

Influence of Starch on the Properties of Carbon-Black-Filled Styrene–Butadiene Rubber Composites

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ABSTRACT: The influence of starch on the properties of carbon-black-filled styrene–butadiene rubber (SBR) composites was investigated. When the starch particles were directly melt-mixed into rubber, the stress at 300% elongation and abrasion resistance decreased evidently with increasing starch amount from 5 to 20 phr. Scanning electron microscopy observations of the abrasion surface showed that some apparent craters of starch particles were left on the surface of the composite, which strongly suggested that the starch particles were large and that interfacial adhesion between the starch and rubber was relatively weak. To improve the dispersion of the starch in the rubber matrix, starch/SBR master batches were prepared by a latex compounding method. Compared with the direct mixing of the starch particles into rubber, the incorpora-

tion of starch/SBR master batches improved the abrasion resistance of the starch/carbon black/SBR composites. With starch/SBR master batches, no holes of starch particles were left on the surface; this suggested that the interfacial strength was improved because of the fine dispersion of starch. Dynamic mechanical thermal analysis showed that the loss factor at both 0 and 60°C increased with increasing amount of starch at a small tensile deformation of 0.1%, whereas at a large tensile strain of 5%, the loss factor at 60°C decreased when the starch amount was varied from 5 to 20 phr. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2254–2260, 2009

Key words: composites; mechanical properties; viscoelastic properties

INTRODUCTION

As far as the mechanical properties (tensile strength, stiffness, abrasion resistance, fatigue resistance, etc.) are concerned, most elastomers would be of no practical value if they were not reinforced. For many years, fine nanosized particles of carbon black (CB) and, more recently, silica have been incorporated into rubber compounds at about a 20–25% volume concentration to provide major improvements in the physical mechanical properties. Why do CB and silica confer outstanding reinforcement compared to fillers with larger particle sizes? Some simple general criteria, which emphasize the importance of particle size, structure, and surface activity, have been commonly accepted. The concept that the size of the reinforcing particle is the primary factor in rubber

reinforcement and that such materials were nanocomposites was first introduced around 2000.^{1,2} The reinforcing effect of CB and silica is attributed primarily to their very small particle size, which is on the order of nanometers rather than micrometers. However, CB is derived from petroleum resources, and the incorporation of CB and silica into rubbers is very energy-consuming. To reduce the dependence on petroleum resources and energy consumption, the development of new kinds of reinforcing fillers that could replace CB has attracted increasing interests in recent years. Starch, obtained from renewable resources, is of great potential because of its low cost, abundant supply, and environmental amity. Goodyear Tire Co., for example, uses a new starch-based material called BioTRED to partially replace CB and silica to reduce tire weight and rolling resistances and simultaneously decrease the energy consumption in the production processes.^{3–5} However, starch particles are about 5–20 μm ,⁶ which is in the nonreinforcing filler range for rubber, and with a lot of hydroxyl groups on its surface, starch is extremely polar; this leads to low interaction with nonpolar rubbers applied for the tire tread, such as styrene–butadiene rubber (SBR) and natural rubber,

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TABLE I
Compositions of the CB/SBR Composites with Starch (phr/100 phr Rubber)

	Sample				
	S0/WS0	S5/WS5	S10/WS10	S15/WS15	S20/WS20
CB	60	55	50	45	40
Starch	—	5	10	15	20
Zinc oxide	3	3	3	3	3
Stearic acid	2	2	2	2	2
Accelerator CZ	1.36	1.36	1.36	1.36	1.36
Sulfur	1.7	1.7	1.7	1.7	1.7
Aromatic oil	6	6	6	6	6
Antioxidant 4010NA	1.0	1.0	1.0	1.0	1.0
Antioxidant RD	1.0	1.0	1.0	1.0	1.0
Paraffin wax	1.0	1.0	1.0	1.0	1.0

4010NA, CZ, and RD are trade names. CZ, N-cyclohexyl-2-benzothiazyl sulfonamide; RD, polymerized 2,2,4-trimethyl-1,2-dihydroquinoline; 4010NA, N-isopropyl-N'-phenyl-p-phenylene diamine.

which makes it difficult to finely disperse starch in the rubber matrix.

