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Influence of chemical characteristics of RAP binders on the mechanical properties of binders and mixes

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Abstract

Utilization of recycled asphalt materials in the asphalt layer construction has emerged as an important rehabilitation option for asphalt pavements. The properties of recycled asphalt material will be different from those of the initial (virgin) asphalt mixture, due to the aging of the binder. Resilient modulus is an important material parameter used for the design of pavements. The mechanical behaviour of mix and binder is expected to be influenced by the chemical composition of the binder. In this study, the effect of the chemical composition of virgin and reclaimed asphalt pavement (RAP) binders on of resilient modulus (M_r) of RAP mixes has been evaluated. This is done by testing different RAP mixes prepared using bitumen samples containing different proportions of RAP binder. RAP mixes prepared using one aggregate gradation (mid-point gradation recommended by the Ministry of Road Transport and Highways for Bituminous Concrete -1) and different RAP contents (0, 15, 25, 35 and 45%) with VG 30 as virgin binder were tested for their resilient modulus value at different temperatures (15, 25 and 35 °C) and frequencies (0.5, 1, 1.5 and 2 Hz). The chemical composition of the binder blends was evaluated with the help of Fourier transform infrared spectroscopy (FTIR). The relationship between chemical indices and rheological parameters has been examined and the ketones, aliphatics and aromatics are found to have good correlation with the rheological properties. The relation between chemical makeup and resilient modulus has also been examined and the relations are presented in the paper.

Keywords: RAP mixes; resilient modulus; FTIR spectroscopy; chemical composition

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1. Introduction

Use of reclaimed asphalt pavement (RAP) material in the preparation of hot asphalt mixes has increased significantly over the past few years as one of the logical and economic options for reuse of aggregates and binder and for the alleviation of the problem of disposal of the bituminous layers removed from in-service pavements. Reclaimed asphalt pavement material, when used for hot mix asphalt (HMA) mixture preparation, changes the properties of the binder and mixture obtained. This is due to the presence of aged binder in the RAP material. The strength and brittleness of the HMA mixture tends to increase with the percentage of RAP added to the mixture (Daniel and Lachance, 2005; Izaks et al., 2015; Nofereni et al., 2017; Yan et al., 2017). Resilient modulus of the bituminous mixture is an input parameter for many flexible pavement design procedures, including the flexible pavement design guidelines followed in India (IRC 37-2012). The mechanical properties and performance characteristics of bituminous mixes are influenced by the loading frequency and mix temperature.

The chemical composition of the binders influences the mechanical behaviour of the binders and mixes. Fourier transform infrared spectroscopy is generally used to identify and quantify the functional groups present in the binders. Ketones, sulfoxides and alcohols are commonly quantified to represent the oxidation characteristics of the asphalt binders. Along with the formation of molecules that impart viscosity to the asphalt binders, the formation of secondary bonds also imparts stiffness/viscosity to the binders. The quantity of aliphatics and aromatics in the binder also influence the viscosity of it. The secondary bonds tend to disrupt due to the application of heat or loading. The modulus/stiffness of the mixture depends on the presence of primary and secondary bonds in the asphalt binder. The viscoelastic response and the properties of the binders or mixes depends on the chemical composition specially the percentage of oxides, saturates (aliphatics) and aromatics which impart viscous properties to the material. The present study is a step forward to understand the relationship between chemical makeup of the binders and the mechanical properties of the mixtures, especially for the RAP mixes.

2. Objective and Scope

The objective of the present study is to investigate the effect of the chemical makeup of the binders on the rheological properties of RAP binders and the resilient modulus of mixes with RAP binders. The scope of the study is as follows

- Characterization of the materials (binders, aggregates and RAP material) used in the present study was done. Bituminous concrete -1 mid-point gradation specified by Ministry of road transport and highways (MoRTH, 2013) has been used to prepare mixes with 0, 15, 25, 35 and 45 % RAP in them.
- Design binder contents for all the five mixes were determined using Marshall mix design method
- Resilient modulus tests were conducted on the specimens prepared at respective design binder contents for three temperatures, 15, 25 and 35 ^{o}C and for four frequencies, 2, 1.5, 1 and 0.5 Hz.
- RAP-virgin binder blends were prepared corresponding to the RAP binder to virgin binder ratios obtained from the mix design exercise. Fourier transform infrared spectroscopy was carried out on the RAP – virgin binder blends to determine the intensities of different functional groups in the binder blends.
- The relation between the chemical makeup and the rheological properties of binders has been examined. Also, the relation between chemical indices and the resilient modulus of the bituminous mixtures was examined.

