

## Effect of Activated Crumb Rubber on the Properties of Crumb Rubber-Modified Bitumen

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**ABSTRACT:** Bitumen modification was made with the activated crumb rubber concentrate and its efficacy was examined in terms of its consistency and rheological properties. It was found that softening point of the activated crumb rubber-modified bitumen increased while its penetration and elastic recovery decreased compared with the nonactivated crumb rubber system. Based on contact angle results, the activated crumb rubber-bitumen system was found to be more wettable and exhibited better adhesion to the substrate than those of other systems. The shifting of glass transition temperature towards higher temperature and the occurrence of inter-mix phases in the activated crumb rubber-bitumen system supported its superior temperature resistance. The difference in viscosity obtained between the activated and nonactivated crumb rubber systems is attributed to the high swelling of activated crumb rubber and its soluble fractions in the bitumen as viewed in scanning electron images. High complex modulus and low phase angle of the activated crumb rubber system over the entire range of temperatures indicated its reduced temperature susceptibility and more elasticity. The activated crumb rubber-bitumen system meets the requirements of commercial standard specification. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

**KEYWORDS:** differential scanning calorimetry (DSC); glass transition; rheology; morphology; swelling

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### INTRODUCTION

Disposal of used and discarded tyres has posed a significant environmental threat world wide every year due to the fire hazards and also habitat for insects/rodents.<sup>1,2</sup> Over recent years, the recycling industry has invested in modern technologies to produce crumb from tyre rubber while removing steel, fibers, and other contaminants.<sup>3–7</sup> One of the means for utilizing crumb rubber is in the bitumen as rheology modifier for making rubberized bitumen<sup>8</sup> because it contains a variety of rubber polymers, predominantly natural rubber and styrene-butadiene rubber. Several attempts<sup>9–19</sup> have been made on the use of crumb rubber in the modification of bitumen for pavement and roofing purposes by one of the two processes namely a wet process or a dry process. In wet processes, beneficial changes in the properties of bitumen can be achieved by the appropriate blending of additives whereas in the dry process, chemical changes in the bitumen such as bond cleavage or stabilization of additives are extremely difficult. Adding crumb rubber into bitumen reduces temperature susceptibility and improves resistance to rutting, low temperature cracking, load associated

fatigue and aging. The extent of improvement in the behavioral performance of the bitumen depends on types and percentage of rubber in crumb and its ratios with bitumen, crumb particle size, carbon black content and processing conditions.<sup>11,20</sup> Since it is cross-linked rubber, the vulcanizate network undergoes limited chemical changes during bitumen blend processing and exhibits crumb rubber sedimentation at the bottom during storage stability test.<sup>21</sup> Because of its thermosetting in nature, the incompatibility problem arises by the existence of low interfacial force between the crumb rubber and bitumen.<sup>22</sup> This in turn, dramatically affects rheological properties of the base bitumen. Unless it is debonded (partially devulcanized), the crumb rubber acts as a flexible filler only. This necessitates rejuvenation of rubber particles by the cleavage of C-S and S-S bonds in their molecular structure to make an effective modifier for bituminous systems.

Earlier studies<sup>13,22–24</sup> have shown that the chemical modification of crumb rubber by the matrix preblending process (matrix asphalt as swelling agents),<sup>13</sup> microwave treatment,<sup>22</sup> high speed agitated desulfuration,<sup>23</sup> and plasticization<sup>24</sup> improves its

compatibility with the bitumen. Various additives such as SBS-linker, wax, polyphosphoric acid,<sup>25</sup> polymeric compatibilizer containing conjugated diene,<sup>26</sup> etc. were also employed in the crumb rubber–bitumen system to prevent sedimentation of particles during hot stage. Two main interaction mechanisms are reported as the binder matrix particles and the liquid phase.<sup>27</sup> Liquid phase modifications are more stable than the matrix modifications. The increased surface area per volume or weight of the fine particles enhances the ability of particles to be swollen by, and thus bond with the binder.<sup>28</sup> Rubber regeneration through swelling/pumping instead of traditional grinding process results in better properties related to storage stability and low viscosity.<sup>29</sup> However, the problem of storage stability is yet to be resolved. Although, in prior art, several attempts have been made on modification of bitumen with the ground crumb rubber, there is scanty information available on use of activated crumb rubber concentrate in making compatibilized bituminous systems.

In this study, the partial devulcanized crumb rubber along with additives (gilsonite and elemental sulfur) was used as an alternative modifier to virgin polymers for making bituminous sealing and waterproofing compounds. The main aim of using an activated crumb rubber in the form of a concentrate is to disperse it uniformly in the bitumen for obtaining homogeneous system and does not separate from bitumen over a long period of time. The resultant blend would provide advantageous properties such as improved elasticity, increased softening point, delayed oxidation of bitumen, enhanced strength and good flow compared with the nonactivated (ordinary) crumb rubber-modified bitumen (CRMB). The improvement in these properties would be expected due to deactivation of radicals onto bitumen formed during partial devulcanization of the crumb rubber. During milling, the swollen crumb rubber would be broken into smaller particles which can be easily mixed with the bitumen during processing of blends. In this paper, we report performance of the modified bitumen made with the crumb rubber concentrate. Efficacy of concentrate in the bitumen was studied in terms of its wettability, phase miscibility and microstructure. The properties of the activated CRMB were discussed vis-à-vis nonactivated crumb rubber system in relation to its conventional as well as rheological parameters and also compared with the requirements of commercial specification.

## EXPERIMENTAL

### Materials

The penetration grade bitumen (softening point, 45°C; penetration, 94 dmm; elastic recovery, <7%) was collected from an Indian refinery. The ground crumb rubber produced by an ambient process was received from a local recycling plant (density, 1.14 g/cm<sup>3</sup>; moisture content, 0.62%; rubber hydrocarbon content, 53%; acetone extract, 10.5%; carbon black content, 29%; ash content, 7.5%).<sup>30</sup> Its mean particle size was 0.37 mm as obtained by the sieve analysis. The cross-link density of ground crumb rubber was 6.5 mol/cm<sup>3</sup>. The coarser grade gilsonite, a high molecular weight oligomeric and polar polynuclear hydrocarbon was used as a modifier procured locally (mineral content, 5%; softening point, 160°C; penetration, < 2 dmm;

solubility in CS<sub>2</sub>, ~ 85 wt %). Since gilsonite is a natural asphalt, it readily disperses into bitumen to form a stable binder.

### Preparation of Samples

The crumb rubber was partially devulcanized in the presence of petroleum tar through thermo-mechanical treatment in an open two roll mixing mill for 2–3 h in the temperature range of 210–230°C. The resulting mass was swollen by the absorption of oil fraction of petroleum tar. The percent devulcanization of the crumb rubber was in the range of 18–20%. It is essential to note that the treated crumb should retain its “free powder flow” characteristic. The treated rubber so obtained was mixed thoroughly with the elemental sulfur in a mixer at slow speed and then compounded with gilsonite for 10 min at an ambient temperature to produce dry crumb rubber concentrate.

The bitumen was preheated at 180°C in a double jacketed vessel with a high shear mixer (peddle type). The crumb rubber concentrate was added gradually into it and mixed well with the help of stirrer at a low speed for 30 min followed by a high speed mixing (1200 rpm) for 1.5 h. The concentration of crumb rubber in the bitumen was optimized at ~11 wt % in view of its workability and also meets requirements of the specification.<sup>31</sup> The base bitumen was also processed in a similar fashion as applied in the case of modified bitumen for comparison purpose. The blends were stored in the containers for testing work.