To achieve a fine dispersion of starch in the rubber matrix, we developed a novel dispersion technique: the compounding of rubber latex with starch paste and then cocoagulation of the mixture;⁷ we call this the *latex compounding method* (LCM). In LCM, the size of starch granules in rubber matrices was greatly reduced to smaller than 1 μm , and the starch/rubber composites exhibited better mechanical properties relative to the corresponding starch/rubber composites prepared by direct blending.⁶ In the meantime, with LCM, starch/rubber master batches can be obtained. Compared with the common method of mixing the filler into rubber by mechanical shear force, LCM saves energy. To improve the interfacial strength between the polar starch and nonpolar rubbers, resorcinol-formaldehyde resin and silane coupling agents were used to *in situ* modify starch/SBR composites prepared by LCM,^{8,9} and the tensile strength of a starch/SBR composite containing 10 phr starch modified *in situ* with resorcinol-formaldehyde and N- β (aminoethyl)- γ -aminopropyl trimethoxy silane reached up to 16.4 MPa, which was an improvement of about sixfold.

In this study, we investigated the structure and properties of CB/SBR composites containing starch/SBR master batches prepared by LCM, in which starch was used to partially replace CB, and the starch amount ranged from 5 to 20 phr. We expect that this study should promote the research of developing starch into a reinforcing filler for rubber.

EXPERIMENTAL

Materials

SBR latex (23% starch) was received from Jilin Petrochemical Co. (Jilin City, China); corn starch (100%

amylopectin, 12 wt % moisture content) was from Changchun Dacheng Special Corn Modified Starch Development Co., Ltd. (Changchun, China).

Preparation of the starch/SBR master batch and CB/SBR composites with starch

About a 5% starch aqueous suspension was stirred at 90°C in a water bath for 1 h until the solution became transparent. When the solution was cooled to ambient temperature, a starch paste was obtained. Starch paste and the rubber latex were mixed and stirred vigorously for 0.5 h, and then, about a 2 wt % calcium chloride aqueous solution was added to cocoagulate the SBR latex and starch paste. The coagulum was then washed several times with water and dried in an oven at 80°C for 18 h to a moisture content of about 10%. The starch/SBR master batch was then obtained.

The compounds were mixed with a two-roll mill at 50–60°C by a standard procedure; the compositions are shown in Table I. The total amount of starch and CB (N234, the type of carbon black) was 60 phr. Samples were named according to the following scheme: S stands for direct-blending starch, and WS stands for a starch/SBR master batch; the number after the letter(s) represents the starch content. The compounds were vulcanized for the optimum cure time [i.e., the time needed to achieve 90% of the cure (t_{90})] at 150°C under 15 MPa pressure, and t_{90} was measured with a disk rheometer (P355B2, Beijing Huanfeng Chemical Industry Machine Experiment Factory, Beijing City, China).

Characterization

Scanning electron microscopy (SEM) images were taken of the abrasion surfaces of composites with an

TABLE II
Properties of the CB/SBR Composites with Different Starch Loadings

	Sample				
	S0	S5	S10	S15	S20
t_{90} (min)	11.27	11.40	11.91	11.60	11.20
Shore A hardness	76	73	72	70	69
Stress at 300% (MPa)	17.9	13.1	10.0	8.1	6.9
Tensile strength (MPa)	27.9	26.2	26.1	25.1	23.2
Elongation at break (%)	460	670	848	919	922
Permanent set (%)	10	14	16	18	18
Tear strength (kN/m)	42.7	43.0	45.9	40.7	39.4
Akron abrasion (cm ³ /1.61 km)	0.0516	0.0738	0.1214	0.1484	0.2221

S-250-III scanning electron microscope from Cambridge Corp. (Cambridge, UK).

