Improving Asphalt Binder Properties Using Recycled Polyethylene Terephthalate and Natural Liquid Rubber

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Abstract. This paper investigates adding two types of polymer to asphalt binder in different proportions to demonstrate the effect of their mechanical properties on the asphalt. A 10% addition of polyethylene terephthalate (PET) is used in this research with different percentages of liquid natural rubber (LNR at 2%, 4%, 6%, and 8%). The natural rubber chemically is heated to increase the surface area to achieve the best penetration and to overcome phase separation issues caused by the difference in the densities of the rubber and asphalt. The asphalt tests showed improvement in the structures and viscosity, with a reduced softening point and improvements in temperature susceptibility with increases in the natural rubber ratio. The FTIR spectroscopy confirmed that the asphalt modification is a physical process, and other tests showed an increase in the asphalt binder resistance at low temperatures.

1. Introduction

Asphalt may be described as a solid or a viscous liquid consisting mainly of mineral oils with a variety of high molecular weight hydrocarbons with varying proportions of oxygen, nitrogen, and sulphur [1]. Asphalt is used in the paving of roads, but suffers from restrictions of temperature, softening when the temperature is high and cracking when the temperature is low; these effects, in addition to damage caused by traffic and high load weights will damage the road more quickly and cause an increase in maintenance costs. This makes it necessary to improve the properties of asphalt [2, 3]. Researchers have tried to use different types of additives to modify the original asphalt material to increase its resistance [4, 5], as when modified, the asphalt material in the elastomer is characterised by its ability to extend, which increases its resistance to withdrawal as shown by the Toughness and Tenacity tests [6-9]. Various types of polymers can be used to improve asphalt specifications in order to increase fatigue resistance. One of the materials used in improving the properties of asphalt is polymer fibres. [10]. A relatively high proportion of plastics can be used in asphalt mixtures by replacing part of the mineral aggregate with an equal weight of plastic waste polymers [11-16]. Polyethylene terephthalate (PET) is suitable substance for use in improving asphalt [17], and several PET characteristics, such as being a two-part aromatic and fibrous thermoplastic polymer with a high melting point and glass transition rate, being non-sensitive to common solvents and humidity, and being chemically inert and brittle, are of interest in such amendments [18]. Figure 1 shows the structure of polyethylene terephthalate and its recycling code.

![Polyethylene Terephthalate Recycling Code and structure](image-url)
Natural rubber (NR) is a group of about twenty different species of polymeric formulas that share mechanical behaviours, also known as rubber behaviours. Natural Rubber is emulsion of isoprene Poly isoprene cis 1-4 (Figure 2) with 35% hydrocarbons in the form of small particles of 0.5 Micron width scattered in water [19].

![Figure 2. Structure of Natural rubber Poly isoprene cis 1-4](image)

This paper explains the importance of compatibility between the polymers added to an asphalt bond in a poly phase system and the effect on the properties of modified asphalt. These include thermal and chemical treatment of natural rubber to obtain a liquid density of convergence with the asphalt bond to avoid the process of phase separation, which often occurs when adding rubber pieces, as well as the effect of hydrogen bonding between the hydroxide group in rubber with the carbonyl group in polyethylene terephthalate and its effect on the mechanical properties of natural rubber [20-22]. Figure 3 shows the hydrogen bonding between polyethylene terephthalate and natural rubber.

![Figure 3. Natural rubber pyrolysis process](image)

### 2. Experimental process

#### 2.1. Materials

##### 2.1.1 Plastic

Plastic compounds are manufactured compounds that are generally difficult to decompose using microorganisms because specific enzymes with certain actions are required to break down particular bonds. Molecules of plastic contain long-form chains with a large numbers of carbon atoms that are linked with each other by strong bonds. They are thus not affected by the various decomposition factors in the environment such as water, oxygen, and microorganisms, so when they enter the environment, they remain intact for long periods causing continuous pollution. It is thus important to find different ways to dispose of them, including their use in improving asphalt.

| Physical properties          |  
|------------------------------|
| Chemical formula             | \((\text{C}_{10}\text{H}_{8}\text{O}_4)\text{n}\)  
| Abbreviation                 | PET  
| Classification               | Thermoplastic  
| Molecular orientation in solid phase | Semi-crystalline  

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Several water bottles were collected after use, washed, and dried. These were indirectly treated thermally and then cut into very small pieces and ground using a milling machine. Sieve analysis revealed that 38.37% of the PET passed through a 0.300 mm sieve, 31.3% through a 0.600 mm, and 22.5% through a 0.425 mm sieve. Figure 4 shows the various stages of this process.

