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THERMAL TREATMENT OF PITCH–POLYMER BLENDS

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Coal-tar pitch was modified by addition of polystyrene, poly(ethylene terephthalate), unsaturated polyester and coumarone-indene resin. The optimum conditions for production of homogeneous binary pitch–polymer blends containing 10% *w*/*w* of the polymer were established. Softening points, contents of toluene and quinoline–insoluble matters and rheological properties of the blends were determined. The yield of solid fraction in semi-coking the blends was also found. The effect of polymers on the coal-tar pitch blend properties was evaluated. Some pitch–polymer blends were then carbonized to carbon sorbents used for purification of water and wastewater.

Keywords: *carbon material, coal-tar pitch, polymer*

Introduction

The coal-tar pitch is a multicomponent mixture of organic compounds, mainly polycyclic aromatic hydrocarbons. Aromatic hydrocarbons are essential components of pitch substances, promoting formation of anisotropic carbon materials [1]. Therefore, it is a good raw material for manufacturing graphite electrodes, carbon anodes and sorbents [2]. Unfortunately, the high content of carcinogenic hydrocarbons, like benzo(a)pyrene [3], limits the use of coal-tar pitch in many areas.

To decrease the content of carcinogenic compounds in the coal-tar pitch, an addition of polymers (including plastics wastes) was formerly recommended, according to results of some studies carried out at the Institute of Chemistry of the Warsaw University of Technology in Płock [4]. In particular, the addition of thermoplastics [5–7], polysaccharides, polyurethanes, epoxy and unsaturated polyester resins [8] as well as some polymer containing wastes was taken into consideration [9, 10]. A considerable decrease in benzo(a)pyrene content in the polymer-modified pitch was observed in the case of unsaturated polyester resins [4].

Addition of a polymer causes the change of chemical composition of pitch and influences the process of its carbonization. The main purpose of the studies presented was to describe the changes of the pitch properties after its modification with polymers.

Experimental

Commercial coal-tar pitch, product of Węglopochodne Ltd., Kedzierzyn Koźle, Pl, (softening point 68.5°C, penetration $8.3\cdot10^{-4}$ m at 50°C, toluene–insoluble matter 20.2%, volatile matter 62.1%) was used. Four polymeric modifiers were selected. Polystyrene (PS), ‘Owispol-S’ grade, average molecular mass 304000, softening point 130°C (by Vicat method), free styrene content below 0.25%. Coumarone-indene resin (CIR), high melting grade, softening point of 114°C (by ring and ball method). Unsaturated polyester resin (UP), ‘Polimal 138’ grade, 40–50% solution of unsaturated polyester in styrene, density 1030–1040 kg m^{-3} at 25°C. Poly(ethylene terephthalate) (PET), wasted mineral water bottles, softening point 257°C (by Vicat method), hardness 12.23 HB (by Brinell method), melt flow index 0.18 g/10 min.

The pitch–polymer blends were prepared by mixing individual components and homogenizing the mixture by stirring at 100–320°C for 0.5–6 h. The homogenization temperature was chosen as low as possible to eliminate the degradation of polymers in the blend. In all cases, the same amount of polymer (10 mass%) was added.

Softening point was determined by the ring and ball method, according to the PN-EN 1427:2001. Penetration was determined at 50°C by the standard method (100 g mass, working time 5 s), according to PN-EN 12591:2004. The content of toluene–insoluble matter (TI) was determined at 110°C (0.05 MPa) (sample mass 3 g, toluene extraction time 1 h), according to the PN-ISO 6376).

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The determination of rheological properties of the blends was carried out in rotating viscometer Rheotest RN 3.1 (Rheotest HAAKE Medingen GmbH Co., Germany) in the cylindrical measurement system. The flow and viscosity curves were determined at 90–150°C.

All blends were carbonized at 520°C for 2 h under argon (flow rate 5 L h^{-1}, heating rate 5°C min^{-1}). The formation of the mesophase structures was followed by polarized light optical microscopy. The semi-coke samples of particle size 0.3–1.2 mm were mounted in epoxy resin, ground, and polished on alumina powders. A Zeiss Neophot 2 microscope equipped with a phase sensitive plate was used for qualitative observations of optical texture and taking photographs of selected areas. Anisotropic content of the semi-cokes was assessed quantitatively from the polished surfaces by point counting technique using a Reichert Zetopan 5 microscope with an attached point counter [11, 12].

Kinetics of the mesophase formation were determined at 450°C for 2 h.

Results and discussion

The physical and chemical properties of pitch–polymer blends are shown in Table 1.

Three groups of blends were distinguished, according to the content of TI matter.

The first group contained the blends with the PET additive and gave a rise in TI by 10%, because PET remained insoluble in toluene even at high temperatures. Therefore, any interactions between the polymer and pitch components did not take place as PET was insoluble also in the bitumen medium. However, a formation of composed micellar regions, probably consisting of α components and polymer macromolecules, was observed as the dominant physical interaction. The high softening points confirmed the assumption.