When rolling, a tire is deformed by the load exerted on it. This repeated deformation causes energy loss, which is mainly due to the viscoelastic properties of the rubber compounds used to make the tire. The surface deformation of a tire is responsible for grip, and it occurs at frequencies between 10^4 and 10^6 Hz because of the roughness of the road surface. According to the time–temperature equivalent principle, the loss factor ($\tan \delta$) of the composite at 0°C and 10 Hz can be used to characterize the grip; the structural deformation of a tire is responsible for its rolling resistance and it occurs every time the wheel completes a full revolution. The frequency range is 10–150 Hz according to the velocity; the strain of the tire rubber compounds varies within the range 0–15% (the typical value for cars and trucks). The $\tan \delta$ of the composite at 60°C and 10 Hz can be used to characterize the rolling resistance. So, the dynamic viscoelastic properties of the composites were investigated with a rubber processing analyzer (RPA 2000, Alpha Technological Co., Ltd., Akron, OH) and a dynamic mechanical thermal analyzer (DMTA V, Rheometrics Science Corp., Piscataway, NJ)

The dynamic storage modulus (G') and $\tan \delta$ of the composites as a function of strain were measured with the RPA 2000. A strain sweep from 0.28 to 100% was operated at 60°C and 10 Hz.

$\tan \delta$ of the vulcanizate as a function of the temperature was measured by dynamic mechanical thermal analysis (DMTA) in the tension mode at 10 Hz and $3^\circ\text{C}/\text{min}$; in the temperature range -100 to 0°C , the strain was 0.01%; in the temperature range 0 – 100°C , the strain was 0.1 or 5%.

RESULTS AND DISCUSSION

Properties of the CB/SBR composites containing direct-blending starch particles

The properties of the CB/SBR composites containing direct-blending starch particles are presented in Ta-

ble II. The t_{90} values of five samples remained almost the same, which indicated that the incorporation of starch had little effect on the vulcanizing behavior of the composites. With increasing starch content, the hardness, stress at 300%, tensile strength, and abrasion resistance decreased, as expected. The cause was that starch particles remained almost the same size as the original, about 5–20 μm , in the nonreinforcing filler range for rubber, much larger than the size of the CB particles. The elongation at break and permanent set increased with increasing starch content.

SEM micrographs of the abrasion surfaces of samples S0, S5, S10, S15, and S20 are shown in Figure 1. With increasing starch loading, the number of holes left by the starch particles on the surface of the composites increased, and the surface became more uneven; this suggested that the interfacial strength between the starch and rubber matrix was weak. To improve the properties of CB and starch filled with SBR, starch/SBR master batches instead of directly mixed starch were incorporated into the CB/SBR system.

Properties of the CB/SBR composites containing starch/SBR master batches

The properties of the CB/SBR composites containing starch/SBR master batches are presented in Table III. The addition of starch/SBR master batches prolonged the curing time of the composites, which was different from the incorporation of directly mixed starch particles. This may have been due to the fact that the surfaces of the smaller starch particles had more hydroxyl groups exposed with the starch/SBR master batches and absorbed curing agents. With the increase in the starch content, the hardness, stress at 300%, and tensile strength decreased; this was the same trend that the composites containing directly mixed starch exhibited, but it seemed to go down more steeply. A possible explanation is the decrease in the crosslinking density of the composites

