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Investigation of the Effects of Adhesion Promoters on the Adhesion Properties of Rubber/Steel Cord by a New Testing Technique

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ABSTRACT: The effects of adhesion promoters, cobalt decanoate and PN759 (modified resorcinol) on the static and dynamic adhesion properties of rubber/steel cord in a carcass recipe are examined. A new testing method with special rubber/steel cord specimens was developed. It was found that cobalt decanoate could improve the static adhesion and favored the dynamic adhesion of rubber/steel cord so that adhesive failure mainly occurred in rubber phase. A resorcinol-formaldehyde-silica promoting system was deleterious to adhesion stability, but improved initial adhesion strength. PN759 improved the dynamic mechanical properties compared with resorcinol for the carcass vulcanizates at strains less than 10%. PN759 instead of resorcinol slightly improved the static and dynamic adhesion and the probability that adhesion failure occurred in the interphase was similar to that occurring in the rubber phase. The dynamic "pull-out forces" for samples with 1.0 phr cobalt decanoate first increased and then decreased with the increase in the number of fatigue cycles and reached a maximum at 100,000 fatigue cycles. The covered rubber on the "pulled-out" cord after fatigue appeared to form a screw thread form and the greater pull-out force corresponded to more uniform and narrower screw threads. SEM images indicated that un-dispersed filler agglomerates could be the initiating factor for adhesive failure. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

INTRODUCTION

The Carcass and the bead are the major load-bearing structures of tires; they help to sustain inflation pressure, they carry the load, counteract impact, and cope with horizontal stress. Thus, it is very important that steel cord, as the framework material in the carcass, has excellent adhesion to the rubber compound. Van Ooij et al. found that copper sulfide (CuxS) and zinc sulfide formed during vulcanization in the rubber/steel cord interface, where CuxS, chemically bonded with cured rubber, formed CuxS–Sx–rubber sulfide bridges to achieve adhesion. Thus, CuxS was necessary and crucial for adhesion and zinc sulfide or zinc oxide with semiconductor properties was a key factor for adjusting the amount of copper and sulfur for CuxS.[1–5] CuxS with a high surface area in the adhesion interphase is necessary for the mechanical interlocking of the rubber compound to the brass-plated steel cord, but an adverse effect is observed with an excess of the copper sulfide layer.[6] Although the initial adhesion strength is significant, hysteresis effects and heat build-up are also important, due to the inherent viscoelasticity of rubber with severe dynamic stress in tire service which decrease adhesion with time. In addition, the rubber compound matrix degrades and stiffens due to thermal, oxygen, and humidity ageing and these effects accelerate ageing of the adhesion interface.[6–10] Thus, the adhesion of rubber to steel cord is crucial for driving safety and the service life of tires.

Initial adhesion and adhesion retention of rubber compounds to brass-plated steel cord are particularly significant in radial tires. Although many researchers have attempted to study the influence of adhesives on rubber/steel cord adhesion properties,[11,12] most researches have concentrated on static adhesion without simulating the loading and fatigue life during real service conditions. Jamshidi[13] evaluated the dynamic adhesion from the static adhesion in the model cord–RFL–rubber system. Brantseva[14] created a new device for studying the dynamic adhesive strength in fiber–polymer systems under impact loading ("Pull-out" technique), the interface between polymer and steel wire was formed by polymers of different chemical nature (epoxy resin, polysulfone). Chandra[15] developed a new dynamic test for steel cord/rubber adhesion using a Monsanto Fatigue-to-Failure Tester and cord pull-out tests were conducted before and after cyclic extension.

This article introduces a novel testing technique for the dynamic adhesion of rubber/cord by first summarizing the

Table I. Recipes of Rubber Compounds

Component	Chemical or trade name	Content (phr)[a]
Natural rubber	SCR5	100
Peptizer	B	0.3
Carbon black	N326	55
Silica	175GR	10
Activator	ZnO	8
Activator	Stearic acid	1
Antioxidant	4010NA	1
Antioxidant	RD	1.5
Accelerator	CBS	1.2
Adhesion promoter	HMMM	5
Insoluble sulfur	S	5

[a] Parts per hundred polymer.

advantages/disadvantages of existing test methods. The new method focuses on simulating the cyclic loading of carcass in the real service. It is very simple, reliable, and does not require extra capital investment.

EXPERIMENTAL

Major Experimental Materials

Natural rubber (SCR5), Hainan Rubber Industry Group, China; Carbon black (N326, CTAB surface area: 120 m^2/g), Cabot Corporation; Silica (175GR, CTAB surface area: 150~180 m^2/g), Rhodia, France; HMMM (Hexamethoxy methyl melamine, $C_{15}H_{30}N_6O_6$), Fujian Qianning Additives, China; Cobalt decanoate ($C_{20}H_{38}O_4Co$, Co: 20–21 wt %), Shepherd Company; PN759 (Phenol–formaldehyde resin), Shanghai Qixiang Chemical, China; Steel cord (3 + 8 × 0.33 HT, Plating composition: 63.5 ± 1.0% Cu, 36.5 ± 1.0% Zn), Bekaert in Belgium; Other chemicals included Peptizer (B), 4010NA (N-isopropyl-N'-phenyl-p-

phenylene diamine), RD [poly(1,2-dihydro-2,2,4-trimethyl-quino-line)], CBS (N-cyclohexyl-2-benzothiazole-sulphenamide) and in-soluble sulfur were purchased from the market.

Formulations

The basic recipes for the rubber compounds are shown in Table I, the contents of other adhesion promoters are variable.

Specimen Preparation and Testing

Rubber Compound Preparation. The master batches were mixed using an internal mixer (XSM-500, Ke Chuang, China) according to ASTMD-3184. The ingredients (except the cura-tives and partial adhesives) for master batches were mixed for 8.5 min at a rotor speed of 55 rpm and 60°C and dumped at about 120°C; the final batch (including CBS, Sulfur, and HMMM) was mixed using a 2-roll mill (BL-6175, Bolon, China) for 5 min and finally re-milled into flat sheets for press curing.

Vulcanization Characteristics and Physical Mechanical Prop-erties. Rheocurves were recorded using rheometer (MDR2000, Alpha Technology) at 151°C according to ASTMD-3182. The curing was carried out on a cure press (VC-150T-FTMO-3RT, Jiaxin Electric Company, China) at 151°C for a time to allow for tc90.

The Shore A hardness was measured using a durometer (LX-A, Mingzhu, China) according to ASTMD-2240.

Tensile properties were measured using a Universal Material Tester (Z020, Zwick, Germany) with a crosshead of 500 mm min^{-1} according to ASTMD-412.

The crosslink density was measured using a NMR Crosslink Density Spectrometer (MR-CDS3500, Dr. Kuhn Innovative Imaging Corporation, Germany).

Dynamic Mechanical Properties. Strain sweeps were carried out using a rubber process analyzer (RPA2000, Alpha Technology) with strain range of 0.28–100% at 60°C and a frequency of 1 Hz.

Rubber/Steel Cord Specimens Preparation and Adhesion Test: A New Testing Technique. Brass-plated steel cord: 3 + 8 × 0.33 high tensile (HT), the steel cord surface was cleaned with ethanol.

Rubber/steel cord specimens are shown in Figure 1. The dimen-sions of the rubber bars prepared by compression molding (see above) were 12.5 × 12.5 × 195 mm.

The dynamic adhesion test is shown in Figure 2. The specimens were subjected to flex fatigue with tension deformations of 4.0 mm at room temperature. After a certain number of tensile fa-tigue cycles, the steel cords between the two rubber bars were immediately cut into two equal lengths and the T-pull-out forces measured using a Zwick tensile tester at a crosshead speed of 50 mm/min according to ASTM-2229. The average "pull out force" was considered as the result.

