such contributions. Since no single trait has been identified as a sufficiently important parameter for early evaluation in the present study, performance of the clones are evaluated through a growth index computed with simultaneous emphasis on girth, canopy characteristics and anatomical parameters. The index takes into account the extent of environmental influence in the expression of the traits through the weights attached to each trait. The top ranking clones in terms of the growth index are therefore, the ones which exhibited a high mean performance for traits which have a comparatively low environmental component of variation. Clones RRII 6, RRII 208, RRIM 605, PB 311, RRII 105 and PB 260 which exhibited growth indices greater than the general mean could be considered superior in terms of adaptability to the stress situations existing in the Konkan tract.

ACKNOWLEDGEMENT

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Indian Journal of Natural Rubber Research, 5 (1&2) : 229-237, 1992

STUDIES ON MICROCELLULAR SOLES BASED ON NR-EVA BLENDS

Alex T. Koshy, Baby Kuriakose, Sabu Thomas and Siby Varghese

Koshy, A. T., Kuriakose, B., Thomas, S. and Varghese, S. (1992). Studies on microcellular soles based on NR-EVA blends. *Indian Journal of Natural Rubber Research*, 5 (1&2) : 229-237.

Blends of natural rubber (NR) and ethylene vinyl acetate copolymer (EVA) were evaluated for technological properties relevant to microcellular sheets for hawai sandals. The effects of blend ratio and loading of precipitated calcium carbonate and china clay on the cell structure and technological properties were studied. The results indicated that with increase in the proportion of EVA in the blend, abrasion resistance, split tear strength, compression set and shrinkage were increased. The pattern of the microcells changed with EVA content of the blend and this was found to influence the properties. Between china clay and calcium carbonate the latter imparted higher split tear strength and expansion and lower compression set and abrasion resistance.

Key words: Natural rubber, Ethylene vinyl acetate, Blends, Microcellular sole, Cell structure.

Alex T. Koshy, Sabu Thomas, School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills, Kottayam 686 562 Kerala, India; Baby Kuriakose (for correspondence) and Siby Varghese, Rubber Research Institute of India, Kottayam 686 009, Kerala, India.

INTRODUCTION

Various types of polymers and their blends are used in footwear to achieve specified combination of properties such as light weight, wearing comfort, stiffness and durability (Duttagupta, 1975; Preyer, 1955; Varkey *et al.*, 1989; Hole, 1970). Though the wear and tear properties of microcellular solings cannot match those of a high quality solid material, they are light and therefore comfortable to wear and usually have high flexural strength. Conventionally a blend of natural rubber (NR) or styrene-butadiene rubber (SBR) with high styrene resin, SBR 1958, is used for making microcellular soles. SBR 1958 improves hardness, stiffness, abrasion resistance etc. of microcellular soling. Supply of styrene for the production of SBR is reported to be decreasing (Elliot, 1974). Attempts have been going on to develop a substitute for SBR 1958 in footwear application. Thermoplastic polyurethane and plasticised polyvinyl chloride have already made in- roads into this field. A promising alternative for SBR 1958 in microcellular soles appears to be ethylene-vinyl acetate copolymer (EVA) which possesses an overall balance of properties. EVA has excellent stress crack resistance, flex resistance and weather resistance compared to SBR 1958 and other polymers such as 1,2 polybutadiene. The present work attempts to evaluate the effect of

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blend ratio and fillers on the mechanical properties of microcellular soles based on NR-EVA blends. Scanning electron microscopic (SEM) observations were made on the microcellular sheets to study the variations in cell structure with blend ratio and type of filler.

EXPERIMENTAL

Materials

NR used for the study was ISNR-5 (light colour). EVA was Exxon 218 of Exxon Chemical Company, USA having vinyl acetate content of 18 per cent by weight, melt flow index 1.7 g/10 min, density 0.939 g/cm^3 and Vicat softening point 64°C. All other ingredients used were of commercial grade.

