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The Influence of Polyethylene on the Rheological Properties of Trinidad Lake Asphalt and Trinidad Petroleum Bitumen

R. Maharaj, A. Balgobin and D. Singh-Ackbarali
University of Trinidad and Tobago, O'Meara Industrial Estate,
O'Meara, Arima, Trinidad and Tobago, West Indies

Abstract: In this study the influence of different amounts of low density polyethylene (LDPE) on the rheological properties such as complex modulus and phase angle of Trinidad Lake Asphalt (TLA) and 60/70 penetration refinery bitumen, Trinidad Petroleum Bitumem (TPB) was studied. Changes in the complex modulus and viscoelastic properties in the polymer modified blends were studied using a controlled dynamic shear rheometer. The results confirmed that LDPE has an enormous potential to be used as a modifier of TLA and TPB. The abundance of waste polyethylene in Trinidad renders the material environmentally attractive for improving the use of asphalt and bitumen. The incremental addition of LDPE to TLA resulted in an increase in the complex modulus, G* (stiffness) which appeared to plateau at approximately 3%. The influence of LDPE resulted in a viscosity maximum (highest phase angle) for the blend containing 1% LDPE. The influence of the addition of various amounts of LDPE to TPB on the phase angle was sporadic however a significant increase in the G* (stiffness) of the TPB blends were observed the maximum stiffness measured at 2% LDPE.

Key words: TLA, bitumen, rheological properties, complex modulus, phase angle

INTRODUCTION

Asphalts and bitumen are both used together with mineral aggregates to construct roads today. The performance of these road pavements depend on the properties of the asphalt and the bitumen which are the only deformable components in the mixture. Both these systems have thermal susceptibilities and often experience low temperature cracking in cold environments as most bitumen have been shown to exhibit an apparent glass temperature near zero degrees Celsius and hence its physical behavior moves from ductile to brittle (Kortschot and Woodhams, 1984). The cracking phenomenon is attributed to thermal shrinkage stresses and further damage occurs due to weathering, moisture damage, frost heave, heavy traffic or embrittlement due to the chemical oxidation of functional groups within the asphalt. Engineers are required to also develop asphalt mixes that provide pavement stability during the high temperature periods to avoid creep and distortion of the material. Research has shown that these limitations can be overcome and the properties such as the bulk modulus can be significantly modified by blending a polymeric material with asphalt and bitumen to improve the viscoelastic behavior while maintaining their own advantages.

Work is done by Masson *et al*. (2001) demonstrated the increased resistance to weathering of bitumen blends containing styrene-butadiene and styrene-butadiene-styrene

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Corresponding Author: Rean Maharaj, University of Trinidad and Tobago,
O'Meara Industrial Estate, O'Meara, Arima,
Trinidad and Tobago,West Indies

copolymers. Blanco *et al*. (1995) used fluorescence microscopy to study the phase morphology changes associated with polymer modified asphalt and concluded that phase morphology is critical in the study of polymer modified asphalt microstructure as well as the choice of optimal polymer content and base asphalt required to produce modified asphalt with desirable properties. Lu and Isacsson (2000) studied the artificial aging of polymer modified binders and found that the effect of aging on the chemistry and rheology of the modified binders was influenced by the nature of the base bitumens and was strongly dependent on the characteristics of the polymers. These observations were confirmed by Wen *et al*. (2001), who showed the superior physical and flow properties of waste rubber and polypropylene modified bitumen. Fawcett *et al*. (2002) studied blends of a bitumen with homopolymers containing small quantities of different semicrystalline polyolefins and found that the properties of binary polymer blends are not associated solely with the components, certain polymer-bitumen interactions may also be significant. Singh *et al*. (2003) employed micronized Poly Vinyl Chloride (PVC) pipe waste as a soft filler in making bituminous products and the results of the study indicated that the optimized mix can be used as waterproof roof mastic as an alternative to conventional bituminous materials. Research has shown that polyethylene is one of the most effective additives (up to 6% wt.) mainly due to its relatively low glass transition temperature (Jew *et al*., 1986).

A technical report on the Rheology of Bitumen-Polyolefin Blends previously done in 1982 suggested that since polyethylene is a solid crystalline material below its melting transition temperature it assumes the role of a filler material when the bituminous material is soft and deformable and this accounts for the changes in rheological behavior and by extension the mechanical properties of the material.

