

Polyphosphoric acid (PPA) in road asphalts modification

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Please cite as: CHEMIK 2012, **66**, 12, 1340-1345

Introduction

Asphalt binders are commonly used in the pavement construction. To meet the raising requirements for durability of the road surface, alternative methods of improving binder have been developed. The wide range of viscoelasticity is essential to achieve long-lasting road surface, as it ensures consistency of asphalt's rheological state in extreme service temperatures. Modifiers applied for improving asphalt's viscoelasticity are [1]: elastomers, plastomers, synthetic resins, crumb rubber, metal-organic compounds, sulfur, natural asphalts and paraffins. Also polyphosphoric acid can be used for this purpose – pros and cons of its application are subject of this paper.

Bituminous binders

Bituminous binders are materials of organic origin whose binding and hardening is caused by the temperature-related change of adhesion and cohesion of their molecules [1]. Those thermoplastic materials are divided into tars and asphalts due to their origin. Tars are produced by destructive distillation under pyrolysis from the organic materials (coal, lignite, wood, peat). Because of their toxicity and low quality they are not used in construction industry.

Asphalt, also known as bitumen, is the mixture of hydrocarbons which are naturally occurring or obtained from crude oil distillation. The composition of asphalt is very complex and depends both on the origin and on the method of crude oil processing. Asphalts, especially modified, are also thixotropic – they flow like a liquid when a sideways force is applied. The properties of asphalt are function of temperature and duration of load.

Bitumens are used as binders in asphalt concrete, a composite material used in the construction of road layers. It also contains mineral aggregate, filler and additives. All compounds are glued together by asphalt, so despite its low content (ca. 5%) its effect on properties of concrete and, therefore, on the pavement performance is critical.

The physical and rheological properties of asphalt are dependent on its composition, chemical structure and colloidal structure.

Colloidal structure of asphalt

Due to the complexity and a large number of molecules with different chemical structure, the structure of asphalt is divided into fractions of similar properties. There are several methods for extracting those asphalt group components [1 ÷ 3]. Bitumen is often characterized by its chromatographic fractions, the maltenes and the asphaltenes, soluble and insoluble in n-heptane, respectively. The maltenes can be fractionated further into saturates, aromatics and resins [2]. The asphaltenes consist mainly of highly condensed polycyclic aromatic hydrocarbons of average molecular weight 2-15 kDa [2]. Asphalt is commonly modeled as a colloid, with maltenes as the continuous phase and micelles of asphaltenes stabilized by associated resins as the dispersed phase [4]. There is no evident border between dispersed and continuous phase.

Asphalt's composition and its colloidal structure determines its physical and rheological properties. The penetration increases with increasing share of saturates and decreases with increase of asphaltenes and resins; changes in softening point and ductility are opposite. High content of asphaltenes increases viscosity, whereas resins contribute to the adhesion of asphalt to aggregate [3].

Asphalts classification

In the USA until 1970s asphalts were classified due to their penetration at 25°C, (ASTM D946), during 1980 ÷ 90s due to their viscosity at 60°C (ASTM Standard D3381). From 1990s Superpave Performance Grade (PG) classification is introduced. It is based on relation between the binder's properties and the conditions under which it is used. Asphalts are reported as PG X-Y, where X is the average seven-day maximum pavement temperature, Y is minimum pavement design temperature [1]. Introduction of this classification system has forced changes in the design of asphalt binders. To meet stiffness requirements in regions with extreme climatic conditions is not possible without asphalt binder modification. In Poland, as in many other European countries, the base of asphalt classification is their penetration at 25°C. Road bitumens are classified according to PN-EN 12591.

Polymer modified bitumen (PMB) are classified according to PN-EN 14023:2011. Polymer modified bitumens are reported as PMB X/Y-Z, where X/Y-penetration range at 25°C, Z- lowest softening point.

Modification of asphalts, polymer modifiers

Modified bitumen is asphalt whose chemical or rheological properties were modified by addition of chemical compound [3]. First polymer modified bitumens were produced in first half of the XX century; in Poland – in 1990s. Earliest modifiers were natural rubber latex, sulfur and rubber; firstly synthetic modifiers were polychloroprene (CR) and styrene-butadiene copolymer (SBS), which is most commonly used nowadays.

