J. Rubb. Res., **15(3)**, 167–178

Properties of Carboxylated Nitrile Latex Film with Varying Thickness

H.M. LIM*#, K. VIVAYGANATHAN* AND M.Y. AMIR-HASHIM*

Increasing price of raw materials and operational cost have triggered glove manufacturers to produce gloves with fewer amounts of material while meeting the minimum requirements for the intended application. Examination gloves in particular, are getting thinner from approximately 7 to 9 grams to 3 to 5 grams. In this study, the physical properties of latex films made from carboxylated acrylonitrile butadiene latex (XNBR), a typical base material for an examination glove, are assessed to elucidate any differences due to the thickness of the film. XNBR latex films of different thicknesses were prepared at a laboratory scale. The XNBR latex was compounded with a varying dosage of zinc oxide (ZnO) to vary the expected ionic crosslink density of the films. The mechanical properties of these films were evaluated. This study confirmed that with increasing loading of ZnO, the physical properties specifically, the tensile strength and the modulus values increased, while the extension tended to be lower and tear strength poorer. As expected, the thicker films had higher physical properties compared with thinner ones. Although heat ageing may not affect XNBR films much, results indicated that XNBR films subjected to accelerated ageing showed higher tensile strength with lower elongation at break value than the unaged films. Crosslink density was estimated using the equilibrium swelling method. The role of ZnO is clear in XNBR film formation as the overall crosslink density of XNBR-ZnO film increased with increased amounts of ZnO. However, there is no clear relationship between the physical properties and the estimated crosslink density in this study.

Keywords: carboxylated acrylonitrile butadiene latex; XNBR; nitrile; examination glove; crosslink density; zinc oxide; physical properties

Traditionally, natural rubber latex (NRL) is the preferred base material for thin latex products such as medical examination gloves as it provides high tensile strength and elongation at low modulus. Thus, NRL gives comfort, feel and strength for examination gloves in a medical situation. Over the years, increasing concern on the potential allergen due to NRL protein towards those who are allergic to latex spurs glove makers to provide a synthetic alternative to NRL[1]. Fearing high insurance claims due to complications related to NRL allergy, some medical institutes have declared a "latex safe" hospital and have instilled a policy of discouraging NRL based products in the hospital[2].

*Rubber Research Institute of Malaysia, Malaysian Rubber Board, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia.
Corresponding author (e-mail: evelyn@lgm.gov.my)

Sensing the opportunity for nitrile as the best alternative to replace NRL for medical gloves, nitrile manufacturers continue to work on the specific properties of examination gloves application including improving the comfort needed for better acceptance of the material to NRL. Carboxylated nitrile latex (XNBR) is a copolymer of acrylonitrile, butadiene and methacrylic acid. As XNBR is known to be a harder material compared to NRL, research and development has been geared towards developing soft and high relaxation nitrile gloves to provide better tactile sensitivity and dexterity for its end users[3–5]. Nitrile gloves exhibit comparable barrier protection as NRL gloves with the added advantages of providing good puncture and chemical resistance. Furthermore, the synthetic glove does not easily degrade under storage, allowing stocking of the glove for a longer period than an NRL glove that is known to be biodegradable.

As a result of the above, NRL gloves although comfortable to use, face increasing competition from emerging alternative synthetic materials, especially the nitrile and PVC gloves for single use general examination hand protection. Based on a recent survey, the market share between NRL and nitrile gloves is estimated to be in the ratio of 70:30[6] and the trend is moving rapidly towards substituting NRL gloves with nitrile mainly due to costs. Nevertheless, NRL gloves remain the main barrier material of choice attributed to its high wet gel strength, good tensile and tear strengths, high elasticity, softness and "green image".

With the continued surge of natural latex price over the recent years[7] and increases in other materials as well as energy needed for production, the glove manufacturers have no choice but to strategise accordingly. This includes producing nitrile examination gloves which are at present better in overall cost effectiveness compared to producing NRL examination gloves. Most manufacturers have either expanded their nitrile glove production capacity or switched their current NRL glove production line to produce nitrile gloves[8]. One clear advantage of nitrile gloves is that the manufacturer can produce much thinner gloves than NRL ones at lower energy consumption, thus saving huge overheads in raw materials and energy.

