# Some Factors Affecting Dipped Nitrile Latex Films

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Dipped Nitrile latex films were prepared by spontaneous gelation using a solution of ~28% calcium nitrate in water. When the pH of the compound was adjusted to >12 using 5 wt% KOH solution, the mechanical (tensile and tear) properties were found to be better compared with compounds prepared at pH~9. The tear properties were especially higher when the films were not leached, although the leached films gave a higher tensile strength. The nitrile latex films could be cured using sulphur or zinc oxide. Higher tearing resistance was obtained from the zinc oxide cured films. The zinc cured nitrile latex films also tend to give higher elongation at break values. Higher tear strength values were also observed for films such as silane-modified silica and titanium dioxide. Carboxylate groups were identified by FTIR and Raman spectroscopy in films obtained from the latexes whose pH values were raised to 12; the carboxylic moieties were observed in films obtained from latexes at pH 9.

Key words: dipped nitrile latex; mechanical properties; FTIR; Raman spectroscopy; latex films; STEM; SEM; compounding

Nitrile latex is typically prepared by emulsion polymerisation of butadiene and acrylonitrile monomers. Functionalisation of the butadieneacrylonitrile polymer was achieved with the addition of carboxylic acid monomers such as acrylic, methacrylic, itaconic or fumaric acids<sup>1</sup>. The resulting latex system is known carboxylated nitrile (XNBR) latex. as Carboxylation (functionalisation) of nitrile (NBR) latex allows greater colloidal stability to be achieved<sup>2</sup>. In addition, the carboxyl groups are capable of hydrogen bonding (H-bonding). ionic-bonding and covalent bonding<sup>1.3,4</sup>. The commercial production of nitrile latex is on the increase due to the growth

in demand for latex to manufacture products such as gloves<sup>5</sup>. The preparation of XNBR latex varies among producers, hence finer adjustments may become necessary during the processing of XNBR latex in the production process.

In general, the ratio and the amount of vulcanising ingredients used in the preparation of XNBR latex films are known to influence tensile properties<sup>6,7</sup>. XNBR latex films can be vulcanised using similar ingredients as those employed for the vulcanisation of natural rubber (*cis*-1,4 polyisoprene) latex. However, a higher zinc oxide (ZnO) to sulphur

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(S) ratio (unlike NR latex formulations) is usually employed for XNBR vulcanisation systems Divalent metal cations<sup>89</sup> such as  $Zn^{2+}$ ,  $Ca^{2+}$  and  $Mg^{2+}$  can be utilised with the carboxylic acid groups to form ionic crosslinking Trivalent metal cations such as Cr<sup>3+</sup> have been shown to confer higher tensile strength compared with  $Zn^{2+}$  or  $Ca^{2+}$  when utilised in a 95/5 ethyl acrylate/acrylic acid latexes at a molar concentration ratio of 1.1 Among the amons studied, OAc in Ca(OAc), was found to have a greater effect on the cast films than  $NO_3$  for  $Ca(NO_3)_2$  or Cl for CaCl, ZnO is used in the XNBR formulation to induce crosslinking involving the carboxylic acid moieties of the XNBR latex particles Classically, ZnO is an accelerator-activator for the sulphur vulcanisation system where sulphur and at least an accelerator, also a zinc compound, are used Hence, ZnO has dual roles when it is utilised in the XNBR formulation A minimum concentration must be present if all of the carboxylic acid groups are to form ionic crosslinking by the reaction with ZnO Theoretically, for a 5% degree of carboxylation about 2.4 p h r of ZnO<sup>10</sup> is required Notice that anhydrous Ca(NO<sub>3</sub>)<sub>2</sub> is typically used as a coagulant for the preparation of dipped films for XNBR as well as NR latexes. Its use, therefore may have a consequence on the formation of the XNBR latex films There are many factors to consider in the preparation of films from XNBR latex The tensile properties of nitrile latex films not only depend on the ratio of the vulcanising ingredients but also on the level of the vulcanising ingredients employed and the type of XNBR latex used<sup>6</sup> The time and temperature of film drying and curing would also influence the film formation and film properties This paper describes some of the work carried out to examine factors associated with the compounding and dipping processes for the preparation of nitrile latex films

