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AN EFFECT OF POLYMERS ON THERMAL STABILITY OF BITUMENS

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Abstract

Results of studies dealing with an effect of polymers (selected kinds) and plasticizer on thermal stability of coal-tar pitch were presented.

Factors being decisive in miscibility of composition constituents and instability of bitumen – polymer – plasticizer mixtures were determined.

Keywords: bitumens, polymers, thermal stability

Introduction

What the bituminous materials, so widely applied in building industry and highway engineering, require is to improve their thermal resistance and mechanical strength. One of the methods that leads to improve these properties is modification of petroleum-derived or coal-derived bitumens by means of polymers. Compositions based on petroleum asphalts are examples confirming the usefulness of this approach. The literature pertaining to the modification of petroleum bitumens by polymers is very extensive. For the most part, these works deal with the physical modification of asphalts by means of plastics, with the intention of obtaining homogeneous mixtures [1–5].

Combining coal-derived bitumens (especially coal-tar pitch) with polymers has generated a significantly smaller level of interest. Nevertheless, studies on modification of coal-tar pitch by means of asphalts, plasticizers and polymers were undertaken.

Experimental

Figure 1 presents main directions of the studies which were realized. A special attention was given to these dealing with an effect of selected polymers and plasticizers on thermal stability of coal-tar pitch.

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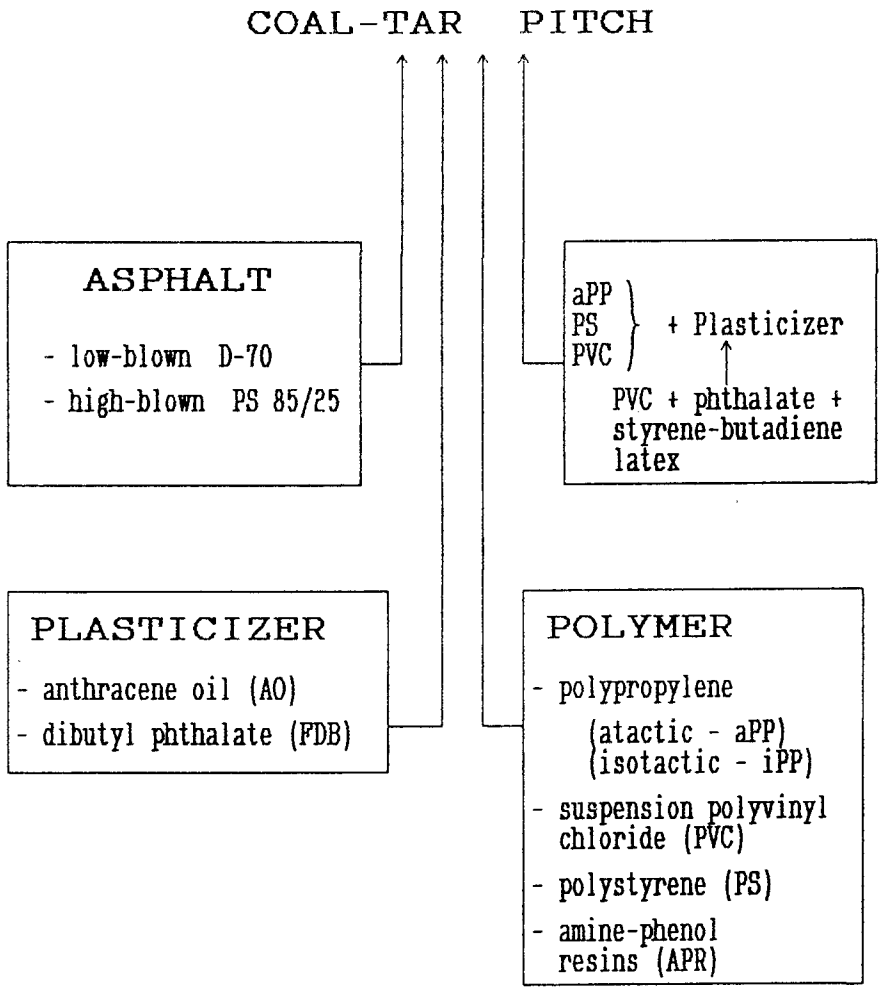


Fig. 1 Essential directions of investigation concerning modification of properties of coal-tar pitch

Used in the studies, coal-tar pitch had: softening point (87°C), density at 25°C (1236.7 kg/m^3) and comprised components insoluble in toluene (21.45% w/w).

