J. nat. Rubb. Res., 4(2), 107–118

Steam Sterilisation Resistance of Latex Films

NG KOK POON*

The steam sterilisation resistance of natural rubber latex films cured by conventional high sulphur and a sulphur-donor, dithiodimorpholine is examined. Changes in physical properties such as tensile strength, modulus and elongation at break and chemical crosslink density of the vulcanisates after steam treatment are monitored. The effect of addition of antioxidants on steam sterilisation is also investigated. A comparison is made between pre- and post-vulcanised films. The superiority of the sulphur-donor cure system is demonstrated.

Natural rubber latex which gives vulcanisates of high strength and extensibility, is widely used in the production of various medical items[1] such as surgical gloves, catheters, medical tubing, *etc.* Disposable medical items are normally packed and then sterilised. The pack keeps the product sterilised inside it until the product is withdrawn for use. Sterility has to be achieved to the level of less than one bacterium surviving among one million bacteria after the sterilisation process. The sterilisation can be performed in a steam autoclave at elevated temperatures, usually at 121°C or 132°C; or by gamma or electron-beam radiation, the minimum dose is 2.5 Megrads. Another method widely applied for polymer products is by bathing the product in ethylene-oxide gas.

In the case of sterilisable surgical gloves, latex formulation giving high temperature ageing resistance necessary to protect the items during sterilisation, is an additional requirement. An efficient vulcanisation (EV) system, giving mainly thermally stable monosulphidic and disulphidic crosslinks and much less main chain modification, of low sulphur/thiuram cure system can be employed[2].

This paper examines closely the steam sterilisation resistance of latex films cured by conventional high sulphur and a sulphur-donor cure system based on dithiodimorpholine (DTDM). The latter cure system has been claimed to be superior in steam sterilisation resistance[3,4]. The advantages of DTDM are:

- It gives a high degree of crosslink, with disulphidic and carbon-carbon bonds which are stable to thermo-oxidation.
- It is regarded to be a low toxicity material, giving less biological activity than thiuram system and therefore it can be employed in the production of medical goods.

EXPERIMENTAL

A commercial grade of natural rubber latex concentrate of high-ammonia (HA) type was used throughout the study. Compounding ingredients added to the latex were either in the form of solutions, emulsions or dispersions. The chemical dispersions were prepared by ball-milling for at least 48 h before use.

The formulations employed are shown in *Table 1*.

Preparation of Prevulcanised Latex

The formulations used were *A* and *B* as shown in *Table 1*, except that for *Formulation B*, thiourea at 1.0 p.h.r. was added as an additional cure activator[5].

The latex compounds were prevulcanised at 70°C for 150 min with constant stirring. After the prevulcanisation, the latex compounds were cooled down immediately and subsequently clarified before use. Clarification was done by passing the latex through a clarifier bowl of a Westfalia LWA 205-1 laboratory centrifuge machine.

*Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia

TABLE 1. COMPOUND FORMULATIONS

Compound	Formulation	
	A	B
NR latex	100	100
Potassium hydroxide	0.4	0.4
Potassium laurate	0.2	0.2
Zinc oxide	0.5	0.5
Zinc diethyldithiocarbamate (ZDC)	0.75	1.0
Zinc mercaptobenzothiazole (ZMBT)	—	1.0
Sulphur	1.4	—
Dithiodimorpholine (DTDM)[a]	—	3.0
Antioxidant 2246	1.0	1.0

All figures are expressed in dry weights.

[a]Sulphasan R (Monsanto)

Film Preparation and Testing

Latex films were prepared by casting the latex compounds at 23°C ± 2°C on levelled glass plates to a thickness of about 1 mm. After drying, the films were removed, talced and subsequently cured in an air-circulating oven at a temperature of 100°C or 120°C. The films were leached in cold water for at least 16 h and were air-dried at 23°C ± 2°C till clear, usually requiring at least another 72 h.

The stress-strain properties of the films were determined according to *BS 903 Part (A2) (1971)*, and relaxed modulus (MR100) at 100% elongation by a MOD tester. Chemical cross-link measurements were carried out using the method described earlier[6].

Sterilisation Procedure

Steam sterilisation was performed in a commercial high pressure steam steriliser, Natal Autoclave 330, Mark III model. The temperature of sterilisation was set at either 121°C or 132°C. A 30-min cycle with a 1-h interval between sterilisation was selected for the study.

RESULTS AND DISCUSSION

Vulcanisation Kinetics of Latex Films

The vulcanisation kinetics of latex films cured by sulphur and sulphur-donor (DTDM) systems is shown in *Figure 1*. Two different temperatures were used for the different cure systems, in view of the rather slow cure rate of sulphur-donor system at 100°C. Optimum cure time to 100% (t_{100}) was determined for each of the cure systems. These are summarised below:

Cure system	Temperature (°C)	t_{100} (min)
A (S/ZDC)	100	30
B (DTDM/ZDC/ ZMBT)	120	25

All the latex films used in the study were subsequently cured with the optimal conditions determined above.

Changes in Physical Properties of Latex Films on Steam Sterilisation

When latex films were subjected to steam sterilisation at 121°C and 132°C, it was observed that generally there was a reduction in tensile strength and modulus, with an increase in elongation at break. However, the extent of change was less at 121°C. *Figure 2* shows changes in tensile strength, modulus at 300% elongation (M300) and elongation at break with steam treatment for conventional high sulphur cure system *(Formulation A)*, while *Figure 3* shows similar changes for the sulphur-donor cure system based on DTDM *(Formulation B)*.

