# The performance of Epoxidised Natural Rubber modified asphalt using nano-alumina as additive

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## HIGHLIGHTS

- Sonication significantly reduced the agglomeration of the nanoalumina.
- Nanoalumina improved the stability of the polymer modified asphalt in hot storage.
- Adding nanoalumina improved the temperature susceptibility and rheological properties of the polymer modified asphalt.
- Adding nanoalumina improved the adhesion of the polymer modified asphalt.

## ARTICLE INFO

## ABSTRACT

Polymers are commonly used for improving the physical and rheological properties of asphalt. Several methods have been suggested to increase the compatibility between polymers and asphalt. Adding of nanoparticles to asphalt can improve the performance of polymer modified asphalt. This study is about evaluating the performance of Epoxidised Natural Rubber (ENR) modified asphalt using nanoalumina ($Al_2O_3$) as Additive. In this study, an ultrasonic device was used to disperse $Al_2O_3$ at 2, 4, and 6 wt% into base asphalt (BA) and ENR using a high shear mixer. The effects of $Al_2O_3$ addition on the base asphalt and Epoxidised Natural Rubber modified asphalt (ENRMA) were then investigated, including the physical properties, storage stability, rheological properties and microstructure of the binders. High compatibility between $Al_2O_3$ and ENR led to a better dispersion of ENR in the asphalt, improving the rheological properties of the binder. Based on dynamic shear rheometry tests, $Al_2O_3$ reduces the temperature susceptibility of the asphalt and facilitated polymeric modification by improving the compatibility, increasing the viscosity, stiffness, adhesion and elastic behaviour of the binders. $Al_2O_3$ also improved the rutting resistance behaviour at high temperatures. The best results were recorded for polymer-modified asphalt containing 6% $Al_2O_3$ compared to the base asphalt without any $Al_2O_3$.

## 1. Introduction

Asphalt, a long-established and valuable engineering material, can be enhanced through the use of polymer additives as modifiers. Various polymer modifiers can impart different characteristics to composites when added. Polyethylene (PE), ethylene vinyl acetate (EVA), rubber and styrene butadiene styrene (SBS) block copolymers, have been identified as useful asphalt modifiers [1].

Many researchers are still working to mitigate the drawbacks of polymer modified asphalt materials, in order to prolong their use in pavement engineering [2]. One of the major shortcomings of pure polymer modifiers is that most polymers are thermodynamically incompatible with asphalt, due to the large differences in density, polarity, molecular weight and solubility between the polymer and asphalt [1]. This can result in delamination of the composite during thermal storage, which is not readily apparent and adversely affects the material when used in construction.

Compatibility is the major factor influencing even dispersion and composite stability in such polymer/asphalt systems.

Consequently, researchers have sought to prepare uniform nanomaterials that can be stably dispersed in asphalt matrix. Unfortunately, nanomaterials tend to aggregate to cause spot segregation, resulting in uneven microstructures in the composite and leading to force field distortion, which has a negative impact on the nanomaterial properties. A lack of dispersion in the added nanomaterials over time (poor stability) will cause the microstructure of the composite to gradually change during transportation and storage, or during application on pavements [2].

The type of nanomaterial present can play a positive role in improving the properties of asphalts modified with polymer additives. Pamplona et al. investigated the thermal storage of asphalt modified with SBS and vermiculite and montmorillonite (OVMT and OMMT) [3]. The presence of OVMT improved the storage stability of the SBS-modified asphalt, as phase separation is a major obstacle for the use of SBS in paving. Dhawo et al. investigated the storage stability of a nanosilica-polymer modified asphalt and found that adding 6 wt% nanosilica stabilises the binders at high temperatures [4]. Furthermore, nanosilica significantly improved the rutting resistance and fatigue of the binder. Markanday et al. have shown that nanoclay can promote compatibility between asphalt and polymer (ethylene-co-vinyl acetate), and that high compatibility between clay and polymer leads to better dispersion of the polymer in the asphalt [5], influencing the final rheological properties of the binder. Similarly, Galooyak et al. reported improved storage stability when a nanoclay was added to a SBS–asphalt blend [6]. Goh et al. prepared nanoclay and carbon-microfibre-modified asphalt, and reported improved mechanical properties and water resistance in the resulting asphalt mixtures [7]. Shaban et al. investigated nanoalumina ($Al_2O_3$) modified asphalt and found that nano-$Al_2O_3$ promotes rutting resistance at high temperatures, while promoting fatigue resistance at intermediate temperatures [8]; they also found a stable form of nano-$Al_2O_3$ modified asphalt after storage at high temperatures. According to Ramez et al. (2014, 2016), the storage stability of epoxidized natural rubber (ENR) modified asphalt depends primarily on the ENR content [9,10]. However, the rheological parameters indicate that ENR increased the binder's stiffness and elasticity behaviour at high temperatures. Adding ENR decreases the rutting for the binder at high temperatures, while improving the fatigue behaviour at intermediate and low temperatures. Furthermore, ENR modified hot mix asphalt (HMA) is less susceptible to moisture damage compared to unmodified HMA [11]. The rheological properties indicated that 6% ENR is the optimum amount to add as a modifier in asphalt [9].

