



Carboxylated acrylonitrile butadiene-natural rubber latex blends with methyl methacrylate grafted natural rubber latex: mechanical properties and morphology

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Abstract

Commercially available carboxylated acrylonitrile butadiene latex (XNBR) was physically blended with natural rubber latex (NR) at varying blend ratios to investigate its effect on the mechanical properties and morphology. Methyl methacrylate grafted natural rubber latex (MG) was added to the latex blends as a third polymer to study whether it could enhance the mechanical properties of the latex blend films. It was found that the tensile strength of the blend films irrespective of composition decreased when the two latexes were blended as compared to the virgin latex films. The modulus 300 decreased while the elongation at break and tear strength of the blend films increased gradually as the ratio of NR increased in the blend films. It was found that the MG did not enhance the mechanical properties of the XNBR/NR blend films under the current experimental condition. AFM phase imaging analysis revealed enhanced polymer distribution and evidence of NR-MG-XNBR interactions.

Keywords Carboxylated acrylonitrile butadiene latex · Natural rubber latex · Blend · Methyl methacrylate grafted natural rubber latex · Phase imaging

Introduction

Carboxylated acrylonitrile butadiene latex (XNBR) known as nitrile latex commercially and natural rubber latex (NR) are the main raw materials used in the production of disposable examination gloves. The COVID-19 pandemic has accelerated the demand for disposable gloves in the healthcare sector. In 2020, Malaysian glove manufacturers produced 60% nitrile gloves and 40% NR gloves [1], supplying about 240 billion pieces of rubber gloves and meeting almost 70% of global glove demand [2].

XNBR is a type of synthetic latex prepared by emulsion polymerisation of butadiene, acrylonitrile and methacrylic acid where the monomers are derived from petroleum feedstock. The advantages of XNBR gloves include having good tensile strength and oil resistance. NR containing *cis*-polyisoprene particles is sourced from the commercially

cultivated rubber trees. It has high tensile strength, good elasticity, low stress relaxation and high resistance to tear and fatigue. It is widely used in medical devices, tyres, automotive components and other applications.

New products with unique properties can be developed by blending commercially available polymers, which cannot be achieved by a single polymer [3]. The properties of polymer blends are affected by the composition, morphology and interfacial interactions between the polymers [4]. The polymer blends are generally classified as either miscible or immiscible. A miscible polymer blend has a single-phase homogeneous structure with one glass transition temperature. When a polymer blend exhibits more than two phases, the blend is immiscible. It can be made compatible by modifying the interface between the polymer phases. Interfacial agents known as compatibilisers are used to reduce the interfacial tension and improve the adhesion between the polymer phases [5]. The compatibiliser employed generally contains hydrophobic and hydrophilic parts that can align along the interfaces between the two polymer phases, thus increasing interactions and compatibility between the phases [6].

The latex blending technique for film dipping purposes has garnered much interest from many researchers. The

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selection of polymers in these blends mainly involves NR and commercially available synthetic latexes. Some of the latex blends studied are natural rubber/carboxylated acrylonitrile butadiene (NR/XNBR) [7–9], natural rubber/styrene butadiene (NR/SBR) [10], natural rubber/chloroprene (NR/CR) [11] and triple latex blend system of natural rubber/chloroprene/carboxylated acrylonitrile butadiene (NR/CR/XNBR) [12]. The objective of blending the latexes is to obtain improved physical properties, as well as oil and chemical resistance in the finished product. However, improvement in oil or chemical resistance with reduction in physical properties has been often observed in these studies. Despite the numerous studies on latex blends, the introduction of a third polymer to enhance compatibility between the polymer phases is somewhat lacking. The present study is aimed at investigating the influence of blend composition and the introduction of methyl methacrylate grafted natural rubber latex (MG) as a third polymer in latex blends with emphasis on the mechanical properties and morphology of the NR/XNBR blend films. MG is commercially available and has a similar chemical identity with XNBR and NR; it is prepared by graft copolymerisation of poly (methyl methacrylate) on the polyisoprene unit in NR.

