

Modification of coal tar pitch by chemical method to reduce benzo(a)pyrene

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Coal tar pitch (CTP) comprises mainly polycyclic aromatic hydrocarbons, some of which are carcinogenic in nature. Among these, benzo(a)pyrene (B(a)P) is one of the most prominently reported carcinogens and its presence in CTP is a cause of concern for environmentalists. B(a)P gets released into the atmosphere during processing of CTP for various applications and is the cause of adverse effects on human health and the environment.

In the present study, CTP has been modified using different modifiers to reduce the content of B(a)P. This involves not only the analysis for content of B(a)P in CTP by HPLC, but also deals with the several physico-chemical properties before and after modification of CTP. It has been observed that the B(a)P content can be reduced almost to the extent of 80% by chemical modification. On comparing the physico-chemical properties of CTP before and after modification, it has been observed that there is no noticeable change. Thus, modified CTP can be effectively used for various applications, without the potential hazards of B(a)P.

Keywords: Benzo(a)pyrene, carcinogens, chemical modification, coal tar pitch.

COAL tar pitch (CTP) is a mixture of condensed aromatic hydrocarbons and heterocyclic compounds^{1,2}. Its major constituents are polycyclic aromatic hydrocarbons (PAHs). Some PAHs present in CTP have been found to be carcinogenic or mutagenic^{3–12}. One of the strongest carcinogens among the PAHs is benzo(a)pyrene (B(a)P)^{13,14}. CTP is used for several industrial applications: as a binder for aluminium smelting electrodes, roofing material, for surface-coating, in black varnishes, and as pipe-coating enamels¹⁵. During the processing as also for different applications, CTP is subjected to thermal treatment. On heating, PAHs such as B(a)P get released in the environment thereby causing potential environment hazards.

Due to this, restrictions on B(a)P content in CTP are being applied by the regulatory agencies. The manufacturers of CTP need to adopt a process to reduce B(a)P in CTP.

Modifications of CTP (or in other words of B(a)P) will provide relief to the processors as their workplace as well as the surroundings will not be exposed to the high levels of B(a)P. This will solve an important issue of reducing pollution due to the emission of high doses of this carcinogenic PAH.

The allowable concentration of B(a)P in technical products, fixed at 50 ppm, according to German regulations, is incomparably lower than what exists for not only in the crude pitch (1.5–2.5 wt%)^{16,17}, but also for commercial pitch-containing products such as road binders, building sealants or insulating materials, etc. in India. In other words, the pitch products in India can easily be termed as toxic substances, based on their B(a)P content.

Several attempts have been made to remove B(a)P from CTP. Zielinski *et al.*¹⁸ studied the effect of addition of various polymers on the content of B(a)P in CTP. They reported reduction to the extent of 46 wt% of B(a)P content in a compound containing 4.7% PVC, anthracene oil and butadiene/styrene rubber latex with CTP and when heated for 1 h at 120–150°C.

Zielinski¹⁹ studied the polymer effects on chemical and physical colloidal structure of CTP and on the compatibility of pitch–polymer blend constituents. Reduction of B(a)P concentration through dilution of CTP with a polymer reportedly suppressed carcinogenicity¹⁹.

Ciesinska *et al.*²⁰ conducted investigations on the effect of polyetherols on B(a)P content in CTP. The studies showed a substantial decrease in B(a)P content of CTP when polyoxyethylenes or polyethylene glycols of varying molecular weight were reacted with B(a)P.

Zielinski *et al.*²¹ studied the effect of the products obtained from the glycol recovery step of waste fraction from PET on the thermorheological properties of CTP and on the reduction of B(a)P content in the pitch. With approximately 30 wt% of the residue from the glycol recovery step of PET waste added to the pitch, B(a)P content was found to be reduced by about 90%.

