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# Amelioration of Bitumen Characteristics via Natural Rubber Latex and Chlorine Gas

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**Abstract**

The influence of natural rubber along-side with chlorine gas on the bitumen blends characteristics have inspected. The modification performed through passing chlorine gas on molten bitumen mix prepared using bitumen and rubber latex of variety percentages. Penetration, penetration index, ductility and softening point have tested. In addition, viscoelasticity, rutting resistance and thermal stability have measured using dynamic shear rheometric analysis and differential scanning calorimetry, respectively. The chlorination has confirmed via Fourier-transform infrared spectroscopy analysis and asphaltene ratio determination. The acquired data showed an improvement in the thermal stability besides obvious enhancements in the viscoelasticity and rutting performance of the resulted blends. The results give clear advantage, for potential usage of such blends in the road paving application. © 2020 NIODC. All rights reserved.

*Keywords: asphaltene; rubber latex; chlorine; bitumen; scanning calorimetry; rheometer; viscoelasticity; rutting performance.*

## 1. Introduction

Natural rubber with its unique structure has found its way to the bitumen industry. it has a versatile application now days; Hence, one of its usages is as an additive material for bitumen to improve the latter elasticity, resistance to high temperature, and durability, besides other required specifics. Bitumen in known as the crude petroleum residuum, a result of losing its light fractions naturally or manufactory [1]. In this study, the term bitumen is used preferentially, however we may asphalt interchangeably with for citation literature.

Rubber latex (RL) has proved as a modifier for bitumen; the process shows it is more efficient to costs, usage levels, storage preparation, and stability compared to the powder type or waste tires. Besides, using rubber-latex for modifying bitumen gives peculiarity to international rubber producers [2].

The literatures of using rubber latex to improve asphalt pavement are limited. Mixing asphalt at higher level of heat with latex makes the rubber particles swell and like a sponge absorbs the light components in asphalt, namely Oils [3]. However, the water contents of latex can be controlled by elimination at a low level of heat [2].

A researcher performed a modification using a heavy-duty mixer with variables of rubber latex, temperature and time. The latex was varied between 1-12% weight, whereas the heating and mixing time varied between 150-200°C and 10 to 90 min, respectively. The outcome was the suitability of latex for the modification with optimum latex content of 9% while the optimum blending temperature was 150°C and blending time was10 minutes [4, 5].

Applying crumb rubber contents of 5, 10 as well as 15%, besides 5% and 10% of latex to fabricate asphaltic binders has an advantage; since the results from both Layer-Parallel Direct Shear (LPDS) test and bond test did not favor one another, the conclusion was that both crumb rubber and latex-bitumen binder are superior in bitumen processing [6].

Furthermore, treating rubber compounding with anti-oxidant and natural latex during the vulcanization operation. The asphaltic rubber reveals that either contents improved certain specification like dropping in penetration, rising in softening and penetration index. The asphaltic-rubber comparing to the asphalt

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penetration (pen) 60 is low temperature susceptibility [7].

Latex of ratio (2.5, 5.0, 7.5 and 10)% has used with bitumen (pen 60/70) and evaluated penetrability, softening point and viscosity; in addition ductility, loss upon heating and dynamic shear rheometer. The addition of latex led to hardened the bitumen, increases the viscosity and provides better resistance against rutting [8].

Natural rubber (NR) domains in the asphalt were also obtained with Polyphosphoric acid (PPA) addition. An incorporation of 0.3% weight of sulphur based on NR content in NR/PPA-modified asphalt was found to substantially increase the toughness and tenacity of the obtained asphalt from its vulcanizing effect. These three modifiers can provide complementary effects in asphalt property enhancement. In addition, the optimal formula to produce asphalt mixture with high stability for road pavement application was 3.2% wt. of NR, 2% wt. of PPA and 0.3% wt. of sulphur [9].

In another research, 5 to 10% observed an increase in softening point (w/w) addition of liquid natural rubber. The ductility decreased with soft bitumen, while some improvements were noticed with blown bitumen at 10% loading. Penetration values consistently decreased in both cases. Resistance to shear also increased and was maximum near 5 to 10% (w/w) of rubber. Another observation, the shear stress for all bituminous samples increased proportionality with the shear rate. For soft bitumen, the dependency of viscosity on the temperature was prominent up to 100ºC [10, 11].

On other side, natural rubber latex can improve the rheological characteristics of modified asphalt emulsion residue. According to the study, the best amount of latex to the prepared emulsion asphalt was 7% while the mixing time 20 min. [12].