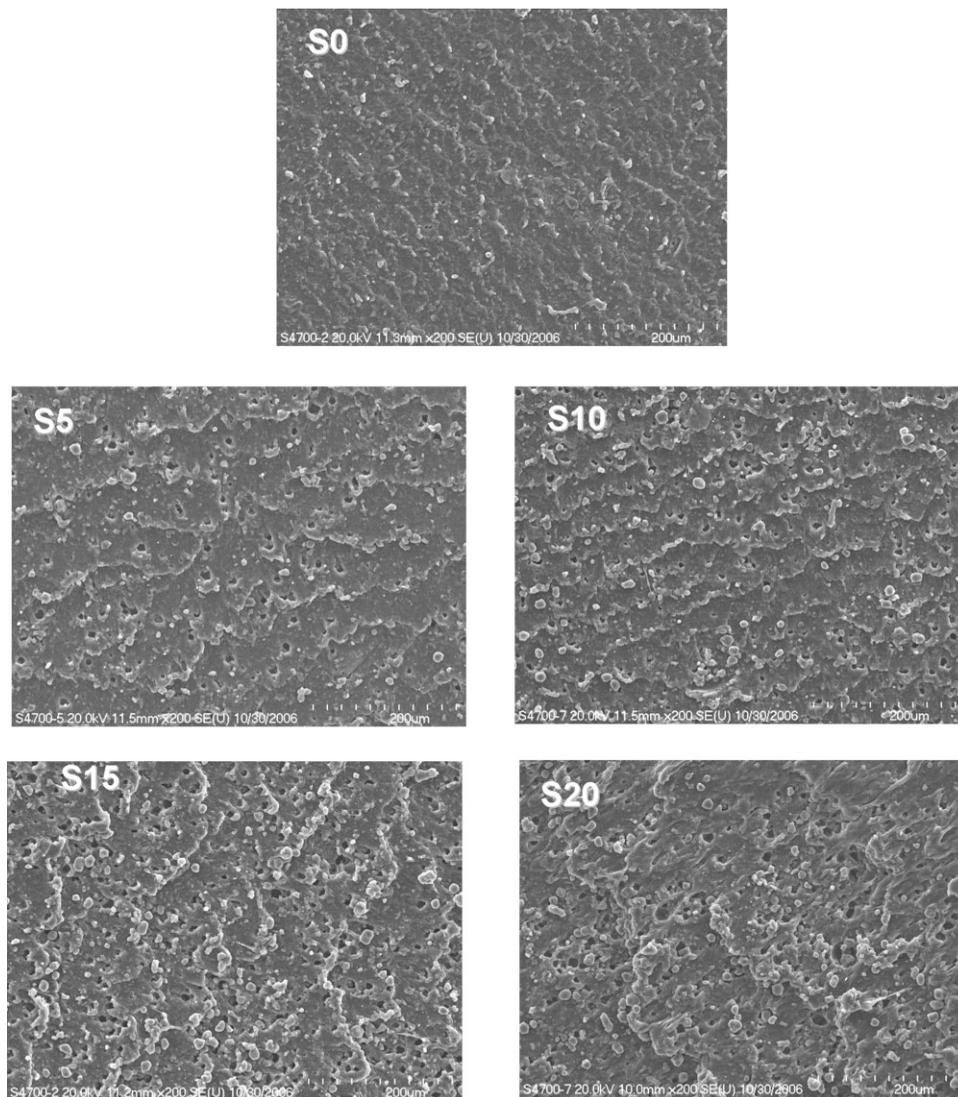


Figure 1 SEM micrographs of abrasion surfaces of S0, S5, S10, S15, and S20.

with starch/rubber master batches, as discussed previously.

The abrasion properties of the CB/SBR composites with starch/SBR master batches are presented in Figure 2. Similar to the composites with directly

blended starch, the abrasion resistance of the composites containing starch master batches decreased with increasing starch content. The abrasion properties of the composites with starch/SBR master batches was improved relative to the corresponding

TABLE III
Mechanical Properties of the CB/SBR Composites with Starch/SBR Master Batches

	Sample				
	WS0	WS5	WS10	WS15	WS20
t_{90} (min)	11.15	15.87	16.88	17.92	19.28
Shore A hardness	78	75	72	70	69
Stress at 300% (MPa)	17.1	10.3	7.7	6.6	4.7
Tensile strength (MPa)	25.0	23.6	22.3	20.6	19.4
Elongation at break (%)	441	618	658	665	728
Permanent set (%)	12	24	24	24	30
Tear strength (kN/m)	57.7	55.9	56.1	51.6	47.3

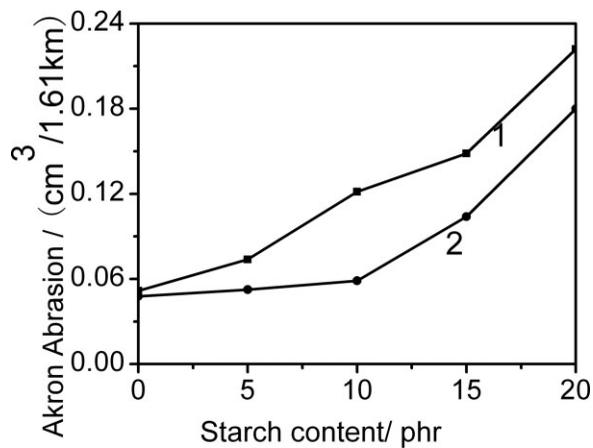


Figure 2 Abrasion properties of CB/SBR composites with different starch loadings: (1) direct-mixing starch and (2) starch/SBR master batches.

composites containing an equivalent amount of directly blended starch.

