

# Rheological Properties of Polyethylene and Polypropylene Modified Bitumen

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**Abstract**—This paper presents a part of research on the rheological properties of bitumen modified by thermoplastic namely linear low density polyethylene (LLDPE), high density polyethylene (HDPE) and polypropylene (PP) and its interaction with 80 pen base bitumen. As it is known that the modification of bitumen by the use of polymers enhances its performance characteristics but at the same time significantly alters its rheological properties. The rheological study of polymer modified bitumen (PMB) was made through penetration, ring & ball softening point and viscosity test. The results were then related to the changes in the rheological properties of polymer modified bitumen. It was observed that thermoplastic copolymer shows profound effect on penetration rather than softening point. The viscoelastic behavior of polymer modified bitumen depend on the concentration of polymer, mixing temperature, mixing technique, solvating power of base bitumen and molecular structure of polymer used. PP offer better blend in comparison to HDPE and LLDPE. The viscosity of base bitumen was also enhanced with the addition of polymer. The pseudoplastic behavior was more prominent for HDPE and LLDPE than PP. Best results were obtained when polymer concentration was kept below 3%

**Keywords**—Polymer modified bitumen, Linear low density polyethylene, High density polyethylene, Polypropylene.

## I. INTRODUCTION

**B**ITUMINOUS binders are widely used by paving industry [1]. Approximately 95% of the almost 100Mt of bitumen produced worldwide each year is utilized by paving industry, where it is used as binder for mineral aggregate to form bituminous mixes[2]. Continuous increase of wheel loads, tyre pressure and change in climatic condition severely affect the performance of bituminous mix pavements. Modification of virgin bitumen with synthetic polymer binder provides a way to overcome new technical demands [3]. The most commonly used polymer globally include approximately 75% elastomeric modified binder, 15% plastomeric and remaining 10% belongs to either rubber or other modification [4].

This study focus on the use of thermoplastics, linear low density polyethylene (LLDPE), high density polyethylene (HDPE) and polypropylene (PP) as modifying polymer for the 80pen base bitumen. Concentrations of all polymers were kept till 5% by weight of the bitumen. Bitumen when blended with polymer forms a multiphase system, a phase rich in asphaltene not absorbed by the polymer [5] which enhances the viscosity by the formation of more complex internal structure [6].

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While mixing either using mechanical or chemical method the differences in molecular weight and polarity of base bitumen and polymer has critical affect on compatibility [7]. Although polyolefin do not significantly increase the volume of blend but increases the viscosity, even this minor volumetric change was because of the structural change in the PMB blend. Polyethylene which belongs to plastomer gives rigidity to the binder and reduces the deformation under load [6]. The affect of this is more profound when the concentration of polyethylene was kept below 1% by weight of the base bitumen [8]. For LLDPE the concentration up to 2.5% shows better results in terms of Marshall Stability, resilient modulus, water susceptibility and fatigue life of the modified binder [5]. Thermoplastic when mixed with bitumen even at ambient temperature increases the viscosity and thus stiffness at service temperature but unfortunately do not show any significant elastic behavior [7].

Polyethylene morphology is strongly affected under stress and deformation as sliding of chains with respects to entanglements occurs at the nodes [9]. Addition of bitumen improves deformation resistance as the viscosity of blend enhanced tremendously which is observed with increase in softening point and decrease in penetration values [5]. PMB blend also shows a two-phase morphology, depending on the polymer type, concentration, base bitumen composition and the aromaticity (lower molecular weight polar naphthenic), the system can have an asphalt-rich phase with a homogeneous dispersion of polymer spheres or continuous polymer-rich phase with dispersion of asphaltene globules in it [10]. When a polymer and compatible base bitumen are mixed, the polymer strands absorb part of the low molecular weight oil fraction of the base bitumen and become swollen [11]. When the polymer-rich phase becomes the continuous phase due to the relatively higher fraction of swollen polymer, the swollen strands connect together at nodes and form a three dimensional network. This network significantly affects the mechanical properties of the binders and ultimately the bituminous binder mixes [11]. Thus the rheology of the multiphase systems is very complex due to instability of the mix as bitumen and polymer having different density and viscosity at 25°C and 160°C, which ultimately influence morphology but still no theory is available till now why polymers are good as modifier [12].