Plastics are widely used in everyday life and since they are resistant to biological degradation, they contribute immensely to environmental pollution (Colak *et al*., 2003). Reprocessing of waste plastics by melting has been proven unsuccessful as the process results in thermo-mechanical reductions and losses in their properties (Tzankova *et al*., 1997). The addition of waste plastics into bituminous materials has become a viable option for not only improving the physical properties of the bituminous mixes but as a safe method of disposal of the waste material. Polyethylene is a long chain hydrocarbon molecule derived from the polymerization of ethylene. Ethylene is the most produced organic compound in the world; global production of ethylene exceeded 107 million metric tones in 2005, (Chemical and Engineering News, July 10, 2006). The Solid Waste Management Company of Trinidad and Tobago (SWMCOL) performed waste characterization studies on components of household waste taken to the different landfill sites on a daily basis in 1995. This study showed that on a daily basis plastics make up between 13-20% of the total waste component dumped at each of the three landfill sites surveyed.

There exists a clear relationship between the differences in the quality of asphalt (different compositions) from different sources and the resulting performance qualities is well known (Oyenkunle, 2006, 2007; Andersen and Speight, 2001; Trejo *et al*., 2004). Asphalts conformation with the same specifications can often produce pavements of varying physical properties, performance and serviceability. Consequently, bitumen and asphalt materials may interact with additives differently. Research investigating the influence of polymeric materials on the mechanical properties of TLA and TPB is limited.

The most famous natural deposit of lake asphalt is the Trinidad Lake Asphalt (TLA), which occurs naturally in the form of a 100 acre lake located on the island of Trinidad in the West Indies. The material basically comprises a mixture of bitumen, water and very fine mineral matter. Trinidad lake asphalt is well known for its consistent properties, stability and durability and is widely used for bridge and airport applications where high stability surfaces are required. Trinidad lake asphalt is a well established commercial product and typically, a 50:50 blend of TLA and bitumen is adopted in the production of TLA modified mastic asphalt (Widyatmoko and Elliott, 2008).

This study intends to investigate the influence of low density polyethylene (LDPE) on the rheological properties of Trinidad Petroleum Bitumen (TPB) and Trinidad Lake Asphalt (TLA). This study utilizes a controlled stress Dynamic Shear Rheometer (DSR) which measures fundamental viscoelastic properties across a range of temperatures and frequencies. The rheology of bituminous materials and bituminous blends containing LDPE would provide a preliminary indication of the mechanical properties and performance of the resulting bituminous blends. Additionally incorporating LDPE into bituminous materials can be used as a recycling option in Trinidad and Tobago and hence reduce the harmful environmental effects of waste polyethylene on the environment.

MATERIALS AND METHODS

Samples of commercial low density polyethylene (LDPE) resins were obtained from Ansa Polymer Limited; Trinidad Lake Asphalt (TLA) and refinery bitumen (60/70 Penetration), TPB, were obtained from Lake Asphalt of Trinidad and Tobago Limited and Petroleum Company of Trinidad and Tobago Limited, respectively. This study was conducted during the months of May and June, 2009.

Approximately 250 g of the TLA and TPB was placed in aluminum cans and heated to 180°C using a Thermo Scientific Precision (Model 6555) Mechanical Convection Oven. The material was mixed using a digital IKA (Model RW20D) Overhead Stirrer, at 3000 rpm. Masses of LDPE resin was added gradually (5 g min^{-1}) to produce TPB-LDPE blends equivalent to 0, 0.5, 2 and 3% of LDPE by weight and TLA-LDPE blends equivalent to 0, 0.5, 1, 2 and 3% of LDPE by weight. The mixtures were mixed for a further 15 min and at the end of mixing process, each blend was split into four cans and transferred to an oven at 180°C, under static conditions and in an oxygen-free environment. After the desired period of curing, the cans were taken out and the molten mixtures were then cast into a ring stamp with 25 mm diameter and 1 mm thickness for subsequent rheological testing. Before testing, the samples were cooled at room temperature and stored in a Fisher Isotemp Freezer at -20°C (Polacco *et al*., 2004). Samples were analyzed using a Controlled Dynamic Shear Rheometer (ATS RheoSystems). The test geometries were plate-plate (diameters 25 and 1 mm gap) Viscosity measurements were conducted in the temperature range 20-140°C and frequency range was 0.1-15.91 Hz. The maximum strain was kept below the limit of the linear viscoelastic region.

