

# Investigation on Thermo-Rheological Properties and Stability of SBR Modified Asphalts Containing Palygorskite Clay

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Received 9 September 2008; accepted 7 February 2009

DOI 10.1002/app.30223

Published online 28 April 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** One problem of polymer-modified asphalts (PMAs) is the poor compatibility between polymer and asphalts. In this article, the effects of palygorskite clay (PC) and organomodified palygorskite clay (OPC) on the rheological and morphological properties of styrene butadiene rubber (SBR) modified asphalts are investigated. The dynamic mechanical analysis (DMA) of PC and SBR/PC (OPC) modified asphalts before and after ageing has been characterized by dynamic shear rheometer (DSR). The results indicate that the degree of SBR modification is a function of asphalt-polymer compatibility. When the polymer concentration is higher, it produces a highly elastic network which increases the viscosity, complex modulus, and elastic response of the mixture, particularly at high service temperatures. However, ageing of the SBR and SBR-PC mixtures result in a decrease

in the elastic response of the modified asphalts. It also have been confirmed that the morphology observed by optical microscopy and scanning electron microscope (SEM) revealed the better compatibility between SBR/PC and asphalt. The storage stability of binder is improved significantly. Compared with PC, OPC shows better effect in improving viscoelastic properties and rutting resistance of the mixture, which contributes to the better improvement of interfacial adhesion based on larger size between layers in OPC-modified asphalts. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2524–2535, 2009

**Key words:** polymer-modified asphalts; organic palygorskite; SBR; rheological properties; dynamic mechanical analysis

## INTRODUCTION

### Background

Pavement defects, such as rutting at high temperatures, crack initiation, and propagation in the low temperature region, are due not only to traffic loads but also to the thermal susceptibility of asphalt.<sup>1</sup> The use of polymer-modified asphalts (PMAs) to achieve better asphalt pavement performance has been studied for a long time. The properties of PMAs are dependent on the polymer characteristics, content, and asphalt nature, as well as the blending process. Elastomers and plastomers are typically used in asphalt modification, such as styrene butadiene rubber (SBR), styrene-butadiene-styrene triblock copolymer (SBS), and polyethylene (PE).

SBR has been widely used as a binder modifier.<sup>2–4</sup> An Engineering Brief from 1987 available at the US Federal Aviation Administration website<sup>5</sup> describes the benefits of SBR-modified asphalt in improving

the properties of bituminous concrete pavement and seal coats. Low-temperature ductility is improved, viscosity is increased, elastic recovery is improved, adhesive and cohesive properties of the pavement are also improved. According to Becker et al., SBR latex polymers increase the ductility of asphalt pavement,<sup>6</sup> which allows the pavement to be more flexible and crack resistant at low temperatures, as found by the Florida Department of Transportation. SBR modification also increases elasticity, improves adhesion and cohesion, and reduces the rate of oxidation, which helps to compensate for hardening and aging problems.<sup>7</sup> Elastomers such as SBR has a significant effect on the results of the ductility test at both 4 and 25°C; while SBR-modified asphalts have high ductility at all temperatures whereas SBS-modified asphalts tend to have lower ductility.<sup>8</sup>

### Effect of polymer modification on asphalt rheology

Asphalts may present either elastic or viscous behavior, or a combination of both, depending on the temperature and the time over which the asphalt is observed. An adequate viscoelastic response of the asphalt is fundamental to ensure a good performance of the road

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pavement. SHRP Highway Research Program<sup>9</sup> proposes a series set of tests which involve rheological methods to replace conventional less reliable trials.<sup>10</sup>

Base asphalts (unmodified) usually have a glass transition temperature around  $-20^{\circ}\text{C}$ . It can be observed that the transition from a viscoelastic to a Newtonian liquid above  $60^{\circ}\text{C}$ . Pavement temperatures during the service life are between  $-30$  and  $60^{\circ}\text{C}$  (except for extreme climates, where they can be as low as  $-40^{\circ}\text{C}$  and as high as  $80^{\circ}\text{C}$ ), and paving asphalt is usually characterized by its dynamic material functions.<sup>11</sup> At high temperatures, when asphalt is pumped or poured (between  $140$  and  $180^{\circ}\text{C}$ ), it behaves as a classical Newtonian fluid and thus its shear viscosity is of practical interest. Addition of several percent of polymer, a marked increase in complex modulus ( $G^*$ ) at high temperature (low frequency) is obtained, further increasing the polymer content results in increased complex modulus.<sup>1</sup> The addition of polymer results in a significant decrease in phase angle, especially over the range of intermediate to low angular frequency. Although the addition of polymer increases both the storage and loss modulus of asphalt, polymer is more effective in increasing storage modulus.

### Mineral modification on asphalts

One problem of PMAs is the compatibility between the polymer and the asphalt. For this case, some researchers have focused on mineral (and organomodified mineral) modification on asphalt in recent years. SBS/ kaolinite clay (KC) compounds have been successfully used to improve the high temperature storage stability of SBS-modified asphalts. The improvement in high temperature storage stability could be attributed to the KC in the SBS/KC compounds because KC can decrease the difference of densities between SBS and asphalts. Montmorillonite (MMT) and organomodified montmorillonite (OMMT) modified asphalts exhibited higher complex modulus, lower phase angle, and enhanced viscoelastic properties, which improve its resistance to rutting at high temperatures. Organomodified mineral showed better effect in modification for the formation of exfoliated structure in modified asphalts. The modification mechanism may probably that polymer chains can intercalate into the interlayer of clay, which makes the clay dispersed into the polymer matrix at nanometer scale. These lead to the significant improvements in the thermal, mechanical, and barrier properties of the polymers.<sup>12,13</sup>

### Research objective and scope

palygorskite clay (PC) is a clay mineral characterized by a microfibrillar morphology, low surface charge,

highly magnesium content, and high specific surface area. PC containing soils occur almost exclusively in arid and semiarid areas of the world.<sup>14</sup> PC has some particularly desirable absorbency, colloidal rheological properties, and catalytic properties, in comparison with other clay minerals.<sup>15</sup> The compatibility between nonpolar superpolymer and PC with polar hydroxyl is poor.

However, despite considerable research in this area, mineral/PMA blends have still not been comprehensively characterized, due to the complex nature and interaction among mineral, asphalts, and polymer system.<sup>12</sup> In our previous work, we synthesized organic palygorskite by microwave method. The classical properties of palygorskite and organic palygorskite-modified asphalts were characterized.<sup>16</sup> In this article, modified asphalts were prepared by melt blending with PC and organomodified PC (OPC), respectively. We presented a laboratory evaluation of the fundamental rheological characteristics and morphology of SBR-modified asphalts containing PC and OPC, respectively. PMAs had been produced by means of laboratory mixing using different polymer contents. The effects of PC (OPC), polymer content, and asphalts-polymer compatibility on the morphological properties of the PMAs had been evaluated by means of optical microscopy and scanning electronic microscope (SEM), respectively. The fundamental rheological (viscoelastic) properties of the PMAs had been determined using dynamic (oscillatory) mechanical analysis and presented in the form of temperature-dependent and frequency-dependent rheological parameters.

