

# Vitrinite reflectance property change during heating under inert conditions

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## Abstract

The aim of the study was to determine optical properties of vitrinite, subjected to temperatures within the range of 400–1200 °C for durations of 1–7 h, in an argon atmosphere. The samples of vitrinite concentrate (Vt content 90%,  $R_r = 1.17\%$ ) were inserted in the furnace at room temperature and subjected to a heating rate of 60 °C/min.

To assess the effects of the experiment, random reflectance as well as apparent maximum and minimum reflectances of vitrinite were measured on the raw and thermally treated concentrates. Employing the method and computer programme of W.E. Kilby, the true maximum, intermediate and minimum reflectances of vitrinite as well as reflectance anisotropy and Reflectance-Indicating Surface (RIS) shapes were evaluated.

Transformation of vitrinite subjected to heating is influenced more by the increase of temperature than the time applied. During the plastic stage (400–500 °C), vitrinite is subjected to substantial chemical and physical alteration. It is manifested by chemical decomposition, significant mass loss and mesophase appearance. Porosity, relief, reflectance and bireflectance of the vitrinite grains increase with heating. At the temperature of 1200 °C, random vitrinite reflectance reaches 6.62% with bireflectance of 3.46%. Mesophase at 1200 °C was characterised by mean reflectance equal to 9.25% and a bireflectance of 13.35%.

The reflectance character of vitrinite changes from biaxial negative into biaxial positive–negative. However, the original RIS shape, resulting from the tectonic regime during the main phase of coalification, is not fully transformed until heated to 1200 °C. Reflectance character of mesophase is consistently biaxial negative. The internal structure of mesophase is thought to be better organised than the internal structure of vitrinite.

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## 1. Introduction

Coalification results in rebuilding of the molecular structure of organic substances under the influence of increasing temperature and pressure. Increased temperature results in increased reflectance values, whereas

the pressure regime controls the internal structure of vitrinite. Reflectance anisotropy is determined mostly by alignment of aromatic lamellae in response to stress regimes during coalification (Wege, 1954; Cook et al., 1972; Hower and Davis, 1981a,b; Levine and Davis, 1984, 1989a,b; Kilby, 1985; Murchison, 1991). Reflectance anisotropy is graphically depicted by Reflectance-Indicating Surface (RIS; optical indicatrix), an ellipsoid, axes of which are proportional to the maximum ( $R_{max}$ ), intermedi-

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ate ( $R_{\text{int}}$ ) and minimum ( $R_{\text{min}}$ ) reflectance values (Hevia and Virgos, 1977). The relationships between the axes define the reflectance character of vitrinite. Taking into consideration RIS shape and orientation of its principle axes, it is possible to draw conclusions about tectonic processes, which took place during coal metamorphism (Hower and Davis, 1981b; Levine and Davis, 1984, 1989a; Kilby, 1988; Komorek, 1996; Komorek et al., 1997; Pozzi, 1996; Morga, 2000). It was also ascertained that vitrinite from the boundary between low volatile bituminous coal and semianthracite ( $R_r = 1.8\text{--}2.0\%$ ) is characterised by distinct ordering of aromatic lamellae. The lamellae can compose clusters that are 50–100 Å in size (Taylor et al., 1998).

Studies of the influence of temperature and pressure on coal reflectance properties revealed that during short heating times, vitrinite reflectance increases and anisotropy changes begin at temperatures of about 400 °C (Goodarzi and Murchison, 1972; Murchison, 1991). Within the range of 350–500 °C, coal undergoes softening. Highly metamorphosed coals do not soften at any temperature (Jasieńko et al., 1997; Murchison, 1991; Taylor et al., 1998). In the plastic stage, rebuilding and increase of the internal ordering of coal structure occur. The external indication of this process is the formation of mesophase, which is the transitional phase between the liquid and the solid phase. Mesophase is characterised by the formation of circular bodies that grow and aggregate at the cost of the original constituents as temperature rises. This process continues until the anisotropic structure of coke is formed after resolidation. Coke formation occurs at temperatures between 500 and 800 °C, depending on the coal rank (Jasieńko et al., 1997).

The objective of the study was to:

- characterise changes of reflectance, reflectance anisotropy and RIS shape of vitrinite subjected to temperatures between 400 and 1200 °C for times of 1–7 h, in an argon atmosphere; and
- compare reflectance properties of vitrinite and mesophase.

An inert gas was used to eliminate possibility of chemical influence of gases on vitrinite during heating.

## 2. Method

The coal tested in this study was a channel sample, collected from Seam 833/1 (18°38'40"E; 50°20'50"N) within the "Gliwice" mine, in the town of Gliwice (the NW part of the Upper Silesian Coal Basin). It was crushed to a 0.1-mm size fraction and a vitrinite concentrate was obtained by gravity separation (mixture of CCl<sub>4</sub> and toluene). The 300 mg samples of vitrinite concentrate were heated in a Carbolite pipe oven at temperatures of 400, 500, 600, 800, 1000 and 1200 °C for times of 1, 3, 5 and 7 h, in an argon atmosphere. The gas flow was 4 l/min. Heating commenced at room temperature and increased at the rate of 60 °C/min in furnace. After heating, the samples were prepared as polished grain mounts for microscopic examination in the reflected light.

To examine the effects of heating, the following analyses were carried out:

- Petrographic examination of vitrinite concentrate.
- Measurements of random reflectance as well as apparent maximum and minimum reflectances of vitrinite and mesophase.