Fisher *et al.* demonstrated that the XNBR film which is a harder and relatively stronger material than NRL can therefore be made much thinner than an NRL latex film while retaining the attributes of puncture resistance[9]. As the trend of nitrile gloves are towards thinner and lighter gloves compared to earlier production, it is deemed necessary to investigate the properties of these thin films, particularly the properties that govern the films' barrier performance which influences the usefulness of the intended product. In this study, varying dosages of zinc oxide were added to the XNBR intended to increase the crosslink density, namely the ionic crosslink of the XNBR film, along with an investigation into the physical properties of XNBR films of different film thickness.

EXPERIMENTAL

Materials and Methods

Commercial grade XNBR was used to prepare the XNBR films. Aqueous dispersions of sulphur, zinc oxide and ZDBC were prepared by ball milling under standard conditions. All of these materials are of industrial grade.

Preparation of XNBR Compound

The XNBR was compounded according to the formulation in *Table 1*. The stabiliser

TABLE 1. XNBR COMPOUND FORMULATION

Ingredients	Part per hundred rubber (p.p.h.r.)
45% XNBR	100.0
10% SDS	0.2
5% Potassium hydroxide	1.8
50% Sulphur	1.0
33% ZDBC	1.0
50% Zinc oxide	0.5 - 2.0

sodium dodecyl sulphate (SDS) was added before the pH of the latex is raised, followed by the addition of vulcanising ingredients.

Preparation of XNBR Films

In the preparation of dipped films, the total solids content of the XNBR was reduced to a different percentage with distilled water to obtain different film thickness. Unglazed porcelain plates were first heated to 70ºC before dipping into a 20% calcium nitrate solution. The plates were oven dried in an air oven set at 70ºC before dipping into the latex compound for 10 seconds. The resulting wet films were air dried under room conditions for 10 min before being subjected to leaching in distilled water for 2 minutes. The leached films were then dried in the oven set at 80 ± 5ºC for 10 min before heating up to 100 ± 5ºC and then again to 110 ± 5ºC for 10 min respectively. The films were then removed from the oven and cooled to room temperature, before being powdered with USP grade corn starch and stripped off the plates.

Mechanical Properties of XNBR Films

The tensile properties of the unaged films and heat aged films at 70ºC for 7 days were determined using an Instron 5565 testing machine according to the *ASTM D412* test method with a crosshead speed of 500 mm/min. The test was conducted under room temperature conditions (25 ± 1ºC).

The tear strength values of the unaged and aged films were obtained by tearing prepared test samples using an Instron 5565 testing machine according to the *ISO 34* test method. The test was conducted under room temperature conditions using a crosshead speed of 100 mm/min.

The stiffness values of the XNBR films were determined using a RRIM modulus tester. For each film, a bongo shaped test piece was cut and then stretched to 100% strain on the tester. After one minute, the force was recorded as the load and the relaxed modulus value of the film was calculated.

SEM Micrograph

Morphology of the XNBR films was observed using scanning electron microscopy (SEM). The test portion of each film was cut and placed onto the specimen stub with carbon double sided tape. The specimen was then prepared for examination by evaporative coating with an ultra-thin layer of platinum under high vacuum. The JOEL SEM 5300 was operated at 2 kV and the images were captured.

Determination of XNBR Films Crosslink Density

The crosslink density of the film was determined by equilibrium swelling a pre-weighed test sample in acetone, based on the Flory-Rehner equation[10]. As the expected vulcanisates contain both ionic and covalent crosslinks, it is necessary to distinguish the ionic crosslink density from covalent crosslink density. To estimate the total crosslink density, samples were first swollen in acetone under room temperature conditions for 72 hours. The samples were then taken out from the glass bottles and excess solvent was blotted off the sample using filter paper. Each of the samples were immediately weighed on an analytical balance and then dried in a vacuum oven to remove all the solvent and reweighed. The volume fraction of rubber in the swollen gel, V_r is obtained using *Equation 1*.

$$V_r = \frac{(m_1/\rho_1)}{(m_1/\rho_1)+(m_2/\rho_2)} \quad \ldots 1$$

Where m_1 and m_2 are the weights of the polymer (XNBR) sample and solvent, and ρ_1 and ρ_2 are the densities of the polymer and solvent respectively. The elastically active network chain density, ΔV_T representing the total crosslink density (ionic and covalent crosslinks) is calculated using *Equation 2* (Flory-Rehner equation).

$$V_T = \frac{\ln(1- V_r) + V_r + \chi V_r^2}{V_s (V_r^{1/3} - V_r/2)} \quad \ldots 2$$