## MATERIALS AND EXPERIMENTAL

### Materials

Asphalt, AH-90 paving asphalt, was obtained from the Lanzhou Petroleum Asphalt Factory, Gansu Province, China.

SBR was produced by the Lanzhou Petrochemical Co., Ltd., China. It was a star-like SBR, containing 27.3 wt % styrene, 0.64 wt % water soluble, 0.37 wt % volatile fraction, and viscosity ( $ML_{1+4}$   $100^{\circ}\text{C}$ ) 48–55.

PC with an average particle size of 100 mesh, purchased from Linze Powder-Material Factory, Gansu Province, China.

### Preparation of OPC

The purification of PC was as follows: PC was immersed in solvent of water (1 : 10) for 24 h, and prepared using a high shear mixer at room temperature and shearing speed of 4000 rpm for 10 min. After being stored for 24 h, suspending liquid was centrifuged and transferred to a desiccator at

105°C. The PC was prepared with an average particle size of 325 mesh.

In this study, microwave irradiation method was used. Desiccated PC and cetyltrimethyl ammonium bromide (molar ratio of 3 : 1) were blend by ultrasonic wave for 30 min, and then exposed to microwave irradiation for 5 min.

### Preparation of modified asphalts

All the modified asphalts were prepared using a high shear mixer at 165–175°C with a shearing speed of 3000–4000 rpm for 50 MIN. Asphalt (500 g) was heated to become a fluid in an iron container, then upon reaching about 175°C, the modifier (PC, OPC, SBR/PC, and SBR/OPC) was added to the asphalts.

### Dynamic mechanical analysis

The most commonly used method of fundamental rheological testing of bitumen was by means of dynamic mechanical analysis (DMA) using oscillatory-type test. It is generally conducted within the region of linear viscoelastic response. These oscillatory tests were undertaken using dynamic shear rheometer (DSR). It applied oscillating shear stresses and strains to samples of bitumen sandwiched between parallel plates at different loading frequencies and temperatures.

A temperature sweep was applied over the range 40–90°C at a fixed frequency of 10 rad/s and variable strain. The strain was chosen to be as small as possible to ensure measurement in the linear region, but large enough to allow sufficient torque readings.

A sample of about 1.0 g was put onto the lower plate. After the sample was heated to become molten, the upper parallel plate was lowered to contact tightly with the sample and trimmed. The final gap was adjusted to 1.2 mm. All the samples were held at a defined, constant temperature for 10 min, and then the temperature was varied in 2°C increments. Various viscoelastic parameters, such as  $G^*$ ,  $G'$ ,  $G''$ , and  $\Delta$  were collected automatically. A frequency sweep was applied over the range 0.1–100 rad/s at a fixed temperature of 75°C. An approximately 1.0 g sample was put onto the lower plate. After the sample was heated to flow, the upper parallel plate was lowered to contact tightly with the sample and the sample trimmed. The final gap was adjusted to 1.0 mm. All the samples were held at the defined temperature for 10 min and then conducted the frequency sweep from higher levels to the lower ones.

### Viscosity measurement

The viscosity properties of asphalt samples were determined by a rotational viscometer (Model DV-

$\alpha$ -Pro, Brook-field Engineering Inc, USA) according to ASTM D 4402.

### High-temperature storage properties

After mixing, some of the prepared modified asphalt was transferred into a aluminum toothpaste tube (32 mm in diameter and 160 mm in height). The tube was sealed and stored vertically in an oven at 163°C for 48 h, then taken out, cooled to room temperature, and cut horizontally into three equal sections. The samples taken from the top and bottom sections were used to evaluate the storage stability by measuring their softening points. Softening point was measured in accordance with ASTM D36. If the difference between the softening points of the top and the bottom sections was less than 2.5°C, the samples were considered to have good high-temperature storage stability. If the softening points differed by more than 2.5°C, the modified asphalt was taken as unstable.

### Standard ageing procedure

The ageing of the modified polymer asphalts was performed using two methods. The rolling thin film oven test (RTFOT, ASTM D 2872) simulates the changes in the properties of asphalt during the plant hot mixing and the lay down process. The second method, pressure ageing vessel (PAV) uses the residue from RTFOT test and is representative of the long term ageing due to *in situ* ageing.<sup>17</sup>

### Morphological analysis

Optical microscopy was used to study morphology of mineral clay and PMAs. A drop of heated sample was placed between microscope slides. Samples were observed under different magnification at room temperature in an optical Olympus microscope.

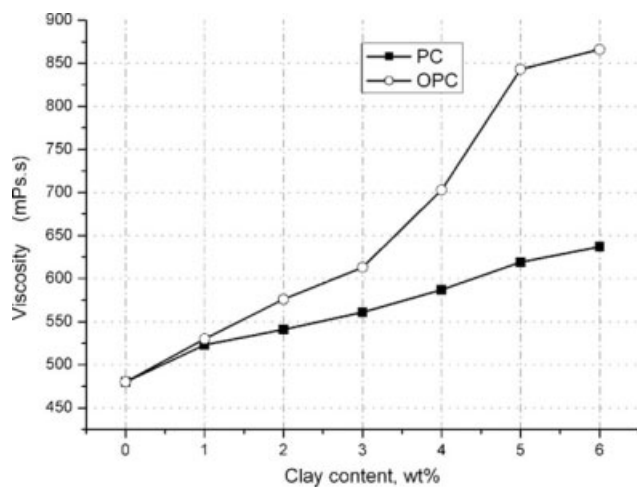
Samples were immersed in absolute alcohol in a beaker and dispersed by a low power ultrasonic instrument for half an hour. Then a drop of sample was taken out from the beaker for morphological observation. The observation was performed on a SEM, S-450 with a resolving power of 4.5  $\mu\text{m}$ .

## RESULTS AND DISCUSSION

### Viscosity behavior

The effect of viscosity on asphalt binder's workability is very important in selecting proper mixing and compacting temperatures. Most modified asphalt binders are non-Newtonian fluids at mixing and compacting temperature range *in situ* currently. Figure 1 shows the effect of types and concentrations of PC on viscosity. The viscosity of the modified





**Figure 1** Effect of PC and OPC content on viscosity at 135°C.

asphalts tends to increase when the contents of PC and OPC increased. The viscosity increases quickly for OPC content between 3 and 5 wt %, but the viscosity of the PC-modified asphalt increases slowly at all contents.