Petrographic composition was determined according to ISO-7404-3. All reflectance measurements were carried out according to Polish Standard PN-92/G-04524 and ISO 7404-5/1984, with the use of a Zeiss microscope Axioskop, in immersion oil ( $n_o = 1.518$  at 23 °C). From each of the samples, a minimum of 100 readings for both vitrinite and mesophase (if occurs) were taken.

Employing the method and computer programme of Kilby (1985, 1988), the true maximum, intermediate and minimum reflectances of vitrinite and mesophase, as well as their reflectance anisotropy and RIS shapes were evaluated.

Relative mass loss of the vitrinite concentrate during heating was also determined. This was done according to the formula:

$$\frac{m_1 - m_2}{m_1 - m_0}$$

where:  $m_0$ —mass of a quartz boat;  $m_1$ —mass of a quartz boat and vitrinite concentrate before heating;

$m_2$ —mass of a quartz boat and vitrinite concentrate after heating.

### 3. Results

Maceral analysis showed that the vitrinite concentrate contained 90% vitrinite, 8% inertinite and 2% liptinite. Random reflectance of raw vitrinite ( $R_{vr}$ ) was 1.17% (standard deviation  $s_r=0.06\%$ ) (Table 1). The values of the true maximum ( $R_{vmax}$ ), intermediate ( $R_{vint}$ ) and minimum ( $R_{vmin}$ ) reflectances were 1.28%, 1.16% and 1.01%, respectively. Bireflectance ( $R_{vbi}$ ) was 0.27%. Vitrinite had a slightly negative biaxial RIS shape.

The study shows that vitrinite transformation during heating is influenced more by the temperature increase than the duration of heating (Figs. 1–4; Table 1). As the relationships are similar for all heating times, only the data dealing with the 1-h heating interval will be discussed.

With temperature increase, vitrinite shows gradual chemical decomposition resulting in the increase of pore size and quantity, as well as an increase in the relief of the grains (Fig. 5). At 500 °C, mesophase formation begins. Mesophase bodies at first are small and circular (Fig. 5d–f). At 800 °C, they begin to aggregate and constitute the major part of the grain (Fig. 5g,h). The product of continued heating is highly porous coke, characterised by the occurrence of anisotropic domains (Figs. 5i–l).

In general, as the temperature of heating increases, the vitrinite reflectance values increase. However, at 400 °C, random reflectance of vitrinite ( $R_{vr}$ ) is even lower (1.08%) than that measured on the raw concentrate (1.17%). Taking into consideration standard deviation values for the two samples, the difference is negligible in statistical terms.

At 500 °C, however, the reflectance increases rapidly, and is accompanied by significant concentrate mass loss (17.42%). With further temperature increase, random reflectance ( $R_{vr}$ ) as well as the true maximum

Table 1  
Optical properties of vitrinite in raw concentrate and after heating

Sample	$T$ [°C]	$t$ [h]	$R_{vr}$ [%]	$S_{vr}$ [%]	$R_{vmax}$ [%]	$R_{vint}$ [%]	$R_{vmin}$ [%]	$R_{vbi}$ [%]	$R_{vmean}$ [%]	$R_{vst}$
2	–	–	1.17	0.06	1.28	1.16	1.01	0.27	1.15	–3.67
2.1	400	1	1.08	0.05	1.20	1.11	0.93	0.27	1.08	–10.89
2.2	400	3	1.06	0.05	1.17	1.07	0.95	0.22	1.06	–2.20
2.3	400	5	1.09	0.06	1.25	1.10	0.96	0.29	1.10	1.14
2.4	400	7	1.06	0.06	1.18	1.04	0.90	0.28	1.04	0.00
2.5	500	1	1.48	0.10	1.61	1.49	1.37	0.24	1.49	0.00
2.6	500	3	1.67	0.13	1.80	1.62	1.41	0.39	1.61	–2.54
2.7	500	5	2.05	0.17	2.34	2.04	1.70	0.64	2.03	–5.43
2.8	500	7	2.19	0.17	2.54	2.24	1.94	0.60	2.24	0.00
2.9	600	1	2.79	0.26	3.08	2.70	2.33	0.75	2.70	0.00
2.10	600	3	3.07	0.31	3.63	3.12	2.48	1.15	3.08	–4.31
2.11	600	5	2.82	0.27	3.63	2.92	2.25	1.38	2.93	0.60
2.12	600	7	3.42	0.27	4.03	3.33	2.65	1.38	3.34	0.60
2.17	800	1	4.46	0.52	5.88	4.48	3.48	2.40	4.61	5.50
2.18	800	3	5.42	0.36	6.44	5.46	4.23	2.21	5.38	–4.50
2.19	800	5	5.71	0.52	6.76	5.46	4.03	2.73	5.42	–1.57
2.20	800	7	5.68	0.42	6.88	5.67	4.46	2.42	5.67	0.00
2.25	1000	1	6.13	0.56	7.43	6.12	4.95	2.48	6.17	1.80
2.26	1000	3	6.14	0.68	7.74	6.24	4.55	3.19	6.18	–2.02
2.27	1000	5	5.65	0.61	6.90	5.70	3.72	3.18	5.44	–8.06
2.28	1000	7	6.52	0.66	7.98	6.51	4.94	3.04	6.48	–1.14
2.33	1200	1	6.62	0.90	8.36	6.66	4.90	3.46	6.64	–0.53
2.34	1200	3	6.54	0.90	8.45	6.35	5.00	3.45	6.60	7.15
2.35	1200	5	6.56	0.88	8.40	6.65	4.97	3.43	6.67	0.67
2.36	1200	7	6.04	1.51	8.55	6.45	4.50	4.05	6.50	1.22