Observation of Covered Rubber on the "Pull-out" Cord. The rubber remaining on the "pulled-out" cord surface was exam-ined using a stereoscopic zoom microscope (SMZ1500, Nikon Corporation, Japan). Three steel cords from each specimen were chosen for micrographing.
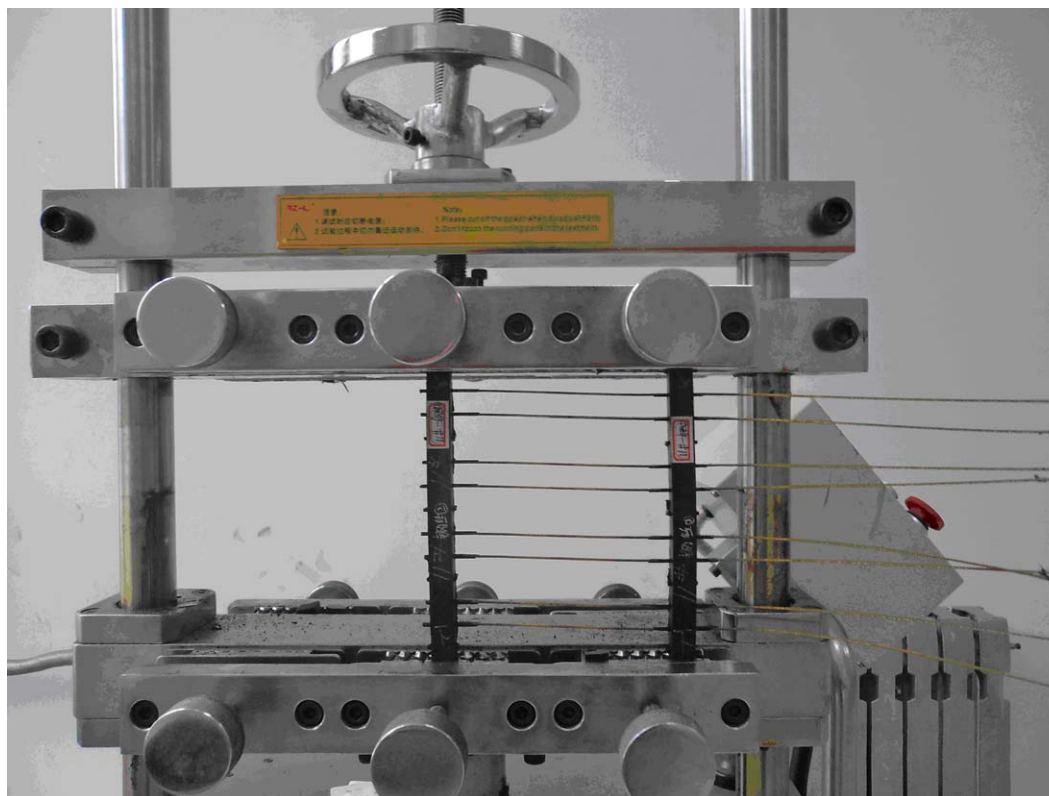

Figure 1. Rubber /steel cord specimen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. Dynamic flex fatigue testing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scanning Electron Microscopy (SEM). The surfaces of cured rubber torn from steel cord were observed by scanning electron microscopy (SEM; JSM-7500F, JEOL, Japan) to investigate changes to the interfaces between rubber and steel cord after flex fatigue. The surfaces were coated with gold prior to examination.

RESULTS AND DISCUSSION

The effects of adhesion promoter cobalt decanoate, a methyl acceptor PN759, and the dynamic fatigue cycles on the adhesion properties of rubber/brass-plated cord were examined.

Effects of Cobalt Decanoate Contents on Adhesion Properties
The adhesion promoter, cobalt, has been reported to retard the formation of zinc sulfide and stimulate the formation of CuxS, which should improve both initial adhesion and adhesion retention.[16] Using the basic formulation for the rubber compound given in the "Formulations" Section the addition of cobalt decanoate was varied from 0 phr to 3.0 phr.

Table II. Carcass Compound Properties with Different Cobalt Decanoate Loadings

| Cobalt decanoate (phr)	0	1.0	2.0	3.0
Maximum torque (MH) (dN·m)	34.22	37.16	37.35	43.46
Minimum torque (ML) (dN·m)	1.91	3.17	2.78	2.57
MH-ML (dN·m)	32.31	33.99	34.57	40.89
tc10 (min)	2.90	2.86	2.99	2.81
tc90 (min)	19.78	14.15	13.41	12.26
Crosslink density by MR-CDS $\times 10^{-4}$ (mol/cm^3)	1.42	1.46	1.53	1.66
Tensile strength (MPa)	22.0	23.5	23.0	23.8
Tear strength (KN/m)	58.7	51.3	78.8	59.7
Elongation at break (%)	445	586	568	488
100% Modulus (MPa)	4.1	4.2	4.5	5.0
300% Modulus (MPa)	15.2	12.8	13.0	15.6
Hardness (Shore A)	68	77	72	74
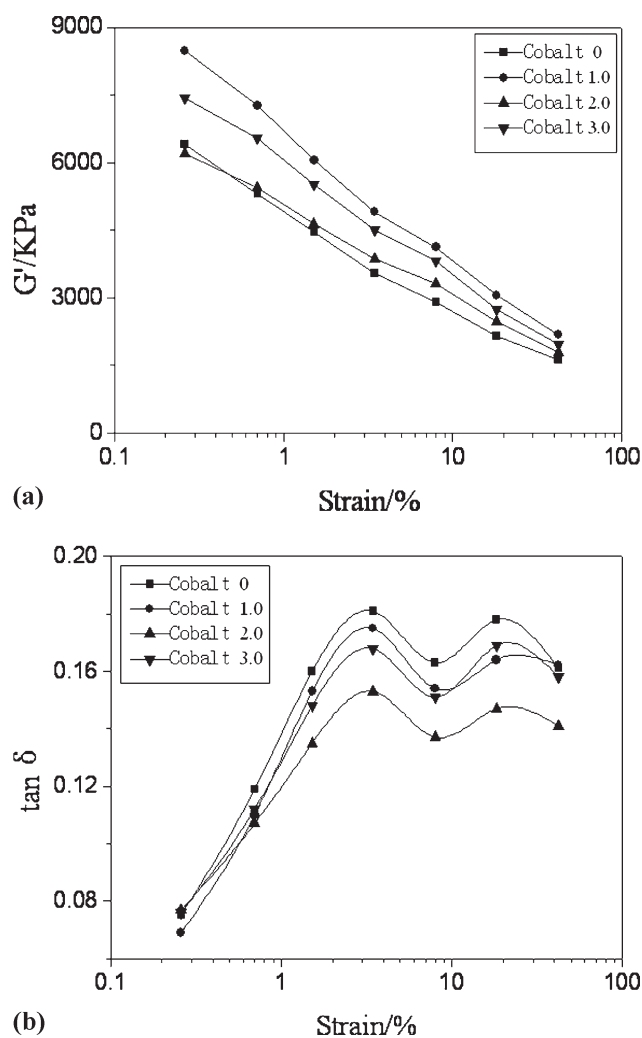
Figure 3. Dynamic mechanical properties with different cobalt decanoate loadings. (a) G' versus Stain and (b) tan δ versus Stain.