3. Materials and Methods

3.1. Materials

The RAP material used for the present study was collected from KULPI plant located on national highway NH-117. Aggregates and VG30 (virgin) binder were collected from an ongoing construction site at Salboni, West Bengal. RAP binder was extracted from the RAP material using Trichloroethylene solvent in order to determine the gradation of RAP aggregates and the content and properties of the binder. The RAP binder content is 3.96 %. Bituminous concrete, a commonly used surface course mixture with nominal maximum aggregate size of 19 mm, was selected for the present study. The binder extracted from RAP material and VG30, VG40 virgin binders were characterized to determine basic properties like penetration, softening point and viscosity at 60 ºC. Gradations of the RAP aggregates and BC-1 midpoint are given in Table 1. Properties of VG30 and RAP binder are presented in Table 2.

Table 1: Gradations of RAP aggregates and BC-1 midpoint

Sieve size, mm		26.5	19	13.2	9.5	4.75	2.36	1.18	0.6	0.3	0.15	0.075
Cumulative % passing	RAP aggregates	100	99	96	91	60	39	23	16	11	7	5
	BC-1	100	95	69	62	45	36	27	21	15	9	5

Table 2: Properties of binders

Binder	Penetration at 25ºC, dmm	Softening point, ºC	Viscosity at 60ºC, P	Kinematic viscosity at 135ºC, cSt
RAP	15	82	346000	-
VG30	61	52	3516	522

3.2 Bituminous mix design

Five mixes with midpoint gradation of bituminous concrete-1 (MoRTH, 2013) with different percentages of RAP were designed to determine the optimum binder contents (OBC). Marshall method of mix design with 75 blow compaction was adopted to determine the optimum binder contents. 100 mm diameter Marshall samples were prepared for different RAP contents and binder contents. The mixing and compaction temperatures were determined using Brookfield viscometer corresponding to viscosity levels of 0.17±0.02 Pa.s and 0.28± 0.03 Pa.s (ASTM D2196-15) respectively. For each of the mixes, RAP material and binder were heated to the mixing temperature corresponding to the binder used. Virgin aggregates were heated separately to a temperature that was 0.5 ºC higher for each percent of RAP material going into the mix and mixed before adding the preheated binder (MS-2 seventh edition, 2015). The binder content corresponding to 4% air voids was selected as the optimum binder content. The properties of the mixes prepared at 4% air void content are tabulated in Table 3.

Table 3: Marshall test parameters for RAP mixes

Mix type	Virgin binder	OBC, %	Stability, kN	Flow, mm	VMA, %	VFA, %
0% RAP	VG30	4.7	13.1	2.9	15.8	74.4
15% RAP	VG30	4.7	16.4	2.6	15.7	73.4
25% RAP	VG30	5.0	15.3	3.4	16.0	75.6
35% RAP	VG30	5.2	16.5	3.3	16.3	75.4
45% RAP	VG30	5.5	18.3	3.4	16.3	76.1

3.3 Characterization of RAP blends

RAP binder blends were prepared by mixing extracted RAP binder and virgin binder (VG30) in required proportions at the mixing temperature determined for virgin binder. The RAP binder blends were prepared by mixing the RAP binder extracted from the RAP material with VG30 binder at mixing temperature of VG30. Characterization of binder blends was done to determine properties such as penetration, softening point, dynamic viscosity at 60 ºC and complex modulus. The properties of different RAP binder blends are given in Table 4.