However, these attempts did not help in the removal of B(a)P from crude or thermally treated CTP. Removal of B(a)P from crude as well as processed CTP has been reported to be difficult, as the physical properties of this particular compound do not differ significantly from other PAHs contained in the pitch^{22,23}. Thus, because of the complexities of the matrix as also due to the fact that the physical properties of B(a)P are similar to those of the other PAHs, optimizing the method for reduction, specially of B(a)P in CTP has always been a challenge.

The objective of this study is to ascertain whether the B(a)P content of a binder-grade CTP can be reduced by chemically treating the CTP with selected chemicals. It has been reported^{24–27} that if B(a)P is converted into its derivatives by chemical modifications, it can be rendered harmless. The proposed mechanism for this type of chemical modification can be described according to the reaction sequence as given in Figure 1.

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Binder-grade CTP having general properties such as softening point (SP) 112.7°C (by ring and ball method), toluene-insolubles (TI) as 43.2%, quinoline-insolubles (QI) as 13.6%, procured from local sources have been used in the study. Unsaturated polyester resin (UPR) of grade CR-600 was procured from Crystic Resin, India. CR-600 is a product of polycondensation of di-ethylene glycol, propylene glycol, styrenated maleic anhydride and phthalic anhydride, with specific gravity (at 25°/25°C) of 1.04.

Polyethylene glycols (PEG) of different molecular weights (300, 400, 600 and 6000) were procured from Loba Chemicals, India. Propylene glycol (PG) and styrene were procured from S.D. Fine-Chem Ltd, Mumbai, India.

Redistilled laboratory-grade solvents were used for extraction. Water and acetonitrile were of HPLC grade (Ranbaxy Fine Chemicals, India). Reference standard of B(a)P (97% purity) was purchased from Supelco, USA. Silica gel 60 (particle size 0.063–0.200 mm) and sodium sulphate (AR grade) were purchased from Merck, India.

CTP was treated with different modifiers as mentioned below: PEGs of different molecular weights (300, 400, 600 and 6000); PG, styrene and UPR.

Modification of CTP was done following the procedure mentioned below: First, 500 g of pitch was heated in a round bottomed flask along with the modifiers PG and styrene and using the catalyst (1 wt% of modifier), to 115°C with constant stirring and maintaining the nitrogen atmosphere for an extended duration of 7 h. The gaseous effluents were collected using traps so as to avoid them from entering the atmosphere. In the case of PEGs, the modification reaction was carried out at 160°C for 7 h duration with constant stirring and maintaining the nitrogen atmosphere.

Modification with UPR was done by dividing the homogeneous mixture of CTP and UPR into two equal

parts and then both parts were made to react in a particular sequence. First, an accelerator (Co-naphthanate, 0.20 wt% of UPR) was added to one part and an initiator (benzoyl peroxide, 10 wt% of the resin) was added to the second part. The first part was heated and once melted, with constant stirring, the second part was added to it for modification.

In all the cases described above, progress of the reaction was monitored after each hour by checking the B(a)P content till the completion of the reaction. The reaction product was collected under hot conditions after completion of the reaction.

B(a)P content in CTP was determined by HPLC using a modular HPLC system (Waters, USA) under the chromatography conditions given in Table 1, and the method as described elsewhere²⁸. B(a)P percentage in the samples was calculated with reference to the peak response of reference standard of B(a)P.

The reaction using PEGs of different molecular weights was carried out for an extended time period of 1–7 h and progress of the reaction was recorded after every hour, in order to find changes in parameters such as B(a)P content, SP, QI content, TI content, coking value (CV) and specific gravity (SG). The results observed for varying amounts of modifiers are presented in Tables 2–5 for PEGs, PG, styrene and UPR respectively. As the modification reaction was found to be complete (based on observations which indicate no further reduction in B(a)P content) after 5 h, the results are reported here only for reactions carried out up to 5 h in all cases.

Reactions using PG, styrene and UPR were also carried out with reaction temperature different from the one used for PEGs as a modifier. The results of B(a)P content of CTP modified with PEGs of different molecular weights are presented in Figure 2.