Cure Characteristics and Physical Mechanical Properties of Carcass Compound. The cure characteristics of carcass compounds with different cobalt decanoate loadings are given in _Table II. It can be seen that MH and MH-ML increased with an increase of the cobalt decanoate loading while tc90 decreased, and the tc10 remained essentially unchanged. Crosslink density measured by MR-CDS also increased as the cobalt loading increased, suggesting that cobalt decanoate had little effect on scorch safety, but improved cure rate and cure degree remarkably. Tensile strength, 100% modulus, and hardness increased by incorporating cobalt decanoate into the rubber compounds due to a significant increase in crosslink density with more single disulfide bonds.[17,18] Additionally, it is worth noting that at a cobalt loading of 2.0 phr a maximum in tear strength was achieved.

Dynamic Mechanical Properties of Carcass Vulcanizates. Storage modulus G' and loss factor tan δ as function of strain for vulcanizates with different cobalt decanoate loadings are shown in Figure 3. It can be seen that cobalt decanoate improved the modulus of the vulcanizates [Figure 3(a)] and

lowered their tan δ [Figure 3(b)]. This can be explained by the participation of cobalt decanoate in the curing process to improve the crosslink structure and crosslink density (*Vide supra*). A detailed examination of the results, shown in Figure 3, suggests that the compounds with 2.0 phr cobalt decanoate had the smallest Payne Effect and the best filler dispersion.[19–21] An improved filler dispersion should improve energy dissipation during dynamic fatigue cycles and hinder the peeling of rubber from the steel cord. Thus, the rubber compound with 2.0 phr cobalt decanoate had the best dynamic mechanical properties and should exhibit the best dynamic adhesion.

Static and Dynamic Adhesion Properties. Specimens and test results are shown in Figures 1 and 2 and described in the "Experimental" section. The number of flex cycles was fixed at 200,000. The T-pull-out forces and rubber coverage can be seen in Table III. In addition, the surfaces of pulled-out steel cords were examined by stereoscopic zoom microscope; examples are shown in Figure 5.

The amount of rubber coverage (Figure 4) was estimated and the results are given in Table III. Comparing all the "rubber coverage before fatigue" with different cobalt contents in Table III, it can be inferred that the area where the adhesive failure occurred moved from the interphase to the rubber phase as the cobalt decanoate loading increased; "rubber coverage after fatigue" showed a similar trend. This suggests that cobalt decanoate enhanced the strength of adhesion. Comparing the rubber coverage before and after fatigue, it can be seen that the samples with 0 phr cobalt showed little change, adhesive failure occurred at the interphase. The adhesive failure in the samples with 1 and 2 phr cobalt decanoate moved from the interphase to the rubber phase so that no exposed steel cord in the fatigued sample could be seen (Figure 4). These observations suggest that the addition of cobalt decanoate imparted an improved adhesion after dynamic fatigue, perhaps because ageing by hot air and humidity occurred during flex fatigue and the formation of CuxS was enhanced in the presence of cobalt decanoate.[1,2] It also can be seen in Figure 4 that rubber coverage for the samples containing cobalt decanoate appeared as a "screw thread" form. We conclude that cobalt decanoate improved the static adhesion and favored the dynamic adhesion of rubber to steel cord so that adhesion failure mainly occurred in the rubber phase.

In Table III, the "pull-out" force before dynamic fatigue is termed "Static pull-out force" and that after dynamic fatigue is called "Dynamic pull-out force." It can be seen that static pull-out force increased with an increase of the cobalt decanoate loading and the amount of rubber coverage increases. It can be inferred that the mobility of copper in the absence of cobalt decanoate is reduced and the increased relative concentration of sulfur at the interface led to the formation of CuS rather than CuxS. The former cannot form Cux–S–Sx–rubber by further reacting with –Sx–rubber. With cobalt decanoate, cobalt cations increased the mobility of both zinc and copper ions, promoting the formation of CuxS[1,6,11,22] and consequently, improved adhesion.

Table III. Adhesion Properties with Different Cobalt Decanoate Loads

Cobalt decanoate (phr)	0	1.0	2.0	3.0
Curing conditions (°C × min)	151 × 25	151 × 20	151 × 18	151 × 18
Rubber coverage before fatigue	25R[a]/75M[b]	25R/75M	50R/50M	75R/25M
Rubber coverage after fatigue	25R/75M	50R/50M	75R/25M	75R/25M
Mean static pull-out force (N)	863	1022	1030	1084
Minimum static pull-out force (N)	847	960	995	1002
Maximum static pull-out force (N)	907	1106	1071	1128
Range of static pull-out force (N)	60	146	76	126
Standard deviation(S) of static pull-out force (N)	36.78	52.72	28.76	39.07
Mean dynamic pull-out force (N)	835	996	1102	1003
Minimum dynamic pull-out force (N)	791	916	1020	934
Maximum dynamic pull-out force (N)	909	1089	1190	1110
Range of dynamic pull-out force (N)	118	173	170	166
Standard deviation(S) of dynamic pull-out force (N)	40.00	68.94	47.58	51.09
Change ratio of pull-out force (%)	−3.2%	−2.5%	+7.0%	−7.5%

[a] R indicates that adhesion failure occurred in the rubber phase; i.e., the adhesion strength of the interphase was greater than the strength of the rubber phase.
[b] M indicates that adhesion failure occurred at the interphase; i.e., the adhesion strength of interphase was less than that of the rubber phase.

It also can be seen in Table III and Figure 4 that the dynamic pull-out forces (after dynamic flex fatigue 200,000 cycles) was lower than that of the un-fatigued samples, except for the sample containing 2 phr cobalt decanoate. This suggests that for the samples without cobalt or with 1 phr cobalt, the rupture of rubber molecular and interface bonding caused by aging during dynamic fatigue dominates and the dynamic pull-out force was reduced; for the sample containing 2 phr cobalt decanoate, the formation of a layer of CuxS, as a result of hot air and humidity ageing, was promoted and the dynamic pull-out force increased. For the sample with 3 phr cobalt decanoate, the layer of CuxS and zinc oxide became too thick and the adhesion and adhesion stability[22–26] decreased, leading to a decrease in the dynamic pull-out force. The greater the pull-out force, the more pronounced was the "screw thread" form of the rubber covering the pulled-out steel cord as can be seen in Figure 5.

Effects of Resorcinol–Formaldehyde–Silica Adhesion Promoting Systems on Adhesion Properties

Conventionally, the hexamethoxy methyl melamine (HMMM, a methyl donor) and resorcinol (a methyl acceptor adhesive) resin system is the most widely used adhesion promoting system in carcass of radial tires.[27] Phenol–formaldehyde resin PN759, as a methyl acceptor, is a non-self-curing thermoplastic modified resin with a low softening point (85–102°C). PN759 is "environment-friendly" since it contains <1% of free resorcinol,[28,29] which reduces the sublimation of resorcinol during mixing and curing at high temperature. In this section, the

effects of resorcinol and PN759 on rubber/steel cord adhesion properties are reported.

