

# Low-Density Polyethylene/Silica Compound Modified Asphalts with High-Temperature Storage Stability

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**ABSTRACT:** Low-density polyethylene (LDPE) modified asphalts with improved high-temperature storage stability are prepared by incorporating silica into the LDPE compounds. The effect of silica on the high-temperature storage stabilities, dynamic rheological and mechanical properties, and morphologies of the modified asphalts are studied. It is found that the LDPE/silica ratio in the compound has a great effect on the high-temperature storage stability. The modified asphalts are stable when the ratio of LDPE/silica is around 100/60 (w/w). The silica content in the modified asphalts is less than 3.2%, and it has a slight influence on the

mechanical properties of the modified asphalts. Silica can improve the rheological properties of the modified asphalt to some extent. The high-temperature storage stability can be increased by a decreasing density difference between the LDPE/silica compound and the asphalt or in terms of equalizing the polarity differences between asphalt and LDPE by silica. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 472–479, 2006

**Key words:** low-density polyethylene; silica; asphalt; stabilization; rheology

## INTRODUCTION

Asphalt is an aggregate binder that is widely used in road pavement. Unfortunately, high-temperature rutting and low-temperature cracking of asphalt cement or coating layers due to severe temperature susceptibility limits its further application.<sup>1</sup> Therefore, it is necessary to modify asphalt. Polyethylene (PE) has been found to be one of the most effective polymer additives for the modification of paving asphalt, because it minimizes low-temperature cracking and reduces rutting at elevated seasonal temperatures under heavy loads.<sup>2–4</sup> Unfortunately, PE separates from the asphalt when stored at high temperature, which is the major obstacle to the application of PE modified asphalts in paving.<sup>5</sup> Many measures have been used to resolve the problem, such as reactive blending and steric stabilizers.<sup>6–9</sup> In previous work, styrene–butadiene–styrene (SBS) modified asphalts with high-temperature storage stability were successfully prepared by the equal-density method (premixing SBS and filler to prepare modified asphalt).<sup>10–12</sup>

It is well known that the performance of rubber compounds with respect to such properties as tensile strength and tear and abrasion resistance can be im-

proved by incorporating carbon black and silica into rubbers. Silica is a useful additive to tire treads not only to reduce resistance but also to reduce heat build-up.<sup>13–16</sup> When silica is added to asphalt, it can improve the high-temperature, aging, and wear resistances of asphalt roads.<sup>17</sup>

In the present work, low-density PE (LDPE) modified asphalts with good high-temperature storage stability were prepared by incorporating silica into LDPE and mixing this into asphalt. Asphalts modified by directly adding LDPE and silica were also prepared for comparison. The effects of silica on high-temperature properties, high-temperature storage stability, and mechanical and rheological properties were analyzed.

## EXPERIMENTAL

### Materials

Asphalt (AH-90 paving asphalt) was obtained from the Zhenhai Petroleum Asphalt Factory. The physical properties of the asphalt were 90-dmm penetration (25°C, ASTM D5), a softening point of 46.5°C (ASTM D 36), and a viscosity of 0.35 Pa s (135°C, ASTM D 4402). The chemical characteristics of the asphalt are provided in Table I. The generic fractions were determined using thin-layer chromatography with flame ionization detection.

High dispersion silica (7000 GR, Degussa) was supplied by Red Avenue Chemical Co., Ltd. LDPE (N220) was provided by Shanghai Petroleum and Chemical

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TABLE I  
Chemical Composition of AH-90 Asphalt

Component	Content (wt %)
Asphaltenes	6.30
Resins	32.75
Saturates	6.29
Aromatics	54.67

Products Co. Ltd. The melting index is 2.0 g/10 min (190°C, 2.16 kg).

Ethylene-propylene-diene rubber (EPDM, ethyl-diene norbornene type, 4770R) was supplied by DuPont Co. with an ethylene content of 70%.

### Preparation of LDPE/silica compounds

LDPE and silica were mixed to form LDPE/silica compounds in a HAAKE rheometer at 150°C with a rotation speed of 50 rpm. The shearing time was 5 min.

