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Influence of surface area and size of crumb rubber on high temperature properties of crumb rubber modified binders

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Abstract

There are many variables of crumb rubber modifier (CRM) and asphalt binder, affecting the interaction of the CRM with the binder when crumb rubber modified binder (CRM binder) is produced. In this study, the influence of the surface area of CRM blends on the high temperature properties, i.e., the complex modulus (G^*), the phase angle and high temperature grade of the CRM binders was investigated. To this end, the surface areas of CRM particles were measured using the BET (Brunauer, Emmett and Teller) tester, while weighted average particle size of CRM blends was calculated based on their graduations and then used as a size index. High temperature properties of CRM binders were measured using Dynamic Shear Rheometer (DSR) test. A total of 108 CRM binders were produced using different combinations of these variables. Results observed from this study indicated: (1) the surface area of the ambient CRM was twice as large as that of the cryogenic one, leading to a much higher G^* and phase angle of the CRM binders; (2) the phase angle and G^* were affected by both the surface area and average size; however, the average size is the predominating factor; and (3) ambient CRM binders were produced about 3 °C in high temperature grade higher than cryogenic CRM binders.

Keywords: Surface area; BET; CRM binder; High temperature; DSR

1. Introduction

Asphalt binders modified by using crumb rubber modifier (CRM) have shown improved performance in pavements over the base binders because of the interaction of CRM with the base binders. This interaction changes the physical properties, viscosity and rheological properties of the CRM modified binder (CRM binder) [5,9,2,11], leading to a high resistance to the rutting of pavements [6,13,8].

The interaction process of CRM with binder is, essentially, rather complicated, depending on the variables of CRM and binder (i.e., type, percentage, size, grade, etc.) in addition to the mixing condition (temperature, mixing time, etc.). There have been a few of researches identifying the influence of these individual variables on the interaction. Miknis and Michon [10] presented a research on the application of nuclear magnetic resonance imaging to crumb rubber modified asphalt. This technology may lead to the study of different interactions between crumb rubbers and asphalt, such as swelling by asphalt molecules, possible dissolution of rubber components in asphalt, and devolatilization and crosslinking in rubber. Gaulliard and Leblanc [7] investigated the swelling kinetics of vulcanized rubber particles using a torque rheometer. A mathematical model was developed that indicated the physics involved in the process of solvent uptake by the rubber particles. Tortum et al. (2005) [15] studied the optimum condition for tire rubber

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in asphalt concrete using Taguchi method. The study indicated it was possible to get a best performance of the mixtures at optimum condition of rubber gradation, mixing time and temperature, aggregate gradation, the ratio of rubber to binder. Shen and Amirkhanian [14] studied the influence of the CRM microstructures of two types of commonly used CRM on the properties of CRM binders.

From these literatures, it was concluded that swelling of the rubber particles due to the absorption of light fractions into the rubber particles, and stiffening of the residual binder phase are the main mechanism of the interaction [1,3,14]. Since the process of swelling reduces the free space between rubber particles, they have less freedom to move into the binder matrix to move around. Therefore, this swelling causes a significant increase in the mass viscosity of the binder matrix as compared to the neat binder or the binder early in the interaction process. Finer particles will swell earlier, developing higher binder modification than coarser ones [1]. In addition, finer particles will achieve maximum swelling earlier than coarse particles, while coarse particles have a higher potential for swelling than do fine particles [1]. The absorption/swelling capacity of a rubber particle is related to the crude source, the penetration grade of the binder and the nature of the CRM [3].

The size effect on the interaction is one of the important issues to understand the mechanism of the interaction. The surface area and the particle size are the two aspects of the size effect that should be considered since the surface area and particle are naturally related. Most of the research available on the size effect did not pay much attention to the influence of surface area.

1.1. Objectives and scope

The objective of this study is to investigate the effects of the surface area and the average size of CRM blends on the high temperature properties of the modified binders.

To this end, the surface areas of the two kinds of CRM (ambient and cryogenic) were measured using a BET (Brunauer, Emmett and Teller) tester. The high temperature properties of 108 CRM binders produced under various combinations were measured, and the influence of the CRM variables on the G*, the phase angle of the CRM binders, was statistically investigated.

