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Research paper

Effect of NR/NBR ratio on mechanical properties and crosslink concentration of NR/NBR blend latex film

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Abstract

It is a common practice to blend two elastomers of different properties with a view to combine the best properties of each in terms of its technical and economic values. Nitrile rubber (NBR) is blended with natural rubber (NR) to meet the requirements for very good oil resistance as well as high mechanical strength. The former is a polar rubber and provides very good oil resistance, while the latter is non-polar and provides excellent mechanical properties. Numerous works on rubber blends that have been reported are based on dry rubber. On the contrary, the work on rubber blends base on latex received less attention than the dry rubber. This paper describes the work on NR latex and NBR latex blends. NR and NBR were blended at several ratios incorporating NBR up to 50% to study their effect on the mechanical properties and crosslink concentrations. The glass transition temperatures, T_g and the morphology of NR/NBR latex blends were determined to verify the compatibility of the blends. The results indicated that tensile strength (TS) showed a good linear relationship with loadings of NBR. The decreased in TS with decreased in NR content of the blends was associated with low crosslink concentrations in the rubber blends. Both elongation at break (EB) and tear energy are affected non-linearly by the presence of NBR indicating the incompatibility of the two rubber components.

***Keywords**: NR: NBR blends; tensile strength; crosslink concentration; tearing energy; glass transition temperature (T_g)*

1. Introduction

Natural rubber (NR) latex has been an outstanding material and has proven long track record in latex dipped products. It possessed strain induced crystallization behavior at high deformation strains [1] which contribute to NR latex excellent mechanical properties such as high tensile strength (TS), high elongation at break (EB), high tear resistance, high elasticity and high flexibility [2]. However, NR is non-polar and shows relatively poor swelling resistance towards hydrocarbon oil [3]. When the rubber is swollen, it tends to lose its tensile strength and tear strength. The decrease in these strengths is associated with the loosening of cohesive bonds and low intermolecular forces between rubber molecular chains [4].

In contrast, nitrile rubber (NBR) is polar. Unfilled NBR vulcanizate have low mechanical properties since NBR is a non-strain crystallizing rubber [5]. However, being polar NBR shows good swelling resistance against hydrocarbon oil [6]. Due to the contrasting properties of NR and NBR, blending the two rubbers would result in a material well balanced in terms of strength and swelling resistance.

Nevertheless, the compatibility and miscibility of a blend is not easy to achieve with materials of contrasting properties since a separate phase with low attraction force existed across the phase boundaries[2]. To enhance compatibility of polymer blends, two factors need to be considered; which are the physical forces and chemical bonding of two or more different polymers. The degree of compatibility of two rubbers is important since it contribute to the mechanical properties of the blends produced[3].

This paper describes the work on the effect of NBR loading and crosslink density on the tensile and tear strengths of NR/NBR latex blends since these two properties are very important in rubber gloves applications. Along the way, the compatibility of the blends was assessed from the morphology and glass-transition temperature, T_g of the resulting NR/NBR blends. The crosslink concentration of the rubber blends was estimated from the Mooney-Rivlin plot obtained from a simple extension measurement technique. This study will lead to improvement of mechanical properties of blending two lattices which can be practically used for production of latex products in industry.

2. Methodology

2.1. Chemicals & Materials

In this study, commercially available high ammoniated (HA) NR latex with a total solid content of 60% and acrylonitrile-butadiene rubber (NBR) latex (X6311 from Synthomer, Malaysia) with medium acrylonitrile content (32% - 35%) and total solid content of 45% were selected.

All the compounding ingredients that were used are of commercial grade. Sulphur dispersion was used as a cross linking agent, zinc oxide (ZnO) as an activator, zinc diethyldithiocarbamate (ZDEC) acts as the accelerator, complex phenol-alkanes (Wingstay-L) acts as an antioxidant; and potassium hydroxide (KOH) and potassium laurate act as stabilizers. Potassium hydroxide (KOH) and potassium laurate were supplied by Excelkos Chemicals Sdn. Bhd. Sulphur, zinc oxide (ZnO), zinc diethyldithiocarbamate (ZDEC) and antioxidant came as 50% dispersion from Excelkos Chemicals Sdn. Bhd.