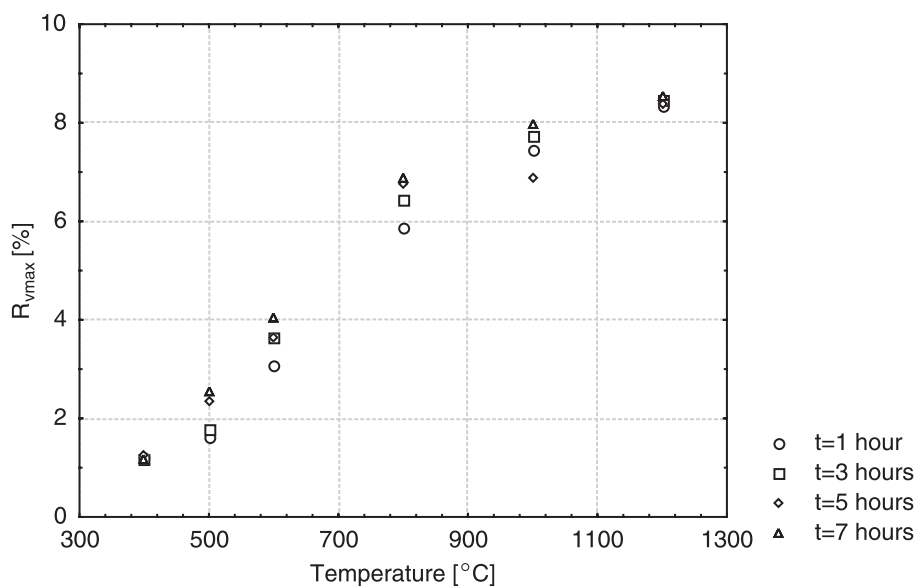


Fig. 1. Relationship between the true maximum reflectance of vitrinite ( $R_{vmax}$ ) and temperature ( $T$ ).

( $R_{vmax}$ ), intermediate ( $R_{vint}$ ) and minimum ( $R_{vmin}$ ) reflectances of vitrinite progressively rise (Fig. 1, Table 1), but at different rates, which results in the gradual increase of bireflectance values ( $R_{vbi}$ ) (Fig. 6).

At 600 °C,  $R_{vr}$  is 2.79%, at 800 °C it is 4.46%, and at 1000 °C, it has increased to 6.13%. Beyond 1000 °C, the true minimum reflectance ( $R_{vmin}$ ) becomes stable. Finally, at 1200 °C, random reflectance equals 6.62%

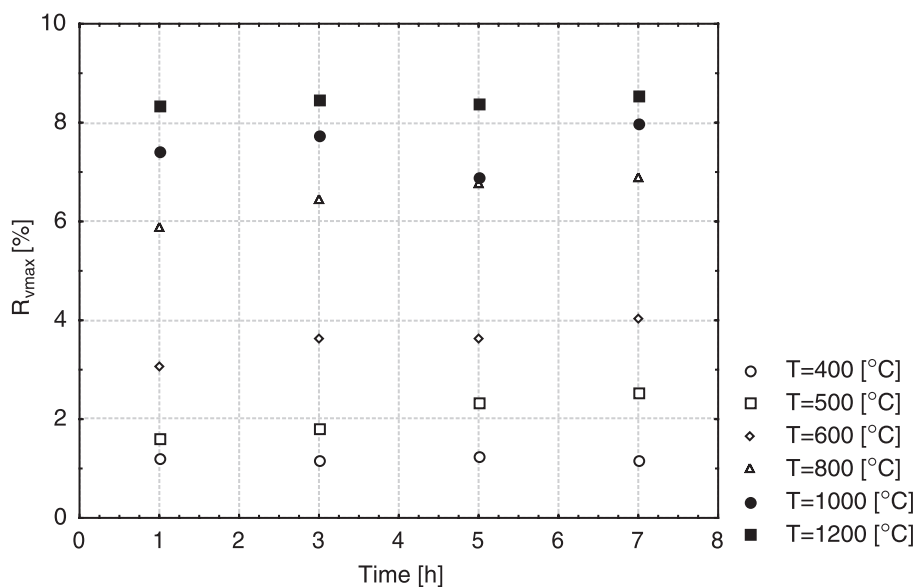


Fig. 2. Relationship between the true maximum reflectance of vitrinite ( $R_{vmax}$ ) and time ( $t$ ).

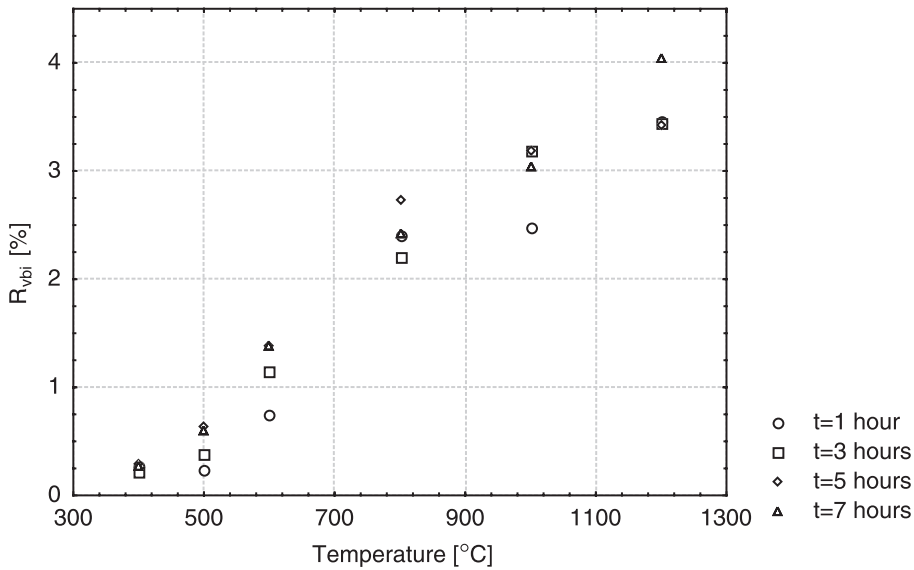


Fig. 3. Relationship between vitrinite bireflectance ( $R_{vbi}$ ) and temperature ( $T$ ).