# Formulations for XNBR Latex Films

It was earlier mentioned that carboxylation of the butadiene-acrylonitrile latex confers colloidal stability Commercial XNBR latex is also stabilised with at least one external surface-active agent (details are not usually disclosed), which is anionic in nature Further additions of 'stabilisers' such as potassium hydroxide and ammonia solutions are usually made as part of the compounding formulations The vulcanising ingredients comprising S, an accelerator e g zinc diethyldithiocarbamate (ZDEC) and ZnO are similar to those employed for NR vulcanisation system. However, the ratio of S to ZnO in terms of phr for these two systems differ, S is employed at higher amounts (0.5 p h r - 2 p h r) and ZnO in lower amounts (0.2 phr - 0.5 phr) in NR latex whereas ZnO is employed at levels of  $1 ph_1 - 2 ph_r$  in XNBR latex with lower S levels of 0.5 p h r = 1 p h r The employment of S in the vulcanisation of XNBR involves the formation of sulphidic crosslinks between the butadiene chains while the ZnO vulcanisation would involve crosslinking of the carboxyl moleties

#### EXPERIMENTAL

## **Preparation of Compounds and Films**

48C40 XNBR<sup>®</sup> latex having an acrylonitrile content of 26% ( $T_{k}$  of -25°C), was used in the preparation of the following films The pH of the compound was adjusted using 5 wt% potassium hydroxide (KOH) solution The iecipe employed for the preparation of the compound is given in *Table 1* Latex compounds were prepared at a total solid content of ~30% The pH values and the viscosity measurements made on the latex compounds for a period of 30 min and 24 h was allowed for homogenisation. The latex compounds containing the various amounts of KOH solution remained stable.

Thin films of about 0.07 mm - 0.15 mm were prepared by spontaneous coagulation of the nitrile latex compound using coagulantcoated formers in a dipping process. The dipped films were prepared by the immersion of ceramic plates into ~28% of anhydrous calcium nitrate solution. The ceramic plates were first heated at 50°C and a latex dwell time of 10 s was employed. Wet-gel leaching of the dipped films was done by immersing the wet-gels for 2 min into the distilled water, which was kept at 50°C. Drying of the films involved two stages at 50°C and 80°C for 20 min each, respectively. Nitrile latex films require longer drying times compared to NR latex films of similar formulation and thickness<sup>11</sup>. The curing of the films was subsequently undertaken by heating the dried films at 120°C for 20 min.

# **Mechanical Properties**

Dumbell specimens were prepared according to ISO 37: 1994. Tensile measurements were carried out on the Instron 5565 at RH of 65%, ambient temperature of 25°C and crosshead speed of 500 mm/min. Each data value is a mean reading obtained from at least 5 specimens. The trouser tear test pieces were also prepared according to ISO 34-1; 1994. A RH of 65%. an ambient temperature of 25°C, a crosshead speed of 100 mm/min. sample rate of 4.0 pts per second and a full-scale load range of 0.5 kN were employed using the same instrument (Instron 5565). At least 5 tests specimen were also prepared for each data value. Tear strength determinations were undertaken for each direction of the latex films. The average values were subsequently reported since the longitudinal and across values were found to be similar (S.D. of ~1 N/mm). All of the test samples were conditioned for 24 h at a relative humidity of 60% - 70% over silica gel at room temperature (~25°C) in a cabinet, before the tests were undertaken.

# Extent of Swelling

A circular disc of 23 mm diameter was cut from the film and immersed in 30 mL of chloroform in a sealed container for 48 h at room temperature. The swelling index was calculated by weight. This is the difference between the weight of the swollen disc and the original weight of the disc divided by the original weight of the disc. Duplicate determinations were carried out.

