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Formulations for Heat Resistant Chlorinated Natural Rubber Latex Films

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The high temperature ageing resistance of natural rubber latex films prepared from five different formulations was studied as a function of chlorine concentration and film thickness. Results obtained showed that among other things, formulations that gave films of higher modulus showed better retention of tensile strength after ageing for 22 h at 100°C.

The extractable protein contents of all the chlorinated films, as determined by modified Lowry Microassay against Bovine Serum Albumin, were less than 0.03 mg/g except for the formulation that contained diphenyl guanidine.

Chlorination is widely used for producing powder-free gloves. One of the advantages of the process is that it reduces the water extractable protein contents (EP) of latex products to very low levels[1]. Such reduction of EP is highly desirable in view of the allergy problem[2,3]. Although its exact mechanism is not clearly understood, chlorination is by far the most effective method for EP reduction[4,5,6].

The process is also widely used in the manufacture of catheters and household gloves as an additional process to eliminate the usage of powders. Due to the thick physical profile of these products, problems of physical deterioration caused by chlorination is minimal. However when it is applied to medical gloves where their thickness is approximately 0.2 mm and below, judicious control of the process is essential. Otherwise, it will result in the gloves having poor physical properties particularly after high temperature ageing at 100°C for 22 h.

A paper was published in 1993 on chlorination of gloves[1], explaining the theoretical and practical aspects of chlorination and changes in physical properties after chlorination at different level of free chlorine concentrations. Under the process conditions studied, the properties of the final product were shown to be below specification as required by the *ASTM* standard. Further storage of the product above the ambient temperature is expected to result in further deterioration in properties. The purpose of this work is to overcome these problems by developing suitable formulations to give latex films which are resistant to high temperature ageing.

GENERAL PROCESS OF CHLORINATION

In general, the chlorination process involves attachment of chlorine atoms onto the backbone of natural rubber molecules on the surface of the latex films. Free chlorine atoms required can be produced by either dissolving chlorine gas in water or by reacting hypochlorite solution with acid to release the chlorine.

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A general procedure for producing chlorinated gloves is given as follows:

Procedure	Conditions
Gloves	Washed
Water	Gloves : Water 1 : 20
Chlorine	Min. 700 p.p.m. Max. 1000 p.p.m.
Tumble/agitation	Time
Washed	Water
Neutralisation	Sodium thiosulphate Ammonia
Washed	Water
Inversion[a]	
Soaking[b]	Time
Drying	Low temperature
Cooling	Room temperature
Packing	Aired

[a]If double chlorination is required, repeat process
[b]Optional

Gloves should possess good physical properties and may be washed with water if necessary prior to the chlorination process.

EXPERIMENTAL

A series of formulations with different curative systems were prepared, as shown in *Table 1*. *Formulation A* uses a single accelerator system and *Formulations B,C,D* and *E* have either two or three combinations of accelerators amongst which synergistic effects were expected to take place. Films of thicknesses 0.1, 0.2, and 0.4 mm were prepared by the normal coagulant dipping. After leaching for approximately 5 min at 70°C, the dipped films were cured at 100°C for 20 min. They were then exposed to various concentrations of chlorine solutions for 15 min, washed with water, neutralised and washed again before drying at 50°C in an air circulated oven. The dried films were then kept for 24 h in a dessicator before the unaged properties were measured. The ageing process was carried out under two conditions, 22 h at 100°C and 7 days at 70°C, after which the tensile properties of the films were tested.

The water extractable protein values of the films were determined by the Rubber Research Institute of Malaysia modified Lowry micro-assay against Bovine Serum Albumin (BSA) standard.

RESULTS AND DISCUSSION

Figures 1-15 show the plots of tensile strength values of latex films of varying thickness *versus* chlorination concentrations for the five formulations investigated.

Tensile Strength Values

Unaged samples. As shown in *Figures 1, 4, 8, 10,* and *13* the tensile strength values of unaged samples ranged from 22 MPa to 38 MPa. They were not affected by increase in chlorine concentration or changes in film thickness. The unaged values for *Formulations A* and *B* were approximately 25 MPa and improved to above 30 MPa in *Formulations C, D* and *E*. The required value by *ASTM* specification is 21 MPa, indicating that all formulations are capable of meeting the specified requirements.

Aged for 22 h at 100°C. All samples of *Formulations A* and *B* were severely affected by ageing as illustrated in *Figures 3* and *6*. The tensile strength values deteriorated by approximately 30% to 50%. The deterioration was most marked when the film thickness was 0.1 mm. Since the values after ageing were below 16MPa, *Formulations A* and *B* were not suitable for chlorinated gloves. However better performance was observed in *Formulation C* as shown in *Figure 9*. All the values were above the specification with the exception of

TABLE 1. FORMULATIONS WITH VARYING LEVELS OF CURATIVES

Item	Formulation (parts by dry weight)				
	A	B	C	D	E
High ammonia latex	100	100	100	100	100
Potassium hydroxide	0.3	0.3	0.3	0.3	0.3
Potassium laurate	0.2	0.2	0.2	0.2	0.2
Zinc oxide	0.4	0.4	0.25	0.4	0.4
Zinc dibutyldithiocarbamate	1	0.3	0.7		
Zinc diethyldithiocarbamate		0.6		0.2	0.2
Zinc mercaptobenthiozole		0.3	0.2	1	1
Diphenyl guanidine					1
Sulphur	1	1.5	0.7	2	1
Winstay L	1	1	1	1	1
Titanium dioxide	5	5		5	5