![Figure 4. PET used (A) Disposable Bottle, (B) melted waste PET (C) Granules of waste PET.](image)

### 2.1.2 Rubber

Natural rubber was used due to its low cost and ready availability [20-22]. The natural liquid rubber prepared in the laboratories of the Chemistry Department, University of Babylon, where 25 g of natural rubber NR was cut into very small pieces and melted gradually using toluene (175 mL) with heating at 150 °C, being continuously stirred with the help of a magnetic motor for 3.5 hours. This process is shown in Figure 5.

![Figure 5. (A) Natural Rubber NR, (B) Small pieces of natural rubber (C) Natural rubber after dissolution](image)

#### 2.1.3 Asphalt Binder

The asphalt material used has a penetration grade of 40 to 50, being a type often used in pavements (road surface layers) in Iraq; Table 2 shows the physical properties of the asphalt binder as determined by the Babylon Structural Laboratory.

| Property                  | Value                  |
|---------------------------|------------------------|
| Density                   | 1.37 g/cm³             |
| Melting point             | 250 °C                 |
| Thermal conductivity      | 0.15 – 0.24 W/m. K     |
| Monomers                  | Terephthalic acid, Ethylene glycol |
| General properties        | Transparency to visible light and microwaves. Very good resistance to ageing. Wear and heat. Lightweight. Impact and shatter resistant. Good gas and moisture barrier properties. |
Table 2: Physical properties of the asphalt binder

| Properties                        | Methods                        | Class requirements | Values       |
|-----------------------------------|--------------------------------|--------------------|--------------|
| Penetration (25 °C, 100 g, 5 min) | Iraqi Standard No. 9           | 40 - 50            | 46 (0.1 mm)  |
| Softening point (ring & ball)     | Iraqi Standard No.1987/10       | -                  | 44 °C        |
| Ductility (25 °C, 5 cm/min)       | Iraqi Standard No. 160          | 100 <              | 120 cm       |
| Flash point (cleaveland open – cup)| AASHTO T- 48                   | 232 °C <           | 245 °C       |
| K. Viscosity (mm²/sec,130 °C)     | AASHTO T 201                    | 400-800            | 544          |

2.2. Methods
Various tests are available to determine the physical, mechanical, and rheological properties of modified asphalt binder to allow awareness of improvement in one or more such properties.

2.2.1. Modified Asphalt Preparation
In this paper, a wet preparation process was used. Several 500g samples of asphalt were heated using an oven until it became liquid. Then, a quantity of PET powder equal to 10% of weight of the asphalt was added to the each sample of heated asphalt along with a different percentage of LNR (2%, 4%, 6%, and 8%) of the asphalt weight. This was done in the high shear mixer, and the LNR added initially with the PET powder added to the mixture after 10 minutes. The mixing temperature was 175 °C, and the mixing speed was 1500 rpm; the mixing time was 60 min., to produce a homogeneous mixture. The polymer-modified asphalt specimens were then sealed in containers and stored for further testing.

2.3. Laboratory Testing
Penetration, Softening point, and Ductility testing were carried out at the Bail Structural Laboratory, while the rotational viscosity test was carried out at the road laboratory at the Faculty of Engineering, Karbala University. The attenuated total reflectance Fourier transforms infrared spectroscopy (ATR-FTIR) were done at the College of Science, University of Babylon, using a BRUKER single reflection zinc selenide prism in the transmission mode to acquire the spectra of LRM samples in wavenumbers ranging from 4,000 to 500 cm⁻¹. Atomic force microscopy AFM tests were done at the College of Materials Engineering, University of Babylon.

2.3.1 Traditional bitumen tests
2.3.1.1 Penetration testing
The consistency of a penetration grade is measured by the penetration test. In this test, a needle of specified dimensions is allowed to penetrate a sample of asphalt [25]. To carry out this test, the samples were thus smelted and cooled and penetration was calculated using a standard penetration device. The amount of penetration is a distance of ten millimetres vertically penetrated by a standard needle in a sample of material at a constant temperature. The standard settings for penetration (100 g, 25 °C and 5.0 sec) were used on a Penetrometer P734, on the bitumen base and on PMB at 10% polymer concentrations of polyethylene terephthalate with natural liquid rubber at 2%, 4%, 6%, and 8% weight of asphalt.

