



# Effect of poly phosphoric acid (PPA) on creep response of base and polymer modified asphalt binders/mixtures at intermediate-low temperature



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## HIGHLIGHTS

- PPA and polymer (SBR, SBS) are used to modified asphalt in combination.
- Creep response of modified asphalt at intermediate and low temperature is investigated.
- Modification penetration test is proposed to evaluate creep rate of modified binders.
- Creep rate of binders decreases after adding PPA.
- Mixtures crack earlier and faster within a small temperature range after adding PPA.

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## ABSTRACT

As an alternative to conventional polymer modifiers, poly phosphoric acid (PPA), presenting good compatibility with asphalt, has been proved to affect thermo-rheological properties of asphalt and its mixtures. In this paper, effect of poly phosphoric acid (PPA) on creep response of base, polymer (SBS, SBR) modified asphalt binders/mixtures at intermediate-low temperature were investigated by several tests. Bending beam rheometer test (BBR) and modified penetration test based on indentation technique were used to measure intermediate and low temperature creep response of binders. Tensile stress restrained specimen test (TSRST) was applied to evaluate thermal cracking of mixtures. Results showed that addition of PPA slightly decreased creep stiffness of both base and polymer modified asphalt binder before aging, and accelerated aging level after short and long term aging. Modified penetration test indicated that creep rate change at intermediate temperature was slower after adding PPA, particularly for base binders whose creep rate declined a lot. In tensile stress restrained specimen test (TSRST), addition of PPA improved fracture strength and accelerated viscoelastic-elastic transition as well as weakened stress relaxation. Especially base asphalt mixtures cracked earlier and faster within a small temperature range after mixing PPA, which is undesired for low-temperature loading. Therefore PPA may have negative effect on asphalt mixtures and is more applicable with SBR and SBS modified asphalt with respect to low temperature performance.

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## 1. Introduction

Asphalt binder is one of the most common materials used in pavement engineering with excellent performance at different climatic conditions. However, conventional asphalt binders do not always perform as expected and cannot meet technical requirements because of heavy traffic loads and severe weather conditions. Common distresses related to asphalt binder, such as

moisture damage, rutting, thermal cracking and fatigue cracking take place at early stage of pavement service life [1,2]. Studies have indicated that pavement constructed with polymer modified asphalt binders possesses greater resistance to rutting, thermal cracking and fewer fatigue damage, stripping and less temperature susceptibility. Among these polymers, styrene butadiene styrene (SBS) and styrene butadiene rubber (SBR) are frequently used in road pavement [3,4].

SBS is a kind of block copolymer able to improve elasticity of original asphalt [5]. A strong bonding strength between asphalt and aggregates is developed owing to network structure created

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by SBS, contributing to retarding low temperature thermal cracking, enhancing resistance to high temperature deformation and obtaining a durable and long-lasting pavement [6–10]. SBR, consisting of styrene and butadiene, forms reinforced network structure in asphalt significantly increasing ductility and elastic recovery [11]. The Florida Department of Transportation [12] found that application of SBR resulted in elasticity increase, adhesion and cohesion improvement, oxidation rate reduction for asphalt. However, there are two main drawbacks in these polymer modifiers. On the one hand, polymer modified asphalt binder has poor workability. There is a tendency for polymer to separate from asphalt binder making asphalt binder unstable at high temperature, which brings serious technical limitations. On the other hand, higher content of polymer addition ranging from 4 to 5 wt% means a large pressure on financial cost. Therefore, it is necessary to find some alternative modifiers acting as substitution or supplement.

PPA (poly phosphoric acid) usually presents good compatibility with asphalt and has been widely adopted in asphalt to change rheological properties with small amounts recently [13,14]. PPA modified asphalt binder was studied through component analysis, rheological experiments and conventional tests, and found that colloidal structure of asphalt binder was varied by gel behavior of PPA further enhancing rutting resistance [15–19]. Edwards et al. [20,21] found PPA had considerable positive effects on rheological behavior of a non-waxy asphalt binder at low temperature. Zhang and Wang [22] proposed PPA decreased ductility of asphalt binders and negatively influenced binder at low temperature. Besides, Susanna Man Sze Ho et al. [23] maintained that PPA had no effect on resistance to thermal cracking.

Though literatures are available on effect of PPA on rheological performance of asphalt binders at low temperature, results were inconsistent. It has been suggested that PPA composite polymer asphalt binder is of superior properties and economic merit [24,25], thus it is necessary to dig into low temperature rheological performance of such binders and mixtures. In this paper, effect of poly phosphoric acid (PPA) on creep response of base, polymer (SBS and SBR) modified asphalt binders/mixtures at intermediate-low temperature were investigated by bending beam rheometer (BBR) test, modified penetration test, and tensile stress restrained specimen test (TSRST) to verify previous research and provide a reference for dual-modified binders and mixture.