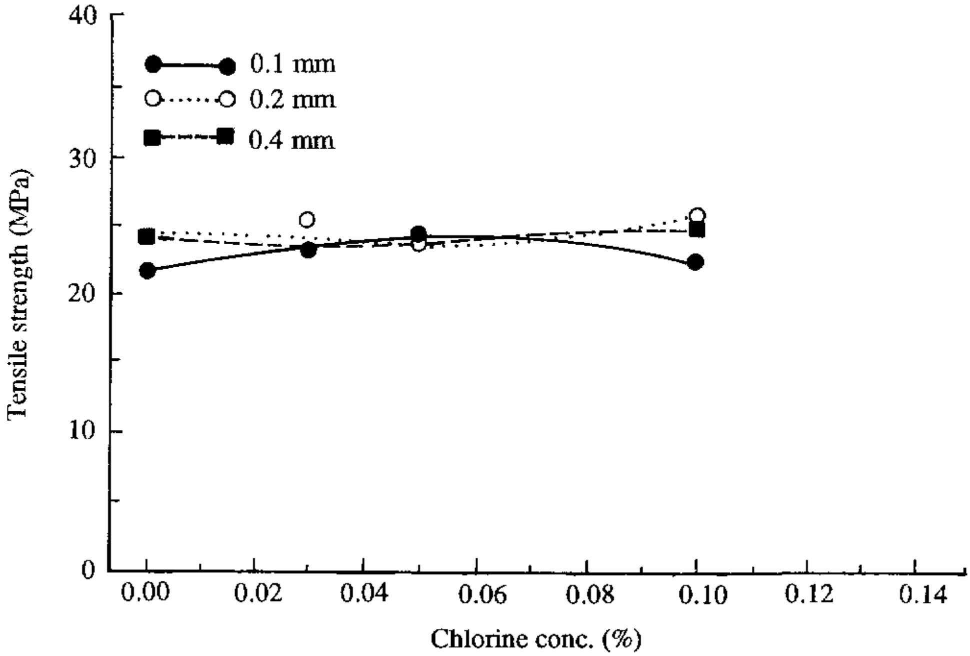

Figure 1. Tensile strength versus *chlorine concentration (Formulation A: unaged).*

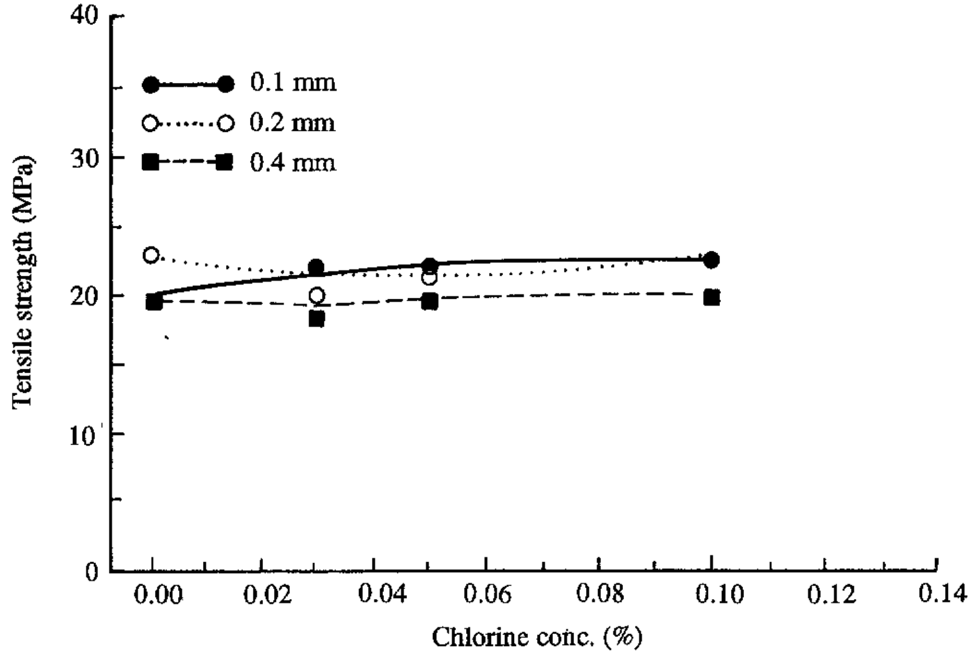

Figure 2. Tensile strength versus *chlorine concentration (Formulation A: aged 70°C).*