Natural Rubber-Asphalt (NRA) obtained from mixing AC 60/70 with ammonia concentrated latex at the content of 1-13 percent (best ratio was 9% latex) by total weight were used to mix with limestone to produce asphalt concrete samples. Because of its availability, natural latex is preferable for roads paving in the NR-latex producing countries and for improving and service life of asphalt pavement [3].

The microscopic ability to spread and asphalt storage stability of grade (pen 60/70) mixed with 6% of rubber latex (using surfactant as incorporating agent and without it) had been investigated. They assessed the prepared samples under unaged besides short term ageing conditions and asphalt blends storage stability at 180 °C for 72 hours. Observing morphology of the asphalt-latex binders' surfaces was performed using optical polarizing microscopes. The results revealed the detection of the formation of globular agglomerated microstructures [6].

Another important property to get suitable performance requirements of bitumen pavement is asphaltene equilibrium. Previous research has indicated that increasing asphaltene contents decreases asphalt temperature susceptibility [13].

The asphaltene is the major responsible viscoelasticity of asphalt blends and raising the asphaltenes contents increases asphalt mixes stiffness and viscosity resulting in penetration and creep compliance decrease [13].

Increasing the asphaltene contents (from 0 to 4.18 vol%) showed strengthen in the polar network (mostly asphaltenes) and hence elasticity property to the whole binder [14].

In another research, four asphalts were fractionated into three generic fractions according to Corbett procedure and re-blended into asphaltenes /aromatics/ saturates ternary mixtures in various ratios, then aerial oxidative aging at about 88, 94 and 100°C for 5-33 days. Rheometer and FTIR were used to observe the changing in the chemical and physical characteristics [15].

The concluded that the saturates (mostly maltenes) have a significant impact on the asphaltene contribution on the viscosity for the aged blends suggesting that the aromatics fraction is solely responsible for the formation of asphaltenes as an asphalt oxidizes [15].

From another point of view, chlorinated products of oil-rich component are likely to find use as plasticizers or binders, where improved water resistance, coupled with solvent resistance, is required whereas chlorination of resins or resin-rich bitumen is unlikely to have any industrial application since it gives hard and brittle products [16].

Another observation is, the bitumen chlorination though gives hard products but controlling the chlorine gas ratio and incorporating other modifiers like plastics into asphalt led to enhance asphalt properties [1, 17, 18].

It was reported that chlorination of asphalt increased its resistance to hardening and further treatment with chlorine does not result in a significant increase in resistance to hardening but may lower the ductility of the asphaltic mixes to a point where it is no longer useful for highway construction [1].

The objective of this research is to modify and characterize the conventional properties of the natural rubber-latex (NRL) modified bitumen binders (in the presence and absence of chlorine gas as homogenizer factor) by using empirical test methods as well as estimating the asphaltene ratio and its effects on the latex-asphaltic mixtures.

## 2. Materials and Methods

### 2. 1. Materials

Base (virgin) bitumen of 80/100 penetration grade has been provided by Petronas company, Malaysia. Conventional tests, including softening point, penetration and ductility, were conducted to recognise the properties of it. The specifications of the base bitumen were illustrated in table 1.

Natural rubber latex high ammonia (HA) was provided by Titan Teraju SDN. BHD. The properties of NRL are shown in table 2.

Chlorination of the blends is achieved by applying chlorine gas ~ 100%. Caustic soda (30%) solution is utilized for excess gas catcher.

### 2. 2. Bitumen binder modification

The addition of NRL were carried out by adding the latex to molten bitumen in different percentage (1, 3, 5, 7, 9 and11%) and stirred for 2 hours with a heavy shear mixer, shearing rate about 350-400 rpm at maintained temperature of 160°C to avoid agglomeration of NRL with bitumen. The specimen represented by (VL1%, VL3%, VL5%, VL7%, VL9%, VL11%) respectively.

Finally, the obtained specimens were treated with chlorine (using similar conditions in the premodification) to obtain chlorinated natural rubber latex-bitumen blends represented by (VLCL1%, VLCL3%, VLCL5%, VLCL7%, VLCL9%, VLCL11%) respectively. All blending ratios of the samples in the experiments are listed in table 1 & 2.

### 2. 3. Conventional bitumen tests

Penetration, softening point and ductility have measured according to ASTM standards [19-21] respectively.