2. Materials used and test procedures

2.1. Materials

Ambient and cryogenic crumb rubbers of three different sizes of −14 mesh (−1.35 mm), −30 mesh (−600 μm) and −40 mesh (−425 μm) along with two percentages of 10% and 15% by weight of the binder were used to make the CRM binders. Three base binders including two binder sources (I, C) and two grades (PG64-22; PG52-28) were used. A mixing temperature of 176 °C, three mixing times of 15, 30 and 45 min and a high shear mixer (Servodyne Mixer Head, 20-900 RPM, 70 oz-in torque) were used to produce the blends at a mixing speed of 700 rpm by the blade mixer. These mixing conditions were used to match those used in the field. Table 1 shows the test combinations of binders produced with different variable in this study. The properties of the binders are listed in Table 2.

Sieve analysis was conducted to get the gradation of the 6 CRM blends with various sizes according to ASTM D 5644-01 [4]. At the same time, sieving was conducted to get relative uniform particles that are retained on one sieve and passed the sieve above for the use of surface area measurements. The gradation of the crumb rubber is shown in Table 3.

The measurement of the surface area of the CRM retained on sieves was conducted using gas sorption (adsorption and absorption), a widely used and accurate method for total surface area measurement. This method provides very high resolution data and has a very wide applicability. Krypton gas was used in this study using COULTER™ SA 3100™ Series Surface Area and Pore Size Analyzers [12]. For this testing, the samples are prepared for surface area or analysis by out-gassing. This process removes adsorbed gasses and moisture from the surface of the samples. The surface area was calculated using the BET method, which assumed that the first layer of molecular adsorption on the surface involves adsorbate–adsorbent energies. The subsequent layers involve the energies of vaporization (condensation) of the adsorbate–adsorbate interaction. The following equation was used to calculate the surface area:

$$S_{\mathrm{BET}} = V_{\mathrm{M}} \times N_{\mathrm{A}} \times A_{\mathrm{M}}/M_{V}$$

where S_{BET} is the BET surface area; V_{M} is the volume of monolayer; N_{A} is the Avogadros number; A_{M} is the volume

Table 1
CRM binders produced

Variables	Number of the variable
Binders (A)	Three: I PG64-22, C PG64-22, C PG52-28
Mesh sizes (B)	Three: −14#(1.35 mm), −30#(0.6 mm), −40#(0.425 mm)
% of CRM (C)	Two: 10% and 15%
Mixing time (D)	Three: 15, 30 and 45 min
Type of CRM (E)	Two: ambient and cryogenic
Number of CRM binders (N)	$N = A \times B \times C \times D \times E = 3 \times 3 \times 2 \times 3 \times 2 = 108$

Table 2
Properties of the three base binders

Items	Source I PG64-22	Source C PG64-22	Source C PG52-28
Rotational viscosity @ 135C (Pa s)	0.39	0.58	1.80
G*/sin(delta) @ 64C (kPa)	1.28	2.03	N/A
G*/sin(delta) @ 52C (kPa)	N/A	N/A	1.98

Table 3
Gradations (retained, %) of the 6 CRM blends used

CRM type	Ambient blend			Cryogenic blend		
Sieve no. (μm)	−14 Mesh	−30 Mesh	−40 Mesh	−14 Mesh	−30 Mesh	−40 Mesh
14 (1350)	0					
16 (1180)	2.9			0		
20 (850)	26.8			36.3	0	0
30 (600)	26.3	0	0	36.8	0.5	0.7
40 (425)	17.0	39.2	9.0	22.9	65.3	7.7
50 (300)	10.3	41.5	31.9	0.8	30.6	45.7
80 (180)	7.7	6.2	32.9	0.0	0.0	34.4
100 (150)	1.4	2.0	7.6	0.0	0.0	4.1
−100 (75)	7.6	11.1	18.6	3.7	3.9	7.4

Table 4
Surface area of the ambient CRM for various mesh sizes ($n = 3$)

Sieve no. (μm)	Std. dev.	Average (m^2/g)	C.V. (%)
16 (1180)	0.0006	0.016	0.04
20 (850)	0.0010	0.028	0.04
30 (600)	0.0006	0.040	0.01
40 (425)	0.0032	0.047	0.07
50 (300)	0.0000	0.064	0.00
80 (180)	0.0114	0.103	0.11
100 (150)	0.0012	0.152	0.01
−100 (75)	0.0053	0.170	0.03

adsorbed; M_V is the cross-sectional area occupied by the each adsorbate molecule.