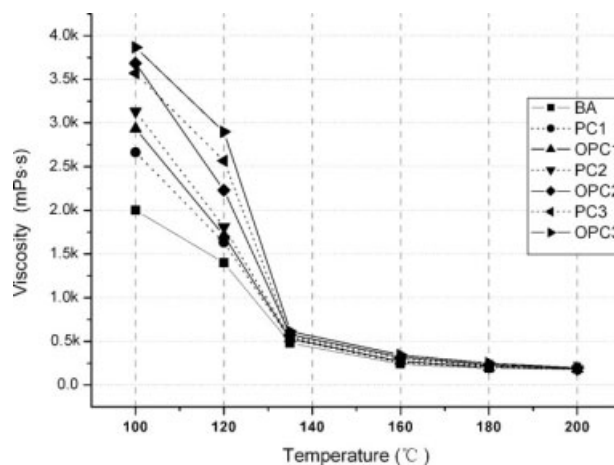
The viscosity of the PC- and OPC-modified asphalts is higher than that of the original asphalt, as shown in Figure 2. There are large difference among various PC or OPC contents when temperature less than 135°C. According to Superpave binder specification limits, the viscosity at 135°C must not be greater than 3 Pa s. Test results show that the viscosity of PC- and OPC-modified asphalt binder is 0.56 and 0.61 Pa s at the content of 3 wt %, respectively. The result indicates that the viscosity of modified asphalt binders at 135°C can meet the requirement of the related construction temperature. With the increasing of PC and OPC contents, the viscosity of asphalt binder increases.

OPC have greater effect on viscosity of binder compared to PC. OPC has greater size of layers than PC, the displacement of the zeolitic water molecules upon partial dehydration of the clay material occurred.<sup>18</sup> Further dehydration enables the formation of bonds between terminal Mg(II) and the small molecules to afford wave-like structure which results in the rapid increase of the viscosity.<sup>16</sup>

### Dynamic viscoelastic properties

#### Effect of PC on dynamic rheological properties

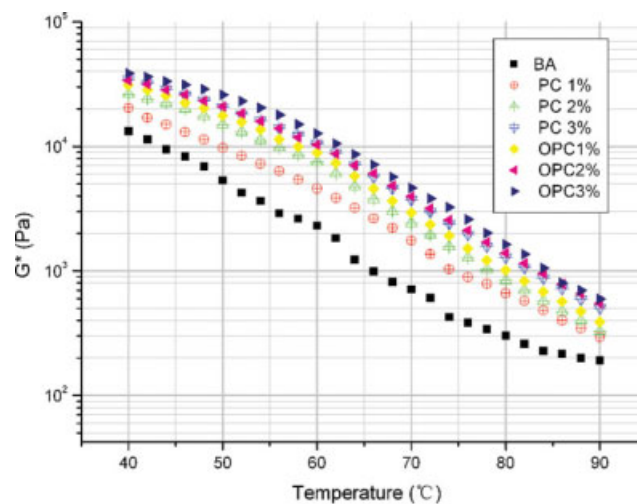
Figure 3 shows the temperature dependency (40–90°C) of  $G^*$  for the different contents of PC- and OPC-modified asphalts. The obtained results indicate that both PC- and OPC-modified asphalts show an increase in the  $G^*$  compared with the base asphalt, especially at relatively low temperatures. At higher temperatures, the increase in  $G^*$  is relatively



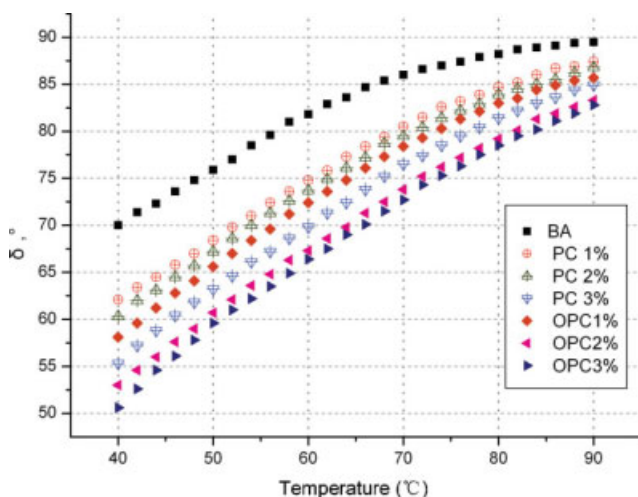
**Figure 2** Viscosity of asphalt mixing with PC and OPC versus temperature.

small. It can be seen that with the increase of modifier contents, the  $G^*$  value of the modified asphalts increases significantly. Compared to PC-modified asphalts, OPC-modified asphalts exhibit higher  $G^*$ . As can be observed in Figure 3, the slope of  $G^*$  curve of modified asphalts is slightly larger than the one of the base asphalts. These results suggest that both PC and OPC can improve the viscoelastic behaviors of modified asphalts.

Measurement of phase angle ( $\delta$ ) is generally considered to be more sensitive to the chemical and physical structure than complex modulus for the modification of asphalts. The deduction in  $\delta$  value exhibits a more elastic behavior of asphalt.<sup>12</sup> Figure 4 shows the result of phase angles against temperature. Compared to base asphalt, the phase angles of all modified asphalts decreased at the same temperature. The decreasing extent of phase angle becomes



**Figure 3** Curves of  $G^*$  vs. temperature (10 rad/s) for the asphalts modified with different contents of PC and OPC. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

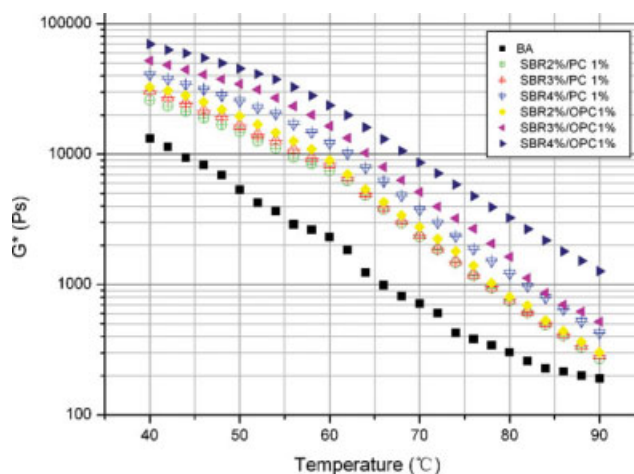


**Figure 4** Curves of phase angle ( $\delta$ ) vs. temperature (10 rad/s) for the asphalts modified with different contents of PC and OPC. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

greater when the content of modifier increases. This trend reveals the increase in elastic properties of the modified asphalt. In addition, the OPC-modified asphalts exhibit lower phase angle than PC, which may be caused by their respective dispersing structures in asphalts. When OPC content exceeds 2 wt %, the  $\delta$  values are very small.