# **Preparation of Compounding Ingredients** (Fillers)

Coupsil 8113® and titanium dioxide were prepared as 20% and 50% dispersions by ball milling each of the preparation for 48 h. As for the preparation of the dispersion of Coupsil 8113<sup>®</sup>, developments in viscosity of the dispersion was obtained when higher concentrations at 30% - 50% dispersions were prepared, thus limiting the preparation of the dispersion to 20%. Cab-O-Sperse LT 121<sup>®</sup> was supplied and used as 15% dispersion. The Cab-O-Sperse LT 121<sup>®</sup> is a fumed silica stabilised with potassium hydroxide, the particles of which are said to exist as branched chain aggregates where the chains can be mechanically entangled but loosely packed<sup>15</sup>. Coupsil 8113<sup>®</sup> obtained from Degussa is a silane-modified silica; this particular grade has a nitrogen surface area of  $175 \text{ m}^2/\text{g}$ .

# Scanning Electron Microscopy (SEM) and Scanning Transmission Electron Microscopy (STEM)

The SEM [Joel SEM (TL 63)] examination and imaging were done under high vacuum after the sample (fillers) was coated with a conducting ultra-thin layer of gold. For the imaging of the nitrile latex, STEM (Philips CM12/STEM) was employed. The latex was first exposed to 1% osmium tetroxide solution for 12 h. Separation was then obtained by centrifugation at 10 000 r.p.m. for 5 min. The reacted latex particles were carefully transferred onto a 'formvar'-coated 200 mesh copper grid, viewed and imaged as a whole mount.

# Fourier Transform Infrared (FTIR) Analysis

For FTIR spectroscopic analysis, thin films of thickness about 0.05 mm were cast from the latex as received or from latex whose pH values were adjusted using 5 wt% KOH solutions. The films were thoroughly dried at room temperature, before samples were cut and the spectra obtained after 32 scans with signal gain and resolution of 4.0, respectively. The spectrometer employed was the Magna System 560 (Thunderdome smart accessory) with a DTGS KBr detector.

# RESULTS AND DISCUSSIONS

As the pH increased from 9 to 11, the viscosity of the compound increased but then decreased with a further increase in the pH from 11 to 12 (*Table 1*). The carboxyl groups are susceptible to neutralisation. which is accompanied by an increase in the viscosity of the latex (as occurs with alkali-swellable latex)<sup>12</sup>, the XNBR latex particles becoming swollen with water from the aqueous phase. Some of the XNBR latex particles, which have a higher carboxyl content, might even dissolve under the highly alkaline conditions. The dissolved carboxylate chains may subsequently be absorbed onto the latex particles, thus conferring electrostatic and steric

Compound ingredient	A (p.h.r.)	B (p.h.r.)	C (p.h.r.)
XNBR <sup>a</sup>	100.0	100.0	100.0
КОН	0.5	2.5	5.2
S	1.0	1.0	1.0
ZDBC <sup>b</sup>	1.0	1.0	1.0
ZnO	2.0	2.0	2.0
pH	9.2	10.9	12.3
Viscosity (cps)	5.0	44.0	16.5
Spindle 1, speed 60 r.p.m.			

TABLE 1. COMPOUNDS OF XNBR LATEX, RECIPE AND LATEX VISCOSITY

<sup>a</sup>XNBR Grade 48C40<sup>®</sup> (Synthomer)

<sup>b</sup>Zinc Dibutyldithiocarbamate

stability to the nitrile latex. The increase in the viscosity is due primarily to the ionisation of the carboxyl acid groups. Subsequent drop in the viscosity is the result of the shielding of ionised carboxylic acid groups by the cations of the alkali<sup>12</sup> and also of a dilution effect.