RESULTS

Figures 1-4 show the variations of Bulk Modulus, G* (Pa) and Phase Angle (degrees) with a range of Frequencies (Hz) at different temperatures for TPB and TLA, respectively. It can be seen in Fig. 1 and 2 that TPB exhibited a higher phase angle and lower bulk modulus than TLA (Fig. 3, 4) over the same temperature range. Figure 1 show that at 333 K and at a frequency of 4.0 Hz, TPB was almost completely viscous (phase angle 88.4 degrees) whereas Fig. 3 showed a phase angle of 54.2 degrees for TLA. At these conditions of temperature and frequency, G* for TLA was approximately 2000 times that of TPB. The phase angles for TPB and TLA increased and the values of G* decreased with increasing temperature. For example at a load frequency of 15.9 Hz the phase angle for TPB increased from between 18 to 86.4 (Fig. 1) and the G* values decreased 36 times (Fig. 2) as the

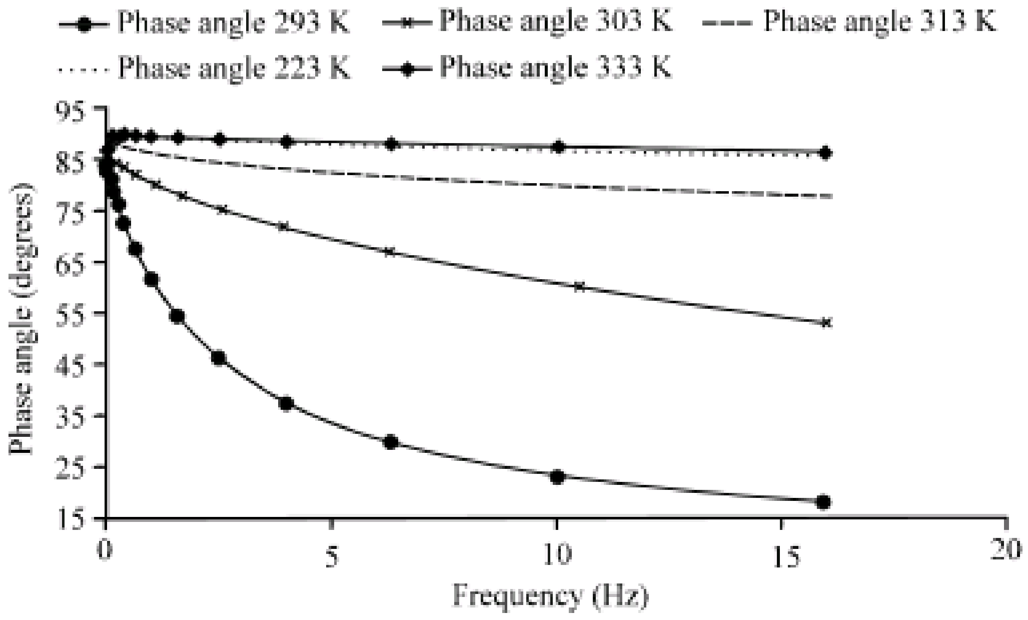

Fig. 1: Variations of phase angle (degrees) with a range of frequencies (Hz) at different temperatures for refinery bitumen 60/70 penetration (TPB)