2.2. Preparation of NR/NBR latex blends

Blends of NR/NBR compound were prepared according to the formulations given in Table 1. Briefly, NBR latex was compounded with 0.5 pphr ZnO and adjusted to pH 10 with 10% KOH before blending with NR latex compound. NR latex was compounded with the remaining vulcanizing ingredients in a separate container. Compounded NBR latex mixture was then added slowly into the NR latex compound.

The NR/NBR latex blends was stirred at 100 rpm and allowed to mature under room temperature. The compounded latex blends were then filtered by using filter cloth to minimize air bubbles which could lead to air entrapment and contamination during casting. Latex films of the blends were casted on glass plates and were allowed to dry until it can be peeled off from the glass plate or until the latex films became translucent. They were further dried at ambient temperature until a constant weight of the films was obtained. Finally, the latex films were dried in an oven at 80°C for 30 minutes followed by post-vulcanization at 120°C for a further 30 minutes[4]. Below table are the formulations for Sample 1 (S1), Sample 2 (S2), Sample 3 (S3), Sample 4 (S4), Sample 5 (S5), Sample 6 (S6) and Sample 7 (S7) according to different ratio.

Table 1: Formulation of NR/NBR latex blends.

Ingredients, phr	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
60% HA Latex	100	90	85	80	75	50	0
45% NBR Latex	0	10	15	20	25	50	100
10% Potassium hydroxide	0.2	0.2	0.2	0.2	0.2	0.2	0.2
20% Potassium laurate	0.5	0.5	0.5	0.5	0.5	0.5	0.5
50% Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
50% ZDEC	1.0	1.0	1.0	1.0	1.0	1.0	1.0
50% Zinc Oxide	1.0	1.0	1.0	1.0	1.0	1.0	1.0
50% Antioxidant	0.5	0.5	0.5	0.5	0.5	0.5	0.5

2.3. Characterization of NR/NBR latex blends.

2.3.1 Determination of glass transition temperature (T_g)

Glass transition temperature (T_g) was determined using Differential Scanning Calorimetry (DSC) Netzsch DSC 200 F3. Samples were heated under nitrogen gas, N_2 environment at a flow rate of 50 ml/min from $10^oC – 100^oC$.

2.3.2 Morphology of blended films

The morphology of rubber blends contribute to the dynamic and mechanical properties of the blends. Characterization of morphology of rubber blends can be achieved by various microscopic techniques. In this study, the blends were examined initially by metallurgical microscopy that was connected to an image analyzer. Transmitter Reflected Metallurgical Microscope Olympus BX51 was used. Thin-sectioned samples cut at 1cm length and 1 cm width was observed at 1000× magnification.

2.4 Determination of Mechanical Properties

2.4.1 Tensile Test

Tensile strength was conducted according to ISO 37 test method by using dumbbell shaped test pieces (75 mm long with central neck 25 mm long and 3.6 mm wide). The test pieces were pulled at a constant rate (500 mm/min) by an Instron 5569 Tensile Test Machine. The modulus M100, M300, elongation at break and tensile strength were recorded. The test was conducted at the temperature of 23ºC.

2.4.2 Tear measurement

Tear measurements were conducted by separating the legs of the trouser test-piece at a uniform rate by using an Instron 5569 tensile machine. The test was carried out at 23ºC. The tearing energy, T, for the trouser test-piece was calculated using equation (1).

$$T = F (\lambda + 1) / h \qquad (1)$$

where F is the force to propagate tearing, λ is the extension ratio in the legs of the test- piece and h is the average nominal thickness of the test-piece.

2.5 Determination of crosslink concentrations of NR, NBR and NR/NBR latex blends.

There are two common methods to determine the crosslink concentration of vulcanized rubber network, namely the equilibrium swelling measurement and the simple extension measurement [7]. In this study, the crosslink concentrations of the blended films were determined by simple extension measurement method due to its simplicity and reliability. The simplicity arises from the fact that it avoids the requirement of the rubber-solvent interaction parameter which is required in the equilibrium swelling measurement. The rubber-solvent interaction parameter for rubber blends is still not known [8]. Furthermore, it is considered as an environmentally accepted method since it depends only on calculation and no hazardous solvents were used. Fig. 1 shows the C_1 Stress Relaxation Machine built in-house for carrying out the simple extension measurement technique.