Table IV. Formulations with Different Contents of Adhesives

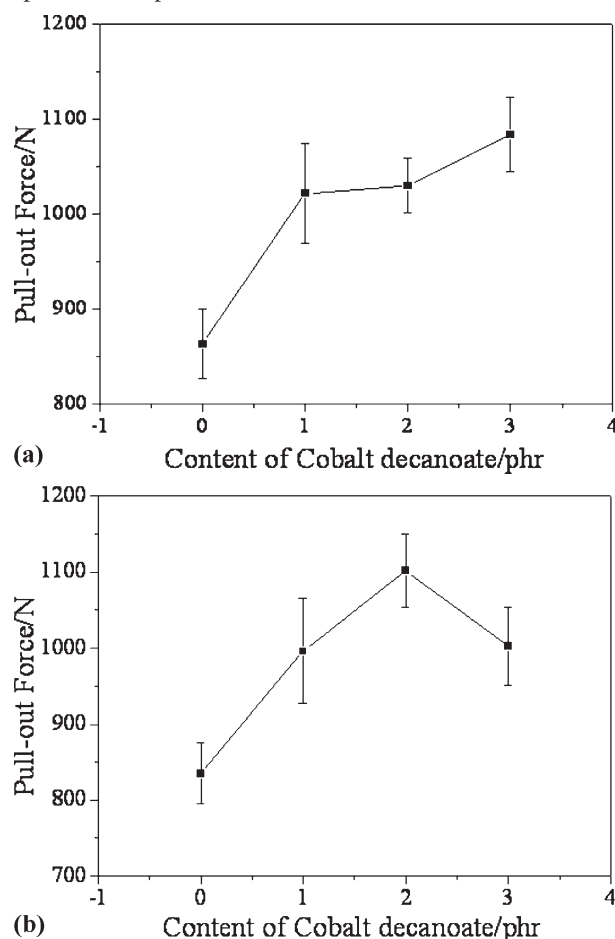| Specimen No.	1	2	3	4	5
Resorcinol (phr)	0	1.5	0	0	0
PN759 (phr)	0	0	1.5	2.0	3.0

Figure 4. Effects of cobalt decanoate contents on pull-out forces of steel cord. (a) Un-fatigued and (b) Fatigued 200,000 cycles.
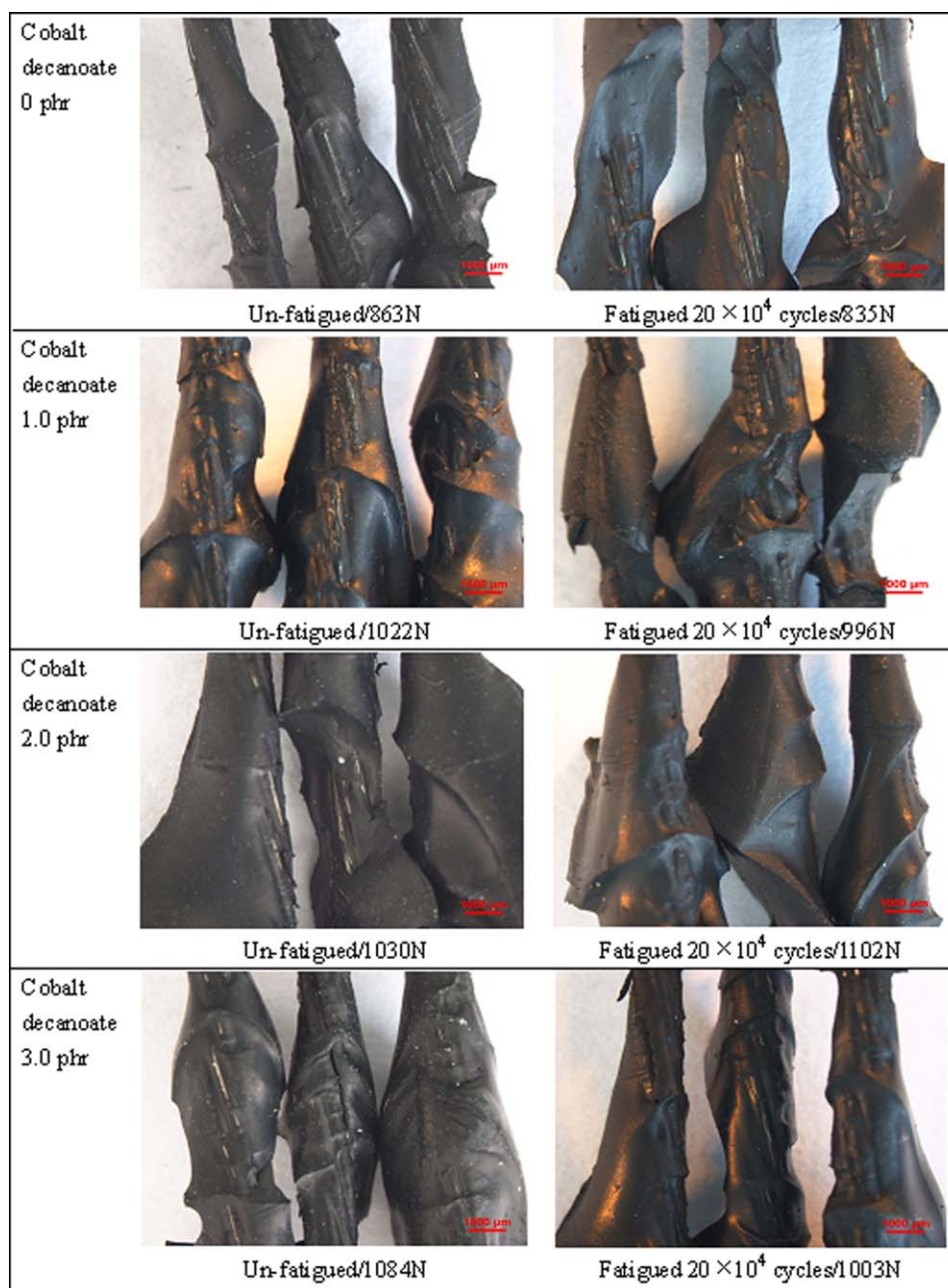
Figure 5. SZM Micrographs of rubber coverage on pulled-out steel cords with cobalt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Using the basic formulation for the rubber compound given in the "Formulations" section, the addition of resorcinol and PN759 from 0 phr to 3.0 phr (Table VI) was studied.

Cure Characteristics and Physical Mechanical Properties of Carcass Compound

The cure characteristics and mechanical properties of carcass compounds with different amounts of adhesives are shown in Table V. It can be seen that tc90 and MH–ML of the compounds increased when they included adhesive (No. 2–No. 5) but the mechanical properties of the vulcanizates were hardly affected. It is suggested that resorcinol–formaldehyde–silica

adhesion promoting systems decreased the curing rate and slightly increased crosslink density. The latter was confirmed by MR–CDS measurements. This can be explained by the adsorption effect of HMMM for amine accelerators which leads to a decreased curing rate[27] and increases the mobility of sulfur in the compound. On the other hand, the formation of linear and three-dimensional phenol–formaldehyde resin by resinification of resorcinol with HMMM increased crosslink density. In addition, the hydroxyl moiety of the phenol–formaldehyde resin can condense with methyl and C=C double bonds to form a co-vulcanizate network. This, in turn, may interpenetrate with the three-dimensional phenol–formaldehyde network.[28–30] The

Table V. Adhesion Properties of Rubber/Steel Cord with Different Adhesives

Specimen No.	1	2	3	4	5
Curing conditions (°C × min)	151×25	151×30	151×35	151×35	151×40
Rubber coverage before fatigue	25R[a]/75M[b]	50R/50M	50R/50M	50R/50M	50R/50M
Rubber coverage after fatigue	25R/75M	75R/25M	50R/50M	50R/50M	25R/75M
Static pull-out force (N)	863	1014	1040	1058	981
Minimum static pull-out force (N)	847	884	1004	969	813
Maximum static pull-out force (N)	907	1115	1107	1207	1160
Range of static pull-out force (N)	60	231	103	238	347
Standard deviation of static pull-out force (N)	36.78	92.40	36.15	77.67	130.98
Dynamic pull-out force (N)	835	922	943	873	840
Minimum dynamic pull-out force (N)	791	810	853	828	787
Maximum dynamic pull-out force (N)	909	996	1048	951	900
Range of dynamic pull-out force (N)	118	186	195	123	113
Standard deviation of dynamic pull-out force (N)	40.00	65.90	70.13	44.39	37.09
Change ratio of pull-out force (%)	−3.2%	−9.1%	−9.3%	−17.5%	−14.4%

[a] R indicates that adhesion failure occurred in the rubber phase; i.e., the adhesion strength of the interphase was greater than the strength of the rubber phase.