### 2.4. FTIR Analysis

The measurements of Perkin Elmer FTIR spectroscopy were occurred (to all treated samples) in the wave number range 400 - 4000 cm$^{-1}$, and 64 scans were recorded at 4 cm$^{-1}$ resolutions.

### 2.5. Asphaltene precipitation method

Asphaltene precipitation method through the calculation of asphaltene precipitation ratio according to ASTM standards [22].

### 2.6. Thermal analysis

The differential scanning calorimetry (DSC) was applied using PerkinElmer DSC6. We performed the measurement using 10 mg sample sealed in an aluminium sample pan. Each sample was heated from 30 - 250ºC at 10ºC/min to get the results and curves.

### 2.7. Dynamic shear rheometer specification (DSR)

Dynamic shear rheometer analysis was performed to characterize the viscoelasticity bitumen mixtures, as well as the prepared binders, at different ranges of temperature. DSR measures complex shear modulus represented by (G*), and phase angle represented by (δ). The analysis temperatures were from 46ºC to 82ºC, with 6ºC increment.

The impact of rubber latex with and without chlorine gas on G* and δ has examined. The G* indicates bitumen deformation resistance, while δ represents the ratio between elasticity and viscosity during the shear load. The test sample diameter and thickness were 25 mm and 1 mm, respectively.

## 3. Results and discussion

### 3. 1. Empirical Tests Results

The results from applying empirical tests are recorded in the table 1 and 2.

**Table 1:** Specifications result of base and latex-bitumen blends.

| **Sample No.** | **Latex%** | **Asphaltene%** | **Softening point, ºC** | **Ductility, cm** | **Penetration, 0.1 mm, 25ºC** | **PI** |
|---|---|---|---|---|---|---|
| **V** | 0 | 5 | 50 | 100 | 90 | 0.3457 |
| **VL1** | 1 | 5.6 | 54 | 94 | 85 | 1.1927 |
| **VL3** | 3 | 6.7 | 57 | 84 | 81 | 1.7423 |
| **VL5** | 5 | 7.35 | 59 | 68 | 76 | 1.9764 |
| **VL7** | 7 | 8.1 | 64 | 53 | 69 | 2.6818 |
| **VL9** | 9 | 9.3 | 68 | 45 | 60 | 2.9969 |
| **VL11** | 11 | 10 | 74 | 41 | 57 | 3.8099 |

The addition of NRL shows proportional scale-up in the softening with latex contents increase. Contrary, increasing latex contents led to a decrease in the penetration and the ductility, respectively. The addition of the polymer ideally decreases the oily contents of the bitumen which gives tougher binders. This is in agreements with the results from [1, 2].

The determination of PI is considered as a function for the thermal susceptibility of bituminous binders where the values may vary from -3 to 7 [23]. Referring to the table 1 and 2, the natural rubber-latex has improved the susceptibility of the bituminous binders to the temperature change which is preferred in the paving and constructing application.

**Table 2:** Specifications result of base and chlorinated latex-bitumen blends.

| Sample No. | Latex% | Asphaltene% | Chlorine Content% | Softening Point, C$^o$ | Ductility cm | Penetration (25C$^0$,0.1mm) | PI |
|---|---|---|---|---|---|---|---|
| **V** | 0 | 5 | - | 50 | 100$^+$ | 90 | 0.3457 |
| **VLCL1** | 1 | 6.25 | 0.423 | 62 | 62 | 58 | 1.7997 |
| **VLCL3** | 3 | 7.5 | 0.63 | 64 | 51 | 51 | 1.8398 |
| **VLCL5** | 5 | 8.45 | 0.855 | 70 | 38 | 47 | 2.6691 |
| **VLCL7** | 7 | 9.9 | 1.085 | 79 | 26 | 44 | 3.8468 |
| **VLCL9** | 9 | 11 | 1.218 | 85 | 17 | 39 | 4.3324 |
| **VLCL11** | 11 | 12 | 1.475 | 92 | 13 | 32 | 4.6837 |

Another point, is the increase of asphaltene ratio with that of the amount of latex in the binder means the polarity of the bitumen has increased and therefore led to more agglomeration and thus the colloidal system stability of the bitumen has been improved. In addition, chlorinated latex-bitumen blends have shown the same behaviour observed in the addition of NRL with a softening increase and reversely a great decrease in the ductility and penetrability, respectively. We can refer this to the addition of chlorine, which makes the bitumen less oily and thus becomes stiffer and tougher [7, 17].