Where $V_s = 73.4$ cm^3/mol is the molar volume of acetone and χ is the XNBR-acetone interaction parameter, taken as 0.345 according to reference[11]. To determine the covalent crosslink density, samples were swollen in the mixture of acetone and dichloroacetic acid (90:10 in mass) for 120 h to destroy the ionic crosslinks. The solvent was replaced with acetone and swollen for another 72 hours. Samples were then taken out from the bottle, excess solvent was blotted from the sample using filter paper and immediately weighed and dried in a vacuum oven and reweighed[12]. The covalent crosslink density, V_{T1} is calculated using the equation above. The ionic crosslink density, V_{T2} is obtained using *Equation 3*.

$$V_{T2} = \Delta V_T - V_{T1} \quad \ldots 3$$

RESULTS AND DISCUSSION

Tensile properties are among the important criteria to gauge the usefulness of rubber articles. *Figure 1* shows the tensile properties of the XNBR film at different thicknesses. The relatively high tensile strength of XNBR is ascribed to the presence of an ionic cluster (assembly of ionic groups) formed by the reaction between the carboxyl groups and zinc oxide[13,14]. Zinc oxide appeared to boost the tensile strength, but tended to level off after a dosage of 1.5 p.h.r. Improving crosslink density (*Figure 6*) certainly contributed to better tensile strength values of the XNBR films. Gauging from the tensile strength (TS) values whereby the thickness of the films was normalised, results clearly suggest that a thicker XNBR film gives a higher strength value than a thinner film with the same dosage of vulcanising ingredients. It is reasonable to expect that a thin film is easily ruptured due to incoherent formation of film due to low amounts of material. However, all the films including the thinnest (0.04–0.05 mm) achieved the minimum TS values expected for nitrile examination gloves.

On the actual force when breaking the test sample, without normalising the thickness as in the TS values, there are significant differences in the force at break value of XNBR films with different thicknesses (*Figure 2*). The force at break (FaB) is the raw force in Newtons, required to rupture the film with

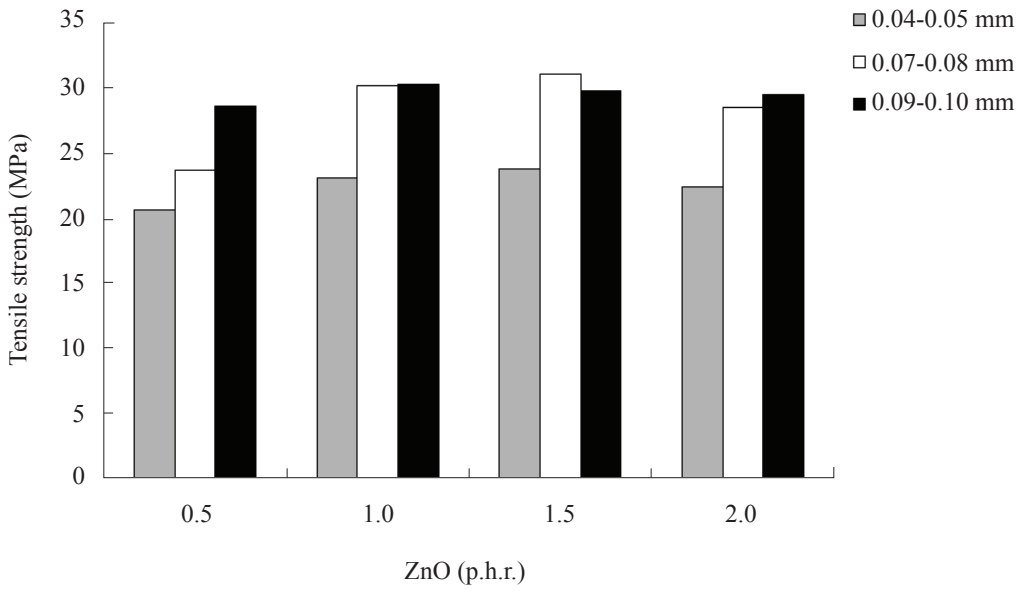

Figure 1. Tensile properties of XNBR films at different thicknesses.