### Preparation of modified asphalts

All modified asphalts were prepared using a high shear mixer (Weiyu Machine Co., Ltd.) at 180°C with a rotation speed of 4000 rpm and a shearing time of 40 min. Asphalt (600 g) was first heated to become a fluid in an iron container. Then, upon reaching about 180°C, silica, LDPE, or LDPE/silica compounds were added to the asphalts.

### High-temperature storage stability test

After mixing, some of the modified asphalt was transferred into an aluminum toothpaste tube (32-mm diameter, 160-mm height). The tube was sealed and stored vertically in an oven at 163°C for 48 h. Then, it was 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 of the LDPE modified asphalts by measuring their softening points and viscosities at 135°C. If the difference between the softening points of the top and bottom sections was less than 2.5°C while the viscosities for the top and bottom sections were nearly the same, the samples were considered to have good high-temperature storage stability. If the softening points differed by more than 2.5°C or the ratio of the two viscosities was above 1.1 or below 0.9, the LDPE modified asphalt was considered unstable.

### Rheological characterization

A strain-controlled rheometer (Advanced Rheology Expanded System, Rheometric Scientific) with parallel

plate geometry (25-mm diameter) was used to determine the rheological behavior of the asphalts before and after modification. Temperature sweeps from 30 to 90°C with 2°C increments were applied at a fixed frequency of 10 rad/s and variable strain. In each test about 1.0 g of sample was placed on the bottom plate, which covered the entire surface; the plate was then mounted in the rheometer. After the sample was heated to become a melt, the top plate was brought into contact with the sample and the sample was trimmed. The final gap was adjusted to 1 mm. The actual strain and torque were measured to calculate the various viscoelastic parameters such as the complex modulus ( $G^*$ ) and phase angle ( $\delta$ ). Temperature sweep tests were performed within the linear viscoelastic range of the materials.

### Swelling measurement

About a 1-g sample of LDPE/silica (100/60) compound was suspended in an aluminum toothpaste tube in which preheated fresh asphalt had been poured. After the tube was stored in an oven at 160°C for a given time, the sample was taken out for density and weight tests. The ratio of swelling ( $S$ ) is calculated according to the following equation:

$$S = m_1/m_0 \quad (1)$$

where  $m_0$  and  $m_1$  are the weights of LDPE/silica compound before and after swelling, respectively.

### Density test

Swelled LDPE was taken out of the asphalt for the density test (ASTM C1166, test method for vulcanized rubber) after getting rid of the asphalt adhesive to the LDPE.

### Gel content analysis

About 1 g of EPDM/silica (100/60) compound was wrapped in filter paper, and the outside was covered with copper mesh in case of leakage. Three identical wrapped samples were immersed in *n*-heptane solvent for 4 days. Then, they were taken out and dried in a vacuum oven at 80°C to constant weight. The gel content is calculated according to the following equation:

$$\text{gel \%} = 100(G_1 - G_2)/(G_0 - G_2) \quad (2)$$

where  $G_0$  is the sample weight before extraction,  $G_1$  is the sample weight after extraction, and  $G_2$  is the weight of silica in the sample.

**TABLE II**  
Effect of Silica Content on Properties  
of Original Asphalt

Silica content (%)	Softening point °C	Viscosity at 135°C (Pas)	Top softening point <sup>a</sup> (°C)	Bottom softening point <sup>a</sup> (°C)
0	47.5	0.30	47.5	47.5
1	47.5	0.30	48.0	48.2
2	48.0	0.31	49.0	48.8

<sup>a</sup> Stored in an oven at 163°C for 48 h.

### Morphological analysis

A small drop of the asphalt was placed between two heated microscope glass slides and squeezed to form a thin film. The morphology of the asphalt was observed under an optical microscope (Leica Co.) with a magnification of 400×.