2.3.1.2 Softening Point test
This method is used to measure asphalt’s tendency to flow at high temperatures when placed on roads; the ring and ball softening test is thus a standard test for the determination of asphalt strength [25]. The method also helps to control the production of asphalt in refineries and, in the production of asphalt, to determine the standard temperature at which asphalt moves from solid to liquid states, when a steel ball weighing 3.55 grams falls into contact with the base plate 2.5 mm away.

2.3.1.3 Ductility test
This test shows the ability of asphalt to adhere to the aggregate in the asphalt mixture, estimating the gravitational potential of the asphalt bond, allowing evaluation of the asphalt adhesivity [25].

2.3.1.4 Temperature Susceptibility:
Viscosity is inversely proportional to temperature. The stability of asphalt penetration at different temperatures (15, 25, and 35 °C) is thus verified under the same conditions of pressure and time to show the sensitivity of the asphalt to high and low temperatures [25]. A 45° C temperature test was added to test asphalt behaviour at a higher temperature.

2.3.1.5 Rotational viscosity RV
The rotational viscosity test was performed at different temperatures (135, 155, 165, and 175 °C), using a programmable viscous viscosity device; rotational viscosity measurements were made for both the undamaged asphalt bond and all polymer ratios.

2.3.2 Morphological, Chemical and Structural Characterization
This study focused on the influence of morphology, chemical and structural characterisation and storage on the mechanical performance of asphalt mixes, in particular permanent deformation and fatigue characteristics.

2.3.2.1 Attenuated total reflectance Fourier transforms infrared spectroscopy (ATR-FTIR)
The AASHTO T 302-05 [23] was used as a standard means to assess the ATR-FTIR of asphalt. This method was used because of the ease of treatment of asphalt samples, in addition to the absence of overlap between the asphalt samples and materials required. The preparation of the sample for examination ensured good measurement speed and accuracy of the results when the light passed through the surface layer of the material; the corresponding spectra were recorded and then used to indicate the functional groups of materials. The polymer-modified asphalt sample was heated in the oven to 100 °C until the asphalt assumed viscosity. About 10 g of asphalt was placed on waxy paper cut slightly larger than the surface of the ATR crystal, with sufficient material used to produce a layer covering the crystal face. The thickness of the asphalt on paper was about 1 mm. The ATR extensions were installed according to the manufacturer’s instructions. The material was allowed to cool for several minutes before the asphalt surface was placed in direct contact with the upper face of the prepared ATR crystal [23]. The air bubbles were removed to ensure that the material was in direct contact with the ATR crystal. In this method, total internal reflectance of infrared light in a non-absorbing prism is used, and thus contact of the absorbing substances with the prism surface attenuates the internally reflected light and provides an infrared absorption spectra so that, when light passes through the surface layer of the material, the corresponding spectra are recorded and used to map the material’s functional groups [24].

2.3.2.2 Atomic force microscopy (AFM)
AFM was used to investigate phase changes due to modifications and to link small-scale changes to chemical and biological performance of the modified binder. The use of AFM as a tool in various documented modifications of asphalt has allowed the morphology of the rubber phase and its interaction with the asphalt bonding structure to be studied at different concentrations in different particle sizes [26], as shown in Figure 13.