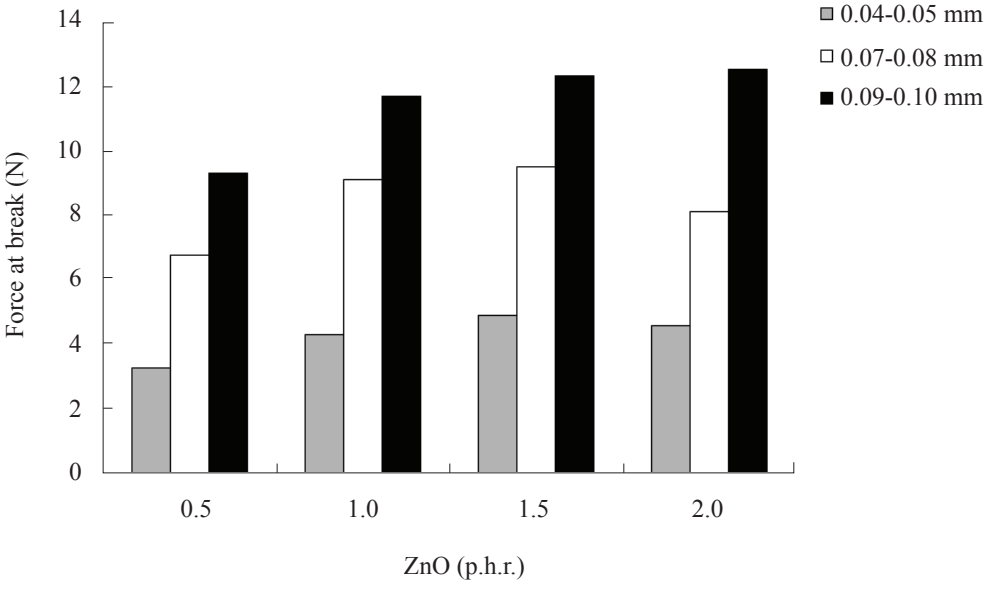

Figure 2. Force at break values of XNBR films at different thicknesses.

thicker films expected to be higher. Similar to the TS value, the FaB value increased with a higher dosage of zinc oxide. The thinnest film showed a sharp drop in FaB value achieving values of less than 6 N even at a high ZnO dosage.

Elongation is an important property in predicting the extensibility of the glove, for its performance and durability during the donning of the glove. At 0.5 p.h.r. of ZnO, the XNBR film achieved elongation at break (EB) value (*Figure 3*) of above 600%. With increasing loading of ZnO, it is thought that the ionic crosslink due to Zn^{2+} will stiffen the XNBR film leading to a reduction in EB value. The thin film of high ZnO content ruptured at low EB and may not be suitable for the examination glove application.

Soft or low modulus characteristic is desired in gloves made from polymer material. Theoretically, the soft property is achieved either by having a very thin film or reducing the elastic modulus of the material. The stress relaxation properties of the XNBR film at different thicknesses is shown in *Figure 4*. The relaxed modulus value was amplified with high dosages of ZnO, indicating the apparent increase in the physical crosslink density of the film. On the other hand, there was no clear indication that stiffness increased with thickness. Nonetheless, thin gloves are perceived by many as contributing to better tactile sensitivity and dexterity to the material. In the case of commercial nitrile latex gloves, the softness of the glove was an intrinsic property of the XNBR latex due to undisclosed manner of preparation by the manufacturer of examination gloves. Even though it is known that XNBR examination gloves provide high TS strength over NRL latex gloves, XNBR may not fare well with NRL gloves in terms of tearing property. It was noted that the tear strength (*Figure 5*) of the XNBR film moved in the opposite direction to its TS values with increasing crosslink density. It was reported that the decrease in the tear strength of XNBR is due to the high stiffness of the XNBR film[4]. The occurrence of this phenomenon is indefinite, either, due to the increased crosslink density or related to the inherent properties of XNBR.

The study also investigated the effect of heat aged XNBR films to see any improvement in property due to elevated heat. The heat ageing properties of the XNBR films is shown in *Table 2*. The increase in the TS value of the heat aged film may indicate that further crosslinking between polymers took place at elevated temperatures. Both EB and tear strength values showed substantial decrease after heat ageing. The major factor contributing to EB reduction appears to be the dosage of ZnO rather than film thickness (*Figure 6*).