Listed in Tables 4 and 5 are the surface areas of the two types of CRM. The porous ambient CRM has a much larger surface area than that of the flat cryogenic one. Tables 6 and 7 show the total calculated surface area and average size of all the 6 blends; respectively. Table 8 presents surface area of the CRM per gram of CRM binders.

Table 5
Surface area of the cryogenic CRM for various mesh sizes ($n = 3$)

Sieve size (μm)	Std. dev.	Average (m^2/g)	C.V. (%)
16 (1180)	0.0006	0.009	0.07
20 (850)	0.0031	0.013	0.24
30 (600)	0.0017	0.018	0.10
40 (425)	0.0122	0.026	0.47
50 (300)	0.0059	0.031	0.19
80 (180)	0.0078	0.042	0.19
100 (150)	0.0021	0.061	0.03
−100 (75)	0.0322	0.105	0.31

Table 6
Total surface area of the 6 blends

Blend size	Surface area (cm^2/g)	
	Ambient	Cryogenic
−14 Mesh (1.35 mm)	560	210
−30 Mesh (0.60 mm)	730	300
−40 Mesh (0.425 mm)	1020	410

Table 7
Average size of the 6 CRM blends (μm)

Mesh size (mm)	Ambient	Cryogenic
−14 (1.35)	544.2	631.1
−30 (0.60)	313.5	375.0
−40 (0.425)	218.5	247.5

Table 8
Surface area (cm^2/g) of the CRM per gram of CRM binders

Type	CRM size	10% CRM	15% CRM
Ambient	−14 Mesh	5.1	7.7
	−30 Mesh	6.7	10.0
	−40 Mesh	9.2	13.8
Cryogenic	−14 Mesh	1.9	2.9
	−30 Mesh	2.8	4.1
	−40 Mesh	3.7	5.6

3. Results and discussions

3.1. Phase angle, delta

Figs. 1 and 2 show the influence of the surface areas of the both ambient and cryogenic CRM blends on the phase angles obtained from DSR testing at test temperatures of 76 °C, for binders with 10% CRM and 82 °C with 15% CRM. The test temperatures of 76 and 82 °C were the high temperature grades of CRM binders with 10% and 15% CRM, which were determined from the DSR test, respectively. Since the three different mixing times did not produce a statistical significant difference in the phase angle, the values in these figures are average of those obtained from the three mixing times. Generally, the phase angles of the CRM binders increased as the surface area of the CRM increased with the two exceptions of the samples made by C PG52-28 and I PG64-22 when mixed with 15% of the cryogenic CRM. Furthermore, in many cases moderate and high correlations of the phase angle and

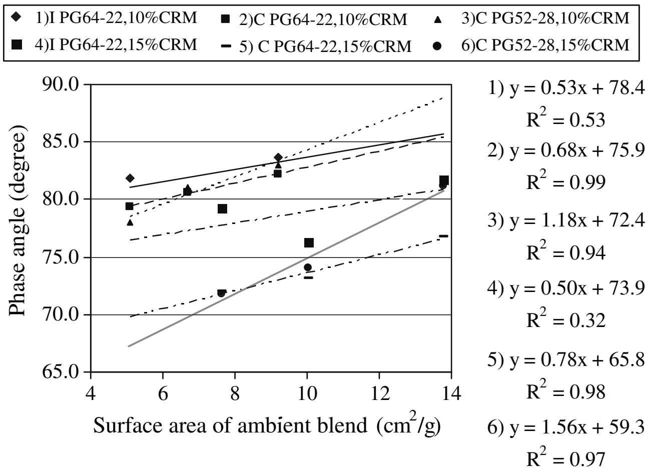

Fig. 1. Phase angle versus surface area of ambient blends.