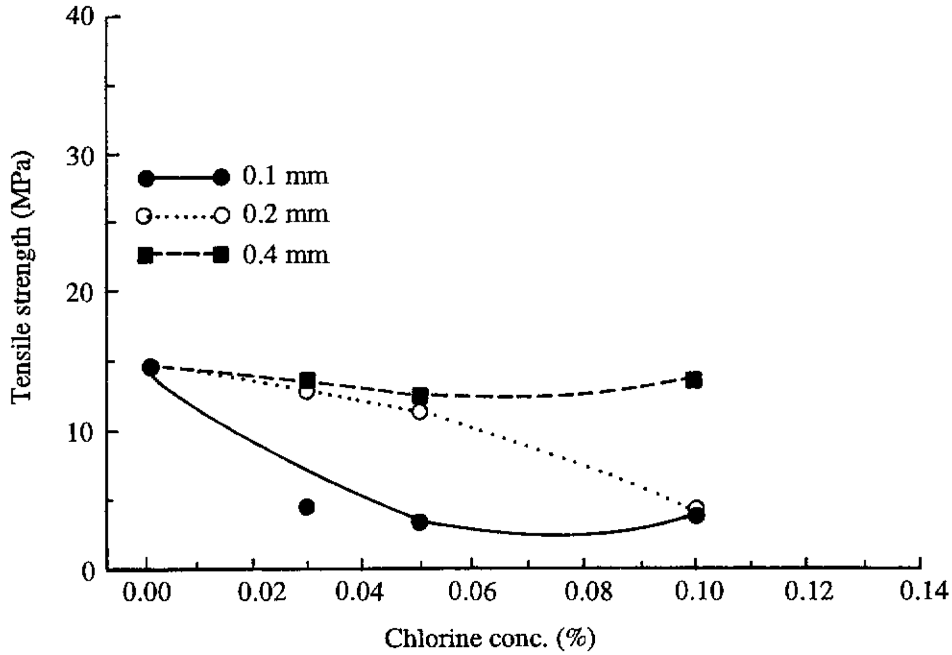

Figure 3. Tensile strength versus *chlorine concentration (Formulation A: aged 100°C, 22 h).*

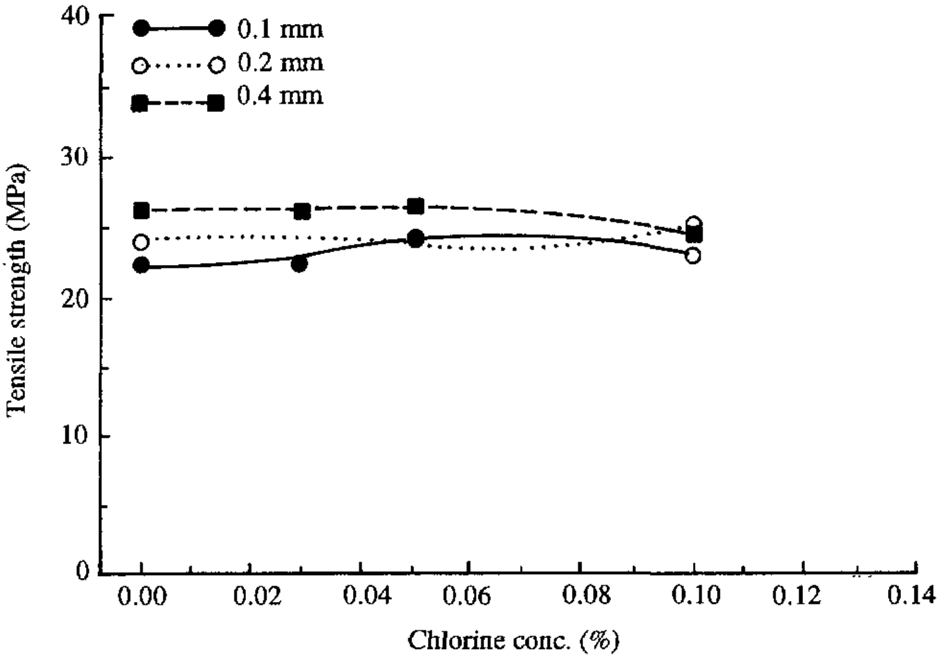

Figure 4. Tensile strength versus *chlorine concentration (Formulation B: unaged).*

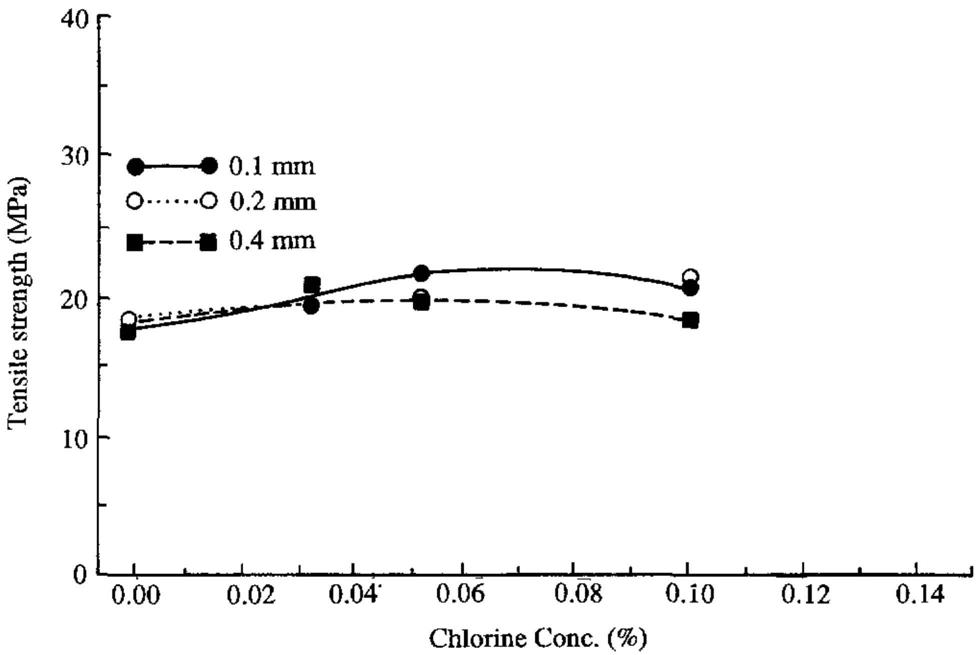

Figure 5. Tensile strength versus *chlorine concentration (Formulation B: aged 70°C).*