In this study, the estimation of crosslink density was done on the XNBR films of thickness ranging from 0.07 to 0.08 mm mainly to understand the relationship between crosslink density and physical properties of the XNBR film. Due to the carboxylate group and the carbon-carbon double bond in the XNBR films, two types of crosslinks were expected, namely the ionic crosslink from ZnO interacting with carboxylate group and the sulphur crosslink from the electrophilic reaction of the butadiene group. Assuming that sulphur crosslink is constant due to constant sulphur content and by varying the ZnO levels in the study, it was hypothesised that any further increase in the formation of crosslinks should be due to the ionic type crosslink. At low ZnO dosage, the estimated ionic crosslink density was expected (*Figure 6*). There were less divalent metal ions (Zn^{2+}) to provide the expected linkages between the carboxylate groups in the XNBR. By increasing the ZnO dosage, the estimated ionic crosslink density increased to almost comparable to the estimated covalent sulphur

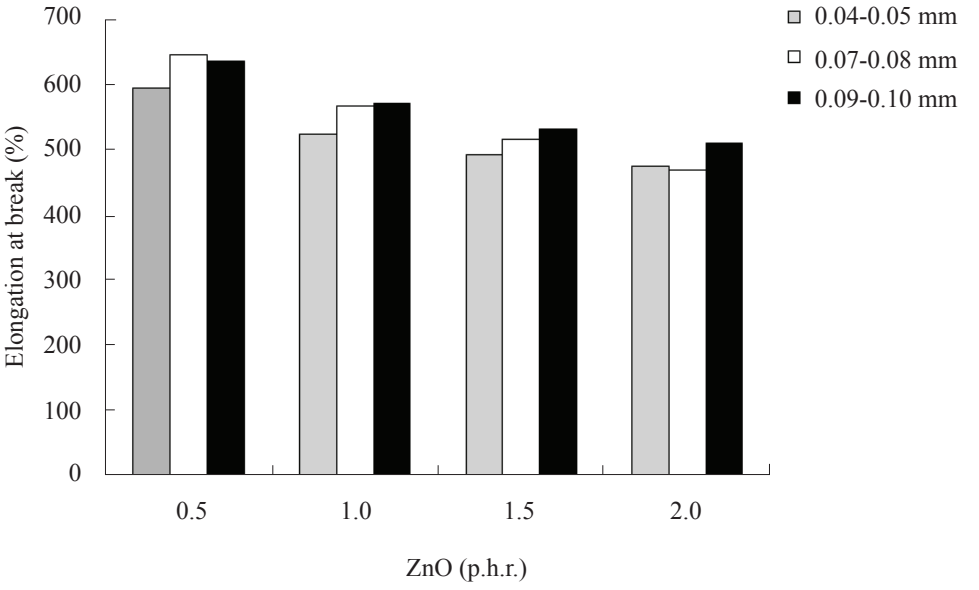

Figure 3. Elongation at break value of XNBR films at different thicknesses.

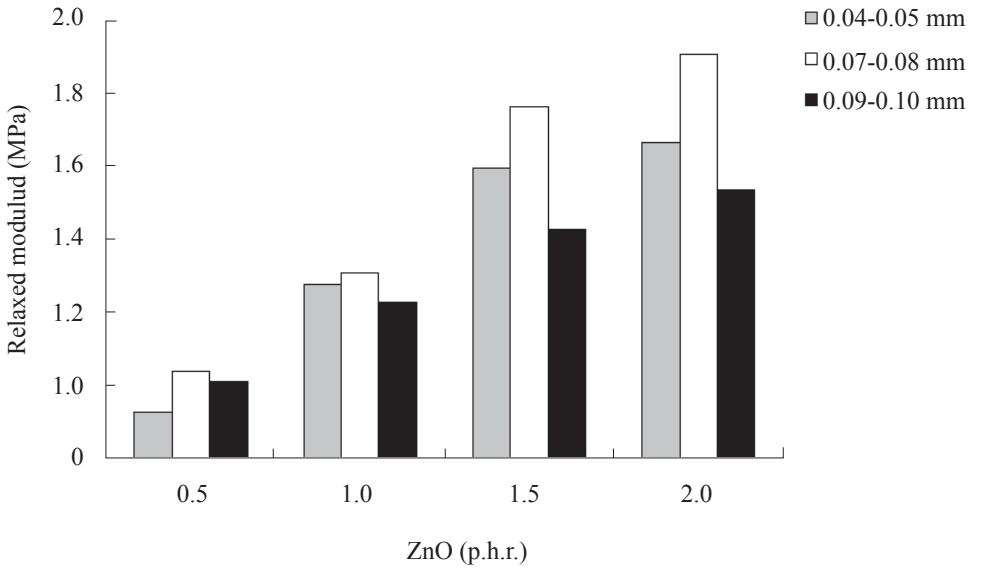

Figure 4. Relaxed modulus value of XNBR films at different thicknesses.

