Correlation between PRI and tensile strength retention of natural rubber after Geer-oven ageing

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Significant direct correlation between *PRI* (Plasticity Retention Index) and heat ageing resistance of unprotected conventional high-sulphur pure gum vulcanizates (as measured by percent retention of tensile strength after Geer-oven ageing at 70°C) is shown for a large number of crude natural rubber samples. Replacement of benzothiazole-2-thiol (MBT) by *N,N'*-diphenylguanidine (DPG) will not change this significancy of correlation.

INTRODUCTION

An unproctected suphur/CBS (*N*-cyclohexyl 2-benzothiazole sulphenamide) gum compound formulation was previously used to show the relationship between heat ageing resistance (measured by percent retention of tensile strength after 14 days at 70°C and Plasticity Retention Index) for a number of market grades having *PRI* values ranging from 10 to over 90[1]. However, that relationship has not been statistically evaluated. An unprotected gum compound was employed in the investigation, since any effect of the oxidation characteristics of the raw rubber on vulcanizate behaviour would be immediately apparent in gum vulcanizates not containing antioxidant[1].

It was recognized that types of natural rubber containing high levels of natural antioxidants will give the best ageing resistance[2].

The aim of this work is to determine whether a direct correlation exists between results of the *PRI* test and those of the tensile strength retention test of unprotected conventional high-sulphur gum vulcanizates (after 1 week and 2 weeks of Geer-oven ageing at 70°C).

EXPERIMENTAL

The Geer-oven ageing tests were carried out using unprotected conventional high-sulphur gum vulcanizate formulations, i.e. a high-sulphur/MBT gum vulcanizate formulation and a high-sulphur/DPG gum vulcanizate formulation. (See *Table* 1).

An average press cure-time of 40 min (for both compounds) was applied. Therefore, the initial tensile strength values were obtained from specimens vulcanized at optimum-cure or slightly over-cure conditions.

Eighty-one Thin Pale Crepe samples were prepared from latex of the experimental gardens of BPP Bogor with varied preparative method, i.e. by varying the dose and type of chemical additive (without additive, 0.02 and 0.06 phr Cu-acetate, 0.02 and 0.06 phr Mn-acetate, 0.02 and 0.06 phr Cu-oxide, 0.02 and 0.06 phr Mn-oxide), the duration of wet coagulum storage (0, 7 and 14 days), and the number of passes through the crepe-mill (8, 16 and 24 passes). The dose of formic acid for coagulation of field latex was 3 g per kg of dry rubber and the wet crepes were dried at 34°C for 10 days.

Each crude rubber specimen was homogenized before compounding; the compound ingredients were mixed, cured, and stored in accordance with ASTM procedures for the standard formulation ASTM-IA[3]. The tensile strength and Geer-oven ageing tests were also performed conform with ASTM procedures[3]. The *PRI* determinations were carried out in line with the normal procedure[4].

The *TSRI* (Tensile Strength Retention Index) was calculated from the formula:

$$TSRI = \frac{\text{Tensile strength after ageing}}{\text{Tensile strength before ageing}} \times 100$$

The distribution-free Spearman's rank difference method for the correlation of rankables was employed in addition to the conventional product–moment method. The use and computation of Spearman's rank difference method is free of the assumption that the correlated variates are normally distributed[5].

RESULTS

The results of these experiments show a highly significant direct correlation between *PRI* (of the crude natural rubber samples) and percent tensile strength retention, when above mentioned high-sulphur/MBT gum and high-sulphur/DPG gum compound formulations are employed in the tensile strength retention test. *Table* 2 shows the correlation coefficients and coefficients of determi-

Table 1 The compound formulations employed in the experiments

	Parts by weight	
	Formulation-A	Formulation-B
Raw natural rubber	100.0	100.0
Sulphur	3.0	3.0
MBT (Benzothiazole-2-thiol)	1.0	–
DPG (*N,N'*-diphenyl-guanidine)	–	1.0
Zinc oxide	5.0	5.0
Stearic acid	1.0	1.0

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Table 2 Correlation coefficients and coefficients of determination for the relationships between *PRI* of the crude natural rubber samples (x) and *TSRI* of their unprotected conventional high-sulphur/MBT gum and high-sulphur/DPG gum vulcanizates (y); compound formulation as recorded in *Table 1*

	Correlation coefficients and coefficients of determination	
	PRI (y) vs. *TSRI* after 1 week at 70°C (x)	*PRI* (y) vs. *TSRI* after 2 weeks at 70°C (x)
Compound formulation		
MBT gum	r = 0.50 r_{rd} = 0.55 r^2 = 0.25 r^2_{rd} = 0.30	r = 0.76 r_{rd} = 0.76 r^2 = 0.58 r^2_{rd} = 0.58
DPG gum	r = 0.83 r_{rd} = 0.81 r^2 = 0.69 r^2_{rd} = 0.66	r = 0.88 r_{rd} = 0.85 r^2 = 0.77 r^2_{rd} = 0.72

Number of crude rubber samples = 81
Degrees of freedom = 79
$r_{0.001}(70)$ = 0.38 (from r—table)
$r_{0.001}(80)$ = 0.36 (from r—table)
r = correlation coefficient (conventional product-moment method)
r_{rd} = correlation coefficient (Spearman's rank difference method)
For $n > 8$: $r = r_{rd}$

nation obtained. A graphical presentation of the linear relationships between *PRI* and *TSRI* (Tensile Strength Retention Index) by using the high-sulphur/MBT gum compound formulation is given in *Figures* 1 and 2.