Preparation of compounds

Blends of NR and EVA were prepared in a laboratory model internal mixer (Shaw Intermix KO) set at a temperature of 80°C and a rotor speed of 60 rpm. NR was masticated for 2 min and then blended with EVA for 2 min. Fillers and other ingredients were added to the blend at the fourth minute and it was dumped at the sixth minute. The compound was sheeted out in a two roll mill. The formulations of the compounds are given in Table 1. Zinc oxide and stearic acid were included in the formulation since they are reported to activate the blowing agent and zinc stearate acts as a lubricant/release agent (Hofmann, 1989).

Moulding of sheets

Microcellular sheets were moulded in a 45 x 45 cm hydraulic press having steam heated platens. The mould was loaded with 3 per cent excess of the mix on volume basis. The temperature and pressure of moulding were 160°C and 10.5

Table 1. Formulations of mixes

Material	Calcium carbonate										China clay				
	F	G	H	I	J	G'_1	G'_2	G'_3	G'_4	G'_5	G''_1	G''_2	G''_3	G''_4	G''_5
Natural rubber	50	40	30	20	0	40	40	40	40	40	40	40	40	40	40
Ethylene-vinyl acetate	50	60	70	80	100	60	60	60	60	60	60	60	60	60	60
Zinc oxide	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Stearic acid	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Zinc stearate	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Styrenated phenol type antioxidant	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Precipitated calcium carbonate	75	75	75	75	75	45	60	75	90	105	—	—	—	—	—
China clay (soft grade)	—	—	—	—	—	—	—	—	—	—	45	60	75	90	105
Paraffinic oil	3.0	3.0	3.0	3.0	3.0	1.8	2.4	3.0	3.6	4.2	1.8	2.4	3.0	3.6	4.2
Dicumyl peroxide (40% active)	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Diethylene glycol	—	—	—	—	—	—	—	—	—	—	0.9	1.2	1.5	1.8	2.1
Azodicarbonamide (ADC)	5.0	5.0	4.5	4.0	3.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0

MPa respectively. The compound was precured in the mould for a period necessary to attain 80 per cent of the maximum torque as measured using a Monsanto Rheometer. The expanded sheets were then post-cured for 3 h at 80°C to complete the curing process.

Testing

The sheets were tested for properties such as relative density, hardness, change in hardness after ageing, split tear strength, compression set, heat shrinkage, flex resistance etc. as per the relevant test procedures given in BIS-10702-1985. Abrasion resistance was tested using DIN abrader as per DIN 53516, with a load of 5 N. The relative expansion of the microcellular sheets was measured immediately after taking out the sheets from the mould and expressed as percentage linear expansion with respect to the size of the mould cavity. All other tests were done only after post-curing the sheets.

Cell structure

Using a JEOL 35 C model scanning electron microscope, observations on cell structure were made. For this, freshly cut samples were sputter coated with gold and photomicrographs taken at 100x magnification.

RESULTS AND DISCUSSION

For preparing microcellular sheets, blends having NR: EVA ratios 50 : 50, 40 : 60, 30 : 70, 20 : 80 and 0 : 100 were used. These blends are designated as F, G, H, I and J, respectively. The effect of fillers was evaluated in blend G only. This was because, for DCP cured NR-EVA blends, better technological properties were shown by those blends which contained a higher proportion of EVA (Koshy *et al.*, 1990). The concentration of blowing agent was varied so as to get the same expansion for the microcellular sheets prepared from the blends containing different proportions of NR and EVA. Linear expansion of the sheets before post-curing was about 100 per cent of the mould dimensions. However, in the case of compounds G_1' to G_5' and G_1'' to G_2'' the concentration of the blowing agent was kept the same to study the effect of filler on expansion level of the microcellular sheets.

