



# Effect of APAO on the aging properties of waste tire rubber modified asphalt binder

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## HIGHLIGHTS

- Asphalt binders modified with WTR and APAO were aged in TFOT and PAV process.
- WTR/APAO modified asphalt has higher resistance to aging.
- WTR/APAO modified asphalt behaves better resistance to permanent deformation.
- WTR/APAO complex modification helps increase the resistance to fatigue cracking.
- APAO strengthened the network in WTR modified asphalt.

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## ABSTRACT

Amorphous poly alpha olefin (APAO) was added into the waste tire rubber (WTR) modified asphalt and its effects on aging properties of WTR modified asphalt were investigated. Thin Film Oven Test (TFOT) and Pressure aging vessel (PAV) test were conducted to simulate the short-term and long-term aging respectively. Conventional properties including penetration, softening point, and viscosity were tested; Dynamic Shear Rheometer (DSR) test were conducted both to evaluate the properties of asphalt. The results showed that higher percentage retained penetration, lower softening point increment, and smaller viscosity aging index were gained after adding APAO to WTR modified asphalt. Closer  $G^*$  and  $\delta$  curves, smaller  $G^*$  ratios due to the introduction of APAO confirmed the improved aging resistance. Higher  $G^*/\sin\delta$  at high temperature and smaller  $G^* \cdot \sin\delta$  at intermediate temperature indicates WTR and APAO are beneficial to improving resistance to permanent deformation and fatigue cracking. Fourier Transform Infrared Spectroscopy (FTIR) measurements revealed that the double bonds in APAO and WTR were consumed for building a strengthened network in WTR modified asphalt and this may explain the better anti-aging properties of WTR + APAO compound modified asphalt.

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## 1. Introduction

Asphalt, though widely used as construction materials in pavement, has inevitable inadequacies, which results in road pavement suffering rutting at high temperatures, cracking at low temperatures and fatigue at room temperatures. These problems are especially urgent to be solved with rapid climate change and fast development of transportation. The past two decades have proved an efficient method by modifying asphalt with polymers, among which waste tire rubber (WTR) is one of the most attracting modifier for being environmentally friendly, comprehensively effective, and economically feasible [1–4].

Despite the advantages, the insoluble properties and poor storage stability of WTR modified asphalt hinder its wide and further

application [5–7]. When searching to overcome these shortcomings, another polymer amorphous poly alpha olefin (APAO), attracted the authors. APAO is one kind of non-polar and saturate plastic material, which has good miscibility with both asphalt binder and rubber [8,9]. In the authors' previous study, APAO was chosen as the second modifier accompanied with WTR, and the results indicates that WTR and APAO compound modification improved the high temperature performance, rutting resistance and storage stability of asphalt binders [10]. However, BBR test results in the previous study show that at low temperature this kind of WTR and APAO modified asphalt can't meet the qualification when temperature is lower than  $-6\text{ }^\circ\text{C}$  thus it is highly recommended for pavement in hot regions but not for that in chilling areas.

The properties of asphalt changes in physical and chemical properties during the production, road laying and years of use, which is called aging [11,12]. Aging process occurs in two types, (1) short-term aging during the construction phase of asphalt

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concrete and (2) long-term aging induced by traffic loads and environmental factors. The overall process is affected by various factors such as heat, sunlight, oxygen, etc. [13,14]. The aging behavior of rubber modified asphalt was already investigated by some researches [15–18]. A. Ghavibazoo, et al., conducted the dynamic shear rheometer and Fourier transform infrared spectroscopy test on rubber modified asphalt before and after TFOT aging. The results revealed rubber retarded asphalt oxidization through the release of antioxidants and the interaction between rubber and asphalt continued during its aging through absorption of aromatics and swelling [15]. Huang studied the rheological properties of crumb rubber modified asphalt before and after long-term oxidative aging. The results showed that addition of crumb rubber in both surveyed asphalts reduced viscosity build-up with aging [16].

However, the effect of APAO on the aging properties of asphalt lack research at present. And the composite influences of WTR and APAO on thermal aging properties of asphalt have not been studied. As another important aspect of the asphalt assessment, especially for this kind of WTR and APAO modified asphalt recommended for using in hot regions, the ability to resist aging is worth studying carefully and this is the focus of this article.

In this study, three different percentages (0%, 4% and 6% wt.) APAO were mixed with WTR (15% wt.) modified asphalt. These ratios of WTR and APAO were selected based on the results of the authors' former study [10]. TFOT and PAV equipment were used to simulate the short-term and long-term aging process. Various research methods including penetration, softening point, viscosity, rheological test and FTIR spectra were used to investigate the physical properties and structural characteristics before and after aging.

## 2. Experimental

### 2.1. Materials

Asphalt binders with the penetration grade 70# (penetration: 60–80), obtained from the SINOPEC Shanghai Petrochemical Company Factory, was chosen as the base asphalt. The properties of base asphalt binders were shown in Table 1. Waste tire rubber (WTR 80 mesh) was produced from grinded tires by He De Li rubber powder co., LTD in Wuhan, China. Physical properties of used WTR were listed in Table 2. Moreover, APAO 2385 manufactured in the company of HUNTSMAN in American was also utilized as a modifier, whose properties were shown in Table 3.