Experimental

Materials

Commercial grade of medium modulus pre-vulcanised NR, carboxylated butadiene acrylonitrile latex (XNBR) with a medium acrylonitrile (ACN) level, having ACN content between 26 and 30% and methyl methacrylate grafted natural rubber latex (MG) known by the trade name GAPOLY PM 30, containing 30% of poly (methyl methacrylate) were used in this study. Aqueous dispersions of sulfur, zinc oxide, zinc dibutyldithiocarbamate, zinc diethyldithiocarbamate and antioxidants were prepared by ball milling in the laboratory under standard conditions.

Methods

Preparation of latex compound

The XNBR was compounded according to the formulation as described in the earlier paper by using 1 phr of ZnO [13], while the MG was compounded with sulfur, zinc diethyldithiocarbamate, zinc oxide and antioxidant at 1 phr each. Both latexes were compounded prior to further use. The NR was used as received.

Preparation of latex blends

The XNBR/NR and the XNBR/NR/MG blends were prepared by mechanically stirring the latexes at varying blend ratios as shown in Table 1. The compound was stirred for 24 h prior to dipping.

The amount of MG to be incorporated into the XNBR/NR blend was determined by evaluating the tensile properties and elongation at break of the XNBR/NR blend films at equal composition in the presence of 5, 10 and 15 phr of MG. Reduction in both tensile strength and elongation at break of the blend films were observed when 10 and 15 phr of MG was incorporated as compared to the 5 phr MG. For both 10 phr of MG and 15 phr of MG blend films, the tensile strength reduced by 10.9 and 8.3%, while the elongation at break reduced by 7.1 and 11.7%, respectively. The reduction in mechanical properties with a higher dosage of MG was probably due to the stiffening effect of MG. Hence, 5 phr of MG was selected in the study.

Preparation of latex films

In the preparation of dipped films, the total solids content of the latex blends was reduced to different percentages with distilled water to obtain a film thickness of 0.08 ± 0.02 mm. Unglazed porcelain plates were first heated to 70 °C before dipping into a calcium nitrate solution. The plates were oven dried in an air oven set at 70 °C before dipping into the latex compound for 10 s. The resulting wet films were air dried under room conditions for 10 min before being subjected to leaching in distilled water for 2 min. The leached films were then dried in the oven set at 80 °C for 10 min before heating up to 100 °C and then again to 110 °C for 10 min, respectively for blend films containing XNBR as its major

Table 1 Formulation of XNBR/NR and XNBR/NR/MG blends

Latex type	Blend (phr)									
XNBR	100	80	80	60	60	40	40	20	20	0
NR	0	20	15	40	35	60	55	80	75	100
MG	0	0	5	0	5	0	5	0	5	0

component. For films having NR as its major component, the films were cured at 100 °C for 30 min. The films were then removed from the oven and cooled to room temperature, before being powdered with corn starch and stripped from the plates.

Mechanical properties of latex films

The tensile stress–strain properties of the unaged and aged (70 °C/7 days) films were determined according to the ISO 37 test method. Five dumb-bell standard test pieces were cut from the film and stretched in a universal testing machine, INTRON 3365 with a crosshead speed of 500 mm/min. The test was conducted under room temperature conditions (25 ± 1 °C). The median value with standard deviations of the property is recorded.

The tear strength of the unaged and aged (70 °C/7 days) films were determined according to the ISO 34 test method. Five trouser test pieces were cut from the films and the tearing force is applied by a universal testing machine, INTRON 3365 with a crosshead speed of 100 mm/min until the test piece breaks. The test was conducted under room temperature conditions (25 ± 1 °C). The median value with standard deviations of the property is recorded.