#### Effect of SBR on palygorskite-asphalts blends

Isochronal plots of complex modulus ( $G^*$ ) vs. temperature, at 10 rad/s, for SBR/PC and SBR/OPC are shown in Figure 5. The influence of SBR on the  $G^*$  of the SBR/PC- and SBR/OPC-modified asphalts is dependant on the SBR content. With the increase of SBR content, the  $G^*$  of the asphalt is dramatically promoted. When the SBR content is higher than 2%, a maximum  $G^*$  reached. The plots in Figure 5 also show a considerable difference in the degree of modification between PC and OPC. The difference of  $G^*$  between PC (OPC) and SBR/PC (OPC) modified asphalts are shown in Table I. SBR/OPC-modified asphalts show a more pronounced increase in  $G^*$  and improved temperature susceptibility with



**Figure 5** Curves of  $G^*$  vs. temperature (10 rad/s) for the asphalts modified with different contents of SBR/PC and SBR/OPC. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

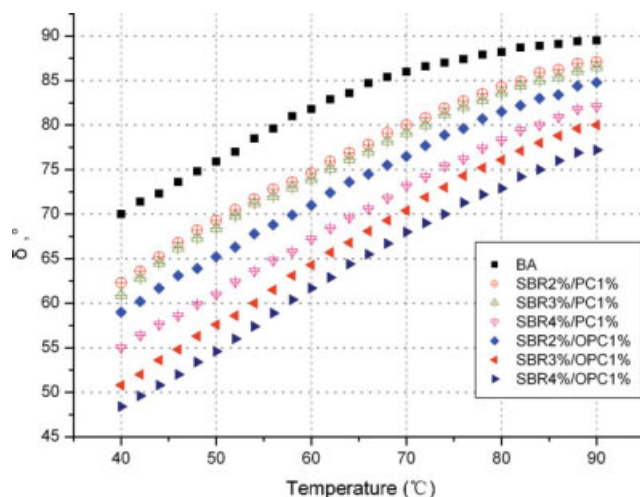
increasing polymer content. The obvious increase of  $G^*$  in SBR addition indicates that a dominant polymer network is formed which results in a sharp increase in the slope of the  $G^*$  isochrones of high content of SBR modification at medium temperature (near 60°C). The isochronal plots at 10 rad/s (1.6 Hz) for the two clay groups in Figure 5 tend to be more comparable.

Phase angle isochrones at 10 rad/s for the SBR/PC and SBR/OPC are presented in Figure 6. The figures clearly illustrate the temperature dependence of the modified asphalts and the effectiveness of SBR. With the increasing temperature, the phase angles for the base asphalts approach 90°, therefore, predominantly viscous behavior, whereas SBR begins to significantly improve the elasticity of the modified asphalts. A plateau region situated at high temperatures which indicates the presence of polymer network formed in modified asphalts. This plateau demonstrates the ability of the polymer to form a continuous elastic network when dissolved/dispersed in the asphalts.

However, no obvious differences are observed between PC (OPC) and SBR/PC (OPC) modified asphalts at low content of SBR as shown in Table I.

**TABLE I**  
Comparison of  $G^*$  Between PC (OPC) and SBR/PC (OPC) Modified asphalts

Temp. (°C)	$G^*$ (Pa)				$\delta$ (degree)			
	PC1	SBR2/PC1	OPC1	SBR2/OPC1	PC1	SBR2/PC1	OPC1	SBR2/OPC1
40	203336	25984	31037	32691	62.1	62.3	58.1	59
50	9743	14859	17641	19693	68.4	69.3	65.6	65.2
60	4597	7461.9	8922	9033	74.8	74.6	72.4	71
70	1756	2330	2769	2939	80.5	80	78.4	76.5
80	663.4	7456	803.6	1015	84.7	84.3	83	81.5
90	294.2	269.9	390.11	302.6	87.4	87.1	85.7	84.8



**Figure 6** Curves of phase angle  $\delta$  vs. temperature (10 rad/s) for the asphalts modified with different contents of SBR/PC and SBR/OPC. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

For SBR/PC (OPC) modified asphalts, particularly at low polymer contents (2%), the phase angle is a slightly increasing function of temperature with both the maximum and minimum phase angle parameters being indistinguishable. Differences in the plots of phase angle vs. temperature and the data in Figure 6 and Table I can be related to the differences in the molecular interaction (i.e. dispersion, swelling, and compatibility) among the base asphalts, PC (OPC), and SBR.

PMA displays enhanced viscoelastic properties with mineral modification which improve resistance to rutting at high temperature. Organic-modified mineral shows better effect in improving physical properties and rutting resistance of asphalts, which contribute to their structure in organic modification.<sup>13</sup>

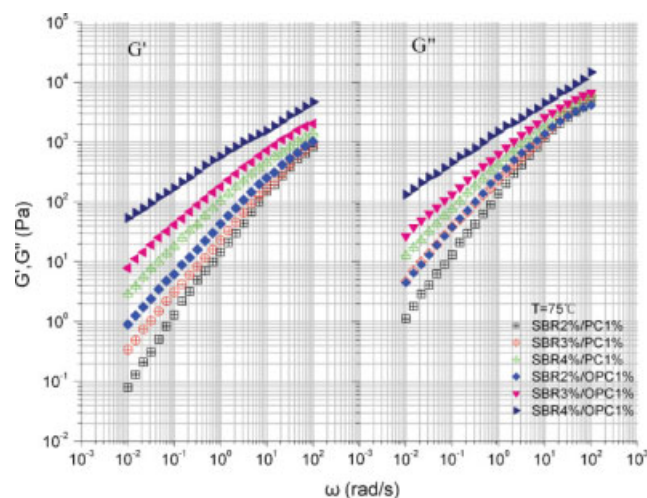
### Rheological master curves

The rheological characters allowed building master curves from the dynamic data taken in isothermal frequency sweep tests. The time-temperature superposition principle is found to hold for all the investigated materials and the horizontal shifting factor was satisfactorily described by the WLF relation. It can provide more information than with a single temperature test and allows the asphalts characteristics to be predicted for some specific frequency zones which are technically interesting but experimentally out of reach.<sup>19,20</sup> Test temperature, 75°C, is chosen since it is at high temperatures where the polymer phase significantly contributes to the improvement of the viscoelastic characteristics of the asphalts.

At 75°C, binders soften sufficiently, and polymer relaxation processes are the main contribution to the bulk rheological behavior of the complex mixture.<sup>21</sup> As can be observed, the addition of SBR to the base asphalts increases both the storage ( $G'$ ) and loss modulus ( $G''$ ) over the entire range of frequency studied for all the systems tested. In Figure 7, the master curves of  $G'$  and  $G''$  for SBR/PC (OPC) modified asphalts are reported. Thus, both samples exhibit higher values of the  $G''$  than the  $G'$  in the experimental frequency, having  $G''$  and  $G'$  slopes close to each other, respectively. These results demonstrate the predominantly viscous characteristics of these materials at 75°C. At lower frequencies, the curves differentiate but those relative to 2% SBR and 3% SBR remain very close to each other. The behavior of 4% SBR is qualitatively different.