Cell structure

Effect of blend ratio

In microcellular soles, the cells are mainly of closed type. Figures 1 to 5 are the photomicrographs of the cut edges of the microcellular sheets prepared from blends F to J, respectively, as seen under a scanning electron microscope. From these figures, it is evident that as the proportion of EVA in the blend was increased, the cells became larger and attained a more uniform structure. The larger cell size of the EVA rich blends is due to lower melt viscosity of such blends which facilitates increased blowing with unit weight of the blowing agent. The non-uniformity of the cells in those blends in which the proportion of EVA is reduced can be due to non-uniform

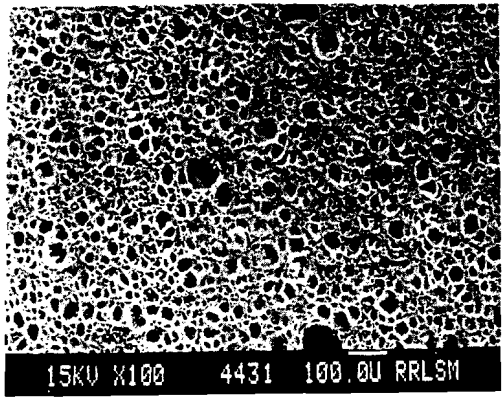

Fig. 1. SEM photomicrograph of NR-EVA (50:50) blend

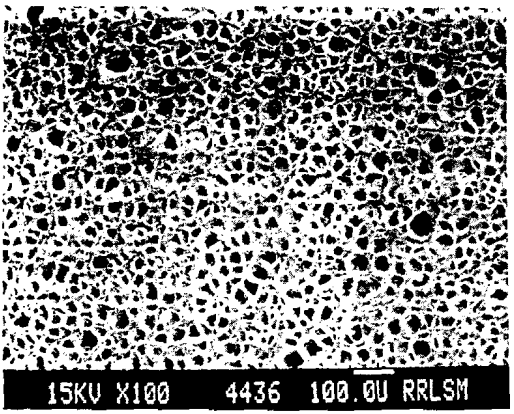

Fig. 2. SEM photomicrograph of NR-EVA (40:60) blend

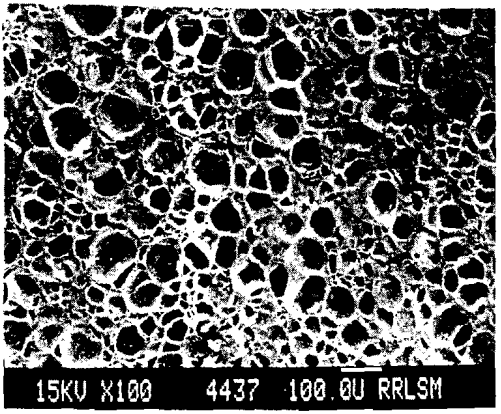

Fig. 3. SEM photomicrograph of NR-EVA (30:70) blend

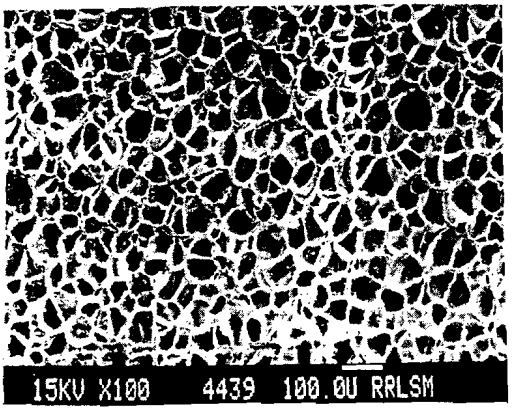

Fig. 4. SEM photomicrograph of NR:EVA (20:80) blend

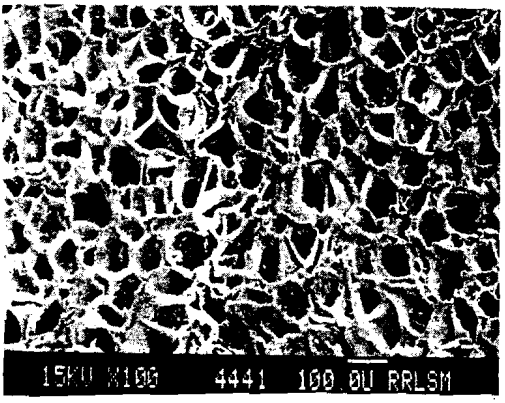

Fig. 5. SEM photomicrograph of NR:EVA (0:100) blend

distribution of the blowing agent between EVA and NR phases. In the NR phase, distribution of the blowing agent can be less due to its non-polar nature . But the dispersion of the blowing agent in this phase will be better since the viscosity of the blend increases as the proportion of NR is increased. This will lead to smaller size for the cells formed in such blends. The non-uniformity in cell structure of such blends can also be due to the difference in extents of blowing of the two phases.

Effect of filler

