INVESTIGATION OF PERFORMANCE OF BITUMINOUS MIXES USING THE BINDER MODIFIED WITH POLYPHOSPHORIC ACID

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Abstract: Bitumen, as we know is the most common binding material used for the construction of flexible pavements. It had been a practice to use bitumen as a binding material as no other material gives such binding properties. It is obtained as a residual product in petroleum refineries after higher fractions like gas, petrol, diesel, etc. are removed.BIS defines bitumen as a black or dark brown non-crystalline soil or viscous material having adhesive material properties derived from petroleum crude either by natural or by refinery processes. Bitumen has got wide range of uses. It is used in construction of roads, runways and platforms, waterproofing material, for flooring of factories and go downs, tank foundations, etc. In the design of flexible pavement construction, the Marshall stability of the mix design is defined as a maximum load carried by a compacted specimen at a standard temperature of 60^0C .Marshall stability test is the performance prediction measure conducted on the bituminous mix. In the present work, it is proposed to investigate for the behavior of bituminous mixes prepared with bitumen modified with Poly Phosphoric Acid (PPA). The optimum binder content will be found using Marshall Stability method. It is proposed to investigate for the stability and flow values and other properties in the design mix will be evaluated.

1. Introduction

Asphalt binders are commonly used in the pavement construction. To meet the raising requirements for durability of the road surface, alternative methods of improving binder have been developed. The wide range of visco-elasticity is essential to achieve long-lasting road surface, as it ensures consistency of asphalt's rheological state in extreme service temperatures. Modifiers applied for improving asphalt's visco-elasticity are elastomers, plastomers, synthetic resins, crumb rubber, metal-organic compounds, sulfur, natural asphalts and paraffin's. Also polyphosphoric acid can be used for this purpose – pros and cons of its application are subject of this paper.

1.1Bituminous binders

Bituminous binders are materials of organic origin who's binding and hardening is caused by the temperature-related change of adhesion and cohesion of their molecules. Those thermoplastic materials are divided into tars and asphalts due to their origin. Tars are produced by destructive distillation under pyrolysis from the organic materials (coal, lignite, wood, peat). Because of their toxicity and low quality they are not used in Construction industry. Asphalt, also known as bitumen, is the mixture of hydrocarbons which are naturally occurring or obtained from crude oil distillation. The composition of asphalt is very complex and depends both on the origin and on the method of crude oil processing. Asphalts, especially modified, are also thixotropic – they flow like a liquid when a sideways force is applied. The properties of asphalt are function of temperature and duration of load.

Bitumen's are used as binders in asphalt concrete, a composite material used in the construction of road layers. It also contains mineral aggregate, filler and additives. All compounds are glued together by asphalt,

So despite its low content its effect on properties of concrete and, therefore, on the pavement performance is Critical. The physical and rheological properties of asphalt are dependent on its composition, chemical structure and colloidal structure. Polyphosphoric acid (PPA) Polyphosphoric acid (CAS 8017–16–1) is a polymeric product of thermal dehydration and polycondensation of orthophosphoric acid (H3PO4).Beside orthophosphoric forms, it contains a mixture of polymeric forms whose content increases with increasing acid concentration. Commercially available PPA is a mixture of linear polyacids of general formula HN+2PnO3n+1, where n ≥ 2. Those acids are produced either from the dehydration of H3PO4 at high temperatures or by heating P2O5 dispersed in H3PO4. In the latter method, longer chains are obtained. Polyphosphoric acids are highly hydroscopic and easily hydrolyze in moist air. Its viscosity and physical form at room temperature depends on the content of P2O5. PPA main's application is production of high quality liquid fertilizers, but it is also a substrate of numerous chemical synthesis. PPA is available in various grades, the naming of which can be confusing as the percentage often exceed 100%. It is effect of calculation of H3PO4 concentration on the base of P2O5 content in this inorganic polymer. For the asphalt's modification, concentration of 105, 110 and 114% H3PO4 are used (75.9, 79.8 and 82.6% P2O5, respectively). PPA is produced mainly in China and in the USA. One of very few in Europe and Poland's only producer of PPA is Inorganic Chemistry Division "IChN" of Fertilizers Institute, located in Gliwice. PPA production is based on their own, original solution of multi-sectional electro thermal evaporator, which provides a controlled production of 100-114% H3PO4 acid (73-82% wt.P2O5). The plant's production capacity total is 30-45 kg per hour.