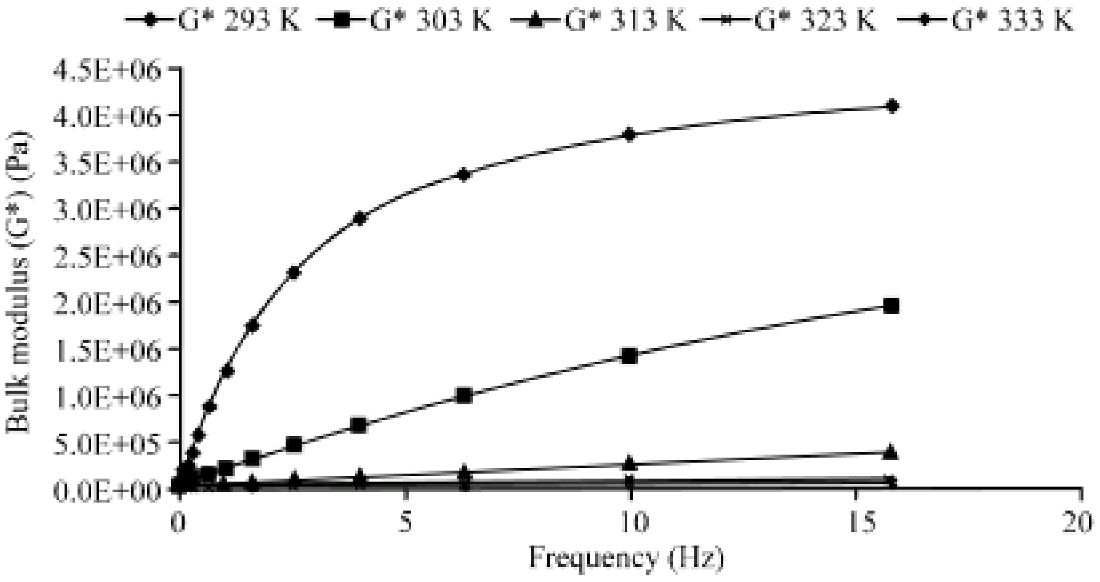

Fig. 2: Variations of bulk modulus, G* (Pa) with a range of frequencies (Hz) at different temperatures for refinery bitumen 60/70 penetration (TPB)

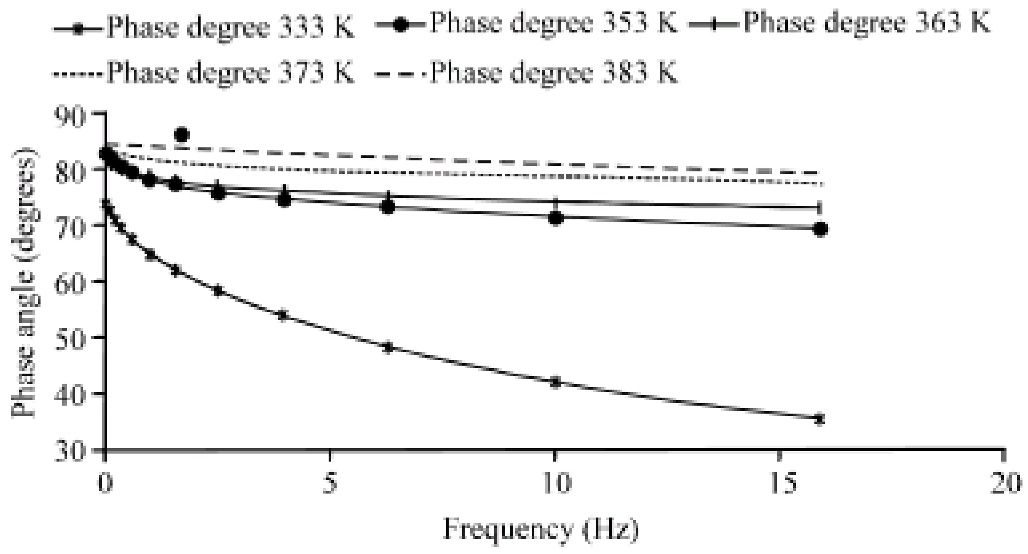

Fig. 3: Variations of phase angle (degrees) with a range of frequencies (Hz) at different temperatures for Trinidad Lake Asphalt (TLA)

temperature moved from 293 to 333 K whereas for TLA phase angle increased from between 35.5 to 79.4 (Fig. 3) and the G* values decreased 50 times (Fig. 4) as the temperature increased from 333 to 383 K.