From the results of B(a)P content as shown in Table 2 and Figure 2, it can be seen that as the PEG content was increased from 10 to 30 phr, the B(a)P content decreased. When PEG of molecular weight 6000 was used, reduction in B(a)P content was sharp, from 1.22% for 0 phr of PEG to 0.42% for 20 phr. However, by further increasing the PEG content, slight reduction in B(a)P content was observed. Thus, on analysing the results, it was found that maximum reduction in B(a)P content (i.e. up to 70%) was observed in the case of PEG with higher molecular

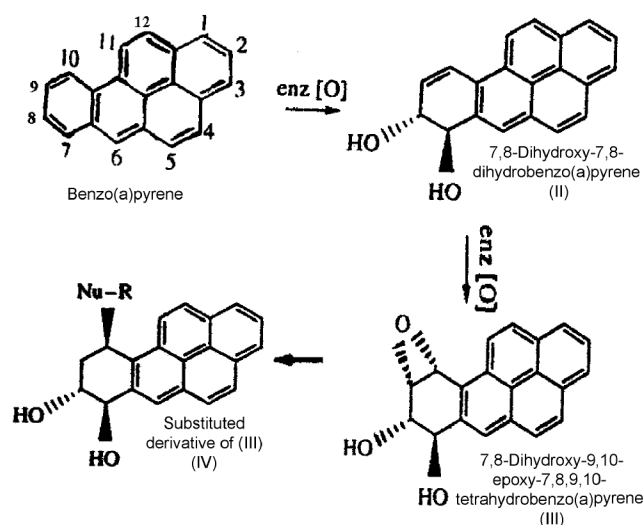


Figure 1. Reactions of benzo(a)pyrene (B(a)P) causing conversion of carcinogenic component(II) to substituted non-carcinogenic component(IV)^{24–27}.

Table 1. Chromatography conditions to determine benzo(a)pyrene content in coal tar pitch

Column	: Phenomenex C18 (250 mm × 4.60 mm; 10 μm; stainless steel)
Mobile phase	: Acetonitrile : Water (80 : 20)
Flow rate	: 0.5 ml/min
Detector	: Fluorescence (excitation 254 nm; emission 400 nm)
Temperature	: 30°C
Injection volume	: 10 μl

Table 2. Properties of CTP (BG1) modified by PEGs of various molecular weights

PEG added		Time (h)	SP (°C)	QI content (%)	TI content (%)	CV (%)	SG	B(a)P content (wt%)
Mol. wt.	phr*							
–	0	0	112.7	13.6	43.2	54.3	1.28	1.22
300	10	5	113.3	13.4	40.6	54.2	1.28	0.94
300	20	5	115.2	12.9	35.0	54.1	1.29	0.73
300	30	5	119.3	11.0	33.1	54.2	1.29	0.57
400	10	5	113.3	13.5	41.2	54.2	1.29	0.90
400	20	5	115.3	12.0	34.6	54.0	1.29	0.69
400	30	5	119.9	10.6	32.7	54.3	1.29	0.54
600	10	5	113.6	13.5	40.2	54.1	1.29	0.84
600	20	5	115.6	12.9	34.2	54.0	1.29	0.62
600	30	5	120.1	10.1	31.6	54.0	1.29	0.51
6000	10	5	115.7	13.4	43.3	53.7	1.29	0.70
6000	20	5	123.9	13.7	43.0	53.6	1.30	0.42
6000	30	5	129.1	13.8	42.7	53.1	1.30	0.40

*phr = parts per hundred of coal tar pitch used.