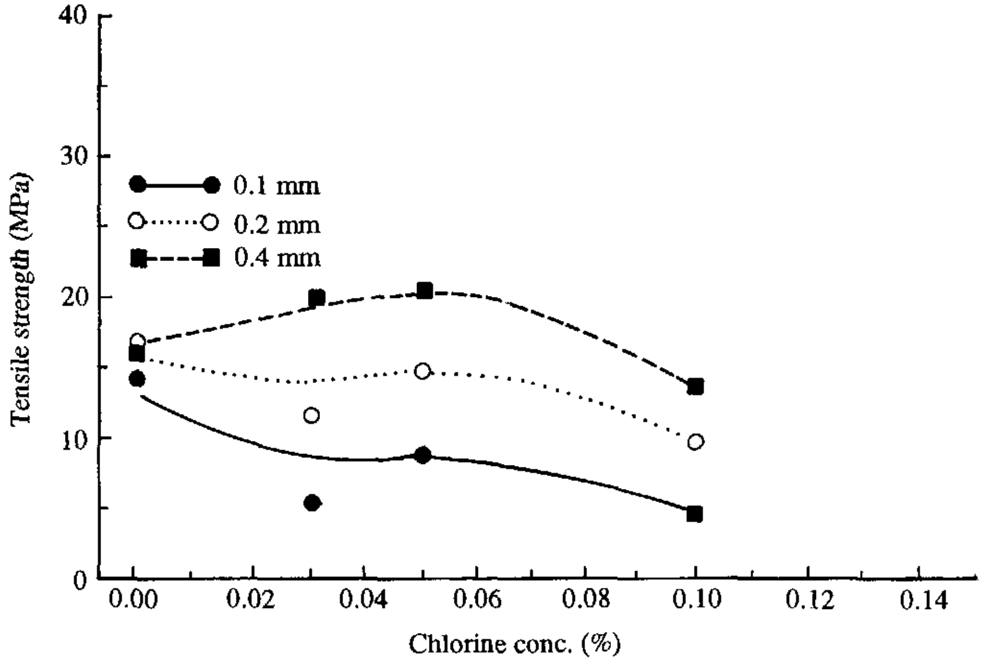

Figure 6. Tensile strength versus *chlorine concentration (Formulation B: aged 100°C).*

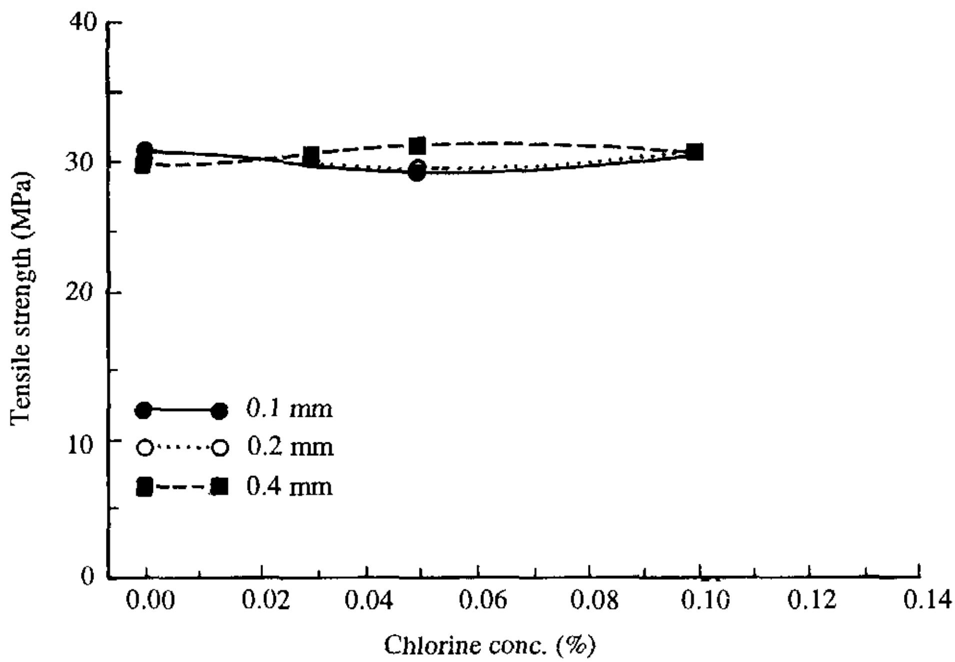

Figure 7. Tensile strength versus *chlorine concentration (Formulation C: unaged).*