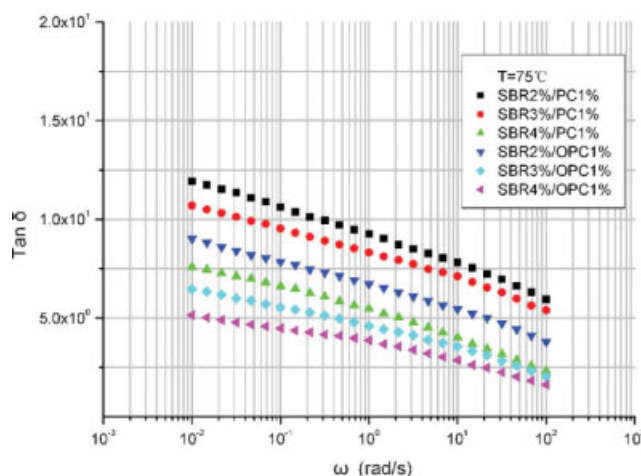
It is well-known that the polymer may dissolve and/or disperse into the maltenic medium, enhancing the mechanical properties of the mixture. These results indicate that PMAs show a viscoelastic behavior. High content of SBR/OPC (4%) modified asphalts show a plateau region at low and intermediate frequencies with values of the  $G''$  higher than the  $G'$ . This observation indicates a remarkable enhancement of the mechanical properties for SBR/OPC-modified asphalts at this temperature.

The frequency dependence of phase angle at 75°C is shown in Figure 8. The phase angle master curves for the SBR/PC (OPC) modified asphalts show a reduction in phase angle with modification and the presence of a phase angle plateau at intermediate loading frequencies. The phase angle plateau is an indication of the presence of polymer elastic networks or entanglements in the PMAs. A marked difference can be observed among the modified



**Figure 7** Frequency sweep tests in the linear viscoelasticity range for SBR/OP- and SBR/OPC-modified asphalts at 75°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]





**Figure 8** Evolution of the  $\tan \delta$  with frequency for SBR/OP and SBR/OPC-modified asphalts at 75°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

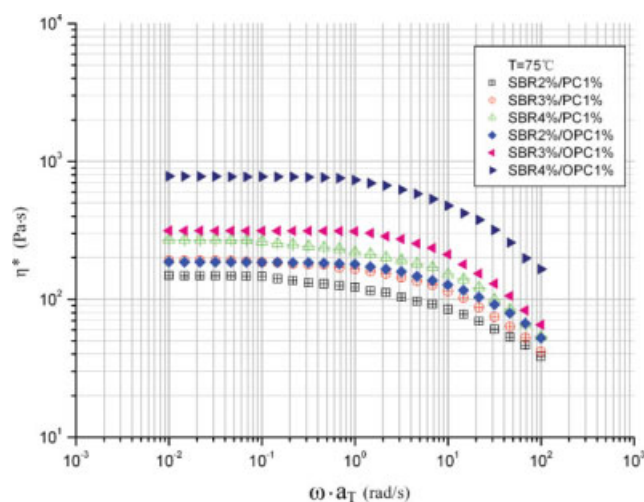
asphalts with high polymer content (4 wt % in this study). Also a significant difference between the two kind of mineral groups occurs at entire frequencies where the nature of the polymer network is dependent on the compatibility of the PMAs system. The polymer network for the SBR/OPC-modified asphalts results in a larger extent of continued reduction in phase angle (increase elastic response) at low frequencies when compared with SBR/PC-modified asphalts. The differences in the plots of phase angle versus frequency can be related to the differences in the structure of OPC and molecular interaction between base asphalts and SBR/PC (OPC) modified asphalts. To draw a more definite conclusion, detailed investigations on the chemistry (e.g. molecular weights and functional groups) of the base asphalts are necessary.

The viscosity of asphalts strongly depends on its constitutive components and the interactions. The presence of foreign solid particles such as PC and OPC in the asphalts matrix contributes to the enhancement of the asphalts viscosity. The adsorption capacity and concentration of these particles and polymer are determining factors. The steady-state flow properties of the polymer-modified asphalts studied are shown in Figure 9. This figure includes the values of the complex viscosity ( $\eta^*$ ), to study if the Cox-Merz rule is followed out.<sup>22</sup> The data obtained in the frequency–temperature superposition method is used to obtain the master curves, which implies the use of a shift factor  $a_T$ . With the addition of different contents of SBR/PC and SBR/OPC binders, an increase of the  $\eta^*$  of the PMAs, particularly at low frequency is observed. The effect of PC addition on the  $\eta^*$  is similar to that of OPC at low contents. As illustrated in Figure 9, for blends

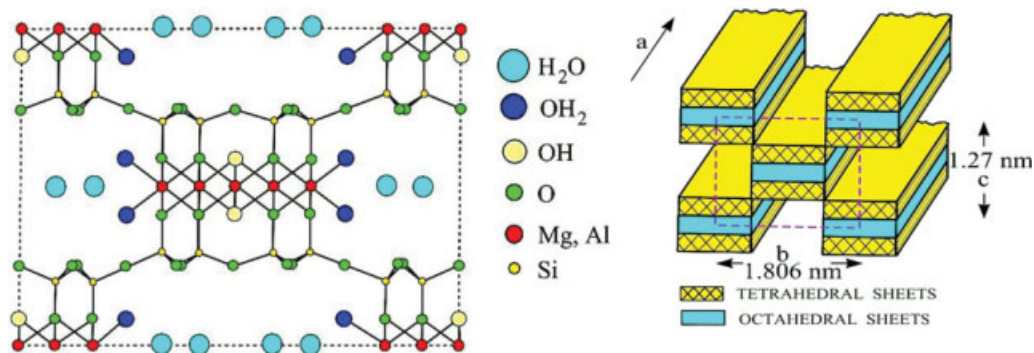
composed of 2–4% SBR/PC and 2–3% SBR/OPC, the curves describing the evolution of the  $\eta^*$  with the frequency is superposed. However, the asphalts modified with high content of SBR (4%) show an obvious increase in  $\eta^*$  over the whole experimental shear rate. This behavior may be due to the presence of strong interactions among the polymeric microphases.

For the PMAs, all the curves were similar from a qualitative point of view. Starting at low shear rates, there is a Newtonian plateau up until a limit shear rate, where shear thinning behavior started. The shear thinning is more or less homogeneously distributed along the shear rate axis and, in this respect, the only anomaly is the slope change observed. In SBR/PC-modified asphalts, the shear thinning behavior occurs at the frequency of  $10^{-1}$  to  $10^1$  rad/s. While in SBR/OPC-modified asphalts, it starts at the frequency at  $10^1$  rad/s. In shearing, a breakage of the network structure and the asphaltic colloidal structure occurs when a critical value of shear-stress is reached. With regard to the viscosity measurements, these materials reasonably hold the Cox-Merz rule.