Table 3. Properties of CTP modified by PG

PG added (phr)	Time (h)	SP (°C)	QI content (%)	TI content (%)	CV (%)	SG	B(a)P content (wt%)
0	0	112.7	13.6	43.2	54.3	1.28	1.22
10	5	113.6	13.5	41.1	54.3	1.29	0.53
20	5	118.1	13.3	37.6	54.2	1.29	0.45
30	5	123.4	12.1	36.7	54.1	1.32	0.43

Table 4. Properties of CTP modified by styrene

Styrene added (phr)	Time (h)	SP (°C)	QI content (%)	TI content (%)	CV (%)	SG	B(a)P content (wt%)
0	0	112.7	13.6	43.2	54.3	1.28	1.22
10	5	112.9	13.4	39.2	53.1	1.29	0.62
20	5	112.7	13.4	37.6	52.4	1.31	0.61
30	5	113.2	13.5	38.1	51.3	1.30	0.58

weight (~6000) compared to that with low molecular weight (~300).

The decrease in B(a)P content with increasing molecular weight of PEG can be explained by the higher stability of carbocations derived from PEGs with higher molecular weight, which show higher alkylating activity. The efficiency of reduction in B(a)P increased with increasing concentration of PEG.

As seen from Table 3, the reaction of CTP with PG results in reduction of B(a)P content from 1.22 to 0.43% for 0 to 30 phr of PG respectively. It may be noted that maximum reduction for PG is marginally lower than that of PEG (molecular weight 6000); it can be considered at par with PEG-6000.

In the reaction of styrene with CTP, reduction in B(a)P content is much less than that obtained with PEG and PG, indicating that the alkylation of CTP with styrene is less effective than that of PEG and PG (Table 4). In the case of styrene, minimum B(a)P content obtained at 30 phr of

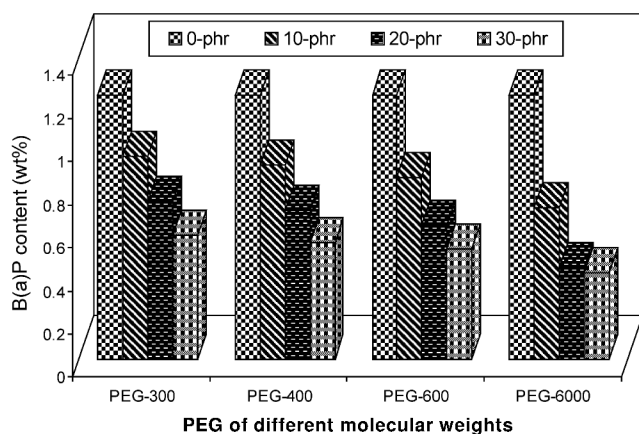
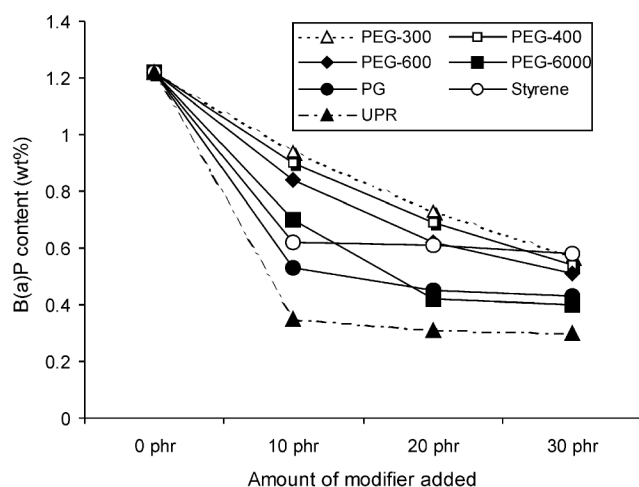
styrene is 1.22–0.58 wt% compared to ~0.40 wt% for PG and PEG of 30 phr.

From Table 5, it is clear that B(a)P content of CTP reduces as the concentration of UPR is increased. B(a)P content of the reaction product obtained by the reaction of CTP with 10 phr of UPR carried out at 160°C for 5 h was reduced to 0.35% from the original B(a)P content of 1.22 wt% of CTP. It is observed that there is a further reduction of B(a)P content to 0.23 wt% when the concentration of UPR is further increased to 30 phr. Further reduction beyond 10 phr of UPR may have occurred due to the dilution factor more than due to any chemical change.