## RESULTS AND DISCUSSION

### Silica modified asphalts

The silica modified asphalt was first studied in order to learn more about the LDPE/silica compound modified asphalt. The effects of silica on the properties of asphalt are given in Table II. It is shown that a small amount of silica has only a small effect on the softening point and high-temperature storage stability of asphalts. The silica used here is a precipitated type and belongs to a nanofiller with very fine particles. Although the modification of the microscope used here is only 400×, the particles of the silica are too fine to see. The morphology of asphalt shows little change, regardless of whether silica was added, as shown in Figure 1.

### LDPE/silica compound modified asphalts

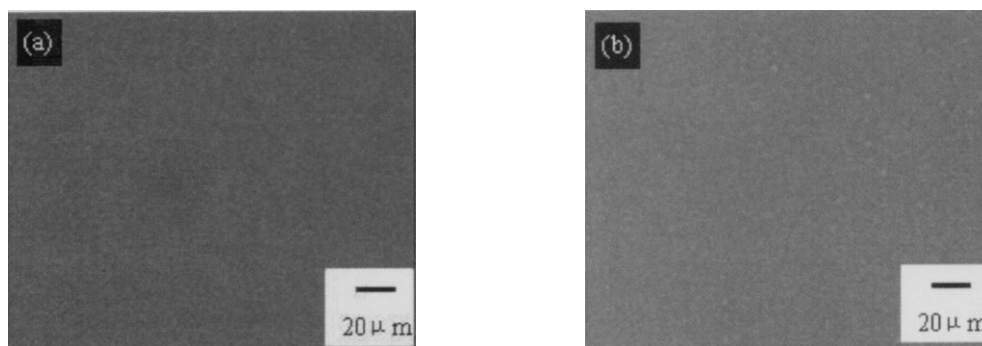
High-temperature storage stability and morphology

Minimum compatibility between the polymer and asphalt is necessary to avoid separation during storing,

pumping, and applying the asphalt and to achieve the expected properties in the pavement.<sup>18</sup> Stability tests can determine whether the polymers during mixing are strong enough to resist separation of the polymer in the condition in which it is stored. Two approaches have been accepted to ascertain if phase separation occurred during the high-temperature storage stability test: softening point variation and phase compatibility. The softening points between the top and bottom of the samples after the high-temperature storage stability test should not be higher 2.5°C in order to show that there is no substantial phase separation (storage stability).

The high-temperature storage stability of LDPE/silica compound modified asphalts are presented in Table III. Obviously, for asphalts modified by LDPE in the absence of silica, the differences in the softening points and viscosities are large, which implies that the phase separation of the LDPE/asphalt mixture is serious. The LDPE modified asphalt was unstable even when the LDPE content was decreased to 3%. With increasing LDPE content, the modified asphalt was becoming increasingly unstable. When the LDPE content was increased to 5%, LDPE seriously separated from the asphalt.

The asphalt modified with 4% LDPE was still unstable when the LDPE/silica ratio was 100/20 or 100/40. When the ratio was 100/60, the storage stability of LDPE/silica compound modified asphalt was improved significantly. For the asphalt modified by directly adding LDPE and silica, it was still unstable even when the ratio of LDPE/silica was 100/60. Thus, it can be concluded that the LDPE/silica compound is critical to obtain high-temperature storage stability of LDPE modified asphalt. When the ratio of LDPE/silica was 100/80, the softening point or viscosity of the bottom was higher than that of the top, indicating that the asphalt modified by the 100/80 LDPE/silica compound was still unstable when stored at high temperature. When the LDPE content increased to 5% or decreased to 3%, a modified asphalt with high-temperature storage stability was obtained by incor-



**Figure 1** Micrographs of (a) original asphalt and (b) 2% silica modified asphalt.

**TABLE III**  
**Effect of Silica Content on High-Temperature Storage Stabilities of Asphalts Modified by LDPE/Silica Compounds**