There are three different dispersion techniques in asphalt modification: mechanical stirring, high shear mixing and sonication. Khattab et al. developed a dispersion technique for carbon nanofibres, combining sonication and high shear mixing techniques to achieve the highest degree of dispersion [12]. Ultrasonic devices are suitable for low-viscosity materials and small volumes of material. Mechanical stirring is a common technique to disperse particles or nanoparticles in liquid systems. However, the major advantage of using a high shear mixer to disperse nanoparticles is the added efficiency when manufacturing large amounts of nanocomposites.

In this study, three types of binders were used: (1) base asphalt (BA), (2) ENR modified asphalt (ENRMA) with 6% ENR (vs. BA weight), and (3) $Al_2O_3$ modified ENRMA. Different levels of $Al_2O_3$ (2, 4, and 6%) were used as additives to modify the ENRMA, labelled as PMN2, PMN4, and PMN6 respectively. The objective of this study is to characterize the physical and rheological properties of Asphalt/ENR/Nano-Alumina composites, so that the Al2O3 (2, 4, and 6%) were chosen based on some previous studies used different Nano-particles as modifiers with asphalt/polymer composites [5,6,13,14]. The binders were evaluated in terms of conventional properties (penetration, softening point, viscosity), storage stability, rheological properties as studied by dynamic shear rheometry (DSR), adhesion as studied by atomic force microscopy (AFM), and the microstructure as determined by Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and X-ray diffraction (XRD).

## 2. Materials & methods

### 2.1. Materials

The asphalt used in this study is 80/100 penetration grade, supplied by the asphalt factory at Port Klang, Malaysia. ENR was obtained from the Malaysian Rubber Board under the trade name of ENR 50, with 53% epoxidization and passed through a 2.36 mm mesh sieve prior to shearing with asphalt. $Al_2O_3$ was obtained from Accumet Materials Co., USA. The physical properties of the asphalt, ENR and $Al_2O_3$ used here are shown in Table 1.

### 2.2. Preparation of binders

Binder preparation was divided into three phases. First, the nanopowder was sonicated in 100 mL of methylene for 5 min to disperse the agglomerated $Al_2O_3$, using a Sonic Ruptor 250 Ultrasonic Homogenizer (USA). A piezoelectric ultrasonic transducer was operated at a resonance frequency of 20 kHz, with an ultrasonic tip having a cylindrical-shaped medium-intensity ultrasonic processor 19 mm in diameter and 10.5 cm in length. The device can accommodate 25–500 mL of substance, and was operated at 50% of its maximum amplitude, delivering energy to the samples at a rate of 1900–2100 J/min. Energy was applied in cycles of 2 s to prevent the suspensions from overheating. Second, ENRMA was produced by mixing ENR (6 wt% vs. asphalt) with base asphalt. All binders were prepared using an IKA T25 digital ultra turrax high shear mixer with dispersing element number S25, at 160 ± 1 °C and 8000 rpm for 1 h. ENR was added to the asphalt when the temperature stabilized at 160 ± 1 °C. Third, $Al_2O_3$ (dispersed in the methylene) was manually poured into the ENRMA, and the high shear mixer was allowed to run for an additional 30 min. Solution addition was performed gradually at a constant rate to avoid foaming.

The morphology of $Al_2O_3$ was investigated by TEM as shown in Fig. 1. While the high shear mixer is not enough to disperse the nanoparticles on its own (Fig. 1a), the use of sonication significantly reduced the agglomeration of the nanoparticles (Fig. 1b & c).

### 2.3. Conventional binder tests

Many conventional tests were conducted on the base asphalt and the modified asphalt according to ASTM standards, such as penetration, softening point, and viscosity tests (using the Brookfield Model DV-III) [15–19]. Consistency was measured using penetration tests, where a softer consistency indicates higher penetration. A liquefied sample was cooled to 25 ± 0.5 °C, and a penetrometer was used to measure penetration via the application of a standard needle to the sample at 25 ± 0.5 °C [15]. For softening point tests, two horizontal asphalt disks cast-heated in supported brass rings and each supporting a steel ball at a controlled rate in a liquid bath were prepared. Here, the softening point is the mean temperatures where two sufficiently softened disks allow their respective asphalt enclosed balls to descend 25 mm [16].

**Table 1**
Base asphalt and ENR material properties.

| Material | Properties | Value | Specification |
|---|---|---|---|
| asphalt 80/100 | Penetration @ 25 °C | 83 | ASTM D5 |
| | Softening point (°C) | 44.5 | ASTM D36 |
| | Specific Gravity | 1.03 | ASTM D70 |
| | Viscosity @ 80 °C (Pa·s) | 12.6 | ASTM D4402 |
| | Ductility (cm) @ 25 °C and 5 cm/min | >100 | ASTM D113 |
| ENR | Size (before shearing) | 2.36 mm | |
| | Specific Gravity | 0.94 | |
| $Al_2O_3$ | Alpha, white, hydrophilic contains 5–10% theta, Fe < 10 ppm | | |
| | Purity | +99% | |
| | APS | ~80 nm | |
| | Morphology | spherical | |