The sulphur-donor system was observed to give higher modulus than the conventional high sulphur cure system. The superiority of the sulphur-donor cure system could be seen, particularly at a higher temperature of steam sterilisation of 132°C. *Table 2* summarises the percentage retention of tensile strength (TS), M300 and elongation at break (EB) for both the cure systems, after five and ten cycles of steam treatment at 132°C.

The sulphur-donor cure system *(B)* retained about 80% of its original tensile strength after ten cycles of steam treatment at 132°C, while the conventional high sulphur cure system retained only about 50% of its original tensile strength.

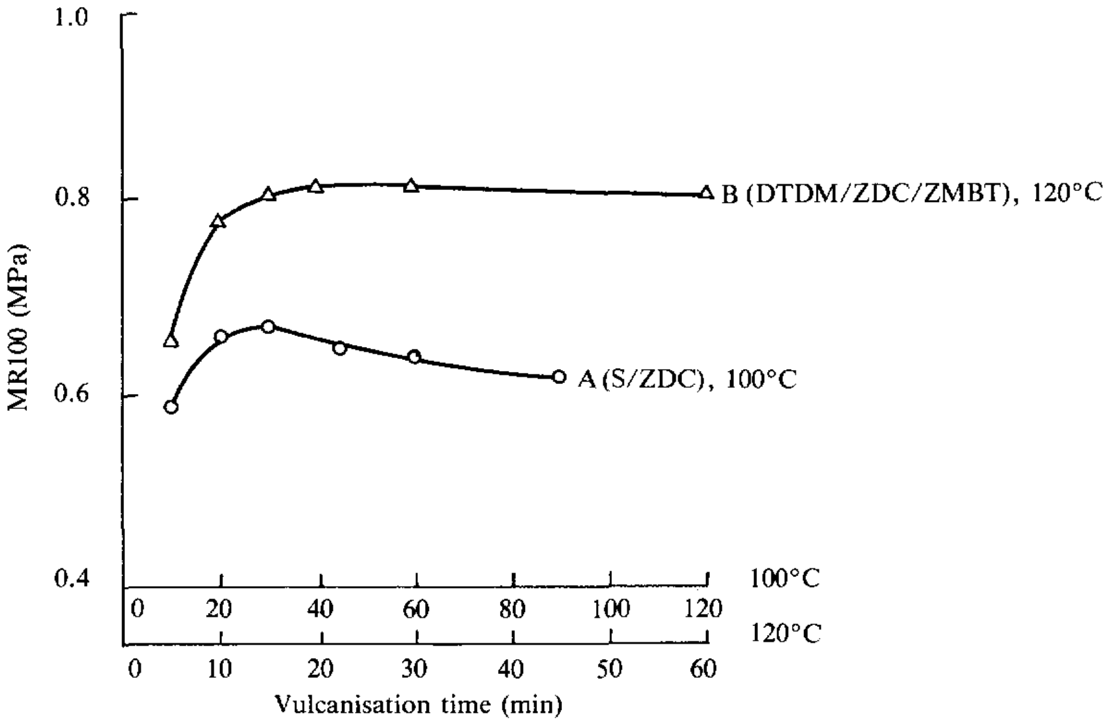

Figure 1. Vulcanisation kinetics of latex films of conventional high sulphur (S/ZDC) and sulphur-donor (DTDM/ZDC/ZMBT) cure systems.

Effect of the Presence of Antioxidants on Steam Sterilisation Resistance of Latex Films

Several commercial non-staining antioxidants, at 1 p.h.r., were evaluated for their effectiveness in protecting the latex films against steam sterilisation. *Figures 4* and *5* show changes in tensile strength, M300 and elongation at break for the conventional high sulphur cure system and the sulphur-donor system, respectively.

The presence of an antioxidant did not, in general, bring about improvement in steam sterilisation resistance of the latex films. This could be probably due to the fact that the ageing under the condition of pressurised steam was closer to anaerobic ageing, due to the limited availability of free oxygen. The extent of degradation would therefore be determined by the type of cure system. Protection offered by the antioxidants would be mininal as such. Furthermore, it has been established previously[7] that, under anaerobic ageing condition, the peroxide and EV cure systems offer the best protection. The superiority of the sulphur-donor cure system of the latex films and the independence of antioxidant would suggest that ageing under pressurised steam was of the anaerobic type.

Steam Sterilisation Behaviour of Prevulcanised and Post-vulcanised Latex Films

With the frequent use of prevulcanised (PV) latex in the production of latex dipped goods, it is therefore useful to examine its steam sterilisation characteristics and compare its performance with a post-vulcanised (POST V) latex compound.

The MR100 values for these two types of latex films were determined and these are shown in *Table 3*.