Formulation		Viscosity at 135°C (Pas)		$\eta_t/\eta_b$	$S_t$ (°C)	$S_b$ (°C)	$S_t - S_b$ (°C)
LDPE (wt %)	LDPE/silica (w/w)	Top	Bottom				
3	100/0	1.422	0.522	2.724	76.5	48.2	28.3
	100/60	0.572	0.592	0.966	50.0	50.8	-0.8
4	100/0	1.658	0.788	2.104	80.5	50.5	30
	100/20	1.702	0.751	2.266	83.5	50.8	32.7
	100/40	1.546	0.800	1.933	75.0	52.0	23.0
	100/60	0.808	0.825	0.979	55.5	54.0	1.5
	100/60 <sup>a</sup>	1.652	0.808	2.045	81.0	52.0	29.0
	100/80	0.792	1.692	0.468	51.0	80.0	-29.0
5	100/0	2.082	0.908	2.293	>90	54.0	>36
	100/60	0.905	0.892	1.015	59.0	60.5	-1.5

$\eta_t$ , top viscosity;  $\eta_b$ , bottom viscosity;  $S_t$ , top softening point;  $S_b$ , bottom softening point.

<sup>a</sup> Asphalt, LDPE, and silica were added directly.

porating 100/60 LDPE/silica compound into the asphalt, as shown in Table III.

The morphologies of the top and bottom sections of LDPE/silica compound modified asphalts after high-temperature storage are shown in Figure 2. In the top section LDPE aggregated to form coarse particles whereas in the bottom section the LDPE particles were small [Fig. 2(a)], which demonstrated that LDPE modified asphalts were unstable during high-temperature storage in the absence of silica. When adding silica into the asphalt (100/40 LDPE/silica ratio), there was an obvious difference in the morphologies between the top and bottom sections of the modified asphalts, which implied that the modified asphalts were still unstable after high-temperature storage [Fig. 2(b)]. Nevertheless, when a large amount of silica was added, there were no obvious differences in the morphologies between the top and bottom sections of the modified asphalts, indicating that the modified asphalt was stable after high-temperature storage [Fig. 2(c)]. When the ratio of LDPE/silica was 100/80 [Fig. 2(d)], the LDPE in the bottom section aggregated to

form coarse particles whereas in the top section the LDPE particles were small, consistent with the change of the softening point between the top and bottom section with increasing silica content.

Therefore, the silica content in the LDPE/silica compound is critical to obtain asphalt with high-temperature storage stability. If the silica content in the LDPE/silica compound was too high or too low, the high-temperature storage stability of the modified asphalt was lost.

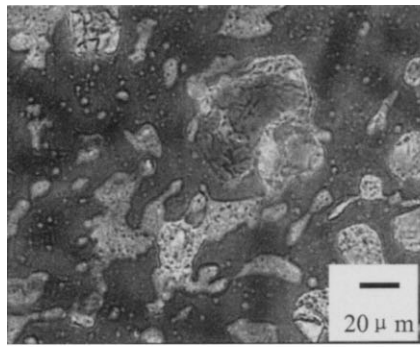
#### Viscosity, softening point, and needle penetration

The effects of silica on the viscosity, softening point, and needle penetration of the modified asphalt are provided in Table IV. With increasing LDPE content, the softening point and viscosity of the asphalt become higher and higher but the needle penetration decreased. The influence of silica on the softening point, viscosity, and needle penetration of the LDPE modified asphalts was independent of the LDPE content. With increasing silica content, the softening point

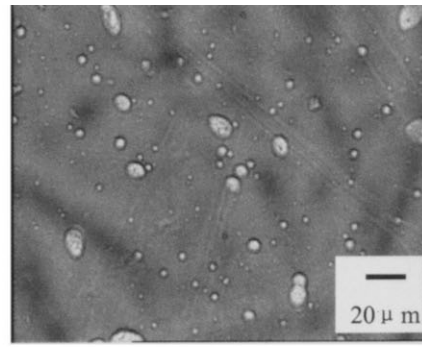
**TABLE IV**  
**Typical Properties of LDPE/Silica Compound Modified Asphalts**