### 2.2. Preparation of samples

Modified asphalt samples were prepared according to the procedure shown in Fig. 1. At first, base asphalt was heated to  $165 \pm 5$  °C in a heating oven for 30 min. Then pre-weighed WTR and APAO were carefully poured into the oven, followed by 30 min blending with a medium-shear radial flow impeller at the speed of 5000 r/min and at the temperature of 180 °C. Bubbles produced in the blending were removed by another 20 min stirring in a propeller mixer at low speed of 1000 r/min. After that, the modified asphalt was poured into specific molds for further analysis.

15%WTR, 15%WTR + 4%APAO and 15%WTR + 6%APAO modified asphalt were prepared by adding different ratios of WTR and APAO respectively. The objective of this research is to analyze the influence of APAO on the aging performance of WTR modified asphalt, so only 15% WTR were adopted in WTR modified asphalt. These ratios were selected based on the authors' former study and they are identified to represent the changing trends of asphalt properties when modified with WTR and APAO [10].

**Table 1**  
Properties of 70# asphalt.

Properties	Values
Penetration (25 °C, 100 g, 5 s)/0.1 mm	64.6
Penetration index (PI)	-0.93
Softening point/°C	48.7
Ductility (15 °C, 5 cm/min)/cm	138.7
Viscosity/Pa·s(135 °C)	0.41
Viscosity/Pa·s(180 °C)	0.09

**Table 2**  
Properties of WTR.

WTR index	Values
Residue on sieve/%	8
Ash content/%	7.6
Density/(g/cm <sup>3</sup> )	3.65

**Table 3**  
Properties of APAO.

APAO index	Values
Penetration (100 g/25 °C/5 s)/0.1 mm	30
Softening point/°C	165
Viscosity/cP(190 °C)	40,000

### 2.3. Analysis methods

#### 2.3.1. Aging of modified asphalt

The thin film oven test (TFOT, ASTM D1754) was conducted to simulate the short-term aging process of modified asphalt. 50 g of asphalt was placed in an iron pan, sitting on the tray. The tray and pan undergo horizontal revolution at settled temperature. In order to analyze the short-term aging systematically, the aging was conducted at 163 °C for 0 h, 1 h, 2 h, 3 h, 4 h, and 5 h. After that, pressure aging vessel (PAV) equipment was used on samples after 5 h TFOT aging, aiming to simulate the long-term aging process according to ASTM D6521.

#### 2.3.2. Conventional properties test

Test methods of penetration, softening point, and viscosity were conducted according to ASTM D5, D36, D4402 and the rubber asphalt standards, respectively.

#### 2.3.3. Rheological characterization

Rheological properties were gained by testing asphalt samples on a Smart Pave 101 Rheometer (Anton Paar, Austria) and the procedure was conducted according to ASTM D7175. The temperature sweep test was conducted under strain-controlled mode at the constant frequency of 10 rad/s, with testing temperature ranging from 42 °C to 82 °C at increment speed of 2 °C/min. The strain level was 10% for unaged and TFO aged asphalt binder. The strain level was 1% for PAV aged asphalt binder. The plate used was 25 mm in diameter the gap between parallel plates was 1 mm for unaged and TFO aged asphalt binders. In addition, the plate used was 8 mm in diameter and the gap between parallel plates was 2 mm for PAV aged asphalt binders.

#### 2.3.4. FTIR spectroscopy

A FTIR spectrometer (Infinity-1) was used to analyze the functional characteristics of asphalt binders; including base asphalt, 15% WTR, and 15% WTR + 4% APAO modified asphalt before and after aging. At first, these samples were separately dissolved by CS<sub>2</sub> to prepare the bitumen/CS<sub>2</sub> solutions with concentration of 5 wt%. Immediately after low-speed mixing into uniform dispersion, for each group one drop of bitumen/CS<sub>2</sub> solution was transferred by a digital display shifter onto a 0.1 mm height blankly scanned KB<sub>r</sub> cell. After the CS<sub>2</sub> totally evaporated, there formed a thin film. Finally, these film samples were scanned by the FTIR spectrometer in wavenumbers from 400 to 4000 cm<sup>-1</sup>.

## 3. Results and analysis

### 3.1. Penetration

Penetration is useful in evaluating the consistency of asphalt at intermediate service temperatures [19]. Fig. 2 shows the penetrations of asphalt samples at 25 °C before aging and those after 1 h, 2 h, 3 h, 4 h and 5 h TFOT aging. It can be seen that penetrations of all samples linearly decrease with increasing time. Linear fitting is convincing because R<sup>2</sup> are higher than 0.95 for all samples. However, slopes of each sample, representing the descent speed, differ with the ratios of WTR and APAO. It can be seen that penetration slopes of 70#, 15%WTR, 15%WTR + 4%APAO, 15%WTR + 6% APAO are -3.8936, -1.2986, -0.9049, -0.5897, respectively. Higher slope represents faster penetration descent. This indicates that the effect of short-term aging on penetration of 70# asphalt is the most significant, followed by 15%WTR, 15%WTR + 4%APAO

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