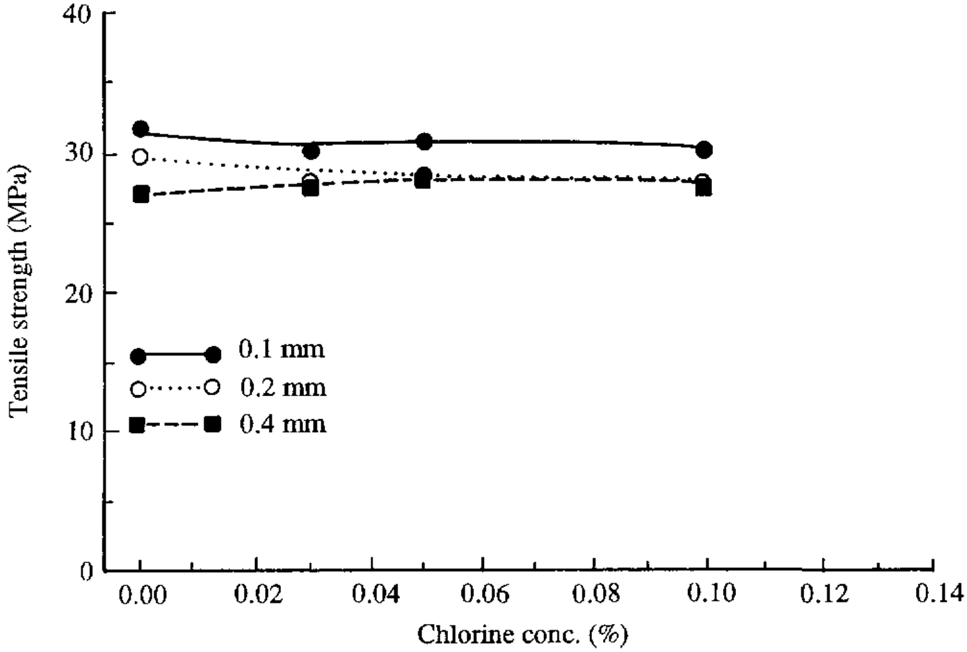

Figure 8. Tensile strength versus *chlorine concentration (Formulation C: aged 70°C, 7 days).*

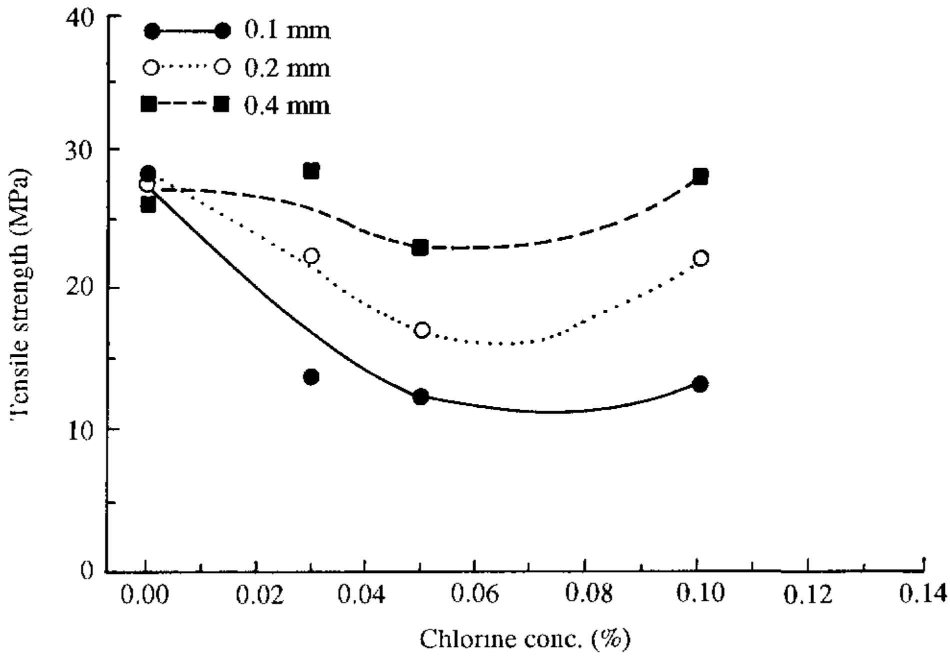

Figure 9. Tensile strength versus *chlorine concentration (Formulation C: aged 100°C, 22 h).*

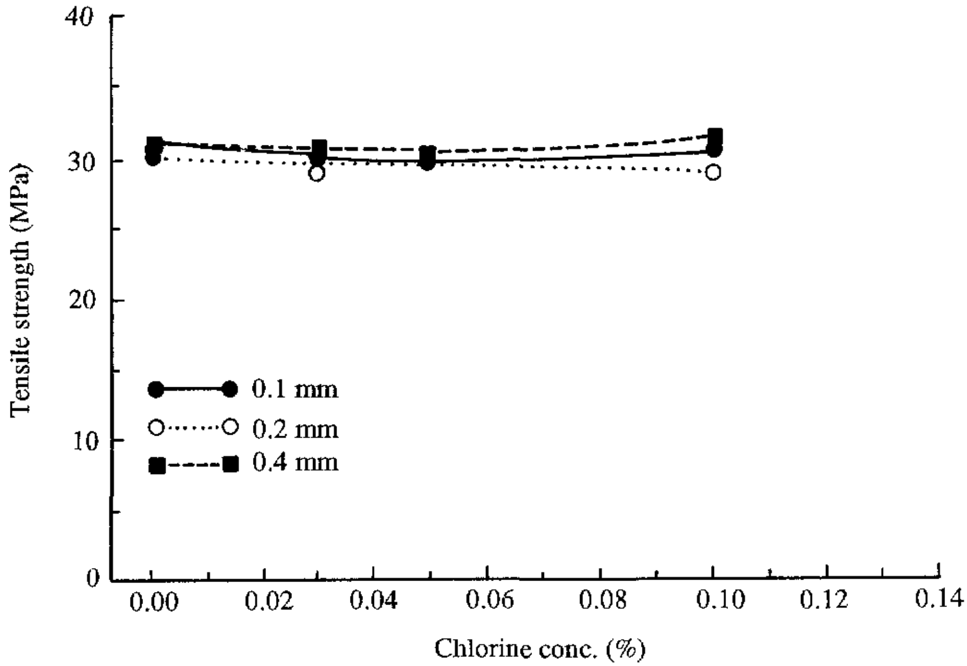

Figure 10. Tensile strength versus *chlorine concentration (Formulation D: unaged).*