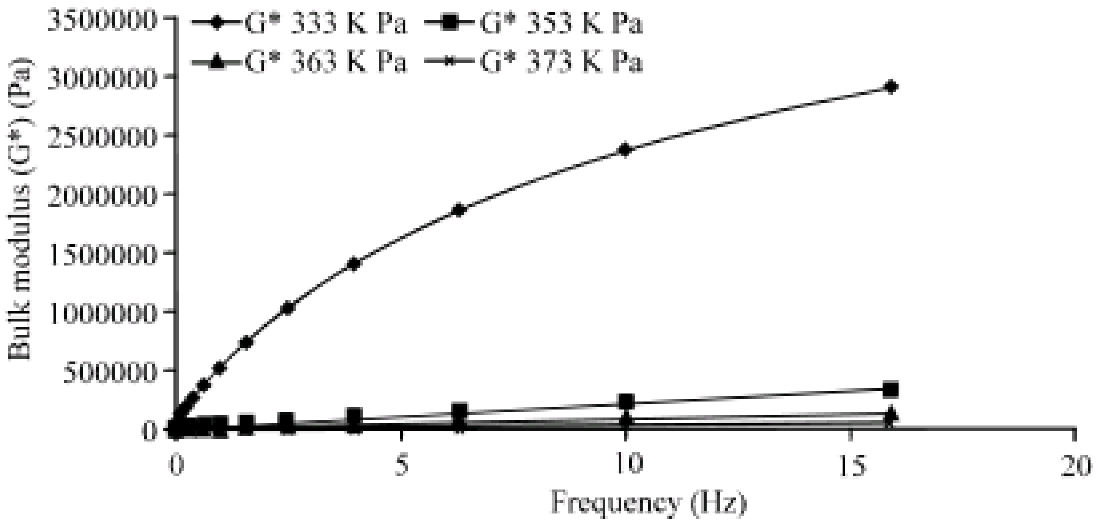

Fig. 4: Variations of bulk modulus, G* (Pa) with a range of frequencies (Hz) at different temperatures for Trinidad Lake Asphalt (TLA)

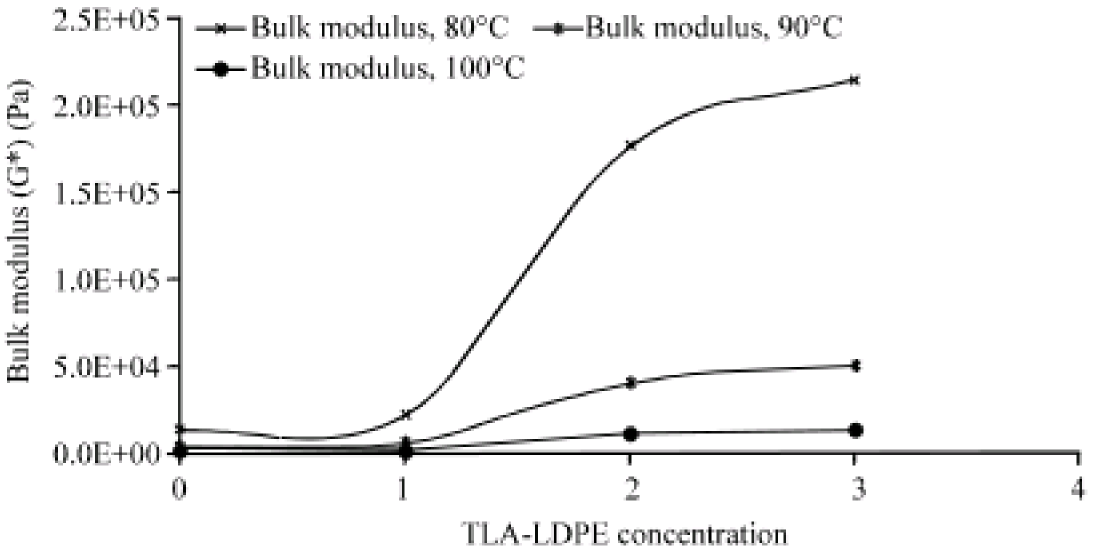

Fig. 5: Variations of bulk modulus, G* (Pa) with the different concentrations of the TLA-LDPE blends (%) at different temperatures at 0.4 Hz