## 2. Materials and methods

### 2.1. Raw materials

#### 2.1.1. Asphalt and modifiers

Asphalt used in this paper was base asphalt from Dongming in China. The main technical properties are shown in Table 1

**Table 1**  
Physical properties of Dong Ming 70# asphalt.

Items	Value	Specification limits
Penetration (25 °C, 100 g, 5 s)/0.1 mm	68.2	60–80
Ductility (5 cm/min, 15 °C)/cm	>100	≥100
Ductility (5 cm/min, 10 °C)/cm	35	≥25
Softening point/°C	53.2	≥46
Flashing point/°C	287	≥260
Paraffin content/%	1.6	≤2.2
Density (15 °C)/g/cm <sup>3</sup>	1.006	Measured value
Solubility/%	99.78	≥99.5
TFOT 163 °C, 5 h	Weight loss/%	0.46
	Penetration ratio/%	63.5
	Residual ductility (15 °C)/cm	31
	Residual ductility (10 °C)/cm	8

according to Chinese specification [26]. Star-like SBS with 40 wt% styrene produced by Beijing Yanshan Petrochemical Company and SBR with 27.3 wt% styrene from Lanzhou Petrochemical Co. Ltd. were chosen as polymer modifiers. PPA containing 79.3% phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>) was provided as a chemical modifier. Basic physical properties of PPA was presented in Table 2.

#### 2.1.2. Asphalt mixtures

Dense graded asphalt mixture (AC-13) with maximum nominal aggregate size of 13.2 mm was selected based on Chinese specification [27]. Gradation of AC-13 is shown in Fig. 1. Sample ID and volumetric parameters of mixtures were listed in Table 3. Three control groups are AC, AS, AR samples, and different amount of PPA was added forming AP, SP and RP. It is noted that optimal asphalt content of AC, AS, AR samples was determined to be same with AP, SP, RP, thus their volumetric values were not measured.

### 2.2. Sample preparation

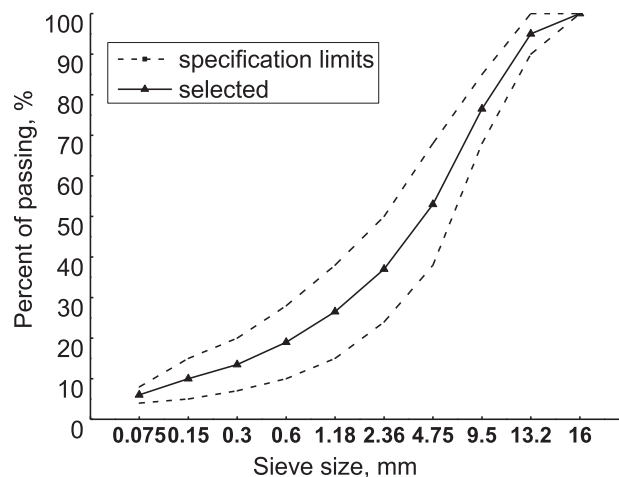
For modified binder only with PPA, it was firstly heated to 150–160 °C and then blended with 1%PPA stirring over 30 min at a constant speed. Large amount of bubbles appeared when stirring, indicating that chemical reactions triggered by base asphalt and PPA brought some gas, thus stirring should not stop until bubbles vanish.

For SBS or SBR modified binder, base asphalt was heated to almost 160 °C and then a certain amount of polymer modifiers was blended stirring for 10 min to obtain A1 or B1 before shearing at a speed of 4000 r/min for 60 min at 175–180 °C (for SBS modified) or 165–170 °C (for SBR modified). Finally A2 and B2 were used as SBS or SBR modified asphalt.

For composite modified binder, same process as SBS or SBR modified type was followed first. Afterwards PPA was added into the blends and sheared for 30 min at the speed of 4000 r/min

**Table 2**  
Physical properties of poly phosphoric acid.

Items	Value
Concentration of P <sub>2</sub> O <sub>5</sub> /%	79.3
Vapor pressure (25 °C)/Pa	$2.66 \times 10^{-6}$
Surface tension/(N/cm)	$80 \times 10^{-5}$
Specific heat/(J/(g·°C))	1.487
Density at 25 °C/(g/cm <sup>3</sup> )	1.964
Boiling point/(°C)	420



**Fig. 1.** Gradation of AC-13.

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