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Studies on microcellular soles based on natural rubber/polyethylene blends

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Microcellular (MC) soles based on NR/polyethylene blends were developed as possible replacements for the conventional NR/HSR soles. The mechanical properties of the soles suggest that 80/20 NR/LDPE blends can be used for light weight good quality soles. 80/20 blends of NR/HDPE are also found to be promising base materials for good quality soles. A part of HSR in a NR/HSR blend was replaced by LDPE and the effect of replacement on the mechanical properties was evaluated. It is found that 70/15/15 NR/HSR/LDPE and 60/20/20 NR/HSR/LDPE based MC soles show better mechanical properties than NR/LDPE based MC soles. © *1999 Kluwer Academic Publishers*

1. Introduction

Microcellular (MC) soles have the advantages of wearing comfort, light weight, high flexural strength and low cost. The production of microcellular expanded soling is a major activity in rubber industry and a substantial quantity of polymers is utilised for this purpose. Microcellular soling can be manufactured from a variety of rubbers, plastics and their blends. Usually Natural rubber/High styrene resin (NR/HSR) blends are used for the manufacture of microcellular soles. NR/HSR based microcellular soling material possesses high abrasion resistance, fairly constant Mooney viscosity and cure characteristics, high resistance to crack initiation, crack growth etc. [1].

NR/HSR based microcellular soling has high density and high shrinkage resulting in comparatively low wearing comfort. In the present paper we report the suitability of NR/LDPE and NR/HDPE blends for production of microcellular soles. The effect of partial replacement of LDPE by HSR was also investigated. The properties of microcellular sheets based on NR/LDPE, NR/HDPE and NR/LDPE/HSR were evaluated and compared with NR/HSR based microcellular soles.

2. Experimental

2.1. Materials used

- Natural Rubber (NR): ISNR-5 (Supplied by RRII, Kottayam).
- SBR 1958: High styrene resin (HSR) (Supplied by Synthetics and Chemicals).
- Low Density Polyethylene (LDPE), High Density Polyethylene (HDPE) were supplied by IPCL, India.
- Zinc Oxide, stearic acid, Vulcafor F, Dicumyl peroxide (DCP), sulphur, precipitated silica, china clay, naphthenic oil, styrenated phenol, diethylene glycol, Dinitroso pentamethylene tetramine (DNPT) were all commercial grade. NR/HSR crumb.

2.2. Preparation of NR/LDPE blends

NR/LDPE blend was prepared on a Brabender Plasticorder model PL 3S employing a rotor speed of 60 rpm and a temperature of 150 °C. LDPE was first melted and homogenised for one min and then masticated NR was added and mixed for 3 min [2]. HSR in the form of a sheet was then added on a mixing mill and the blends were compounded according to the formulation given in Table I NR/HDPE blends were also prepared by the above procedure.

2.3. Preparation of microcellular sheets

The optimum cure times (time to reach 90% of the maximum torque) of the compounds were determined using a Goettfert Elastograph model 67.85. Microcellular sheets were moulded in an electrically heated hydraulic press at 160 ± 2 °C. The mould was filled with three per cent excess of the compound on a volume basis. The compounds were precured in the mould up to 80% of their respective optimum cure times. The expanded precured sheets were then post cured in an air oven for 2 h at 80 °C.

2.4. Test methods for mechanical properties

The mechanical properties like relative density, hardness, compression set, split tear strength, heat shrinkage, and water absorption were evaluated according to relevant Indian Standards. The flex resistance, in

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TABLE I Formulation for NR/LDPE or NR/HDPE based MC sheets (parts per hundred of rubber)

Ingredients	I	II
NR	80	80
HSR	—	—
HDPE/LDPE	20	20
Zinc oxide	3	3
Stearic acid	6	4
Precipitated silica	20	20
China clay	80	80
NR/HSR crumb	25	25
Wood rosin	2	2
Styrenated phenol	1	1
Vulcafor F	1.2	—
Sulphur	2.25	—
Dicumylperoxide (40% active)	—	5
Naphthenic oil	3	3
Diethylene glycol	1.5	1.5
DNPT	6	6

number of cycles (for initial crack development) and cut growth at the end of 100,000 cycles were tested using a Ross flexing machine as in IS 3400 (part 16)—1974. Abrasion resistance was tested using a DIN abrader as in DIN 53516 standards with a load of 5 N.