Fig. 1: C1/Stress relaxation machine built in-house

The test piece is a long parallel strip of vulcanized rubber of uniform thickness of about (120 × 3.2 × 1) mm. The thickness of the test piece was measured by a thickness gauge and the average thickness was recorded. The two ends of the test piece were clamped tightly to avoid slippage by the clamps attached to the C_1 machine. The test piece was pulled at various pre-determined extensions. The force was recorded after 3 minutes at each extension. Then the test piece was pulled to the next pre-determined extension and the force was recorded 3 minutes later. This same sequence was repeated until at least twelve readings were obtained. The Mooney-Rivlin relationship as shown in equation (2) [9] is used to determine C_1.

$$f = 2A_o (\lambda - \lambda^{-2}) [C_1 + C_2\lambda^{-1}] \qquad (2)$$

where f is the force to elongate a vulcanized rubber strip to an extension ratio λ, C_1 is the elastic constant obtained at the intercept of the $f/2A_o (\lambda - \lambda^{-2})$ versus λ^{-1} plot, and C_2 is a measure of the degree of chain entanglements obtained from the slope of the straight line portion of the plot. A_o is the cross-sectional area of the test-piece measured in the unstrained state.

Finally, equation (3) was used to calculate the crosslink concentration, $[X]^1$:

$$C_1 = [X]\rho RT \qquad (3)$$

where ρ is density of rubber, R is the molar gas constant and T is the temperature in Kelvin. Density of NR rubber, (ρ) = 0.92kg/m^3. Density of NBR rubber, (ρ) = 1.17kg/m^3. Molar gas constant (R) = 8.314 J/mol.K. Temperature (K) = 298K. The unit of crosslink concentration is in mol kg^{-1} RH. RH refers to rubber hydrocarbon.

3. Results and Discussion

3.1 Effect of Blend Ratios on the Crosslink Concentration and Glass Transition Temperature of NR/NBR Blended Films

Table 2 shows the corresponding T_g values measured of the samples. The T_g of the various rubber blends S2, S3, S4, S5 and S6 showed single Tg values close to the Tg value of NR latex film, S1. The T_g of a polymer is influenced by several factors such as the main back bone structure, chain flexibility, side group, polarity and steric hindrance [10].

Table 2: T_g of various samples S1-S7

Samples	S1	S2	S3	S4	S5	S6	S7
T_g/^{o}C	-65	-65	-61	-61	-58	-55	-23
Crosslink Concentration/[X] (mol kg^{-1} RH)	0.05	0.03	0.035	0.036	0.030	0.022	0.044

NBR is a copolymer of acrylonitrile and butadiene rubber; the structure of which is as shown in Fig. 2.

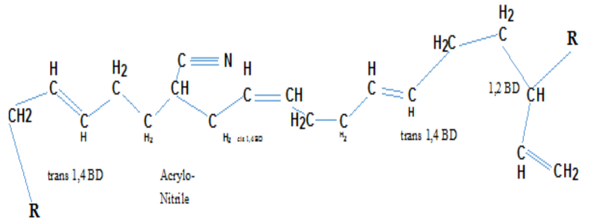

Fig. 2: Chemical structure of NBR rubber

In the case of NBR, the main factor affecting the T_g is its polarity and concentration of the side group acrylonitrile (ACN) ^{3}. The higher the ACN content, the higher is the polar attraction and the greater is the hindrance to molecular mobility imposed by the ACN side group. The NBR latex used in this project is of medium ACN content (32%-35%) showing a T_g value of -23^{o}C. When NBR is blended with NR rubber the total ACN content is reduced further to (16%-18%). Because ACN concentrations were low they do not contribute significantly to the overall T_g values of the blends; and for this reason only one T_g values were detected for the blend samples S2, S3, S4, S5 and S6. Nevertheless the T_g values of the NR component increased from samples S2 to S6 with increased loading of NBR suggesting the reduction in NR properties as more NBR were added to the blends. The reduction in the NR properties is discussed in the next section.

A single T_g values observed in the blends could be attributed to the dilution of the ACN component by NR molecules depressing the significance of ACN contribution. Hence only one T_g values was detected. One may be misled as to associate the single T_g values to homogeneity of the blends. It is well known that NR and NBR are incompatible and blends of NR/NBR should show separately two T_g values of the individual components [6].