Similar lines can be graphically drawn for the application of the high-sulphur/DPG gum compound formulation in the *TSRI* test.

DISCUSSION AND CONCLUSION

The correlation between results of the tensile strength retention tests (with Geer-oven ageing for 7 and 14 days at 70°C, using unprotected conventional high-sulphur/DPG gum or high-sulphur/MBT gum compound formulations and an average press cure time of 40 min at 140°C) and results of the *PRI* test is significant.

The use of above mentioned specific gum compound formulations in this work shows that a low *PRI* indicates a relatively lower percent tensile strength retention after heat-ageing of the rubber, as compared with a high *PRI*. Also, according to the graphs in *Figures* 1 and 2, and the data in *Table* 2, a better correlation would be achieved with a more severe Geer-oven ageing.

The incorporation of an appropriate man-made antioxidant in the mixes can improve the heat-ageing resistance of low *PRI* rubbers[1]. It is also known that unprotected gum vulcanizates prepared with the so-called synergistic combination of MBT and DPG, as their

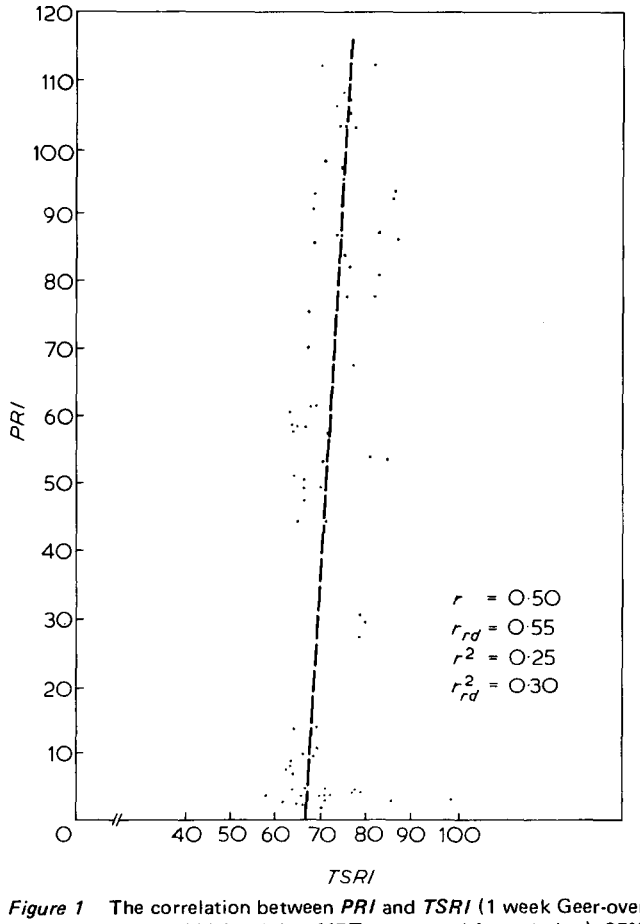

Figure 1 The correlation between *PRI* and *TSRI* (1 week Geer-oven ageing, unprotected high-sulphur MBT compound formulation); 25% of the variances of *TSRI* is associated with variances of *PRI*

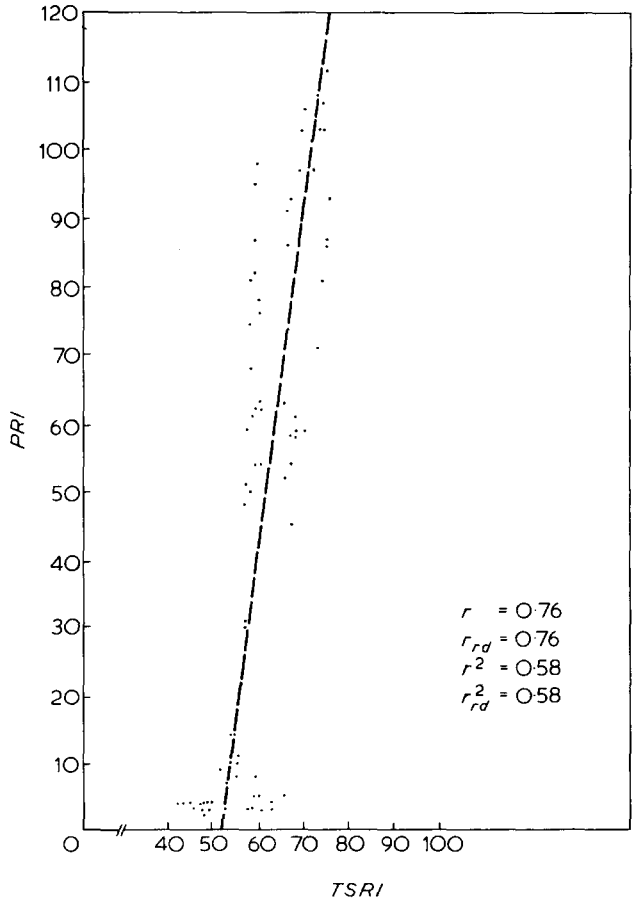

Figure 2 The correlation between *PRI* and *TSRI* (2 weeks Geer-oven ageing, unprotected high-sulphur MBT compound formulation); 58% of the variances of *TSRI* is associated with variances of *PRI*

accelerating systems show poor correlation between heat-ageing behaviour and *PRI*[6]. It was also claimed previously that efficient vulcanization systems show no marked dependence of ageing behaviour on *PRI*[7]. For these reasons only well selected conventional unprotected high-sulphur gum compound formulations with a good ability for reversion, and definitively, optimum-cured or slightly over-cured specimens should be employed in the tensile strength retention test.

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