Hardness was measured using a Shore A Durometer. Split tear strength was tested using a Zwick universal testing machine model 1445. Cut test pieces of 25 × 100 mm along and across the direction were used. Each test piece was prepared by splitting it midway between the top and the bottom surface at a distance of 30 mm from one end which eventually forms two tongues. The two tongues of the test pieces were clamped between the jaws of the UTM and allowed to separate at a constant rate of 75 mm/min. At least four specimens per sample were tested for each property and the mean values are reported.

3. Results and discussion

Table II shows the properties of MC sheets prepared using sulphur as curing agent for both NR/LDPE based and NR/HSR based MC sheets. NR/LDPE based MC sheets show increased expansion compared to NR/HSR based MC sheets. The increase in expansion is due to the presence of LDPE which is thermoplastic in nature. The degree of crystallinity in sulphur cured NR/LDPE systems is lower than that of pure LDPE because sulphur crosslinks in NR retards the crystallisation of LDPE [2]. Relative density decreases with increase in expansion of the MC sheet. Hardness and split tear strength show marginal decrease in 80NR/20LDPE based MC sheets. This decrease in properties may be due to the presence of uncured LDPE phase, since LDPE phase does not get cured in presence of sulphur and Vulcafor F. Compression set shows an increase in the case of the NR/LDPE based MC sheets. Water absorption and heat shrinkage were found to be high for NR/LDPE based MC sheets. This increase in water absorption is due to the presence of more open cells, resulting from higher expansion [3]. This is also confirmed from increased heat shrinkage of NR/LDPE based MC sheets.

Properties of MC sheets prepared with partial replacement of HSR by LDPE are shown in Table II. Expansion of the NR/HSR/LDPE based MC sheets is marginally high and it increases as the concentration of the LDPE increases as expected. Relative density of the MC sheets decrease with increase in concentration of LDPE in NR/HSR/LDPE based blends. As the amount of LDPE in the blend increases, hardness, split tear strength and water absorption decrease. This may be due to the increased expansion of the MC sheet. Low water absorption shows the presence of lower amount of open cells [4]. Abrasion resistance decreases with LDPE content in the blend. But a 60NR/20HSR/20LDPE based MC sheet shows improvement in abrasion resistance compared to a 70NR/20HSR/10LDPE blend based MC sheet. Compression set increases with increase in the amount of LDPE. This may be due to part of the curing ingredients dissolving in PE phase and hence is not available for crosslinking. But as the amount of HSR in the blend increases marginal improvement in hardness and compression set are observed. This is probably due to the self reinforcing character of HSR. Water absorption of 60NR/20HSR/20LDPE based MC sheet is higher,

TABLE II Mechanical properties of MC sheets prepared using sulphur as curing agent

NR	80	80	70	70	70	60	60
HSR	—	20	30	15	20	20	40
LDPE	20	—	—	15	10	20	—
Initial expansion (%)	78.57	73.81	76.19	77.38	72.57	72.62	71.43
Expansion after 5 min (%)	50	41.66	47.62	48.8	48.8	47.2	35.71
Expansion after 24 h (%)	41.66	33.3	35.71	38.09	38.09	38.09	29.76
Optimum cure time 160 °C min	8	8.9	8	8.1	8	9	8
Expansion ratio	2.634	2.139	2.39	2.505	2.546	2.579	2.259
Relative density	0.445	0.471	0.458	0.367	0.418	0.443	0.452
Split tear strength (kg)	3.07	3.69	4.04	2.76	2.37	2.48	4.59
Abrasion loss (mm^3)	470	426.7	446.7	440.69	461.5	451.36	420.0
Compression set (%)	13.07	7.9	8.40	12.0	14.57	13.94	10.49
Water absorption (% by mass)	0.128	0.1	0.106	0.0964	0.096	0.114	0.102
Hardness (Shore A)	37	48	49	45	44	44	51
Heat shrinkage (%)	4.56	3.54	3.59	3.67	3.60	3.71	6.23
Flex resistance in cycles							
(a) Initial crack	>60000	>60000	>60000	>60000	>60000	>60000	>60000
(b) Cut growth at the end of 100,000 cycles (%)	<600	<600	<600	<600	<600	<600	<600