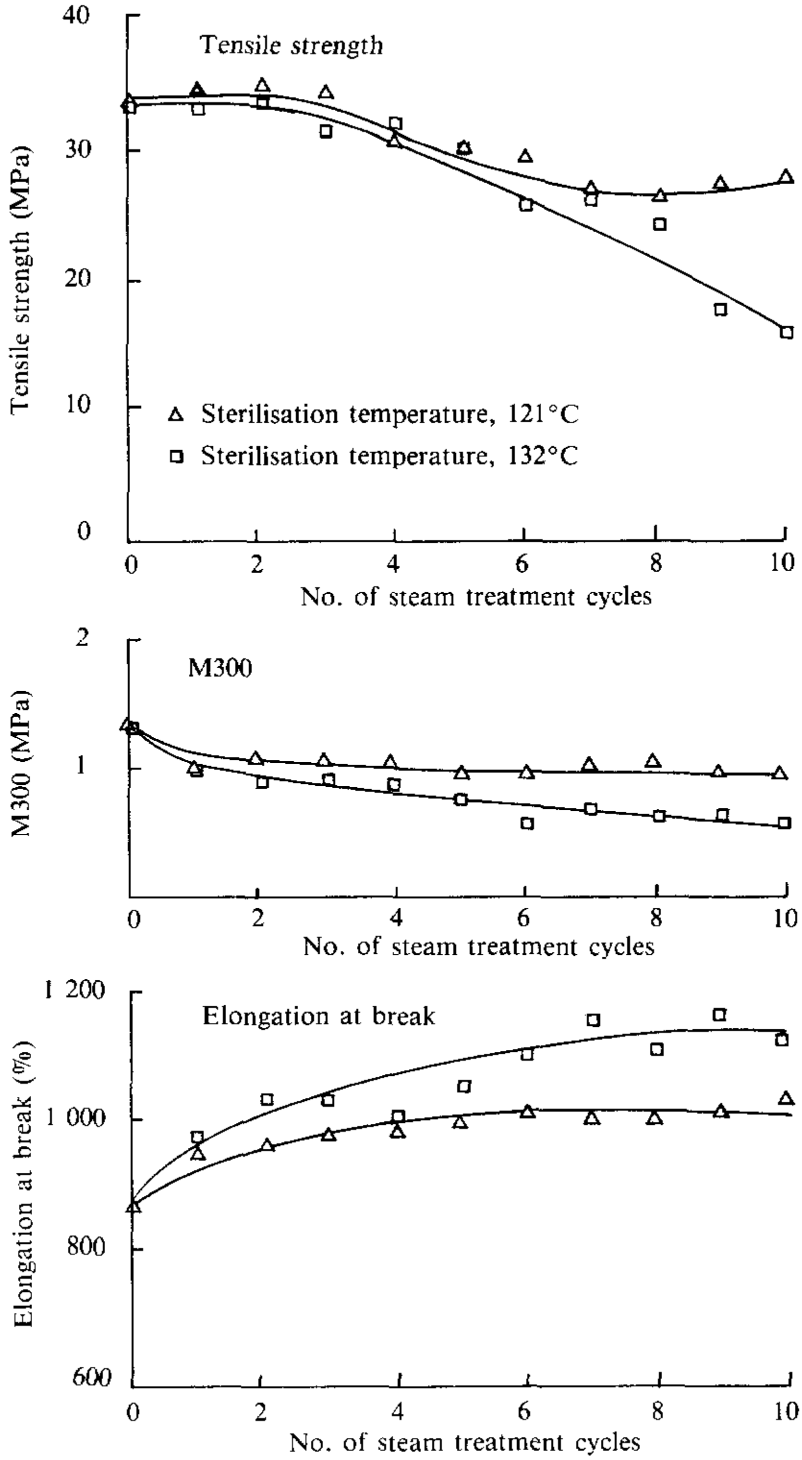

Figure 2. Effect of steam sterilisation on tensile strength, M300 and elongation at break for Cure System A.