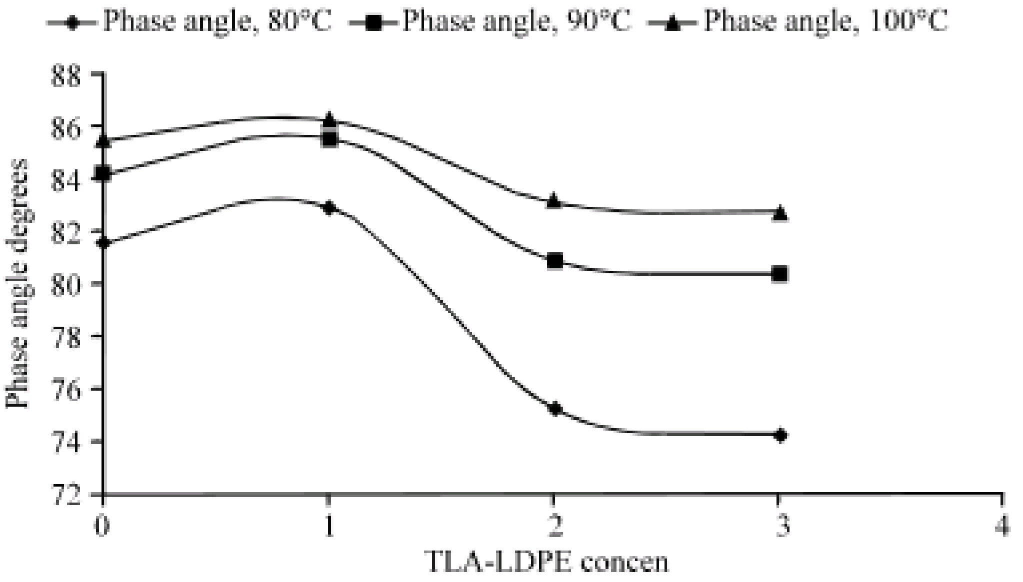

Fig. 6: Variations of phase angle (degrees) with the different concentrations of the TLA-LDPE blends (%) at different temperatures at 0.4 Hz

Figure 5 shows the effects of the addition of LDPE on the bulk modulus of TLA. The addition of LDPE to TLA resulted in a significant increase in the values of G*. This increase appeared to plateau between 2 and 3% LDPE. This was consistent with previous findings (Yeh *et al*., 2005). At 80°C the increase in G* due to the addition of 3% LDPE was approximately tenfold. Figure 6 shows the effect of the addition of LDPE the phase angle of

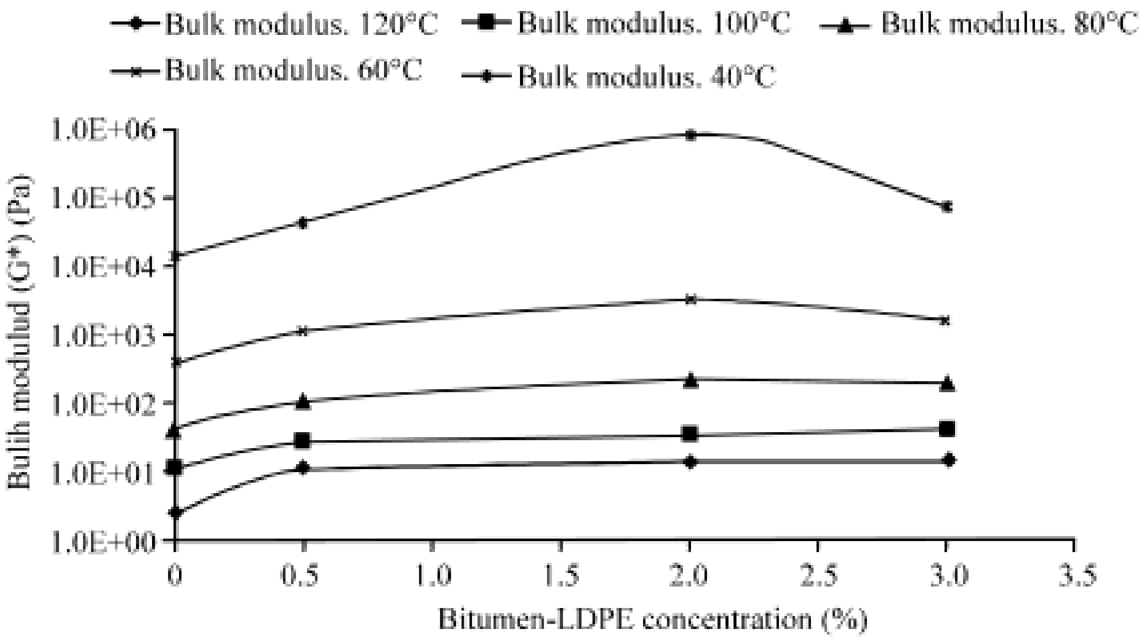

Fig. 7: Variations of bulk modulus, G* (Pa) with the different concentrations of the TPB-LDPE blends (%) at different temperatures at 0.4 Hz

