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# Modification of Asphalt using Castor Oil Based Polyurethane

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**Abstract:** ***Asphalt is the most used binder for road paving due to its adhesive and water proofing properties. Since bitumen (asphalt) has low softening point and thermal stability, making it prove to permanent deformation and fatigue. In order to maximize it resistance to permanent deformation and to reduce the fatigue, bitumen used to be modified with various additive. Normally additive used for the modification are styrene butadiene styrene (SBS) co-polymer, reactive ethylene terpolymer, ethylene vinyl acetate rubber etc. by using polyurethane (PU), can have added advantage of easy handling and more durability etc. Pre-added polyol to bitumen make it more flowable and liquid to make it ease of handling. In the present work, different reaction parameters such as the effect of reaction time, effect of catalyst and effect of OH to NCO ration was optimized. PU modified asphalt shows hardness value i.e. 21-32mm and softening point i.e. 53$^0$C-63$^0$C. Unmodified asphalt have the 89mm hardness value and 43$^0$C softening temperature.***

**Keywords:** Asphalt; Pre-polymer; Binder; Toluene diisocyanate; Polyurethane

## 1. Introduction

The invention of polyurethane (PU) was done by Otto Bayer and his coworkers at the laboratories of I.G. Farben in Leverkusen, Germany in the 1937. Since then, polyurethane has been used in different industrial applications and more recently in civil engineering and geotechnical applications [1]. The initially aliphatic diisocyanate and diamine forming polyurea was focused, later polyurethane obtained from an aliphatic diisocyanate and glycol was used as it produced the interesting properties of polyurethane. Polyisocyanates became commercially available in the year 1952, soon after the commercial scale production of polyurethane was witnessed (after World War II) from toluene diisocyanate and polyester polyols. In the years of 1952-1954, different polyester-polyisocyanate systems were developed by Bayer [2].

Polyurethane are found practically everywhere in our modern world and are used in a wide variety of applications such as disposable packaging for food, in the cushioning and insulation material. It is hard to go a day without coming across some sort of polymeric foam [3].

Over the years, the chemistry, material properties and application techniques of polyurethane have been developed and improved. As polyurethane are light in weight, insulation quality, quick reaction time and high expansion rate; polyurethane has been used to repair pipeline leaks, for curtain walls, install in-situ foam piles without excavation and in asphalt modification for the road construction. The polyurethane is use to raise sunken concrete roadway, to improve the performance and to increase load bearing capacity [4,5].

Asphalt is act as the glue that holds a hot mix asphalt pavement together. Asphalt shows fluid-like and solid-like i.e. elastic characteristics there so, it is in the class of a viscoelastic materials. These types of materials are largely temperature dependent, as it behaves more like a solid at low temperatures and more like a liquid at high temperatures. These excessive behavior can leads to negative effect on pavement performance. Even sometimes cracking may also takes place due to stiffness and deformation may occur if it is too fluid. An ideal temperature range exists for asphalt, in which it displays the right combination of viscous and elastic properties for good pavement performance [6,7].

Different materials are mixed with asphalt to improve its properties and performance i.e. its natural viscoelastic behavior. There are two main classes of polymers used for this purpose: elastomers (i.e styrene-butadiene rubber and styrene-butadiene-styrene block copolymer), which enhance strength at high temperatures, as well as elasticity at low temperatures; and plastomers (i.e. polyethylene and ethylene vinyl acetate), which enhance strength but not elasticity [8]. Other than these, hydrated lime, elemental sulfur and crumb rubber prepared from scrap tires are used as modifier for asphalt [9].

Asphalt modification is done to enhance the performance of asphalt by widening the range between the asphalt's high- and low temperature grades, in pavement carrying a very high traffic volume and slow moving heavy vehicles [10]. This paper focuses on the use of polyurethane in the modification of asphalt used as binder for road construction. In the present work, polyurethane obtained from toluene diisocyanate and castor oil was used for asphalt modification. These modified asphalt may used for the road construction. The properties of modified polyurethane modified asphalt such as hardness and softening point were determined.