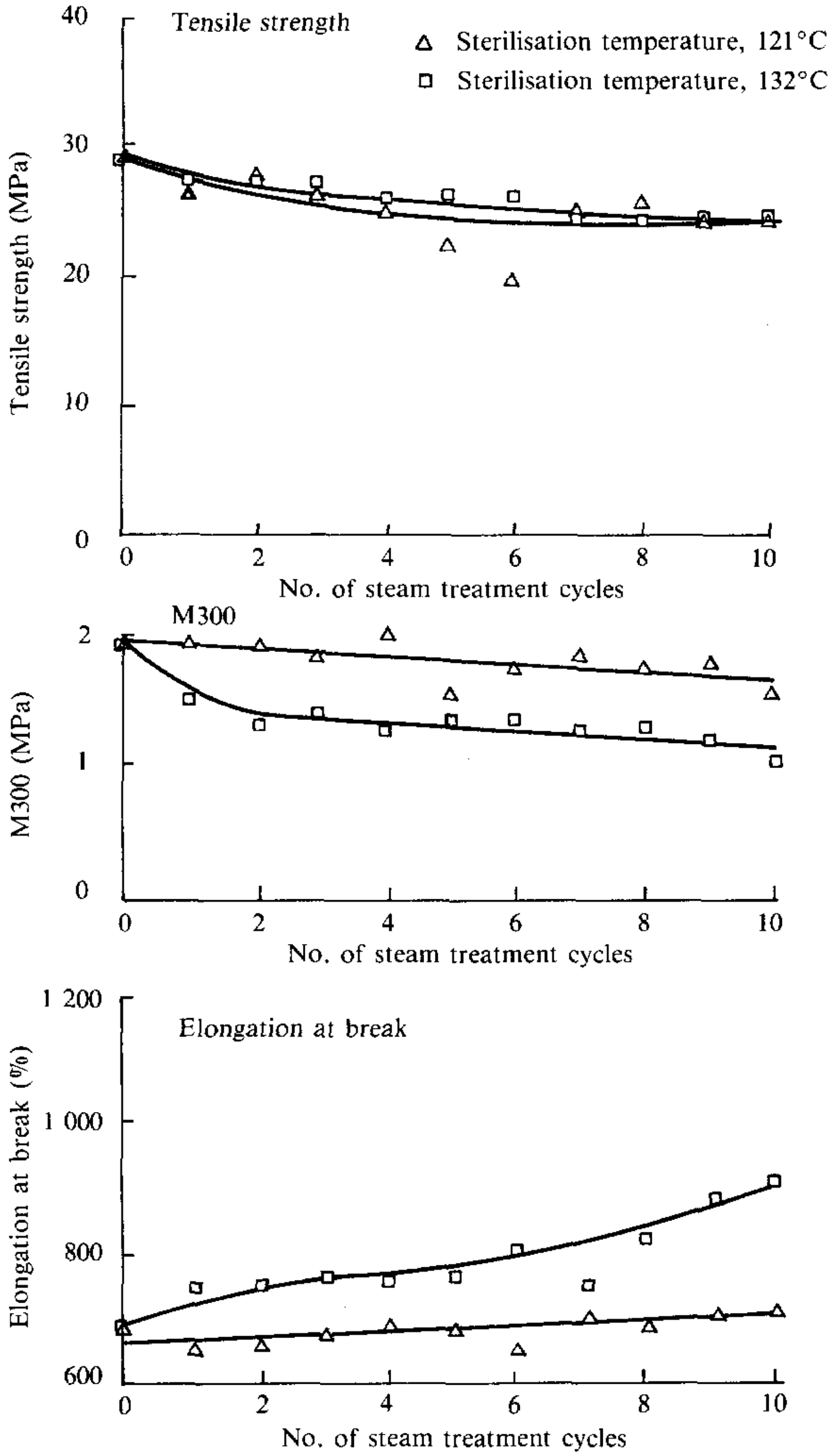

Figure 3. Effect of steam sterilisation on tensile strength, M300 and elongation at break for Cure System B.

TABLE 2. RETENTION IN PHYSICAL PROPERTIES AFTER STEAM TREATMENT

Steam treatment (cycles)	Retention in physical property (%)					
	Cure System A			Cure System B		
	TS	M300	EB	TS	M300	EB
5	91	58	122	87	68	110
10	50	44	130	81	52	130

TABLE 3. RELAXED MODULUS (MR100) OF PREVULCANISED AND POST-VULCANISED LATEX FILMS

Cure System	MR100 (MPa)
A, PV	0.74
B, PV	0.82
A, POST V	0.66
B, POST V	0.86

Higher values of MR100 were obtained for the sulphur-donor cure system for both the prevulcanised and post-vulcanised latex films, indicating the higher state of cure achieved.

The changes as a result of steam treatment in tensile strength, M300 and elongation at break are shown in *Figures 6, 7* and *8* respectively for post-vulcanised and prevulcanised latex films at 121°C and 132°C. Overall, little difference was observed between prevulcanised and post-vulcanised latex films. Reduction in tensile strength, M300 and increase in elongation at break after steam treatment were observed for both types of latex films.

Changes in Chemical Crosslink Density

The changes in physical properties as a result of steam sterilisation of latex films were expected to relate to changes in the chemical crosslink density of the vulcanisates. *Table 4* shows changes in the chemical crosslink density for the prevulcanised and post-vulcanised latex films subjected to various steam treatment.

Higher values of retention of chemical crosslink density were generally obtained for the sulphur-donor cure system, indicating the inherent stability of the crosslinks. After ten cycles at 132°C, about 45% of crosslink density was still retained in the case of sulphur-donor system, compared to only about 13% for the conventional high sulphur cure system.

CONCLUSION

A sulphur-donor cure system based on DTDM has been confirmed to be superior in terms of steam sterilisation resistance to a conventional high sulphur cure system. A reduction in tensile strength, modulus and an increase in elongation at break have been observed, the severity of which depends on the extent and the temperature of sterilisation. There is no difference in steam sterilisation resistance behaviour between prevulcanised and post-vulcanised latex films. The presence of an antioxidant in the latex films does not give protection against steam sterilisation. This is probably due to the anaerobic nature of ageing with the limited supply of free oxygen in the autoclave.

The superiority of the sulphur-donor cure system could be explained by the higher crosslink density and the greater stability of the crosslinks when subjected to steam treatment, typical of an EV cure system.

ACKNOWLEDGEMENT

This work forms part of the research programme of the Rubber Research Institute of Malaysia. The experimentl assistance rendered by Puan Zahara Haniff and Miss Har Mun Lin is gratefully acknowledged. Thanks are also extended to Mr Wong Niap Poh and Dr Loo Cheng Teik for their useful discussion, and to Dr A. Subramaniam, Head of Polymer Research and Process Division for his valuable comments and encouragement.