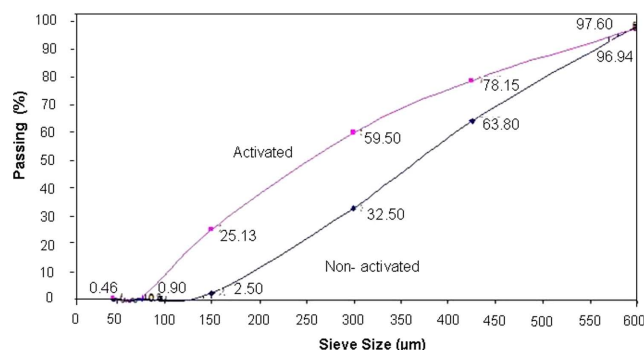
### Test Methods

**Conventional Tests.** The softening point of the samples was measured by a ring and ball method as per ASTM D 36-09. In this test, two disks of sample were cast into a shouldered ring and then, they were heated at a constant rate of 5°C/min in a glycerin bath. The temperature at which bitumen disks soften and sag downward under the weight of a standard steel ball was noted as a softening point.

The penetration test was performed according to ASTM D 5-06 under the condition of applying a 100 g weight on the penetration probe for 5 s at 25°C and reported in tenths of millimeters.

The elastic recovery of the bitumen blends was determined according to IS: 1208-1978.<sup>32</sup> In this test, the specimen was elongated upto 100 mm at a speed of 50 mm/min at 15°C and cut it into two halves at the mid point. After 60 min, length of the recombined specimen was recorded by placing an elongated cut half of the piece back into position just touching the fixed half of test specimen.

**Modulated Differential Scanning Calorimetry (MDSC).** MDSC (Model Q 200, TA Instruments Inc.) of the samples (0.26–0.37 mm) equilibrated at –80°C was carried out between –80°C and 150°C at a heating rate of 2°C/min under a nitrogen atmosphere. A slow heating rate was selected to allow for a good deconvolution. Modulation with ± 0.8°C amplitude for 60 s was employed. The resultant reversing (heat capacity component) and nonreversing (kinetic component) signals of the samples were recorded.



**Figure 1.** Particle size distribution of activated and nonactivated crumb rubber particles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### FTIR Microscopy

FTIR microscope (Perkin Elmer, AutoIMAGE/GX Spectrum) with ATR crystal was employed to collect spectra of the bituminous samples. To avoid the unevenness, the thin film of sample was used instead of KBr pellet. The samples were placed on a movable X-Y stage of the microscope. The size of tantalum aperture was kept at  $100 \times 100 \mu\text{m}$ . The locational mapping on the surface of samples was carried out with the help of an AutoIMAGE and their FTIR spectra were recorded under a micro-ATR mode at  $4 \text{ cm}^{-1}$  resolution with the accumulation of 64 scans.

### Scanning Electron Microscopy (SEM)

The morphology of the activated and nonactivated crumb rubber particles and their bituminous blends was examined on a Scanning electron microscope (Leo 435 VP). Before examination, the samples were coated with Au/Pd thin film to render them conductive.

### Contact Angle Measurement

The contact angle of the processed base bitumen and CRMBs was measured using a sessile drop technique with the help of Dynamic contact angle analyzer (VCA Optima, AST Products). Distilled water and formamide were used as probe liquids in the experiment. The specimen of size  $10 \text{ mm} \times 10 \text{ mm}$  was mounted on a microscope stage and adjusted to the horizontal position. An aliquot of probe liquid ( $0.5 \mu\text{L}$ ) was dropped onto surface of the sample with the help of a micro-syringe. A photograph was taken 10 s after the probe liquid had been dropped. AutoFAST analysis imaging system was used to capture a droplet image and automatically calculates contact angle with no user intervention. Five measurements were made for each sample. The surface energy of samples was calculated from the contact angle data using surface energy software (SE-2500).

### Rheological Test

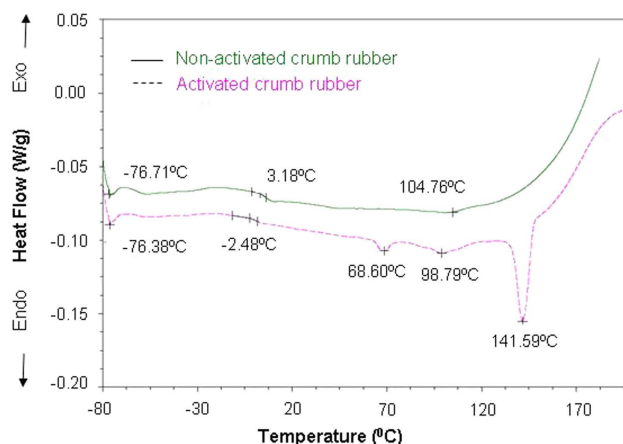
The rheological test of bitumen blends was carried out on a stress-controlled rheometer (Bohlin, Gemini 200) using 25 mm parallel plate geometry with 1 mm gap under viscometry and oscillation modes. The viscosity of samples was measured in the temperature ranged between  $60^\circ\text{C}$  and  $135^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$  under 0.24 Pa shear stress. In the oscillation mode, a temperature sweep was performed within the linear visco-elastic region from

$5^\circ\text{C}$  to  $85^\circ\text{C}$  with an increment of  $6^\circ\text{C}$  at an angular speed of 10 rad/s using plate and plate geometry to record complex modulus and phase angle. A Black diagram between complex modulus and phase angle was also drawn for all the samples to view a modification effect. The dynamic shear test was conducted on the samples between  $5^\circ\text{C}$  and  $85^\circ\text{C}$  at 10 rad/s using 25 mm parallel plate geometry as per TP5 (AASHTO Designation: Standard specification for performance graded asphalt binder).