3.2 Effect of Blend Ratios on the Mechanical Properties of NR/NBR Blended Films

Table 3 shows the various mechanical properties measured for the blended NR/NBR films. The results shows a general trend in the decreased of tensile strength (TS) and elongation at break (EB) (also as shown graphically in Fig. 3 with increasing NBR concentrations in the blends. Two major factors that affect the TS of NR/NBR latex blend are the extent of strain-crystallization and energy dissipation (hysteresis) which is influenced by the T_g of the material^2. In the case of 100% NR, the TS is very high, which is 36.69 MPa as compared to NBR, 6.35 MPa. This is because of strain-crystallization effect. The crystals act as reinforcing fillers and increased the hysteresis of the rubber and enhanced TS [7]. In the case of NBR, it is a copolymer of butadiene and acrylonitrile, the low TS is associated with its lack of stereo regularity^2.

Table 3: Mechanical properties of samples S1 – S7

Samples	Tensile Strength (TS) (MPa)	Elongation at break (EB) (%)	Tearing Energy (kJm^{-2})	M100	M300
S1	36.69	523.73	101.63	1.11	2.82
S2	30.92	497.23	125.54	5.64	8.27
S3	27.45	615.95	140.37	9.04	10.42
S4	24.56	489.25	137.00	7.38	9.59
S5	19.35	478.20	114.57	2.06	10.25
S6	11.24	297.62	76.94	5.39	6.74
S7	6.35	195.12	11.89	6.13	7.94

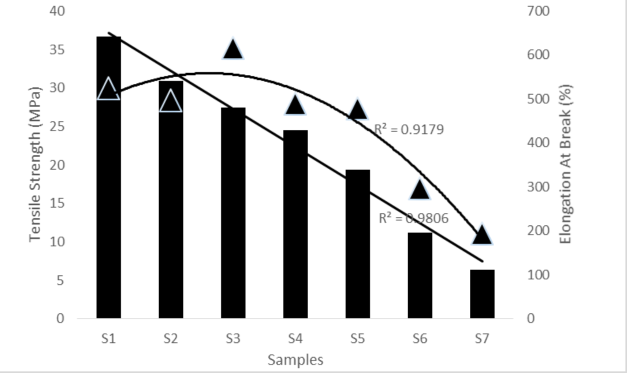

Fig. 3: Tensile strength, ▲ and elongation at break, ■ of the various NR/NBR latex blends

It was also observed that TS showed a good linear relationship with the blends composition (refer Fig. 3). The low total concentration of ACN in the blends does not contribute significantly to the decreased in the TS values of the blends hence showing the linear relationship. The overall TS of the blends are affected only by the presence of NR rubber.

Blank NR, S1 with the highest crosslink concentration (see Table 2) showed the highest TS. However, when lowering NR content in the latex blends (S2-S6), the crosslink concentration of the blends decreases. The NR phase is unable to strain-crystallize to its fullest because the crosslink concentration is too low to support high stresses to ease reorientation and molecular alignment necessary to undergo strain crystallization^4. Hence TS decreased with decreased in NR content in the blend.

The results of tearing energy in Fig. 4 shows, the tearing energy were affected by the presence of NBR. They showed a non-linear relationship with blends composition. The non-linear relationship can be attributed to the incompatibility of NR and NBR [11] causing poor interfacial adhesion between NR and NBR phases.