September 1988

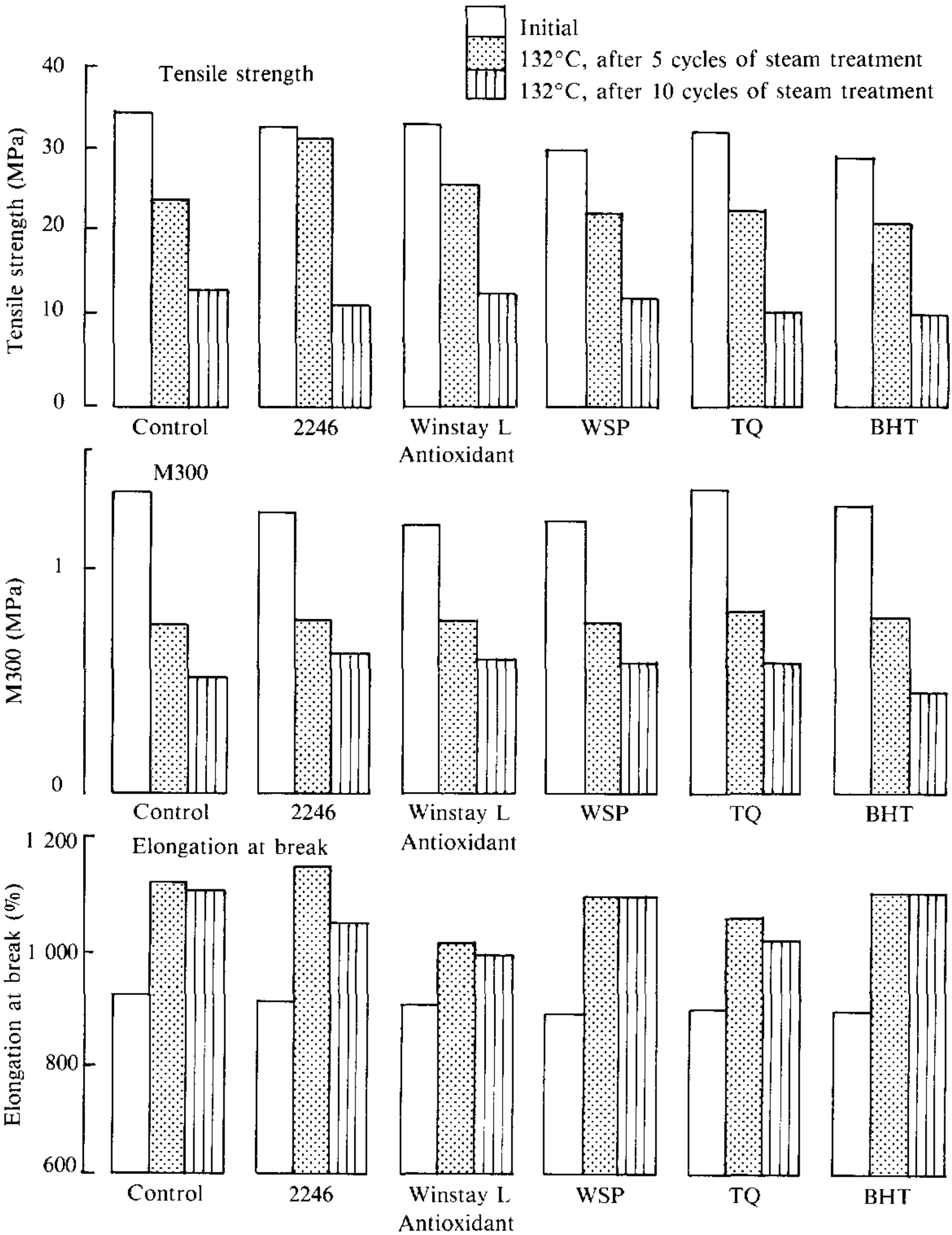

Figure 4. Variation of tensile strength, M300 and elongation at break with antioxidant type after steam treatment for Cure System A.