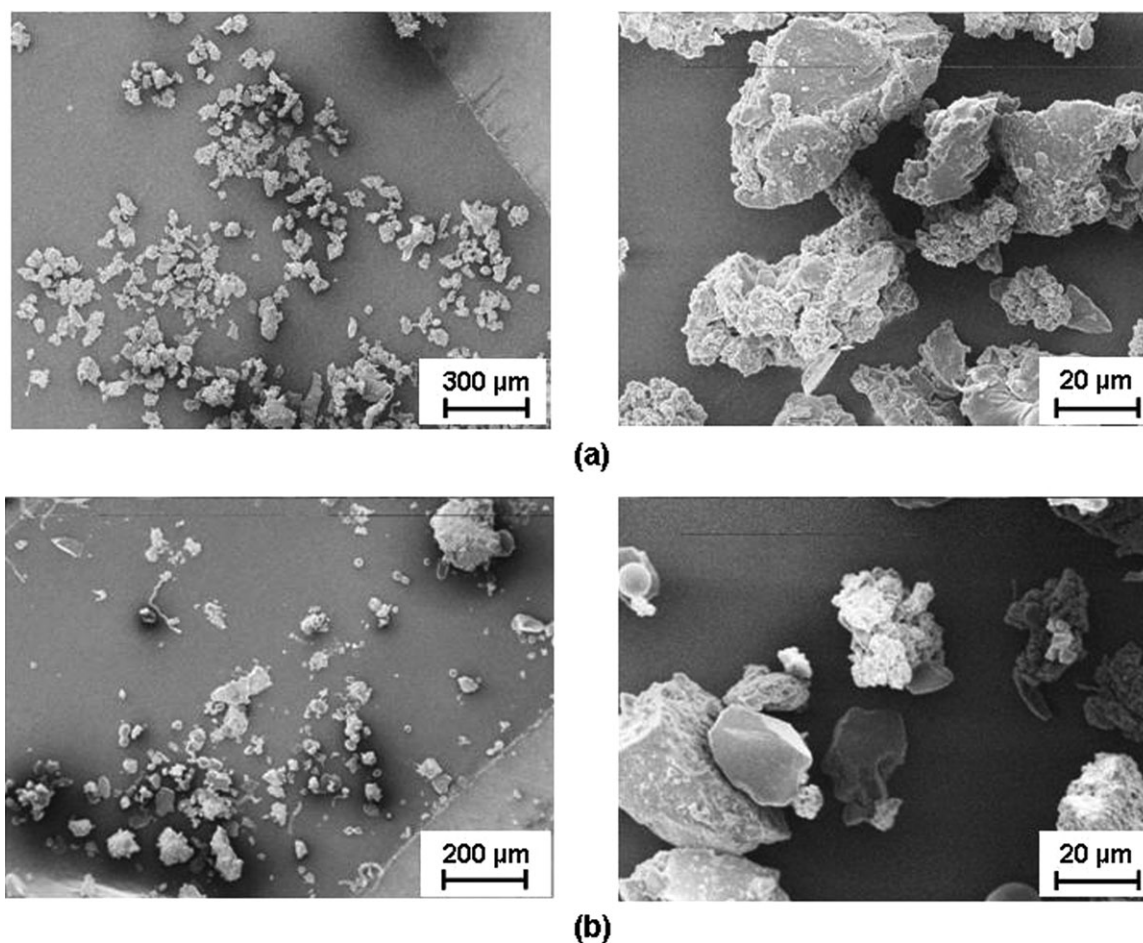
## RESULTS AND DISCUSSION

### Effect of Activation

The particle size distribution of activated and nonactivated crumb rubber is given in Figure 1. As a result of treatment, the crumb rubber particles were finer and seem to be uniformly distributed. The activated crumb particles retained 75% on a  $150 \mu\text{m}$  sieve whereas the nonactivated retained 98%. Its average particle size was  $260 \mu\text{m}$  compared with  $370 \mu\text{m}$  for the nonactivated crumb rubber. Fineness modulus of the activated crumb rubber was also slightly higher. DSC traces of the activated and nonactivated crumb rubber are given in Figure 2. After activation, the crumb rubber exhibited transition at  $-2.48^\circ\text{C}$  compared with  $3.18^\circ\text{C}$  of the parent sample. The presence of melt endotherms at  $68.60^\circ\text{C}$ ,  $98.79^\circ\text{C}$ , and intense  $141.59^\circ\text{C}$  clearly indicated that the crumb rubber had changed from its thermosetting type (cross-linked) to thermoelastic state due to devulcanization. Because of such changes, it is believed that the activated crumb rubber could provide an elastomeric character to the bitumen. As shown in SEM micrographs (Figure 3), the nonactivated crumb rubber has irregular particle shape with fragmented porous surface morphology. The particles were large and seem to be agglomerated. Several holes scattered onto their surfaces [Figure 3(a)]. Contrary to this, the surface of activated crumb particles was quite smooth and the particles were less segregated [Figure 3(b)]. The efficacy of activation can also be viewed in the microstructure of the crumb rubber-modified bitumen (Figure 4). The activated crumb rubber particles were swollen and well dispersed [Figure 4(b)]. The good dispersion of particles may be attributed to the breaking



**Figure 2.** DSC traces of activated and nonactivated crumb rubber. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



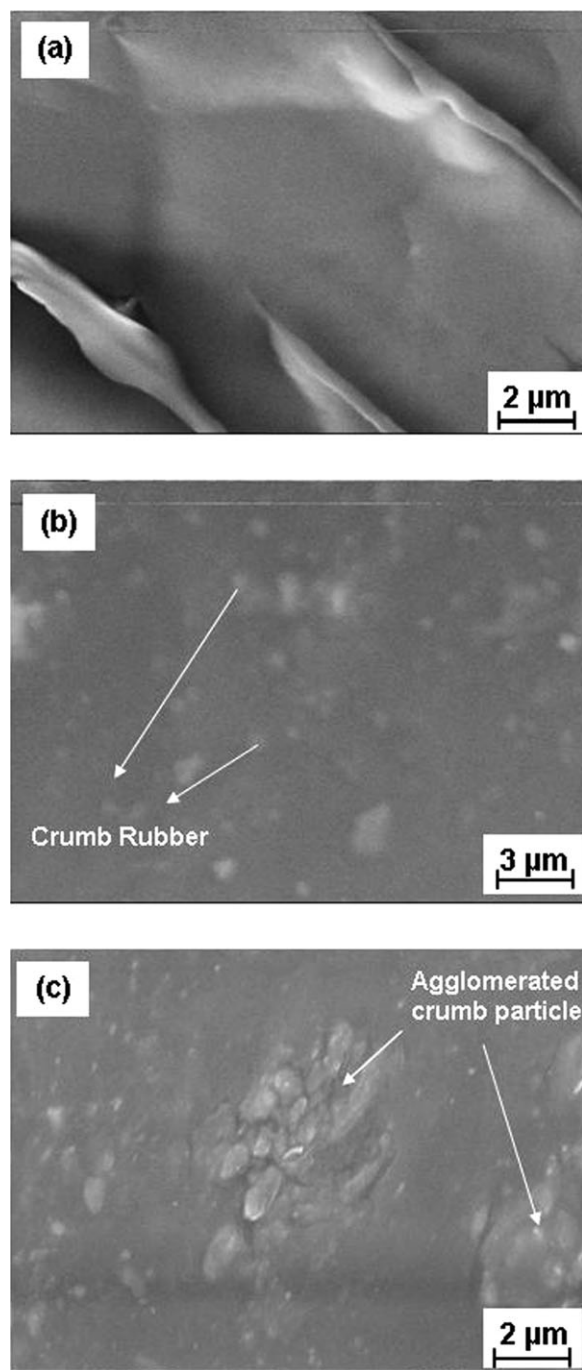
**Figure 3.** SEM micrographs of crumb rubber particles (a) nonactivated (b) activated.

of particle-particle bonds during activation process and the wetting characteristics. Once the particles are wetted, the bond failed to reform leading to a reduced agglomeration.<sup>33</sup> In the case of nonactivated crumb rubber, the agglomeration of particles in the bitumen was clearly visible which affects performance of the binder [Figure 4(c)]. The difference in surface morphology also occurred probably due to the partial dissolution of rubber particles in the bitumen by absorption of its maltene fraction.