Atomic force microscopy (AFM) visualisation

AFM samples were prepared as described in the latex film preparation procedure in the previous section in this paper, using smaller dipping plates and omitting the anti-tack powder. Without stripping, the dipped films were viewed under a Park System NX10 AFM at the view size of $10 \mu\text{m} \times 10 \mu\text{m}$. All images were captured using the Non-contact Mode and we report the surface topography and phase image of these samples.

Results and discussion

Mechanical properties

The tensile strength of XNBR/NR blend films with and without MG at different blend ratios is shown in Fig. 1. The tensile strength of virgin XNBR and NR films were 37.3 and 20.2 MPa, respectively. Generally, the tensile strength of the blend films irrespective of composition decreased when the two latexes were blended as compared with its virgin latex films, respectively. A similar observation has been reported by other researchers [7, 8]. In comparison with the virgin XNBR film, the tensile strength of the latex film dropped by 24% when 20 phr of NR was blended. The tensile strength further decreased to more than 50% when 40 phr of NR was blended. By blending 40 phr of XNBR, the tensile strength

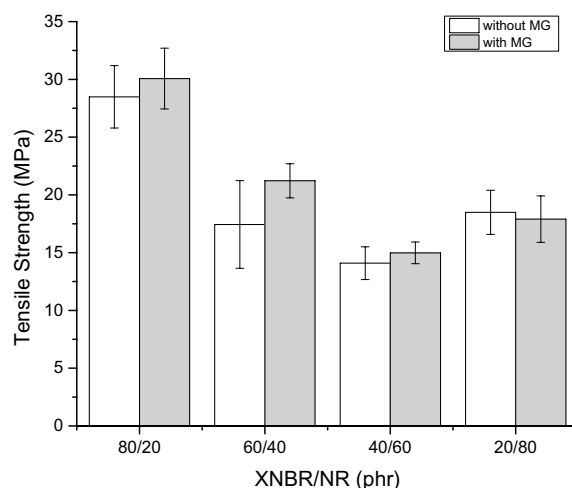


Fig. 1 Tensile strength of the XNBR/NR blend film with and without MG

of the latex film was the lowest among all the latex blends and decreased by 30% compared with the virgin NR film. It is likely that the inherent tensile strength of the XNBR did not contribute to the latex blend film properties with the current physical blending method. This observation is similarly reported by Ruhida et al., although the intention is to produce a vulcanisate with the best properties from each component, a decrease in tensile strength is observed with the lowest tensile strength recorded at 50/50 (XNBR/NR) film [14].

The mechanical properties of polymer blends are known to depend on the morphology and dispersion of each component in the blend. Latex blending often leads to immiscibility due to differences in polymer polarity and a third component is added to enhance the mechanical properties of the film by increasing interactions between the polymer phases [15]. MG contains both polar and non-polar components that may align along the interfaces between the XNBR and NR phases, thus enhancing its tensile properties, where XNBR has greater polarity than NR [15]. The increase in tensile strength could be either attributed by better interaction between the polymer phases or due to MG, which has been shown to enhance the stiffness of film [16]. In this study, incorporation of MG in the XNBR/NR blends did not enhance the tensile properties of the films as evident from the overlapping of error bars in Fig. 1. Elsewhere, it has been reported that incorporation of 5–35% MG did not show any incremental effect on the tensile strength of NR/MG blend films [17].

The modulus 300 of XNBR/NR blend films with and without MG at different blend ratios is shown in Fig. 2. The modulus 300 of the blend films decreased gradually as the ratio of NR increased in the blend films, and a similar trend has been observed by another researcher [7]. The