Obtained PPA has very good quality parameters, making it suitable for many applications. PPA as an asphalt modifier first patent on use of PPA in asphalt modification was published in 1973. Addition of PPA to binder results in increase of softening point with no effect (or sometimes small decrease) in low-temperature brittleness, as PPA does not oxidize asphalt. This leads to improve maximum service temperature (or useful temperature range). However, also decrease in low-temperature properties was observed, it seems to be depending on base asphalt composition.

Main advantages on use of PPA in asphalt modification are:

• Good compatibility of PPA with asphalt: no phase separation during the long-term storage.
• Modified bitumen characteristics: increased viscosity without oxidation, softening point improvement, lower penetration at room temperature, improved stiffness.
• Pavement characteristics: reduced rutting, increased resistance to thermal and fatigue cracking, increased resistance on moisture, increased durability due to better binder adhesion to aggregate.
• Facilitated processing: ease of pumping, operating at lower temperatures, reduced emissions from asphalt operations.
• In addition with polymers: lower polymer consumption, possible lower temperature processing, synergetic effect of both additives,
Cost reduction.

Since 1990s, researches on using PPA in conjunction with polymers to improve quality of road bitumen's are conducted. The major benefit of this particular combination is synergistic effect– possible reinforcement of both modifications effects on asphalt. It has been observed for binder elasticity, thermal cracking resistance, and resistance to permanent deformation. Moreover, PPA improves adhesion and may eliminate the need for antis tripping agents. In addition, the stability of binder during long-time storage in elevated temperatures is increased. Overall cost of using modified asphalt binders is reduced by using fewer modifiers, possible elimination of antis trips, and energy savings from lowering operating temperatures. Addition of PPA may reduce reaction time with some polymers.
Polymers linked with PPA are: Effect of PPA on crumb rubber modified asphalt has been investigated since 2003, with good results. PPA improves viscosity, stability during storage, elastic recovery and reduces the amount of asphalt needed to create the blend. Binder containing 5-8% gum and 0.5-1% PPA has similar characteristics to asphalt modified with PPA and polymer.

1.2. Effect of PPA in Asphalt

Asphalt is typically described as a colloidal substance, in which a dispersed phase, consisting of asphaltenes, is covered by a protective layer of polar resins and the continuous phase consists of a mixture of aromatic and saturate oils. The asphaltenes consist of complex polyaromatic compounds aggregated together showing a lamellar structure. The polarity of each component of the asphaltene controls the degree of association, mainly through hydrogen bonding. Typically, the addition of PPA to asphalt (0.2 to 1.5%) increases the asphaltene content and concurrently reduces resin concentration. As opposed to a typical asphalt oxidation process, the increase of asphaltene is not related to oxidation of the asphalt but to an increase of the polarity of the asphaltene-PPA-resin complex.

The reactions between the asphaltene component and PPA are not yet completely understood due to the extreme complexity of the asphaltene composition. However, it has been reported that asphaltene phosphorylation may occur, but this appears to be asphalt dependant. Also, the PPA acidity definitely contributes tremendously to the asphaltene structure reorganization. The exact nature chemical reactions are still under investigation using model compounds.
The PPA modified asphaltene significantly affects the rheology of the asphalt binder giving the PPA modified binder the capacity to resist higher temperatures and stress level conditions more than neat asphalt.