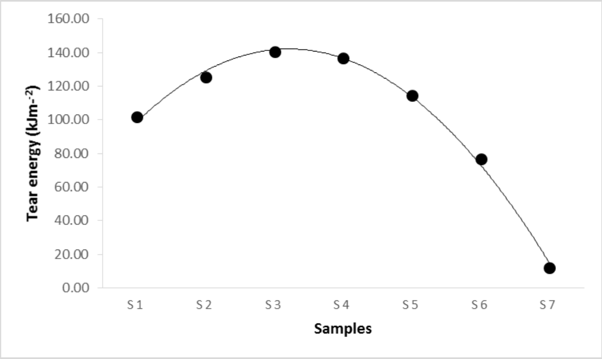

Fig. 4: Tearing Energy of the various NR/NBR latex blends

Analysis of modulus at 100% elongation (M100) and 300% elongation (M300) of Table 3 revealed the following information: (i) All blended samples showed higher M100 and M300 compared to blank NR latex films. (ii) S2, S3, S4 and S5 showed M300 values higher than both blank NR and NBR. (iii) S3 and S4 showed higher M100 values than both blank NR and NBR. The increase in M100 and M300 indicate that the rubber is hard. There are 2 factors that influence the hardness which are crosslink concentration and T_g of the rubber[10]. For a given T_g, normally, the hardness increases with increasing crosslink concentration. For given crosslink concentration, the hardness increases with increasing T_g. For the case of NR (S1), it has the highest crosslink concentration, but lowest T_g, yet it gave the lowest M100 and M300. For the case of NBR (S7), its crosslink concentration is lower than that of NR, but the T_g of NBR is much higher than T_g of NR. But the M100 and M300 of NBR is higher than M100 and M300 of NR. It appears that the T_g is more dominant factor than crosslink concentration to affect M100 and M300. However, there is no systematic trend on M100 and M300 the effect of increasing NBR concentration in the NR/NBR blend.

It is clear that the best tensile strength together with good elongation at break, good crosslink concentrations and tearing energy is shown by S3 an S4 samples with NR/NBR ratios of (85:15) and (80:20) respectively. The values of elongation at break for these two samples were above 600% while the tensile strength is maintained at high values of 27.45 and 24.56 MPa. The crosslink concentrations were averaged at 0.035 mol kg^{-1} RH and tear energy at an average value of 138.69 kJm^{-2}. The tearing energy is the highest compared to the other samples. These observations could be associated to the combination of the right crosslink concentration and T_g of the blend that contributed to high mechanical strengths. The results contrasted those reported by Ismail[11] possibly due to the different grade of NBR compound used.

3.3 Morphological Study

Fig. 5 shows the phase contrast micrographs of the different NR/NBR latex blends. S2 with 90:10 latex blends ratio showed a fine and uniform textured surface. S3 and S4 showed homogeneous textures as well which explained the high mechanical properties observed for these two samples. However, as the NBR content was increased further in S5 and S6, the texture becomes rougher with formations of agglomerated structures in the blends. These agglomerated structures were dominant in S6 with NR/NBR latex blend ratio of 50:50. This observation is in line with the low values of TS and tearing energy of S5 and S6. Insufficient interaction and poor interfacial adhesion between the two phases of NR and NBR caused agglomeration and consequently reduction in the TS and tearing energy.

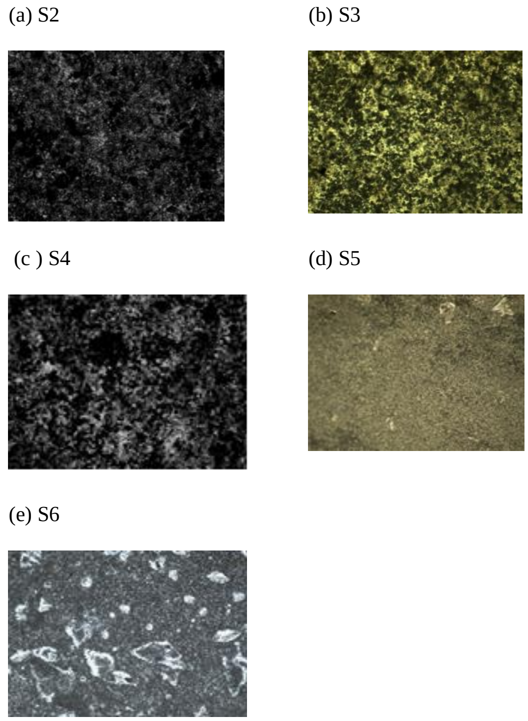
(a) S2
(b) S3
(c) S4
(d) S5
(e) S6

Fig. 5: Phase contrast micrographs of S2, S3, S4, S5 and S6 NR/NBR latex films. All micrographs are obtained at l000× magnification.

4. Conclusion

Latex blends of NR and NBR at various percentages of NBR concentration were prepared. It can be concluded from the results that, NR/NBR latex blends are incompatible as can be seen from the deviation from linearity of EB and tear energy. T_g shifts of blends towards T_g of NR suggested minimum contribution of NBR due to the low content of ACN in the NBR samples. Tensile properties of the blends are generally improved with the increasing NR component because of good mechanical properties of NR. Samples S3 and S4 with NR/NBR blend ratios of (85:15) and (80:20) respectively showed good properties in terms of high tensile strength and high tear energy; and with high elongation at break and acceptable crosslink concentration.

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