LDPE content (wt %)	LDPE/silica compound (w/w)	Softening point (°C)	Viscosity at 135 °C (Pas)	Needle penetration at 25 °C (dmm)
3	100/0	49	0.550	67
	100/60	49	0.560	66
4	100/0	50	0.800	53
	100/20	50	0.800	52
	100/40	50.5	0.802	53
	100/60	51	0.808	52
	100/60 <sup>a</sup>	51	0.808	52
	100/80	51	0.810	50
5	100/0	53.5	0.872	46
	100/60	54	0.875	45

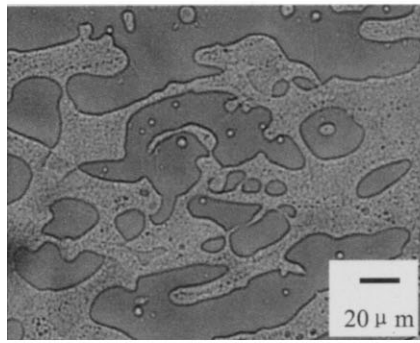
<sup>a</sup> Asphalt, LDPE, and silica were added directly.



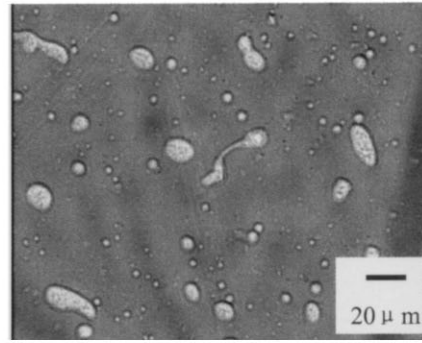
(a) Top



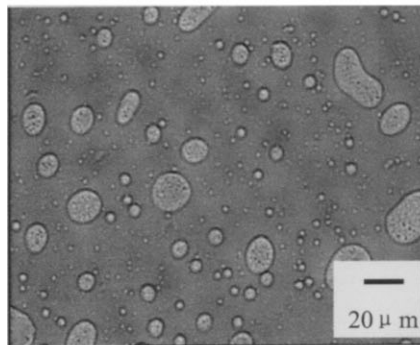
(a) Bottom



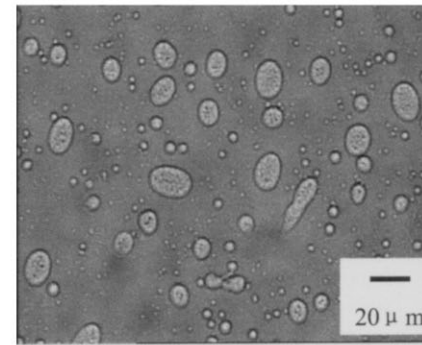
(b) Top



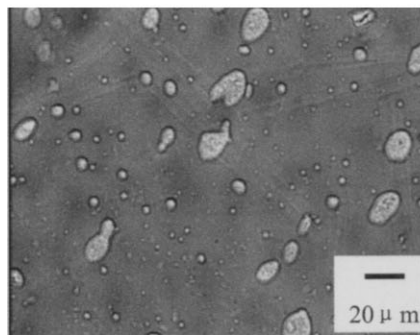
(b) Bottom



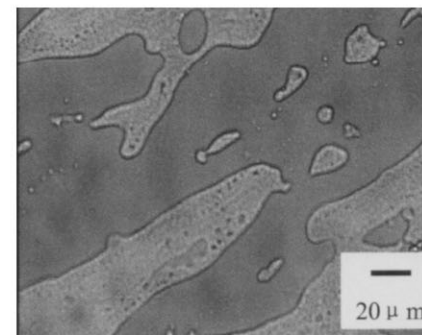
(c) Top



(c) Bottom

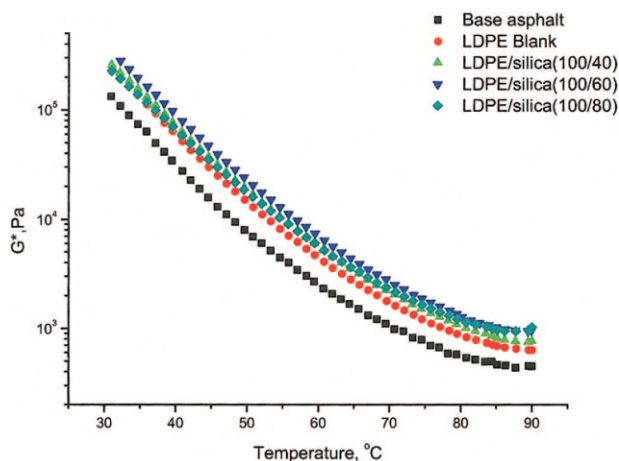


(d) Top



(d) Bottom

**Figure 2** Micrographs of the 4% LDPE/silica compound modified asphalts after high-temperature storage for (a) 100/0, (b) 100/40, (c) 100/60, and (d) 100/80 (w/w) LDPE/silica modified asphalts.



**Figure 3** Isochronal plots of the complex modulus ( $G^*$ ) versus temperature at 10 rad/s for asphalts modified by different contents of LDPE/silica compound. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

and viscosity of the asphalt increased a little whereas the needle penetration decreased to some extent. There was no significant difference of properties regardless of whether silica was added directly or indirectly (incorporating LDPE/silica compound into the asphalt).

### Rheological properties

The most significant effect of polymers on asphalt is the improvement of elasticity. There is a strong correlation between rutting resistance at high temperature and elastic modulus. Increasing elastic modulus is to be expected because it reflects a promising rutting resistance at high temperature.