TABLE III Mechanical properties of MC sheets prepared using DCP as curing agent

NR	80	80	70	70	70	60	60
HSR	—	20	30	15	20	40	20
LDPE	20	—	—	15	10	—	20
Initial expansion (%)	67.86	82.14	69.05	90.48	96.43	71.43	96.43
Expansion after 5 min (%)	36.9	48.8	38.09	55.95	61.9	39.28	63.1
Expansion after 24 h (%)	29.76	41.66	30.95	45.24	53.57	32.14	57.14
Optimum cure time 160 °C min	9	9	8	9	8.6	8	7
Expansion ratio	2.35	2.78	2.9	3.31	3.57	2.56	3.47
Relative density	0.49	0.3799	0.4863	0.3469	0.3206	0.475	0.308
Split tear strength (kg)	3.67	3.35	3.59	2.89	2.95	4.08	3.30
Abrasion loss (mm^3)	510	623	523.80	553.4	586.9	495	595
Compression set (%)	7.1	9.42	10.4	12.96	14.35	13.13	14.39
Water absorption (% by mass)	0.112	0.141	0.112	0.169	0.175	0.071	0.196
Hardness (Shore A)	34	22	34	32	30	38	28
Heat shrinkage (%)	6.41	8.60	8.1	7.44	8.45	7.9	7.68
Flex resistance in cycles							
(a) Initial crack	>60000	>60000	>60000	>60000	>60000	>60000	>60000
(b) Cut growth at the end of 100,000 cycles (%)	<600	<600	<600	<600	<600	<600	<600

TABLE IV Properties of NR/HDPE blend based Microcellular soles

	DCP cured	S cured
NR	80	80
HDPE	20	20
Initial expansion (%)	94.05	90.47
Expansion after 5 min (%)	66.70	63.07
Expansion after 24 h (%)	54.76	52.38
Expansion ratio	3.51	3.13
Relative density	0.306	0.325
Split tear strength (kg)	2.99	2.60
Abrasion loss (mm^3)	570.9	556
Compression set (%)	15.94	18.94
Water absorption (% by mass)	0.138	0.115
Hardness (Shore A)	25	27
Heat shrinkage (%)	2.02	1.04
Flex resistance in cycles:		
(a) Initial crack	>60000	>60000
(b) Cut growth at the end of 100,000 cycles (%)	<600	<600

due to the presence of more open cells. Heat shrinkage of the NR/HSR/LDPE based MC sheets is found to be almost constant. Flex resistance of all the samples are found to be within the specification limits given in Indian Standards as shown in Table II.

Table III shows the properties of MC sheets prepared using DCP as the curing agent. Expansion of peroxide crosslinked MC sheets is comparatively higher compared to NR/HSR/LDPE based MC sheets prepared with sulphur as curing agent. Consequently relative density is also found to be lower in DCP cured MC sheets. Properties generally improve as the amount of LDPE in the blend increases as shown in Table III. Split tear strength of the MC sheets prepared using DCP as curing agent is found to be higher than that of the MC sheets prepared using sulphur as curing agent. This may be due to the curing of LDPE phase also in presence of DCP which also results in slightly lower compression set. But heat shrinkage and water absorption are higher compared to sulphur cured MC sheets. This is due to the higher expansion of the MC sheets, which produces more open cells. Abrasion loss shows marginal increase compared to sulphur cured MC sheets. This is due to the weaker cell walls resulting from higher expansion [4]. Hardness of MC sheets with DCP as curing agent shows a decrease. It can be explained by the fact that the network is so dense and brittle that the hemispherical indentor of the Durometer penetrates and slightly breaks the vulcanizates with the consequental drop in hardness [5]. This effect is also observed for DCP cured samples at high temperature. Flex resistance of all the samples is found to be within the specification limit given in Indian Standards.

Table IV shows the properties of 80NR/20 HDPE based MC sheets. Properties suggest that the 80 NR/20 HDPE blend is a potential candidate for making MC soles.

4. Conclusions

1. 80/20 NR/LDPE or NR/HDPE blend can be used for making light weight Microcellular soles.

2. A part of HSR in the 70/30 NR/HSR and 60/40 NR/HSR blend can be replaced by LDPE to improve properties like hardness, split tear strength, abrasion resistance etc.

3. 70/15/15 NR/HSR/LDPE or 60/20/20 NR/HSR/LDPE blend can be used for making light weight and good quality MC soles.

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