In short to know about the internal structure of polymer modified bitumen, rheological studies of the PMBs is the only answer. As wide range of properties can be attained from an individual polymer thus a complete comprehensive study with

understanding of fundamental properties is essential. The development of new polymer blends of specific properties is the most difficult task as it is related to the behavior of the multi phase formation which controls the rheology of the PMB and its mechanical properties. The objective of this paper is thus to investigate the characteristics of the polymer modified bitumen PMB using empirical test, and relating its rheological characteristics to its mechanical properties at the later part of this study.

## II. METHODOLOGY

### A. Materials

Materials used in this study includes 80/100 penetration grade base bitumen obtained from PETRONAS refinery at Malacca, Malaysia. The polymer used for modification supplied by Titan Polyethylene Malaysia, were Linear low density polyethylene LLDPE, High density polyethylene HDPE and Polypropylene Resin PP. LLDPE and HDPE were in pallet form while Polypropylene was in powder form.

### B. Sample Preparation

Samples were prepared using melt blending technique. The bitumen about 400gm was heated in oven till fluid condition and polymer was slowly added, while the speed of the mixer was maintained at 120 rpm and temperature was kept between 160°C and 170°C. The concentration of PP, LLDPE and HDPE used, were 0.5, 1.0, 1.5, 2.0, 2.5, 3 and 5% by weight of blend. Mixing was continued for 1 hr to produce homogenous mixtures. The modified bitumen was then sealed in containers covered with aluminum foil and stored for further testing. Empirical test such as penetration, softening point and viscosity were then conducted on the prepared samples.

### C. Laboratory testing

Test on the prepared samples were conducted according to ASTM [13] method to characterize the properties of PMBs. The different percentage of polymer concentration provides a wider range of results which helps in analysing each type of the polymer blend at particular concentration. The rheological test includes penetration at 25°C, softening point and viscosity test. The test results of base bitumen are presented in Table I.

TABLE I  
 CONVENTIONAL PROPERTIES OF BASE BITUMEN

Grade	80/100 pen
Penetration (dmm)	84
Softening point °C	53
Penetration Index	0.5
Viscosity (Pa s)	0.44

#### 1) Penetration (ASTM D-5)

The standard 100g, 25°C and 5sec penetration test was

performed both on base bitumen and PMB with the concentration of polymer varying between 0.5%- 5% by weight of the bitumen. The results of the test are shown in Table II.

#### 2) Softening Point (ASTM D-36)

Ring and ball is the standard test to determine the consistency of the bitumen, which represent the temperature at which a change of phase from solid to liquid occurs. It is the temperature at which standard 3/8 inch steel ball weighing 3.55gm fall and touches the base plate which is 2.5mm away. The results are shown in Table III.

#### 3) Viscosity (ASTM D-4402)

Viscosity test was conducted using Brook Field viscometer on virgin and polymer modified bitumen. The dynamic viscosity measurement were made at 135°C. The test was carried out on all polymers up to the concentration of 3% and viscosities measurements were made on increasing shear rates (shear stresses).