Table 2 shows the results for tensile property measurements and tear strength determinations performed on nitrile latex films, which were not aged. For a compound with a pH of > 12, the tear resistance values for the resulting films were found to be higher than those prepared from compounds of lower pH values. This was especially evident when the films were not leached. In contrast, the unleached films showed low tensile strength values. While wet-gel leaching resulted in a dramatic increase in tensile strength values from 25 MPa to about 40 MPa, the tear strength values obtained under the same conditions were lower. In this experiment, 2 p.h.r. of ZnO and 1 p.h.r. of S were used. The elongation-at-break values of the films were in the range of 550% - 600%. The pH values of the compounds in combination with the leaching protocol have contrasting

effects on the tensile and tear properties of the XNBR latex films. It may also be possible that under higher pH conditions, the curing agents employed may have a higher degree of activation for complexes to form, favouring an increase in crosslinking efficiency.

In order to obtain further information on the influence of the curing agents on the films properties, XNBR latex compounds of pH  $\sim$ 12 were prepared with either sulphur or zinc oxide at various levels. *Table 3* gives the tensile properties and the tear strength values for the unaged XNBR latex of various formulations.

The XNBR films prepared with 2.0 p.h.r. or 3.0 p.h.r. of ZnO alone showed higher elongation at break in the range of about 710%. Comparable elongation at break was obtained for the XNBR films cured with S at a lower concentration of 1 p.h.r. compared with an elongation at break value of 550% when 3 p.h.r. of S was used. The tensile strength did not appear to be dependent on the type of crosslinks present for these films; values in the range of 34 MPa – 36 MPa were

Film (Unaged)	Thickness (mm)	Tensile strength (MPa)	M100 (MPa)	M300 (MPa)	Elongation at break (%)	Tear strength (N/mm)
A/L	0.105	32.0	3.0	6.6	600	4.3
A/U	0.104	23.0	2.5	5.0	580	4.2
B/L	0.100	33.0	3.5	.7.3	560	4.2
B/U	0.105	22.0	3.1	6.2	550	4.1
C/L	0.107	42.0	3.2	6.8	620	5.8
C/U	0.108	25.0	3.0	5.6	600	7.5

TABLE 2. TENSILE AND TEAR PROPERTIES OF CURED-XNBR DIPPED FILMS

L: Leached

U : Unleached

Films	Tensile strength (MPa)	Elongation at break (%)	M100% (MPa)	M300% (MPa)	M500% (MPa)	Tear strength (N/mm)
D/L	34.0	550	2.8	6.0	25.3	4.7
D/U	26.0	560	2.8	5.7	18.9	4.5
E/L	36.0	680	1.9	3.6	9.8	5.3
E/U	22.0	690	1.6	2.9	6.8	6.1
F/L	36.0 (34.0)	690	2.3	4.2	9.9	6.3
F/U	23.8 (22.0)	710	2.2	4.0	8.6	8.1
G/L	36.0	720	1.9	3.4	8.2	6.0
G/U	24.0	740	1.7	3.1	6.4	7.6

### TABLE 3. TENSILE PROPERTIES OF DIPPED XNBR LATEX FILMS PREPARED WITH ONLY ONE TYPE OF CURATIVE

Figures in parentheses were repeated median values accumulated from at least 5 specimens, for each set. D: sulphur - 3.0 p.h.r.; ZDBC - 0.5 p.h.r.

E: sulphur — 1.0 p.h.r.; ZDBC — 0.5 p.h.r.

F: ZnO — 3.0 p.h.r. G: ZnO — 2.0 p.h.r.