To interpret the rheological properties mentioned earlier, the internal structure of the PMAs has to be considered. Figure 10 demonstrates the schematic projection of PC structure. PC had an interstitial vacancy, and  $M^{2+}$  is an exchangeable cation.<sup>2</sup> The linked ribbons represent a 2 : 1 layer that was continuous along the  $a$ -axis, but of limited lateral extend along the  $b$ -axis. Rectangular channels, formed through the pleating of sheets, contain exchangeable  $Ca^{2+}$  and  $Mg^{2+}$  cations, zeolitic water, and water



**Figure 9** Complex viscosity ( $\eta^*$ ) master curves obtained using frequency–temperature superposition method and a reference temperature of 75°C.  $a_T$  is the shift factor which accounts for the frequency–temperature equivalence. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 10** A schematic projection of PA structure. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

molecules bound to coordinatively unsaturated metal ion centers at the edges of the ribbons. When PC was added into asphalt, displacement of the zeolitic water molecules upon partial dehydration of the clay materials occurred.<sup>19</sup> Further dehydration enables the formation of bonds between terminal Mg(II) and the small molecules to afford wave-like structure. The microstructure showed good inter-layers cohesion with uniform wave-like layers, and the interface does not reveal any debonding showing that a significant improvement of interfacial adhesion was obtained. However, at the same time the mechanical properties demonstrated that the polymer islands were not simply dispersed in the asphaltic phase. With SBR added, further displacement of the clay materials occurred. When the content of SBR increased, promotion of the size between layers was seen. The explanation might be that the displacement among asphalt, SBR, and PC (OPC) at interstitial vacancy of PC occurred. Therefore, the SBR macromolecules form a continuum, which bridges between two or more polymer-rich zones. Thus, a physical network where "rigid" SBR domains are interconnected through polymer chains is formed. As a consequence, there are domains with very different "mobility," determined by both their dimension and the number and strength of bridges that bond them to other domains.<sup>16</sup>

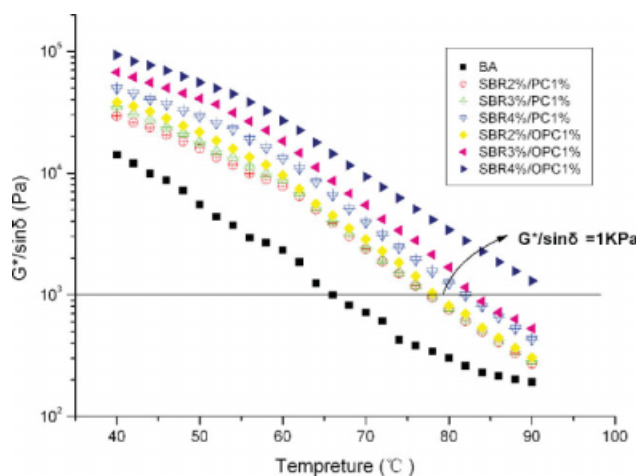
#### SHAP test

It is known that the temperature of the bitumen binders when  $G^*/\sin \delta$  is equal to 1 kPa is defined as a criterion for the high temperature (good viscoelastic) performance of bitumen in SHRP (Strategic Highway Research Program) tests.<sup>2,23</sup> Plots of  $G^*/\sin \delta$  versus temperature are displayed in Figure 11. Results reveal that the maximum temperature is improved when any of the modifiers are added. The resulting temperature of base asphalts and modified asphalts are determined as 65°C and above 78°C from the testing data obtained. The best results are

obtained when 4% of SBR/OPC is mixed with base asphalts at the temperature of 90°C. This indicates that the SBR/PC (OPC) modified asphalts have a higher performance grade than base asphalts. It is also known that higher  $G^*/\sin \delta$  values are found to correlate with higher rutting resistance.

#### Changes in the rheological properties after laboratory ageing

Changes in the properties of aged PMAs are dependent on a combined effect of asphalt oxidation and polymer degradation. In previous work, Lamontagne et al. compared the aging with the Rolling Thin Film Oven Test (RTFOT) and demonstrated that 1 h of aging corresponds to 2 years of road use and further confirmed that the RTFOT test have a moderated effect on the asphalt aging.<sup>24</sup> The changes in  $G^*$ ,  $\delta$  and  $G^*/\sin \delta$  are shown in Table II with the selected temperature of 60°C (values of other temperatures are not given). The effects of short-term



**Figure 11** Curve of  $G^*/\sin \delta$  versus temperature for SBR/PC and SBR/OPC-modified asphalts. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



TABLE II  
Comparison of Complex Modulus, Phase Degree and Rutting Factors before and after RTFOT by DMA

Temperature (60°C)	G* (Pa)		$\delta$ (degree)		Upper limit temp. (°C) G*/sin $\delta$ = 1 kPa	
	Orig.	Aged	Orig.	Aged	Orig.	Aged
BA	2309.3	4800	81.8	76.4	64	70
PC1	4597	10975	74.8	70.7	74	80
PC2	7456.1	12247	73.7	69.3	78	80
PC3	10597	16765	69.8	67.9	82	86
OPC1	8922.7	12484	72.4	68.4	80	84
OPC2	10321	18091	67.3	65.7	82	88
OPC3	12697	22336	66.4	62.8	84	90
SBR2/PC1	7461.9	11397	74.6	71.4	76	82
SBR3/PC1	8443.6	12086	73.9	69.4	76	80
SBR4/PC1	12137	15631	67.2	66.9	80	88
SBR2/OPC1	9033.6	13692	71	67.8	78	84
SBR3/OPC1	16469	23764	64.3	62.5	82	90
SBR4/OPC1	23703	37650	61.7	59.6	>90	>90

aging of RTFOT indicate that the simulating aging in the laboratory increases  $G^*$ . Aging makes the asphalt binder less temperature sensitive in  $G^*$ . For aged asphalts there is still significant difference between unmodified and modified binders in their  $G^*$ . The desired effect of polymer modification is to provide a polymer network that imparts elastic stability at higher temperatures and this is indicated by a decrease in loss tangent.<sup>25</sup> One aging mechanism is an irreversible one, characterized by chemical changes in the asphalt. The processes contributing to aging include oxidation, loss of volatile components, and exudation. The second mechanism is a reversible process called physical hardening which may be attributed to molecular structuring, i.e. the reorganization of asphalt molecules or asphalt microstructures to approach an optimum thermodynamic state under a specific set of conditions.<sup>26</sup> Generally, asphalt aging is a process of in service auto-oxidation. Under severe aging conditions, i.e. increasing the temperature, decreasing asphalt film thickness, increasing oxygen pressure and using combinations of these factors, free radical reaction taking place. In this case, aging results in a significant shift of the entire phase angle in the direction of more elastic (relatively less viscous) behavior indicating that a variation from a more sol-like (viscous and less structured) to a more gel-like (elastic and more structured) behavior has occurred.

### High-temperature storage properties

The compatibility between polymer and asphalt is necessary during storage, pumping, and to achieve the expected properties in the pavement.<sup>27</sup> Stability tests can determine whether the interactions created between the polymer and the asphalts during mixing are strong enough to resist a separation of the polymer in the conditions in which it is stored. Table

III shows the high-temperature storage stability of SBR/PC (OPC) modified asphalts. Obvious differences in the softening points are detected in base asphalt, indicating that base asphalt is unstable. With the addition of PC and OPC, the storage stability of SBR/PC- and SBR/OPC-modified asphalts are improved significantly. No marked differences in the softening points of modified asphalts are seen.

