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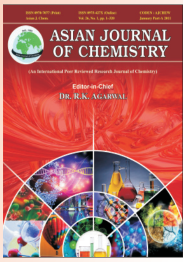

Surface Modification of Coal Powder by Using Different Coupling Agent†

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To compare the superficial capacity of coal powder, the coupling agents such as γ-methacryloxypropyl trimethoxy silane (KH-570), vinyltrimethoxysilane (SG-Si171) and di(dioctylpyrophosphato)ethylene titanate (NDZ-311) were used as modifiers to modify its surface activity. The structural changes and properties of the unmodified and modified coal powder were characterized by Fourier transform infrared spectroscopy, sedimentation stability experiment, thermogravimetric analysis (TGA) and contact angle measuring instrument. The results showed that the coupling agent bonds were tightly coated onto the surface of coal powder and formed an organic coating layer. Thermogravimetric analysis and contact angle measuring instrument indicated that coupling agent molecules were absorbed or anchored on the surface of coal powder particles, which favoured hindering the aggregation of coal powder particles.

Keywords: Coal powder, Coupling agent, Surface modification, Organic coating layer.

INTRODUCTION

Coal is the complex substance with high carbon content. The molecules of it are composed of different aromatic and aliphatic structural units of ether bonds, aliphatic carbon-carbon bonds, aromatic bonds and other bridge bonds linking. The electrophilic active sites of the aromatic and aliphatic structures can react as substituent, alkylation, acylation[1]. The strong hydrogen bonds between aromatic and aliphatic macromolecules can be opened and the van der Waals forces are lowered by Friedel-Crafts alkylation reaction under mild conditions, while it has little effect on the structure. Therefore, Friedel-Crafts alkylation reaction is often used as surface modification of coal powder[1-3]. During the reaction, each unit of three-dimensional structure in the coal is connected by the aliphatic hydrocarbon chains or ether bonds and most of oxygen existed in the coal as hydroxyl. Silanols or titanate on the coupling agent, after hydrolysis, can graft with surface hydroxyl of coal powder particles[4-6]. The grafting reaction can improve the performance of bond properties between the powder and polymer material.

In this work, in order to compare the surface activity of coal powder, KH-570, SG-Si171 and NDZ-311were used to modify coal powder. On the one hand, silanols or titanate as the side group [-Si–OCH_3 or -Ti-OO-] on the main chain of coupling agent may react with -OH which are on the surface of coal powder particles containing active hydrogen. On the other hand, the main chain of coupling agent has the similar structure or polarity with some polymers such as BR, NR, NBR, *etc*. and provides them with great compatibility.

The dispersion of coal powder particles as well as the stability mechanism of colloidal dispersion was discussed in anhydrous ethanol. The surface hydrophobicity and efficiency of coupling agent used as a modifier were also studied.

EXPERIMENTAL

Native coal with M_{ad} 1.7 %; A_d 9.96 %; V_{daf} 32.4 %; $F_{C,d}$ 59.85 % was obtained from XinJi Coal Preparation Plant of Huainan (Anhui, China). γ-Methacryloxypropyl trimethoxy silane (KH-570), vinyltrimethoxysilane (SG-Si171) and di(dioctylpyrophosphato) ethylene titanate (NDZ-311) were purchased from Nanjing Shuguang Chemical Group Co., Ltd. in China. Other reagents were of analytical grade and used as received.

Surface modification of coal powder: Before modification, native coal powders were dried at 80 ºC in a vacuum oven for 10 h to remove the adsorbed moisture on their surface. Then, 1 g native coal powders were dispersed in 150 mL anhydrous ethanol with the aid of the ultrasonic agitation and an amount of coupling agent (10 wt % of coal powder) was

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added into the flask. The reaction was refluxed at 70 °C for 5 h with agitation. After the reaction, the product was filtered and washed using anhydrous ethanol for some time and dried under vacuum for 10 h.

Instrumental analysis: The structures and properties of the modified coal powder were characterized by using FTIR, TGA and CAMI. The photos of dispersion stability on coal powder in anhydrous ethanol were obtained by digital camera. FTIR spectra of coal powder were carried out on spectrometer (Nicolet Co., Nexus-870, USA). The content of intercalated coupling agent was determined by TGA on thermalanalyzer (SDT 2960, USA), the samples were scanned from 30-900 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Surface hydrophilicity of coal powder was investigated by CAMI (Kino Co., SL 200C, USA) at room temperature, a content of water was dropped on the sample surface and the contact angle was taken.

Dispersion stability of coal powder in anhydrous ethanol: Sedimentation stability experiment was achieved in sedimentation tubes. Typically, 0.1 g coal powder particles were dispersed in 100 mL anhydrous ethanol at room temperature. After a definite time, the stability of dispersion was estimated from photographs of dispersed coal powder particles after standing.