Increased attention in asphalt modifiers can be attributed to the following factors [6]:

- increasing traffic volume, loads and tire pressures, causing increased pavement rutting and cracking
- environmental and economic issues – possibility of recycling waste and industrial byproducts (tires, roofing shingles, glass, ash) with achieving benefit in pavement properties
- public agency willingness to fund higher-cost asphalt additives for longer service life of pavement and its less maintenance.
- Bitumen is modified to enhance the functional properties of asphalt concrete and the lifetime of pavement. Most important issue is to extend the range of viscoelasticity.

Binder and polymer have to be miscible to form homogeneous mixture, without destroying colloidal structure of asphalt. Compatibility

affects the long-term storage behavior as it prevents polymer phase separation. Miscibility depends on structure and properties both asphalt's and polymer's.

Asphalt can be modified with elastomeric or plastomeric polymers. The first results in improved elastic recovery after removing applied stress, broaden range of viscoelasticity, reduced risk of rutting and reduced prone to thermal and fatigue cracking. Plastomers make bitumen stiffer but more prone to permanent deformation; low-temperature properties of such modified asphalt are not better than base asphalt [3].

The most popular polymer modifiers suitable for mixing with asphalt are: atactic polypropylene (APP), polychloroprene (CR), ethylene-vinyl-acetate (EVA), polybutylene (PB), styrene-butadiene-styrene (SBS), synthetic styrene-butadiene-rubber (SBR), natural rubber latex, ethylene-propylene-diene terpolymer (EPDM), ethylene-methyl acrylate and ethylene-butyl acrylate (EMA, EBA) and styrene-isoprene-styrene (SIS).

Polyphosphoric acid (PPA)

Polyphosphoric acid (CAS 8017 16 1) is a polymeric product of thermal dehydration and polycondensation of orthophosphoric acid (H_3PO_4). Beside orthophosphoric forms, it contains a mixture of polymeric forms whose content increases with increasing acid concentration. Commercially available PPA is a mixture of linear polyacids of general formula $H_{n+2}P_nO_{3n+1}$, where $n \geq 2$. Those acids are produced either from the dehydration of H_3PO_4 at high temperatures or by heating P_2O_5 dispersed in H_3PO_4 . In the latter method, longer chains are obtained. Polyphosphoric acid is highly hygroscopic and easily hydrolyze in moist air. Its viscosity and physical form at room temperature depends on the content of P_2O_5 [6]. PPA main's application is production of high quality liquid fertilizers, but it is also a substrate of numerous chemical synthesis.

PPA is available in various grades, the naming of which can be confusing as the percentage often exceed 100%. It is effect of calculation of H_3PO_4 concentration on the base of P_2O_5 content in this inorganic polymer. For the asphalt's modification, concentration of 105, 110 and 114% H_3PO_4 are used (75.9, 79.8 and 82.6% P_2O_5 , respectively).

PPA is produced mainly in China and in the USA. One of very few in Europe and Poland's only producer of PPA is Inorganic Chemistry Division "IChN" of Fertilizers Institute, located in Gliwice. PPA production is based on their own, original solution of multi-sectional electrothermal evaporator [7], which provides a controlled production of 100-114% H_3PO_4 acid (73-82% wt. P_2O_5). The plant's production capacity total is 30-45 kg per hour. Obtained PPA has very good quality parameters, making it suitable for many applications.

PPA as an asphalt modifier

First patent on use of PPA in asphalt modification was published in 1973 [8]. Addition of PPA to binder results in increase of softening point with no effect (or sometimes small decrease) in low-temperature brittleness [10], as PPA does not oxidize asphalt. This leads to improve maximum service temperature (or useful temperature range). However, also decrease in low-temperature properties was observed [11], it seems to be depending on base asphalt composition.

Main advantages on use of PPA in asphalt modification are:

- Good compatibility of PPA with asphalt: no phase separation during the long-term storage
- Modified bitumen characteristics: increased viscosity without oxidation, softening point improvement, lower penetration at room temperature, improved stiffness
- Pavement characteristics: reduced rutting, increased resistance to thermal and fatigue cracking, increased resistance on moisture, increased durability due to better binder adhesion to aggregate

- Facilitated processing: ease of pumping, operating at lower temperatures, reduced emissions from asphalt operations
- In addition with polymers: lower polymer consumption, possible lower temperature processing, synergetic effect of both additives, cost reduction.