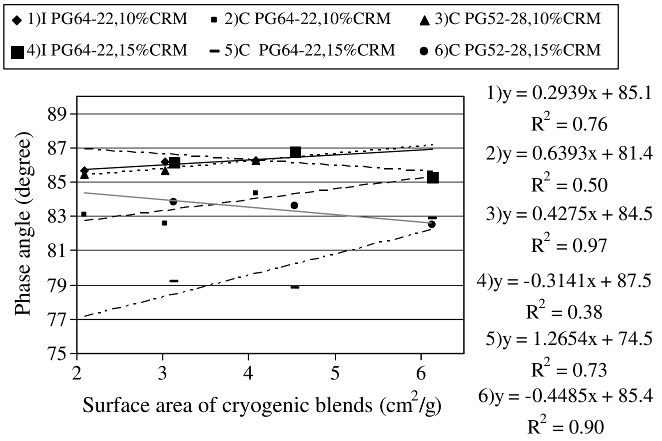

Fig. 2. Phase angle versus surface area of cryogenic blends.

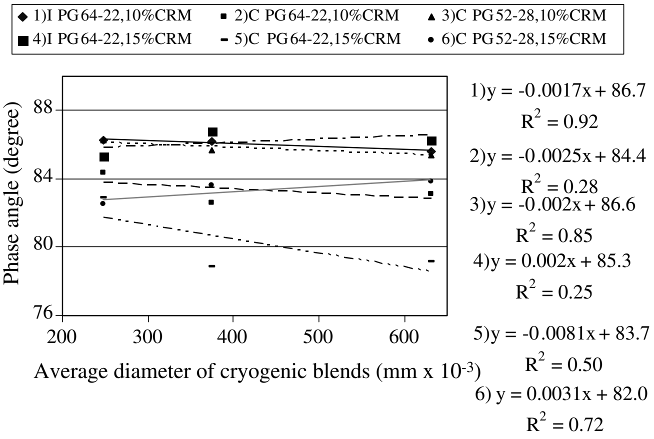

Fig. 4. Phase angle versus average size of cryogenic blends.

the surface area were found. The influence of the surface area on the phase angle demonstrated separately in these two figures is in essence the resulting size effect including the particle mesh size and surface area since the CRM blends with a high surface area correspond to fine meshes of the CRM.

It was observed that the phase angle strongly depends on the type of the CRM used to produce the modified binder. The modified binders containing ambient CRM produced phase angles that were less than the ones containing cryogenic CRM. For example, the two blends having the same surface area of 6.0 cm^2/g, the phase angles ranged from 82° to 87° for the cryogenic CRM binders and 67–81° for ambient CRM binders. Thus, the average difference in the phase angle corresponding to this surface area was 9°. This difference may be resulted from the particle average size since the ambient CRM with a surface area of 6 cm^2/g has a finer mesh size than the cryogenic.

Figs. 3 and 4 show the influence of the average size (diameter) of the rubber particles on the phase angles of the modified binders. Generally, the curves showing the phase angle and the average size are much flatter than those showing the phase angle and the surface area, indicating that the phase angles were not as obviously affected by the average sizes of the CRM blend as by the surface areas. In most cases (4 of the 6), the phase angle of the CRM binders decreased as the average diameter increased, depending on the type of the CRM. In this study, ambient CRM produced lower phase angle than the same size cryogenic CRM did with the two exceptions, namely, C PG52-28 and I PG64-22 made with 15% of cryogenic CRM. The correlations between the phase angle and the average diameter, in majority of cases, are relatively good. As we can see, all of the cases have a high R^2 for either ambient or cryogenic binders.

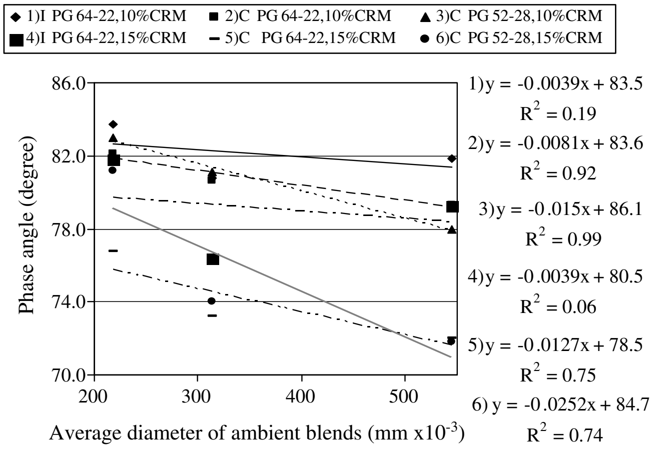

Fig. 3. Phase angle versus average size of ambient blends.