## III. ANALYSIS OF RESULTS

### A. Penetration Results

From the result shown in Table I for base bitumen and in Table II and Figure 1, the sharp decrease in the penetration value of 84 dmm for base bitumen to 36dmm for LLDPE and HDPE and 33 for PP at 0.5% concentration of polymer shows that increase in the hardness of the PMB was because of the use of the high molecular weight polymer HDPE with melt flow Index of 0.9g/10 min for LLDPE and 0.09g/10 min. The PP although have melt flow index of 8g/10min shows lesser value of penetration, thus to make a decision on the basis of melt flow index is not an ultimate answer as these values depend on the force and pressure applied during determination of melt flow index for a particular type of polymer. It is obvious from the observation that thermoplastics influence more on the penetration with the increase in the viscosity of the bitumen [1] as can be observed by the decrease in the value of penetration with the increase in concentration of polymer. The Polyethylene at temperature above 160°C is in melt state as melting temperature of LLDPE, HDPE and PP is 122°C, 135°C and 165°C, it absorb some oil and release low molecular weight fraction into the bitumen which increases the viscosity of the PMB[8]. Thus it increases the viscosity by the end of mixing process, and by the time it cools harden mixture was formed. The hardening of the bitumen can be beneficial as it increases the stiffness of the material, thus the load spreading capabilities of the structure but also can lead to fretting or cracking [1]. This can be evaluated at later stage of this study by performance tests. The results obtained by the penetration are highly controversial although being widely used by paving industry as penetration needle displaces a relatively small volume of fluid [14].

TABLE II  
 PENETRATION TEST RESULTS

Polym er %	HDPE Penetration (dmm)	LLDPE Penetration (dmm)	PP Penetration(dmm)
0.5	36	36	33
1	32	35	34
1.5	28	30	35
2	22	30	30
2.5	21	27	30
3	23	25	28
5	23	13	15

TABLE III  
 SOFTENING POINT TEST RESULTS

% Polymer	HDPE °C	LLDPE °C	PP °C
0.5	52	50	53
1.0	51	53	54
1.5	52	54	54
2.0	58	53	55
2.5	62	54	55
3.0	67	60	55
5.0	79	67	59

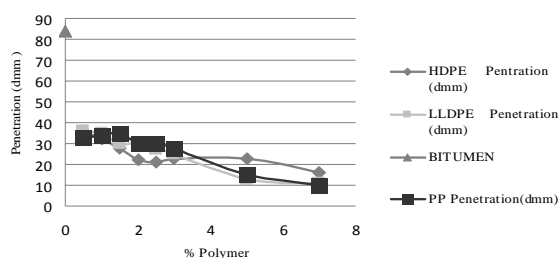


Fig. 1 Penetration results for HDPE, LLDPE, PP and Bitumen

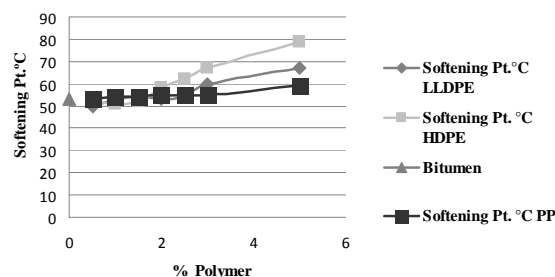


Fig. 2 Softening point of HDPE, LLDPE, PP and Bitumen

### B. Softening Point Results

The results obtained from the ring ball shown in Table II and Figure 2 shows that there is no great difference in the softening temperature for PMBs up to 1.5 % concentration of polymer in bitumen as compared to base bitumen as thermoplastics modification does not significantly affect the softening point as compared to the penetration [1]. One of the cause was the internal structure formed by polymer seems to be thermodynamically stable which do not significantly affect the softening point of the PMB, but as the concentration of polymer increases HDPE and LLDPE shows rapid increase in softening point in comparison to PP. This can be considered as positive sign and can be further checked with the performance test at the later stage of this study, whether it enhance the pavement performance characteristics in terms of rutting, fatigue and temperature susceptibility. From Figure 2 it can also be observed that PP offer lesser variation in softening point which may be due to homogeneity achieved during blending of PP with base bitumen as PP is in powder form, which reflects that it may offer better rutting resistance at higher temperature when tested later.

