INVESTIGATIONS ON REDUCING THE BENZO(A)PYRENE CONTENT OF COAL-TAR PITCH

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Introduction

Bitumens, like coal-derived tars and pitches, as well as petroleum asphalts, have been widely used in many branches of industry and economy [1]. A dramatic limitation of the application areas for bitumens of coal origin is currently observed, due to the carcinogenic action of some bitumen-containing polycyclic aromatic hydrocarbons, especially benzo(a)pyrene (BAP). This hazardous condition was the reason for shutting down plants involved in the coking of coal-tar pitch in Poland and Germany [2,3]. As a result, many research studies on decreasing BAP content in bitumen materials have been performed.

According to literature reviews [4], a considerable reduction in BAP content could be achieved by changing the conditions under which coal-tar pitch is manufactured, especially by decreasing the coal coking temperature [5]. Other workers [6,7] have attained lower BAP concentrations by modifying the pitch properties through oxidation, ultraviolet irradiation [8], or by extraction with low-boiling solvents [8,9]. Polymers not only improve the properties and applicability of bitumen-containing materials [1], but also can play an important role in decreasing their carcinogenicity. The current work studies how the properties of coal-tar pitch are affected by specific high molecular weight substances at elevated temperatures.

Experimental

The following materials were used: Polish coal-tar pitch (R & B softening point, 68.5^{o}C; toluene insolubles, 17.2% w/w; BAP content, 1.83% w/w), suspension-grade polyvinyl chloride (PVC, molecular weight, 139,000; Fikentcher number, 66.9), polystyrene (PS, molecular weight, 304,000; Vicat softening point, 103^{o}C), polyethylene terephthalate waste (PET) and unsaturated polyester resin (UPR, 40-50% styrene solution).

The study was performed stepwise. In the first step, the pitch was heated at 150 to 430^{o}C for 6 h to determine the effect of temperature on the pitch properties. The procedure was executed both with and without removal of distillate. In the second step, the molten pitch was blended with the various polymers: with PVC from between 120 and 350^{o}C for 0.5 to 4 h, with PS from between 240 and 350^{o}C for 0.5 to 4 h, with PET from between 260 and 350^{o}C for 1 to 6 h, and with UPR at 160^{o}C for 3 to 5 h. The products were analyzed for softening and dropping points, penetration (temperature relationship), as well as for BAP content and the amount of toluene-insoluble material. The BAP content was determined using the UV-VIS spectroscopic method [10].

Results and Discussion

The results (Table I) show that the structural changes in the heated pitch are demonstrated by a decrease in penetration and increases in softening point, dropping point and toluene-insolubles content. Changes in these properties became substantial in systems whose temperature was greater than 380°C. The observed decrease in BAP content from 1.83% to 1.48% w/w was not caused by its evaporation because no BAP was found in the distillate fractions. There was very little change in the BAP content for pitch mixtures heated at temperatures below 380°C. As a result, the changes in BAP content in this temperature range can be explained only by chemical interactions between the polymer and the pitch.

It has been found that homogeneous pitch-polymer blends can be obtained under the following conditions:

- an anthracene oil or dibutyl phthalate-plastified PVC up to 10% w/w and below 130°C,
- PS up to 10% w/w and below 310°C,
- PET and UPR, each up to 30% w/w and below 260°C,
- UPR up to 30% w/w and at 110°C, and after subsequent crosslinking at 140 to 160°C.

An individual selection of blending parameters, however, was necessary for each polymer. Temperature was an especially important property. It can be assumed that the elevated temperature contributes to an increase in the amount of toluene-insoluble material. This is due to a simultaneous destruction of polymer molecules and the polycondensation of pitch components, which is also evidenced by an increase of softening point and a decrease of penetration. No correlation, however, between this occurrence and a change in BAP content has been observed.

The largest reductions of BAP content were achieved with pitch-polymer blends containing either PET at 30%; UPR at 30%; or a system comprised of PVC at 4.76%, anthracene oil at 22.63% and butadiene-styrene copolymer latex at 4.76%. The corresponding decreases in BAP content were 72%, 80-90%, and 46%, respectively. Amounts of polyester additive and the effect on BAP content in coal-tar pitch are presented in Fig. 1. The polyester resin used in these compositions was modified additionally by initiators: naphthenate cobalt and hydroperoxide of methyl ethyl ketone. The substantial decrease in BAP content in the case of UPR modification was independent of crosslinking of the resin. The changes in BAP content are likely connected to some chemical interactions between the pitch and the polymer. It has also been found that the plastified PVC-containing pitches can be used in many applications, such as the manufacture of insulating and sealing materials for the building industry [1].

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	Softening Point (°C)	Dropping Point (°C)	Penetration ($\times 10^{-4}$ m, 50°C)	Toluene Insolubles (% w/w)	BAP Content (% w/w)
Original Pitch	68.5	82.0	8.3 ± 1.5	17.20	1.83 ***
Pitch after 6 h of heating without removal of distillate at (°C)					
150	72.0	85.5	9.3 ± 1.4	18.04	1.81
250	76.0	88.0	4.5 ± 1.1	19.98	1.82
300	75.0	87.5	5.3 ± 0.5	20.50	1.77
350	77.0	88.0	5.3 ± 0.6	23.68	1.79
380 *	83.0	97.0	1.3 ± 0.5	27.84	1.71
Pitch after 6 h of heating with distillate removal at (°C)					
350 - 400	88.0	102.5	—	32.20	1.64 **
400 - 430	111.0	130.0	—	52.59	1.48 **

Table I. Properties of thermally treated coal-tar pitch.

* 4 h.
** in terms of 100 g of pitch.
*** distributed into acetone-solubles (1.72%), acetone-insolubles (0.08%), and toluene-insolubles (0.03%).

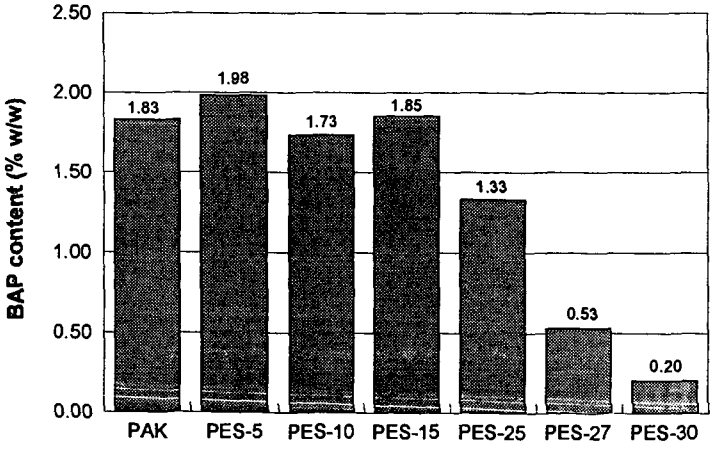

Fig. 1. Benzo(a)pyrene content in coal-tar pitch modified by polyesters. PES-5 relates to a composition of coal-tar pitch containing 5% w/w polyester resin.