

Development of Polybutadiene (BR)–Polyethylene (LDPE) Blend Based Microcellular Soles for Low-Temperature Applications

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ABSTRACT: Microcellular (MC) soles based on polybutadiene (BR) and low-density polyethylene (LDPE) blends for low-temperature applications were developed. A part of BR in BR–LDPE blend was replaced by natural rubber (NR) for property improvement. The BR–NR–LDPE blend-based MC sole shows good technical properties. Sulphur curing and DCP curing were tried in BR–LDPE and NR–BR–LDPE blends. Study shows that sulphur-cured MC sheets possess better technical properties than DCP-cured MC sheets. 90/10 BR–LDPE and 60/30/10 BR–NR–LDPE blend combinations are found to be suitable for low-temperature applications. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 277–281, 2000

Key words: polybutadiene; low density polyethylene; microcellular soles; low temperature applications; technical properties; abrasion resistance

INTRODUCTION

Microcellular soles possess lightness, stiffness, high abrasion resistance, and hardness and are used in footwear. The elastic properties of rubber change as the temperature is changed. The term “low-temperature stability of rubber” refers to the retention of its elastic properties when cooled below 0°C.^{1–3} The problem of low-temperature flexibility of vulcanized rubber arises from the fact that its high elastic properties are evident only within a limited temperature range because of the relaxation characteristics. This temperature range depends not only on the nature of rubber but also on the conditions of deformation, especially at the time of application of the force. On cooling, a rubber loses its rubberiness as the polymer passes through its glass transition temperature (T_g), or by crystallization.³ As the temper-

ature is reduced toward the T_g , the specimen becomes increasingly stiff or “logy,” loses resilience, and increases modulus and hardness. The low temperature properties depend on the T_g of a polymer. The molecular factors controlling T_g are chain stiffness, interchain attraction, molecular symmetry, copolymerization, branching and crosslinking, and, finally, solvents and plasticizers. So, for optimum low-temperature properties, a low T_g is required.³

In this article, microcellular (MC) soles for low-temperature applications are proposed to be developed using a blend of polybutadiene [T_g (–100°C)] and low-density polyethylene [T_g (–25°C)]. MC sheets based on NR–BR–LDPE ternary blends are also proposed to be developed.

EXPERIMENTAL

Materials Used

The polybutadiene rubber (BR) was Cisamer-01, supplied by Indian Petrochemical Limited, Vado-

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Table I Formulations for Sulphur-Cured BR-LDPE and NR-BR-LDPE Blends

Ingredients (Phr)	Mix Number						
	A	B	C	D	E	F	G
NR	—	—	30	30	—	30	30
BR	90	80	60	50	90	60	50
LDPE	10	20	10	20	10	10	20
ZnO	4	4	4	4	4	4	4
Stearic acid	6	6	6	6	6	6	6
China clay	60	60	60	60	70	70	70
Precipitated calcium carbonate	40	40	40	40	—	—	—
NR-HSR microcrumb	25	25	25	25	—	—	—
HAF black	—	—	—	—	30	30	30
Naphthenic oil	5	5	5	5	5	5	5
SP	1	1	1	1	1	1	1
Wood rosin	2	2	2	2	2	2	2
Vulcafor F	1.2	1.2	1.2	1.2	1.2	1.2	1.2
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Sulphur	2	2	2	2	2	2	2
DNPT	6	6	6	6	7	7	7

dara [cis 1,4 configuration (%) 96; raw mooney viscosity [ML(1 + 4)100°C] 44]. Low-density polyethylene (LDPE) was Indothene 24 FSO40 grade, supplied by Indian Petrochemicals Limited, Vadodara (density at 23°C: 0.922 gm/cm³; melting point, 105–110°C). Natural rubber (NR), ISNR-5, was supplied by RRII, Kottayam.

Zinc oxide, stearic acid, naphthenic oil, DNPT (dinitroso pentamethylene tetramine), DCP (dicumyl peroxide), vulcafor F, sulphur, wood rosin, styrenated phenol, precipitated silica, china clay, and HAF black were commercial grade.

Preparation of BR-LDPE Blend

Blends of polybutadiene rubber (BR) and low density polyethylene (LDPE) were prepared by melt-mixing the polymers in a Brabender plasticorder model PL 3S at a rotor speed of 50 rpm at 150°C. LDPE was added, and 1 min was given for its melting, then BR in the form of a sheet was added, and 4 more min were given for blending.