L: leached; U: unleached

recorded. The leached films in all cases exhibited higher tensile strength values. Higher sulphur concentration gave films with higher moduli. These data clearly demonstrated the ability of the XNBR latex to cure in the presence of only one type of curing agent either S or zinc oxide to give acceptable tensile properties. From the tear property data, the nitrile films also showed a higher resistance to tearing when the zinc oxide was used alone, implying a contribution of the ionic crosslinks to the reinforcement of the films to tearing. The increase in tearing resistance is more pronounced in the unleached films. Some of the films prepared above were subjected to swelling. Hasegawa<sup>13</sup> used methyl ethyl ketone (MEK) in the swelling of XNBR latex films; he showed that MEK is a stronger solvent

compared to toluene. On the other hand, Ghosal *et al.*<sup>7</sup> employed methanol, which is a more polar solvent to examine the effect of AN content in the films on the solvent resistance of XNBR films. Methanol was found to have no effect on the films (A-G) prepared in our experiments. While much MEK was found to be absorbed into these films, chloroform was also found to be a very effective swelling agent. The swelling indices of some of the XNBR latex films in chloroform were determined (Table 4).

Interestingly, there appeared to be a lack of integrity for the films cured with ZnO in the absence of sulphur, although the tear resistance was higher. Tensile strength values of about 34 MPa - 36 MPa and substantial

Films	Swelling index			
A/L	10.9			
A/U	11.1			
B/L	10.4			
B/U	10.6			
C/L	14.2			
C/U	11.4			
D/L	7.5			
D/U	7.6			
F/L	Sample broke (disintegrated)			
F/U	Sample broke (disintegrated)			

TABLE 4. SWELLING INDICES OF DIPPED XNBR LATEX FILMS PREPARED WITH ONLY ONE TYPE OF CURATIVE

A — S: 1.0 p.h.r.; ZDBC: 0.5 p.h.r.; ZnO: 2.0 p.h.r.; pH: 9.2

B — S: 1.0 p.h.r.; ZDBC: 0.5 p.h.r.; ZnO: 2.0 p.h.r.; pH: 10.9

C — S: 1.0 p.h.r.; ZDBC: 0.5 p.h.r.; ZnO: 2.0 p.h.r.; pH: 12.3

D — S: 3.0 p.h.r.; ZDBC: 0.5 p.h.r.; ZnO: 0.0 p.h.r.; pH: 12.3

extension of about 700% were obtained for these films. It is not likely that there was reversion (overcure) or degradation of the crosslinks in the films prepared in the presence of zinc oxide alone, because the retention in tensile properties of these films after they underwent accelerated aging tests (22 h at 100°C) was very good. For example, the aged films prepared with 2 p.h.r. of zinc oxide gave an average tensile strength value of 39 MPa and an average elongation-at-break value of 690% for the leached films (G/L/Aged). The unleached films (G/U/Aged) also showed an improvement in tensile strength with an increase in the average tensile strength value to 28 MPa and an average elongationat-break value of 710% after the films were subjected to ageing. In addition, for the leached films prepared with 3 p.h.r. of zinc oxide alone a high tensile strength value of 39 MPa and an average elongation-at-break value of 740% were obtained for the aged films. The corresponding tensile strength and elongationat-break values for the unleached films which were aged (containing 3 p.h.r. of ZnO as the only cure agent), were 36 MPa and 740%, respectively. The swelling indices for the films prepared with a higher concentration of S (3 p.h.r.) gave the lowest values, which not only show that a higher degree of crosslinking was achieved but also that the films had better integrity. For solvent (chemical) resistance, the XNBR latex films require sulphur crosslinks.

### **Effect of the Addition of Fillers**

XNBR latex films tend to have lower resistance to tearing compared to NR latex films. The effects of the addition of fillers such as Cab-O-Sperse LT 121<sup>®</sup> (Cabot Corporation),

Coupsil 8113<sup>®</sup> (Degussa) and titanium dioxide into the XNBR latex compounds were evaluated. The pH of the compound was kept at pH of ~12. Vivayganathan<sup>14</sup> reported that there was no significant difference observed when fillers were added to the 48C40<sup>®</sup> latex compound at a lower pH of ~9. To aid visualisation of the particle and particle sizes of the fillers used, SEM photomicrographs of the various filler particles before and after the preparation of their dispersions are shown in *Figure 1*. In the compounding, all of the fillers were added at 2 p.h.r. In *Table 5*, the tensile properties of the filled XNBR films are presented.