SEM micrographs of the abrasion surfaces of the composites of WS0, WS5, WS10, WS15, and WS20 are shown in Figure 3. With increasing starch loading, the surface became rougher. In contrast to the surfaces of the composites of S5, S10, S15, and S20, there were no evident holes of starch on the surfaces of WS5, WS10, WS15, and WS20. This could be attributed to the reduced size of the starch particles and the increased interactions between the starch particles and the rubber matrix.

The curves of G' versus strain of the WS0, WS5, WS10, WS15, and WS20 vulcanizates are presented in Figure 4. As shown in Figure 4, G' decreased with increasing starch loading, as expected, and correspondingly, the drop in G' with increasing strain became smaller with composites containing a higher

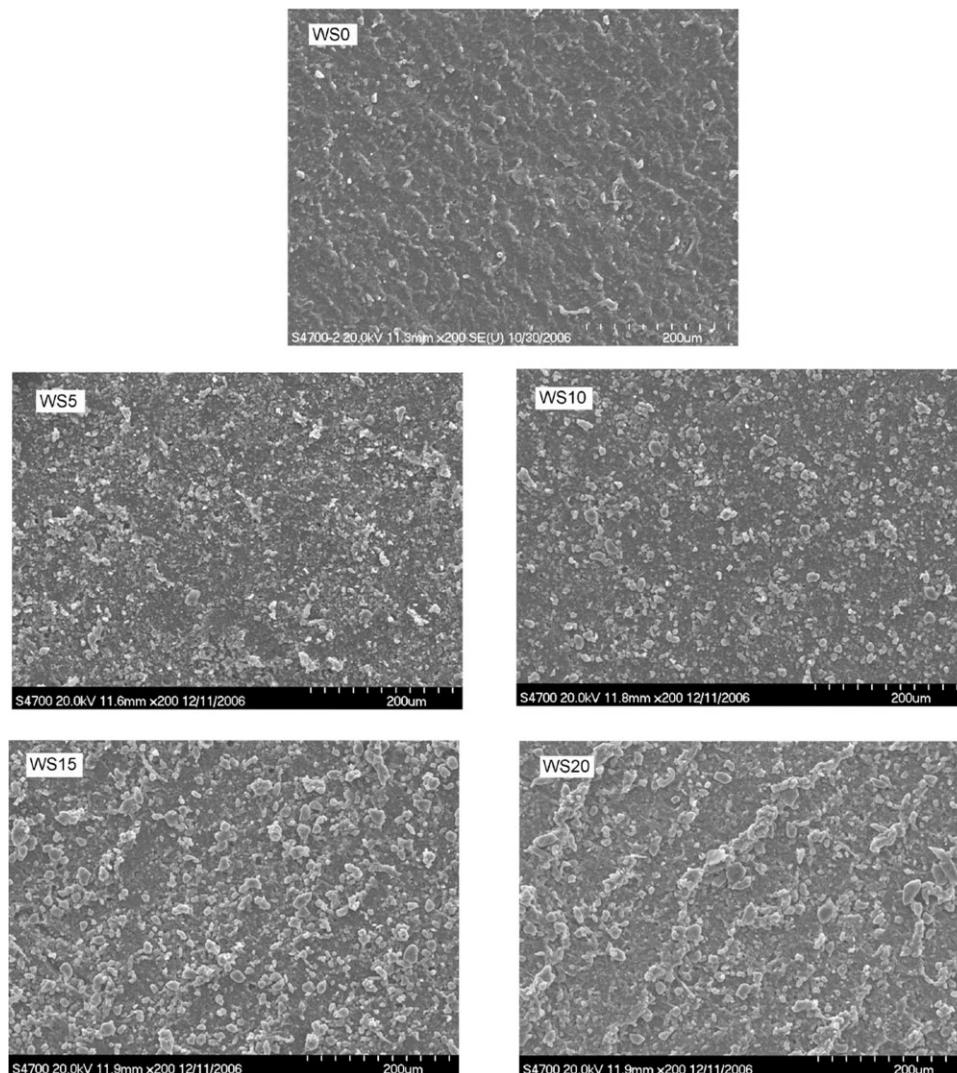


Figure 3 SEM micrographs of abrasion surfaces of WS0, WS5, WS10, WS15, and WS20.