The effect of different modifiers on B(a)P content is also shown graphically in Figure 3. Maximum reduction in B(a)P content in CTP was observed by reacting it with UPR as a modifier. The possible mechanism for the reaction of CTP with UPR was the selected O-alkylation of B(a)P, as reported by Zielinski *et al.*²³. As regards the

Table 5. Properties of CTP modified by UPR

UPR added (phr)	Time (h)	SP (°C)	QI content (%)	TI content (%)	CV (%)	SG	B(a)P content (wt%)
0	0	112.7	13.6	43.2	54.3	1.28	1.22
10	5	118.3	13.7	43.1	53.9	1.29	0.35
20	5	129.3	13.8	43.7	53.2	1.31	0.24
30	5	139.4	13.8	42.3	52.9	1.33	0.23

**Figure 2.** Effect of molecular weight of PEG on B(a)P content.**Figure 3.** Effect of different modifiers on B(a)P content.

effect of the reaction of CTP with PEG of different molecular weights on the physico-chemical properties, it has been observed that there is not much variation in SP, QI content, TI content, CV and SG values, except in the case of PEG-6000, where SP increases from 112.7 to 129.1. Maximum change in SP was observed in the case of UPR, where it increased from 112.7 to 139.4 as UPR content increased from 0 to 30 phr.

The reaction at 160°C for 5 h has been found to produce maximum reduction in B(a)P content; having B(a)P

content as 0.23 wt% compared to 1.22 wt% of the starting pitch. Further, the other physico-chemical properties of CTP remain more or less unchanged after the modifications.

From the present study, it is clear that by subjecting the CTP to chemical modifications, one can bring the B(a)P content down to acceptable limits set for ensuring environmental safety. The outcome of the study provides us with options in this regard. However, it must be noted that while modifying the CTP to achieve reduction in B(a)P content, care must be taken about the safety aspects of the modifiers used. Here, maximum reduction achieved with UPR is also associated with the incorporation of substances such as benzoyl peroxide and naphthanate. Though both these chemicals are allowed to be used in the polymer industry, it is essential to keep environmental safety aspects due to these chemicals in mind. In that case, maybe PEG or PG would be the preferred options.

Based on the present findings it has been concluded that B(a)P content in CTP can be reduced significantly by reacting it with several modifying agents. The best results were obtained with UPR. Reduction of B(a)P has also been observed in the case of other modifying agents such as styrene, PG and PEG of different molecular weights, but maximum reduction to the extent of more than 80% was observed with UPR. The difference in reduction of B(a)P or modification of CTP has been attributed to the alkylating efficiency of the modifying agents. Thus, CTP with lower B(a)P content can be used for various applications as the modification caused little effect on the other properties of CTP.

Considering the fact that the aim of the study was to reduce the B(a)P content of CTP, it is evident from the results that the various modifiers studied here bring about reduction in the following order:

UPR-modified CTP > PEG-modified CTP > PG-modified CTP > styrene-modified CTP

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Reduction in B(a)P content

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Bioactivity of essential oils and sesquiterpenes of *Chloroxylon swietenia* DC against *Helicoverpa armigera*

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Essential oils from the leaves and stems of *Chloroxylon swietenia* DC were obtained by hydrodistillation and the chemical composition was determined by GC and GC–MS. The major identified components in leaf oil were limonene, geijerene, pregeijerene, germacrene D and trans- β -ocimene, while stem oil essentially contained methyl eugenol, limonene and geijerene. Laboratory bioassays of the essential oils and isolated compounds were evaluated for insecticidal and antifeedant activities on *Helicoverpa armigera*. Toxicity was determined by topical application of the total extracts and the isolates at varying concentrations, where leaf oil, stem oil, geijerene and pregeijerene were found to be more toxic than germacrene D and limonene, with LD₅₀ values of 22.3, 26.9, 39.4 and 45.8 μ g/larva respectively. Further, geijerene and pregeijerene displayed maximum feeding deterrence as well with DC₅₀ of 89.8 and

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