and the true maximum, intermediate and minimum reflectance values are 8.36%, 6.66% and 4.90%, respectively. Bireflectance reaches 3.46% (Figs. 3 and 4) and mass loss is 29.50%.

Mesophase bodies at 500 °C are characterised by a high mean reflectance ( $R_{mmean} = 2.35\%$ ) and substan-

tial bireflectance ( $R_{mbi} = 2.77\%$ ) (Table 2). Alteration of mesophase is also affected more by the increase of temperature than the time of heating (Figs. 7–10). The true maximum ( $R_{mmax}$ ) and intermediate ( $R_{mint}$ ) reflectances rise much faster than the true minimum reflectance ( $R_{mmin}$ ).  $R_{mmin}$  is consistently lower than

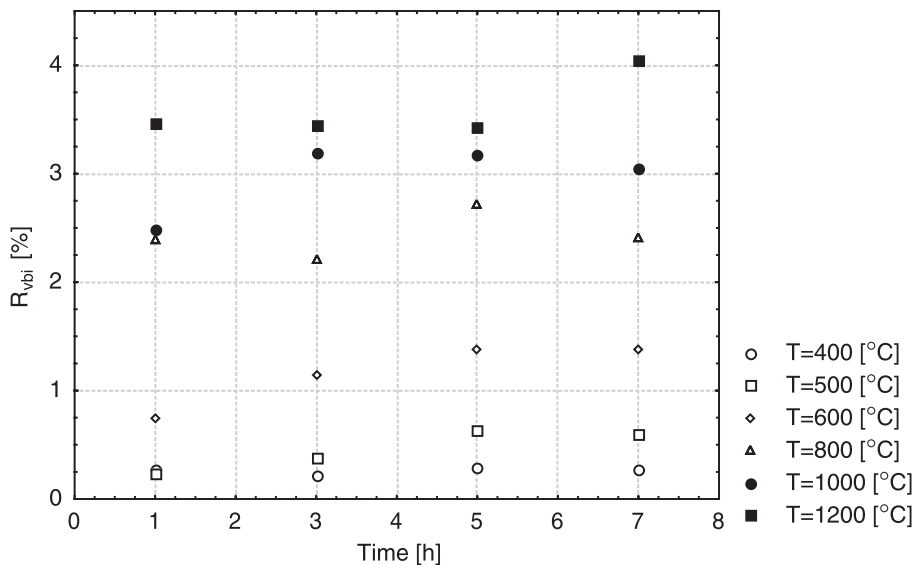


Fig. 4. Relationship between vitrinite bireflectance ( $R_{vbi}$ ) and time ( $t$ ).