As mentioned above, the asphaltenes are aggregated though hydrogen bonding. Additional acidity brought by PPA impacts the association degree of asphaltene. The chemical reactions affect the asphaltene structure, leading to a higher degree of dispersion and thus increasing the viscosity of the asphalt.
The PPA modified binder also shows higher capability for adhesion to aggregate.

2. METHODOLOGY

2.1Materials collection.

The first step is to collect the materials required for the experiments. The different materials required are stated below. The bitumen sample of VG30 grade is chosen and to this sample modification process by using poly phosphoric acid is carried out. After the preparation of samples the filtration and distillation process are carried out using a chemical compound called N-Heptane which is used to separate the oil phase and solid phase of bitumen.

2.2Bitumen:

It was the prime material in our project. By modifying this material with PPA we increased its strength properties. For our project we used the straight run bitumen having VG30 grade which is available in our highway materials laboratory. The bitumen for dense bituminous macadam shall comply with the Indian Standard Specification for viscosity graded bitumen, IS: 73 modified bitumen complying with IS: 15462 or otherwise specified as in the contract.

2.3. Polyphosphoric Acid (PPA) :

PPA is termed as Poly phosphoric acid. It is highly viscous and is having a pH value of 1.PPA obtained from the Orthophospharic acid by the method of Reflux Condensation is used.

2.4. Coarse Aggregate:

Coarse aggregate shall be crushed material retained on 2.36mm sieve and shall be crushed stone, crushed slag or crushed gravel. It shall be clean, strong, durable, of fairly cubical shape and free from disintegrated pieces, organic or other deleterious material and adherent coatings. The aggregates shall preferably be hydrophobic and of low porosity. Coarse aggregates offer compressive and shear strength and shows good interlocking properties.

2.5. Fine Aggregate:

Fine aggregate shall be the fraction passing 2.36 mm sieve and retained on 75μm sieve, consisting of crusher run screenings, natural sand or a mixture of both. It shall be clean, hard, durable, uncoated, dry and free from any injurious, soft or flaky pieces and organic or other deleterious substances. Fine aggregate fills the voids in the coarse aggregate and stiffens the binder.

2.6. Mineral Filler:

The requirement of filler in bituminous concrete shall normally be met by the material passing 75μm sieve in fine aggregate, if any. The filler shall be stone dust, cement hydrated, lime, fly ash or any other approved non-plastic mineral matter. The mineral filler fills the voids, stiffens the binder and offers permeability. In the present project filler of 2μm is used.

3. Experimental Program

3.1. Preparation of PPA modified Bitumen:

Bitumen acid modification was discovered because it turned out to start to make economical sense and seemed to lack the fragility problem of air-blown bitumen's. In particular, polyphosphoric acid (PPA) modification is currently gaining industrial importance since it permits to significantly harden bitumen in an easily controllable way. As a result, the reaction of 2% of PPA to bitumen typically allows for a change of one class of paving grade. Although the oxidative effect of acids was long recognized as well as its similarities with air-blowing, the reactivity of bitumen towards acids is still not completely understood. It is known that not all bitumen's show the same reactivity, depending primarily on their crude source.

Recent work proposed that PPA acts through the neutralization of polar interactions between the stacked asphaltenes molecules, either by protonation of basic sites or by desertification. The overall effect is to increase the salvation of the asphaltenes, increasing in turn the solid fraction and hence, the viscosity.
Other researcher proposed various bitumen-dependent mechanism of PPA modification which also affect the lower weight components of the bitumen: co-polymerization of the saturates, alkyl aromatization of the saturates, cross-linking of neighboring bitumen segments, the formation of ionic clusters and the cyclisation of alkyl aromatics.

3.2Sample preparation: The proper amount of PPA was added to bitumen, at 120^0 C, to reach a level of 2% by weight.