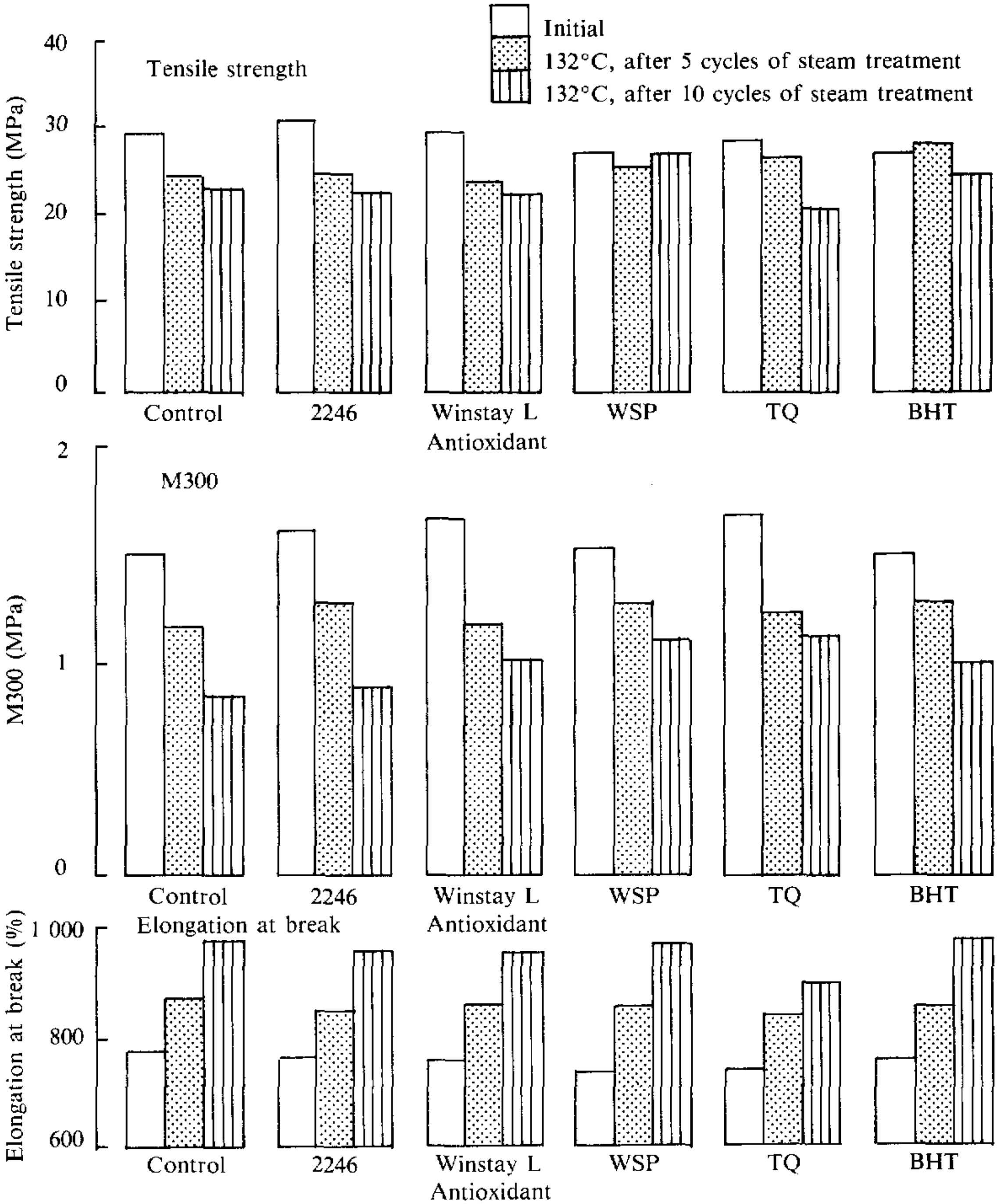

Figure 5. Variation of tensile strength, M300 and elongation at break with antioxidant type after steam treatment for Cure System B.

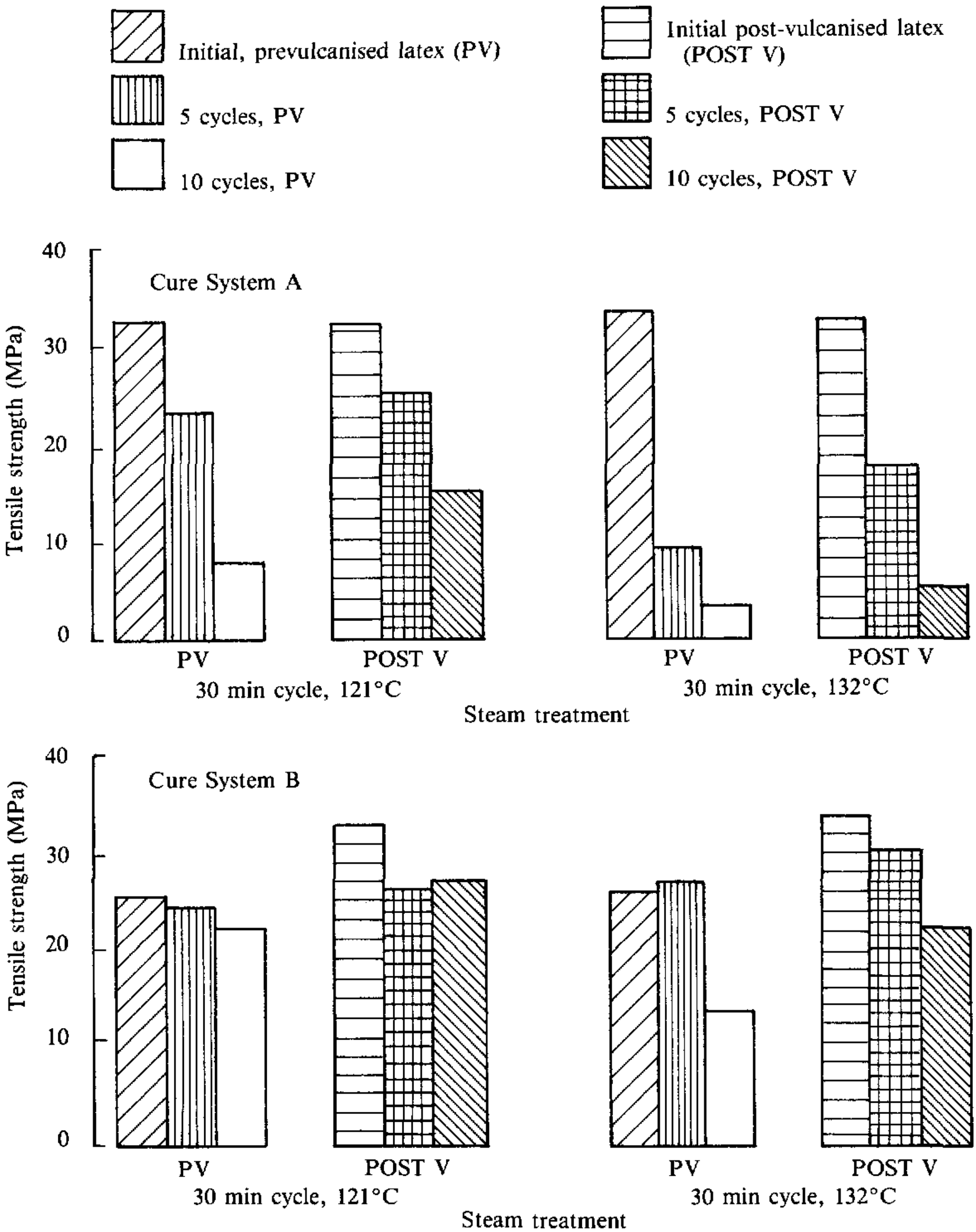

Figure 6. Tensile strength of prevulcanised and post-vulcanised latex films after steam treatment for Cure System A and Cure System B.