[b] M indicates that adhesion failure occurred at the interphase; i.e., the adhesion strength of interphase was less than that of the rubber phase.

interpenetrating network would further decrease the mobility of the sulfur.

Comparing samples No. 2 and 3 in Table V, tc90 and tc10 with PN759 were longer than with resorcinol suggesting that PN759 extended the scorch time and improved processing performance. Comparing No. 3, 4, 5 with No. 2, it can be seen that PN759 slightly improved the physical and mechanical properties of the vulcanizates.

Dynamic Mechanical Properties of Carcass Vulcanizates

The storage modulus G' and loss factor tan δ as function of strain for vulcanizates with different methyl acceptors are shown in Figure 6. It can be seen that methyl acceptor adhesives increase G', tanδ and the Payne Effect $(\Delta G')$[31,32] of the vulcanizates. We presume that although the interpenetration of a resin network

and/or crosslinked network increased the G', the complex co-vulcanizate networks had a negative effect on the uniform dispersion of fillers in the vulcanizates. Rubber compounds with PN759 rather than resorcinol had higher G' and lower tan δ at strains less than 10% and higher tan δ at strains more than 10%. This can be explained by the higher crosslink density restraining the mobility of the rubber molecules for the vulcanizates containing PN759 at lower strain and the destruction of the interpenetrating resin network at greater strain.[28,29] We conclude that PN759 imparted better dynamic mechanical properties to the carcass vulcanizates than resorcinol at strains less than 10%.

Static and Dynamic Adhesion Properties

Specimens and test results are shown in Figures 1 and 2 and described in the "Experimental" section. The number of flex cycles was 200,000. The T-pull-out forces and rubber coverage
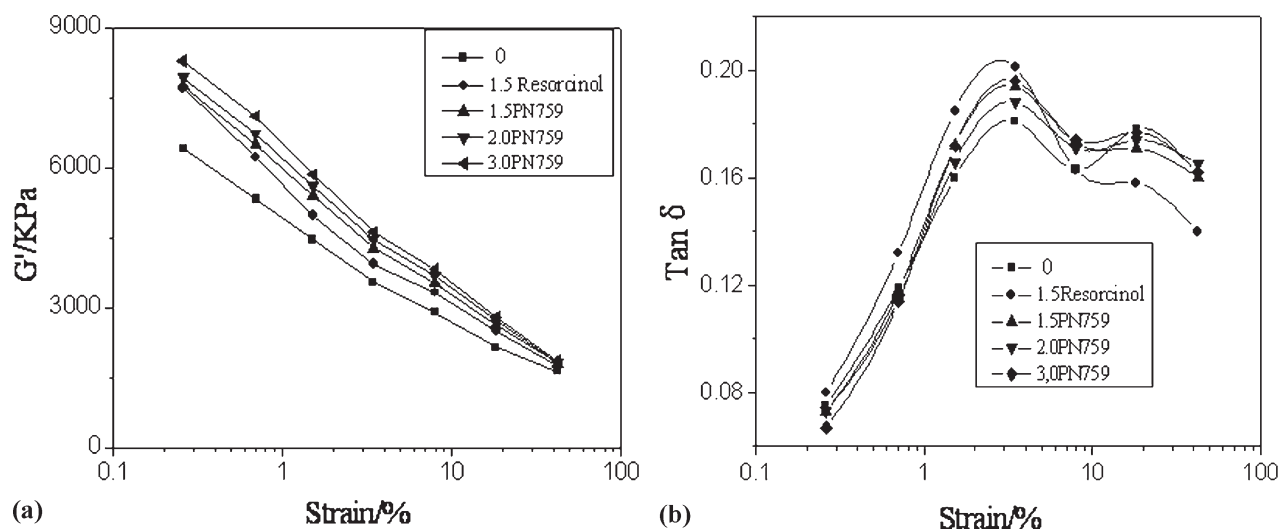

Figure 6. Dynamic mechanical properties of carcass vulcanizates with different adhesives. (a) G' versus Stain and (b) tan δ versus Stain.

Table VI. Adhesion Properties of Rubber/Steel Cord with Different Adhesives

Specimen No.	1	2	3	4	5
Curing conditions (°C × min)	151 × 25	151 × 30	151 × 35	151 × 35	151 × 40
Rubber coverage before fatigue	25R[a]/75M[b]	50R/50M	50R/50M	50R/50M	50R/50M
Rubber coverage after fatigue	25R/75M	75R/25M	50R/50M	50R/50M	25R/75M
Static pull-out force (N)	863	1014	1040	1058	981
Minimum static pull-out force (N)	847	884	1004	969	813
Maximum static pull-out force (N)	907	1115	1107	1207	1160
Range of static pull-out force (N)	60	231	103	238	347
Standard deviation of static pull-out force (N)	36.78	92.40	36.15	77.67	130.98
Dynamic pull-out force (N)	835	922	943	873	840
Minimum dynamic pull-out force (N)	791	810	853	828	787
Maximum dynamic pull-out force (N)	909	996	1048	951	900
Range of dynamic pull-out force (N)	118	186	195	123	113
Standard deviation of dynamic pull-out force (N)	40.00	65.90	70.13	44.39	37.09
Change ratio of pull-out force (%)	−3.2%	−9.1%	−9.3%	−17.5%	−14.4%

[a] R indicates that adhesion failure occurred in the rubber phase; i.e., the adhesion strength of the interphase was greater than the strength of the rubber phase.

[b] M indicates that adhesion failure occurred at the interphase; i.e., the adhesion strength of interphase was less than that of the rubber phase.

can be seen in Table VI. The surfaces of pulled-out steel cords were examined by stereoscopic zoom microscopy and examples are shown in Figure 7.

Comparing the rubber coverage of all the samples before dynamic fatigue, it was found that methyl acceptor adhesives slightly decreased the probability of adhesion failure occurring at the interface, which indicated improved static adhesion strength. This might be explained by the improved crosslink density which could reinforce interfacial adhesion. Comparing the rubber coverage after fatigue, it was found that only sample No. 2 with resorcinol exhibited an increased interfacial adhesion and No. 5, with the most PN759, showed the weakest interfacial adhesion and more exposed steel cord, as shown in Figure 7. This suggests that too much PN759 was deleterious for dynamic

adhesion. The probability that adhesion failure occurred at the interface was similar to that for failure occurring in the rubber phase for the samples with moderate loadings of PN759.