NR-BR-LDPE blends were prepared on the mixing mill. NR was masticated, and then the BR-LDPE blend was added and mixed well for 3 min. Formulations of BR-LDPE and NR-BR-LDPE blends (both sulphur curing and DCP curing of the blends were done) are shown in Tables I and II. The blends were compounded on a two-roll mill, and the optimum cure time was determined at 150°C on a Goettfert Elastograph Model

67.85. MC sheets were moulded at 150°C up to 80% of their optimum cure time. The expanded sheets were then postcured at 80°C for 2 h. Low-temperature flexibility of selected samples (90/10 BR-LDPE and 60/30/10 BR-NR-LDPE blends) were evaluated according to SATRA PM 60-1992 at -5°C.

RESULTS AND DISCUSSION

Properties of Microcellular Soles Based on Sulphur-Cured BR-LDPE and NR-BR-LDPE Blends

Table III shows the cure characteristics and technical properties of S-cured microcellular sheets. The cure characteristics of the compounds show that these blends show the lowest cure time, which can lead to higher expansion of MC sheets. The highest expansion is obtained with the 80/20 BR-LDPE blend, leading to low density and hardness.

The split tear strength of the microcellular sheets based on BR-LDPE blend is low, while abrasion loss is high. The compression set and heat shrinkage are found to increase with LDPE content in the blend. This may be due to the lower extent of crosslinking and higher expansion of the MC sheets. Water absorption decreases with increase in the amount of LDPE in the blend due to the increase in the number of open cells.

Table II Formulations for DCP-Cured BR-LDPE and NR-BR-LDPE Blends

Ingredients (Phr)	Mix Number						
	H	I	J	K	L	M	N
NR	—	—	30	30	—	30	30
BR	90	80	60	50	90	60	50
LDPE	10	20	10	20	10	10	20
ZnO	4	4	4	4	4	4	4
Stearic acid	5	5	5	5	5	5	5
China clay	60	60	60	60	70	70	70
Precipitated calcium carbonate	40	40	40	40	—	—	—
NR-HSR microcrumb	25	25	25	25	—	—	—
HAF black	—	—	—	—	30	30	30
Dicumyl peroxide (DCP) (40% active)	3	3	3	3	3	3	3
SP	1	1	1	1	1	1	1
Wood rosin	2	2	2	2	2	2	2
Naphthenic oil	4	4	4	4	4	4	4
DNPT	5	5	5	5	5	5	5

When a part of BR is replaced by NR, there is a reduction in the expansion of the MC sheet with a corresponding increase in the relative density. Higher expansion is obtained for 30/50/20 NR-BR-LDPE blend with low density. Split tear strength of the MC sheet improves marginally with addition of NR. A 30/50/20 NR-BR-LDPE

blend shows marginal decrease in strength, which may be due to the higher amount of LDPE, resulting in higher expansion. Hardness and heat shrinkage decrease with LDPE content in NR-BR-LDPE blends. When compared to BR-LDPE blends, the hardness and abrasion resistance of these ternary blends are marginally superior.

Table III Technical Properties of Sulphur-Cured Microcellular Soles Based on BR-LDPE and NR-BR-LDPE Blends

Properties	Mix Number						
	A	B	C	D	E	F	G
Optimum cure time at 150°C min	7.5	8	5.5	6	6.6	5.9	6.8
Initial expansion (%)	65.48	67.86	47.62	48.8	50	42.86	47.62
Expansion after 5 min (%)	38.09	39.28	34.52	34.52	36.6	26.9	34.52
Expansion after 24 h (%)	28.57	30.95	25.57	28.57	29.76	27.43	23.81
Expansion ratio	2.3	2.58	1.87	1.9	1.77	1.41	1.65
Relative density	0.519	0.481	0.62	0.604	0.551	0.72	0.709
Split tear strength (kg)	2.68	2.73	2.75	2.69	2.7	2.9	2.99
Abrasion loss (mm ³)	317.7	379.5	304.5	340	363	294.8	296
Hardness (Shore A)	28	27	32	30	38	45	42
Heat shrinkage (%)	2.89	2.84	2.04	2.19	1.79	1.03	1.13
Compression set (%)	11.01	12	9.2	10.3	7.2	7.19	8.2
Water absorption (percent by mass)	0.114	0.129	0.107	0.114	0.098	0.087	0.090
Shrinkage after postcuring (%)	4.04	4.762	3.85	3.92	2.912	2.88	3.0
Flex resistance:							
(a) Crack initiation in cycles	297,970	297,970	275,100	275,100	299,500	290,500	290,500
(b) Crack growth at the end of 100,000 cycles (%)	<600	<600	<600	<600	<600	<600	<600
Low-temperature flexibility at -5°C, KC	1.5		1.5		1.5	1.5	

Table IV Technical Properties of DCP-Cured Microcellular Soles Based on BR-LDPE and NR-BR-LDPE Blends