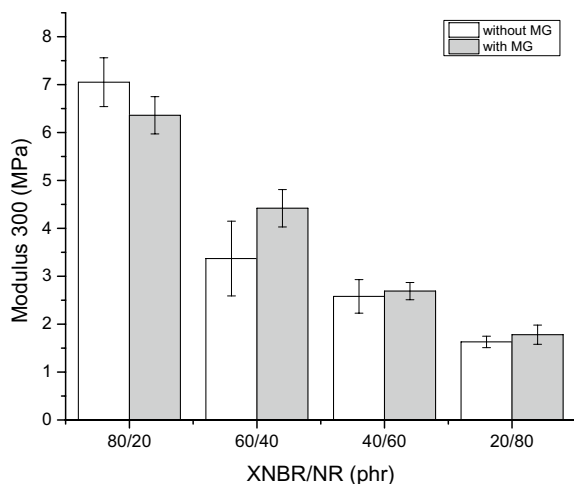


Fig. 2 Modulus 300 of the XNBR/NR blend film with and without MG

modulus 300 of virgin XNBR and NR were 7.9 and 1.4 MPa, respectively. The modulus 300 of the NR film is much lower than that of the XNBR, as NR film is known to be softer. The modulus 300 of the 60/40 (XNBR/NR) blend films decreased to approximately 4 MPa or 50% compared with the XNBR film. However, there was no substantial reduction by only blending 20 phr of NR with the XNBR. The XNBR/NR blends films with higher ratio of NR recorded lower modulus whereby the polymer stretches easier with less resistance. In the form of glove when worn, it will lead to less hand fatigue and will be more comfortable to wear [18]. Similarly in rubber blends, El-Sabbagh and Yehia [19] found that the modulus improved with the increase of the nitrile butadiene rubber component in the natural rubber/nitrile butadiene rubber blend. While the incorporation of MG in the XNBR/NR blends did not enhance the modulus 300 of the films.

The elongation at break of XNBR/NR blend films with and without MG at different blend ratios is shown in Fig. 3. The elongation at break value of virgin XNBR and NR was 530 and 790%, respectively. The elongation at break of the blend films increased gradually as the ratio of NR increased in the blend films, a similar trend was observed by another researcher [7]. Contrary to the tensile strength results, the effects of combined properties inherent in the individual polymers namely the XNBR and NR by blending method was observed in the elongation at break values. The elongation at break of blend films with higher ratio of NR were higher, these films displayed higher elasticity when stretched [20]. Similarly in rubber blends, the reduction in the elongation at break of natural rubber/nitrile butadiene rubber blend is observed with increasing ratio of nitrile butadiene rubber [21]. However, the incorporation of MG did not contribute to the elongation at break of the blend films.

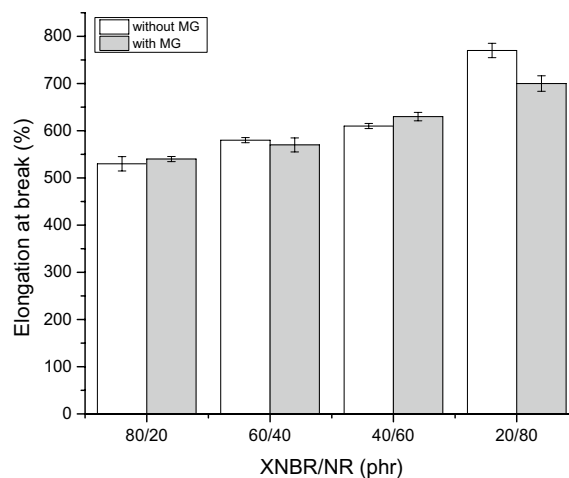


Fig. 3 Elongation at break of XNBR/NR blend film with and without MG

The tear strength of XNBR/NR blend films with and without MG at different blend ratios is shown in Fig. 4. The tear strength of virgin XNBR and NR films were 4.7 N/mm ($s=0.96$) and 7.2 N/mm ($s=0.53$), respectively. Similar to tensile strength, the tear strength of the blend films irrespective of composition decreased when the two latexes were blended as compared with the virgin latex films except for the 20/80 (XNBR/NR) blend film. The tear strength of the blend films increased gradually as the ratio of NR increased in the blend films, and a similar trend was observed by another researcher [7]. The drastic drop in tear strength for the 80/20 film and large standard deviation for the 20/80 film could not be identified, while the incorporation of MG did not enhance the tear strength of all the blend films.