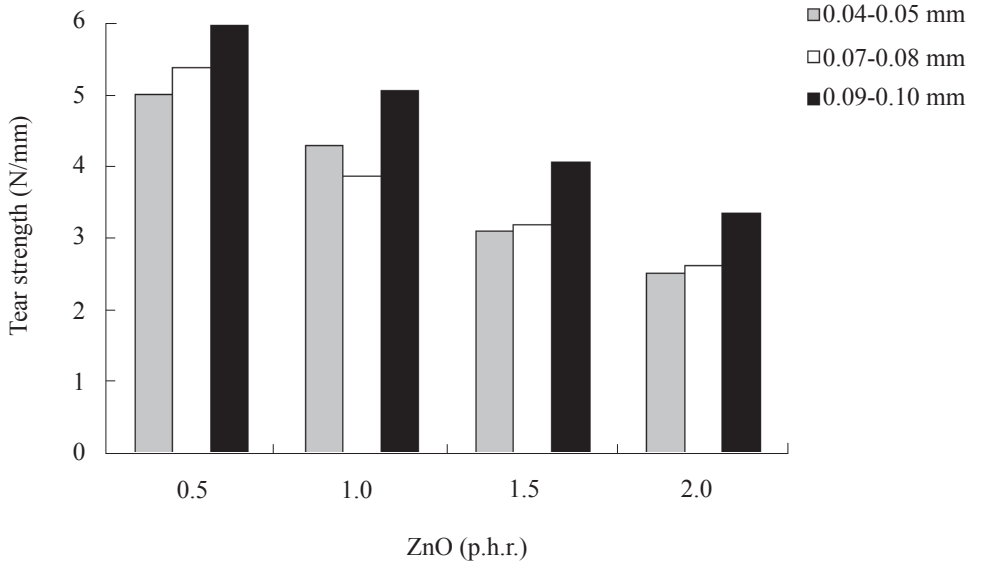

Figure 5. Tear strength of XNBR films at different thicknesses.

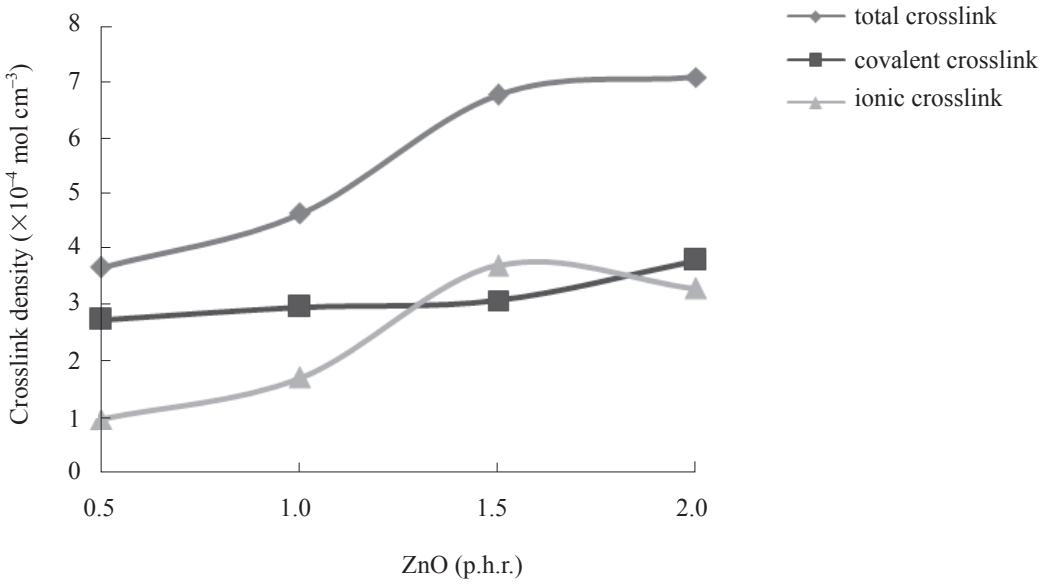

Figure 6. Crosslink density of XNBR films at various ZnO contents.