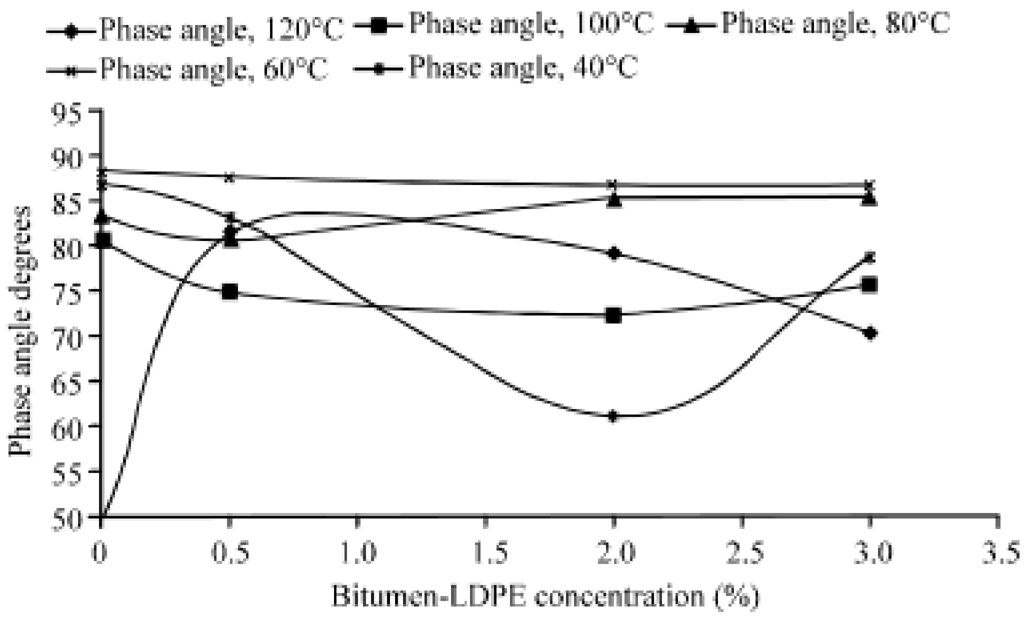

Fig. 8: Variations of phase angle (degrees) with the different concentrations of the TPB-LDPE blends (%) at different temperatures at 0.4 Hz

TLA. An increase in viscosity (higher phase angle) for the blend containing 1% LDPE however further addition of LDPE resulted in a decrease in the phase angle (greater elasticity of the blends) was observed.

Figure 7 shows the effects of the addition of LDPE on TPB which resulted in an increase in the bulk modulus of the material with a maximum occurring at 2% LDPE where the increase of G* of the blend was more than 8 times that of the unmodified material. As seen in Fig. 8 the influence the LDPE on the phase angle of the TPB was sporadic.

As expected the viscosities of the various TLA and TPB blends increased (higher phase angles) and the values of G* decreased as the test temperatures increased (Fig. 5-8). For TLA and TLA blends the temperature induced changes in phase angles and G* generally increased as the concentration of added LDPE increased. For example at a load frequency of 0.4 Hz the phase angle for TLA containing 3% LDPE increased from 74.2 to 82.7 degrees and the G* values decreased from 214900 to 14150 Pa as the temperature moved from 353 to 373 K whereas at 1% the increase in phase angle was from 82.9 to 86.2 and the decrease in the G* was from 23080 to 1979 Pa.