Two-component, coal-tar pitch–polymer compositions were obtained by mixing fused constituents:

- pitch + PVC (or styrene-butadiene rubber latex) at 125°C and for 0.5 h,
- pitch + aPP or iPP at 150–200°C and for 2–2,5 h,
- pitch + PS at 230–305°C and for 1.0 h,

– pitch + amine-phenol resin at 120°C and for 0.5 h.

Plastification of compositions was carried out by preparing, preliminarily, PVC-plasticizer paste or by mixing, preliminarily, plasticizer and pitch [6, 7].

The following determinations were performed on the obtained compositions:

– fragility point (Frass) – T_F
– softening point (Ring and Ball) – T_S
– penetration
– stability index (*SI*) – defining composition stability and estimated according to: $SI = (\rho_L - \rho_U) \times 100\%$, where ρ_U and ρ_L are densities of upper and lower layers of compositions heated for four days at 100°C (for PVC) and at 150°C (for the other polymers) and then frozen out at –25°C. This is modified method of the Tube Test used in determining stability of coal bitumens.

At the same time, for a few selected compositions, the structures were examined by photomicroscopy. The photomicroscopy was performed in polarized light at a magnification of 650X and the specimens were consumed in *n*-hexane.

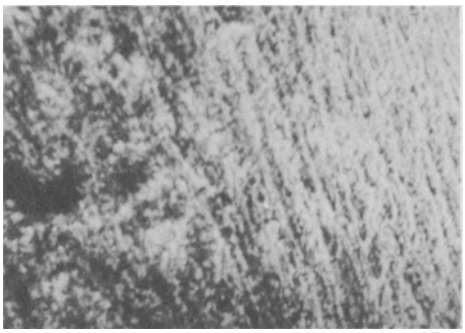
Properties of pitch–polymer compositions are presented in Table 1.

Table 1 Properties of selected coal–tar pitch–polymer compositions

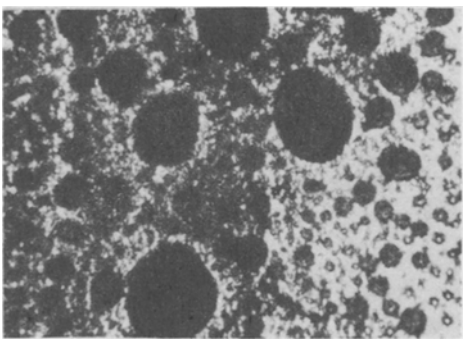
Composition	T_S / °C	T_F / °C	Penetration $\times 10^{-4}$ m (25°C)	Stability index / %
Coal–tar pitch	87.0		0.0	1.06
Pitch + 10% aPP	88.0	–9.5	8.6	10.25
Pitch + 90% aPP	113.6	–11.5	10.2	0.44
Pitch + 5% iPP	87.5		2.6	2.02
Pitch + 5% PVC	88.5		2.5	1.00
Pitch + 10% PVC	114.0		0.0	0.05
Pitch + 5% PS	133.5		0.0	0.95
Pitch + 10% PS	108.0		0.0	13.27
Pitch + 5% APR	86.0		0.0	0.25
Pitch + 10% APR	87.0		0.0	0.51
Pitch + 23.75% FDB + 5% PVC	41.0	–22.5	241.7	0.29

In the case of compositions made up of coal-tar pitch and polymers, certain intrinsic factors play a particular role with regard to obtaining mixtures which are homogeneous and which will not delaminate. These factors include temperature, the time needed to reach homogeneity and the order of addition of

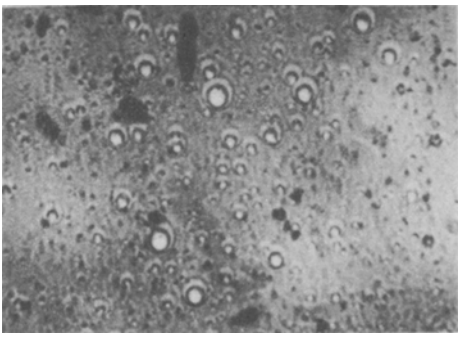
components. Another important factor is the elimination of circumstances which may destroy polymers.



Pitch+PVC (5% w/w)



Pitch+aPP (5% w/w)



Pitch+PS (5% w/w)

Fig. 2 Photomicroscopy of the structures of coal-tar pitch–polymer compositions (transmission optical microscopy, polarized light, magnification ×650)

Beneficial properties were attained only in the case where pitch was combined with polar PVC. Mixtures containing 10% w/w PVC in pitch were homogeneous and stable. The addition of PVC increased the softening point to 114°C, with concurrent lack of improvement in elasticity. This is confirmed by examining selected photomicrographs of the structures of the pitch-polymer compositions (Fig. 2):

– pitch–PVC (5% w/w) – compositions displays a continuous, skeined structure,

– pitch–aPP (10% w/w) – compositions shows distinct spheroidal aggregations of particles expanded in the dispersed phase of the pitch particle polymer,

– pitch–PS (5% w/w) – the polymer particles are uniformly dispersed and sorrounded by solvent layers.