Table 2 shows the thermal ageing properties of both the virgin and blend films. The increase in the tensile strength

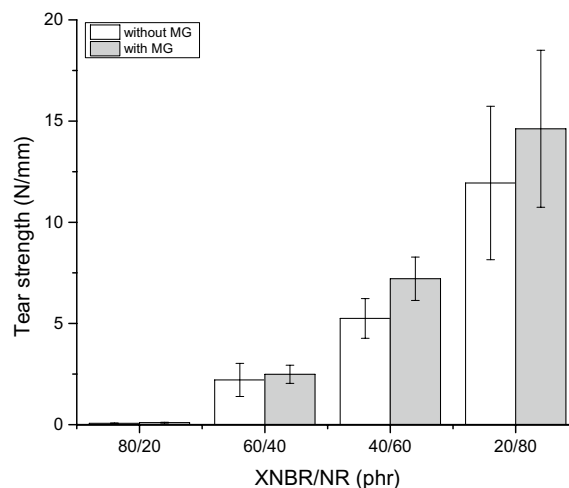


Fig. 4 Tear strength of XNBR/NR blend film with and without MG

Table 2 Virgin and blend films heat ageing properties

Blend films (XNBR/NR) and (XNBR/NR/MG)	Mechanical properties		
	Tensile strength (MPa)	Tear strength (N/mm)	Modulus 300 (MPa)
100/0	38.8 (+4.0)	3.1 (−33.0)	9.5 (+16.8)
80/20	29.1 (+2.1)	2.3 (> +100)	8.2 (+14.6)
85/15/5	33.6 (+11.7)	2.6 (> +100)	7.4 (+14.8)
60/40	23.8 (+36.6)	2.0 (−9.5)	4.5 (+26.6)
60/35/5	20.6 (−2.9)	2.4 (−2.8)	4.8 (+8.3)
40/60	18.4 (+30.7)	11.3 (> +100)	3.2 (+21.8)
40/55/5	17.6 (+17.8)	11.2 (+55.9)	2.8 (+7.7)
20/80	21.3 (+15.4)	7.3 (−38.3)	1.5 (−6.6)
20/75/5	22.5 (+26.1)	9.4 (−35.4)	1.9 (+10.5)
0/100	23.2 (+15.0)	13.3 (+84.6)	1.1 (−18.1)

*The percentage of changes in value compared with unaged films in parentheses ()

in tandem with modulus 300 of the aged films is an indication that further crosslinking between polymers took place at an elevated temperature. The tear strength of the virgin XNBR film, 20/80 (XNBR/NR) and 20/75/5 (XNBR/NR/MG) blend films decreased substantially after heat ageing while other films showed an increase in tear strength. Tear strength reduction of aged virgin XNBR film was observed in our previous study [13].

Morphology AFM analysis

Atomic force microscopy (AFM) provides useful information on the surface of specimens. It captures surface morphology in 2D and 3D modes as well as some mechanical properties. In this study, we try to understand the behaviour of blended rubber films through a microscopic lens. As seen in Fig. 5, both virgin NR and XNBR films were rough on surface but they are distinguishable. The XNBR film surface consists of smaller bumps compared with much bigger and rounder bumps seen on the NR film surface, corresponding to the smaller particle size of XNBR. The surface of all the

films were undulating with height and depth differences that could reach as high as a few microns. No significant variation can be observed between the blends with various ratios, with or without the presence of MG.