Figure 6 is the photomicrograph of the microcellular sheet in which china clay was used as the filler. Comparing with Fig. 2, which contained the same loading of precipitated calcium carbonate, it is seen that the china clay filled compound gave a slightly larger cell size. The uniformity of cell structure is almost identical. From the rheographs of calcium carbonate and china clay loaded compounds it is seen that the

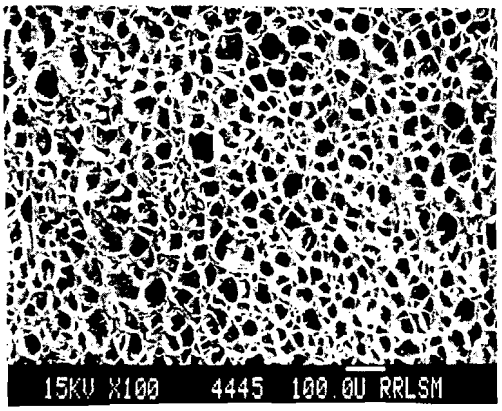

Fig. 6. SEM photomicrograph of NR:EVA (40:60) clay filled blend

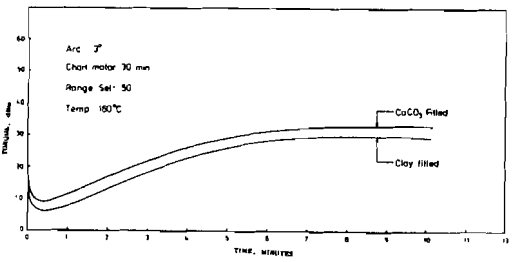

Fig. 7. Rheographs of calcium carbonate and china clay filled compounds

compound containing the former had a higher viscosity (Fig. 7). Hence in this compound the blowing agent will be more finely dispersed which will result in smaller cell size for the expanded sheet.

Physical properties

Relative density and shrinkage

The relative density decreased with increase in EVA content over the range 50 to 70 per cent (Fig. 8). Further increase in EVA content did not cause any appreciable change in relative density. But shrinkage of microcellular sheets showed steady increase with increase in the proportion of EVA in the blend. In microcellular soles, shrinkage that occurs on post-curing or long-term storage is due to loss of gases by diffusion process. The larger cell size and reduced wall thickness of the cells facilitate diffusion of gases from blends having higher proportions of EVA. The combined effects of high permeability and faster diffusion of gases in high EVA blends are reflected in higher shrinkage of such blends.

Hardness and compression set

Hardness of the microcellular soles decreased with increase in EVA content. But compression set increased steadily as the proportion of EVA was increased (Fig. 9). The increase in compression set is due to the residual thermoplastic nature of EVA.