DISCUSSION

Rheology is that part of science that is interested in the description of the mechanical properties of different materials under various deformation conditions when they simultaneously perform the capability to flow and accumulate recoverable deformation; in this case, the rheological properties of bituminous blends are measured using the DSR and variations in the bulk modulus and phase angles were observed. The Bulk modulus represents stiffness, whilst phase angle is normally used to demonstrate the viscoelastic response of bituminous materials. Higher values of phase angle indicate a tendency towards more viscous behaviour, whilst lower values indicate more elastic response. The elastic behaviour (lower phase angle) is generally associated with high stiffness and increased brittleness; while the viscous response (higher phase angle) reflects high ductility and low stiffness.

The observations from Fig. 1 to 4 are consistent with the superior physical properties of TLA as the material was significantly stiffer and more elastic material than TPB. The materials moved from exhibiting an elastic response to an almost viscous liquid. The effect of the load frequency was more pronounced at lower temperatures and affected the phase angle and G* as the response tended to be more elastic and stiffer with increased load frequency.

The effect of the addition of LDPE to TLA on the phase angle produced interesting results. The viscosity of the material increased (higher phase angle) with the addition of 1% LDPE and further addition of LDPE resulted in a decrease of the viscoelastic response (lower phase angle). For practical purposes it is possible to produce a marginally stiffer but more viscous TLA based material by the addition of 1% LDPE. Blending TLA with 3% LDPE produces a material that is significantly stiffer and more elastic.

The addition of LDPE to TPB produced a stiffer but more viscous material by the addition of 2% LDPE. The sporadic results obtained for the phase angle changes due to the addition of LDPE to TPB was also observed by Lesueur (2008), when blending certain asphalts with crumb rubber and attributed this observation to the potential lack of polymer/bitumen compatibility. The dispersion of polyethylene in bitumen occurs above 140°C under high shear. At this point the molten polymer absorbs the maltene components of the bitumen and partially dissolves to form a highly viscous, elastic dispersion (Jew *et al.*, 1986). Since, the dispersion of the polymer molecules within the bitumen is dependent on the absorption of the maltene component of the material, it follows that the chemical composition of an asphalt determines its polymer compatibility. For TLA, the ratio of naphthene aromatic: polar aromatic: asphaltene is approximately equal to one, unlike the other asphalts, which generally have a low proportion of asphaltenes compared with aromatics (Chattergoon *et al.*, 1992).

The lack of compatibility between the TPB and polymer can result in the separation of the polymer and asphaltene phases of the bitumen resulting in measurements of the rheological properties of two separate phases (LDPE and bitumen) instead of one homogenous phase. Incompatibility could have also resulted in an incomplete reaction between the polymer and the bitumen and as a result limited absorption of bitumen molecules. Lesueur (2008) pointed out that in industry cross linking additives can be used to improved polymer/bitumen compatibility.

The unique composition of TLA as well as TPB give rise to unique performance qualities observed and this study provides further evidence of the composition-performance relationship described by Oyenkunle (2006, 2007), Andersen and Speight (2001) and Trejo *et al.* (2004).

CONCLUSIONS

The addition of LDPE in TLA and TPB resulted in changes in the rheological properties of the materials. The addition of LDPE to TLA resulted in a significant increase in the values of G*. This increase appeared to plateau between 2 and 3% LDPE. The effect of the addition of LDPE to TLA on the phase angle resulted in an increase in the viscosity of the material (higher phase angle) with the addition of 1% LDPE and further addition of LDPE resulted in a decrease of the viscoelastic response (lower phase angle). The influence of the addition LDPE on TPB resulted in an increase the bulk modulus of the material, the highest increase observed at 2% LDPE. However, the influence of the LDPE on TPB was sporadic. The changes in the viscoelastic properties of the TLA and TPB blends were temperature dependent as the viscosities of the various blends increased (higher phase angles) and the values of G* decreased as the test temperatures increased.

Variations of the rheological properties reflect variations in the mechanical properties of the various blends. Blends with relatively lower G* and higher phase angles are more ductile and flexible resulting in a more crack resistant material whereas blends with relatively higher G* and lower phase angles are more elastic and deformation resistant.

The results therefore confirm that low density polyethylene has enormous potential to be used as a modifier of TLA and TPB. The abundance of waste polyethylene in Trinidad renders the material environmentally attractive for improving the use of asphalt and bitumen.

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