The average size of Coupsil 8113<sup>®</sup> was larger than that of the other two fillers. The 48C40<sup>®</sup> average particle size is reported to be in the range of 130 nm. STEM

photomicrograph of the 48C40<sup>®</sup> latex particles was obtained and shown in *Figure 2*. It can be clearly observed that the nitrile latex particles are not uniform in sizes.

Higher tear strength values were still clearly observed for the unleached dipped films. Higher values were obtained when Cab-O-Sperse LT  $121^{\textcircled{0}}$  was used as the filler. An average tear strength value of about 9 N/mm was recorded for the unleached films compared to unfilled unleached films whose tear strength values averaged at about 7 N/mm. Other fillers added did not show much difference compared to the control. High tensile strength values were recorded for all the films containing the various fillers. Elongation at break exceeding 600% were also obtained for these films. The addition of fillers appeared to have reduced the moduli

Thickness (mm)	T.S. (MPa)	E.B. (%)	M100 (MPa)	M300 (MPa)	M500 (MPa)	Tear strength (N/mm)
0.11	42.0	620	3.2	6.8	16.9	6.0
0.11	25.0	600	3.0	5.6	13.6	7.6
0.10	38.0	650	2.7	5.5	14.0	6.4
0.11	23.0	660	2.2	4.0	9.5	9.0
0.10	36.0	640	2.6	5.1	13.0	5.3
0.10	25.0	660	2.4	5.0	10.3	7.9
0.10	38.0	620	2.8	6.0	18.0	5.1
0.11	26.0	630	2.5	5.0	11 <b>.7</b>	7.1
	Thickness (mm) 0.11 0.11 0.10 0.11 0.10 0.10 0.10 0.1	Thickness (mm) T.S. (MPa)   0.11 42.0   0.11 25.0   0.10 38.0   0.11 23.0   0.10 36.0   0.10 25.0   0.10 36.0   0.10 35.0   0.11 25.0   0.10 36.0   0.11 25.0   0.10 38.0   0.11 26.0	Thickness (mm) T.S. (MPa) E.B. (%)   0.11 42.0 620   0.11 25.0 600   0.10 38.0 650   0.11 23.0 660   0.10 36.0 640   0.10 25.0 660   0.10 38.0 620   0.11 25.0 660   0.10 36.0 640   0.10 25.0 660   0.10 38.0 620   0.11 26.0 630	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

TABLE 5. TENSILE PROPERTIES OF FILLED XNBR DIPPED FILMS

Control: Formulation C

H: Formulation C filled with Cab-O-Sperse<sup>®</sup> (CoS)

I: Formulation C filled with Coupsil 8113® (Cp)

J: Formulation C filled with Titanium Dioxide (TiO<sub>2</sub>)

L: Leached films

U: Unleached films



Aggregates of particles can be observed; the individual particle size is of sub-micron range.

Figure 1a. SEM micrograph of particles of Cab-O-Sperse LT 121<sup>®</sup> as received.



Figure 1b. SEM micrographs of particles of Coupsil 8113<sup>®</sup> before ball milling (left) and after ball milling (dispersion) (right).



Aggregation of particles can be seen; individual particle size is of sub-micron range.