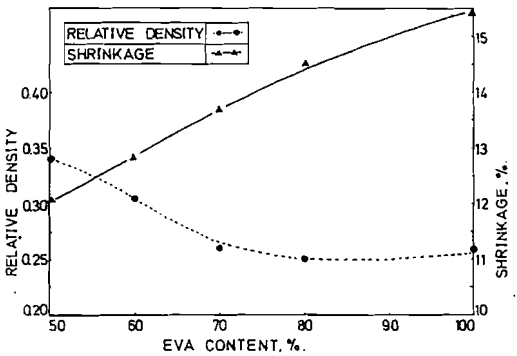

Fig. 8. Variation of relative density and shrinkage with EVA content

Abrasion loss and split tear

Higher proportion of EVA in the blend enhanced the abrasion resistance and split tear strength of the microcellular sole (Fig. 10). These two properties are very important as far as the service life of the product is concerned. The factors which contribute to improvement in these properties are more uniform cell structure of the sole having higher proportion of EVA and

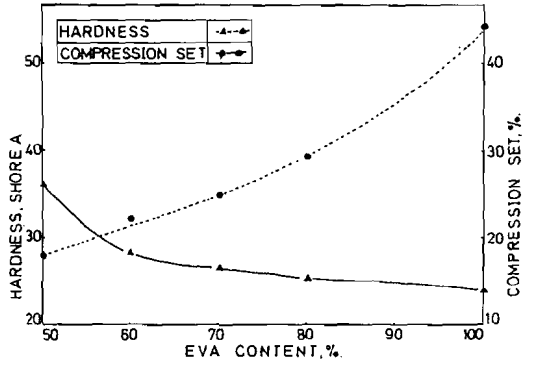

Fig. 9. Variation of hardness and compression set with EVA content

the crystalline nature of EVA. Uniform cell structure helps to take up higher loads by equal distribution of the force applied. Crystalline regions in EVA impart high tear resistance to the product by arresting / diverting the propagation of the tear path.

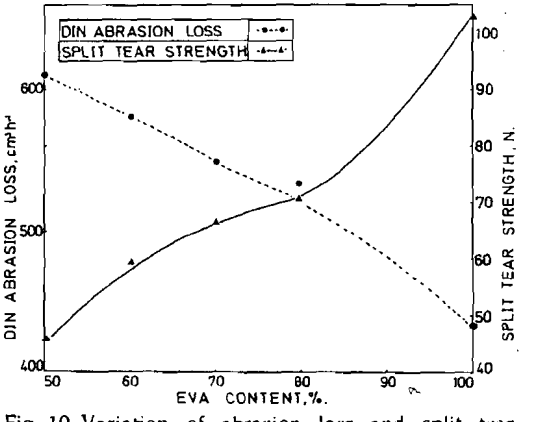

Fig. 10. Variation of abrasion loss and split tear strength with EVA content

Effect of filler on properties

The effects of china clay and precipitated calcium carbonate on the physical properties of the microcellular soles were evaluated, by varying the filler content. All other ingredients, including the blowing agent were kept at the same dosage as that for compound G, except the oil content which was fixed at 4 per cent of the filler

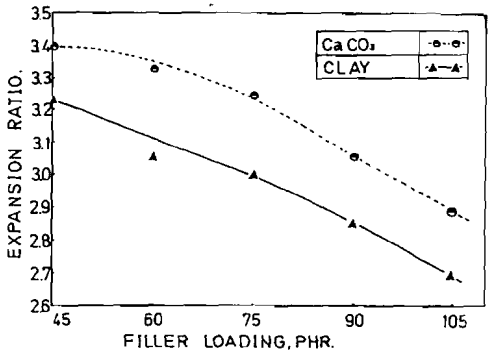

Fig. 11. Effect of china clay and calcium carbonate on expansion

loading. Diethylene glycol (DEG) was added in those compounds which contained china clay as the filler at 2 per cent of the filler level.