The AFM phase imaging may provide more practical information than topography images. If there is more than one material, the phase difference may be significant enough to be detected by the atomic force microscopy. As the cantilever scans through the surface, the drive and response from a material should be constant until a harder or softer material is touched. At this point, the drive remains constant but the response is varying. A phase image in AFM is constructed using the data collected at each point of the scanned area and the data can be presented either as an image or a histogram. Figure 6 shows the phase images and the corresponding histograms of NR and XNBR. These histograms provide affirmative information to differentiate both NR and XNBR, in which the peak for NR was found mainly on the negative region and this phase may be referred to as a softer material [22]. It is noted that there are two peaks on the histogram of the XNBR phase image. The peak on the left could be

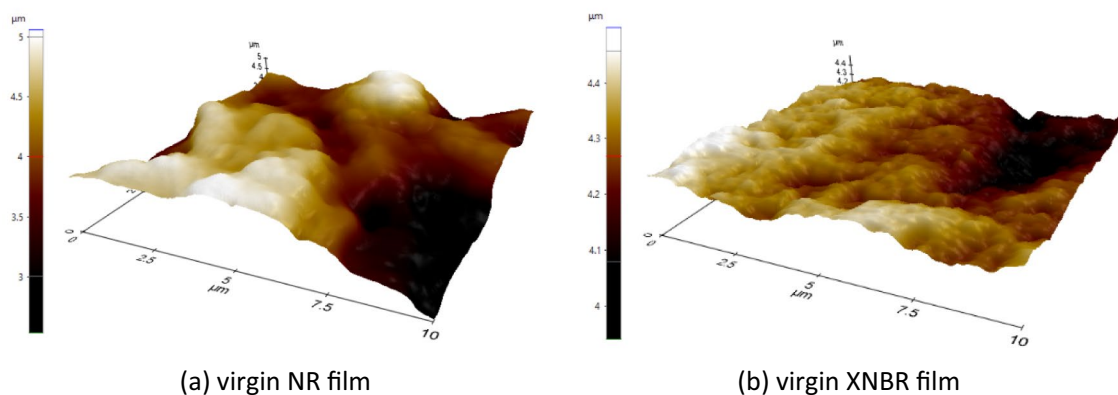
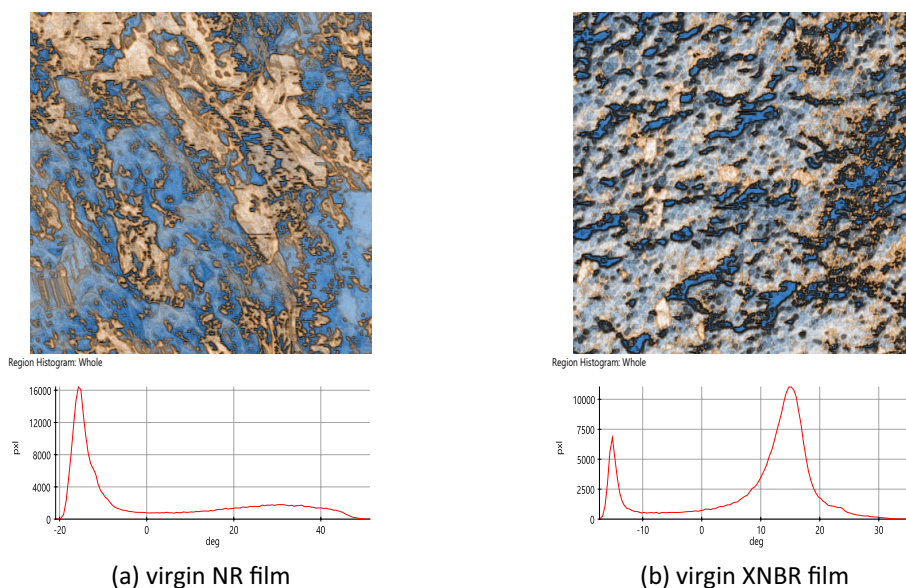


Fig. 5 The 3D topography images of **a** virgin NR film and **b** virgin XNBR film

Fig. 6 Phase images of **a** virgin NR film and **b** virgin XNBR film. Their corresponding histograms are also presented below these images. The dominant peak for NR lies on the negative region as opposed to that of XNBR



some minor component in the XNBR, which may require further investigation. Similarly, a small bump on the positive region was also observed for NR. The existence of MG cannot be identified via histograms but may be observed using the advanced colouration from the 2D phase images.