Differences in the chemical make-up and the colloidal structure of pitch and PP prevented the attainment of mixtures that did not delaminate. In order to obtain homogeneous mixtures of pitch and PS, a temperature range of 260–310°C was required. This led to the destruction of polymer and provided no changes in the properties of the pitch.

Plastification of pitch by means of coal-derived oil fractions (anthracene oil) as well as artificially-produced dibutyl phthalate obtained from industry was studied. It was demonstrated that the most beneficial changes in properties were obtained using the dibutyl phthalate at 25–30% w/w. The dibutyl-phthalate-modified pitch provided new qualities in pitch-plasticizer binders. For example, the fragility point (according to Frass) of pitch-phthalate mixtures is –24°C. Mixtures of pitch and anthracene oil at 20–25% w/w provided similar improvements. Plasticizers radically increase the amount of pitch's dispersed phase thanks to the pitch accepting characteristic properties of petroleum asphalts high in oxygen. The appearance of solvent layers are observed near the points of dispersed particles of pitch.

Conclusions

1. Information in the literature as well as our own results show that the mixing of the components of pitch-polymer compositions are determined by the following factors:

– character of the bituminous raw product. Bitumen should contain large oil fractions for the purpose of dissolving and expanding the polymer. At the same time, bitumen should also contain a relatively large amount of condensed components in order to ensure the durability of the composition's structure. Considering that coal-tar pitches contain large amounts of aromatic hydrocarbons,

which are often condensed, especially advantageous they mix with polar polymers aromatic chain structure;

– structure and amount of polymer. These limit, among other things, the polymer's ability to dissolve and to swell in aliphatic and aromatic fractions of bitumen. The structure and amount of polymer also limits the formation of now colloidal structures resulting in the mutual separation between fragments of the polymer chain and the active components of the bitumen. The essential element is the establishment of the limits of the amount of polymer added to the bitumen. Near these limits, the phases of the dispersion undergo a reversal phenomenon, resulting in the composition moving to an inhomogeneous state and displaying a lack of stability;

– mixing parameters. Especially important are time and temperature, so as to prevent polymer destruction.

2. When adding polymers: PVC or amine-phenol resin or polystyrene (in quantities ≤5% w/w) to coal-tar pitch, thermal stability of the composition became higher. The stability is related to homogeneity of the composition.

3. Modification of coal-tar pitch–polymer composition by plasticizer improves dispersity in dispersion medium of the composition. This has an effect on increase in composition stability.

4. Estimation of stability index and photomicroscopy at the same time can be successfully used for evaluation of stability and homogeneity in bitumen–polymer compositions.

5. Stable, coal-tar pitch–polymer compositions can be employed as a base to obtain insulating seal materials for building industry.

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References

1 UK Patent 1 457 999, 1976.
2 J. Zieliński and A. Bukowski, J. Thermal Anal., 32 (1987) 1797.
3 J. Zieliński and A. Bukowski, Ropa a Uhlie, 29 (1987), 404.
4 J. Zieliński, Erdöl u.Kohle, Erdgas Petrochemie, 42 (1989) 456.
5 J. Zieliński, Studia nad budową i właściwościami kompozycji bitumiczno-polimerowych, Wyd. Pol. W-skiej, Warszawa 1991.
6 J. Zieliński, K. Piotrowska and J. Polaczek, Koks, Smoła, Gaz, 35 (1990) 190.
7 J. Zielińksi and A. Bukowski, Modification of properties of petroleum and coal-tar bitumens by means of oil plasticizers, 36th International Conference on Petroleum, Bratyslava, 1993.
8 G. Zenke, Bitumen, (1973) 11.
9 J. Zieliński, K. Piotrowska and J. Polaczek, Polimery - Tworzywa Wielkocząsteczkowe, 38 (1993) 185.

Zusammenfassung — Ergebnisse von Untersuchungen über den Einfluß von Polymeren (bestimmte Arten) und Weichmachern auf die thermische Beständigkeit von Kohlenteerpech werden dargelegt.
Die Faktoren, die ausschlaggebend für die Mischbarkeit der einzelnen Komponenten und die Instabilität von Bitumen-Polymer-Weichmacher-Gemischen sind, wurden ermittelt.