After mixing, the system was heated up to 160^0 C and maintained at this temperature, under stirring conditions at 600 rpm (RW 20 Digital, IKA, Germany), for 30 min in a closed beaker to avoid any oxidation process. Afterwards, the resulting bitumen was poured into a small sealed cane and then stored in a dark chamber kept at 25^0 C to retain the obtained morphology. Samples ID are reported in Tables 1 and 2 for the 50/70 and for 70/100 penetration grade bitumen respectively and they will be used throughout the text. Specimens for rheological tests were prepared by pouring the molten bitumen in a Teflon mould (10x5x3 mm) and cooling the system at 4^0 C, for 4 min, and then at 18^0 C, for 30sec, to allow the material solidification. Afterwards the sample was removed from the mould and kept at 4^0 C for the last 6 h before testing.

Fig.1 Heating of Bitumen

Fig.2 Sample

4. RESULTS AND DISCUSSION

Various tests were conducted on modified bitumen, aggregates and bitumen mixes and the results obtained are as follows:

4.1Bitumen Penetration Test:

This test was conducted for determining the penetration value of normal bitumen and modified samples. By conducting this test we found the hardness of samples. This test was conducted by using Penetrometer. Following results were observed after conducting the penetration test.

Table No.1 Results of Penetration Test

Sample	Admixture	Dosage (%w/w)	Penetration value (d.mm)
VG 30	PPA	0	64
		0.5	44
		1	40
		1.5	36
		2	31

4.2Softening Point Test:

Softening point is defined as the temperature where the bitumen becomes soft. By conducting this test the softening temperature of modified samples were found. This test was conducted by using ring and ball apparatus. After conducting this test following results were obtained.

Table No.2 Results of Softening Point Test.

Sample	Admixture	Dosage (%w/w)	Softening temperature (◦C)
VG30	PPA	0	47
		0.5	50
		1	53
		1.5	56
		2	59

4.3Ductility Test:

This test was conducted for determining the ductility value of modified samples. Ductility values were noted where the bitumen will sag or break. The test was conducted at room temperature (25^0C). This test was conducted by using briquette mould and ductility machine. New mould was prepared for ductility test with 8mm neck dimension because by using 10mm neck dimension of briquette mould gave values beyond the calibrated values of the ductility machine. The test was conducted at the speed of 1cm/min and 5cm/min. After conducting this test following results were obtained.

Table No. 3. Results of Ductility Test

Sample	Admixture	Dosage (% w/ w)	Ductility value (cm)		
			10mm neck (5cm/ min)	8mm neck (5cm/ min)	8mm neck (1cm/min)
VG30	PPA	0	100+	70.2	71.5
		0.5	82.7	62.5	68
		1	67.5	66.4	67.4
		1.5	46	47.5	48.7
		2	16.5	11.5	17.5

4.4Aggregates:

4.4.1Specific Gravity of Coarse aggregate:

Coarse aggregate shall be crushed material retained on 2.36mm sieve and shall be crushed stone, crushed slag or crushed gravel. Three trials have been conducted for determining the specific gravity of the sample using pycnometer and the results are tabulated as follows:

Table No.4.Results of Specific Gravity of Coarse Aggregate.

S .NO	W1	W2	W3	W4	Specific gravity
1	0.666	1.102	1.789	1.516	2.67
2	0.666	1.111	1.803	1.516	2.81
3	0.666	1.108	1.792	1.516	2.66
	Average				2.7

4.4.2Specific Gravity of Fine Aggregate:

Fine aggregate shall be the fraction passing 2.36 mm sieve and retained on 75μm sieve, consisting of crusher run screenings, natural sand or a mixture of both. Three trials have been conducted for determining the specific gravity of the sample using pycnometer and the results are tabulated as follows:

Table No.5 Results of Specific Gravity of Fine Aggregate

S.NO	W1	W2	W3	W4	Specific gravity
1	0.666	1.102	1.789	1.516	2.67
2	0.666	1.111	1.803	1.516	2.81
3	0.666	1.108	1.792	1.516	2.66
	Average				2.7