The phase image can be presented in enhanced colours as illustrated in Fig. 7. The darker blue colour represents the NR phase as it is corresponding to the negative region in the phase histograms (Fig. 6). The light blue and whitish areas are of the XNBR phase and the bright orange spots are believed to be MG. A better distributed phase with smaller clusters for each polymer can be seen when the MG is present. It is also observed that these bright spots are located

in between the NR and the XNBR phases, bridging the two major polymers, hence resulting in a better polymer distribution.

Conclusion

Latex films were dipped from blends of XNBR and NR in varying ratios in this study. A third polymer, MG, was added to the latex blends to study its functionality in compatibilising the polymer phases. Generally, the tensile strength of the blend films irrespective of composition decreased when the two latexes were blended compared with its virgin latex

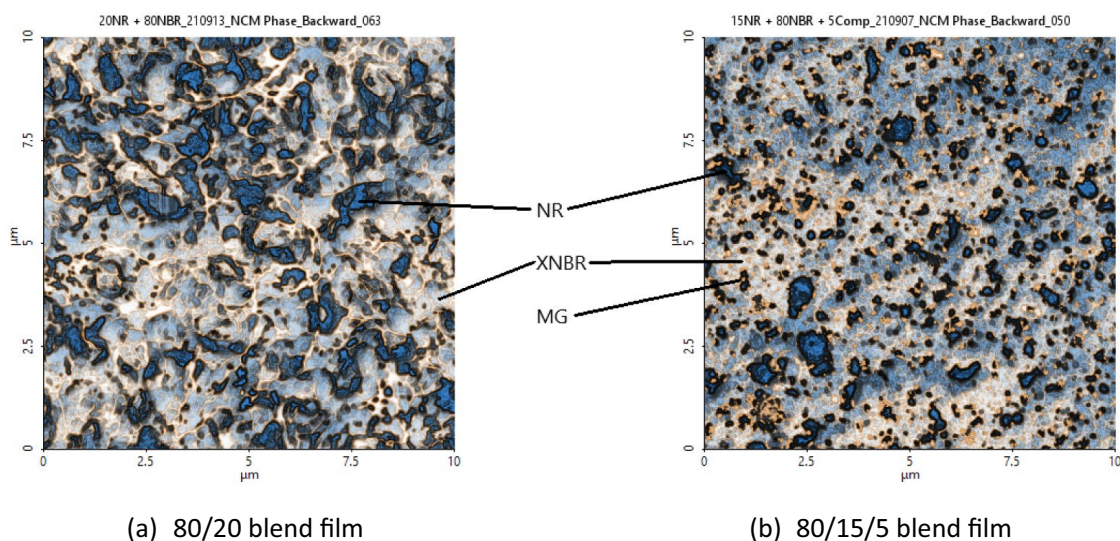


Fig. 7 The AFM phase images of **a** 80/20 (XNBR/NR) blend film and **b** the presence of MG in the 80/15/5 (XNBR/NR/MG) blend film

films, respectively. Upon increasing NR in the blend ratios, the modulus 300 of the blend films decreased gradually with increasing elongation at break and tear strength. The MG did not enhance mechanical properties of the XNBR/NR blend films in this study. For the aged blend films, increase in tensile strength and modulus 300 was observed. AFM phase imaging was found useful in providing information on the distribution of all three types of polymers in the blends and visually confirmed the linkages between them. However, the enhanced polymer distribution did not enhance the mechanical properties of the blend films.

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Declarations

Conflict of interest The authors declared that they have no conflict of interest.

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