Figure 11 shows the effect of loading of china clay and calcium carbonate on expansion of the moulded sheets. Filler loading reduced the expansion of the sheets and this effect was almost identical for both the fillers. However, calcium carbonate showed higher expansion ratio than clay. Compression set of the microcellular sheets increased with filler loading (Fig. 12). In

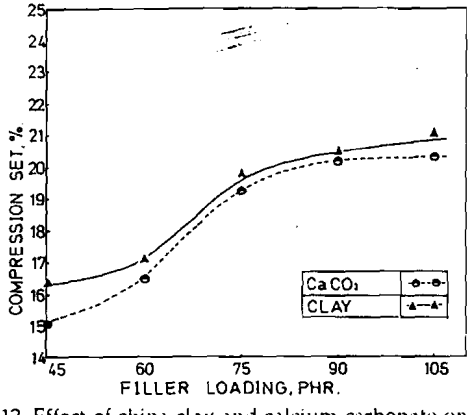

Fig. 12. Effect of china clay and calcium carbonate on compression set

this case, the behaviour of both the fillers was almost identical. However, calcium carbonate showed comparatively lower set. The split tear strength (Fig. 13) was also

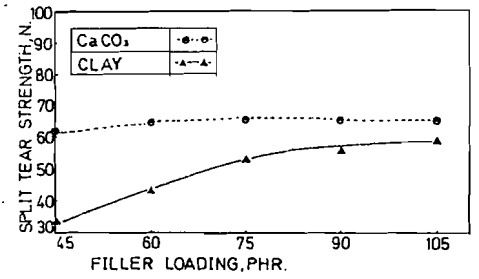

Fig. 13. Effect of china clay and calcium carbonate on split tear strength

better for the calcium carbonate loaded sheets. But the relative increase in split tear with loading was less for calcium carbonate loaded microcellular sheets. Figure 14 shows the effect of filler on shrinkage of expanded sheets. Shrinkage was more for the calcium carbonate loaded compounds at higher filler loadings. This is due to the fact that these sheets had higher expansion ratios compared with the clay loaded samples. However, at 45 phr level, the calcium carbonate loaded compound showed lower shrinkage. Hardness

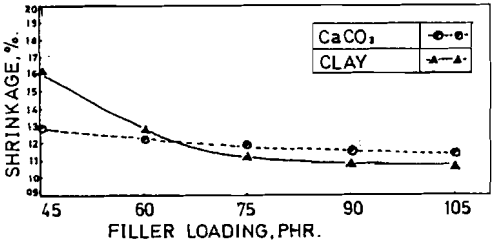

Fig. 14. Effect of china clay and calcium carbonate on shrinkage

(Fig. 15) and relative density (Fig. 16) also increased with filler loading. Both these properties were lower for the sheets containing calcium carbonate since these sheets had higher expansion than those containing china clay. Abrasion loss decreased with increase in filler loading (Fig. 17). But in this case, calcium carbonate loaded sheets showed higher abrasion loss than china clay loaded samples. Comparatively