Since 1990s, researches on using PPA in conjunction with polymers to improve quality of road bitumens are conducted. The major benefit of this particular combination is synergistic effect – possible reinforcement of both modifiers effects on asphalt. It has been observed for binder elasticity, thermal cracking resistance, and resistance to permanent deformation [9]. Moreover, PPA improves adhesion and may eliminate the need for antistripping agents. In addition, the stability of binder during long-time storage in elevated temperatures is increased. Overall cost of using modified asphalt binders is reduced by using less modifier, possible elimination of anti-strips, and energy savings from lowering operating temperatures [9]. Addition of PPA may reduce reaction time with some polymers [9]. Polymers linked with PPA are: SBS [12÷15], EVA [12, 14, 16] and ethylene terpolymer [17].

Effect of PPA on crumb rubber modified asphalt has been investigated since 2003, with good results [9]. PPA improves viscosity, stability during storage, elastic recovery and reduces the amount of asphalt needed to create the blend. Binder containing 5-8% gum and 0.5-1% PPA has a similar characteristics to asphalt modified with PPA and polymer [18].

Mechanism of PPA modification

Modification of asphalt with PPA is a complex physicochemical process. Investigation of reaction occurring between the components of the binder and the PPA is difficult, due to the great number of molecules with different chemical structure and their possible interactions. It has been proven that PPA acts on functional groups with high dielectric constants – hence studies are conducted on bitumen model compounds. As a result of reaction between asphalt and PPA, a decrease in molar weight distribution and a change in asphalt's morphology is observed [10, 19]. Explanation of this phenomenon is based on colloidal structure of asphalt.

According to recently proposed mechanism [10], asphalt's weak bases (pyridines and amphoteric quinolones) form ionic pairs with strongly acidic PPA, thus, PPA displace weak acids such as phenols in their interaction with those bases. The loss of the hydrogen bonds and the release of an alkylated phenol from a larger aromatic structures results in compounds with lower molecular mass. Those lower molecular weight components enrich maltens fraction. PPA is also a catalyst in indole bridge formation. Formed large, covalently linked and therefore, stiffer molecules remain in fraction of asphaltenes. As a result, a decrease in average molecular weight of asphalt components and change in its morphology is observed, due to disintegration of asphaltenes resulting in smaller domains and amplification of the natural segregation of maltenes and asphaltenes. Low molecular weight compounds migrate to maltenes and decrease its T_g , and higher molecular weight covalently linked compounds raise the T_g of the asphaltenes [10].

Reactions of PPA with bitumen is strongly dependent on its chemical composition, which is related to its type and origin; thus properties of modified asphalt can slightly vary [19].

Main heteroatom in asphalt is sulfur, however, both aliphatic and aromatic sulfide groups, were proven to be inert when heated with PPA at 150°C for 1 hour [19]. Other studies [10] showed that reactivity of PPA with asphalt increases with increasing nitrogen and oxygen content. Given that indoles are found in higher concentrations than other functional groups (on second place there are pyridines), its content is expected to play a crucial role in the reaction of binders with PPA.

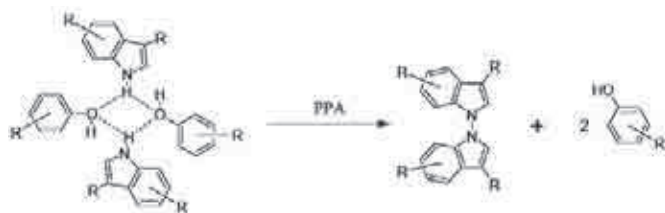


Fig 1. Diagram of a chemical modification of asphaltene through polyphosphoric acid, leading to break down into smaller domains and formation of indole bridges

Technical guidelines for PPA asphalt modification

The following guidelines are based on *Best Practices for PPA Modification of Asphalt* [20] prepared by the Polyphosphoric Acid Subcommittee in cooperation of the PPA producers in USA and on materials from *2009 PPA Workshop* in Minneapolis [21]. Useful information on asphalt technology and requirements can also be found in the *Poradnik Asfaltowy 2011*, developed by PKN Orlen [5].

Acid selection: it is very important to distinguish between polyphosphoric and orthophosphoric acid, the latter confusingly is sometimes named PPA, from *purified phosphoric acid*. Orthophosphoric acid contains free water, which lowers miscibility with asphalt and leads to phase separation during storage, asphalt foaming and steel tanks corrosion. Polyphosphoric acid contains no free water and is completely miscible with asphalt. It is also less corrosive to steel and stainless steel.

Acid concentration of 105 and 115% H_3PO_4 is mostly used in asphalt modification. The amount of PPA required is different for each base asphalt, typically from 0.25% up to 1.5%. There are no recommendations for PPA grade.