4.4.3. Specific Gravity of Mineral Filler:

The mineral filler fills the voids, stiffens the binder and offers permeability. In the present project, a mineral filler of 2μm is used. Three trials have been performed for determining the specific gravity of the sample using specific gravity bottle. The results are tabulated as follows:

Table No.6 Results of Specific Gravity of Mineral Filler

S .NO	W1	W2	W3	W4	W5	Specific gravity
1	49	60	98	90	100	2.93
2	49	61	99	90	100	3.2
3	49	63	100	90	100	2.71
	Average					2.95

4.4.4. Los Angeles Abrasion Test :

Los Angeles Abrasion Test was conducted on the aggregates to determine the percentage wear of the aggregates. The test was conducted for the aggregate grades of A, B and C and the results obtained are as follows:

Table No. 7 Results of Los Angeles Abrasion Value

Grade	A	B	C
Percentage wear	14.36	11.64	15.60

As the values of percentage wear are less than 30%, these aggregates can be used for mixes of pavements.

4.4.5Impact Test:

The impact test is done on the aggregates passing through 12.5 mm sieve and retained on 10 mm sieve and result is as follows:

Aggregate impact value = 13.5%
Aggregate impact value is used to classify the aggregates in respect of their toughness property. As the value of aggregate impact value lies between 10-20%, the aggregate can be classified as strong.

4.4.6Shape Test:

The shape test was conducted to determine the flakiness index and elongation index of the aggregates and the results are as follows:
Flakiness index = 12.15%
Elongation index = 11.26%
The values of flakiness index and elongation index should be maintained as low as possible.

4.4.7. Marshall Stability Test:

Marshall Stability test was conducted to determine the stability and flow values of the bituminous mix samples.

Table No. 8 Results of Marshall Stability Test:

Binder content (%)	Stability value (KN)	Flow (mm)
4.5	14.64	16.42
5	15.85	16.35
5.5	8.48	15.87
6	7.92	16.62

4.4.8. Determination of Optimum Binder Content:

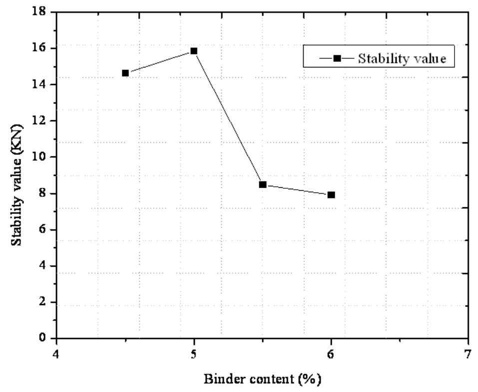
The properties that are of interest include the
Theoretical specific gravity (Gt)
The bulk specific gravity of the mix (Gm)
Percent air voids (Vv)
Percent volume of bitumen (Vb)
Percent void in mixed aggregate (VMA)
Percent voids filled with bitumen (VFB)
The average value of the above properties are determined for each mix with different
Bitumen content of three samples for each mix proportion and the results are tabulated as follows:

Table No.9Parameters for Determining Optimum Binder Content

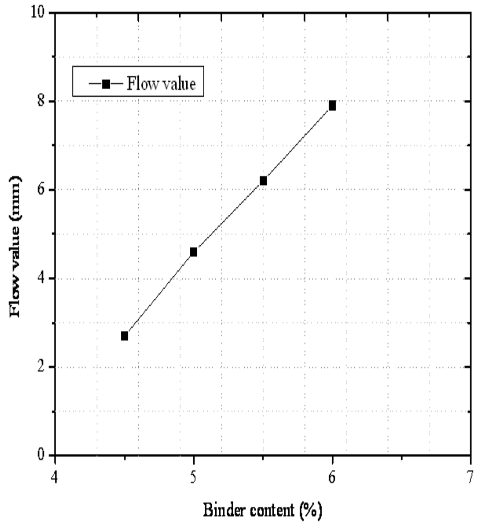
Binder Content (%)	Stability Value KN	Flow mm	Vv %	VMA %	VFB %	Gm
4.5	14.64	2.70	5.45	16.42	66.82	2.44
5.0	15.85	4.60	4.09	16.35	75.10	2.47
5.5	8.48	6.20	6.20	15.87	86.00	2.46
6.0	7.92	7.90	1.80	16.62	89.31	2.45