## 3. 2. Fourier-Transform Infra-red Spectroscopy Results

Figure 1., represents the FTIR-spectra of neat bitumen and the modified binders with latex at different percentages as described earlier. The peaks observed from the FTIR-spectra for the latex-bitumen blends and the chlorinated latex-bitumen blends are not similar to those of virgin bitumen.

It was observed that the peaks 1020, 1220 and 1083 cm$^{-1}$ corresponding to C — O stretching vibration mostly vinyl ether, aliphatic ether respectively, which is found on the rubber spectrum but did not notice on the spectrum of the modified bitumen. As expected, the addition of natural latex has not affected the FTIR-spectra of the virgin bitumen, which support the say that the addition was proceeded through physical blending [1, 10].

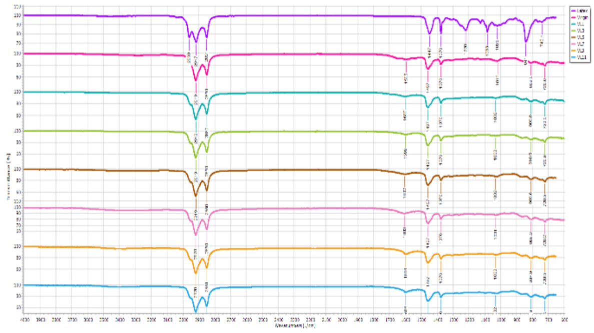

**Fig. 1.** FTIR-spectra of virgin bitumen and bitumen-latex binders.

Figure 2. shows the FTIR Spectrum for chlorinated latex-bitumen binders. The absorption peak, starting at 660 cm$^{-1}$ in comparison to un-modified bitumen belongs to C-Cl stretching bond, providing a firm proof chlorine introduction into the network of bitumen [17, 24].

It is also noticed that the C-Cl peak intensity increases with the latex ratio which is agreed with results from some studies besides ours in the same field [1, 25-26].

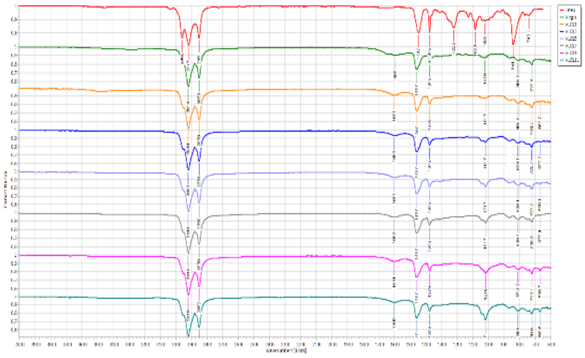

**Fig. 2.** FTIR-spectra of virgin bitumen and chlorinated bitumen-latex binders.

### 3.3. DSC Results

The DSC plots against the temperature of the virgin bitumen and prepared blends are shown in the Figure 3 and Figure 4 respectively, while the data are recorded in Table 3.

**Table 3:** DSC results of virgin bitumen, VL and VLCL

| Sample | Tg, (ºC) | ΔH (J/g) | $\Delta H_f$, (kJ/mole) |
|---|---|---|---|
| **Original Asphalt** | 60.07 | -75.441 | -0.0754 |
| **VL1** | 59.61 | -144.8850 | -0.1449 |
| **VLCL1** | 67.12 | 36.2662 | 0.0363 |
| **VL3** | 61.34 | -198.6622 | -0.1987 |
| **VLCL3** | 65.8 | -115.2618 | -0.1153 |
| **VL5** | 62.23 | -59.7637 | -0.0598 |
| **VLCL5** | 66.73 | -227.4288 | -0.2274 |
| **VL7** | 57.19 | -115.1950 | -0.1152 |
| **VLCL7** | 70.54 | -161.6233 | -0.1616 |
| **VL9** | 68.02 | -68.8121 | -0.0688 |
| **VLCL9** | 69.09 | -211.0083 | -0.2110 |
| **VL11** | 58.01 | -171.4669 | -0.1715 |
| **VLCL11** | 69.11 | -89.9763 | -0.0900 |

The data obtained from the DSC plots of the VL binders show no crucial change in the Tg values, except for sample VL9 (Latex contents 9%). While, the chlorinated latex -bitumen samples have an obvious change in the Tg, though there is no conclusive effect attributed to the chlorination; for example no sharp peak appears in the chlorinated blends. The changes in the Tg of the chlorinated latex -bitumen blends mostly about 16% of the Virgin bitumen. The higher the Tg, means the blends more brittle at cold temperature thus they are meant for areas at which the weather is hot.