TABLE 2. XNBR FILMS HEAT AGEING PROPERTIES

Zinc oxide (p.h.r)	Film thickness (mm)	Physical properties			
		Tensile strength (MPa)	Force at break (N)	Elongation at break (%)	Tear strength (N/mm)
0.5	0.04-0.05	28 (+28 %)	4 (+25 %)	510 (-15 %)	3.2 (-56 %)
	0.07-0.08	28 (+17 %)	7 (+14 %)	550 (-16 %)	4.3 (-23 %)
	0.09-0.10	33 (+15 %)	11 (+18 %)	550 (-14 %)	5.4 (-9 %)
1.0	0.04-0.05	28 (+17 %)	4 (0 %)	490 (-6 %)	2.7 (-59 %)
	0.07-0.08	37 (+18 %)	10 (+10 %)	490 (-14 %)	4.4 (+13 %)
	0.09-0.10	37 (+18 %)	14 (+21 %)	500 (-14 %)	4.0 (-25 %)
1.5	0.04-0.05	28 (+17 %)	5 (+20 %)	440 (-11 %)	2.0 (-55 %)
	0.07-0.08	36 (+13 %)	10 (+10 %)	470 (-8 %)	2.9 (-10 %)
	0.09-0.10	31 (+6 %)	13 (+7 %)	430 (-23 %)	4.3 (+6 %)
2.0	0.04-0.05	28 (+21 %)	5 (+20 %)	440 (-6 %)	1.8 (-38 %)
	0.07-0.08	36 (+22 %)	9 (+11 %)	450 (-2 %)	2.5 (-4 %)
	0.09-0.10	33 (+12 %)	13 (+7 %)	450 (-13 %)	3.6 (+8 %)

* Percentage values in parentheses are the change in value to unaged film

crosslink density. At a much higher dosage, the crosslink densities of both types of crosslinks were expected to approach their optimal level of possible crosslink density to impart better physical properties. Thus, the increased level of ZnO indicated an increase in the overall estimated crosslink density.

Comparing the ionic crosslink density to the films' physical properties as indicated in *Figure 7*, the TS and FaB values of these XNBR films increased with increasing ionic crosslink densities. Hence, it is possible to roughly predict the dosage of ZnO to produce the optimum strength requirement. We see that at 1.5 p.h.r. ZnO content, the plot of the estimated crosslink density tended to level off (*Figure 6*) and this appears to be the highest TS and FaB values recorded in *Figure 1* and *2* and for the heat ageing samples in *Table 2*. The relationship between TS and FaB values for the 0.07 mm to 0.08 mm thickness samples is plotted against their estimated crosslink density values (*Figure 7*) which again point to 1.5 p.h.r. ZnO content as the optimum level of ZnO giving the highest TS values.

SEM Micrographs of XNBR Films

The physical evidence of the XNBR films may be visualised at high magnification of the surface of the films. *Figure 8* shows the morphology of the XNBR films of 0.07 – 0.08 mm thickness. Crack-like lines were quite evident in the lower ZnO dosage films. The actual source of the crack like structure is not known. It is postulated that the lines occurred during the drying stage whereby

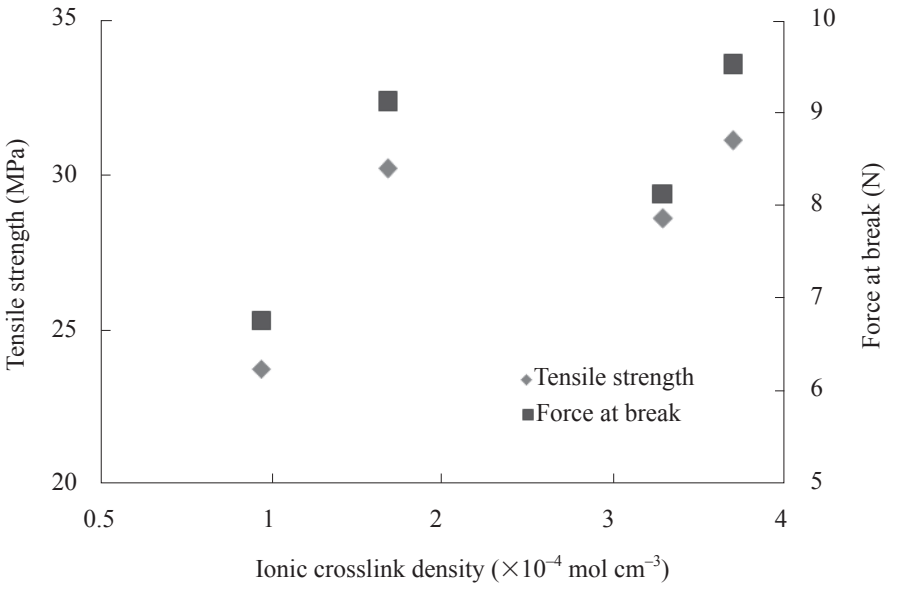

Figure 7. Tensile strength and force at break value versus ionic crosslink densities of XNBR films (0.07-0.08 mm thickness).