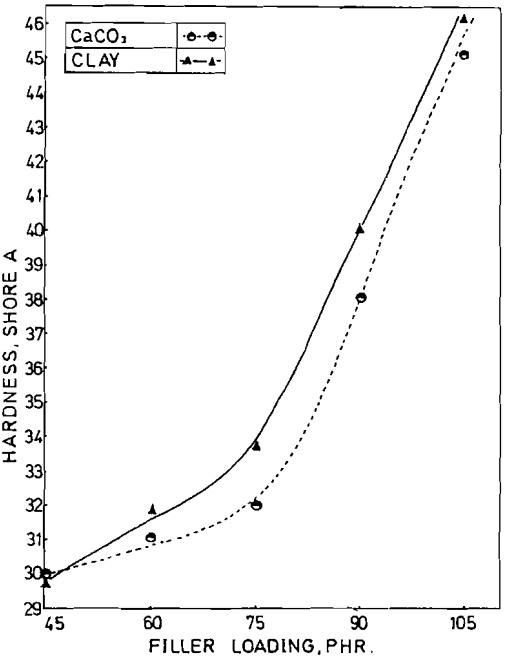

Fig. 15. Effect of china clay and calcium carbonate on hardness

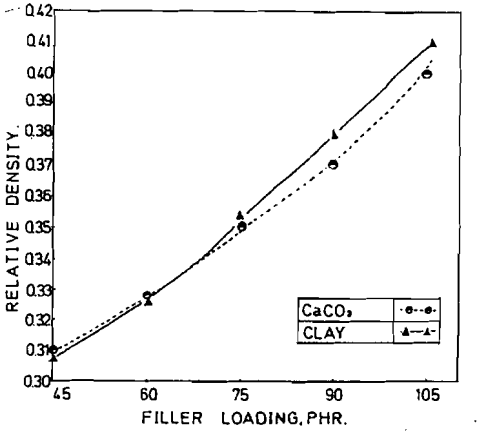

Fig. 16. Effect of china clay and calcium carbonate on relative density

lower split tear and higher abrasion loss of the calcium carbonate loaded sheets is due to higher expansion of the sheets. These two properties depend very much on the strength of the matrix. When expansion is higher, the actual volume of the matrix to take up the load will be lower.

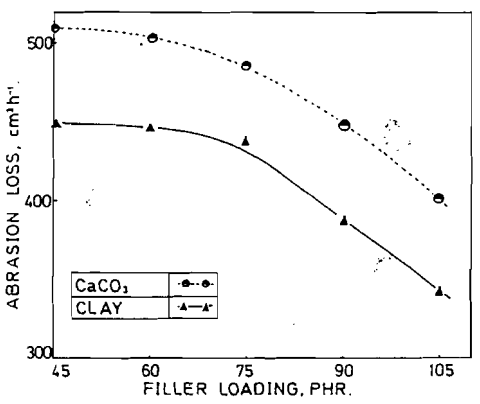

Fig. 17. Effect of china clay and calcium carbonate on abrasion loss

Formulation of compound meeting BIS 10702-1985 specifications

With an understanding of the changes in properties with blend ratio and filler loading, a formulation which can yield microcellular Sheets that meet Bureau of Indian Standards (BIS) specifications for hawai sheets, was developed. The formulation developed and the properties of the sheets prepared using the same are given in Tables 2 and 3 respectively.

Table 2. Formulation to meet BIS 10702-1985 specifications

Polymer blend (40% NR and 60% EVA)	100.0
Zinc oxide	3.5
Stearic acid	1.0
Zinc stearate	2.0
Styrenated phenol type of antioxidant	1.0
Dicumyl peroxide (40% active)	4.0
Calcium carbonate	90.0
Paraffinic oil	3.6
Azodicarbonamide	4.0

CONCLUSIONS

EVA enhances abrasion resistance and split tear strength of microcellular sheets based on NR. It also gives lower density. As the proportion of EVA is increased, compression set and shrinkage are increased. The change in properties with increasing EVA content is basically due to the characteristics of EVA and the accompanying change in cell structure of the microcellular sheet. Between china clay and calcium carbonate, the latter imparts higher expansion and split tear, and gives lower set and abrasion resistance.

Table 3. Physical properties of the microcellular sheet

	Properties	NR-EVA	BIS 10702-1985 specification limits
1.	Relative density	0.45	0.4 to 0.5
2.	Hardness (Shore A)	46	45 ± 5
3.	Change in hardness after ageing at 100°C for 24 h	+2	+5 (max.)
4.	Split tear strength (N)	53	50 (min.)
5.	Shrinkage, 100 ± 1°C, 1 h (%)	2.9	3.0 (max.)
6.	Flex resistance : kilocycles to crack initiation	>400	>60 (min.)
7.	DIN abrasion loss 5 N load (mm^3)	440	—
8.	Compression set (%)	23	25 (max.)
9.	Room temperature shrinkage at 27°C for 2 weeks (%)	1.3	1.5 (max.)

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