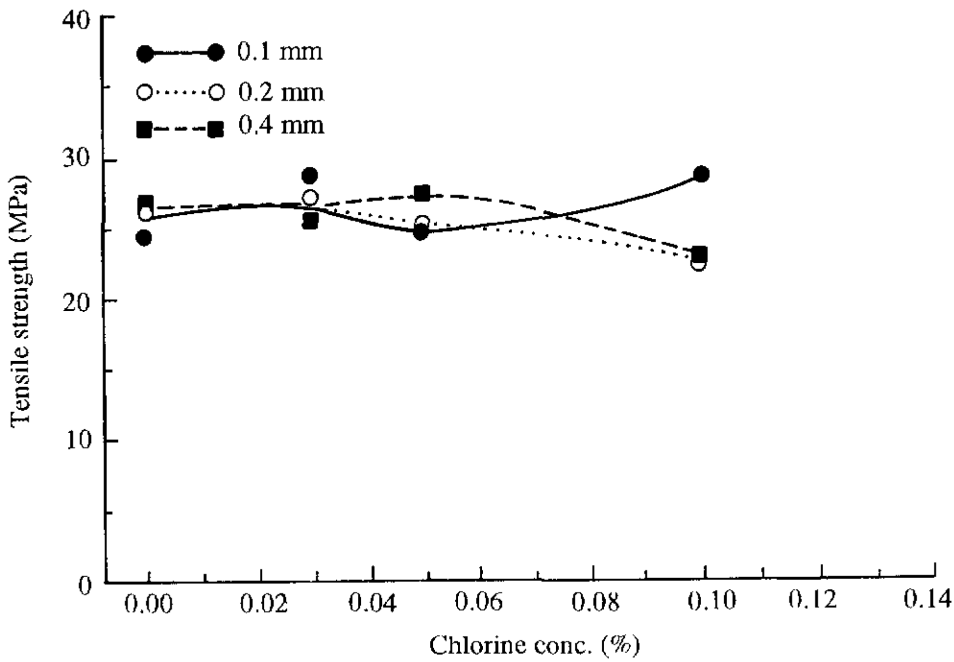

Figure 11. Tensile strength versus *chlorine concentration (Formulation D: aged 70°C).*

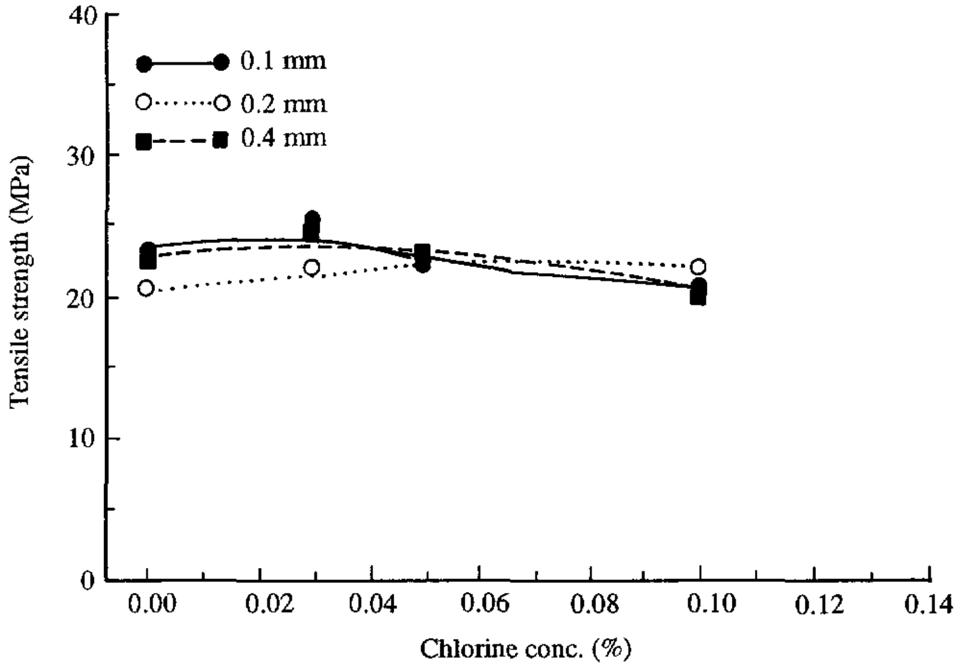

Figure 12. Tensile strength versus *chlorine concentration (Formulation D: aged 100°C).*