Isochronal plots of the complex modulus ( $G^*$ ) versus temperature at 10 rad/s for LDPE modified asphalts are shown in Figure 3. For original LDPE modified asphalt, the isochronal plots show a difference between the base asphalt and the LDPE modified asphalt over the entire temperature range, indicating that LDPE can improve the rheological properties of the asphalt. After the introduction of silica, the isochronal plots show a difference between the LDPE and LDPE/silica modified asphalt, particularly at the upper and lower ends of the temperature range, indicating the silica can improve the rheological properties of the asphalt to some extent. Although there are only minor increases in the  $G^*$  at low temperatures with the introduction of silica, there is considerable evidence of an increase in the  $G^*$  at high temperatures (above 70°C).

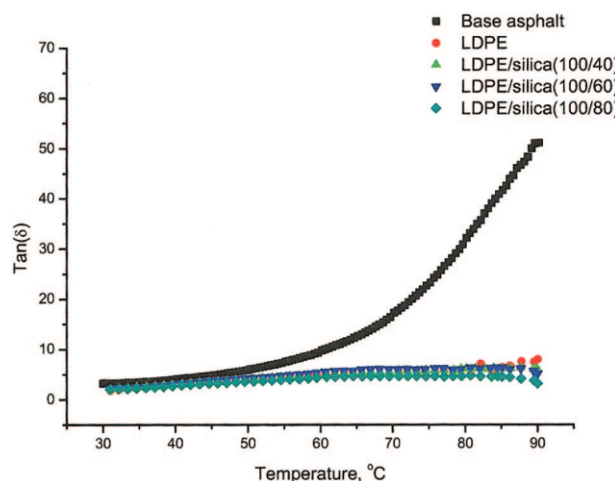
Phase angle isochrones at 10 rad/s for the LDPE modified asphalts are presented in Figure 4. Measurements of  $\tan \delta$  are generally considered to be more

sensitive to the physical structure and therefore the modification of asphalts than the complex modulus. The phase angle isochrones clearly illustrate the improved elastic response (reduced phase angles) of the modified asphalts compared to the base asphalt. Whereas the phase angles of the base asphalt approach 90° and therefore there is predominantly viscous behavior with increasing temperature, the LDPE polymer can significantly improve the elastic response at high temperature. This can be attributed to the viscosity of the base asphalt being low enough to allow the elastic response of the polymer to influence the mechanical properties of the modified asphalt. The plateau region and decreased phase angles at intermediate and high temperatures is synonymous with the plateau region defined for polymers and demonstrates the ability of the polymer to improve the rheological properties of asphalt. The isochronal plots of  $G^*$  and  $\tan \delta$  indicate the degree of LDPE modification at high temperatures (above 50°C).