Table I presents surface energetic characteristics of the processed base bitumen and activated/nonactivated crumb rubber-bitumen systems. The activated CRMB had lowest contact angle values under both water and formamide probe liquids compared with the other systems showing its superior wettability with the substrate. It was also noted that the nonactivated crumb system showed higher contact angles than the processed base bitumen indicating its poor wetting behavior. The work of adhesion of activated CRMB was also higher. These results demonstrate the variability in the physico-chemical nature of all bituminous surfaces. The low contact angle of formamide probe liquid onto bituminous substrate is attributed to its surface solubility that leads to an incorporation of wetting liquid onto surface. The critical surface energy of samples was calculated using Zisman plot between the cosine of contact angle and surface tension of probe liquids. It was found that the critical surface

energy of all samples was negative showing lack of physical roughness. During preparation of the samples from molten to solid state, the forces responsible for surface energy will work to ensure a minimum surface area and eliminate surface roughness.<sup>34</sup> The processed base bitumen surface had low polar component and high dispersive component (nonpolar) of surface-free energy. Because of this, bonding between the bitumen and substrate may not be adequate. When activated crumb rubber was added to the base bitumen, the surface energetic of the resulting system has been changed due to alteration of its chemical composition. As a result, the activated CRMB had higher polar and dispersive components of surface-free energy than the processed base bitumen. The higher polar component of the activated CRMB may be attributed to the diffusion of dissolved portion of crumb rubber to the boundary layer and accumulation of polar groups onto surfaces resulting in good adhesion with the substrates.<sup>34,35</sup> It was also noted that the nonactivated CRMB exhibited lower surface-free energy than the processed base bitumen exhibiting its superior compatibility with substrates.

MDSC traces of the processed base bitumen and activated/nonactivated CRMBs are shown in Figure 5. A broad step change in the base line of reversible curve could be considered to the overlapping of two glass transition temperatures of the amorphous phases of the bitumen.<sup>36</sup> However, when examine the



**Figure 4.** SEM micrographs of crumb rubber-modified bitumens (a) processed base bitumen (b) activated crumb rubber (c) nonactivated crumb rubber.

nonreversible signal, an exothermic peak was observed in the same area. Amorphous wax material is known to crystallize during the glass transition of the bitumen and this is causing the glass transition temperature to appear as possibly two overlapping glass transitions. In the case of nonactivated crumb system, the shifting of glass transition temperature towards lower temperature was noticed with respect to the base bitumen supportive of interaction of soluble fractions of crumb rubber with the bitumen. Contrary to this, the activated CRMB exhibited

transitions towards higher temperature along with an additional endotherm at 105.5°C compared with the base bitumen showing the existence of bituminous matrix of high molecular weight. When base bitumen was modified with the activated crumb rubber, the heat of fusion in the nonreversible curve of the resulting system was reduced to 1.69 J/g from 2.65 J/g of the base bitumen because of self-ordering of saturates/aromatics. The peak height of the exotherm was also reduced. The presence of several transitions indicates that the activated crumb system contains inter-mix phases with flexible chains.

FTIR microscopic images of both processed base and crumb rubber-modified bituminous surfaces under reflectance mode are shown in Figure 6. In the case of nonactivated crumb rubber system, the peak intensities of free  $\text{—OH}$  group ( $3836\text{ cm}^{-1}$  and  $3747\text{ cm}^{-1}$ ),  $\text{—C—H}$  stretching ( $2868\text{ cm}^{-1}$ ) and  $\text{—CO}$  group ( $1698\text{ cm}^{-1}$ ) increased with respect to the base bitumen. The increased  $\text{—C—H}$  peak intensity at  $2868\text{ cm}^{-1}$  may be attributed to the high hydrocarbon content following the solubility of crumb rubber in the bitumen. The new peak at  $1535\text{ cm}^{-1}$  along with a shoulder at  $1471\text{ cm}^{-1}$  and  $1384\text{ cm}^{-1}$  appeared with respect to bitumen peak at  $1488\text{ cm}^{-1}$  ( $\text{—C—H}$  bending). When activated crumb rubber was added to the bitumen,  $\text{—OH}$  peak intensity of samples reduced indicating their moisture-free surface. The peaks in  $2000\text{—}1500\text{ cm}^{-1}$  region disappeared due to dominance of rubbery phase in the bitumen which may prevent generation of the oxidized species such as ketones and carboxylic acids on the surface during aging/processing. It is noted that peak at  $1132\text{ cm}^{-1}$  ( $\text{—C=S}$  stretching) of bitumen disappeared on the surface due to reaction of  $\text{—C=S}$  bond of asphaltenes with allylic group of rubber. The intensity of peak at  $893\text{ cm}^{-1}$  (nonaromatic  $\text{—C=C}$  bond) was relatively reduced with respect to base bitumen due to cross-linked structure. The difference in the spectra of these bituminous samples clearly indicated the existence of chemical interactions between the activated crumb rubber and bitumen. Such interactions may support superior properties of activated crumb rubber-bitumen system over nonactivated ones.

#### Rheological Properties

Rheological properties of the processed base and activated/nonactivated CRMBs are given in Table II. As shown in Figure 7, the viscosity results indicate a pronounced difference between the activated and nonactivated crumb rubber-bitumen systems over the entire range of temperatures. Higher swelling, more soluble fraction of rubber components and finer particles of the activated crumb rubber in the bitumen caused a significant increase in the viscosity. At the start of melting between 60 and 62 °C, the viscosity of nonactivated CRMB was higher than the activated CRMB probably due to its more stiffness. As the shearing starts, the viscosity of nonactivated CRMB decreased attributable to the existence of poor chemical interaction between the bitumen and crumb rubber. Contrary to this, the curve of activated crumb rubber system initially showed a straight line between 60°C and 68°C and then exhibited lesser slope than the nonactivated ones because it swells easily due to disrupted cross-linked bonds resulting higher modification effects. This also implied that there was chemical coupling between the crumb rubber and bitumen. Above 90°C, the

**Table I.** Surface Energetic Characteristics of Processed Base and Activated/Nonactivated Crumb Rubber Modified Bitumens

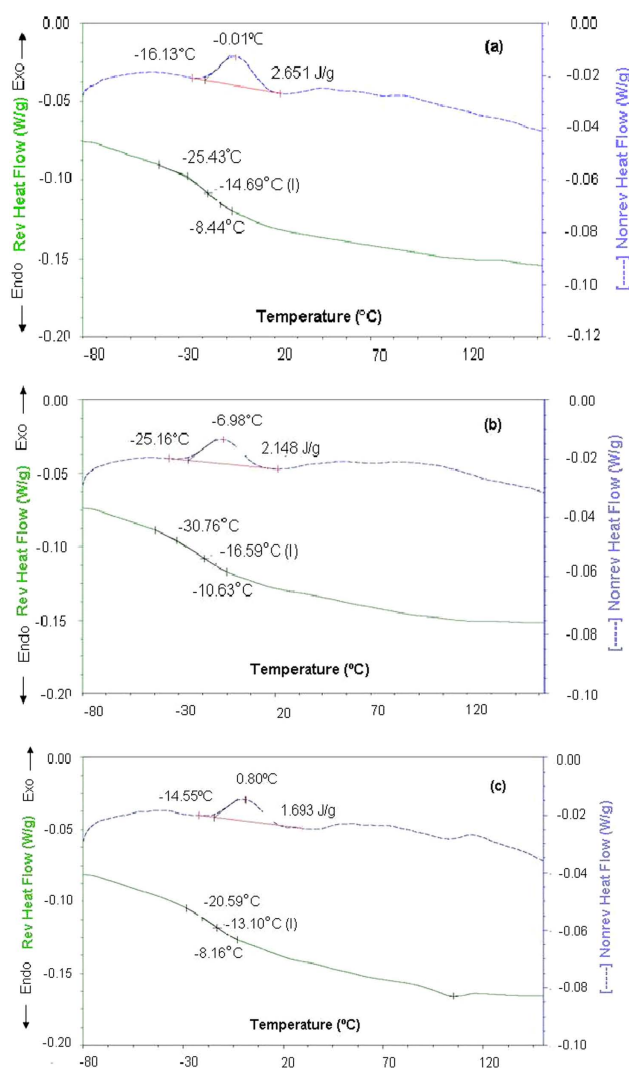
Treatment	Contact angle (°) Probe liquid		Work of adhesion (mJ m <sup>-2</sup> )	Surface-free energy (mJ m <sup>-2</sup> )	Polar component (mJ m <sup>-2</sup> )	Dispersive component (mJ m <sup>-2</sup> )	Critical surface energy (mJ m <sup>-2</sup> )
	Water	Formamide					
Processed base bitumen	104.61 (1.45)	95.42 (3.19)	54.48 (1.83)	12.00 (1.49)	3.72 (0.49)	8.28 (1.89)	-47.44 (2.37)
Nonactivated crumb rubber modified bitumen	108.10 (1.36)	99.14 (1.07)	50.19 (1.65)	10.32 (0.41)	3.06 (0.38)	7.26 (0.26)	-53.48 (2.67)
Activated crumb rubber modified bitumen	93.54 (1.09)	84.92 (3.18)	68.31 (1.55)	17.54 (1.53)	7.24 (0.83)	10.30 (2.29)	-35.62 (1.78)