It can be seen from Table VI and Figure 8 that the static "pull-out forces" increased for compounds containing methyl acceptor adhesives. We assume that resorcinol improved static adhesion strength by forming interpenetrating networks, and that the mechanical adhesion strength induced by the polar functional groups in the rubber phase with the oxidized film of the steel cord also improved static adhesion performance. It also can be seen that 1.5 phr PN759 led to a greater pull-out force than an equivalent amount of resorcinol; perhaps because the volatility of resorcinol reduced the formation of phenol–formaldehyde resin and interpenetrating networks. Comparing all the
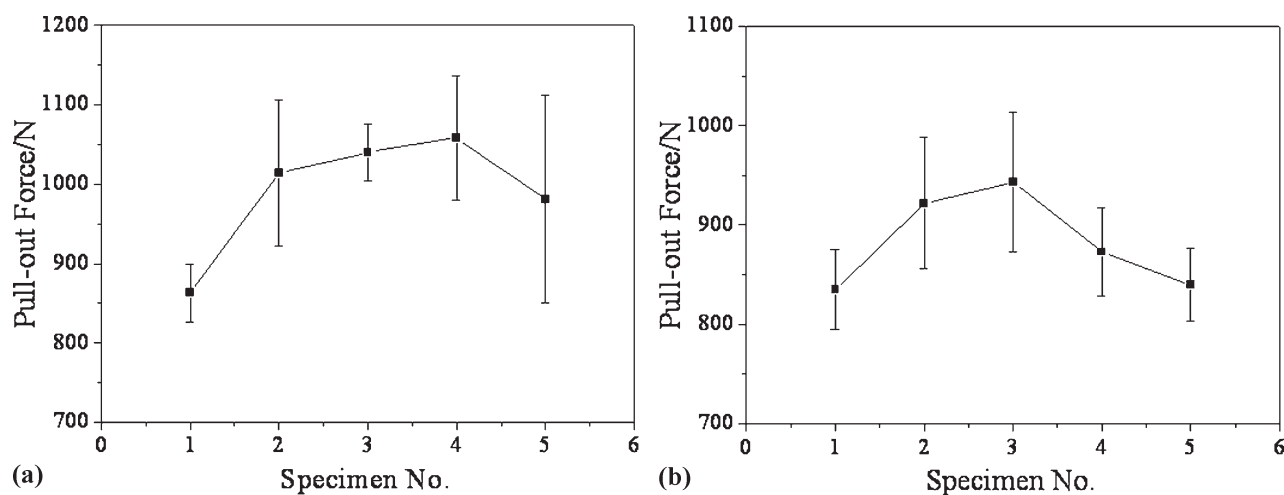
Figure 7. SZM Micrographs of rubber coverage on pulled-out steel cords with methyl acceptor adhesives.
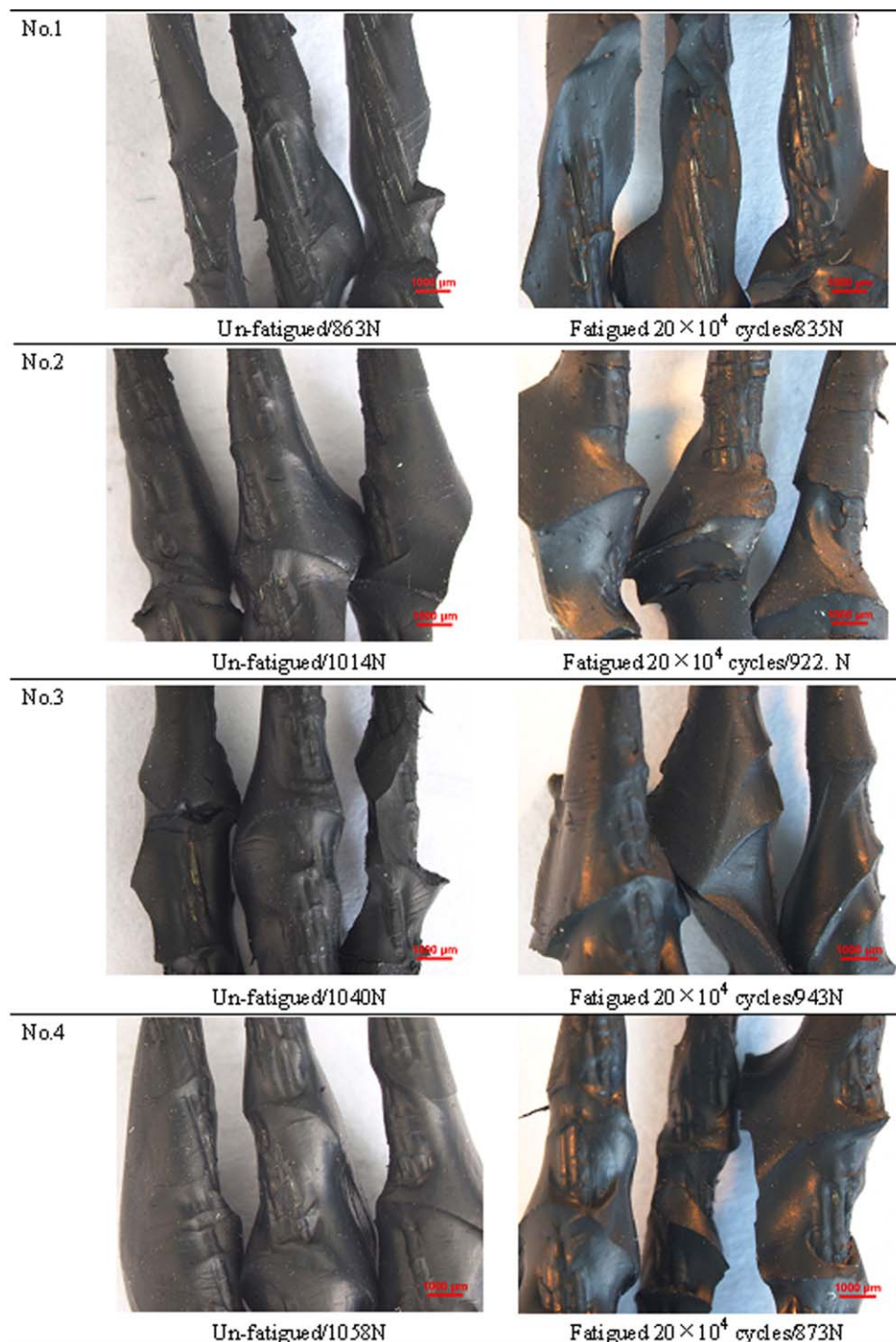
Figure 8. Effects of methyl acceptor adhesives on pull-out forces of steel cord. (a) Un-fatigued and (b) Fatigued 200,000 cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

samples with PN759, it also can be seen that 2.0 phr PN759 was sufficient for 5.0 phr HMMM; further increasing PN759 load had no reinforcement effect on the initial adhesion strength. This can be explained by suggesting that overloading the methyl donor reduced the three-dimensional resin and enhanced the formation of linear phenol-formaldehyde resin. Thus, the confining force of the crosslinked rubber on the steel cord decreased and static adhesion performance became weaker.

After 200,000 fatigue cycles, all the pull-out forces decreased with various change ratios, which indicated that PN759 was not favorable for dynamic adhesion (contrary to the effect of cobalt decanoate). It is presumed that the aging effect predominated with excessive fatigue cycles of 200,000.[33] It also can be seen that pull-out force with 1.5 phr adhesives showed a subtle decrease. However, rubber containing more than enough adhesive exhibited greater hysteresis as can be seen from Figure 6.

Table VII. Adhesion Properties with Different Flex Fatigue Cycles

Fatigue cycles (104×)	0	5	10	15	20	25
Curing conditions (°C × min)	151 × 20	151 × 20	151 × 20	151 × 20	151 × 20	151 × 20
Mean dynamic pull-out force (N)	1022	1041	1074	1054	996	874
Minimum dynamic pull-out force(N)	960	921	957	944	916	663
Maximum dynamic pull-out force (N)	1106	1139	1163	1188	1089	1198
Range of dynamic pull-out force (N)	146	218	206	244	173	535
Standard deviation of dynamic pull-out force (N)	52.72	77.69	67.23	72.02	68.94	188.27
Rubber coverage	25R[a]/75M[b]	50R/50M	75R/25M	75R/25M	50R/50M	50R/50M

[a] R indicates that adhesion failure occurred in the rubber phase; i.e., the adhesion strength of the interphase was greater than the strength of the rubber phase.