Again, the influence of the average sizes of the CRM blends on the phase angle demonstrated separately in these two figures is in essence the resulting size effect including the particle mesh size and surface area.

For example, the CRM having the same diameter of 350 μm produced 74–81° for ambient CRM binders and 81–86° for cryogenic CRM binders. An average decrease of 6.5° in the phase angle was observed for ambient CRM binder compared with the cryogenic. This decrease in the phase angles of the modified binders could be caused by the higher surface area of the ambient CRM blend, consequently a better interaction of the ambient CRM with the binder than cryogenic CRM.

It is believed that the larger the surface area, the quicker and more absorption of light fraction into the CRM; therefore, a faster interaction. Then, the residual asphalt phase of the CRM binders has a lower phase angle (a higher elastic property after more absorption). The finding that the phase angles increased as the surface area increased confirmed that the higher and quicker interaction of CRM with the binders because a larger surface area was not the only factor that affected the phase angle. On the contrary, the size of the CRM blends would be still a more important factor to consider. In a world, the size effect of CRM on the phase angle was caused by both average size and the surface area.

3.2. Complex modulus, G*

Figs. 5 and 6 show the relationships between the average diameter of the CRM blends and the complex modulus, G*, obtained at test temperatures of 76 °C, for binders with 10% CRM and 82 °C with 15% CRM. The three different mixing times did not produce much significant difference in the G*. Therefore, the values in the figures are also the average of those obtained from the three mixing times. The G* increased as the average diameter of the blends increased. This is true for all the modified binders except in one case. Most of the correlations between the average diameter and the G* are good. Five of the 6 cases have a R^2 higher than 0.44 for ambient CRM binders, whereas 5 of the 6 blends have a R^2 higher than 0.45 for cryogenic CRM binders, excluding the case of I PG64-22 binder with 15% of CRM.

Figs. 7 and 8 show the influence of the surface area of the CRM blends on the complex modulus of the modified binders. The G*, in general, decreased as the surface area increased except in one case, i.e., when A PG64-22 is mixed with 15% of cryogenic CRM. The correlations between the G* and the surface area; in the majority of the cases, is relatively good.

Similar to what was discussed above, the influence of the average diameter on the G* in these figures is essentially the size effect including both the average diameter and the surface area of the CRM. In general, a coarser rubber produced a binder with a higher complex modulus of the modified binders. For the same average size of CRM, the G* of ambient CRM binders was found to be higher than that of the cryogenic blends. For instance, for an average diameter of 400 μm ambient CRM, the G* was about 900 Pa, whereas the G* was found to be 700 Pa for the same cryogenic CRM. It is believed that the higher G* values obtained for the ambient CRM, is the result of better interaction of the ambient CRM, i.e., due to the higher surface area of the ambient CRM.

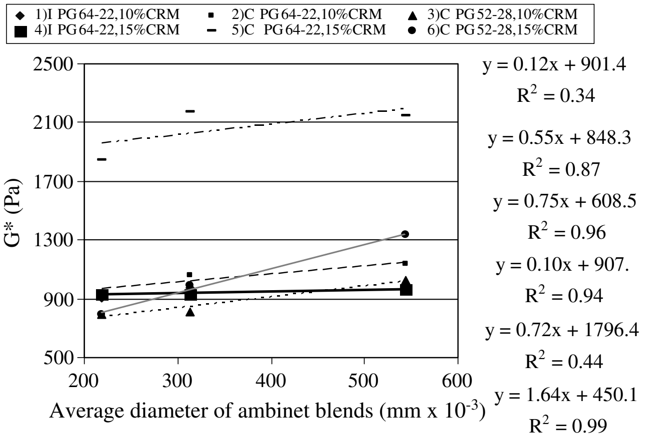

Fig. 5. G* versus average size of ambient blends.

Table 9 shows the regression equations of the phase angle and G* with surface area and diameter of the CRM blends. The regressions can predict the parameters very well.