The second group included the polystyrene-containing blends. The content of TI matter substantially grew up in this group in comparison with unmodified pitch, but in a lower degree than the total content of polymer additive added (10 mass%). Polystyrene is soluble in toluene at elevated temperatures, but the physical interactions also dominated in the system. Simultaneously proceeding chemical interactions were to a lower extent.

The third group contained blends with a changed content of TI matter in relation to the pitch. The blends of pitch with UP and CIR were included into this group, where a good homogeneity could be established in the pitch–polymer system under conservative conditions. The used polymers increased probably the continuous phase of pitch (γ components and some parts of β components) as a result of dominant soluble and swelling processes. The effect was particularly visible in the blends containing UP. The resin is very good soluble both in toluene and in the pitch material. Inside the pitch, the resin acts as a good plasticizer, without any cross-linking during the preparation. It resulted in a decrease in softening points of the blends by 9°C. All blends, except for those with UP, showed a very high load resistance, low values of penetration at 50°C (Table 1) and low melting flow index (Fig. 1). The viscosity curves (Fig. 2) showed that the examined systems can be rated as Newtonian fluid diluted by coagulation process. The rheological curves (Figs 1 and 2) indicated the stable connections as a result of interactions between the blend components. The blends with PET, PS and CIR showed a growing content of coke-forming components (Table 1), while this content in the blend with UP remained unchanged.

The kinetics of carbonization of pitch–polymer blends was determined for the blends with PS, UP and CIR. The blends differed in the optic texture of coke and in its formation efficiency during carbonization [6]. The blends containing 10 mass% of polymers were carbonized at 450°C for 0.5 to 2 h (Table 2).

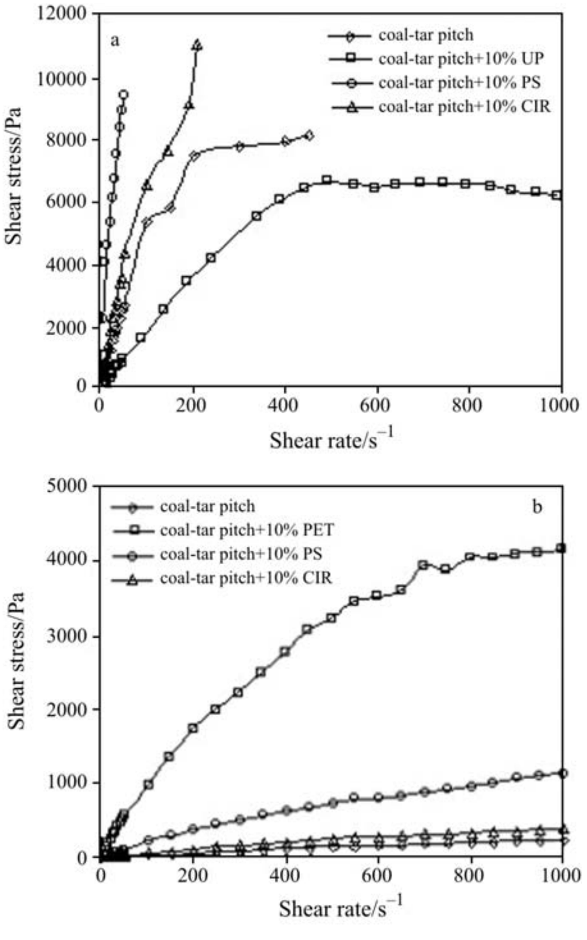

Fig. 1 Flow curves of coal-tar pitch and pitch–polymer blends as determined at a – 100 and b – 150°C

Table 1 Physico-chemical properties of coal-tar pitch–polymer blends

Additive (10%)	Softening point/°C	Penetration at 50°C ($\cdot 10^{-4}$ m)	Toluene-insolubles/mass%	Volatile matter/mass%
no	68.5	8.3	20.1	59.8
PS	90.0	1.2	25.1	63.2
PET	103.0	2.0	31.0	62.7
UP	59.8	204.0	21.3	58.7
CIR	71.5	13.0	19.8	64.9

Table 2 The effect of pitch soaking time on the content of mesophase in carbonizates made of pitch–polymer blends

Additive (10%)	Time of carbonization/h			
	0.5	1.0	1.5	2.0
	Content of mesophase/%			
no	21.7	45.0	52.9	65.2
PS	42.7	57.8	66.5	73.0
UP	26.2	47.6	61.0	65.0
CIR	18.8	41.2	53.6	58.4