Standard deviation is given in parenthesis. Surface tension of water : 72.8 mN m<sup>-1</sup>; surface tension of formamide : 58.4 mN m<sup>-1</sup>.

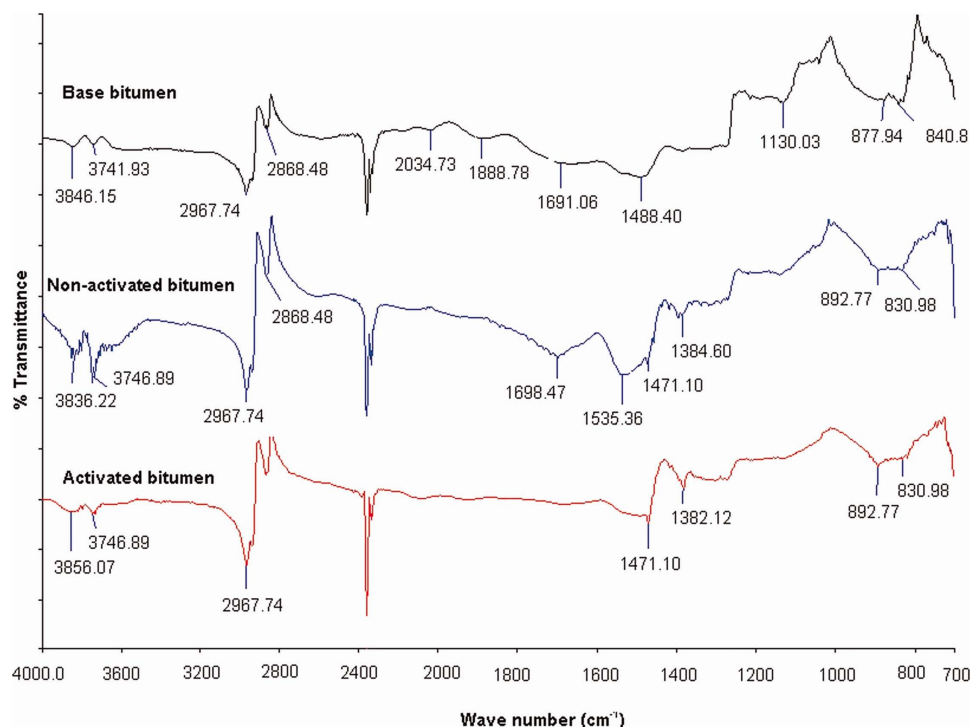
viscosity thinning was significant and its slope was slightly more than the nonactivated system. These two steps thinning of the activated crumb rubber-bitumen system may be considered pri-

marily to the breakdown of physically cross-linked networks and subsequent disturbance in the colloidal structure of bitumen resulting into gel-sol transition.<sup>37</sup> It was also noted that a sudden increase in the viscosity (hardening) of bituminous system occurred after thinning at higher temperature (above 120°C) due to the reversible deformation of elongated rubber drops into original spherical droplets which easily orients towards the flow direction.<sup>38</sup> The viscosity change was also associated with the increase of rubber mass through bitumen absorption. This hardening is more indicative of a filler type modification rather than that of an elastomeric type.<sup>39</sup> The viscosity of activated crumb rubber bitumen at 135°C was 5 Pa. s at 11 wt % loading which can be easily used for sealing and waterproofing purposes.

Figure 8 shows plot of complex modulus versus temperature for the processed base bitumen and CRMBs. As would be expected, the complex modulus decreased as the temperature increased for all the samples. It was observed that the values of complex modulus were nearly the same at low temperatures whereas a pronounced difference occurred between the activated and nonactivated CRMBs at high temperatures. As observed in contact angle data, the existence of polarity onto crumb rubber surfaces created during activation results in improved rubber-bitumen interactions. This can also be evidenced in the FTIR microscopic images of the crumb rubber-modified bituminous surfaces. The polymer and sulfide radicals formed as a result of thermal scission of the crumb rubber are expected to deactivate onto bitumen to form elastomeric bitumen (Scheme 1). These radicals are not combined with each other due to scavenging action of sulfide radicals.<sup>3</sup> The labile hydrogen of allylic group of rubber would also interact with -C=S/-SH group of asphaltenes resulting in a network. The isolated crumb rubber from the crumb rubber-bitumen system was thoroughly washed with carbon tetrachloride followed by their crystallization in hot toluene aimed at to remove the complete physisorbed bituminous fraction. It is noted that the existence of bitumen is still occurred onto crumb rubber as viewed in the SEM supportive of their interaction with bitumen. Compared with nonactivated CRMB, the large glassy and plateau regions in the activated CRMB showed the existence of better elastic network and entanglement as similar to the polymer-modified bitumen.<sup>40</sup> Because



**Figure 5.** Modulated DSC traces (a) processed base bitumen (b) nonactivated CRMB (c) activated CRMB. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6.** FTIR microscopic spectra of base and crumb rubber-modified bitumens. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

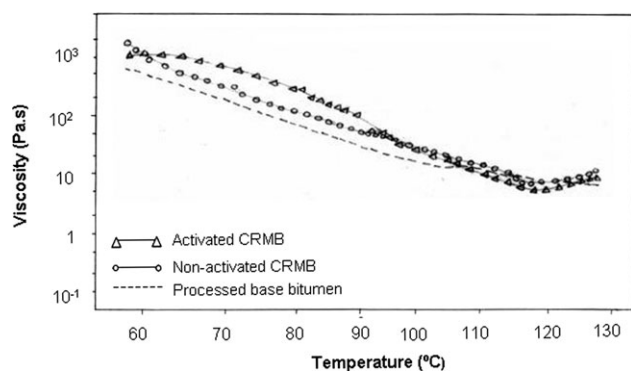
of this, the activated crumb rubber exhibited superior complex modulus at higher temperature favoring its reduced temperature susceptibility. On further examination, it was observed that the complex modulus was dominated by loss modulus (viscous component) after cross over point between both storage and loss moduli (Figure 9). Activation effect can be easily seen at the cross over point and also above 80 °C in terms of a rubbery plateau in the terminal zone. As a result, the activated crumb rubber-bitumen system retained higher storage and loss moduli compared to nonactivated crumb rubber

system. The modified bitumen with nonactivated crumb rubber exhibited a sudden drop of their moduli above 85 °C probably due to the lack of molecular associations between the crumb rubber and bitumen and consequently, the loss of elasticity occurred. The temperature dependence of phase angle is shown in Figure 10. As the temperature increased upto 85°C, the phase angle of samples approached between 80° and 90°. It can be seen that the activated CRMB showed low phase angle than the nonactivated crumb rubber and base bitumen systems. Consequently, more elasticity occurred at both low