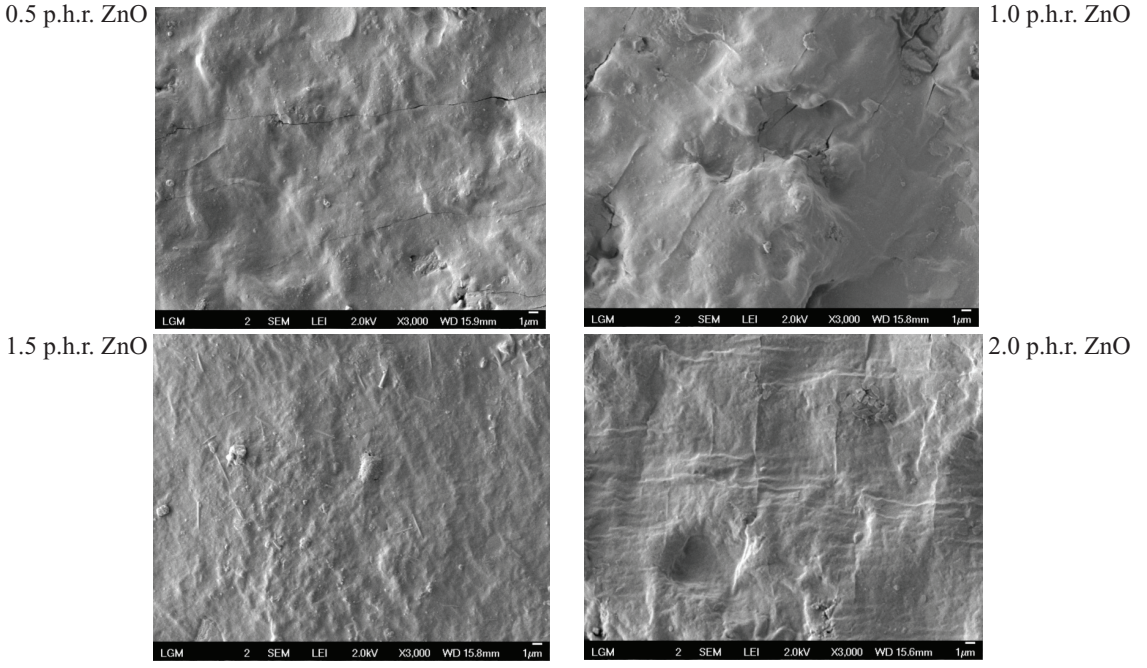

Figure 8. Morphology of XNBR films.

a better coherent film surface was more difficult to achieve due to lack of crosslinking occurring in the films. These crack like lines within the films may weaken the films under stress, which explains the low strength values typically achieved by low ZnO dosage XNBR films.

CONCLUSION

This study proposed that the recent improvement in examination gloves made from XNBR latex is not entirely due to a trend towards producing gloves of ultra thin thickness. As the production of the XNBR latex grade for thin medical gloves application remains a trade secret, it is suspected that the improvement in the feel and better suitability of nitrile for examination gloves application probably lies in the polymer itself. This study confirmed the improvement in the properties of XNBR latex film at specific dosages of ZnO. However, the formation of ionic crosslinks due to ZnO is limited to the available carboxylate group. Further to that, ZnO is also a sulphur crosslink activator and therefore there will be competing reactions for crosslink formation in XNBR films. The fundamental knowledge in this area is still lacking and it is hoped that the results presented in this study lead to more research in the aspect of crosslinking in latex films.

ACKNOWLEDGMENTS

The authors would like to thank the Director General of the Malaysian Rubber Board for the permission to publish this paper and the funding for the project. The authors are also grateful to Mr Syahril Zainul for technical assistance rendered.

Date of receipt: January 2012
Date of acceptance: April 2012

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