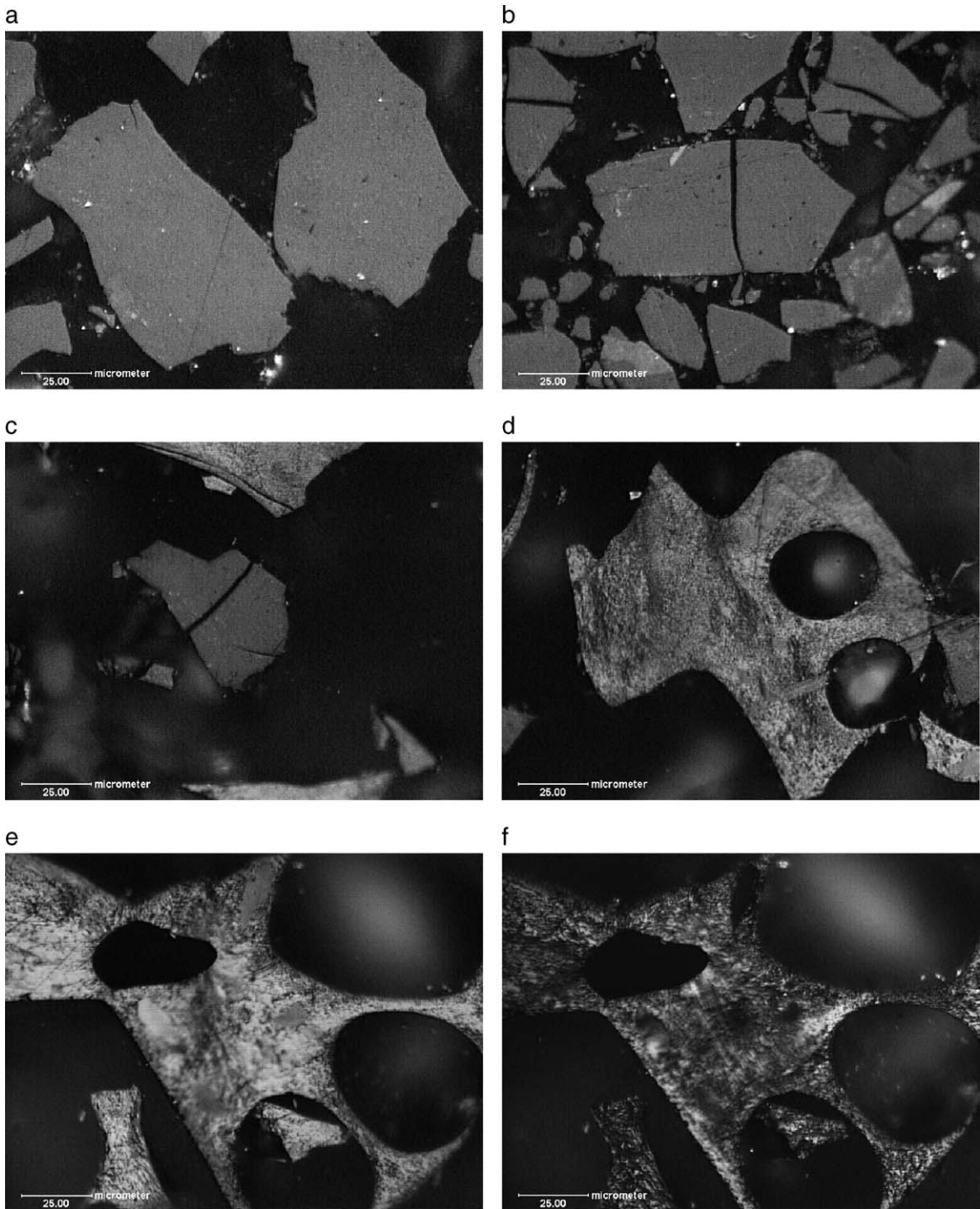


Fig. 5. Different stages of vitrinite alteration and mesophase formation (1-h heating time). (a) The raw concentrate; (b, c) vitrinite grains with no noticeable alteration (b—400 °C; c—500 °C; parallel nicols); (d-l) altered and strongly altered grains with mesophase bodies, which gradually aggregate (d—500 °C; e—600 °C; g—800 °C; i—1000 °C; k—1200 °C; parallel nicols; f—600 °C; h—800 °C; j—1000 °C; l—1200 °C; crossed nicols). In j and l, anisotropic domains can be observed (white and dark zones).



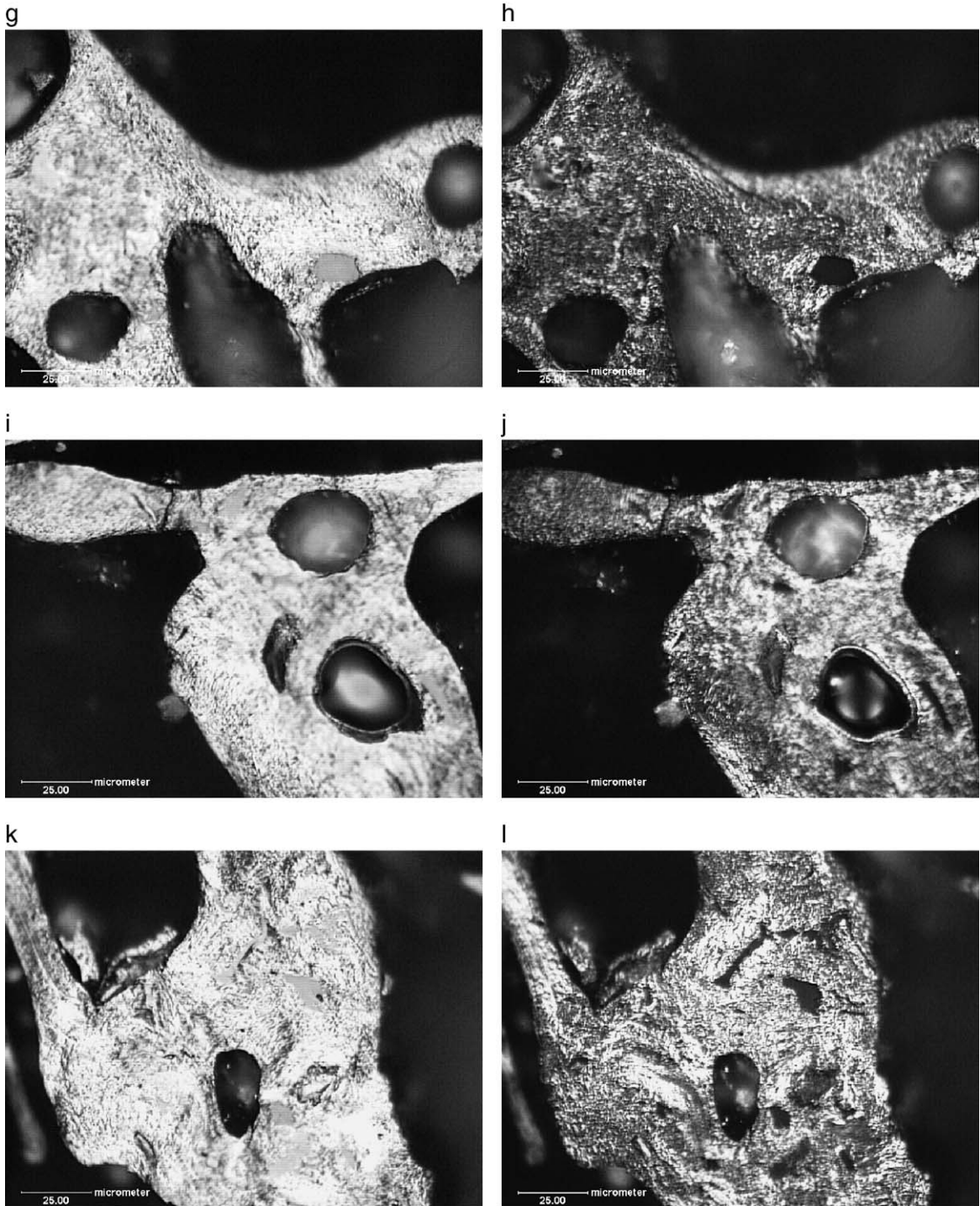


Fig. 5 (continued).