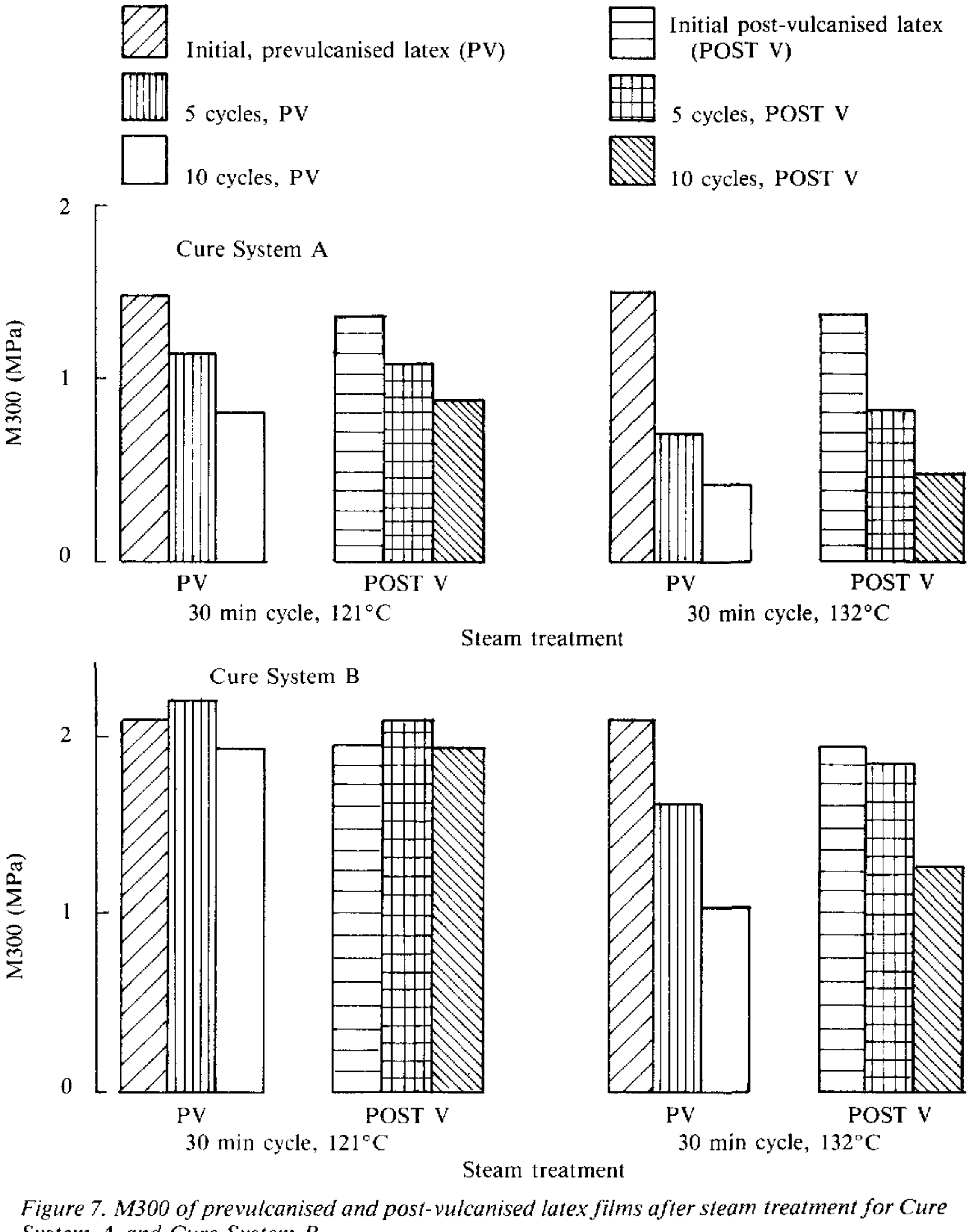

Figure 7. M300 of prevulcanised and post-vulcanised latex films after steam treatment for Cure System A and Cure System B.