[b] M indicates that adhesion failure occurred at the interphase; i.e., the adhesion strength of interphase was less than that of the rubber phase.

Increased heat generation perhaps promoted the formation of excess CuxS; this is brittle and leads to poor adhesion stability.

In summary, methyl acceptor adhesives were deleterious to adhesion stability, but improved static adhesion performance. The pull-out force after dynamic fatigue with adhesives was still better than without the adhesives; PN759 rather than resorcinol slightly improved the static and dynamic adhesion performance.

Effects of Dynamic Fatigue Cycles on Adhesion Properties
Static and Dynamic Adhesion Properties. The test for pull-out force after different flex fatigue cycles with a certain deformation is an effective characterization method to evaluate dynamic adhesion properties of rubber/steel cord compounds. In this section, the influence of the number flex cycles (from 0 to 250,000) on the adhesion between rubber with 1.0 phr cobalt decanoate and steel cord is reported. Specimens and test results are shown in Figures 1 and 2 and described in the "Experimental" section. The T-pull-out forces and rubber coverage can be seen in Table VII and

Figure 9. Effects of flex fatigue cycles on pull-out forces.

Figure 9. In addition, the surfaces of pulled-out steel cords were observed by stereoscopic zoom microscopy and examples shown in Figure 10.

It can be seen from Table VII and Figure 9 that the pull-out force first increased and then decreased with an increase of fatigue cycles and reached a maximum value at 100,000 cycles. The pull-out force at 150,000 cycles, although less than the maximum value was still greater than the static value. However, after 200,000 cycles, the pull-out force was lower than the static value. It can also be seen from Table VII that the rubber coverage of un-fatigued samples indicated that adhesive failure mainly occurred at the interface; the rubber phase was stronger than the interface. The probability of adhesive failure occurring at the interphase became less up to 150,000 cycles but increased again as the number of cycles increased. The adhesion performance of rubber/steel cord articles is influenced by heat generation, cure reversion, and aging during dynamic fatigue.[1,34] It can be inferred from Table VII that the reversion predominates after about 150,000 cycles.

The micrographs of "pulled-out" steel cord are shown in Figure 10. One can see that the exposed steel cord was least after *ca.* 100,000 cycles when the "pull-out force" was the greatest. The covered rubber on the "pulled-out" cord after 100,000 cycles appeared more uniform and more "screw-like" and the "thread" was narrower. These observations suggest that the "pull-out force" correlates with the amount of rubber coverage and surface roughness of the "pulled-out" steel cord.

Surfaces Morphology. The surface of rubber coverage torn from the "pulled-out" steel cord was examined using a scanning electron microscope (SEM; Figure 11). It can be seen that small particles appear on the surface after flex fatigue and the size and numbers of particles increased with an increase in the number of fatigue cycles. One of the particles was chosen and examined at higher magnification (Figure 12). From Figure 12, it can be seen that the particles are filler agglomerates. It is presumed that the filler agglomerates grew from either preformed filler aggregates or un-dispersed agglomerates during flex fatigue because fillers
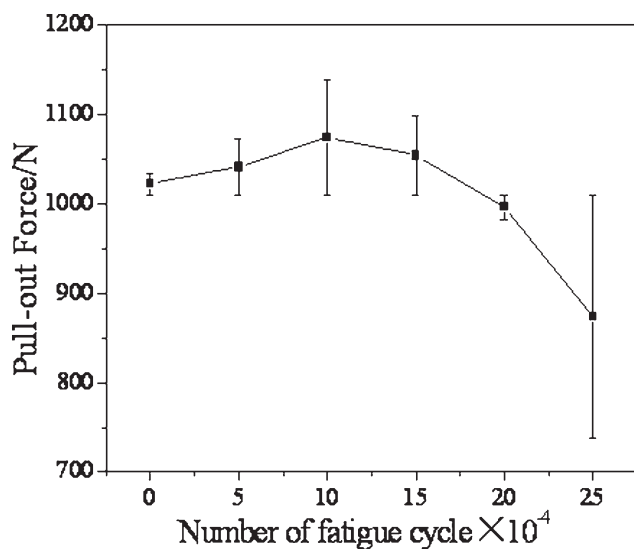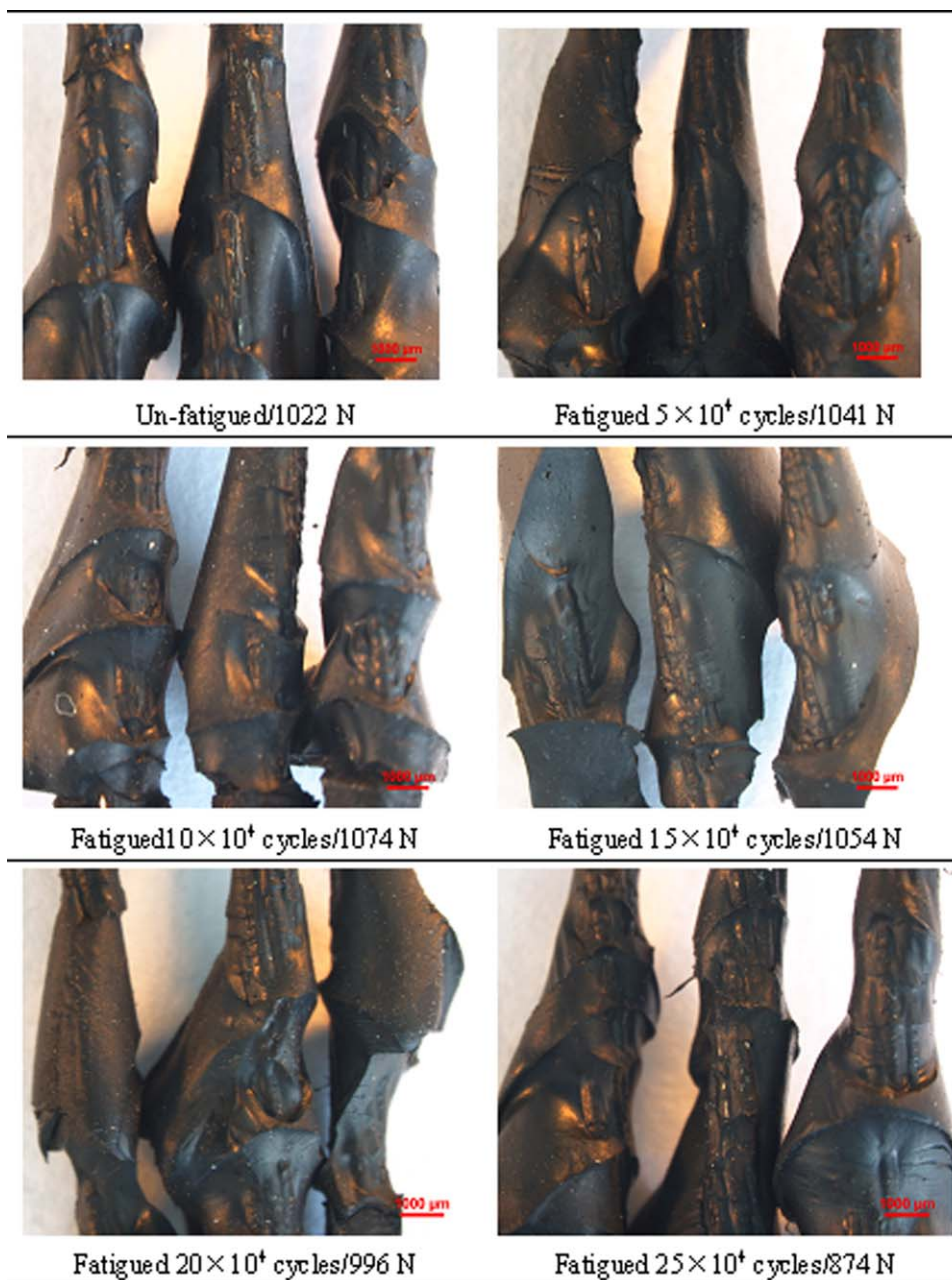
Figure 10. SZM Micrographs of rubber coverage on pulled-out steel cords with different flex fatigue cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in rubber, which were stuck to steel cord, were subject to high internal stress due to the relative motion during flex fatigue and could move around in a wider range and aggregation to larger particles is abetted. Thus, the particle size and number of aggregates increased with the number of cycles. In Figure 11(e) and (f), some cracks appeared after 250,000 fatigue cycles. This might be explained by a stress concentration at the filler agglomerates and that this leads to a potential point for crack initiation. After crack initiation, the cracks propagate leading to failure at the rubber/steel cord interface. Thus, we conclude that un-dispersed filler agglomerates may well be the initiating factor for adhesive failure.