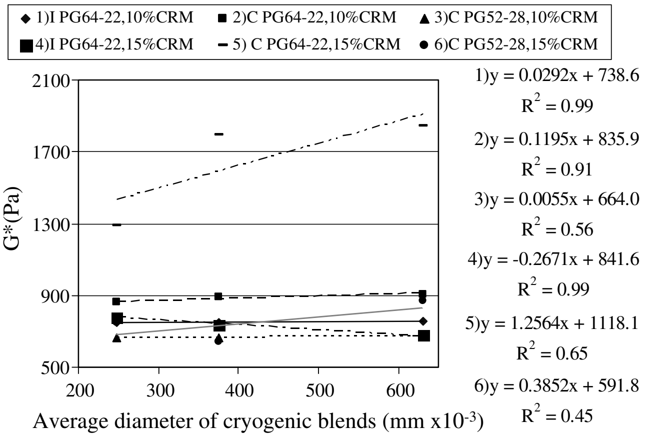

Fig. 6. G* versus average size of cryogenic blends.

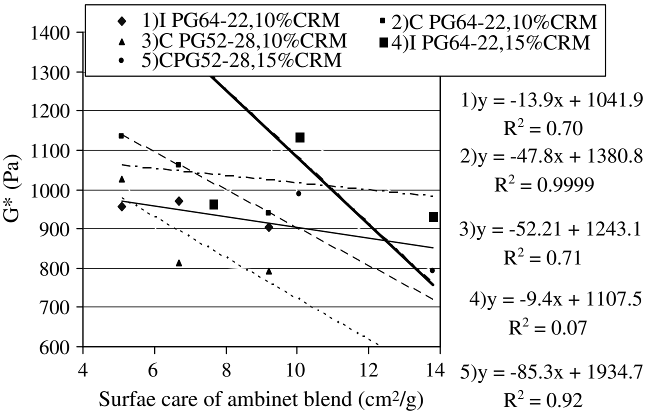

Fig. 7. G* versus surface area of ambient blends.

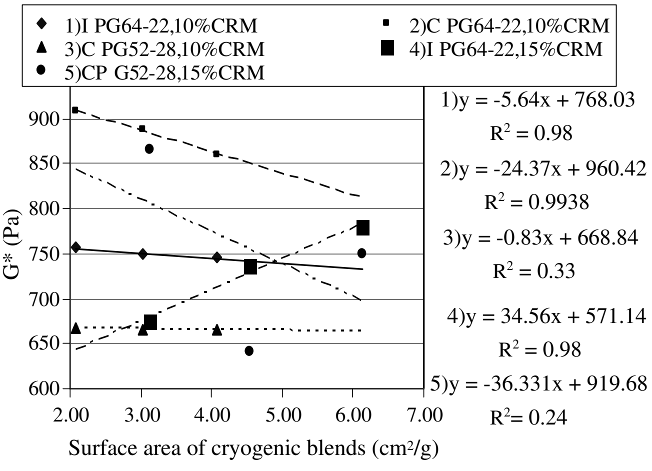

Fig. 8. G* versus surface area of cryogenic blends.

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Table 9
Regression of the DSR parameters with average diameter (*D*) and surface area (*A*)

Source		Regression equations	
Rubber	Binders	15% CRM	
Ambient	I PG64-22	$\delta = 42.0 + 0.035D + 2.1A$	$G^* = 2601 - 1.69D - 85.36A$
	C PG64-22	$\delta = 60.7 + 0.0057D + 0.97A$	$G^* = 3776 - 1.33D - 107.6A$
	C PG52-28	$\delta = 48.4 + 0.012D + 1.97A$	$G^* = 739.5 + 1.34D - 15.7A$
		10% CRM	
	I PG64-22	$\delta = 63.9 + 0.016D + 1.59A$	$G^* = 1306.6 - 0.30D - 33.05A$
	C PG64-22	$\delta = 77.8 - 0.002D + 0.47A$	$G^* = 1371 + 0.0085D - 42.6A$
	C PG52-28	$\delta = 82.3 - 0.011D + 0.30A$	$G^* = 216 + 1.16D + 32.0A$
		15% CRM	
Cryogenic	I PG64-22	$\delta = 88.8 - 0.0037D - 0.42A$	$G^* = 733.5 - 0.16D + 14.0A$
	C PG64-22	$\delta = 47.7 + 0.027D + 4.69A$	$G^* = 5255.5 - 2.76D - 535.5A$
	C PG52-28	$\delta = 990.56 - 0.005D - 1.11A$	$G^* = -1311.9 + 2.23D + 246.4A$
		10% CRM	
	I PG64-22	$\delta = 88.87 - 0.00374D - 0.42A$	$G^* = 1681.6 - 0.89D - 175.5A$
	C PG64-22	$\delta = 66.8 + 0.015D + 3.4A$	$G^* = 2555.1 - 1.55D - 321.1A$
	C PG52-28	$\delta = 82.7 + 0.0017D + 0.76A$	$G^* = 1597.5 - 0.9D - 173.4A$