3. Results and discussion
The results of penetration testing showed that the penetration rate of the modified asphalt increased as the percentage of the added LNR decreased. This is because the polyethylene terephthalate molecules help in increase the strength of the bond between the asphalt particles, and high rates of added LNR cause the resulting asphalt to have a higher hardness than pure asphalt. The value increases with the addition of 6% rubber and then decreases at 8% due to the overlap of rubber with polyethylene terephthalate in asphalt; rubber’s properties include a tendency to increase lubrication and elasticity, and the fine rubber particles have a higher surface area and are therefore more active than other asphalt ingredients. Thus, the introduction of fine rubber particles reduces the temperature of the binder by enhancing the flexible and strong properties of the asphalt at low temperatures [27]. The increase in the spread of oils in the rubber particles negatively affect the cohesive properties of bitumen, however, and reduces the ability of the binder to link to other particles. Therefore, it is recommended to use higher-content asphalt as compared to traditional mixtures or to select asphalt with a high degree of penetration in the design of rubber mixtures [28].
Higher temperatures cause higher degrees of softening, and asphalt sensitivity to heating is used in the classification of asphalt types. Figure 7 shows that the degree of elasticity associated with a 10% ratio of polyethylene terephthalate is due to the ordering of the molecules and their association with each other, especially when the temperature rises, owing to the cohesion or absence of gaps between the chains as they link to each other. The degree of flexibility increases with the ratio of natural rubber to 6% and 8%. The later low degree of flexibility is due to the nature and characteristics of natural rubber, which contains short and linear unsaturated strings, and the effect this has on the mix. When the rubber touches the asphalt, it generally absorbs some of the low molecular weight material and leaves the remaining bitumen with more higher molecular weight (elliptical) substrates, which increases viscosity [29], by allowing spreading of rubber particles, which increases the dimensions of the rubber mesh until a swelling balance is achieved. Factors affecting the rate of swelling include rubber temperature, mixing time of rubber with asphalt, chemical composition of asphalt, and type and size of rubber [30].

Figure 8 shows that polymer hardness and strength increase due to the presence of aromatic rings. These offer a systematic arrangement of the asphalt content, characterised by a high degree of resistance to corrosion due to the semi-crystalline structure of the polymer. The addition of natural rubber at about 6%, causes these to increase slightly, but the increase of the rubber percentage to 8% causes the value to increase significantly due to the mechanical properties of rubber. In addition, there is a slight weight increase of the sample due to increased polymer concentration in the mixture, along with increased viscosity.

The lighter asphalt components penetrate easily into the polymer structure of the rubber. Non-polar components such as alkanes, n-alkanes, and n-alkyl benzenes have a tendency to penetrate through rubber particles, due to the high compatibility of these compounds with the linear polymer chains [31].
Penetration values for each control and PET10%-LNR modified asphalt binder sample at different temperatures are shown in figure 9. These suggest that the addition of different ratios of polymer amends the thermal sensitivity of the asphalt bonds at different temperatures. Cracking resistance is increased significantly with significantly lower crack length, and low temperature thermal sensitivity decreases with 10% polymer polyethylene terephthalate with natural rubber up to the highest value of LNR of 8%. At high temperatures, the thermal sensitivity is highest in pure asphalt and decreases with the addition of LNR at 4%, gradually decreasing further when adding LNR at 8% due to the impact of rubber and its resistance to tensile deformation. Several factors contribute significantly to the extent to which rubber acts as a flexible aggregate, including, rubber content and general grade; when applying the load, the rubber particles absorb the impact energy from deformation, but after the release of the load, the rubber releases this absorbed energy and restores the physical form.

Figure 10 shows the penetration index versus Softening Point for the control and each PET 10% + LNR modified asphalt binder at different temperatures. The temperature index against the softening point at 25 °C and the application of the equation by Pfeiffer and Van Doormaal (1936) and Van der Poel (1954) are shown. At the first addition, PET 10% is affected by increases in temperature susceptibility but with the increase in liquid rubber ratio to 6% and 8%, formation of Sol-Asphalt occurs as asphaltenene are scattered in the oil components due to the difference between the simple densities of rubber and asphalt. This process is less effective at low temperatures.
Asphalt is a thermoplastic material with rheological properties influenced by high temperature and loading time [32]. Treatments and polymer components (carbon black, fillings, polymers and ores) can be transferred from rubber to asphalt and concentrated in the aromatic part of the asphalt [33], which in turn can improve the asphalt’s properties. This is in addition to the beneficial effects that rubber can have on the rheological properties of asphalt, especially at high temperatures [34, 35].

The quality and quantity of both resin and asphalt were studied in this work. When the aromatic content is high, Sol-Asphalt is formed, while with increasing paraffin content, Gel-Asphalt is formed [36, 37].

The most important rheological test of asphalt was proof of penetration (PI), used to establish the idea that the asphalt system is colloidal: through PI the degree of propagation of heavy and polar components within the asphalt matrix can be determined [38].