Compared to original LDPE modified asphalts, the LDPE/silica compound modified asphalts show a similar tendency of the isochronal plots with increasing silica content, as shown in Figure 4. Introduction of silica has little influence on the rheological properties of LDPE modified asphalt, except for a little elastic modification at high temperatures, as compared with original LDPE modified asphalt.

### Mechanism of storage stability

Asphalt is traditionally considered as a dynamic colloid system consisting of a suspension of high molecular weight asphaltene micelles dispersed in a lower molecular weight oily medium (maltenes).<sup>19</sup> The poly-



**Figure 4** Isochronal plots of  $\tan \delta$  versus temperature at 10 rad/s for asphalts modified by different contents of LDPE/silica compound. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

mer modified asphalts may have a tendency to separate into two phases, a polymer-rich phase and a asphalt-rich phase, because the introduction of any polymer will disturb the dynamic equilibrium and reduce the homogeneity of the asphalt system. The case is of the utmost seriousness under quiescent conditions at high temperature.<sup>6</sup>

LDPE modified asphalt can be considered as a suspended system. For a suspended system, the particles in the liquid with the buoyancy force and gravitational force and the falling velocity of the particles in the system follow Stoke's law<sup>20</sup>:

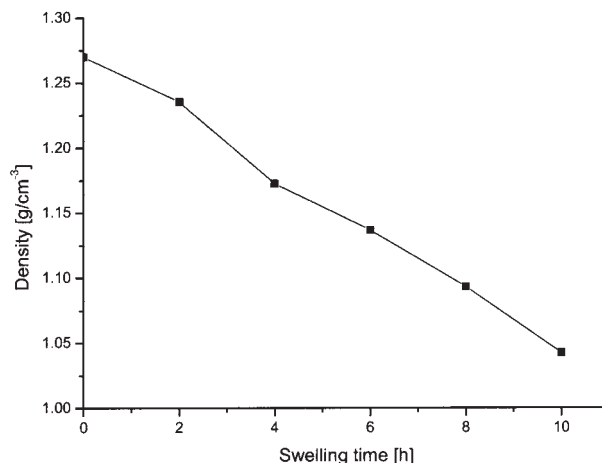
$$V = 2(\rho_0 - \rho_1)gr^2/9\eta \quad (3)$$

where  $\rho_0$  is the density of asphalt,  $\rho_1$  is the density of LDPE,  $g$  is the gravitational force constant,  $r$  is the average radius of the LDPE particles, and  $\eta$  is the viscosity of the modified asphalt.

To prevent the phase separation of LDPE from asphalt, a critical way is to reduce the falling velocity of the particles. As shown in eq. (1), there are two methods to reduce the falling velocity: one is to reduce the particle size and the other is to decrease the density difference.

Because silica has many active functional groups on its surface, chemical or physical interactions with LDPE can form during processing. In previous work, gelling occurred during the processing of SBS/kaolin-clay or natural rubber/silica, which is evidence for the interaction between the polymer and the filler.<sup>10</sup> In the present work, there is some difficulty to directly quantify the gel content of LDPE/silica because the interaction between LDPE and silica might be destroyed at high temperature and the LDPE/silica compound cannot be dissolved at room temperature by a solvent after application of the gel content test at room temperature. Thus, EPDM containing 70% ethylene was selected to simulate the interaction between LDPE and silica. The gel content of EPDM/silica (100/60) was 21.5%, which is evidence for the interaction of EPDM and silica, indicating that there might be a rather strong interaction between LDPE and silica.

The density of the LDPE was 0.91 g/cm<sup>3</sup> and the density of asphalt here was 1.02 g/cm<sup>3</sup> at room temperature. The density of silica is around 1.87 g/cm<sup>3</sup> at room temperature. When the silica attached to LDPE, the density difference decreased and the force for driving separation became zero at a certain content of silica, so the high-temperature storage stability was improved. The results of the LDPE/silica compound swelling measurements are shown in Figure 5. The density of the compound was 1.27 g/cm<sup>3</sup> at the beginning stage of swelling. As the swelling proceeded, the density of the compound was slowly decreased. According to the trend of the curve, the density of the compound had a tendency to reach the density of the



**Figure 5** The density of LDPE/silica compound swelling in asphalt as it varies with time.

asphalt, which implied that the density difference between the LDPE/silica compound and asphalt was minimized. Thus, the system reached a stable condition.