RESULTS AND DISCUSSION

FTIR analysis: It can be seen from Fig. 1(c) of modified coal powder with SG-Si171, 1035 cm^{-1} and 1100 cm^{-1} correspond to Si-O-C absorption bands, while 1310 cm^{-1} correspond to -Si-CH absorption peak. There are some C=C- in the structure of SG-Si171 modified coal, which are broader and stronger than those in unmodified coal (Fig. 1a). Fig. 1(e) shows FT-IR spectra of modified coal powder with KH-570[7-9]. It can be seen that the detection of strong absorption peak at 1720 and 1310 cm^{-1} are attributed to -C=O and Si-CH- groups of the presence of KH-570, respectively. The peak at 1030 and 1150 cm^{-1} correspond to -Si-O-C absorption bands. After modified by KH-570, the absorption of C=C- in coal powder is intensified. From the FT-IR spectra of modified coal powder with NDZ-311 (Fig. 1g), it can be seen that the absorption at 3000-2800 cm^{-1} belonged to the $-CH_2-$, $-CH_3$ groups of NDZ-311. The Ti-O-C absorption bands are observed at 1150 and 1038 cm^{-1}, which coincide with -Si-O- absorption bands of silane coupling agent[10-12]. These indicate that the surface groups of coal powder have changed from -OH to -Si-O-C or -Ti-O-C. The above results prove that the coupling agents are tightly absorbed on the surface of coal powder particles by chemisorption.

Thermogravimetric analysis: Thermal stability of native coal powder and modified coal powder was measured by TGA (Fig. 2). As shown in Fig. 2(a), the decomposition temperature of native coal powder begins at 165 °C and the continuous mass loss can be seen from 165-845 °C. This may be due to the desorption or decomposition of some organic aromatic and aliphatic functional groups or some physical and chemical adsorption substances, *etc*. So, the main weight loss of the native coal powder is 22.9 % at a high decomposition rate in 400-600 °C stage while in 600-845 °C stage the weight loss is at a relative low decomposition rate[10, 13-15].

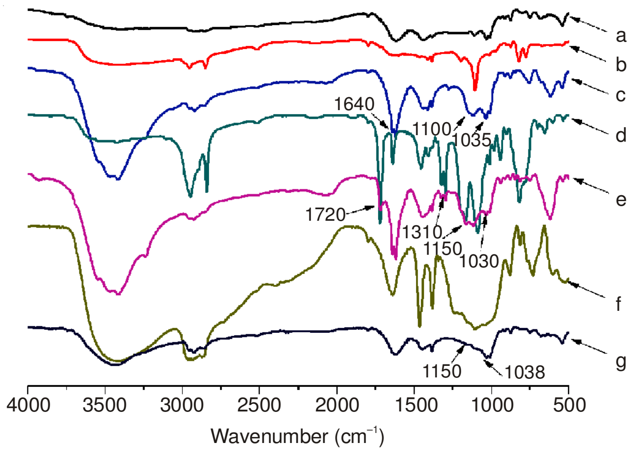

Fig. 1. IR spectra of (a) native coal powder; (b) SG-Si171; (d) KH-570; (f) NDZ-311; modified coal powder with (c)SG-Si171, (e) with KH-570 and (g) with NDZ-311

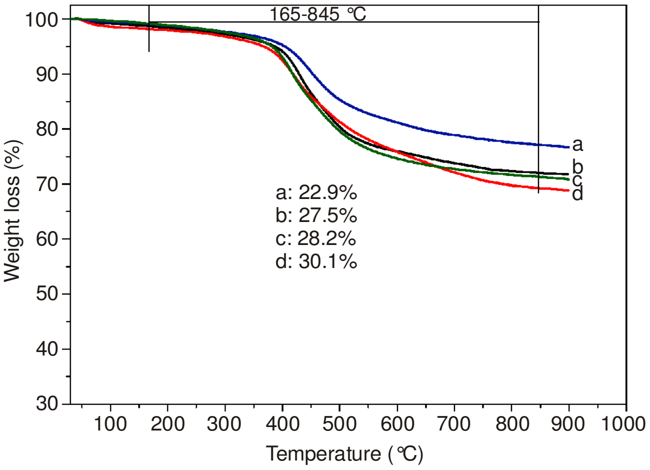

Fig. 2. TGA spectra of (a) native coal powder; modified coal powder with (b) SG-Si171; (c) KH-570 and (d) NDZ-311

Thermal degradation curves of modified coal powder with SG-Si171, KH-570 and NDZ-311 are shown in Fig. 2(b-d), which are similar with Fig. 2(a). But in contrast with Fig. 2(a), the weight losses of Fig. 2(b-d) are 27.5, 28.2 and 30.1 %, respectively. The weight losses of modified coal powder are higher than that of the native coal powder, which is the result of the introduction of the coupling agent. We can get the efficiency of the coupling agent used, which are calculated as following:

$$\text{Using efficiency of SG-Si171} = \frac{27.5\,\% - 22.9\,\%}{10\,\%} 100\,\% = 46\,\%$$

$$\text{Using efficiency of KH-570} = \frac{28.2\,\% - 22.9\,\%}{10\,\%} 100\,\% = 53\,\%$$

$$\text{Using efficiency of NDZ-311} = \frac{30.1\,\% - 22.9\,\%}{10\,\%} 100\,\% = 72\,\%$$

Above analysis showed that using efficiency of modified coal powder with NDZ-311 is the highest while the using efficiency of SG-Si171 is lowest. Therefore, it further illustrates that the coupling agent chains are anchored or grafted on the surface of coal powder.