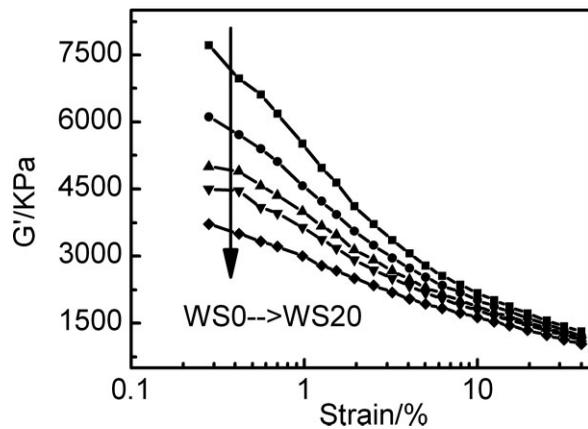


Figure 4 Curves of G' versus the strain for WS0, WS5, WS10, WS15, and WS20 tested with the RPA 2000.

amount of starch. This could be explained by the fact that most of the starch particles were not on a nanometer scale, and correspondingly, the filler network composed of starch and CB became weaker with increasing starch loading. In fact, the drop in the composite G' with increasing strain was related to energy dissipation, and the smaller drop amplitude indicated reduced energy dissipation.

The curves of $\tan \delta$ versus the strain of the WS0, WS5, WS10, WS15, and WS20 vulcanizates are presented in Figure 5. With increasing starch loading, $\tan \delta$ decreased in the shear deformation range of about 1–20%. This suggests that the addition of starch into tire tread should decrease the rolling resistance.

The curves of $\tan \delta$ versus the temperature for the WS0, WS5, WS10, WS15, and WS20 vulcanizates as tested by DMTA at a tensile strain of 0.1% are shown in Figure 6, and the glass-transition temperature (T_g) and $\tan \delta$ values at 0 and 60°C are pre-

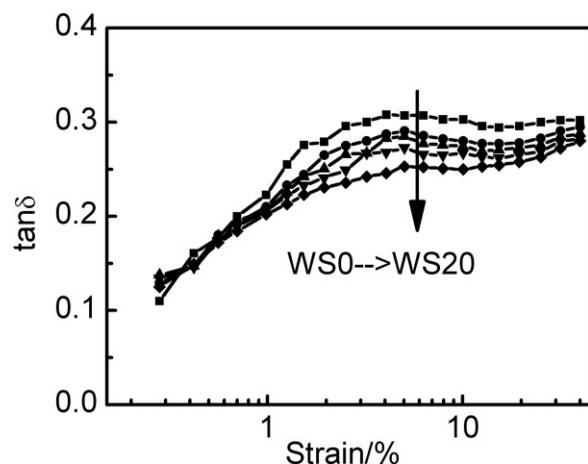


Figure 5 Curves of $\tan \delta$ versus the strain for WS0, WS5, WS10, WS15, and WS20 tested with the RPA 2000.