Table 4: Properties of RAP blends

Binder blend	Penetration, dmm	Softening point, ºC	Viscosity at 60ºC, P	Complex modulus at 64ºC, kPa	Phase angle, δ

VG30	61	52	3516	1.30	87.4
15% RAP	48	57	6243	4.07	85.9
25% RAP	41	60	9643	4.64	85.7
35% RAP	33	62	12470	7.67	84.3
45% RAP	26	65	18780	12.58	83.0

3.4 Resilient modulus test

Resilient modulus (M_R) is an input parameter which represents the material behaviour in many of the pavement design procedures including flexible pavement design method used for Indian roads (IRC 37, 2012). Indirect tension mode is a common mode of testing used for determination of resilient modulus. Resilient modulus is the ratio of applied stress to the recoverable strain at any frequency and temperature. The environmental chamber of universal testing machine (UTM 14.0) available in the laboratory of IIT Kharagpur was used for conditioning the specimens. Resilient modulus testing was carried out according to EN 12697-26 (2012) at test three temperatures: 15ºC, 25ºC, 35ºC and four frequencies 2 Hz, 1.5 Hz, 1 Hz and 0.5 Hz. The load required to achieve a peak deformation of 5 µm was applied. The Poisson's ratio of the mix was assumed to be 0.3, 0.4 and 0.5 for 15, 25 and 35 ºC respectively. The expression given by equation 1 was used for the calculation of the resilient modulus. The resilient modulus jig is shown in Figure 1. Results of the resilient modulus (for each value reported in the table 3 replicates were tested) test are given in Table 5.

$$M_R = \frac{P(\mu+0.2732)}{t*\Delta H} \quad (1)$$

Where, µ is the Poisson's ratio, P is the applied load, t is the specimen thickness, M_R is the resilient modulus and ΔH is the horizontal deformation resulting from the applied load.

Fig 1: Resilient modulus test setup

Table 5: Results of resilient modulus test

Temperature	Frequency, Hz	Resilient modulus, MPa				
		VG30- 0% RAP	VG30-15% RAP	VG30-25% RAP	VG30-35% RAP	VG30-45% RAP
15ºC	2	10485	9267	13357	15954	18328
	1.5	9239	8265	11422	13387	14384
	1	8715	7828	9202	11860	12915

	0.5	7392	6136	7805	11435	11568
25ºC	2	5292	5979	7220	8093	8894
	1.5	4730	5520	6714	7666	8440
	1	4302	4948	6222	7130	7431
	0.5	3227	3858	4939	5795	6121
35ºC	2	2040	2714	3193	3862	4673
	1.5	1807	2387	3006	3478	3581
	1	1644	1897	2635	3031	2871
	0.5	1233	1410	2005	2380	2377

Figure 2 shows graphical representation of the resilient modulus values of different mixes.

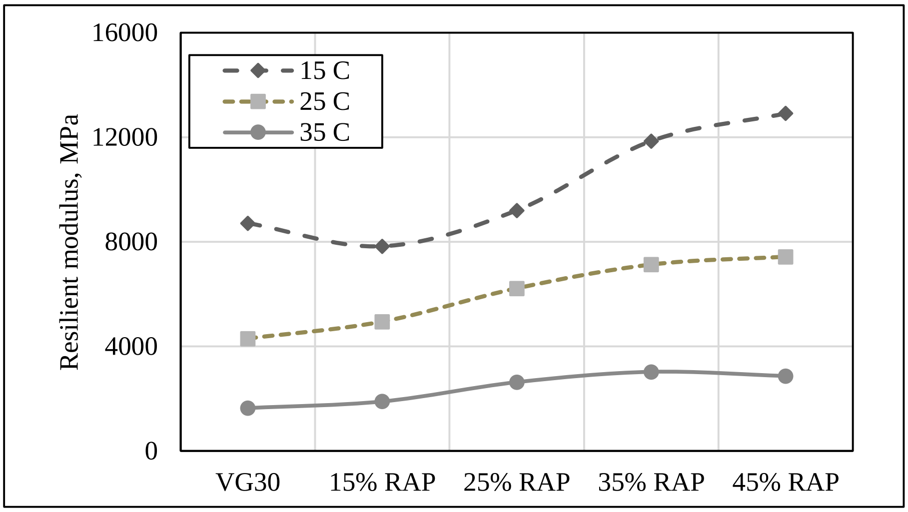

Fig 2: Resilient moduli of different mixes (1 Hz)