**Table II.** Rheological Properties of Processed Base and Activated/Nonactivated Crumb Rubber Modified Bitumens

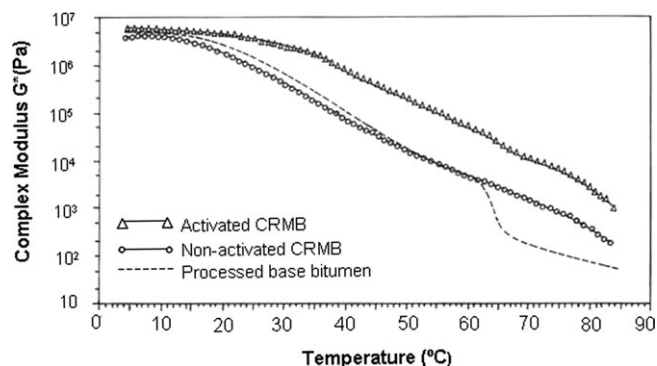
Property	Processed base bitumen	Nonactivated crumb	Activated crumb
Softening point (T <sub>SHRP</sub> ) (°C) (G*/Sin δ, min 1KPa)	59.01 (2.95)	70.90 (3.55)	75.02 (3.75)
G*/Sin δ (KPa)			
46°C	29.90 (1.49)	26.80 (1.34)	216.02 (10.80)
58 °C	4.98 (0.25)	5.50 (0.28)	33.90 (1.69)
Complex modulus, G* (Pa)			
5°C	0.894 (0.045) × 10 <sup>6</sup>	4.07 (0.21) × 10 <sup>6</sup>	5.23 (0.26) × 10 <sup>6</sup>
25°C	0.11(0.005) × 10 <sup>6</sup>	0.955 (0.048) × 10 <sup>6</sup>	3.31 (0.17) × 10 <sup>6</sup>
70°C	169 (8.45)	1480 (74)	11600 (580)
Phase angle, δ (°)			
5°C	11.20 (0.56)	15.20 (0.76)	6.80 (0.34)
25°C	53.01 (2.65)	55.10 (2.76)	24.80 (1.24)
70°C	85.10 (4.26)	82.90 (4.15)	75.20 (3.76)

Standard deviation is given in parenthesis.



**Figure 7.** Viscosity versus temperature curves for processed base and activated/nonactivated crumb rubber-modified bitumens.

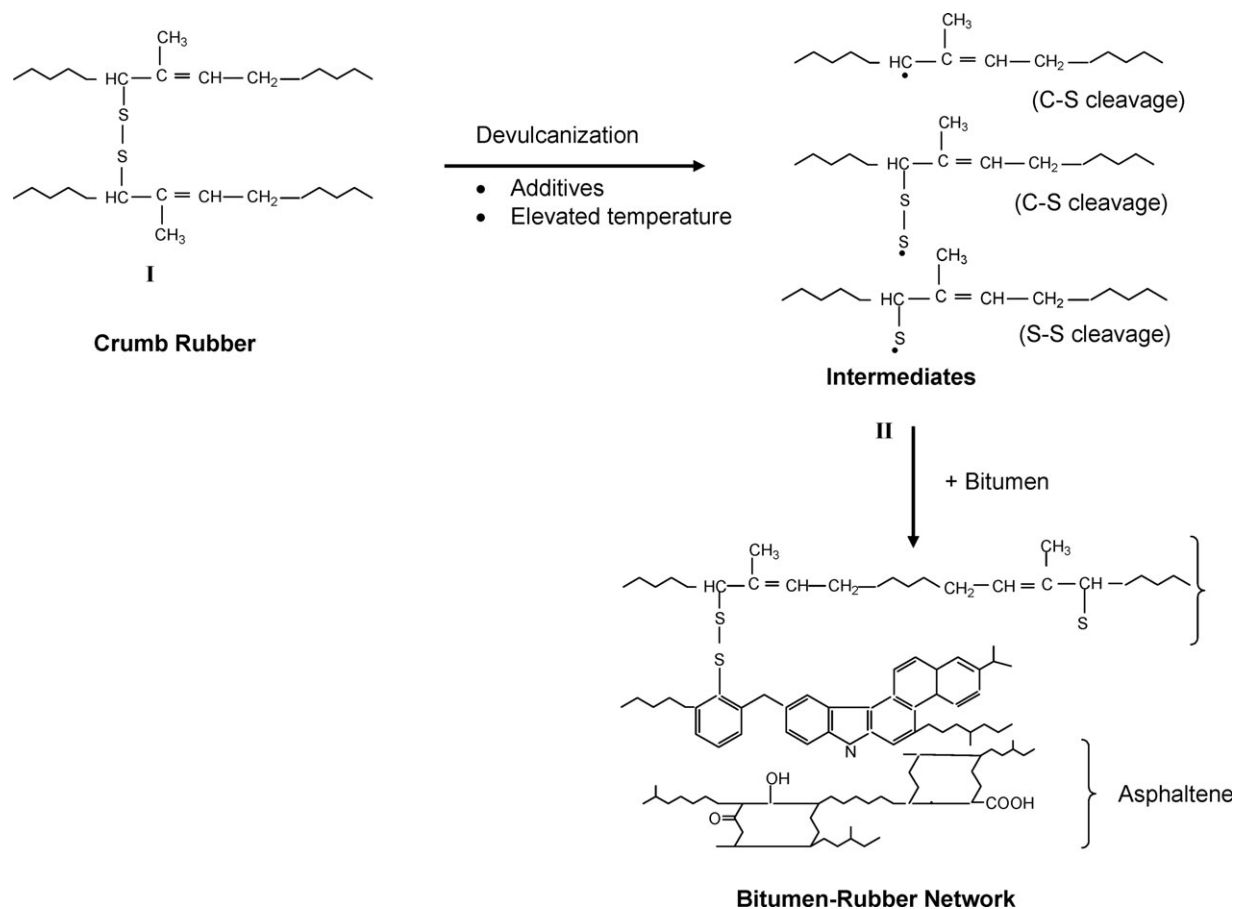
and high temperatures. This improvement is believed to be the dominant character of elastomeric nature of bituminous matrix and also its good compatibility with the residual rubber particles. The effect of activating crumb rubber can also be evidenced in a Black diagram : complex modulus versus phase angle curve (Figure 11). The nature of curve for all samples was almost similar and a shift in the curve occurred as expected towards lower phase angles (more elastic response) at complex modulus of  $< 10^6$  Pa. At phase angle above  $35^\circ$ , the difference was clearly visible between the activated and



**Figure 8.** Complex modulus of processed base and activated/nonactivated crumb rubber-modified bitumens as a function of temperature.