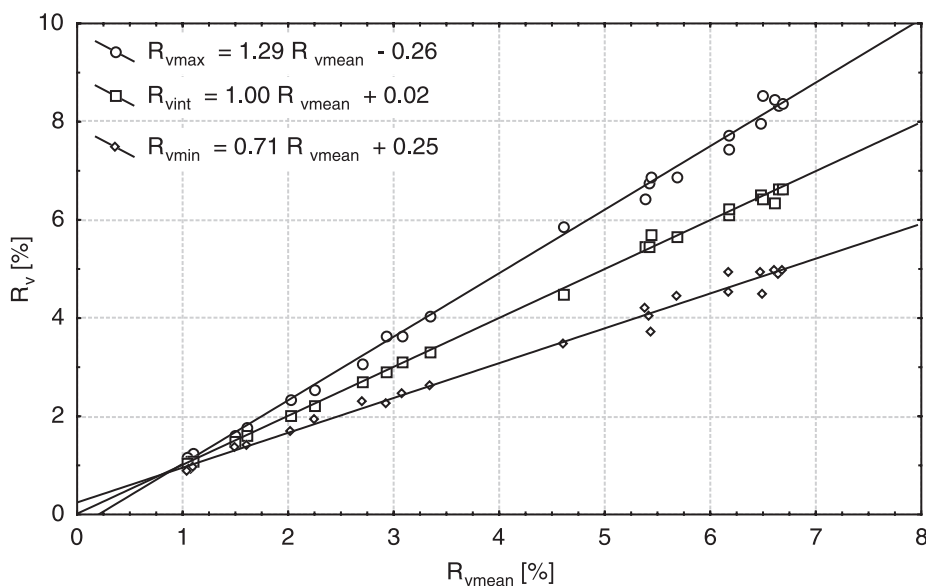


Fig. 6. Relationship between the true maximum, intermediate as well as minimum reflectances, and the coal rank, described by mean reflectance, for vitrinite  $R_{vmean}$ , where  $R_{vmean} = (R_{vmax} + R_{vint} + R_{vmin})/3$ .

the corresponding  $R_{vmin}$  value and shows a relatively low rate of increase (Fig. 11). Due to such intense anisotropy and mosaic structure in mesophase, the true maximum ( $R_{mmax}$ ) or mean ( $R_{mmean}$ ) reflectances

proved to be more precise parameters for the measurement of the degree of thermal alteration than random reflectance. At 1200 °C, the true maximum, intermediate and minimum reflectances reached 15.00%,

Table 2  
Optical properties of mesophase

Sample	$T$ [°C]	$t$ [h]	$R_{mmax}$ [%]	$R_{mint}$ [%]	$R_{mmin}$ [%]	$R_{mbi}$ [%]	$R_{mmean}$ [%]	$R_{mst}$
2.5	500	1	3.71	2.41	0.94	2.77	2.35	-2.09
2.6	500	3	4.01	2.61	1.13	2.88	2.58	-1.03
2.7	500	5	4.20	2.65	0.50	3.70	2.45	-5.35
2.8	500	7	4.35	2.75	0.70	3.65	2.60	-4.07
2.9	600	1	5.76	3.20	0.48	5.28	3.15	-1.00
2.10	600	3	6.08	3.68	0.60	5.48	3.45	-4.07
2.11	600	5	6.00	3.30	0.36	5.64	3.22	-3.30
2.12	600	7	6.88	4.24	0.56	6.32	3.89	-5.43
2.17	800	1	10.05	6.45	0.90	9.15	5.80	-7.01
2.18	800	3	12.02	7.83	1.08	10.94	6.98	-7.71
2.19	800	5	13.20	9.44	0.90	12.30	7.85	-12.70
2.20	800	7	13.05	8.55	1.31	11.74	7.64	-7.71
2.25	1000	1	15.45	10.35	0.90	14.55	8.90	-9.93
2.26	1000	3	15.15	10.20	1.20	13.95	8.85	-9.95
2.27	1000	5	14.55	8.84	1.35	13.20	8.25	-4.50
2.28	1000	7	16.05	10.80	1.50	14.55	9.45	-9.13
2.33	1200	1	15.00	11.10	1.65	13.35	9.25	-13.49
2.34	1200	3	15.15	10.65	1.80	13.35	9.20	-10.65
2.35	1200	5	15.90	11.40	1.65	14.25	9.65	-12.01
2.36	1200	7	15.60	10.65	1.50	14.10	9.25	-9.76