As expected, with increase in temperature, resilient modulus reduced and with increase in the percentage of RAP in the mix resilient modulus value increased. Increase in resilient modulus with increase in RAP content in the mixture supports the research findings of past research studies (Tabakovic et al., 2006; Baron and Zhanping, 2011; Xiao et al. 2011).

3.5 Fourier transform infrared spectroscopy

Infrared spectroscopy is a technique generally used to identify the presence and concentration of functional groups in a material. In the present study, the FTIR NEXUS-870 spectrometer available in the central research facility of IIT Kharagpur was used to carry out the analysis. Binder in the form of a solution (mixed with carbon disulphide) was placed on the pellets which were prepared using spectroscopic grade KBr. Specimen was prepared by placing a drop of the solution prepared (10% by weight - 0.5 g binder dissolved in 5 ml carbon disulphide) on the pellet and allowed to dry for 10 minutes using air blower. In the FTIR spectroscopy, the path of the light beam passing is interrupted by the sample placed in the chamber and the light absorbed for different wavelengths of infrared light (400 – 4000 cm^{-1}) is measured. Figure 3 shows FTIR spectra obtained for different binders.

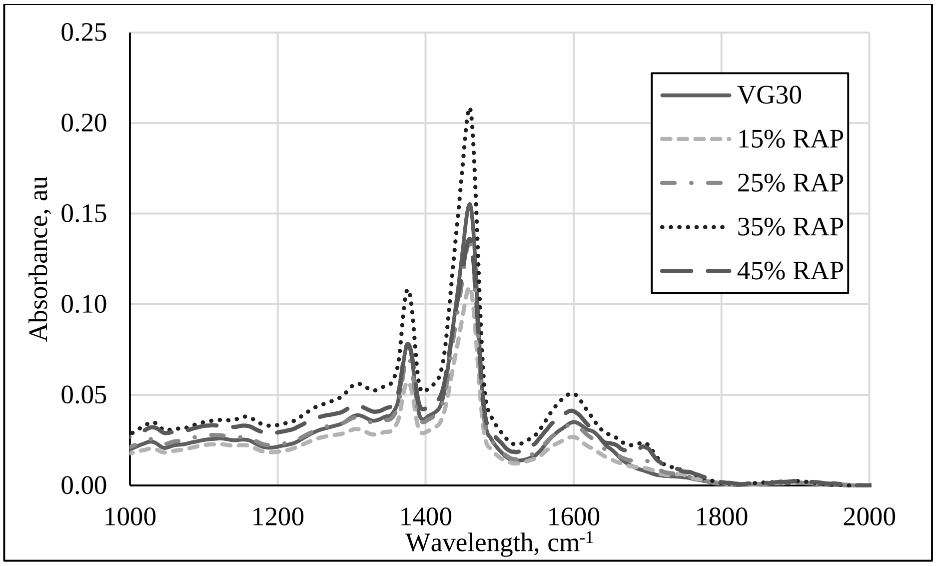

Fig 3: Plot of a FTIR spectra

The changes in the functional groups that indicate the level of aging have been examined using the spectra. The carbon and sulfur atoms present in the binder react with oxygen to form respective oxides during the oxidation process. The quantification of these oxides gives an idea about the aging (oxidation kinetics) the binder underwent. Alcohols are formed along with the ketones and sulfoxides during the binder oxidation process. The aliphatics are the lighter molecular weight molecules present in the binder and next are aromatics, resins and asphaltenes. A higher aliphatics content in the binder indicates softer binder. The quantity of aromatics along with resins present in the binder indicates the viscous nature of the binder. Ketones, sulfoxides, alcohols, aromatics, aliphatics and polar groups (alcohols) were quantified in the form of different indices using equations 2 to 6 (Lamontagne et al, 2001; Liu et al 1998; Singh and Sawant, 2016; Gong et al, 2017). Aging indices calculated for different virgin-RAP binder blends are given in Table 6.