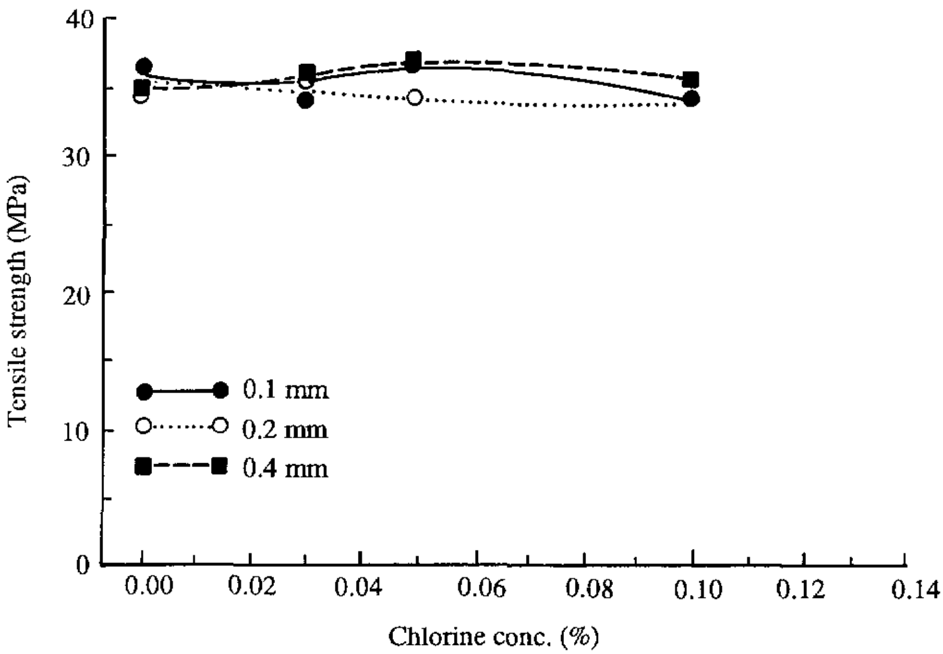

Figure 13. Tensile strength versus *chlorine concentration (Formulation E: unaged).*

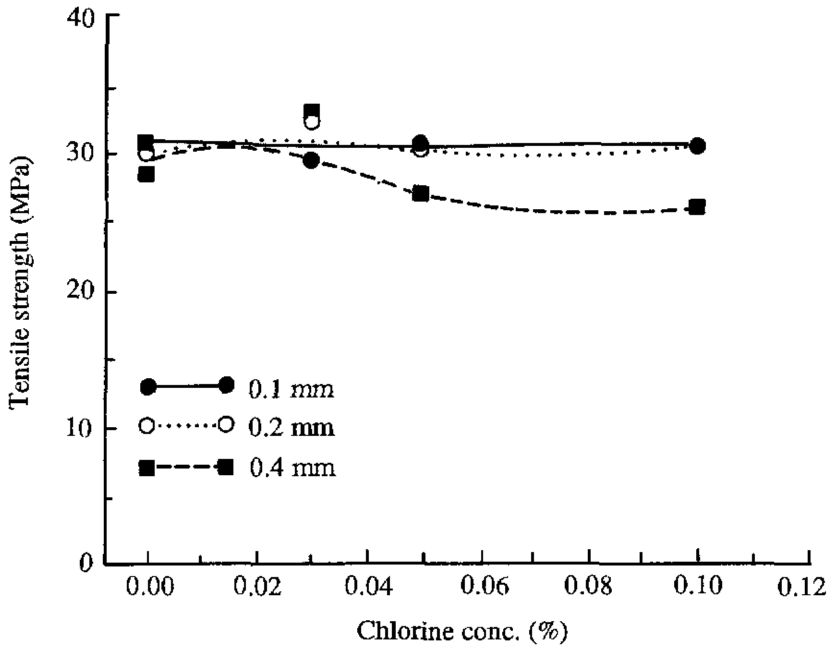

Figure 14. Tensile strength versus *chlorine concentration (Formulation E: aged 70°C).*

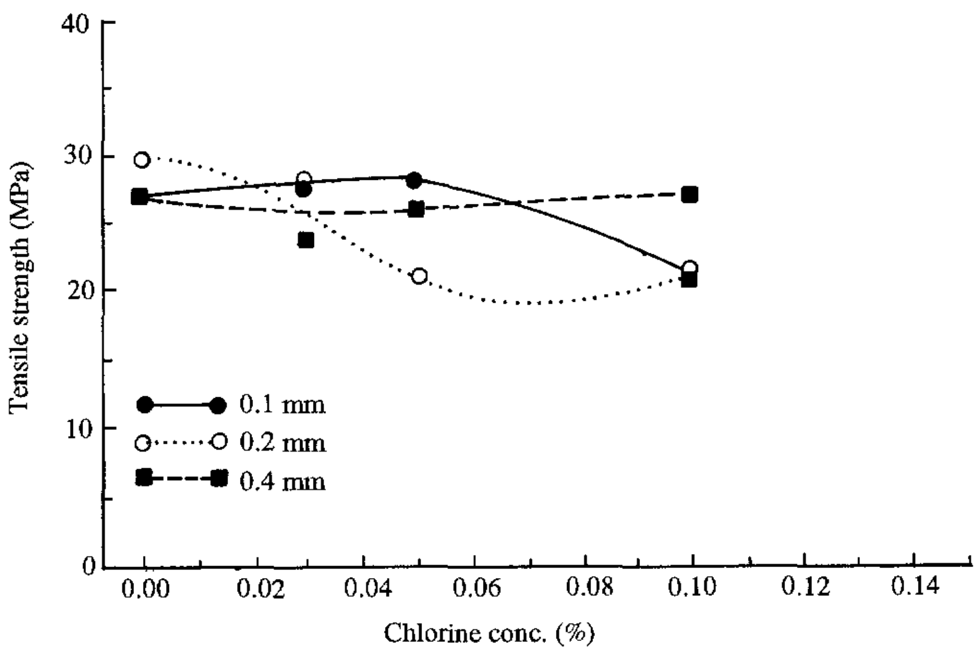

Figure 15. Tensile strength versus *chlorine concentration (Formulation E: aged 100°C).*

samples with thickness of 0.1 mm, which again exhibited poor heat resistance.

Formulations D and *E* exhibited higher aged tensile strength values, (approximately above 70%), as shown in *Figures 12* and *15*. The retention was also unaffected by changes in chlorine concentration and sample thickness. It is worth noting that the results for *Formulation D* were more consistent than those of *Formulation E:* the aged tensile strength values decreased monotonically with increasing chlorine concentration. They were however all above the minimum specification.