## 2. Materials and Methodology

**Materials**

Asphalt (Asp) was purchased from roadways contractor, castor oil based imidazoline (CIM), tin octoate were purchased from Sigma Aldrich. Toluene diisocyanate (TDI) and xylene were purchased from Merck India Private Ltd. Solvents and other chemicals were used of A.R grade and used after routine purification.

**Methodology**

***Synthesis of polyurethane pre-polymer***

Polyurethane pre-polymer (PUP) was prepared by using castor oil and toluene diisocyanate (TDI). Pre-polymerization was carried out at $80^0$C temperature under nitrogen atmosphere for 1hour reaction time. Reaction system consist the four neck round bottom flask, motor stirrer and heating source.

***Modification of asphalt***

Asphalt modification was done using castor oil (C.O.) and PUP. Asphalt was heated to convert into semi-liquid asphalt. The liquid asphalt i.e. 65%, 70%, 75% and 80% was taken into dry and clean glass beaker. Desired amount of castor oil contains 0.3% CIM catalyst was added to decrease the viscosity or flow/stirring property of liquid asphalt. PUP was added to the above mixture at $120^0$C temperature. Reaction mixture was continuously stirring for 30minutes using motor stirrer. After reaction time, mixture was poured into the aluminium paper dish. Stand it at room temperature for 3 to 4 hours till cured PU modified asphalt was obtained.

***Hardness determination***

The determination of hardness of PU modified asphalt was carried out using penetrometer shown in figure: 1.

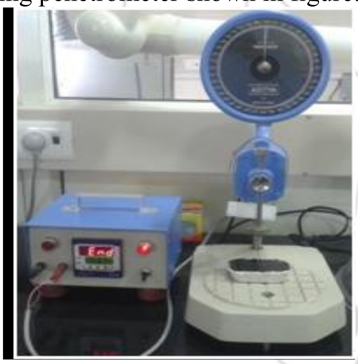

**Figure: 1 Penetrometer**

***Softening point determination***

The determination of softening point of PU modified asphalt was carried out using softening point apparatus shown in figure: 2.


**Figure 2:** Softening point apparatus

## 3. Result and Discussion

In addition to improving pavement performance at locations with extreme hot-cold temperature variations, there are other potential benefits of using polymer modified binders in hot mix asphalt construction. Polymer-modified binders typically are thicker than unmodified binders and tend to show improved adhesive bonding to aggregate particles. These properties result in a thicker binder coating on the aggregate particles that does a better job of holding the particles together. Thicker binder usually takes longer to become brittle from oxidation, so the durability of the pavement can be improved. The better adhesion helps to minimize drain down at the time of construction, and also helps to reduce the tendency of the pavement to ravel once it has aged.

**Properties of PU modified asphalt**

Hardness and softening point value of PU modified asphalt are tabulated in table: 1 and table: 2 respectively.