SBR/PC (OPC) modified asphalt can be considered as a suspended system. Stoke's law demonstrate the falling velocity of the particles in a suspended system<sup>13</sup>:

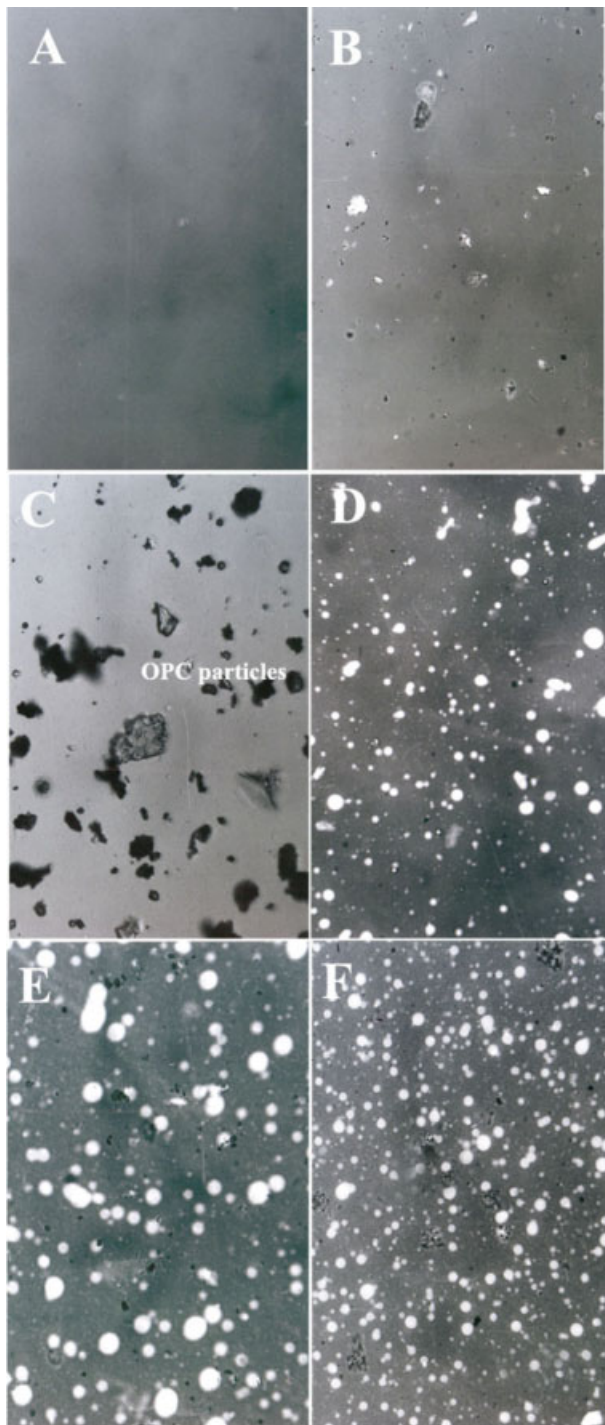
$$V = \frac{2gr^2(\rho_0 - \rho_1)}{9\eta} \quad (1)$$

where  $g$  is the gravitational force constant,  $r$  is the average radius of the SBR particles,  $\rho_0$  is the density of asphalt,  $\rho_1$  is the density of SBR, and  $\eta$  is the viscosity of the modified asphalt. As shown in eq. (1), there are two ways to prevent the phase separation of SBR from asphalt. One is to decrease the density difference and one is to reduce the particle size. The density of the SBR was about 1.2 g/cm<sup>3</sup> and the density of base asphalt here was 1.013 g/cm<sup>3</sup> at

TABLE III  
High-Temperature Storage Stability of SBR/PC and SBR/OPC-Modified Asphalts

SBR content	Softening point (°C)		$S_t - S_b$ (°C) <sup>a</sup>
	Top	Bottom	
BA	47	42.2	4.8
SBR2/PC1	53.4	50.8	2.6
SBR3/PC1	55	53.8	1.2
SBR4/PC1	55.6	54.2	0.8
SBR2/OPC1	54.1	52.3	1.8
SBR3/OPC1	55.4	54.7	0.7
SBR4/OPC1	56.6	56.1	0.5

<sup>a</sup>  $S_t - S_b$  = Top softening point subtract bottom one.



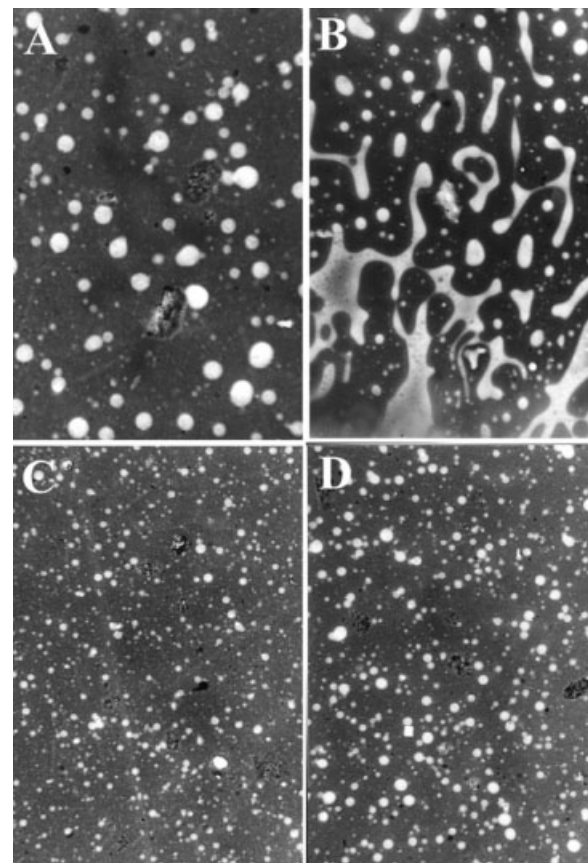
**Figure 12** Morphology development of OPC and SBR/OPC-modified asphalts. (A) Base asphalt; (B) 1 wt % OPC-modified asphalt; (C) 3 wt % OPC-modified asphalt; (D) 2 wt % SBR/OPC-modified asphalt; (E) 3 wt % SBR/OPC-modified asphalt; (F) 4 wt % SBR/OPC-modified asphalt.

room temperature. The density of PC is around  $2.05\text{--}2.32\text{ g/cm}^3$  at room temperature. At high temperatures, the SBR particles swelled in the oily fraction of the asphalt and results in the density difference of the SBR and asphalts became larger. When the PC or OPC attached to SBR, the density