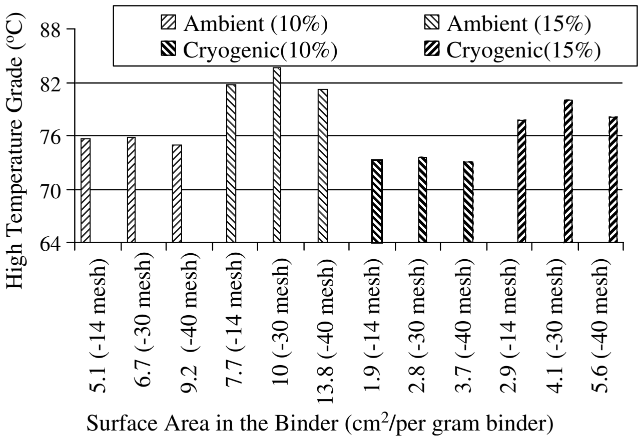

Fig. 9. High temperature grades of modified binders (base binder PG64–22).

3.3. High temperature grade

Fig. 9 shows the high temperature grade of the CRM binders with the surface area of CRM blends contained, which were obtained from DSR tester on CRM binders in original state. This figure indicated the relationship between the high temperature grade and the surface area contained in the binder, however, actually reflected the size effect again, including the surface area and the average diameter of the CRM blends. It could be found that the binders modified by ambient CRM blends have a higher temperature grade of about 3 °C than those modified by cryogenic CRM. This increase was caused by the higher surface area of ambient CRM blends.

4. Summary and conclusions

The size effect of CRM on the high temperature properties of CRM binders was investigated using the surface area of the CRM and the average size of the rubber blends. Surface areas were measured using the BET for the two types of CRM (ambient and cryogenic) of various size blends. Statistical analysis was conducted for investigating the influence of the blend variables on the DSR results, between the DSR parameters and the surface area and the average size of the CRM blends. The following conclusions can be drawn from this study:

1. The ambient CRM particle has a surface area approximately twice as large as that of the cryogenic one, leading to an ambient blend having 2.5 times the surface area of the cryogenic blend. This is because the ambient blend has more fine particles that cryogenic one.
2. The phase angle increased as the surface area of the CRM blends increased when using the same type of CRM for most of the cases discussed. The phase angle decreased as the average diameter of the CRM blends increased. In other words, CRM blend with a larger size produced better elasticity properties of the CRM binder.
3. The G^* of the CRM binders increased as the average diameter of the CRM blends increased, and decreased as the surface area of the CRM blends increased. In other words, CRM blend with larger size produced bigger complex modulus, i.e., better rutting resistance.
4. The high temperature grade of ambient CRM modified binders was about 3 °C higher than that of cryogenic CRM modified binders for the same mesh size. This is the results from the more interaction between ambient CRM with the binder since ambient CRM blend has a bigger surface area.
5. Average diameter of CRM blend was a more influential factor to both the phase angle and the complex modulus than surface area, although surface area affected these two parameters. That is true for both types of CRM.

6. The influence of both surface area and average size on the phase angle and complex modulus was not true for all individuals' cases of the 108 CRM binders discussed in the study. It may be necessary to enlarger the sample size, especially binder sources with sufficient oil fraction, to confirm the complete absorption of oil into the rubber particles.

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