$$\text{ICO} = \frac{Area\ around\ 1700\ cm^{-1}}{Area\ around\ 1460\ cm^{-1} and\ Area\ around\ 1375^{-1}} \quad (2)$$

$$\text{ISO} = \frac{Area\ around\ 1030\ cm^{-1}}{Area\ around\ 1460\ cm^{-1} and\ Area\ around\ 1375^{-1}} \quad (3)$$

$$\text{ICC} = \frac{Area\ around\ 1600\ cm^{-1}}{\sum Area\ around\ 1460\ cm^{-1}, 1375^{-1}, 1700\ cm^{-1}, 1030\ cm^{-1}, 1600\ cm^{-1}} \quad (4)$$

$$\text{ICH} = \frac{Area\ around\ 1460\ cm^{-1} and\ Area\ around\ 1375^{-1}}{\sum Area\ around\ 1460\ cm^{-1}, 1375^{-1}, 1700\ cm^{-1}, 1030\ cm^{-1}, 1600\ cm^{-1}} \quad (5)$$

$$\text{OH/CH} = \frac{Area\ around\ 3450\ cm^{-1}}{\sum Area\ of\ peaks\ present\ in\ 1300\ to\ 3000\ cm^{-1}} \quad (6)$$

Table 6: Aging indices for different virgin – RAP binder blends

Index	VG30- 0% RAP	VG30-15% RAP	VG30- 25% RAP	VG30- 35% RAP	VG30- 45% RAP	100% RAP
ICO	0.038	0.049	0.057	0.062	0.071	0.141
ISO	0.138	0.143	0.148	0.145	0.173	0.200
ICC	0.225	0.226	0.234	0.234	0.246	0.285
ICH	0.666	0.652	0.635	0.634	0.605	0.534
OH/CH	0.699	0.639	0.687	0.764	0.640	1.019

It can be seen that ketones, sulfoxides and aliphatics reduced and aromatics increased with increase in RAP content. The polarity/alcohols present in the binder blends increased till 35% RAP and then reduced. This phenomenon is due to the aggregation of asphaltenes, which agglomerate to reduce the energy of the colloid system.

4. Analysis of results

Complex modulus of a binder relates the applied stress to the strain whereas the phase angle of a binder represents the viscoelastic nature of the binder. Lower the phase angle higher is the elasticity of the binder. Ketones are one of the molecular groups imparting viscosity/stiffness to the binders. Figure 4 shows the relationship between complex modulus and ICO. Figure 5 shows the relationship between the phase angle and ICO.