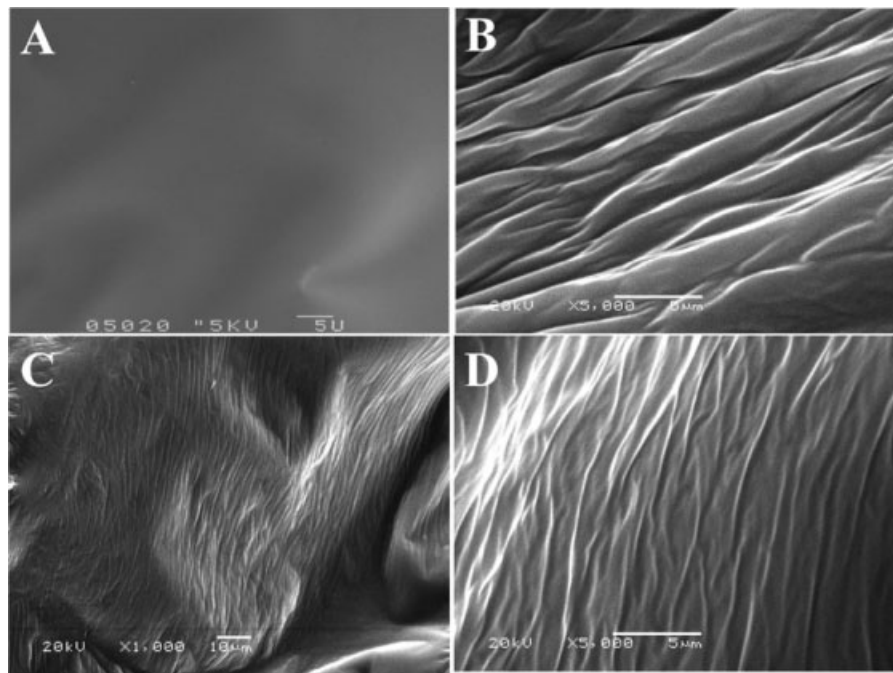
difference is decreased and the force for driving separation becomes zero at a certain content of PC or OPC, so the high-temperature storage stability is improved.

### Morphology

The compatibility between polymer and asphalt is critical to the properties of PMAs.<sup>28</sup> The morphology of PMAs is investigated using optical microscopy by characterizing the distribution and the fineness of polymer in the asphalt matrix. The morphology of SBR/PC (OPC) modified asphalts are shown in Figure 12. The modified asphalts with different contents of OPC and without SBR are shown in Figure 12(B,C). The SBR-modified asphalts with a low polymer content, as shown in Figure 12(D,E). At low polymer content, small polymer droplets swelled by asphalts light fractions appear in a continuous asphalts phase. Although the SBR content increased to 4%, as shown in Figure 12(F), polymer continues



**Figure 13** Morphology of the stability test for SBR/OPC-modified asphalts. A: Micrograph of top of the stability test tube for 2 wt % SBR/PC-modified asphalts. B: Micrograph of bottom of the stability test tube for 2 wt % SBR/PC-modified asphalts. C: Micrograph of top of the stability test tube for 4 wt % SBR/OPC-modified asphalts. D: Micrograph of bottom of the stability test tube for 4 wt % SBR/OPC-modified asphalts.



**Figure 14** A: SEM micrograph of base asphalt; (B) SEM micrograph of 1 wt % OPC-modified asphalt; (C) SEM micrograph of 4 wt % SBR/OPC-modified asphalt; (D) Magnification of 4 wt % SBR/OPC-modified asphalt.

dispersed in the asphalts, a continuous polymer phase tends to appear in the studied systems. The different morphologies seen in Figure 12 are a function of the swelling potential of the nature of the polymer, base asphalts and the polymer content of the PMAs. The rheological characteristics of these modified binders are inevitably affected by the nature of different PMAs. SBR-modified asphalts having a continuous polymer-rich phase generally produce polymeric type modification rather than filler type (stiffening). On the basis of the morphology of the PMAs, SBR4/OPC1 should demonstrate the highest degree of polymer modification.

A continuous and direct approach to study the high temperature storage stability of SBR/PC (OPC) modified asphalts was obtained by observing the morphology at high temperature as a function of time. As shown in Figure 13, the morphology of SBR2/PC1-modified asphalt changed quickly with time. In some part of the analyzed surface, big spots of polymer-rich phase appear [Fig. 13(B)]. The morphology of the polymer "islands" is very different from the previous ones and indicates that the low content of SBR-modified asphalts are not stable when stored at high temperature. However, as for the SBR4/OPC1-modified asphalts, SBR-OPC disperse in the asphalt matrix very homogeneously under the same high shear-stress and at the same high temperature. As shown in Figure 13(D) along with the stored time from 1 to 24 h at 160°C SBR-OPC dispersed more homogeneous, which implied that the SBR-OPC-modified asphalt binder had high temperature storage stability.

Because of its significant improvement of interfacial adhesion it is reasonable that SBR-OPC has significant compatibility with base asphalt and can keep binder more stable stored at high temperature.

In optical microscopy technique it is difficult to measure the real size of polymer inclusions in asphalt matrix. SEM is used to analyze the shape of asphalt, surface texture even PC and OPC distribution in modified asphalts. The typical morphology of base asphalt with SEM is shown in Figure 14(A). As the content of OPC increased up to 1%, modified asphalt is obtained with relatively uniform layers, wave-like surface as shown in Figure 14(B). The size of layers with the minimum of 3 nm and maximum of 4 nm in OPC-modified asphalts. When SBR is added, a relatively uniform wave-like layer surface is observed in Figure 14(C,D). In the SBR/PC-modified asphalt, resemble tendency is observed (The micrograph of SBR/PC are not given for it very similar to OPC addition). When the content of SBR was higher than 3%, remarkable uniformly wave-like layers surface is seen. An increase in the size between layers is detected compared to the absence of SBR.

## CONCLUSION

The addition of PC and SBR to base asphalts, in order to improve its performance for pavement applications has been studied. When PC (OPC) was added into asphalt, good inter-layers cohesion with uniform wave-like layer, and the interface does not



reveal any debonding showing that a significant improvement of interfacial adhesion was obtained. When the content of SBR increased, promotion of the size between layers was seen. The mechanism associated with SBR polymer modification consists of a swelling of the polymer through the absorption of the light fractions of the base bitumen and the establishing of a rubber-elastic network within the modified binder. The improved viscoelastic properties of PMAs had been demonstrated using DMA and the rheological parameters of complex modulus and phase angle. SBR modification has increased the complex modulus and elastic response of the PC- and OPC-modified asphalts, particularly at high temperatures and low frequencies. The extent of polymer modification had differed depending on the nature of the minerals and subsequently the compatibility of the asphalts-polymer system. It is under these conditions that the lower viscosity of the base asphalts allowed the polymeric nature of the SBR polymer network to dominate the rheological properties of the modified binder.

Laboratory simulative short-term ageing of PMAs using the RTFOT, had shown differences in the rheological characteristics of the modified binders after ageing compared with those unaged. Aging improves the temperature susceptibility of asphalt binders and further broadened the relaxation spectrum but also stiffens the asphalt (in both elastic modulus and viscosity) and damages the polymer network.

Stability tests performed combining oscillatory flow and microscopy results reveal that blends which contain low content of PC are susceptible of phase separation after 24 h of storage at 165°C. SBR-OPC had significant compatibility with base asphalt and could keep binder more stable stored at high temperature: no phase separation was detected.

The authors express their sincere thanks to Gansu International Sci.&Tech. Cooperation, China. (031-31).

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