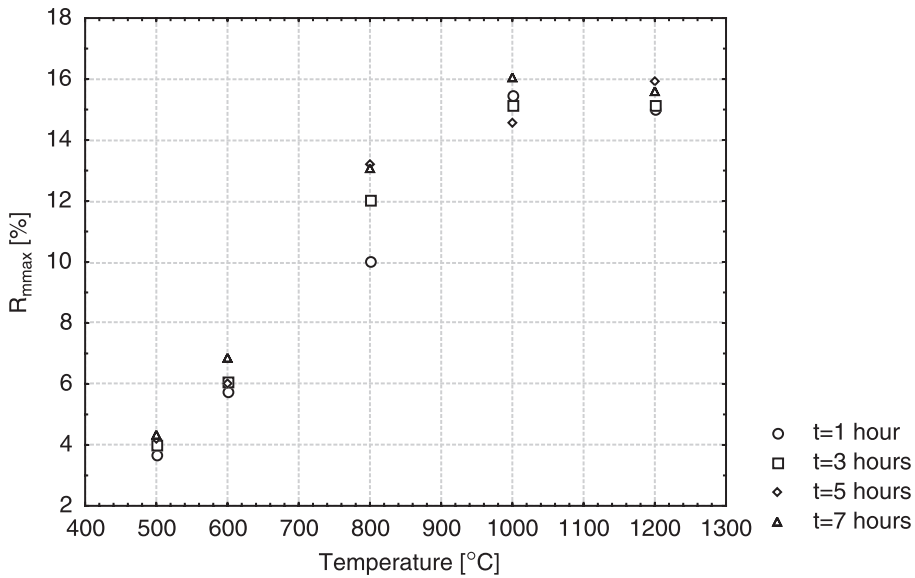


Fig. 7. Relationship between the true maximum reflectance of mesophase ( $R_{mmax}$ ) and temperature ( $T$ ).

11.10% and 1.65%, respectively. The mean reflectance equaled 9.25% and the bireflectance reached 13.35% (Table 2; Figs. 9 and 10).

Taking into consideration the RIS style ( $R_{vst}$ ), it was determined that the RIS shape of vitrinite changes from biaxial negative into biaxial positive–negative

with the temperature increase. Kilby’s diagrams for the samples heated at the temperature of 500 °C and partly 600 °C are characterised by somewhat chaotic distribution of the points, which is thought to be related to disordering of the molecular structure of vitrinite during the plastic stage. Diagrams prepared

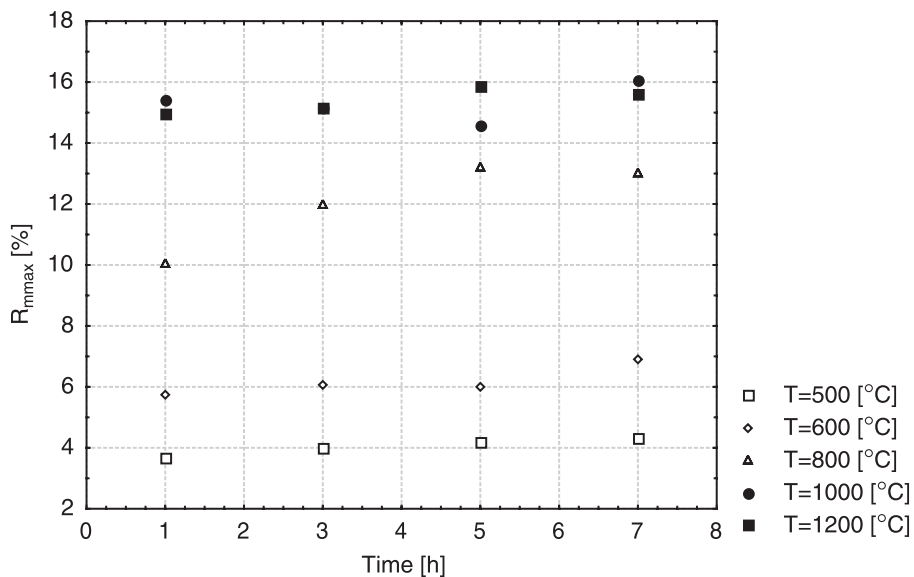


Fig. 8. Relationship between the true maximum reflectance of mesophase ( $R_{mmax}$ ) and time ( $t$ ).

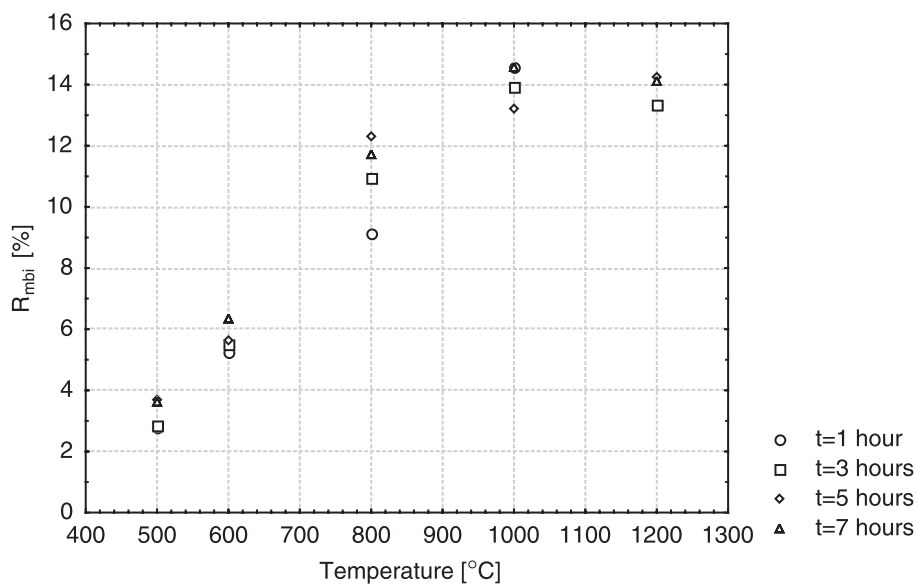


Fig. 9. Relationship between mesophase bireflectance ( $R_{mbi}$ ) and temperature ( $T$ ).

for the samples heated to higher temperatures are much more unequivocal, which suggests increase of the degree of ordering of vitrinite structure during resolidification. Optical character, however, does not change profoundly beyond the plastic stage.