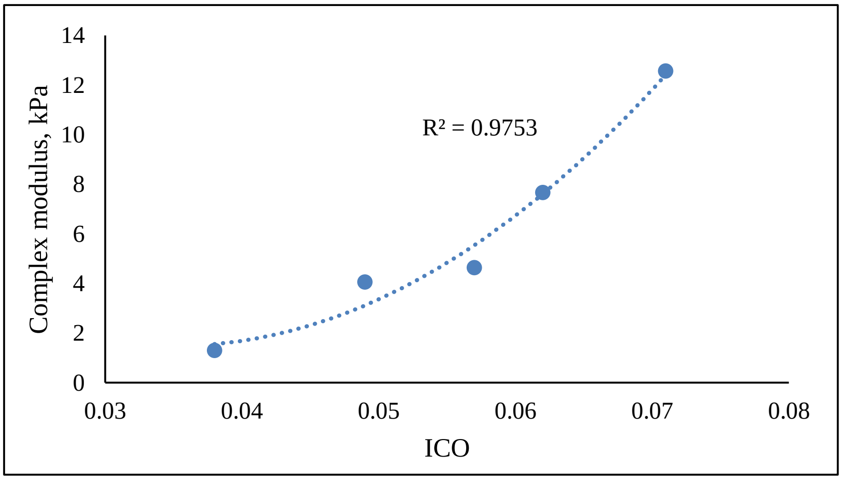

Fig 4: Plot showing ICO vs complex modulus

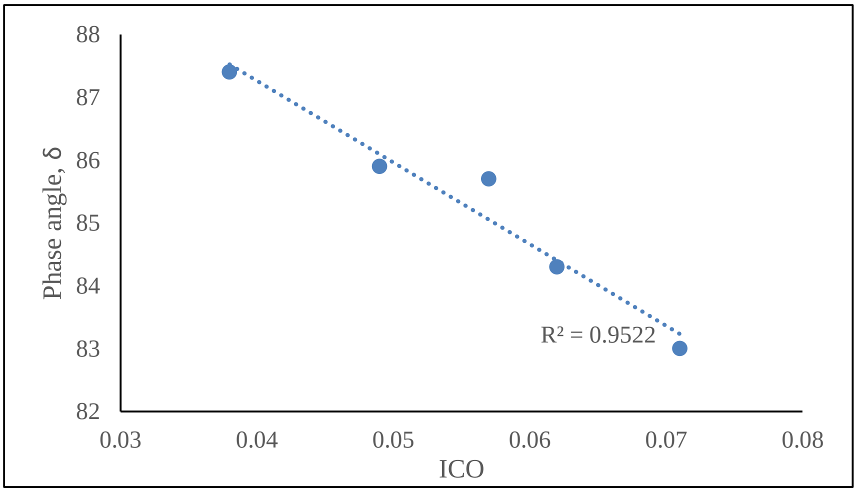

Fig 5: Plot showing ICO vs phase angle

It can be seen that ICO has good correlation with both complex modulus and phase angle. With increase in the ketones present in the binder the stiffness of the binder increased and the phase angle reduced. Similarly, good correlations were found between ICC (aromatics) and ICH (aliphatics) with complex modulus and phase angle. Compared to aromatics, aliphatics had better correlation with G* and phase angle. This can be due to the fact that the combination of aromatics and resin affect the viscous nature of the binders. As there is good relationship between the chemical characteristics of the binders and the rheological behaviour of the binders, an effort was made to examine the relation between the resilient modulus and chemical properties. Figures 6, 7 and 8 show the relationship between resilient modulus at 1 Hz frequency and ICO, ICH and ICC respectively.