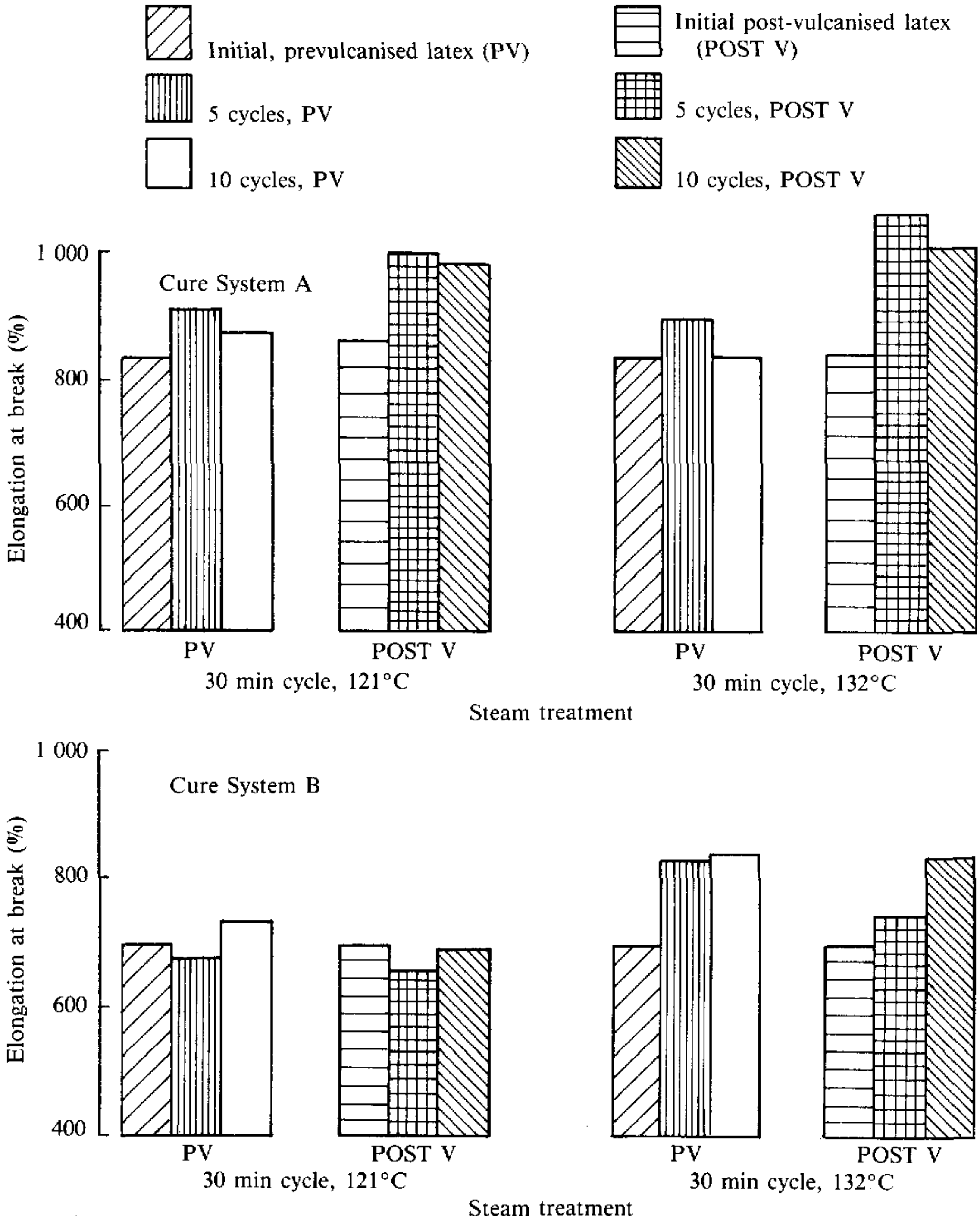

Figure 8. Elongation at break of prevulcanised and post-vulcanised latex films after steam treatment for Cure System A and Cure System B.

TABLE 4. CHANGES IN CHEMICAL CROSSLINK DENSITY OF LATEX FILMS

Steam treatment	*Chemical crosslink density × 10^5* (g mole/g rubber hydrocarbon)			
	A		B	
	PV	POST V	PV	POST V
Initial	3.26	3.41	5.61	4.69
121°C				
After 5 cycles	2.03	2.16	6.25	4.44
	(62)	(63)	(111)	(95)
After 10 cycles	1.45	1.51	4.69	3.95
	(45)	(44)	(84)	(84)
132°C				
After 5 cycles	0.65	0.99	3.91	3.34
	(20)	(31)	(70)	(71)
After 10 cycles	0.40	0.47	2.40	2.18
	(12)	(14)	(43)	(47)

Figures within brackets denote percentage retention in chemical crosslink density.

REFERENCES

1. GORTON, A.D.T. (1983) The Use of Natural Rubber Latex for Products in the Medical and Food Industries. Danish Society of Technologists' Meeting, Denmark, 1983.
2. PORTER, M. (1968) The Chemistry of the Sulphur Vulcanisation of Natural Rubber. *The Chemistry of Sulphides (Tobolsky, A. V. ed)*, p. 165. New York: Interscience.
3. CHERNAYA, V.V. AND ELKINA, I.A. (1975) Vulcanisation of Natural Rubber Latex Films in the Presence of Dithiodimorpholine. *Proc. Int. Rubb. Conf. Kuala Lumpur 1975*, **5**, 49.
4. CHERNAYA, V.V., ELKINA, I.A. AND SHUMSKAYA, N.I. (1978) Production of Latex Articles Used in Medicine. *NR Technol.*, **9(1)**, 8.
5. PHILPOTT, M.W. (1969) Compounding Natural Rubber Latex for Improved Performance. *J. Rubb. Res. Inst. Malaya*, **22(5)**, 441.
6. LOO, C.T. (1974) High Temperature Vulcanisation of Elastomers. Part 2. Network Structures in Conventional Sulphenamide-sulphur Natural Rubber Vulcanisates. *Polymer*, **15**, 357.
7. KNIGHT, G.T. AND LIM, H.S. (1975) Factors Influencing High Temperature Ageing of Large Natural Rubber Components. *Proc. Int. Rubb. Conf. Kuala Lumpur 1975*, **5**, 57.