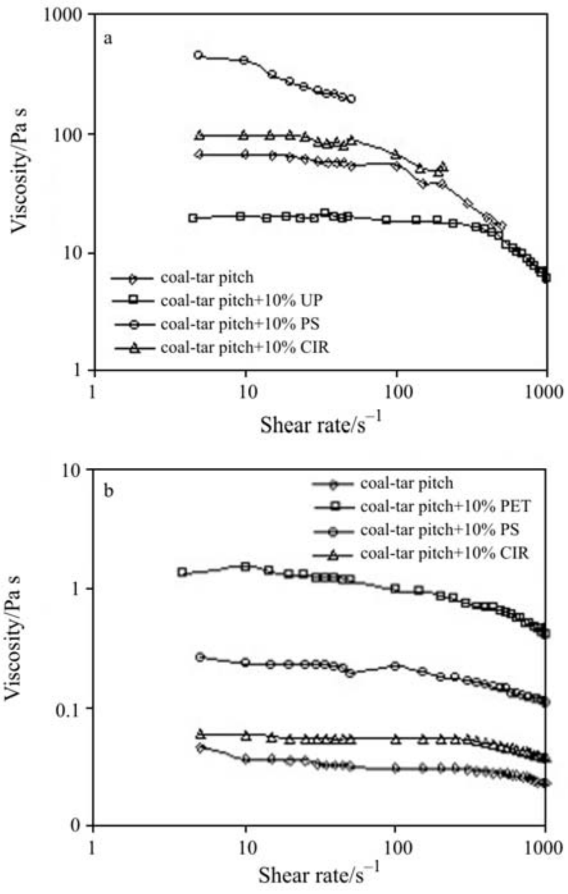

Fig. 2 Viscosity curves of coal-tar pitch and pitch–polymer blends as determined at a – 100 and b – 150°C

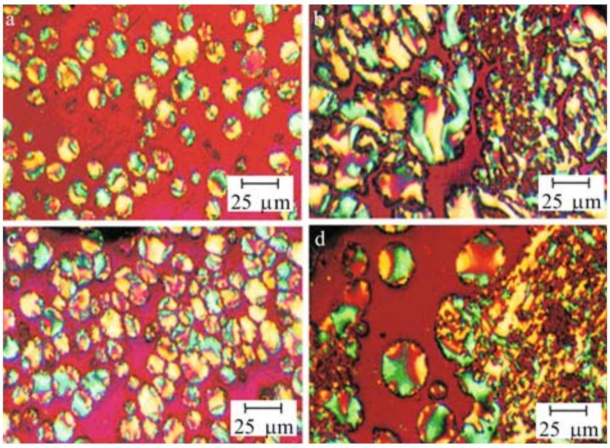

Fig. 3 Microscopic image of pitch and pitch–polymer blend transformations to mesophase (450°C, 1 h; 250× magnification, reflected polarized light): a – coal-tar pitch, b – coal-tar pitch+10% PS, c – coal-tar pitch+10% UP, d – coal tar pitch+10% CIR

In the first period of soaking (below 0.5 h), the polymers had an influence on enlargement of spherical size of the mesophase, except for CIR (Fig. 3). Both PET and UP favored the cumulating α components in the preliminary stage of carbonization in form of a clear separate phase. Besides, all polymers, except for CIR, accelerated the conversion of isotropic pitch to mesophase. The effectiveness of polymers in the conversion at the beginning of carbonization (0.5 h) decreased in a sequence: PS>PET>CIR>UP. The destruction of polymers with heteroatoms in chains, like oxygen, probably favoured the dehydrogenation of pitch.

The ratio of spherical units (particles) to the all mesophase was the highest, especially in first stage (up to 1 h), during carbonization of UP-containing blends (Fig. 3). The UP resins contributed to the development of pitch-originated mesophase. Therefore, the UP-containing pitch–polymer blends can be recommended for manufacturing the spherical mesophase semi-cokes.

In general, the mesophase content in the carbonizates depended on temperature and time of soaking. The throughput of the carbonizates decreased stepwise with the increasing time of soaking.

Conclusions

Stable and homogeneous blends of coal-tar pitch with polymers (added in 10 mass%) were formed independently on the polymer nature but under individual conditions. Conservative homogenization conditions were necessary particularly for preparation and processing the PS-containing pitch blends. The polymer structure influenced the physical properties of coal-tar pitch (softening point, penetration, content of TI matter, course of rheological curves). The properties indicated the proceeding structural interaction between group pitch components and polymers.

In the PET-containing blends, the physical interactions played a dominating role and favoured the formation of micellar areas. Between the pitch components and PS, close to predominant physical interactions, proceeded also chemical interactions, which probably have an influence on properties and structure of the bitumen matter. The UP-containing blends showed quench annealing processes in the pitch surrounding. The addition of CIR, PET and PS to the pitch resulted in an increase in semi-coke yield during the carbonization, what is of an advantage for practical use.

The addition of PU stopped the tendency of mesophase spheres to coalescence, what favours the clear increase in content of spherical form of mesophase and improves the spheres distribution. Coal-tar pitch modified by UP can be considered as a suitably raw material for producing mesophase pitches or spherical mesophases during the carbonization of the blends.

Obtained experimental results indicate the possibility of utilization of thermoplastic wastes, particularly poly(ethylene terephthalate) waste, as pitch modifiers.

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