### C. Penetration Index

Penetration Index is another way of looking at the temperature susceptibility of the bitumen as described by Pfeiffer and Van Doormaal[1]. It is the measure of the deviation of bitumen behavior from Newtonian to non-Newtonian. Bitumen usually have value between +1 and -1 for road construction, while the bitumen with values less than -2 shows Newtonian behavior with brittleness at lower value and those greater than +2 are less brittle, exhibiting high elastic properties under higher strains[1]. From the results shown in Figure 3 all the PI values of this study are less than -0.5 except for higher polymer concentration in the blend. This shows that PMB blends are temperature susceptible. HDPE seems to be more prone to brittleness as the values were more towards the lower side that is -2, while PP shows less variation as the change in their softening point and penetration was less fluctuating, but true relevance can't be made as these values are based on concept that the penetration of the bitumen is about 800 at its softening point [14] which is not true for the polymer modified bitumen.

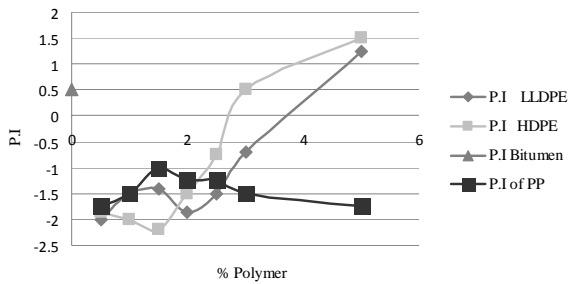


Fig. 3: Penetration Index of HHDPE, LLDPE, PP & Bitumen

#### D. Viscosity of Bitumen and PMB blend

The flow behaviour of the material described in terms of viscosity, exhibits Newtonian and non-Newtonian characteristics depending on the composition and source of the crude. Temperature and loading also affect the behavior describing the viscoelastic properties of the material. The internal structure of the base bitumen also play key role [10]. Bitumen with viscosity of 0.44 at 135°C shows increase in viscosity with the increase in polymer concentration. The non-Newtonian characteristic with the decrease in viscosity with the increase in shear rate was observed for all concentration of polymer in bitumen. These non-Newtonian phenomena are dependent on the shear rate and it influences the internal structure of the PMB [10]. From Figure 4 -Figure 8, shows the non-Newtonian behavior with the decrease in viscosity with increase in shear rate. The fluctuation of viscosity was observed more for HDPE and LLDPE till 2.5% concentration of polymer as shown in Figure 4-8. This mixed behavior with the decrease in viscosity with increase in shear rate and again increase in viscosity do not truly represent non-Newtonian behavior but it represent thixotropic effect. The thixotropic behavior of modified bitumen may be due to reversible breakdown of structure which is commonly found in multiphase system of polymer modified bitumen [15]. It is very difficult to say that polymer modified bitumen purely exhibit shear thinning phenomenon with the decrease in viscosity with the increase in shear rate as shear thickening phenomenon was also observed. This pseudo plastic behavior of PMB may be attributed due to breakdown of structure, or polymer particles existing in equilibrium state being more aligned offering lesser resistance to flow but with the increase in shear rate these offer higher resistance due to agglomeration, aggregation or flocculation of particle in multiphase system as the interparticle forces like Brownian, van der Waals forces become prominent [15]. HDPE and LLDPE as both are not fully dispersed in bitumen because of higher molecular weight exhibit both thixotropy and viscoelasticity at all concentration of polymer in the blend. PP offer less fluctuation as can be observed for all concentration of polymer in the blend as shown in Figure 4-8. One of the main cause of this instability is the tendency of PMB to morphological phase separation which is due to Brownian

coalescence followed by gravitational flocculation and later on end up with creaming [3]. As this viscometer did not allow measurement of viscosity at both higher and lower shear rate, true statement about the shear thickening or shear thinning cannot be made. It was also observed that for HDPE it shows shear thickening behavior at shear rate around 2000 1/sec to 3000 1/sec., which may be due to agglomeration of HDPE particle at higher temperature of 135°C, in which the chain realign and offer more resistance to higher shear stress. The phenomenon which was observed for HDPE and LLDPE may offer better resistance to rutting when analyzed at later stage of this study. More expectation are made for LLDPE and PP as rearrangement of molecules were observed more for these two types of polymer by linear decrease in viscosity with the increase in shear rate but actual behavior can only be obtained when tested for fatigue and rutting at later stage of this study.