Aged for 7 days at 70°C. The retention in tensile strength values after ageing at 70°C for 7 days was above 80% for all samples. It was not significantly affected by changes in sample thickness and chlorine concentration. As shown in *Figures 2, 5, 8, 11* and *14,* the values ranged from 17 MPa to 33 MPa and were above the minimum requirement.

Extractable Protein Contents

The extractable protein (EP) content of all chlorinated films ranged from 0.009 to 0.030 mg/g sample. However for *Formulation E,* the value was slightly higher as compared to other samples. In view of this, only *Formulations C* and *D* were found suitable for production of chlorinated gloves with good heat resistance and low EP contents. *Tables 2* and *3* below show the other tensile properties of chlorinated films of *Formulations C* and *D* (unaged and aged at 70°C for 7 days and 100°C for 22 h). The EB (%) and modulus values were satisfactory and met the requirements of standard specifications.

CONCLUSION

Changing the accelerator system or increasing the thickness of latex films was found to improve the ageing resistance of the films. For less severe ageing conditions (for 7 days at 70°C) all five formulations studied passed the *ASTM* specification. However, when severe ageing condition (for 22 h at 100°C) was used

TABLE 2. TENSILE STRENGTH, MODULUS AND EB VALUES *(FORMULATION C)*

Item	Unaged			Aged (100°C for 22 h)			Aged (70°C for 7 days)		
0% Chlorinated									
Thickness (mm)	0.1	0.2	0.4	0.1	0.2	0.4	0.1	0.2	0.4
Tensile strength	30.73	29.74	29.88	28.36	27.84	26.27	31.78	29.77	27.20
Elongation at break	900	900	850	850	850	830	850	850	800
M100	0.80	0.80	0.90	0.60	0.65	0.70	0.85	0.75	1.00
M300	1.50	1.45	1.55	1.30	1.35	1.55	1.65	1.50	1.75
M500	2.55	2.40	3.00	2.50	2.50	2.80	2.85	3.00	3.35
M700	11.20	10.00	12.25	10.40	8.75	11.80	13.50	15.30	15.00
0 1% Chlorinated									
Tensile strength	29.88	30.36	30.28	13.86	22.83	28.75	30.03	28.27	27.70
Elongation at break	930	900	870	1000	970	870	1000	930	800
M100	1.00	1.00	1.00	0.80	1.00	1.00	0.55	0.65	0.65
M300	1.60	1.60	1.75	1.30	1.45	1.80	1.20	1.35	1.55
M500	2.70	2.80	3.10	2.00	2.15	2.85	2.10	2.20	2.90
M700	9.50	10.75	11.90	3.55	5.10	9.20	6.60	8.25	10.10

TABLE 3. TENSILE STRENGTH, MODULUS AND EB VALUES *(FORMULATION D)*

Item	Unaged			Aged (100°C for 22 h)			Aged (70°C for 7 days)		
0% Chlorinated									
Thickness (mm)	0.1	0.2	0.4	0.1	0.2	0.4	0.1	0.2	0.4
Tensile strength	31.20	30.38	30.61	23.19	20.65	22.51	24.81	26.09	26.79
Elongation at break	800	760	780	700	600	600	620	660	640
M100	0.75	0.75	0.75	1.00	1.00	1.00	1.00	1.00	1.00
M300	2.25	1.75	2.00	2.00	2.50	2.50	2.50	2.50	2.50
M500	3.75	3.75	4.25	5.50	5.50	7.25	5.75	6.25	5.75
M700	22.50	22.00	22.75	–	–	–	–	–	–
0.1% Chlorinated									
Tensile strength	30.26	29.04	31.24	20.32	21.79	19.77	28.83	22.60	23.00
Elongation at break	770	770	760	850	710	660	800	700	690
M100	1.00	1.00	1.00	1.00	0.75	1.00	1.00	1.00	1.00
M300	2.00	2.00	2.00	1.75	1.75	2.50	2.00	2.25	2.50
M500	4.00	3.75	4.00	3.00	3.50	5.00	4.00	4.75	6.25
M700	19.00	19.25	19.00	10.00	14.00	–	17.25	–	–

on thin latex films of 0.1 mm thickness, only *Formulations C, D* and *E* met the specified requirements. Of the three formulations, *C* and *D* are the best in terms of heat resistance and extractable protein content and are therefore recommended.

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REFERENCES

1. NOR AISAH AB. AZIZ (1993) Chlorination of Gloves. *IRTC Latex Protein Wkshop, Kuala Lumpur, 1993.*
2. FOOD AND DRUG ADMINISTRATION (1992) Sensitivity to Latex in Medical Devices. *Proc. Int. Latex Conf. Baltimore, Maryland, USA, 1992.*
3. LOVELL, C.R. (1993) *Relationship between Protein Level and Allergic Response. Latex Protein Allergy: the Present Position.* Crain Communications and Rubber Consultants, Hertford, UK.
4. SUBRAMANIAM, A. (1992) Reduction of Extractable Protein Content in Latex Products. *Proc. Int. Latex Conf. Baltimore, Maryland, USA, 1992.*
5. ESAH YIP (1993) Determination of Extractable Protein in NR Latex Products by HPLC. *IRTC Latex Protein Wkshop, Kuala Lumpur, 1993.*
6. NG, K.P., SUBRAMANIAM, A., ESAH YIP AND MOK, K.L. (1993) Extractable Protein Content of Glove from PV NR Latex. *IRTC Latex Protein Wkshop, Kuala Lumpur, 1993.*