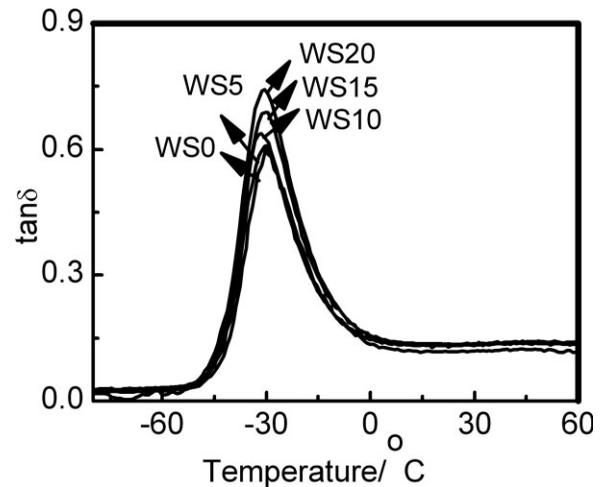


Figure 6 Curves of $\tan \delta$ versus the temperature for WS0, WS5, WS10, WS15, and WS20 at a low tensile strain.

sented in Table IV. The incorporation of starch/SBR master batches increased the $\tan \delta$ values at 0°C, which favors the improvement of the wet-grip properties of tire tread. However, the increase of $\tan \delta$ at 60°C upon starch addition was not expected, which seems to be in disagreement with the RPA 2000 results. A possible explanation could be the different deformation mode and deformation amplitude: the deformation mode during RPA 2000 measurement was shearing, and the deformation was large, whereas the tensile deformation mode was used during the process of DMTA measurement, and further, the strain was very small (0.1%). To clarify this point, DMTA measurement was carried out at a large tensile deformation of 5% in the temperature range of 10 to 100°C, and the results are presented in Figure 7. The trend of the $\tan \delta$ versus temperature curves for WS5, WS10, WS15, and WS20 was different from that of WS0. This may have been due to the combined results of the following two aspects. With decreasing CB amount, the filler network became weaker, and the fraction from filler to filler decreased, which led to a decreased $\tan \delta$; on the other hand, with the increase in starch content, the viscoelastic behavior of starch could have

TABLE IV
 T_g and $\tan \delta$ Values of the CB/SBR Composites with Starch/SBR Master Batches

	Sample				
	WS0	WS5	WS10	WS15	WS20
T_g (°C)	-30.2	-29.7	-31.5	-29.6	-30.4
$\tan \delta$ at T_g	0.6024	0.6093	0.6380	0.6885	0.7423
$\tan \delta$ at 0°C	0.1348	0.1466	0.1472	0.1550	0.1552
$\tan \delta$ at 60°C	0.1178	0.1351	0.1348	0.1364	0.1392

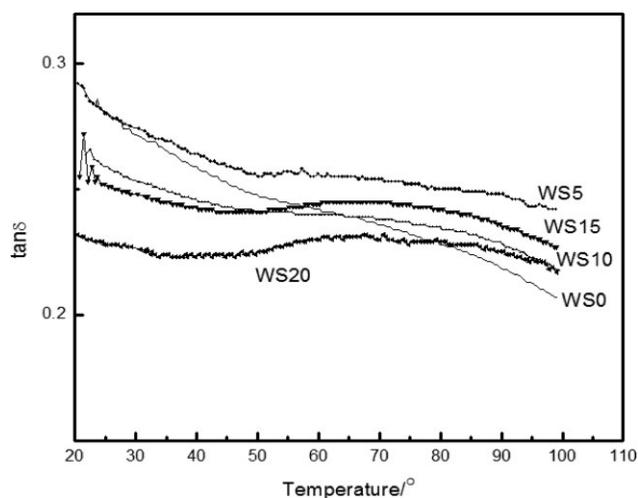


Figure 7 Curves of $\tan \delta$ versus the temperature for WS0, WS5, WS10, WS15, and WS20 at a high tensile strain of 5%.

contributed to the increased $\tan \delta$ because starch is a polymeric filler. As shown in Figure 7, when the starch amount was varied from 5 to 20 phr, $\tan \delta$ decreased, which was consistent with the RPA 2000 results.

CONCLUSIONS

Starch/SBR master batches were prepared by LCM. Compared with the direct mixing of starch particles

into rubber, the application of starch/SBR master batches improved the abrasion resistance of CB-filled SBR composites because of the fine dispersion of starch. Under the condition of small tensile deformation, $\tan \delta$ at both 0 and 60°C increased with increasing amount of starch, whereas in the shearing deformation range of 2–20 or 5% tensile deformation, $\tan \delta$ at 60°C decreased with increasing starch content.

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