The peaks of endo-thermic fusion of the bituminous blends, appearing at approximately at (~80°C), and increasing proportionally with the latex, become less sharp in the chlorinated samples.

The alter in the Tg value endorses the increase of the binder's strength, measured by softening, penetration and ductility for the chlorinated samples [27]. Another observation, the enthalpy (ΔH), and fusion heat ($\Delta H_f$), of both VL and VLCL significantly change to larger values than that of the original asphalt except for VL5, VL9 and VLCL11. The chlorinated binders change appears much larger, which means the intact between the latex and the bitumen has ameliorated which definitely attributed to the existence of chlorine. The enthalpy increase implies that the phase severely separates and induces latex aggregates to crystalise in the bitumen matrix.

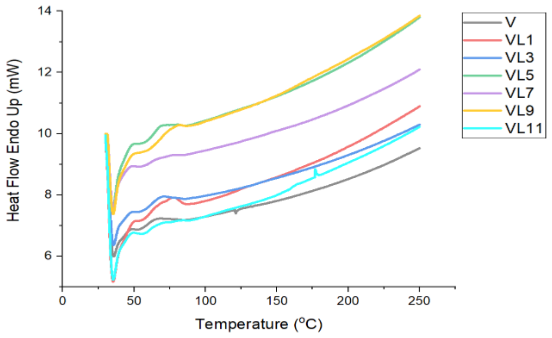

**Fig. 3.** DSC plot of virgin bitumen, latex and bitumen-latex blends.

The enthalpies of the VLCL at higher polymer contents have dropped mostly much compared to the non-chlorinated blends. The binder's hardness increase attributed to the viscosity increase of the bituminous blends while the enthalpies decrease may refer to the enhancement in the phase-crystallinity since the intact between the NR, and bitumen constituents occurred due to chlorine influence. This agrees with the results from references [28, 29]. In our opinion from the environmental perspective, these results are attractive because increasing the latex amount may help reduce the bulk load on the environment (most works prefer polymer contents below 5% because of the severe phase separation) and improve the bitumen characteristics since the distribution and the stability have increased.

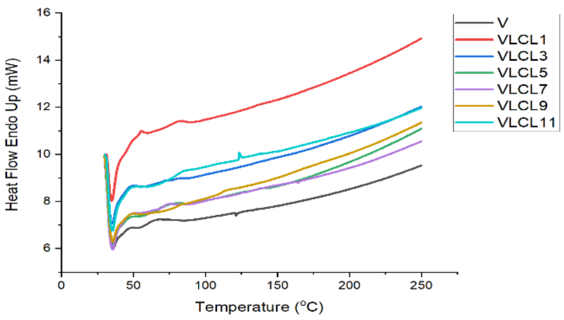

**Fig. 4.** DSC plot of virgin bitumen, latex and chlorinated bitumen-latex blends.

### 3.4. Rheology

Figures 5-8 Show the results of sweep test conducted. The addition of the Latex showed an obvious increase in the G* and a drop in the δ.

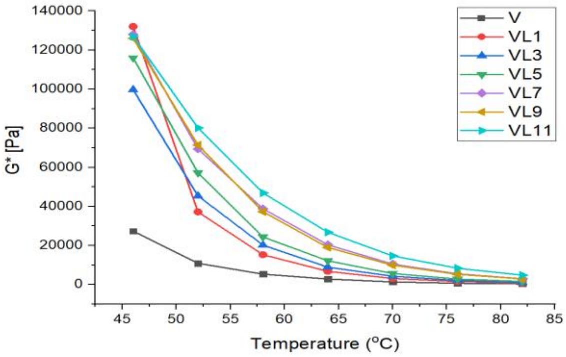

**Fig. 5.** Complex modulus of virgin bitumen, latex and bitumen-latex blends.

In addition, from Figure 5, it can be observed that all blends except VL3, VL5 have G* higher than virgin bitumen of about 126000-132000 Pa, while VL3, and VL5 values of 99000 and 119000 Pa, respectively.