The results of the FTIR spectra are shown in Figure 12 for absorption at 2,919.42 to 2,850.44 cm\(^{-1}\) representing the range of the C-H vibration; 1,375 cm\(^{-1}\) representing the bending vibration of C-H, and 1,459 cm\(^{-1}\) representing the vibration of the expansion of C = C bonds in the aromatics. The FTIR asphalt spectrum contains a high proportion of light aromatic components, and increases in the polymer ratio cause a decrease in the aromatic content of the asphalt at 870 to 675 cm\(^{-1}\). The asphalt rubber peaks are slightly lower than those of the rubber free of additives due to low saturation between rubber and asphalt.
at 1,030 cm\(^{-1}\). The expansion vibration is related to the sulphoxide group, S = O bonds, in asphalt as a result of the release of sulphur added to the asphalt, especially for additions of 2 to 6%. The absorption at 1,737 to 1,738 cm\(^{-1}\) indicates the presence of carboxyl, C = O bonds, which suggest that the oxidation process begins at 2% and then decreases with increases in the proportion of polymer. These results show that the increase in the rubber ratio leads to an improvement in asphalt behaviour, with reduced aging due to the increased oil content of modified asphalt.

Rubberised asphalt showed a different phase topography under AFM, leading to the discovery that some rubber particles may dissolve in asphalt due to the removal of rubber vulcanization. The effect of temperature on binder formation was measured in modified asphalt binder with low polymer percentages [40]. The AFM results showed that the addition of the interactive polymer created areas rich in bee-shaped micro structures with low thermal properties, which were present even at high temperatures, improving binder viscosity at this range of temperatures during service. The chemical structure of the asphalt binder was elegant, and this fine structure plays an important role in the modification of the binder with polymer. Topography (Height sensor), elasticity (DMT modulus), stickiness (Adhesion),
hardness (Deformation) and energy loss (Dissipation) were acquired simultaneously. In addition, the AFM results show different phases such as a stiffer phase (Peri) and a softer phase (Perpetua), and a more viscous phase (Perpetua) and less viscous phase (Peri). The resolution was good enough to resolve the individual temperature behaviours of the mechanical properties moduli of both phases. The modulus behaviour for both phases was very similar at different temperatures [41]. The adhesion strength of the asphalt volumes is one of the basic characteristics that affects the performance under damage caused by asphalt moisture. AFM is one of the few ways to measure adhesion in small-scale asphalt devices [42]. Under moisture, the fine structures are severely affected, and new topographical features observed on the bitumen film surfaces. These suggest that tension, bending and pressure in the presence of water exposure lead to cracking the weakest surface structure points. According to the observed results, the “bees” of the micro structure and the interfaces between that phase and the working phase were the weakest point on the surface tar, and thus the first to break [43]. The AFM data shows that the evolution of adhesive strength appears due to different types of exposure or aging. This discovery supports the concept of traditional aging, which diminishes binder boundaries with aging that may lead to the failure of adhesive bonding between binder and aggregates. Gravity causes the bulk of failures; however, aging will increase polar fractures, reflected by increased adhesion to the surface. Local polar interactions are likely to reduce gravity, and the ratio of micro structures on the surface decreases with exposure and time [44-46].

![Figure 13. Typical AFM images of asphalt binder using topographic 3D](image)

**Conclusion**

1. Two types of polymer were used in this work, PET and LNR.
2. The addition of polymer to the asphalt led to the modification of the asphalt, improving the mechanical, physical, and rheological properties, generally by improving the viscosity.
3. The mixture of rubber, polymer and asphalt is homogeneous due to similar densities, avoiding phase separation and collapse.
4. Increasing the natural rubber ratio increased the physical bonding between asphalt and polymer, which improved the mechanical properties, temperature susceptibility, and crack resistance especially at low temperatures.
5- Rotational viscosity testing showed improvements in the viscosity with increases of polymer additions and high temperatures.
6- Stability and degree of elasticity were affected by the oxidation process, decreasing at 4% and 6% LNR addition, but improving subsequently.
7- Spectral analysis of FTIR showed a difference in the height of the peaks proportional to the ratio addition of polymer to asphalt. The aromatic content decreased with increased ratio of additions, and the density increased by polymer type and mixing ratio.
8- The analysis by atomic force microscope revealed the distribution of the structures and the ratio of the spread and their effects on the mechanical and rheological properties of asphalt.

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