Optical character of mesophase is consistently biaxial negative, but the RIS style ( $R_{mst}$ ) changes progressing towards a uniaxial negative RIS character with increased heating. All Kilby's diagrams for mesophase are explicit, at all temperature levels. This

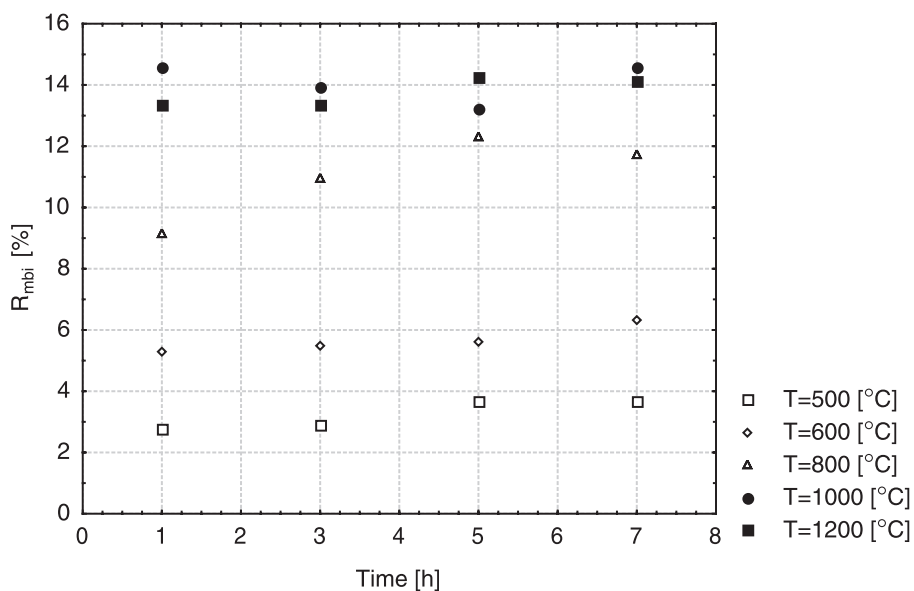


Fig. 10. Relationship between mesophase bireflectance ( $R_{mbi}$ ) and time ( $t$ ).

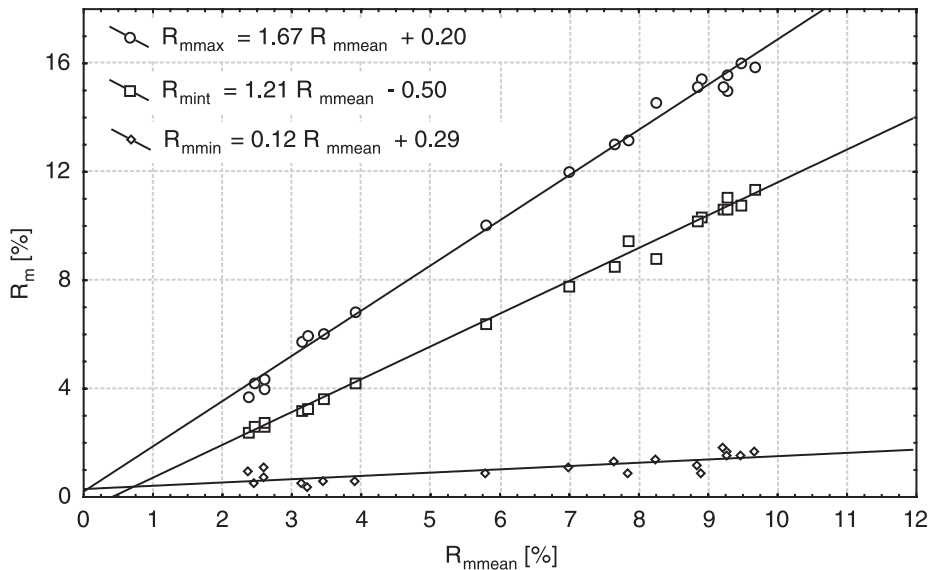


Fig. 11. Relationship between the true maximum, intermediate as well as minimum reflectances, and the coal rank, described by mean reflectance, for mesophase  $R_{m\text{mean}}$ , where  $R_{m\text{mean}} = (R_{m\text{max}} + R_{m\text{int}} + R_{m\text{min}})/3$ .

suggest that the internal structure of mesophase is better organised than the structure of vitrinite.

#### 4. Conclusions

The results of this investigation show that the transformation of vitrinite by heating is influenced more by the increase of temperature than the duration of heating.

At the temperature between 400 and 500 °C, during the plastic stage, vitrinite is subjected to substantial chemical and physical alteration. It is manifested by chemical decomposition, connected with significant mass loss and mesophase appearance. Porosity and optical relief of the grains increase. Reflectance and bireflectance values grow rapidly and RIS character changes. It was also ascertained that the original vitrinite shape of RIS, resulting from the tectonic regime, in place during the main phase of coalification, was not fully transformed by heating to 1200 °C. Vitrinite and mesophase show different behaviours during the experiment. It is thought that structural changes in mesophase, particularly the development and ordering of aromatic lamellae, are more rapid than in vitrinite. The internal structure of

mesophase is probably better organised than the vitrinite structure for the same temperature of heating. This conclusion, however, could be confirmed by other methods, micro-FTIR analysis, for example.

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