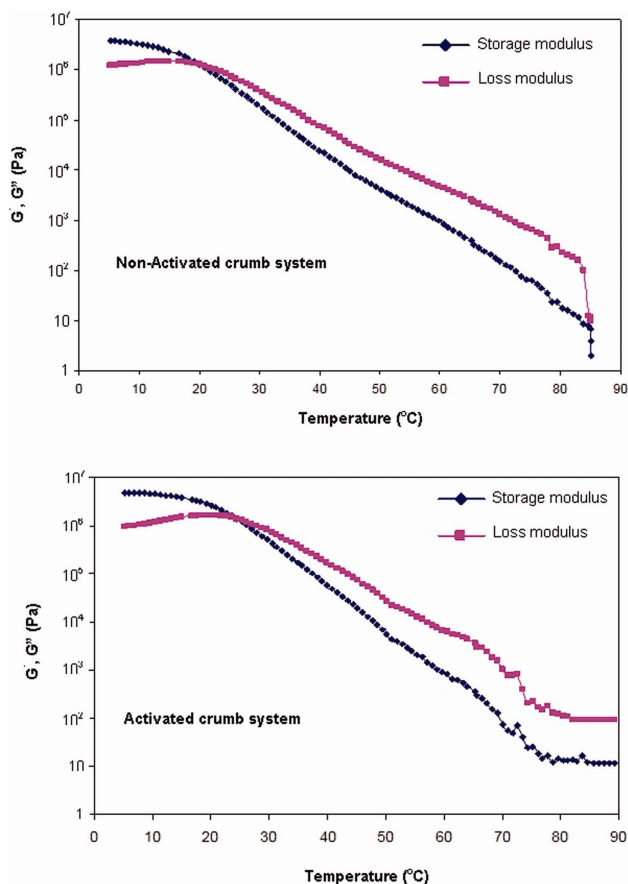
nonactivated CRMBs. This indicates that rheological properties of binder have been altered relatively to be more elastomeric type as those of bituminous type due to soluble fractions of the rubber component.

Figure 12 shows dynamic modulus of samples as a function of temperature under shear mode. A substantial difference in the shear modulus of samples was noticed due to increased interaction between the crumb rubber and bitumen as a result of activation. The value of  $T_{SHRP}$  for the activated CRMB ( $75^\circ\text{C}$ ) was higher than the nonactivated CRMB ( $71^\circ\text{C}$ ) and base



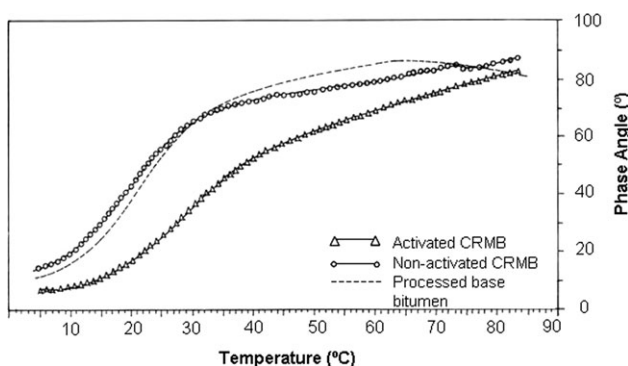
**Scheme 1.** Schematic representation of bitumen-activated crumb rubber interaction.



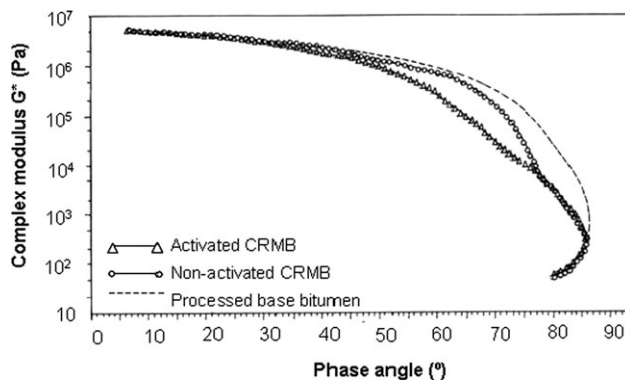


**Figure 9.** Storage ( $G'$ ) and loss moduli ( $G''$ ) of activated and nonactivated crumb rubber modified bitumen. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

bitumen ( $59^{\circ}\text{C}$ ). It was noted that the activated CRMB displayed superior shear modulus ( $G^*/\sin \delta$ ) than those of non-activated CRMB and base bitumen systems. It is mentioned that the criterion adopted by Strategic Highway Research Programme (SHRP) for performance grade asphalt binder is the highest temperature at which  $G^*/\sin \delta$  is more than 1 KPa. The high  $G^*/\sin \delta$  values indicate that the activated CRMB was less susceptible to permanent deformation at high temperatures.<sup>41</sup> The activated crumb rubber is porous and formed a viscous gel



**Figure 10.** Phase angle of processed base and activated/nonactivated crumb rubber-modified bitumens as a function of temperature.

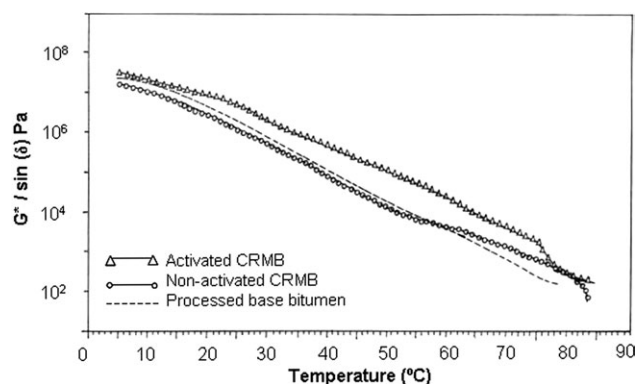


**Figure 11.** Black diagram : complex modulus versus phase angle for processed base and activated/nonactivated crumb rubber-modified bitumens.

due to the absorption of saturates/aromatics of the bitumen leading to a better resistance to deformation.

### Conventional Properties

The properties of the processed base bitumen and nonactivated/activated CRMBs are given in Table III. An increase in softening point and a decrease in penetration for the activated CRMB were observed compared with the nonactivated ones. These improvements are related to the formation of elastic network and also stiffening effect of undissolved rubber particles to the bituminous binder. In order to know phase separation in the system, the samples were stored for three weeks at room temperature. It was found that there were insignificant changes in the softening point and penetration values when compared with the freshly prepared samples. The high swelling and compatibility were achieved through mutual infiltration of components of the crumb rubber and bitumen which might prevent their separation from each other during storage.<sup>13</sup> The elastic recovery of CRMBs increased significantly as compared to the base bitumen. However, it was noted that elastic recovery of the activated CRMB was less than that of nonactivated CRMB due to its stiffness as viewed in penetration and softening point results. The workable viscosity of activated CRMB at  $135^{\circ}\text{C}$  was slightly lower than the nonactivated CRMB and higher than the base bitumen. It was found that the activated crumb rubber bitumen meets the requirements of BIS: 15462-2004.<sup>31</sup>



**Figure 12.** Dynamic Shear modulus versus temperature for processed base and activated/nonactivated crumb rubber-modified bitumens.

**Table III.** Properties of Activated/Nonactivated Crumb Rubber Modified Bitumens as per IS: 15462-2004

Property	IS : 15462 Required value	Crumb rubber modified bitumen	
		Nonactivated crumb	Activated crumb
Softening point (°C)- Fresh			
-Fresh	60 (min)	50 (2.50)	62 (3.12)
- 2 weeks storage		52 (2.60)	63 (3.15)
- 3 weeks storage		55 (2.65)	62 (3.10)
Penetration (dmm)			
- Fresh	< 50	56 (2.80)	35 (1.75)
- 2 weeks storage		54.01 (2.70)	34.81 (1.74)
- 3 weeks storage		54 (2.70)	35 (1.75)
Elastic recovery (%) 15°C	50 (min)	55 (2.75)	52 (2.62)
Viscosity (Pa. s)			
-60°C	-	1900 (95)	1230 (61.50)
-130-150°C	5 (max.)	5.71 (0.29)	5.03 (0.25)

Standard deviation is given in parenthesis.