There might be another explanation. When LDPE is compounded with silica, some silica particles can attach to the LDPE and change the polarity of the compound because the silica is strongly polar and LDPE is apolar. The storage stability of LDPE modified asphalt is obtained by equalizing the polarity differences between asphalt and LDPE by silica.

## CONCLUSIONS

LDPE modified asphalts with improved high-temperature storage stability were prepared by incorporating silica into the LDPE compounds. The effects of silica on the high-temperature storage, dynamic rheological and mechanical properties, and morphologies of the modified asphalts were studied. We found that the LDPE/silica ratio in the compound had a great effect on the high-temperature storage behavior. When the LDPE/silica ratio was too high or too low, the modified asphalt was unstable when stored at high temperature. The modified asphalts were stable when the ratio of LDPE/silica was around 100/60 (w/w). The silica content in the modified asphalts was lower than 3.2%, so the silica content had only a slight influence on the mechanical properties of the modified asphalts. The silica improved the rheological properties of the modified asphalt to some extent. The high-temperature storage property was obtained by decreasing the density difference between LDPE and asphalt or in terms of equalizing the polarity differences between asphalt and LDPE by silica.

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**References**

1. Shingo, K.; Shigeru, T.; Zhan, X. M.; Dewen, D.; Norihiro, I. *Polym J* 2001, 3, 209.
2. Woodhams, R. T. *Int. Pat. WO 87/5313 A1*, 1987.
3. Kuloğlu, N. *J Mater Civil Eng* 1999, 11, 283.
4. Liang, Z. Z.; Woodhams, R. T.; Wang, Z. N.; Harbinson, B. F. *Utilization of Recycled Polyethylene in the Preparation of Stabilized, High Performance Modified Asphalt Binders*; ASTM Special Technical Publication 1193; American Society for Testing and Materials: Washington, DC, 1993; p 197.
5. Lee, N. K.; Hesp, S. A. *Transport Res Record* 1997, 1436, 54.
6. Gao, G. T.; Zhang, Y.; Zhang, Y. X. *China Synth Rubber Ind* 2001, 24, 176.
7. Liang, Z. Z. *Int. Pat. WO 9730121*, 1997.
8. Liang, Z. Z. *Int. Pat. WO 9837146*, 1998.
9. Hesp, S.; Liang, Z. Z.; Woodhams, R. T. *U.S. Pat. 5,708,061*, 1998.
10. Ouyang, C. F.; Wang, S. F.; Zhang, Y.; Zhang, Y. X. *Polym Degrad Stab* 2005, 87, 309.
11. Wang, S. F.; Zhang, Y.; Zhang, Y. X. *Polym Polym Compos* 2003, 11, 477.
12. Ouyang, C. F.; Wang, S. F.; Zhang, Y.; Zhang, Y. X. Presented at the Symposium of the International Rubber Conference, 2004.
13. Fultz, W. C.; Evans, L. R. *Rubber World* 1998, 218, 39.
14. Choi, S. S. *J Appl Polym Sci* 2002, 85, 385.
15. Choi, S. S. *J Appl Polym Sci* 2002, 83, 2609.
16. Luginsland, H.-D.; Niedermeier, W. *Rubber World* 2003, 228, 34.
17. Lesueur, D.; Dekker, D.; Planche J. *Transport Res Record* 1995, 1515, 47.
18. Gorbaty, M. L.; Peiffer, D. G.; McHugh, D. J. *U.S. Pat. 5,348,994*, 1994.
19. Loeber, L.; Muller, G.; Morel, J. *Fuel* 1998, 77, 1443.
20. Hesp, S. A.; Woodhams, R. T. *Colloid Polym Sci* 1991, 269, 825.