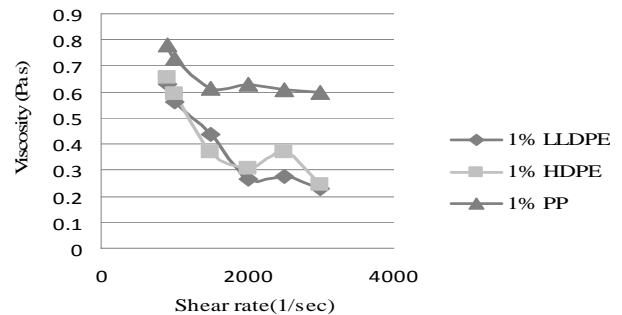


Fig. 4: Viscosity of 1% HDPE, LLDPE and PP

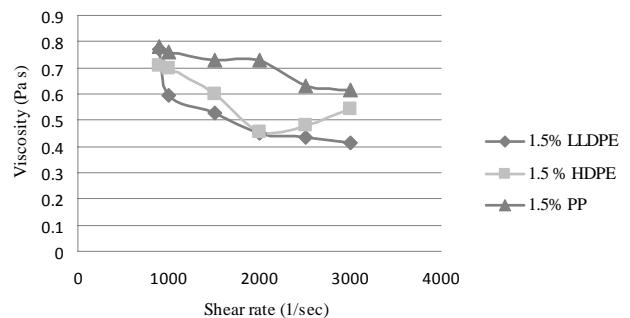


Fig. 5: Viscosity of 1.5% HDPE, LLDPE and PP

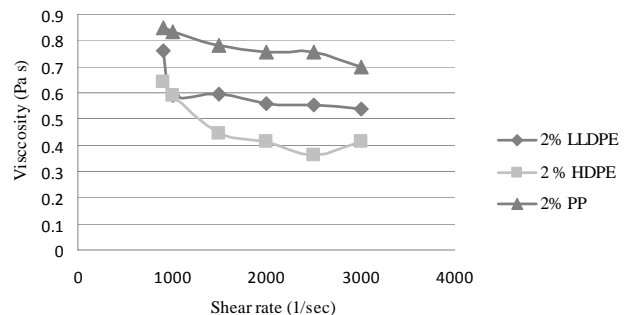


Fig. 6: Viscosity of 2.0% HDPE, LLDPE and PP

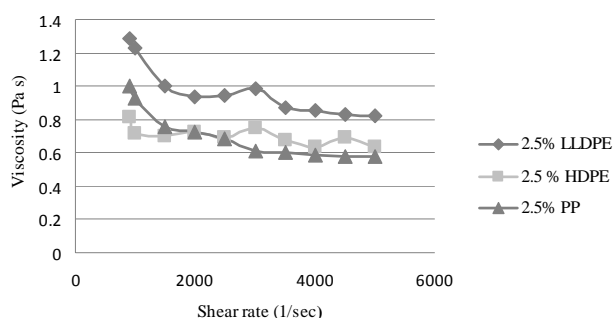


Fig. 7: Viscosity of 2.5% HDPE, LLDPE and PP

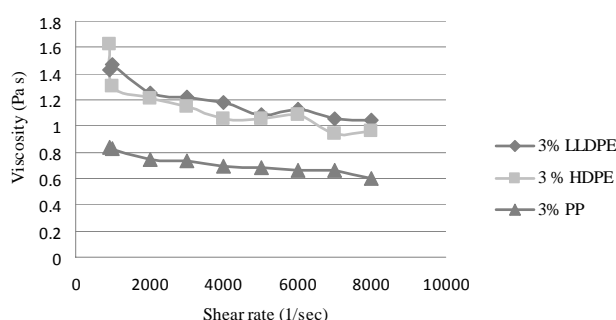


Fig. 8: Viscosity of 3.0% HDPE, LLDPE and PP

#### IV. CONCLUSION

The rheology of 80 pen bitumen was strongly affected by the addition of thermoplastic copolymers as observed by the results of penetration, softening point and viscosity. From all the test results it was revealed that LLDPE & PP modified bitumen shows least variation in penetration and softening point in comparison to HDPE modified bitumen, when the concentration of polymer is kept below 3% which may be due to the formation of thermodynamically stable structure which may offer resistance in terms of rutting, fatigue and temperature susceptibility when investigated at later part of this study. The sharp decrease in the penetration value of virgin bitumen at 0.5% concentration of polymer in the blend shows that even at lower concentration of the polymer in blend rapidly enhances the hardness of the PMB, which may be due to the formation of dispersed polymer network as the viscoelastic behavior of virgin bitumen was strongly influenced by polymer concentration, temperature and penetration grade of the bitumen. The non-Newtonian behavior was observed for virgin bitumen, which was profoundly affected by the addition of polymer in the blend as they as they exhibited thixotropy. Polypropylene with linear structure added in powder form to the base bitumen was easier to blend to produce homogenous blend as observed by the linear decrease in penetration, increase in softening point and increase in viscosity, thus presenting the continuous formation of stable internal structure. HDPE and LLDPE exhibited both

thixotropic and viscoelastic behavior at all concentration of polymer in the blend. HDPE showed shear thickening behavior at shear rate around 2000 1/sec to 3000 1/sec., which may be due to agglomeration of HDPE particle at higher temperature of 135°C and may offer better resistance to rutting.