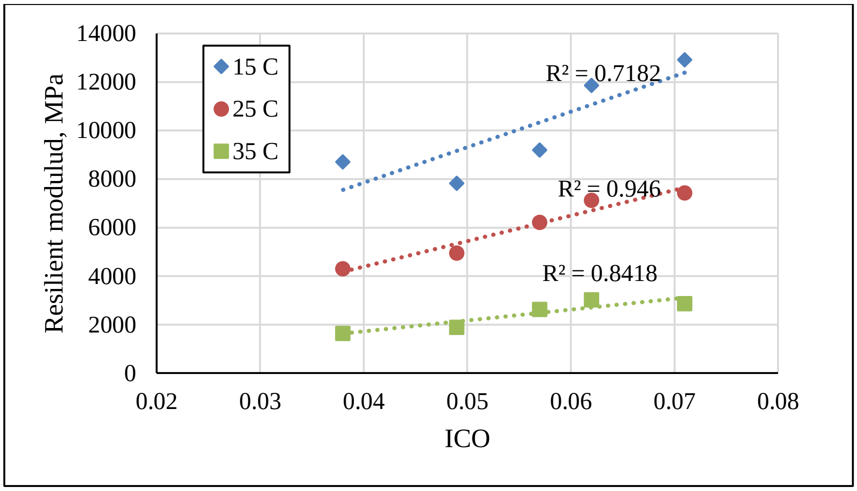

Fig 6: Relationship between ICO and resilient modulus

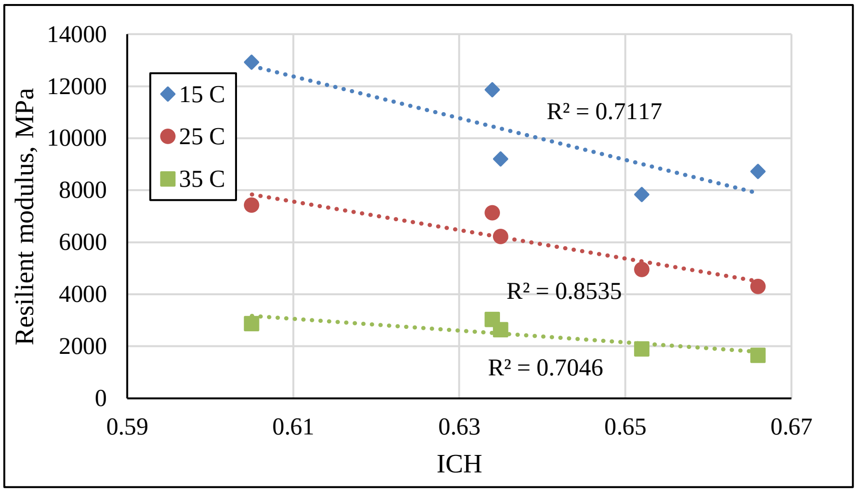

Fig 7: Relationship between ICH and resilient modulus

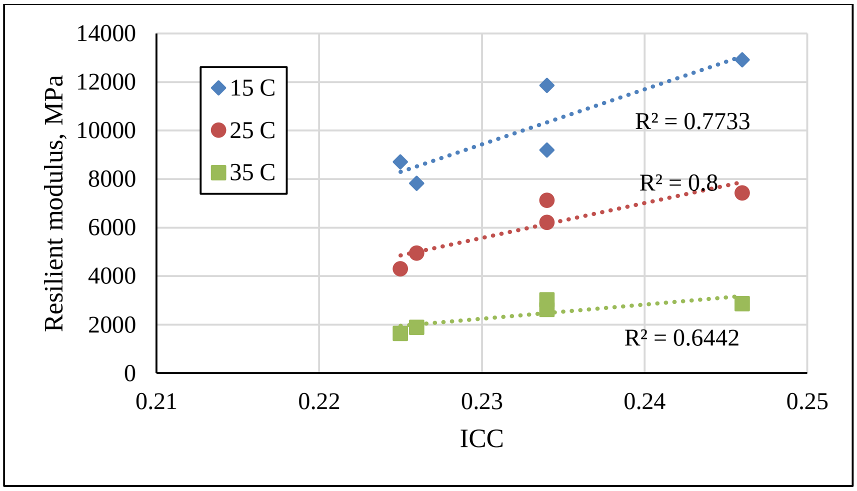

Fig 8: Relationship between ICC and resilient modulus

It can be seen that the chemical makeup of the binders like ketones, aliphatics and aromatics related well with the mixture properties (resilient modulus). Sulfoxides and alcohols (representing polar groups in the binder) did not have good relationship with the resilient modulus values. Sulfoxides did not correlate well due to their instability. Aggregation of asphaltenes happens to reduce the energy of the colloid system by covalent bonding of the polar molecules. This aggregation is probably the reason behind the weak relationship between alcohols and resilient modulus.

5. Conclusions

The present study evaluated the mechanical properties of the asphalt mixtures containing RAP material in terms of resilient modulus and the chemical makeup of the binders has been examined from the data of FTIR spectroscopy. The relationships between the complex modulus, phase angle and the chemical indices were examined. The chemical indices that related well with the G* and phase angle were further used to correlate with resilient modulus of the bituminous mixtures. The following conclusions are drawn from the present study:

- There is an increase in the resilient modulus of the mixtures with increase in RAP content, this is due to the increase of amount of stiffer binder. The increase in the stiffness is due to the increase in the viscosity imparting functional groups like sulfoxides and ketones
- The relationship between the chemical indices and the G* and phase angle was examined and it was observed that the ketones, aliphatics and aromatics correlated well with the rheological properties (G*, δ) of the binders.
- Ketones, aliphatics and aromatics have also been shown to have good correlation with the resilient modulus of the mixes.

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