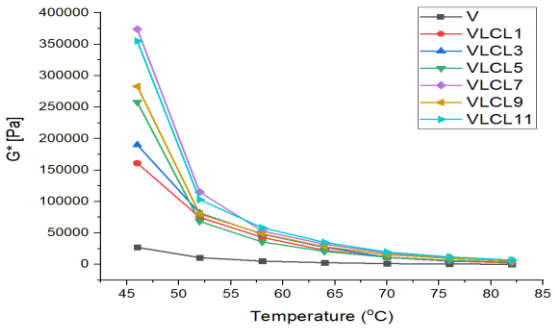

**Fig. 6.** Complex modulus of virgin bitumen, latex and chlorinated bitumen-latex blends.

Chlorinated binders show significant improvement in the G*, between 161000 -355000. It must be said here that VLCL7 has the highest G* values of about 374000 Pa. This means that these binders resist the deformation and are also thermally stable [30].

Reversely, δ of the binders decreases slightly in the order from lower to higher contents of latex, whereas, chlorinated blends conclusively changed at the same order; In this particular, VLCL7 specimen is the best of all blends.

Generally, one can say that the chlorinated binders have the improvement in the rutting resistance in comparison with neat bitumen and unchlorinated blends.

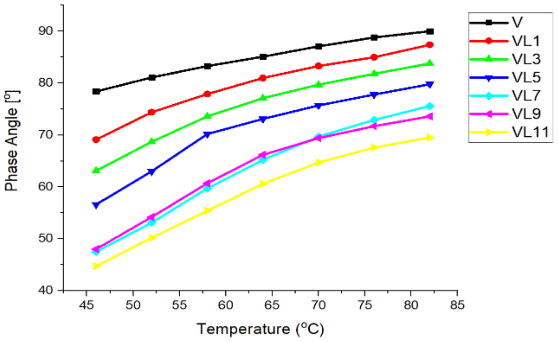

**Fig. 7.** Phase angle of virgin bitumen, latex and bitumen-latex blends.

The phase angle change range for the latex base binders was observed between 44 to 69°, which was lesser than original at low temperature (as the value for virgin asphalt is 78°). This range decreases by rising the temperature and becomes from 69 to 87°, very near to the perfect viscous range (90°) at higher temperature, meaning that the binders do not resist the deformation and it can be referred to the poor distribution and linking in and with bitumen the polymer in this case tend to separate due to the temperature and thus the binder loses it strength to resist the deformation.

As for the VLCL binders, the phase angle decreases from 45 to 56° lesser than the virgin bitumen. VLCL blends at higher content is the best in terms of the complex modulus (higher) and phase angle (lower) which reflects higher rutting resistance values and also has good viscoelastic properties though at lower temperature it is stiff.

The dropping in the δ indicates that viscoelastic properties for VLCL binders change from a prevail viscous-liquid to a prevail elastic-solid trending, revealing the thermal susceptibility enhancements for the binders. The amplitude sweep test shows that the process of chlorination does definitely change the G* and δ for these blends. This is supported by the results from references [13, 5]. As such, it can be expected that chlorinated latex bitumen binders have potential application in the roofing applications.

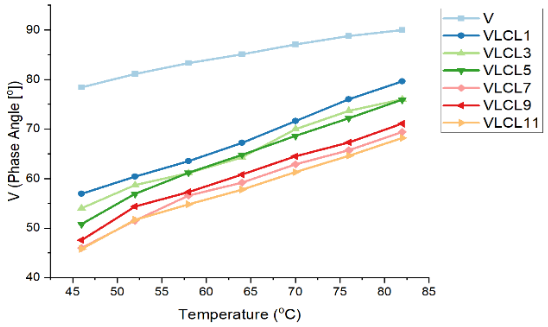

**Fig. 8.** Phase angle of virgin bitumen, latex and chlorinated bitumen -latex blends.

## 4. Conclusion

Bitumen was modified using natural rubber latex and further modification was conducted by the aid of chlorine gas as a chemical modifier agent.

The FT-IR results revealed that the chlorine has introduced to the system chemically, unlike the natural latex which was done physically.

Heat stability of the system shows an enhancement from the results of softening, penetration as well as DSC, but the higher chlorination the higher brittleness which in return suggest that samples with medium chlorination is favoured over the rest of them.

The viscoelasticity of the prepared samples also enhanced clearly due to addition of natural latex and further enhancing has been observed when latexes samples has been chlorinated. The rutting resistance has been enhanced due to latex and chlorine modification and in summary we can conclude that the best addition of latex and chlorine introduction have been obtained in the moderate samples VLCL5 and VLCL9.

Final conclusion is that the addition of latex to the bitumen is favourite with moderate chlorination and the most acceptable ratio is 5% and 9% latex-bitumen.

## Conflicts of interest

The authors declare that they have no conflicts of interest.

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