## CONCLUSIONS

Results indicate that the activated crumb rubber particles were finer and well dispersed in the bitumen compared to the nonactivated particles. The low contact angle of probe liquids on the surface of activated crumb rubber-bitumen system indicated its superior wetting behavior over the other systems. The activated crumb rubber-bitumen system exhibited inter-mix phases as observed in MDSC. The viscosity of activated CRMB at 135°C meets the requirement of commercial standard specification. Higher complex modulus and low phase angle at higher temperature indicated an improvement in the heat resistance of the binders. During 3 weeks storage at room temperature, phase separation in the CRMB was insignificant based on the observations made with the softening points of the top and bottom portions of the stored samples. It was found that the use of crumb rubber concentrate provides superior consistency and rheological properties to the bitumen than the nonactivated crumb rubber. It is suggested that processing of bitumen with the activated crumb rubber concentrate can be adopted in the manufacturing of sealing / waterproofing compounds. It can be used as part or sole replacement of virgin polymers for the bitumen modification depending upon the end uses and also provides a significant amount of cost saving due to high price of virgin polymers. Further experimental work on modification of bitumen with the combined use of the activated crumb rubber and plastomers is under progress.

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## REFERENCES

1. Reading, M. A. In *Rubber from Tyres as Additives to Plastics*; The Recycling Plas IV-Conference of the Plastics Institute of America, Washington, D.C. **1989**, 195.
2. Jang, J. W.; Yoo, T. S.; Oh, J. H.; Iwasaki, I. *Resource Conserve Recycle* **1998**, 22, 1.
3. Adhikari, B.; De, D.; Maiti, S. *Prog. Polym. Sci.* **2000**, 25, 909.
4. Miguel, G. S.; Folwer, G. D.; Sollars, C. J. In *New Developments in the Reuse of Scrap Tyres*; The Waste Management Research Symposium; Society of Chemical Industry (SCI), London, **1997**, 14.
5. Martinez, D. F. U. S. Pat.,5, 304, 576 (**1994**).
6. Isayev, A. I.; Chen, J.; Tukachinsky, A. *Rubber Chem. Technol.* **1995**, 8, 267.
7. Tripathy, A. R.; Williams, D. E.; Farris, R. J. *Polym. Engg. Sci.* **2004**, 44, 1338.
8. McDonald, C. H. U.S. Pat.3,891,585 (**1975**).
9. Bahia, H. V.; Davis, R. *Proc. AAPT* **1994**, 63, 414.
10. Al-Abdul-Wahhab, H. I.; Al-Amri, G. *J. Mater. Civil. Engg.* **1991**, 3, 189.
11. Murphy, M.; Mahony, M. O.; Lycett, C.; Jamieson, I. *Mater. Struc.* **2000**, 33, 438.
12. Kok, B. V.; Colak, H. *Constr. Build. Mater.* **2011**, 25, 3204.
13. Xiang, L.; Cheng, J.; Que, G. *Constr. Build. Mater.* **2009**, 23, 3586.
14. Navarro, F. J.; Partal, P.; Martinez-Boza, F. J.; Gallegos, C. *Fuel* **2004**, 83, 2041.
15. Liang, Z.; Woodhams, R.T. U.S. Pat.5, 79, 215 (**1998**).
16. Charles, H.; Jaroslaw, D.; Wlodzimierz, Z.; Jan D, M. *Petroleum Sci. Technol.* **1997**, 15, 523.
17. Palit, S. K.; Reddy, K. S.; Pandey, B. B. *J. Mater. Civil Engg.* **2004**, 16, 45.
18. Kumar, P.; Mehndiratta, H. C.; Singh, K. L. *J. Sci. Ind. Res.* **2009**, 68, 812.
19. Kumar, C. R.; Fuhrmann, I.; Korger-Kocsis, J. *Polym. Degrad. Stabil.* **2002**, 76, 137.

20. Shen, J.; Amirkhanian, S.; Xiao, F.; Tang, B. *Constr. Build. Mater.* **2009**, *23*, 304.
21. Whiteoak, D. In *The Shell Bitumen Handbook*; 4th ed.' Shell Bitumen UK: Chertsey, **1990**.
22. Yu, G. X.; Li, Z. M.; Zhou, X. L.; Li, C. L. *Petroleum Sci. Technol.* **2011**, *29*, 411.
23. Zhi-Gang, Y.; Xian-Ming, K.; Jian-Ying, Y.; Lian-Qi, W. J. *Wuhan Univ. Technol. Mater. Sci. Ed.* **2003**, *18*, 83.
24. Shunin, D. G.; Filippova, A. G.; Okhotina, N. A.; Liakumovich, A. G.; Samuilov, Y. D. *Russian J. Appl. Chem.* **2002**, *75*, 1020.
25. González, V.; Martínez-Boza, F. J.; Navarro, F. J.; Gallegos, C.; Pérez-Lepe, A.; Paez, A. *Fuel Process Technol.* **2010**, *91*, 1033.
26. Cheng, G.; Shen, B.; Zhang, J. *Petroleum Sci. Technol.* **2011**, *29*, 192.
27. Abdelrahman, M. A.; Carpenter, S. H. *Transportation Res. Record* **1999**, *1661*, 106.
28. Billiter, T. C.; Davison, R. R.; Glover, C. J.; Bullin, J. A. *Petroleum Sci. Technol.* **1997**, *15*, 205.
29. Leite, L. F. M.; Soares, B. G. *Petroleum Sci. Technol.* **1999**, *17*, 1071.
30. TMS: 122 (2002) Techno-Market Survey on Recycling of Tyres, Technology Information, Forecasting and Assessment Council (TIFAC), Department of Science and Technology, Govt. of India, New Delhi-110006.
31. IS: 15462 (2004) Indian Standard Specification Polymer and rubber modified Bitumen (Indian Standard Institution, New Delhi 110002).
32. IS: 1208 (1978) Indian Standard Specification Method of testing tar and bituminous materials: Determination of ductility (Indian Standard Institution, New Delhi 110002).
33. Shenoy, A. V. In *Rheology of Filled Polymer Systems*; Netherlands: Kluwer Academic Publishers, **1999**.
34. Hefer, A. W.; Bhasin, A.; Dallas, N.; Little, P. E. *J. Mater. Civil Engg.* **2006**, *18*, 759.
35. Zakirova, L. Y.; Vol'fson, S. I.; Khakimullin, Y. N. *Polym. Sci. Series C* **2007**, *49*, 149.
36. Singh, B.; Gupta, M.; Kumar, L. *J. Appl. Polym. Sci.* **2006**, *101*, 217.
37. Polacco, G.; Berlincioni, S.; Biondi, D.; Stastna, J.; Zanzotto, L. *Eur. Polym. J.* **2005**, *41*, 2831.
38. Garcia-Morales, M.; Partal, P.; Navarro, F. J.; Martínez-Boza, F. J.; Mackley, M. R.; Gallegos, C. *Rheologica Acta* **2004**, *43*, 482.
39. Airey, G. D. *Constr. Build. Mater.* **2002**, *16*, 473.
40. Lu, X.; Isacsson, U. *Constr. Build. Mater.* **1997**, *11*, 23.
41. Lu, X.; Isacsson, U.; Ekblad, J. *Mater. Struct.* **1999**, *32*, 131.