Figure 1c. SEM micrographs of particles of titanium dioxide before ball milling (left) and after ball milling (right)



Figure 2. STEM micrograph of XNBR latex particles ( $\times$  22000).

slightly. Favourable interaction of the XNBR particles and the Cab-O-Sperse LT 121® particles may have led to a higher tear resistance, unlike the other cases. The size distribution of Coupsil 8113® particles before the preparation of the dispersion was clearly very wide. Particles of sizes greater than 10 µm as well as those of less than 1 µm could be observed. After ball milling, the Coupsil 8113<sup>®</sup> particles as observed in the micrographs had a narrower size distribution but the average particle size was still relatively large (~2  $\mu$ m – 3  $\mu$ m). Nevertheless, this grade of silanised silica, among the silicas produced by Degussa, has the highest nitrogen surface area. The silica that was therefore utilised in this case had the smallest particle size16 among the grades offered. Although the particle size distribution of Coupsil 8113® had reduced, the average size was still larger than that of Cab-O-Sperse LT 121® or Titanium Dioxide. Despite the sub-micron particle size of the titanium dioxide, no reinforcement in tear strength of the XNBR latex films was obtained when it was incorporated at this concentration.

# Fourier Transform Infrared Spectroscopy

Under high pH conditions, the ionized carboxyl chains may have assumed extended conformation. The carboxyl groups that exist (buried) within the latex particles in layers close to the particle surface may have also assumed an extended chain conformation. The distribution of the carboxyl groups within the nitrile latex particles (on the particle surface or buried) and in the dispersion medium would have been dependent on the hydrophilicity of the carboxylating monomer used, the polarity of the comonomers utilised<sup>17</sup> and the polymerisation system employed for the preparation of the nitrile latex. Under high pH conditions, carboxylate anions were observed as is shown in Figure 3.

The acrylonitrile (AN) peak is found at about 2237 cm<sup>-1</sup> wavenumber and this could be taken as the internal reference peak if necessary. Also given in *Figure 3* are the spectra of another grade of XNBR latex 99G43<sup>®</sup> whose pH has been adjusted using 5% KOH solution to give a pH value of



(a) 48C40, pH 9.3; (b) 48C40, pH 12.3; (c) 99G43, pH 9.3 and (d) 99G43, pH 12.3.

Figure 3. FTIR spectra of two grades of XNBR latexes, 48C40 and 99G43 prepared at pH 9.3 and pH 12.3, respectively.

9.3 and 12.3, respectively. The pH values of the 48C40<sup>®</sup> nitrile latex supplied are in the range of 8.2 - 8.6 and for the 99G43<sup>®</sup> nitrile latex, the pH values range between 8.2 - 8.5. The reported difference between these two grades is in the AN content: 48C40<sup>®</sup> has an AN content of 26%, and for 99G43<sup>®</sup>, the AN content is 39%. The glass transition temperatures of the XNBR copolymers are -25°C for 48C40<sup>®</sup> and -10°C for 99G43<sup>®</sup>. For both the grades, under higher pH conditions, the detection of carboxylate peaks could be made. The carboxylate peaks are clearly identifiable at about 1556 cm<sup>-1</sup> and possibly also at about 1398 cm<sup>-1</sup>; the corresponding C=O peaks associated with the carboxylic acid group which are only observed at low pH occur at a higher wavenumber of 1731 cm<sup>-1</sup>. In the latex which was prepared at a high pH (~12) and where the carbonyl group for the COOH had shifted from 1731 cm<sup>-1</sup> to carboxylate at 1556 cm<sup>-1</sup>, the butadiene unsaturation peaks (C=C) which are at ~1640 cm<sup>-1</sup> became prominent in the spectra. Identification of the carbonyl and C=C peaks from the FTIR spectra for the samples acquired was confirmed by Raman spectroscopy since the C=C peak is Raman sensitive while the C=O peak is not.

The addition of KOH solution to the latex caused neutralisation of the carboxylic acid, the particles becoming hydrated. Under these conditions, the carboxylate structures assumed the expanded conformation. During the preparation of the dipped films, when wetgel leaching was carried out, some of the KOH solution was washed away. It is then hypothesized that the carboxyl groups on the surface and in the sub-layers closer to the particle surface had reverted to a collapsed conformation. The expanded conformation of the carboxylate groups may favour interdiffusion of polymer chains before crosslinking takes place. Interparticle crosslinking (crosslinking of the carboxylate groups between particles) is therefore more readily achieved than if the conformation is collapsed. The collapsed conformation may induce intraparticle crosslinking (crosslinking of the carboxylate groups within the particle surface) resulting in films with lower tear resistance. Information concerning the amount as well as the type of crosslinks formed in the latex films under the different conditions is desirable, so that better understanding of the chemistry and the behaviour of film formation from these latexes can be obtained.