The average values of the above properties are determined for each mix with different Bitumen content and the following graphical plots are prepared:

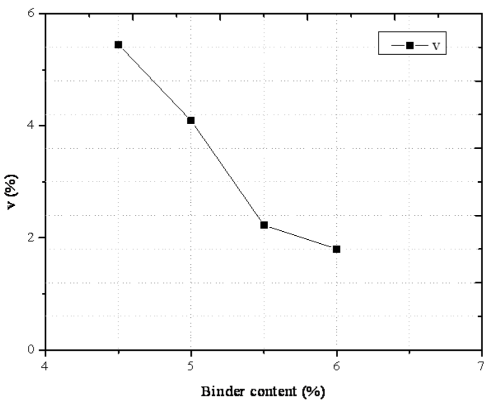
Graph between binder content versus corrected Marshall Stability



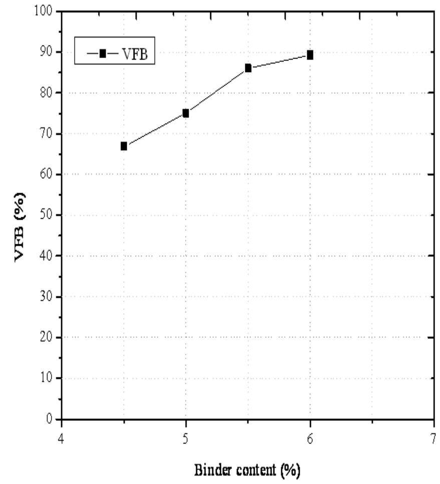
Graph between binder content versus Marshall Flow



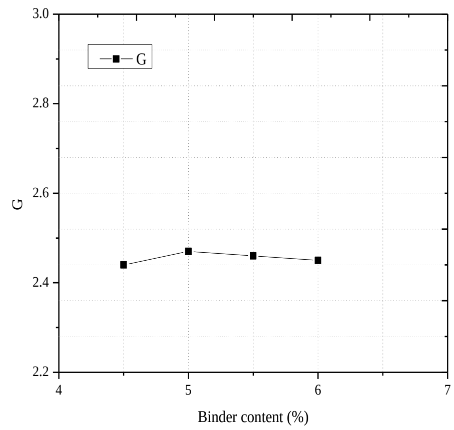
Graph between binder content versus percentage of void (Vv) in the total mix



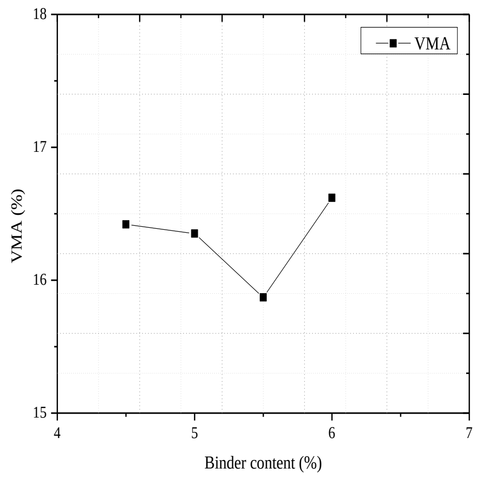
Graph between binder content versus voids filled with bitumen (V FB)



Graph between binder content versus unit weight or bulk specific gr



Graph between binder content versus voids in mineral aggregate (VMA)



4.4.9CALCULATION OF OBC:

By considering the specifications given by MORTH, the value of optimum binder content is calculated as shown below:

Table No.10 Calculation of OBC

S.No	Test property	Value of binder content
1	Volume of voids i.e. @4% Vv	5.14
2	Voids filled in bitumen i.e. @70% VFB	4.8
3	Maximum stability	5
4	Flow value @4.5 mm	5.1
	Average	5.02

5. Discussion:

By increasing the percentage of PPA the bitumen is becoming hard. Because of that reason the values of penetration test and softening point are increasing with increasing dosage of PPA. Maximum values of penetration depth and softening temperature were observed at 2% dosage. But ductility values are decreasing by increasing the PPA dosage. Minimum ductility value at the dosage of 2% PPA. The reason for decreasing the ductility values are by increasing the PPA dosage, the bitumen is becoming hard but is losing its "ELASTIC PROPERTIES".

The stability value for DBM binder course has enhanced. According to MORTH specification, the minimum stability value should be 9 KN. But we got the stability value as 15.85 KN. From the above results, it was observed that stability value of DBM mixes were enhanced due to the usage of PPA modified binder.

6. Conclusions:

Bitumen can be modified by using Polyphosphoric Acid. There exists an Optimum dosage for the modification of bitumen using PPA. The Optimum dosage was observed to be 2% (w/w) of bitumen. Properties of bitumen such as penetration and softening point are greatly enhanced. Ductility of bitumen is observed to be decreasing with increase in PPA dosage. Hardness of bitumen is observed to be increasing with increase in PPA dosage which enables the bitumen to be used in extremely hot climatic conditions. The optimum binder content was observed to be 5% (w/w) of bitumen. The stability value of DBM layer has been enhanced.

7. Scope for Further Study:

Due to time and resource constraints the investigations were limited to 2% dosage. The performance of mixes for higher dosages of PPA can be investigated. Also the influence of acid modification with PPA for polymer modified bitumen can be studied.

8. References:

Abraham H. Asphalt and Allied Substances. 6th Ed. New York: Van Nostrand; 1960.

Aglan H, Dallas NL, Lewandowski LH. In: Seminar of the journal of elastomers and plastics on polymer modifiers for improved performance of asphalt mixtures, 1994, p. 95.

American Society for Testing and Materials Annual book of ASTM standards section 4, vol. 4.03, ASTM-D1559-1993 Philadelphia PA.

ASTM D6927 -Standard Test Method for Marshall Stability and Flow of Asphalt Mixtures.

Bahia, H., Perdomo, D., "Current practices for modification of paving asphalts", Fuel, 41, 4, 1996.
Baldino N, Gabriele D, Oliviero Rossi C, Seta L, Lupi FR, Caputo P. Low temperature rheology of polyphosphoric acid (PPA) added bitumen. Construction Building Materials 2012; 36:592–6.

Baumgardner GL, Masson J-F, Hardee JR, Mena pace AM, Williams AG. Pholyphosphoric acid modified asphalt – proposed mechanisms. Association of asphalt paving technologists, Annual meeting and technical sessions, Long Beach, California; 2005

IS: 1203-1978-Indian standard methods for testing tar and bituminous materials (Determination of penetration)

IS: 1205-1978-Indian standard methods for testing tar and bituminous materials (Determination of softening point)

IS: 1208-1978- Indian standard methods for testing tar and bituminous materials (Determination of ductility).

IS: 2386 (Part I) – 1963 – Method of test for aggregates for concrete (Part I) Particle size and shape.

IS 73: 2006, Indian Code of Practice for Paving Bitumen

IS: 2386(Part IV)-1963 Methods of test for aggregate for concrete Part IV Mechanical Properties.

Thomas K. P., Turner T. F., "Polyphosphoric-acid modification of asphalt binders: Impact on rheological and thermal properties", Road Materials and Pavement Design, Vol. 9, No. 2, 2008, p. 181-205.

Tom Kunnen, Road Science: Journal of modifiers a must in a world of high performance of concrete.
www.pavementinteractive.org.