CONCLUSIONS

An effective characterization means for evaluating the dynamic adhesion performance of rubber/steel cord has been developed.

Cobalt decanoate improved the static adhesion and favored the dynamic adhesion of rubber/steel cord; adhesive failure mainly occurred in rubber phase. The carcass compound with 2.0 phr cobalt decanoate exhibited lower hysteresis and improved static and dynamic mechanical properties.

The resorcinol–formaldehyde–silica promoting system was deleterious to adhesion stability but improved initial adhesion strength. Employing PN759 instead of resorcinol slightly
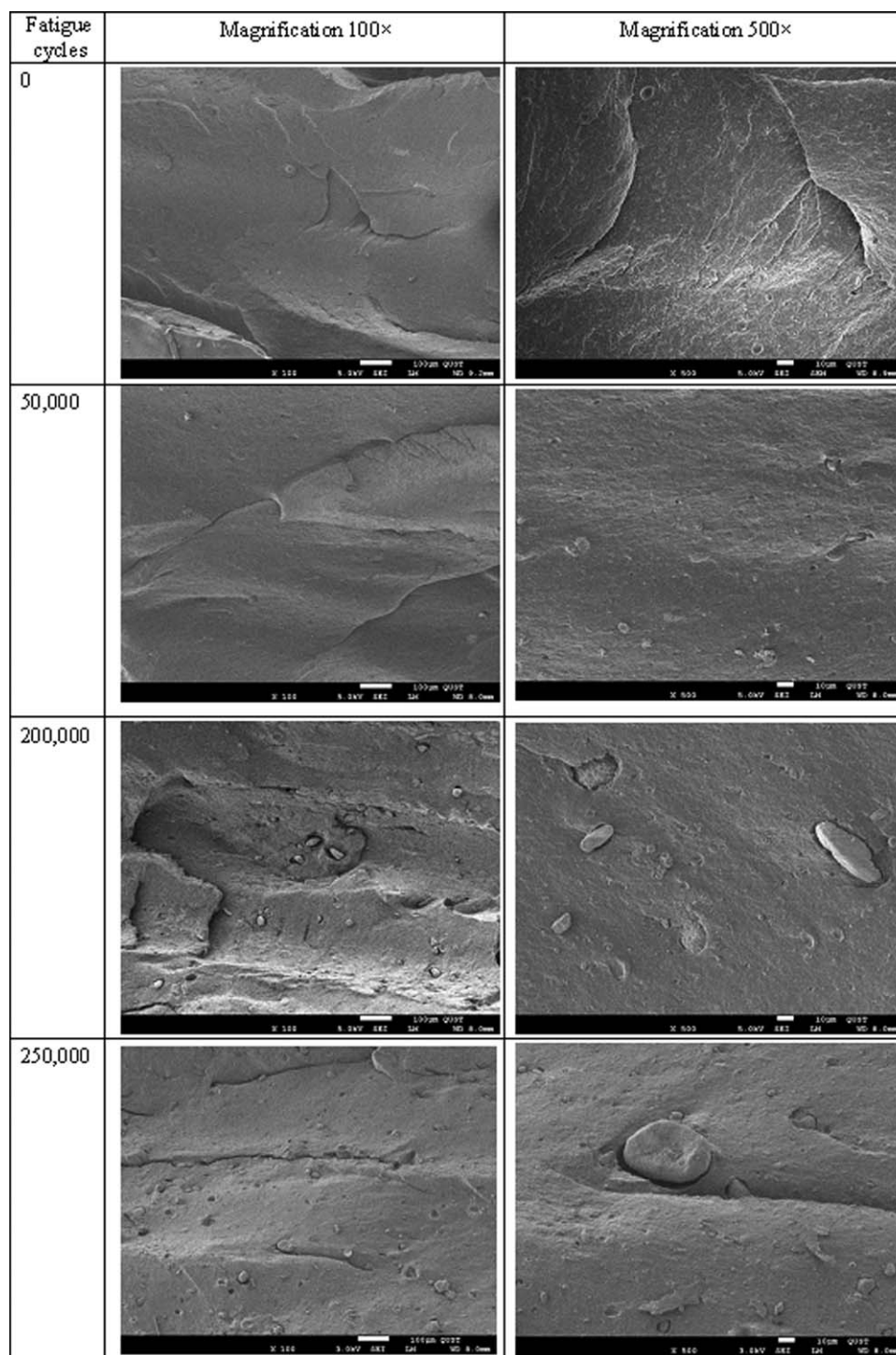
Figure 11. SEM micrographs of rubber coverage surfaces torn from the "pulled-out" steel cord with different flex fatigue cycles.

improved the static and dynamic adhesion performance. The probability of adhesive failure occurring at the interface or in the rubber phase was similar.

The dynamic pull-out force for samples with 1.0 phr cobalt decanoate first increased and then decreased with an increase in the number fatigue cycles and reached a maximum at 100,000 cycles. The covered rubber on the "pulled-out" cord

after fatigue appeared to form a "screw thread" form and the greatest pull-out force corresponded to more uniform and clearer screw-like rubber coverage with finer screw threads.

SEM examination of the surface of the rubber torn from steel cord indicated that un-dispersed filler agglomerates may be the initiating factor for adhesive failure.
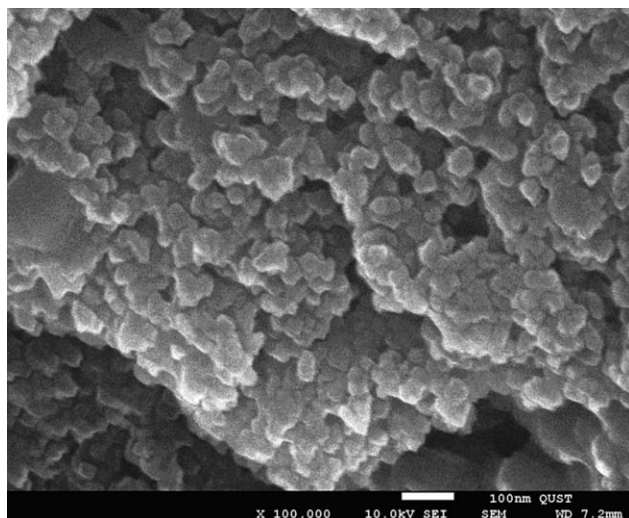
Figure 12. SEM micrograph of particles from the surface (100,000×).

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