Properties	Mix Number						
	H	I	J	K	L	M	N
Optimum cure time at 150°C min	8	8.1	9.9	9.5	10	10.4	11
Initial expansion (%)	80.92	84.52	59.52	72.62	76.19	50	51.19
Expansion after 5 min (%)	41.66	55.95	40.48	48.8	44.05	30.95	33.3
Expansion after 24 h (%)	36.9	40.48	35.71	39.28	38.69	28.57	28.57
Expansion ratio	2.38	2.39	2.10	2.29	2.1	1.74	1.89
Relative density	0.433	0.378	0.445	0.422	0.518	0.607	0.59
Split tear strength (kg)	2.9	2.95	3.01	2.6	3.2	3.81	3.95
Abrasion loss (mm ³)	392	412	311.7	360	328.7	301.4	318.6
Hardness (Shore A)	25	23	27	24	28	32	31
Heat shrinkage (%)	5.49	4.44	2.22	2.89	4.23	3.22	3.34
Compression set (%)	18.67	19.14	17.66	18.65	16.49	15.1	15.95
Water absorption (percent by mass)	0.127	0.138	0.118	0.121	0.11	0.098	0.098
Shrinkage after postcuring (%)	6.30	6.71	5.39	6.01	5.18	4.39	3.61
Flex resistance:							
(a) Crack initiation in cycles	267,500	267,500	250,500	250,500	250,170	250,170	246,516
(b) Crack growth at the end of 100,000 cycles (%)	<600	<600	<600	<600	<600	<600	<600
Low-temperature flexibility at -5°C KC	1.5		1.5		1.5	1.5	

Shrinkage after postcuring also decreases in NR-BR-LDPE blends. However, BR-LDPE blends show excellent flex resistance compared to NR-BR-LDPE blends.

Table III shows the effect of addition of HAF black as filler in NR-BR-LDPE and BR-LDPE blends (Mixes E, F, and G) based microcellular soles. Addition of HAF black improves split tear strength and hardness. In blends with a higher content of rubber, the effect of carbon black on the properties is more pronounced, due to the interaction of carbon black and rubber, which leads to an increase in strength.⁴ Heat shrinkage and expansion of MC sheets decrease with the addition of HAF black. Water absorption and the compression set also decrease with the addition of HAF black. This may be due to the lower expansion of MC sheets. Relative density of MC sheets increase with the addition of HAF black, as shown in Table III. Blends with a higher content of rubber show a higher strength on addition of black, as expected.⁵

Flex resistance of all the samples are within the IS specification. Cracks develop after 292970 and 275100 cycles for BR-LDPE and NR-BR-LDPE blend, respectively. 90/10 BR-LDPE and 60/30/10 BR-NR-LDPE blend-based MC sheets

possess excellent low-temperature flexibility (shown in Table III).

Properties of Microcellular Soles Based on DCP-Cured BR-LDPE and NR-BR-LDPE Blends

Table IV shows the technical properties of DCP-cured microcellular sheets, and DCP-cured microcellular sheets based on BR-LDPE blend achieve a higher degree of expansion and, hence, have lower densities. As the amount of LDPE increases, expansion further increases, and this leads to very low densities. There is a marginal increase in split tear strength for the DCP-cured MC sheets compared to sulphur-cured MC sheets. Abrasion loss and water absorption are comparatively higher for DCP-cured MC sheets due to the higher expansion. Lower hardness is observed for DCP-cured MC sheets.⁶ Heat shrinkage decreases with increase in LDPE content in BR-LDPE blend, and the compression set marginally increases.

When a part of BR is replaced by NR, expansion decreases, and relative density increases. Properties like hardness, compression set, split tear strength, and abrasion resistance are improved. Heat shrinkage and water absorption de-

crease. Shrinkage after postcuring is also found to decrease with the partial replacement of BR by NR. Addition of HAF black in DCP cured compound shows improvement in technical properties, as shown in Table IV.

Flex resistance of DCP-cured MC sheets show comparable values (Table IV). In the case of DCP-cured sheet, crack initiation occurs after 267,500 cycles for BR-LDPE blends. The values obtained at low temperature shows that the 90/10 BR-LDPE and 60/30/10 BR-NR-LDPE blend-based MC sheets are suitable for low-temperature applications.

CONCLUSION

1. Very low-density microcellular soles can be obtained from BR-LDPE and NR-BR-LDPE DCP-cured blends with excellent flex resistance.
2. Sulphur-cured MC sheets possess higher technical properties like hardness, split

tear strength, and abrasion resistance compared to DCP-cured MC sheets.

3. 90/10 BR-LDPE and 60/30/10 BR-NR-LDPE blend-based microcellular soles are found to be suitable for low-temperature applications.

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