Analysis of contact angle: Surface hydrophilicity of coal powder particles was investigated by contact angle measurements as shown in Fig. 3. The contact angle of modified coal powder by SG-Si171, KH-570 and NDZ-311 increase from 61.51-71.42°, 89.53° and 96.63°, respectively in water, suggesting the increased surface hydrophobicity and the decreased surface free energy of coal powder. The efficiency of modification with SG-Si171 is inferior to KH-570 and NDZ-311. These changes of the contact angles are likely due to the hydrophobic carbon backbone of coupling agent. The coal powder particles modified with coupling agent can be easily dispersed in polymer materials than native coal powder particles[4,16,17].

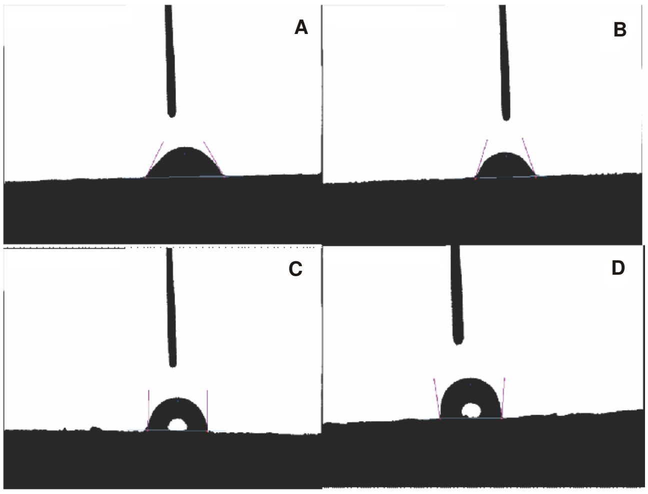

Fig. 3. Contact angle images of (A) native coal powder; modified coal powder with (B)SG-Si171; (C) KH-570 and (D) NDZ-311

Analysis of stability of coal powder dispersion: The dispersion stability of native coal powder and modified coal powder in anhydrous ethanol is shown in Fig. 4. It can be seen that native coal powder and modified coal powder with SG-Si171 have been completely precipitated for 3 days, while modified coal powder with KH-570 and NDZ-311 have a stable colloidal dispersion in anhydrous ethanol. The -OH from coal powder can interacted with $-Si-OCH_3$ or titanate (-Ti-OO-) groups from coupling agents to form (coupling agent-g-coal powder) complex on the surface of powder. Consequently, no matter what reaction occurred, the coupling agents are initially grafted or anchored on the surface of the powder at one or several spots, which fulfills steric hindrance between inorganic particles[4,10,15]. The above factors give rise to the homogeneous dispersion of powder in anhydrous ethanol and maintain a stable colloidal dispersion for a long time. The modified efficiency of KH-570 and NDZ-311 is better than SG-Si171.

Conclusion

Coal powder particles were modified by coupling agent. Results show that coupling agents have been anchored on the surface of coal powder. The modified coal powder particles presented a more stable colloidal dispersion in anhydrous ethanol than that of untreated coal powder and the using efficiency of SG-Si171, KH-570 and NDZ-311 was 46, 53 and 72 %, respectively.

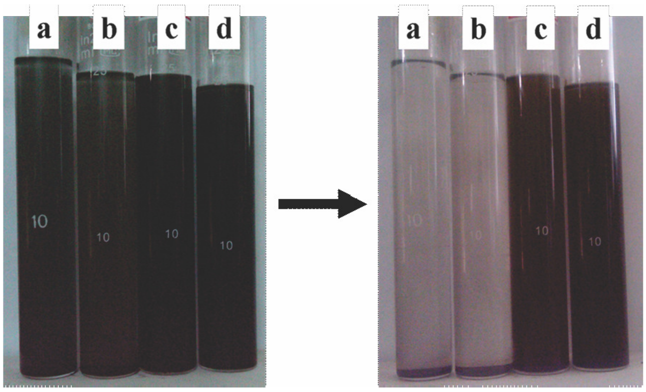

Fig. 4. Photographs of dispersion stabilized of coal powder in anhydrous ethanol by time: (a) native coal powder; modified coal powder with (b) SG-Si171; (c) KH-570; (d) NDZ-311. Left and right are ultrasonic ispersion samples after 10min and 3 days, respectively

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