition under low-temperature conditions (>92 %, beside the cyclic dimer – 4 % and other compounds – 4 %) (Bockhorn, Hornung A., Hornung U. and Weichmann, 1999). It is highly probable that an acid hydrolytic scission of the amide linkage takes place, because coal is a strong hydrogen donor (content in hydrogen 5.5 %, Table 1) and reaction water from coal degradation is formed. Moreover, water from polymer is present. As the result, the conversion times were much more lower with 40 – 50 wt.-% of coal in the mixture, because formation of ϵ -caprolactam is catalyzed.

With high contents of coal in the mixture (60 – 70 wt.-%) the conversion time of copyrolysis increased, as was observed at the temperature of 440 °C (Table 4). The reason is that degradation of coal prevails and influences the conversion time which can be very high with high contents of coal, in another words, with high content of coal the conversion time is higher due to polycondensation reactions of coal tar structures.

At higher temperatures (over 500 °C) carbon monoxide, carbon dioxide, methane, hydrocarbons C_2 – C_4 , ammonia, hydrogen and ϵ -caprolactam were detected during pyrolysis of polyamide 6. Under high-temperature conditions of copyrolysis it can be expected that content in carbon oxides increase with an increasing content of polyamide 6 in the mixture, because formation of CO and CO_2 is very sensitive to thermal attack (Kaminsky, 2002). In this connection we compared the composition of gas obtained under

Table 4 TGA of decomposition of polyamide 6 in the presence of coal at the temperature of 440 °C. Degree of conversion 90 %, the conversion time was calculated for heating rates of 5, 10, 15 and 20 °C min⁻¹ in the temperature range of 350–550 °C (Model Free Kinetics). n – apparent reaction order; E_A , ln Z – parameters of the Arrhenius plot (TGA Kinetics)

Mixture (wt.-% PA6 / wt.-% coal)	Conversion time (min)	n	E_A (kJ.mole ⁻¹)	ln Z
100/0	154.0	0.7	197.7	28.5
60/40	55.9	1.4	271.1	40.3
50/50	85.6	1.7	274.7	41.0
40/60	249.1	3.0	291.4	44.6
30/70	3490.2	3.8	245.9	37.3
0/100	10865.6	-	-	-

Table 5 Composition of gas obtained from pyrolysis of coal alone and copyrolysis of coal with waste polyamides (vol.-%)

Sample	CH ₄	ΣC ₂	ΣC ₃	ΣC ₄	N ₂	CO	CO ₂	H ₂	Sum
Coal	24.8	1.2	0.8	0.5	1.6	6.4	1.7	62.5	99.5
Coal + 60 % polyamides	24.9	3.1	1.1	0.8	0.9	11.1	8.2	48.9	99.0

Table 6 Mass balance of copyrolysis of coal with waste polyamides (wt.-%)

Feedstock	Coke	Tar	Water	Gas	Ammonia and Losses
Coal	72	10	5	10	3
Coal + 60 % polyamides	40	25	9	22	4

high-temperature conditions on a laboratory unit during pyrolysis of coal alone and copyrolysis of coal with 60 wt.-% of waste polyamides (Table 5). As the data in Table 5 prove, amounts of CO and CO₂ were higher in the case of copyrolysis.

Coal tars obtained under high-temperature conditions from bituminous coal differ from those obtained from copyrolysis of polyamide 6 with coal. Due to formation of a significant amount of ε-caprolactam a higher yield of liquid products can be expected in this case in comparison with that from pyrolysis of coal alone. Liquid aliphatics, benzene, toluene, xylenes, styrene, ethyl benzene, indene, naphthalene, stable oils and ε-caprolactam were detected by capillary GC in the case of copyrolysis. In this connection we compared the yields of tar and gas obtained on a laboratory unit during pyrolysis of coal alone and copyrolysis of coal with 60 wt.-% of waste polyamides. As the data in Table 6 prove, these yields were higher in the case of copyrolysis.

CONCLUSION

Kinetic parameters of thermal reactions of coal with polyamide 6 by DSC and TGA were determined, because they yields valuable informations about copyrolysis. In the range of 350 – 500 °C the thermal degradation of coal proceeds, simultaneously, the decomposition of polyamide 6 occurs. The endothermal decomposition of polyamide 6 was promoted by water and hydrogen from the coal degradation, because coal is a strong H-donor. That is why the conversion time of polyamide 6 decomposition was lower in the presence of 40 – 50 wt.-% of coal. With high content of coal the conversion time was higher due to polycondensation reactions of coal tar structures. Under high-temperature conditions the yields of gas and tar from copyrolysis are higher in comparison with those for pyrolysis of coal alone. Also gas and tar compositions are changed. As oils from pyrolysis of

polymers are often unstable, oils from copyrolysis with coal are always stable.

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