#### REFERENCES

- [1] Whiteoak C.D The shell bitumen hand book. Surrey, UK. 2003.
- [2] Didier Lesueur "The colloidal structure of bitumen: Consequences on the rheology and on the mechanism of bitumen modification". *Advances in Colloid and Interface Science*, vol. 145, pp. 42-82, 2009.
- [3] Gonzalez et al "Rheology and stability of bitumen/EVA blends" *European Polymer Journal*, vol.40, pp. 2365-2372, 2004.
- [4] Barresi A, et al. "Use of modified bituminous binders, special bitumens with bitumen additives in pavement applications". *Technical Committee Flexible Roads (C8) World Road Association (PIARC)*, 1999.
- [5] Hadidy Al, Qui Tan Yi "Effect of Polyethylene on life of flexible pavements" *Construction and Building Materials* vol. 23 pp. 1456-146, 2009.
- [6] J.Stastna et al. "Viscosity functions in polymer modified asphalts" *Journal of Colloid and Interface Science*, vol. 259, pp.200-209, 2002.
- [7] Lu.X and Isacson "Compatibilty and storage stability of styrene-butadiene-styrene copolymer modified bitumens" *Journal of Materials and Structure*, vol.30, pp.618-626, 1997.
- [8] Yousefi AA, Kadi A AIT "Composite asphalt binders: Effects of modified RPE on asphalt" *Journal of Materials in civil Engineering*, May, pp.113-123, 2000.
- [9] Drozdov Aleksey. D, Yuan Q "The viscoelastic and viscoplastic behavior of low density polyethylene" *International Journal of Solid and Structure*, vol. 40, pp2321-2342, 2003.
- [10] Sybilski.D "New simplified equation for the computation of absolute viscosity of polymer-bitumens" *Materials and Structure*, vol.30, pp.182-187, April 1997.
- [11] Wekumbura et al., "Destruction and Recovery of Internal Structure in Polymer-Modified Asphalts" *Journal of Materials Civil Engineering*, pp. 227-232, 2007.
- [12] Chen Jian-Shiuh et al. "Asphalt Modified by Styrene-Butadiene Styrene Triblock Copolymer: Morphology and Modal" *Journal of Materials in Civil Engineering* May/June, pp. 224-229, 2002.
- [13] American society for Testing and Materials (ASTM), standard Specification, Section 4, vol. 04-03, 2000.
- [14] Traxler "Asphalt its composition, properties and uses" *Reinhold publishing corporation. Chabman & Hall.Ltd.*, London.1961.
- [15] Bhattacharya Sati N "Rheology Fundamentals and Measurement" chapter 1, Royal Melbourne Institute of Technology. Australia.1997.