**Table 1:** It shows the day wise hardness value for PU modified asphalt

| *Sr. No.* | *Raw Materials (Gms)* | *Hardness (10th mm)* | | | | |
|---|---|---|---|---|---|---|
| | | *Day 1* | *Day 2* | *Day 3* | *Day 4* | *Day 5* |
| 1 | Asp 39.0<br>C.O. 12.0, PUP 9.0<br>CIM 0.5% | 30 | 27.5 | 26 | 24.5 | 23 |
| 2 | Asp 39.0<br>C.O. 12.0, PUP 9.0<br>CIM 0.8% | 39.2 | 34.5 | 29 | 25 | 21 |
| 3 | Asp 42.0<br>C.O. 12.0, PUP 6.0<br>CIM 0.3% | 63 | 46 | 30.5 | 29.3 | 28 |
| 4 | Asp 42.0<br>C.O. 12.0, PUP 6.0<br>CIM 0.5% | 45 | 37.3 | 30 | 28 | 27 |
| 5 | Asp 42.0<br>C.O. 12.0, PUP 6.0<br>CIM 0.8% | 52 | 49 | 46 | 33 | 22 |
| 6 | Asp 45.0<br>C.O. 9.0, PUP 6.0<br>CIM 0.3% | 75 | 63.5 | 49.5 | 39.8 | 31 |
| 7 | Asp 45.0<br>C.O. 9.0, PUP 6.0<br>CIM 0.5% | 47.3 | 40 | 32 | 30 | 29 |
| 8 | Asp 45.0<br>C.O. 9.0, PUP 6.0<br>CIM 0.8% | 55 | 49.5 | 41 | 35.8 | 28 |
| 9 | Asp 40<br>C.O. 05<br>PUP 05 | 60 | 56 | 53.5 | 43 | 32 |
| 10 | Asp 40<br>C.O. 07, PUP 03<br>IM 0.5% | 52 | 48.5 | 45 | 36.4 | 28 |

**Table 2:** It shows the softening point value for PU modified asphalt

| *Sr. No.* | *Raw Materials (Gms)* | *Softening point ($^0C$)* |
|---|---|---|
| 1 | Asp 39.0, C.O. 12.0 PUP 9.0, CIM 0.5% | 63 |
| 2 | Asp 39.0, C.O. 12.0, PUP 9.0, CIM 0.8% | 63 |
| 3 | Asp 42.0, C.O. 12.0 PUP 6.0, CIM 0.3% | 58 |
| 4 | Asp 42.0, C.O. 12.0 PUP 6.0, CIM 0.5% | 57 |
| 5 | Asp 42.0, C.O. 12.0 PUP 6.0, CIM 0.8% | 56 |
| 6 | Asp 45.0, C.O. 9.0 PUP 6.0, CIM 0.3% | 55 |
| 7 | Asp 45.0, C.O. 9.0 PUP 6.0, CIM 0.5% | 53 |
| 8 | Asp 45.0, C.O. 9.0 PUP 6.0, CIM 0.8% | 52 |
| 9 | Asp 40, C.O. 05 PUP 05 | 55 |
| 10 | Asp 40, C.O. 07 TDI-A 03, IM 0.5% | 53 |

***Effect of catalyst***

Effect of catalyst during the modification of asphalt was optimized and the results were tabulated in table: 1 and table: 2. Catalyst plays a very important role for any reaction. Castor oil based imidazoline were used as a catalyst for the process. Concentration of catalyst beyond 0.3% leads to the slight decrease in the hardness value and softening point properties of PU modified asphalt.

***Effect of OH and NCO ratio***

Different ratio of OH to NCO was studied such as 1:1, 1:1.5, 1.5:1 and 1.25:1. But only the result of optimized ratio (i.e. 1.5:1) was shown in table: 1 and table: 2 as other produced very poor result. In case of 1:1, 1:1.5 and 1.25:1 ratio lower hardness value (approx 110) and lower softening point (approx $43^0C$) was obtained. While 1.5:1 ratio produced good hardness value i.e. 21-32mm and softening point i.e. $53^0C$ - $63^0C$.

***Effect of time on hardness value***

Effect of time on hardness of PU modified asphalt was optimized and the results were tabulated in table: 1. As the time increased hardness of modified material also increased. By time modified material become more and more hard, so this was significant and positive result for used as binder for paving application in road construction. After certain days may be beyond $5^{th}$ day the hardness value remains constant.

## 4. Conclusion

PU is thermoplastic and thermoset in nature. Hydrogen bonding plays a key role in determining the properties of final PU product. PU modified asphalt shows the significant results which may help for paving application in road construction. As modified material shows the good improvement in properties such as Hardness and softening point i.e. 21 - 32mm and $53^0C$ - $63^0C$ respectively, this was previously 89mm and $40^0C$ respectively for hardness value and softening point of unmodified asphalt. Pavement application may be smooth as castor oil was added.

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