It may also appear possible that the watersoluble materials *e.g.*, calcium nitrate, which may have been physically trapped, but would have been extracted during the wet-gel leaching process (for the leached films), conferred some form of reinforcement either physically or chemically in the unleached latex films by increasing the tear resistance, but not the ultimate tensile strength of the films. The tensile strength values of the unleached latex films were always lower than in the leached films but the latter would always show lower resistance to tearing compared with the unleached films. Plasticisation conferred to the films by the water-soluble materials (hydrophilicity) may have been dominant in the unleached films, increasing the tear resistance but which can also give lower tensile strength values.

The interaction of chemical forces<sup>18</sup> that may exist within the carboxylate groups in the unleached films may have also increased the resistance of the films to tearing. It may also be possible that the extended carboxylate groups (in films that were not leached) were able to form aggregations, which were still present in the dried films. Some resistance against the propagation of tear may have therefore been realised from the aggregations<sup>19</sup> of the carboxyl moieties. These aggregations may have become disrupted when the latex gels were leached. Having said that, it would appear that such aggregations (if they are dominant in the films and that they do play a significant role in the tear reinforcement) for these nitrile latex films are not favourable for the development of high tensile strength of the films. Ionic interactions<sup>18</sup> have been shown to affect the physical properties of the films prepared from polymers synthesized with ionic groups such as the carboxylic acids. Anthony et al.<sup>19</sup> showed that higher tensile strength, tear strength, modulus and hardness were obtained for ionomeric polyblend (dry-mix) compared to nonionomeric polyblend. For the dipped nitrile latex films, additional considerations such as the presence of the aqueous phase, the pH, the spontaneous coagulation coupled with synerisis (in a dipping procedure involving the use of a coacervant), the presence of the coacervant in the film and the leaching protocol would be necessary. Any of these factors or combinations of these factors appears to have contributed to the contrasting effect of leaching of the dipped nitrile latex films on the tensile strength and the tear strength values.

The higher pH conditions may have also induced favourable formation of curative complexes necessary to induce a higher extent of crosslinking. It was also observed that the ionic crosslinks formed in the nitrile latex films did not appear to be resistant to solvent imbibition disintegration of the nitrile latex films was obtained. This may imply that this type of crosslink structure is less stable Ionic crosslinks cannot resist long term swelling due to the breaking and reforming of the ionic crosslink structures Matner<sup>10</sup> had also stated that the ionic bonds give little or no improvement in chemical resistance

#### SUMMARY

Improvements in tensile strength and tear strength of the XNBR latex dipped films can be obtained when the pH of the compound is high 48C40<sup>®</sup> latex can be cured to give satisfactory film properties with only one cure system  $i \epsilon$  sulphur or zinc oxide The ionic crosslinking in the XNBR latex dipped films appears to influence the tear strength more than the sulphidic crosslinking. The sulphidic crosslinks on the other hand are necessary for the solvent resistance of the films Addition of Cab-O Sperse LT121<sup>®</sup> fumed silica to the XNBR latex compound formulated at high pH did confer some improvement in the tear resistance particularly when wet-gel leaching was omitted The type of crosslinks present in these films did not significantly affect the tensile properties Other fillers examined such as Coupsil 8113®, a silanised silica and a metal oxide titanium dioxide did not show significant changes on the film properties when utilised in the compounds

Carboxylate amons in the XNBR latex was detected when the pH of the latex was increased to J2 This was investigated by FTIR spectroscopy and by Raman spectroscopy

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