Masson et al. [10] proposed an equation to predict the stiffening effect of PPA on asphalt binders with 1% PPA or less. It can be used as a first approximation in the design and production of binders with specific PGs.

Properties of prepared asphalt blend have to be tested for each composition, after adding all additions.

Aggregate and anti-strips: PPA can react with components of asphalt binder. Neutralization reaction that occurs depends on the type of asphalt, aggregate and antistripping agent and may lead to a reduction in elasticity of asphalt and its adhesion to aggregate. PPA does not react with limestone. Reaction with acidic aggregates (e.g. granite) leads to enhance moisture resistance and can eliminate the need for using anti-strip additives.

When required, the anti-strip additives used should be compatible with PPA, otherwise neutralization may occur. Strongly recommended are phosphate esters, due to its proven compatibility. Adhesives based on amines react with PPA, leading to decrease of mixture properties.

Technology: in a plant, PPA should be stored in a dedicated tank, it is recommended that a nitrogen blanket be placed over the material to prevent moisture absorption from air. Preferred tank construction material is 316SS. Laboratory tests proven that the PPA modified asphalt and the head space above the modified binder are not corrosive.

The storage tank, pump, and acid process lines should be heated to maintain PPA in a fluent state. The required handling temperature is approximately 38°C for 105% PPA is and 94°C for 115% PPA.

Safety: asphalt is classified as hazardous due to high temperature required during transport. PPA modified asphalt is as safe as neat asphalt, PPA is not leached and does not migrate from asphalt's mass. Raw polyphosphoric acid is corrosive and should be treated according to MSDS.

Summary

Polyphosphoric acid has been successfully used in the USA for over 10 years. However, it does not gain any interest in Poland, despite

national manufacturer. PPA used in correct way, in the appropriate amount and according to technological guidelines, can significantly improve asphalt properties, thus, improve pavement's performance, its durability and application range. Also using PPA in conjunction with polymer or with crumb rubber is possible and beneficial. On the other hand, incorrect application of PPA technology, as in case of many other polymer modifiers, can result in construction or performance problems. The effect of PPA on asphalts of various origin and on other components of asphalt concrete should be carefully considered during formulation.

Literature

1. Piłat J., Radziszewski P.: *Nawierzchnie asfaltowe*. Wydawnictwa Komunikacji i Łączności 2004.
2. Masson J-F.: *A brief review of the chemistry of polyphosphoric acid (PPA) and bitumen*. *Energy & Fuels* 2008, **22**, 2637-2640.
3. Gawel I., Kalabińska M., Piłat J.: *Asfalty drogowe*. Wydawnictwa Komunikacji i Łączności 2001.
4. Nellensteyn F.J.: *The Constitution of Asphalt*. *Journal of Institute Petroleum Technology* 1924, **10**, 311-325.
5. Błażejowski K., Olszacki J., Peciakowski H.: *Poradnik asfaltowy 2011*. ORLEN Asphalt 2011.
6. Kirk-Othmer Encyclopedia of Chemical Technology, 2nd ed., vol.15. John Wiley & Sons 1986.
7. Patent PL 308863
8. Patent US 3751278
9. *Use of Polyphosphoric Acid in Asphalt Binders*. Phosphate Forum of the Americas 2009.
10. Masson J-F., Collins P., Woods J.R., Bundalo-Perc S., Margeson J.C.: *Chemistry and effects of polyphosphoric acid on the microstructure, molecular mass, glass transition temperatures and performance grades of asphalts*. *Journal of the Association of Asphalt Paving Technologists* 2009, **78**, 403-430.
11. Aflaki S., Tabatabaee N.: *Proposals for modification of Iranian bitumen to meet the climatic requirements of Iran*. *Construction and Building Materiale* 2009, **23**, 2141-2150.
12. Patent WO 9958600
13. Patent US 5880185
14. Patent US 5070123
15. Patent US 5451621
16. Patent US 6136898
17. Patent US 6117926
18. Patent US 2006/0250886
19. Masson J-F., Collins, P.: *FTIR study of the reaction of polyphosphoric acid and model bitumen sulfur compounds*. *Energy & Fuels* 2008, **23**, 440-442.
20. *Best Practices for PPA Modification of Asphalt*. Phosphate Forum of the Americas 2009.
21. <https://engineering.purdue.edu/NCSC/PPA%20Workshop/2009/index.html>, 2009 PPA Workshop Minneapolis, 10.01.2012

Translation into English by the Author

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